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Investigación y desarrollo de fluidos de corte eco-eficientes para el mecanizado de aleaciones de titanio

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A mis padres, Antonio y Mercè,
a mi hermano, Miki
y a mi pareja, Jordi.

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TÍTULO: Investigación y desarrollo de fluidos de corte eco-eficientes para el mecanizado de aleaciones de titanio

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Resumen

Las aleaciones de titanio son muy utilizadas en la industria aeroespacial por sus características excepcionales, como su elevada resistencia mecánica, baja densidad, y buenas propiedades anticorrosivas. Sin embargo, su aplicación se ve limitada por su dificultad para ser mecanizadas. El uso de sistemas de lubricación y refrigeración es extremadamente importante para mejorar la calidad de la pieza mecanizada y alargar la vida útil de la herramienta. En los últimos años, ha habido un mayor interés en el mecanizado sostenible, lo que ha aumentado la demanda de nuevos fluidos de corte específicos para trabajar con materiales difíciles de mecanizar como el Ti6Al4V o el γ-TiAl. Esta Tesis Doctoral tiene como objetivo fundamental la investigación y el desarrollo de nuevos fluidos de corte eco-eficientes para el mecanizado de aleaciones de titanio, que permita aumentar la productividad, la sostenibilidad y la calidad de los procesos de mecanizado mediante una lubricación y refrigeración adecuadas. Se ha realizado un estudio detallado sobre los fluidos de corte eco-eficientes, desde la selección de sustancias utilizadas como materia prima para producir lubricantes sostenibles hasta la formulación del producto, así como el análisis del torneado de aleaciones de titanio usando distintos sistemas de lubricación y refrigeración.

Los fluidos de corte contienen mezclas de compuestos polares, como los ésteres y los tensoactivos, que se adsorben fácilmente en la superficie metálica, formando una película lubricante estable. En este trabajo, se ha establecido una metodología que permite cuantificar la formación de la película lubricante sobre una superficie metálica cuando está en contacto con un fluido de corte. Esto permite investigar el rendimiento de varias sustancias y el efecto sinérgico entre ellas para formular un nuevo fluido de corte eco-eficiente. El rendimiento del fluido mejora al aumentar la formación de la película orgánica en la superficie del metal, lo que depende de la estructura química del éster y de su capacidad de adsorción en la superficie frente a otros compuestos. Cambiando la estructura molecular del tensoactivo, es posible variar la afinidad entre el éster y el sustrato y alcanzar una combinación óptima, que mejora la formación de la película lubricante.

Se ha desarrollado un nuevo fluido de corte eco-eficiente o EcoMWF (del inglés, Eco-efficient metalworking fluid) basados en agua para aleaciones de titanio. Los aceites minerales usados comúnmente en los fluidos de corte convencionales han sido sustituidos por ésteres de poliol, que son biodegradables, provienen de fuentes renovables y han demostrado un excelente rendimiento durante el mecanizado. El fluido de corte desarrollado se ha probado en el torneado de piezas de aluminuro de titanio gamma (γ-TiAl), una aleación de titanio nueva y relativamente poco explorada. Además, se ha comparado su rendimiento con otros sistemas de lubricación y refrigeración sostenibles. Los sistemas considerados en este trabajo son el mecanizado en seco, el aire comprimido frío o CCA (del inglés, Cold compressed air), la mínima cantidad de lubricante o MQL (del inglés, Minimum quantity lubrication), el sistema criogénico y el sistema de inundación. Se ha investigado el impacto del material de la herramienta y de los parámetros de corte en la rugosidad superficial, la redondez, el desgaste de la herramienta y la temperatura de corte para cada sistema de lubricación y refrigeración. Los resultados detallados demuestran que la sostenibilidad del proceso de torneado de γ-TiAl puede mejorarse con el nuevo EcoMWF desarrollado, manteniendo el mismo rendimiento de mecanizado que los fluidos de corte base aceite mineral comúnmente usados.

Abstract

Titanium alloys are widely used in the aerospace industry because of their exceptional characteristics, such as high mechanical strength, low density, and good anti-corrosion properties. However, their application is limited by their difficulty in machining. The use of lubrication and cooling systems is extremely important to improve the quality of the machined part and extend tool life. In recent years, there has been an increased interest in sustainable machining, which has increased the demand for new specific cutting fluids to work with difficult-to-machine materials such as Ti6Al4V or γ-TiAl. The main objective of this PhD Thesis is the research and development of new eco-efficient cutting fluids for the machining of titanium alloys, which allows increasing productivity, sustainability, and quality of machining processes through proper lubrication and cooling. A detailed study on eco-efficient cutting fluids has been carried out, from the selection of substances used as raw material to produce sustainable lubricants to the formulation of the product, as well as the analysis of titanium alloy turning using different lubrication and cooling systems.

Cutting fluids contain blend of polar compounds, such as esters and surfactants, that easily adhere to the metal surface, forming a stable lubricant film. In this work, a methodology has been established to quantify the formation of the lubricant film on a metal surface when it is in contact with cutting fluid. This gives a better knowledge of the performance of various substances and the synergistic effect among them to formulate a new eco-efficient cutting fluid. The performance of the cutting fluid is improved by increasing the organic film formation on the metal surface, which depends on the chemical structure of the ester and its adsorption capacity on the surface against other compounds. By changing the molecular structure of the surfactant, it is possible to vary the affinity between the ester and the substrate and achieve an optimal combination, which improves lubricant film formation.

A new eco-efficient water-based cutting fluid (EcoMWF) for titanium alloys has been developed. The mineral oils commonly used in conventional cutting fluids have been replaced by biodegradable polyol esters from renewable sources and have demonstrated excellent performance during machining. The developed cutting fluid has been tested in turning of gamma titanium aluminide (γ-TiAl) parts, a new and relatively unexplored titanium alloy. In addition, its performance has been compared with other sustainable lubrication and cooling systems. The systems considered in this work are dry, cold compressed air (CCA), minimum quantity lubricant (MQL), cryogenic, and flooded machining. The impact of tool material and cutting parameters on surface roughness, roundness, tool wear, and cutting temperature has been investigated for each lubrication and cooling system. Detailed results demonstrate that the sustainability of the γ-TiAl turning process can be improved with the newly developed EcoMWF while maintaining the same machining performance as commonly used mineral oil-based cutting fluids.

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Índice de símbolos y abreviaturas

CCA	Aire comprimido frío (Cold compressed air)
CLP	Clasificación, etiquetado y envasado (Classification, labelling and packaging)
DOE	Diseño de experimentos (Design of experiments)
EcoMWF	Fluido de corte eco-eficiente (Eco-efficient metalworking fluid)
EO	Grado de etoxilación
ESCA	Espectroscopía electrónica para análisis químico (Electron spectroscopy for chemical analysis)
GHS	Sistema globalmente armonizado de clasificación y etiquetado de productos químicos (Global harmonized system)
GWP	Potencial de calentamiento global (Global-warming potential)
IRRAS	Espectroscopia de reflexión-absorción en el infrarrojo (Infrared reflection absorption spectroscopy)
JCR	Journal citation reports
LN_2	Nitrógeno líquido (Liquid nitrogen)
MQL	Mínima cantidad de lubricante (Minimum quantity lubrication)
MWF	Fluido de corte (Metalworking fluid)
n	Número de etoxilación
O/W	Aceite en agua (Oil in water)
PVD	Deposición física de vapor (Physical vapor deposition)
R	Longitud de cadena de hidrocarburos (Hydrocarbon chain length)
Ra	Rugosidad media aritmética (Arithmetic average roughness)
ToF-SIMS	Espectrometría de masas de iones secundarios de tiempo de vuelo (Time-of-flight secondary ion mass spectrometry)

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Capítulo 1. Introducción

La mejora en el proceso de mecanizado de aleaciones de titanio sigue siendo un reto en la industria metalmecánica, a pesar de su elevada experiencia. Su dificultad se relaciona, principalmente, con el excesivo desgaste y fallo catastrófico de las herramientas, que provoca una disminución de su vida útil y una baja productividad del proceso. La comunidad investigadora ha abordado los retos de las aleaciones de titanio de tres maneras, desarrollando 1) nuevos materiales y geometrías de las herramientas de corte, 2) nuevos procesos de eliminación o adición de material, y 3) nuevos sistemas de lubricación y refrigeración.

Los fluidos de corte se usan para mejorar el proceso de mecanizado, proporcionando lubricación, disipando el calor y eliminando las virutas de la zona de corte. El consumo mundial de los fluidos de corte en 2021 superó los 1,3 millones de toneladas [1]. No obstante, los fluidos de corte son objeto de revisión de la Unión Europea debido a su impacto medioambiental y a los riesgos que conllevan para la salud de los trabajadores [2]. La creciente preocupación por el cambio climático y la necesidad de cumplir las regulaciones impuestas por los gobiernos sobre el uso de materiales peligrosos, han originado una mayor demanda de lubricantes sostenibles. Sin embargo, aún hay pocos fluidos de corte para el mecanizado de metales respetuosos con el medioambiente que estén comercialmente disponibles [3]. El gran desafío es mejorar la eficiencia y la sostenibilidad de estos productos, donde la investigación y el desarrollo de los fluidos de corte se basa principalmente en la experiencia fuertemente relacionada con la industria.

1.1. Necesidad de investigación y desarrollo de fluidos de corte eco-eficientes

La dificultad de mecanizar las aleaciones de titanio se asocia a sus características inherentes, como la baja conductividad térmica, el bajo módulo de elasticidad y la elevada reactividad química a altas temperaturas [4], que provoca un aumento de las temperaturas de corte y una elevada adhesión entre la herramienta y la pieza [5]. Como resultado, la vida útil de la herramienta y la calidad de la superficie mecanizada disminuye. La experiencia de los profesionales en procesos de mecanizado coincide con los problemas descritos en la bibliografía. Los expertos deben trabajar a velocidades de corte baja disminuyendo así la productividad. Las herramientas se desgatan muy rápido, lo que da como resultado un mal acabado superficial de la pieza y/o continuos paros de producción. La zona de corte se calienta mucho e incluso, en algunos casos, se observa la generación de chispas. Además, las virutas resultantes son muy finas y se enrollan, aumentando la probabilidad de que el operario sufra algún corte.

Debido a las dificultades de mecanizar el titanio y sus aleaciones, la aplicación de sistemas de lubricación y refrigeración es extremadamente importante [6]. Generalmente, los fluidos de corte se emplean en el mecanizado para mejorar la calidad de la pieza de trabajo, reducir la corrosión y alargar la vida de la herramienta. Los fluidos de corte basados en agua, también conocidos como taladrinas, son los más usados durante el mecanizado de aleaciones de titanio, gracias a su capacidad de disipar el calor de la zona de corte y lubricar la superficie de la herramienta y la pieza. Sin embargo, la mayoría de estos fluidos contienen aceite mineral y/o productos derivados del petróleo y aditivos peligrosos.

Los fluidos de corte convencionales aumentan los costes del proceso, el impacto medioambiental y el impacto sobre la salud de los trabajadores [7-10]. Una exposición continua y prolongada a los fluidos de corte convencionales puede provocar varios problemas de salud, como la dermatitis y enfermedades respiratorias. Los informes médicos demuestras que los fluidos de corte base aceite mineral son la principal cause de más del 80% de las enfermedades profesionales de la piel [11]. Además, la presencia de agentes nocivos, como los hidrocarburos, los compuestos clorados o sulfurados, agentes liberadores de formaldehído, entre otros, puede provocar varios tipos de cáncer[12]. Todos estos compuestos hacen que las aguas residuales de los fluidos de corte sean peligrosas y no biodegradables, y que las alternativas de eliminación de estos residuos sean costosas [13].

Como alternativas a los fluidos de corte convencionales se está estudiando otros sistemas de lubricación y refrigeración como el mecanizado en seco, la aplicación de mínima cantidad de lubricante, la refrigeración criogénica y/o gaseosa. Sin embargo, en el mecanizado de titanio, la mayoría de estas alternativas no alcanzan los resultados esperados [14-17]. Otra alternativa, objeto del trabajo de esta Tesis Doctoral, es el desarrollo de nuevos fluidos de corte sostenibles. Hay una tendencia creciente hacia la utilización de aceites con base de origen vegetal o sintético, frente a la formulación de aceites minerales medioambientalmente más negativos [18], así como a la eliminación o reducción de las sustancias peligrosas [19]. Continúan aumentando los desafíos en la formulación de fluidos de corte ya que los usuarios finales están exigiendo una mayor eficiencia durante períodos de tiempo más largos y bajo condiciones más severas [20]. Por consiguiente, se requieren nuevas formulaciones de fluidos de corte eco-eficientes para el mecanizado sostenible de materiales difíciles de mecanizar [21,22]. Entendiéndose como fabricación sostenible, "la creación de productos fabricados que usan procesos que minimizan los impactos ambientales, conservan la energía y los recursos naturales, son seguros para los trabajadores, la comunidad y los consumidores y son económicamente sólidos" [23].

A pesar de que existen muchos estudios sobre fluidos de corte, la mayoría están relacionados con metales como el acero y el aluminio, y pocos con aleaciones de titanio [24-26]. La investigación sobre nuevos fluidos de corte se centra, principalmente, en el estudio de nuevas bases lubricantes o de un tipo de aditivo en concreto y, por lo tanto, no puede ser usada directamente como fluido de trabajo. Se necesitan más estudios sobre el comportamiento de las materias primas que componen el fluido de corte, para comprender los factores que influyen en las propiedades del fluido, como la lubricación [27].

1.2. Mecanizado de aleaciones de titanio

Las aleaciones de titanio se usan ampliamente en el sector aeronáutico, aeroespacial y de automoción, gracias a sus excelentes propiedades como su elevada resistencia mecánica, baja densidad y excelente resistencia a la corrosión. También es muy utilizado en aplicaciones biomédicas por su biocompatibilidad

[28]. La aleación Ti6Al4V constituye la mayor parte de la producción de todas las aleaciones de titanio disponibles actualmente [29].

Para cumplir con los requerimientos cada vez más exigentes de la industria aeroespacial y para aplicaciones avanzadas en el sector de la automoción, se han desarrollado nuevas aleaciones como los aluminuros de titanio [30]. La nueva generación de aleaciones de titanio, gracias a su estructura intermetálica [31], tiene propiedades superiores a temperaturas elevadas, permitiendo aumentar hasta un 50% la temperatura de trabajo respecto al Ti6Al4V [32]. Sin embargo, como la mayoría de las aleaciones de titanio, los aluminuros de titanio son extremadamente difíciles de mecanizar [33], incluso más que las aleaciones de titanio comunes [34].

El creciente uso de las aleaciones de titanio, especialmente en el sector aeroespacial que representa el 60% del uso total mundial de aleaciones de titanio [35], ha incrementado la demanda de procesos de mecanizado de estos metales. Mejorar el mecanizado de aleaciones de titanio sigue siendo un reto sin resolverse para las industrias, donde la mayoría de los problemas están relacionados con el alto consumo de herramientas de corte debido al desgaste excesivo como resultado de la generación de altas temperaturas en la zona de corte [36]. Las principales dificultades del mecanizado de aleaciones de titanio se asocian a: la baja conductividad térmica, al endurecimiento por deformación, la alta dureza, el bajo módulo de elasticidad y la elevada reactividad química a altas temperaturas [37].

La baja conductividad térmica (6,67 W/m·K) y el elevado calor específico dificultan la disipación del calor generado en el proceso, provocando un aumento de la temperatura en la zona de corte que acelera el desgaste de la herramienta. A diferencia del mecanizado de aleaciones acero, donde aproximadamente el 50% del calor generado es absorbido por la herramienta, en el mecanizado de titanio es del 80% [38]. La temperatura en la zona de corte puede alcanzar fácilmente los 1000 °C, unos 300-400 °C más que las aleaciones acero para el mismo proceso de mecanizado, provocando un reblandecimiento de la herramienta y acelerando su desgaste [39]. Asimismo, la alta reactividad química del titanio a temperaturas superiores a 500 °C y su afinidad tanto con el recubrimiento como con el material de la herramienta, provoca un desgaste prematuro, principalmente por mecanismos de difusión y adhesión [40].

Las aleaciones de titanio presentan un endurecimiento por deformación de la superficie mecanizada. Este comportamiento afecta a la calidad de la pieza en términos de rugosidad superficial y un aumento significativo de la dureza superficial. Su elevada dureza, que se mantiene a altas temperaturas generadas durante el proceso de mecanizado, se opone a la deformación plástica necesaria para formar las virutas [38]. Esto provoca la formación de una viruta segmentada [41], lo cual produce unas solicitaciones cíclicas, tanto térmicas como mecánicas, en la herramienta, provocando un deterioro más rápido de la misma. Además, el bajo módulo de elasticidad de las aleaciones de titanio (110 GPa para Ti6Al4V) provoca que la pieza de trabajo tienda a alejarse de la herramienta debido a la acción de la fuerza cortante. Esto da lugar a vibraciones perjudiciales para la vida útil de la herramienta y problemas de tolerancia de la pieza [42].

Para superar los problemas anteriormente mencionados y mejorar el proceso de mecanizado, los parámetros de corte, la herramienta de corte y el sistema de lubricación/refrigeración utilizados durante la operación de corte, juegan un papel importante [43-45]. El aumento de la productividad en el mecanizado se puede lograr utilizando velocidades de corte, avances y profundidades de corte más altas.

Sin embargo, con las aleaciones de titanio el incremento de los parámetros de corte es un reto debido al desgaste severo de la herramienta y las alteraciones en la microestructura y dureza de la superficie mecanizada que conducen a un mal acabado superficial [46]. Considerando la dificultad del mecanizado de las aleaciones de titanio, se recomiendan velocidades de corte más bajas para satisfacer la sostenibilidad [47] y los criterios económicos [48].

1.3. Sistemas de lubricación y refrigeración en el mecanizado de aleaciones de titanio

Para un mecanizado eficiente de las aleaciones de titanio es necesario el uso de sistemas de lubricación y refrigeración [49] que permitan disminuir las altas temperaturas alcanzadas durante el proceso de corte, lubricar la zona de contacto entre la herramienta y la pieza, así como evacuar las virutas metálicas de la zona de corte, aumentando así, la vida útil de la herramienta y mejorando la calidad de la pieza final. Sin embargo, el uso de fluidos de corte conlleva mayores costes de mecanizado y problemas medioambientales. Alrededor del 17% del coste de cualquier producto está relacionado con el fluido de corte, y cerca del 80% de las enfermedades de la piel se deben a la niebla y los humos generados por los fluidos de corte [50]. Además, los procesos de almacenamiento, de mantenimiento y de eliminación adecuada del fluido de corte usado suponen un aumento de los costes totales de producción.

El concepto de fabricación sostenible ha adquirido gran interés dentro de la comunidad internacional debido a la preocupación por el cambio climático y las regulaciones cada vez más estrictas impuestas por los acuerdos internacionales. Las empresas están explorando nuevas soluciones para reducir o eliminar completamente los fluidos de corte convencionales a favor de tecnologías más eficientes, menos contaminantes y más económicas [51]. Algunas de las soluciones más interesantes, desarrolladas recientemente, son el mecanizado en seco, el mecanizado con mínima cantidad de lubricante o MQL (del inglés, Minimum quantity lubrication), los sistemas de refrigeración gaseosa y criogénica, los fluidos de corte sostenibles y combinaciones de ellas.

Se ha demostrado que la eliminación o reducción de la cantidad de fluido de corte mediante el mecanizado en seco o el MQL puede ofrecer ventajas significativas en algunas operaciones de corte de aleaciones de aluminio y acero. Sin embargo, en el mecanizado de aleaciones de titanio, la ausencia total de fluido de corte disminuye la disipación del calor y no permite la evacuación de las virutas o partes del material de la pieza de trabajo, lo que hace que queden adheridas en la herramienta. En consecuencia, se produce un desgaste severo y prematuro de las herramientas y un peor acabado superficial de la pieza [52,53].

El mecanizado con MQL consiste en aplicar una cantidad mínima de fluido en forma de gotas de aceite o una mezcla de aire-aceite en la zona de corte. Los fluidos de corte suelen tener aceite mineral como compuesto mayoritario, aunque hay una tendencia a mejorar su sostenibilidad mediante el uso de alcoholes grasos, aceites vegetales o ésteres sintéticos. El sistema MQL es una alternativa prometedora a la sustitución de los fluidos convencionales [54], aunque debido a la baja capacidad de refrigeración del aceite, es necesario seleccionar adecuadamente los parámetros de corte [55], especialmente en el mecanizado de materiales como el titanio, donde la disipación de calor es primordial [56].

La energía térmica transferida a la pieza de trabajo se puede reducir mediante el uso de refrigeración gaseosa, como el aire comprimido [57], o la refrigeración criogénica con nitrógeno líquido (LN_2) o el dióxido de carbono líquido (CO_2) [58]. El fluido se aplica en la zona de corte, absorbe el calor generado y se evapora, sin dejar ningún residuo contaminante en la pieza, en las virutas ni en la máquina-herramienta. Además, el flujo del fluido a presión ayuda a romper las virutas, retirarlas de la zona de corte y recogerlas en forma seca [4]. Sin embargo, la capacidad de lubricar la superficie es menor a otros sistemas de lubricación y refrigeración [56].

Al combinar distintos sistemas de refrigeración/lubricación, se consigue una mejora en el proceso de mecanizado. Por ejemplo, sistemas híbridos de MQL con aire comprimido frío o CCA (del inglés, Cold compressed air) se benefician del poder de lubricación de aceite y de la capacidad de disipar el calor del aire frío comprimido. A pesar de las nuevas alternativas, la industria sigue demandando fluidos de corte para el mecanizado de aleaciones de titanio, donde aún se requiere su uso.

1.4. Fluidos de corte

La elección del fluido de corte es de suma importancia para reducir la fricción y mitigar el desgaste de las herramientas, disminuir la temperatura en la zona de corte y evacuar las virutas. Además, los fluidos de corte deben cumplir los siguientes requisitos:

- No deben ser ni tóxicos ni irritantes.
- No deben ser corrosivos para ninguna parte de la máquina-herramienta, ni sistemas de distribución del fluido, ni de la pieza.
- Deben ser compatibles con la pintura y los elastómeros.
- No deben producir espuma ni aerosoles.
- Deben ser estables a lo largo del tiempo, inhibiendo el crecimiento de microorganismos.
- Debe minimizarse el arrastre del fluido con las virutas.
- No debe dejar residuos para una inspección rápida y su olor no puede ser desagradable.
- Fácil tratamiento del residuo.

Para cumplir con las exigencias de la industria, la mayoría de los fluidos de corte están compuestos por un fluido base, que es la sustancia mayoritaria, al que se le añaden aditivos para alcanzar propiedades específicas. Hay una gran variedad de fluidos base que pueden usarse como alternativas a los aceites minerales, entre los más utilizados se encuentran los aceites vegetales, las polialfaolefinas, los polialquilenglicoles y los ésteres. Teniendo en cuenta la composición de los fluidos de corte, se pueden clasificar en fluidos basados en aceite y fluidos basados en agua.

Los fluidos de corte basados en aceite son productos que se usan directamente, sin diluirlos en agua. Gracias a su elevado contenido de aceite, tienen una elevada capacidad de lubricación y protegen las superficies contra la corrosión. Sin embargo, su capacidad de refrigerar es relativamente baja. Estos tipos de fluido de corte suelen ser más efectivos en procesos de mecanizado con bajas velocidades de corte.

A diferencia de estos, los fluidos de corte basados en agua, también conocidos como taladrinas, tienen mayor poder de refrigeración [59]. Los fluidos de corte basados en agua se suministran en forma concentrada y se diluyen a una concentración del 3-10% en agua para su uso [60]. Las taladrinas pueden clasificarse según su contenido en aceite en: emulsiones y soluciones [61]. Por un lado, las emulsiones se obtienen mezclando agua, aceite y aditivos. El aceite funciona como lubricante, reduciendo la fricción entre las superficies de fricción, mientras que la fase acuosa ayuda a evacuar el calor generado debido a su mayor capacidad calorífica [62]. Por otro lado, las soluciones no contienen aceite y están formados por mezclas de varios aditivos solubles en agua, como agentes anticorrosivos o antiespumantes. Forman una solución transparente o translúcida y proporcionan un mayor efecto de refrigeración debido a su alto contenido en agua [63].

En el mecanizado de aleaciones de titanio, generalmente se usan fluidos de corte basados en agua, debido a la necesidad de refrigerar la zona de corte [26]. Debido a la presión de las regulaciones gubernamentales y a la creciente tendencia social hacia un mundo más sostenible, los usuarios finales están exigiendo una mayor eco-eficiencia de estos productos para poder trabajar con materiales más avanzados y mejorar la sostenibilidad de sus procesos de mecanizado [20]. Esto repercute en un aumento del uso de lubricantes renovables y biodegradables. En los últimos años, ha habido un interés creciente en el uso de aceites vegetales como fluido base para la formulación de lubricantes, como alternativa a los aceites minerales que, a su vez, ha dado lugar a un mayor interés en investigar su potencial como fluidos de corte [64].

Los aceites vegetales tienen excelentes propiedades de lubricidad, biodegradabilidad, características viscosidad-temperatura y baja volatilidad. El impacto medioambiental de los aceites vegetales es menor que el de los aceites minerales. El análisis comparativo del ciclo de vida de los fluidos de corte base aceite mineral y de fuentes renovables para operaciones de mecanizado, muestra la gran reducción del potencial de calentamiento global o GWP (del inglés, Global-warming potential) de los fluidos de corte renovables (Figura 1) [65]. Aunque su precio es significativamente más alto [66], con la tendencia actual a minimizar el uso de lubricante (con MQL), este factor es menos relevante. Sin embargo, sus limitaciones en el rendimiento de estos productos se derivan de las propiedades inherentes del aceite vegetal, como su baja estabilidad térmica y oxidativa [67].

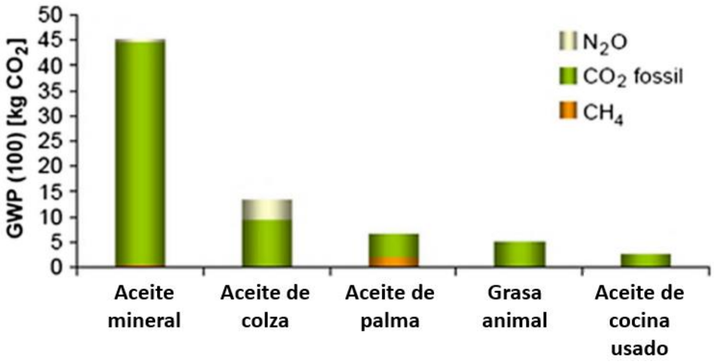


Figura 1. Potencial de calentamiento global (GWP) asociado a distintos fluidos de corte.

Estos inconvenientes pueden ser abordados, por ejemplo, mediante el uso de ésteres sintéticos. Los fluidos base éster han atraído un gran interés tanto de los investigadores como de la industria por su excelente lubricidad [68,69]. Además, los ésteres sintéticos tienen un buen comportamiento en una amplio rango de temperaturas, tienen un índice de viscosidad alto, proporcionan protección contra la corrosión y tienen una alta estabilidad oxidativa [70,71]. Generalmente, los ésteres sintéticos cumplen los requisitos de biodegradabilidad y toxicidad acuática, aunque tienden a ser menos fácilmente biodegradables que los lubricantes a base de aceite vegetal [72].

El éster se adsorbe a la superficie metálica con el extremo polar, orientando la parte hidrocarbonada (ácidos grasos) lejos de la superficie, permitiendo, de este modo, la formación de una película lubricante (Figura 2). En general, la adsorción en la superficie metálica depende de la estructura química del éster, factores tales como la polaridad, la longitud de la cadena y la ramificación de los ácidos grasos, [73] e influye fuertemente en su rendimiento tribológico [74,75]. Por ejemplo, al incrementar los grupos funcionales polares, aumenta la cohesión de la película lubricante en la zona de contacto metálico, mejorando así su eficacia para reducir el desgaste [76]. Las moléculas de éster son más polares que los aceites minerales y, por lo tanto, experimentan interacciones más fuertes con otras moléculas polares (aditivos), así como con las superficies metálicas de los elementos de la máquina [77].

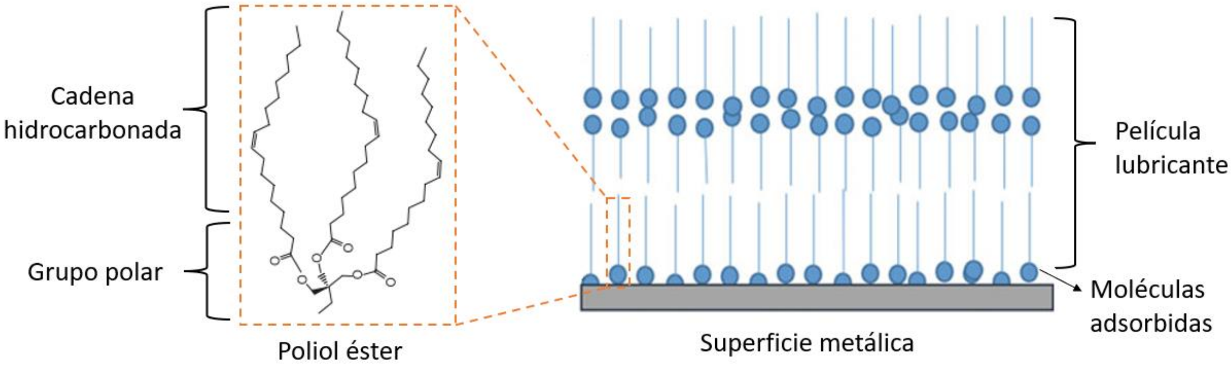


Figura 2. Mecanismo de formación de la película lubricante sobre la superficie metálica.

Al diseñar un fluido de corte sostenible, se presta atención principalmente al fluido base que es el compuesto mayoritario. Sin embargo, algunos aditivos también son considerados toxicológicamente y ecológicamente inaceptables y, por lo tanto, deben excluirse de las formulaciones de lubricantes [78]. Los aditivos son compuestos químicos que se agregan en pequeñas cantidades cuyo objetivo es mejorar las propiedades del lubricante base. Entre los más comunes se encuentran los tensoactivos, los inhibidores de la corrosión, los agentes antidesgaste y extrema-presión, los antiespumantes, los biocidas y los fungicidas. En los últimos años, ha aumentado las restricciones regulatorias en torno al uso de parafinas cloradas, aminas secundarias, ácido bórico y biocidas, especialmente los liberadores de formaldehído [20]. En esta Tesis Doctoral se investiga el comportamiento de distintos compuestos para la formulación de taladrinas para el mecanizado de aleaciones de titanio. Si bien la variedad de aditivos empleados en la industria es muy extensa, este trabajo se centra en los ésteres de poliol, los tensoactivos y los inhibidores de corrosión.

1.5. Justificación de la unidad temática de la Tesis Doctoral

Esta Tesis Doctoral surge de la necesidad de encontrar un fluido de corte eco-eficiente para aleaciones difíciles de mecanizar como son las aleaciones de titanio. De forma simplificada, se pueden definir tres grandes objetivos de la ecoeficiencia [79]:

- Reducir el consumo de recursos: minimizar el uso de energía, materiales, agua y tierra, mejorar la reciclabilidad y la durabilidad del producto.
- Reducir el impacto en el medioambiente: minimizar las emisiones atmosféricas, las aguas residuales, la eliminación de residuos y de sustancias tóxicas, así como fomentar el uso sostenible de los recursos renovables.
- Aumentar el valor del producto: proporcionar mayores beneficios a través de una mejora del rendimiento del fluido, haciendo aumentar la productividad del proceso.

Debido al aumento del uso de aleaciones de titanio, concretamente de Ti6Al4V y las limitaciones de procesar las aleaciones de γ-TiAl, es necesario el diseño de nuevos fluidos de corte sostenibles que permitan mejorar la calidad de la pieza y alargar la vida de la herramienta. Hasta ahora, se han realizado pocos estudios sobre la formulación de fluidos de corte solubles en agua efectivos con aleaciones de titanio [80-82]. Este trabajo proporciona un estudio detallado sobre los fluidos de corte eco-eficientes, desde la selección de sustancias utilizadas como materia prima para producir lubricantes sostenibles hasta la formulación del producto, así como el análisis del torneado de aleaciones de titanio usando distintos sistemas de lubricación y refrigeración.

La cuidadosa selección de las sustancias para formular el fluido de corte eco-eficiente se realiza teniendo en cuenta tanto los criterios para proteger la salud humana y el medioambiente, así como los criterios técnicos y la disponibilidad industrial del producto. El análisis exhaustivo de las materias primas permite identificar las alternativas disponibles a los aceites minerales y otras sustancias peligrosas como el ácido bórico. Cada sustancia tiene una o varias funciones dentro de la fórmula del producto y la interacción entre ellos puede modificar la capacidad de formar la película lubricante y, por lo tanto, la eficiencia del fluido de corte.

Otro factor que se debe tener en cuenta es la afinidad de las sustancias químicas de los fluidos de corte con las diferentes superficies metálicas. Actualmente, el método heurístico es el más común para el desarrollo de fluidos de corte, es decir, identificar una sustancia alternativa, sustituirla dentro del fluido y comprobar si funciona. Esta Tesis Doctoral estudia el comportamiento tribológico de varias sustancias (ésteres y tensoactivos) de una taladrina con una superficie de Ti6Al4V, mediante una nueva metodología desarrollada para poder identificar las sustancias más eficientes para cada material. Esta metodología proporciona una visión útil a los investigadores y a la industria para diseñar nuevos fluidos de corte eco-eficiente específicos para cada material de trabajo y teniendo en cuenta su estructura química y la competencia o sinergia entre las distintas sustancias para formar una película lubricante.

A continuación, el fluido de corte se diseña teniendo en cuenta aquellas sustancias que favorecen la formación de una película lubricante sobre una superficie de Ti6Al4V. La eficacia del producto se estudia, a nivel de laboratorio con un equipo de roscado, que es muy sensible a las propiedades de lubricación y se compara con un fluido de corte convencional. Posteriormente, se realiza un estudio de mecanizado sobre una aleación de γ-TiAl usando varios parámetros de corte con un torno para simular las condiciones reales de mecanizado. El estudio experimental y el modelo numérico demuestra el potencial de nuevos fluidos eco-eficientes para el mecanizado de aleaciones difíciles de mecanizar.

Finalmente, como alternativa a los fluidos de corte por inundación, el torneado de γ-TiAl se realiza con otros sistemas de lubricación y refrigeración. Los sistemas de lubricación y refrigeración tienen una gran influencia en el mecanizado y hay muy pocos estudios realizados en aleaciones de γ-TiAl para mejorar su eficiencia y optimizar los parámetros. De los distintos sistemas en desarrollo, se seleccionan el mecanizado en seco, el MQL, el aire comprimido frío y el criogénico, por su elevada compatibilidad con el medioambiente. Para el MQL se sustituye el aceite mineral por un lubricante base éster por sus propiedades de renovabilidad y biodegradabilidad. Esta información permite conocer los factores más influyentes y las condiciones óptimas del mecanizado para poder minimizar el desgaste de la herramienta y mejorar el acabado superficial de las aleaciones de titanio.

Capítulo 2. Hipótesis y objetivos

2.1. Hipótesis

Para poder desarrollar un fluido de corte eco-eficiente que represente con rigurosidad el proceso de mecanizado para aleaciones de titanio y presente una complejidad moderada, se consideran las siguientes hipótesis:

- El torneado se considera una de las operaciones más comunes del mecanizado y constituye el grueso de la investigación publicada para el mecanizado de aleaciones de titanio. Es una operación sencilla, es decir, un mecanizado sin dificultades geométricas.
- El material de trabajo es homogéneo. La composición química y la estructura de la aleación de titanio es constante en la pieza de trabajo. El cilindro de γ-TiAl usado para el torneado, tiene una geometría perfecta.
- La eco-eficiencia del fluido de corte se valora por aspectos de sostenibilidad y productividad. Por un lado, como indicadores de sostenibilidad se consideran la biodegradabilidad, la renovabilidad y toxicidad de las sustancias químicas utilizadas para la formulación del fluido. Por otro lado, los indicadores de eficiencia considerados son: la calidad de la pieza (en términos de rugosidad superficial y redondez) y la vida útil de la herramienta.
- Los valores de rugosidad superficial alcanzados deben estar dentro de los valores definidos por los requerimientos de la pieza, en este caso para aplicaciones aeroespaciales. No siempre es mejor que sean mínimos, ya que esto implica, generalmente, un aumento de los costes de producción.
- El diseño del fluido de corte se realiza a nivel de laboratorio con una operación de roscado, con un equipo que es más sensible a la capacidad de lubricación. Al no tener disponibilidad de piezas de γ-TiAl para este equipo, el fluido de corte se diseña con una aleación de Ti6Al4V. Se considera que el fluido de corte eco-eficiente desarrollado es válido para las aleaciones de titanio.
- La composición y las propiedades físicas y químicas de los fluidos de corte pueden variar con el tiempo y pueden verse afectadas por contaminación durante el mecanizado. Para el desarrollo de los fluidos de corte, se considera que el envejecimiento y la contaminación tienen un efecto análogo en el rendimiento de los distintos productos.
- Las propiedades de adsorción superficial del fluido de corte se consideran estables en el tiempo. La formación de la película lubricante se estudia con unas probetas de Ti6Al4V, no con la superficie recién mecanizada.

- Las sustancias que se usan para el desarrollo del fluido de corte son comerciales y de uso industrial. Por ello, los tensoactivos investigados presentan cierta polidispersidad en el grado de etoxilación y en la cadena de hidrocarburos.

2.2. Objetivos

El objetivo fundamental de esta Tesis Doctoral es la investigación y el desarrollo de nuevos fluidos de corte eco-eficientes para el mecanizado de aleaciones de titanio, con un menor impacto medioambiental, mayor seguridad para los trabajadores y un aumento de productividad del proceso. Los enfoques para mejorar la eficiencia y sostenibilidad de los fluidos de corte son [65]: 1) Reemplazar el aceite mineral con fuentes renovables y reducir/eliminar las sustancias peligrosas de los fluidos de corte convencionales y, 2) aumentar el rendimiento del fluido de corte (lubricidad y refrigeración) respecto a los fluidos convencionales.

Los objetivos específicos de la investigación se pueden resumir en:

- Estudiar e identificar sustancias que pueden ser empleadas para formular un lubricante sostenible teniendo en cuenta su valor ambiental, en aspectos de biodegradabilidad, renovabilidad y peligrosidad.
- Desarrollar una nueva metodología que permita estudiar la capacidad de formación de una película lubricante considerando el material de trabajo y las interacciones entre las sustancias del fluido de corte.
- Investigar la influencia de la estructura molecular de los ésteres y de los tensoactivos en las emulsiones aceite en agua sobre la capacidad de formar una película lubricante sobre la superficie metálica.
- Promover la adhesión del éster en la superficie metálica mediante el uso adecuado de tensoactivos, con el fin de mejorar las propiedades de lubricidad y anti-desgaste.
- Reducir el número de iteraciones y reducir el coste de desarrollo de producto mediante el uso de modelos de diseño.
- Obtener un fluido eco-eficiente con un rendimiento igual o superior a los fluidos de corte convencionales y demostrar los beneficios de utilizar fluidos de corte sostenibles como alternativa a los aceites minerales.
- Obtener un fluido para los sistemas de lubricación y refrigeración tipo MQL, basados en éster.
- Evaluar los parámetros de corte en el torneado de γ-TiAl con el fluido de corte eco-eficiente en comparación con un fluido convencional. El estudio considera como variables la velocidad de giro del cabezal, el avance y el tipo de herramienta, y como resultados, la rugosidad superficial, la redondez, el desgaste de la herramienta y la temperatura de corte.
- Investigar los efectos de los parámetros de corte en el mecanizado de γ-TiAl bajo diferentes sistemas de lubricación y refrigeración, mediante el análisis de datos con herramientas de diseño para determinar las condiciones óptimas en las operaciones de mecanizado de aleaciones de titanio.

Capítulo 3. Metodología

Para alcanzar los objetivos descritos, esta Tesis Doctoral se divide en tres etapas distintas (Figura 3). En la primera, se establece un nuevo método para investigar la formación de una película lubricante en la superficie de titanio que permitirá optimizar los esfuerzos de la segunda etapa sobre el desarrollo de los nuevos fluidos de corte eco-eficientes para el mecanizado de aleaciones de titanio. Finalmente, en la tercera etapa se estudia el sistema tribológico en una operación de torneado.

Las publicaciones que constituyen este trabajo describen la metodología seguida en cada una de las etapas, dando sentido y mostrando coherencia a lo largo del desarrollo de la Tesis Doctoral. A continuación, se describen los aspectos claves de la metodología seguida para cada etapa.

Desarrollo de un nuevo método para determinar la formación de una película lubricante

Formulación de un fluido de corte eco-eficiente para aleaciones de titanio

Evaluación de varios sistemas de lubricación/refrigeración para el mecanizado de γ-TiAl

Figura 3. Metodología seguida para alcanzar los objetivos de la Tesis Doctoral.

3.1. Desarrollo de un nuevo método para investigar la formación de película lubricante

En esta Tesis Doctoral se establece un método directo para investigar la interacción de distintas sustancias que componen el fluido de corte y su capacidad de formar una película lubricante sobre la superficie de trabajo. Aunque existen algunos métodos tradicionales para evaluar la composición de una película lubricante sobre una superficie, como la espectroscopía electrónica para análisis químico o ESCA (del inglés, Electron spectroscopy for chemical analysis) o la espectrometría de masas de iones secundarios de tiempo de vuelo o ToF-SIMS (del inglés, Time-of-flight secondary ion mass spectrometry), estos métodos no son cuantitativos. Además, requieren equipos complejos y personal altamente cualificado.

El nuevo método desarrollado combina la técnica de espectroscopía de infrarrojos y el análisis del carbono orgánico total, para determinar la cantidad de éster que queda adherido en una superficie metálica en contacto con una emulsión de aceite en agua. El principio del método científico se basa en la determinación del porcentaje de ésteres de la superficie mediante espectroscopia de reflexión-absorción en el infrarrojo o IRRAS (del inglés, Infrared reflection-absorption spectroscopy), gracias a su pico característico (C=O a una longitud de onda de 1735-1750 cm^{-1}), y en la cuantificación de la película orgánica mediante el análisis del carbono orgánico total de la superficie (Figura 4).

La descripción detallada del método está publicada en el artículo científico "*A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification".* Este método permite evaluar la afinidad de las sustancias químicas utilizadas en los fluidos de corte con diferentes superficies metálicas, pudiendo identificar las sustancias más eficientes para cada material.

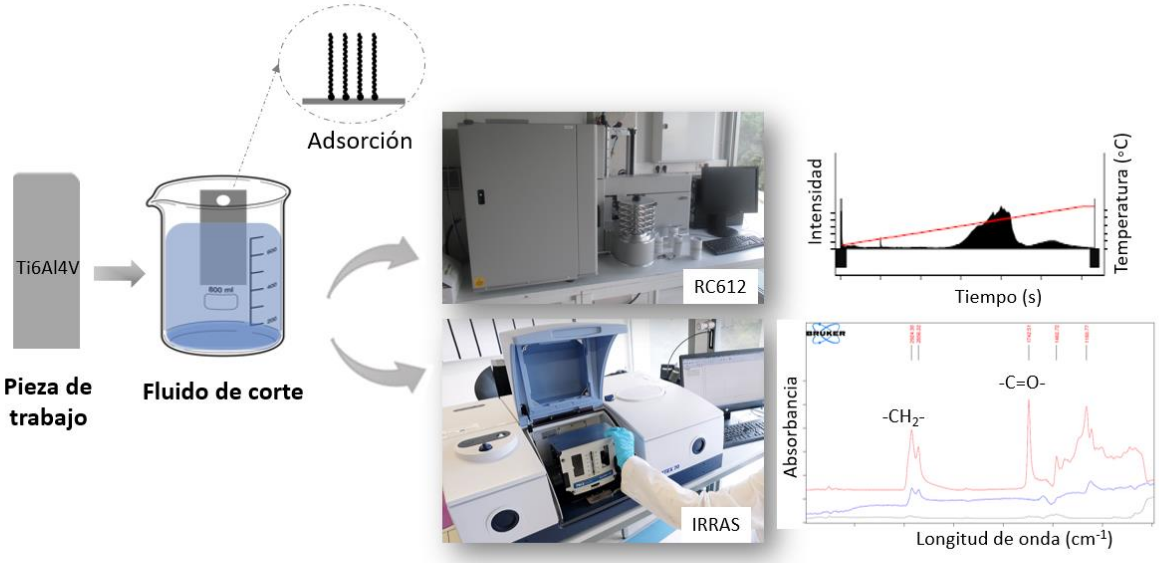


Figura 4. Diagrama de la metodología desarrollada.

3.2. Investigación y desarrollo del fluido de corte para sistemas de inundación

El desarrollo de la fórmula del fluido de corte se divide en varias etapas (Tabla 1). Primero, se hace una selección de sustancias alternativas a los aceites minerales y que minimicen el impacto medioambiental y el riesgo para la salud de los trabajadores. A continuación, se estudia el efecto de la estructura de los tensoactivos y los ésteres en la capacidad de formación de una película lubricante sobre Ti6Al4V para seleccionar la combinación óptima de sustancias que mejoren el rendimiento tribológico. Finalmente, se completa la formulación del fluido de corte para cumplir con todos los requisitos y se estudian sus propiedades.

Tabla 1. Fases de la investigación para el desarrollo de un fluido de corte.

Fases de la investigación	Muestra	Resultado
Selección de las sustancias	Compuesto	Beneficio ambiental
Estudio del tensoactivo	Formula parcial	Función de la sustancia
Estudio del éster	Formula parcial	Función de la sustancia
Formulación completa	Formula completa	Progreso técnico

3.2.1. Selección preliminar de las sustancias

Los fluidos de corte basados en agua, o taladrinas, contienen varias sustancias como tensoactivos, inhibidores de la corrosión, agentes anti-desgaste y extrema-presión, antiespumantes, biocidas y fungicidas. La cuidadosa selección de las sustancias para formular el fluido de corte se realiza teniendo en cuenta los criterios definidos según el Reglamento (CE) n.º 1272/2008 sobre clasificación, etiquetado y envasados de sustancias y mezclas o CLP (del inglés, Classification, labelling and packaging). El Reglamento CLP se basa en el Sistema Globalmente Armonizado de clasificación y etiquetado de productos químicos o GHS (del inglés, Global harmonized system) cuyo objetivo es proteger la salud humana y el medioambiente.

De entre muchos otros agentes lubricantes, los ésteres de poliol han resultado ser muy prometedores como alternativas a los aceites minerales. En la Tabla 2 se muestran las principales propiedades de las sustancias típicas que se usan en los lubricantes sostenibles en comparación con los aceites minerales [83]. La alta biodegradabilidad de los ésteres y su producción a partir de fuentes renovables, reducen aproximadamente cuatro veces la contribución al calentamiento global en comparación a los aceites minerales [84]. Concretamente, esta Tesis Doctoral se centra en los ésteres de poliol obtenidos a partir de la reacción de ácido oleico y alcoholes polihídricos, que son menos susceptibles a la hidrólisis [85].

Tabla 2. Fluidos típicos para lubricantes sostenibles comparados con el aceite mineral.

Propiedad	**Aceite vegetal (canola)**	**Poliol éster**	**PAG (sintetizado de petróleo)**	**Aceite mineral (petróleo)**
Biodegradabilidad	Excelente	Muy buena	Buena	Mala
Toxicidad	Baja	Baja	Baja*	Alta
Lubricación	Excelente	Muy buena	Muy buena	Buena
Estabilidad oxidativa	Mala	Moderada	Buena	Muy buena
Estabilidad térmica	Moderada	Buena	Buena	Buena
Estabilidad hidrolítica	Mala	Moderada	Buena	Muy buena
Precio relativo**	2	4	4	1

**La solubilidad puede aumentar la toxicidad de algunos PAGs*

***Coste comparado con el aceite mineral (1)*

3.2.2. Formulación del fluido de corte

Uno de los factores más importantes para formar una película lubricante con emulsiones de aceite en agua u O/W (del inglés, Oil in water) es la capacidad de las gotas de aceite para mojar la superficie metálica y adherirse a ella. Esto, a su vez, depende del tipo y de la concentración tanto del tensoactivo como del aceite [59]. Para poder conocer el comportamiento de las sustancias dentro del fluido de corte y comprender los efectos sinérgicos o antagónicos entre ellas, se parte de una matriz base simplificada. Esta matriz base se compone, principalmente, de: agua, como fluido para refrigerar, de ácido carboxílico y de una combinación de aminas, para garantizar que el fluido se mantenga dentro del rango de pH entre 8,6 y 9,3. Este rango, ligeramente alcalino, evita la corrosión, minimiza el potencial de dermatitis y controla el crecimiento biológico [86,87]. La concentración del ácido carboxílico y de las aminas que se añaden en la matriz se determina mediante el ensayo de corrosión (descrito en la sección 3.2.3.). Este ensayo permite conocer la concentración mínima necesaria de aditivos protectores de la corrosión que debe tener el fluido para no dañar las superficies.

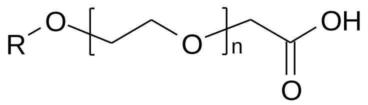
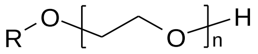
A continuación, se estudia el efecto de la estructura molecular de los tensoactivos para formar una película lubricante con una emulsión O/W. Para ello, se usa una mezcla de dos tensoactivos y un éster de poliol, concretamente, el trioleato de trimetilolpropano, sobre la matriz base (Tabla 3). La mezcla de tensoactivos se compone de un tensoactivo no-iónico, concretamente un alcohol graso propoxilado que ayuda a estabilizar la emulsión, y del tensoactivo de estudio.

Tabla 3. Composición química de las emulsiones (O/W), en concentración molar.

Producto	**Molar**
Éster de poliol	0,0010
Alcohol graso propoxilado	0,0008
Tensoactivo de estudio	0,0012

Para conocer la influencia de la estructura química del tensoactivo en la capacidad de formar una película lubricante, se contemplan tensoactivos de distinta carga (aniónicos y no-iónicos), distinta longitud de cadena de carbonos (R, de C8 a C18) y distinto grado de etoxiliación (EO, de 2 a 10), todos ellos suministrados por Kao Chemicals GmbH. En la Tabla 4 se incluyen las propiedades de cada uno de ellos. Estos fluidos se preparan sin la adición de otros agentes químicos, como extrema-presión o anti-desgaste, para evitar interferencias en los resultados. A continuación, mediante la metodología desarrollada, se estudia cuál es el tensoactivo que promueve la adherencia del éster en aleaciones de titanio y, al mismo tiempo, aporta lubricación.

Tabla 4. Propiedades de los tensoactivos.

Familia química. Carga	**Abreviación**	**Longitud de cadena (R)**	**Número de etoxilación (n)**
Ácidos alquil éter carboxílicos. Aniónico 	AC8E8	C8	8 EO
	AC12E4.5	C12	4,5 EO
	AC12E10	C12	10 EO
	AC18E2	C18	2 EO
	AC18E5	C18	5 EO
	AC18E9	C18	9 EO
Alcoholes grasos etoxilados. No-iónico 	NC8E8	C8	8 EO
	NC12E4.5	C12	4,5 EO
	NC12E10	C12	10 EO
	NC18E2	C18	2 EO
	NC18E5	C18	5 EO
	NC18E10	C18	9 EO

Con la combinación óptima de tensoactivos identificada, se preparan nuevos fluidos de corte, manteniendo constante su concentración molar según la Tabla 3. En este caso, se varía la estructura química del éster de poliol. Los ésteres de poliol, suministrados por Industrial Química Lasem (IQL), se han obtenido a partir de la reacción del ácido oleico con distintos alcoholes. Siguiendo el mismo procedimiento que con los tensoactivos, se estudia la película lubricante formada para identificar el éster que más lubrica y protege la herramienta del desgaste. Esta información, disponible en los artículos correspondientes ("*The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium*" y "*Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys*"), permite identificar la mejor combinación de sustancias que mejoran la capacidad de lubricación del fluido de corte en la matriz base.

Finalmente, se desarrolla el fluido de corte eco-eficiente. Teniendo en cuenta que la mayor parte del fluido de corte es agua, se prepara un producto concentrado que se diluirá al 10% en agua para su uso. Esto permite tener un producto con mayor sustancia activa, un ahorro en costes y transporte, y una menor generación de residuos de envases. Para preparar el producto concentrado, primero se añade monoetanolamina (5,76%), trietanolamina (5,64%) y ácido isononanoico (7,09%) en agua desionizada y se agita. Seguidamente, se añade el alcohol graso propoxilado (13,12%) y el tensoactivo aniónico AC18E9 (10,20%) para reducir la tensión superficial del fluido, pare emulsionar el éster en agua y para mejorar la lubricidad del fluido de corte. El trioleato de trimetilolpropano (6,44%) y un éster fosfatado (12,14%) se adicionan para mejorar las propiedades de anti-desgaste y lubricación. Finalmente, se añade glicol (8,25%) para estabilizar el fluido de corte.

3.2.3. Estudio de las propiedades del fluido de corte

En esta sección, se describen las metodologías usadas para poder caracterizar el fluido de corte a nivel de laboratorio y asegurar que cumple con los requisitos necesarios. El fluido de corte concentrado se diluye al 10% en agua desionizada para estudiar sus propiedades.

a) Lubricidad y desgaste de la herramienta.

Para estudiar las propiedades lubricantes del fluido de corte se hace una operación de roscado, que es muy sensible a la lubricación [88], con el equipo Microtap modelo Labtap 8. Los resultados del Microtap para los fluidos de corte, se correlacionan muy bien con los resultados de los ensayos de taladrado a gran escala, lo que sugiere que este método es un ensayo confiable para el estudio de su rendimiento [89]. Como se observa en la Figura 5, el fluido de corte se introduce en los agujeros de la pieza de trabajo de Ti6Al4V. A continuación, se realiza la operación de roscado a 300 rpm y a una profundidad de 6 mm. El equipo mide el esfuerzo de torsión necesario para hacer la operación durante el mecanizado y se reporta como valor medio en N·m.

Debido al elevado desgaste que sufre la herramienta durante el mecanizado, en cada roscado el valor medio del esfuerzo de torsión aumenta. Estas diferencias entre roscados consecutivos, permite calcular la tasa de desgaste que sufre la herramienta. Para cada fluido de corte, se utiliza una herramienta nueva y con ésta se realizan 15 operaciones de roscado o hasta que la herramienta se rompe.

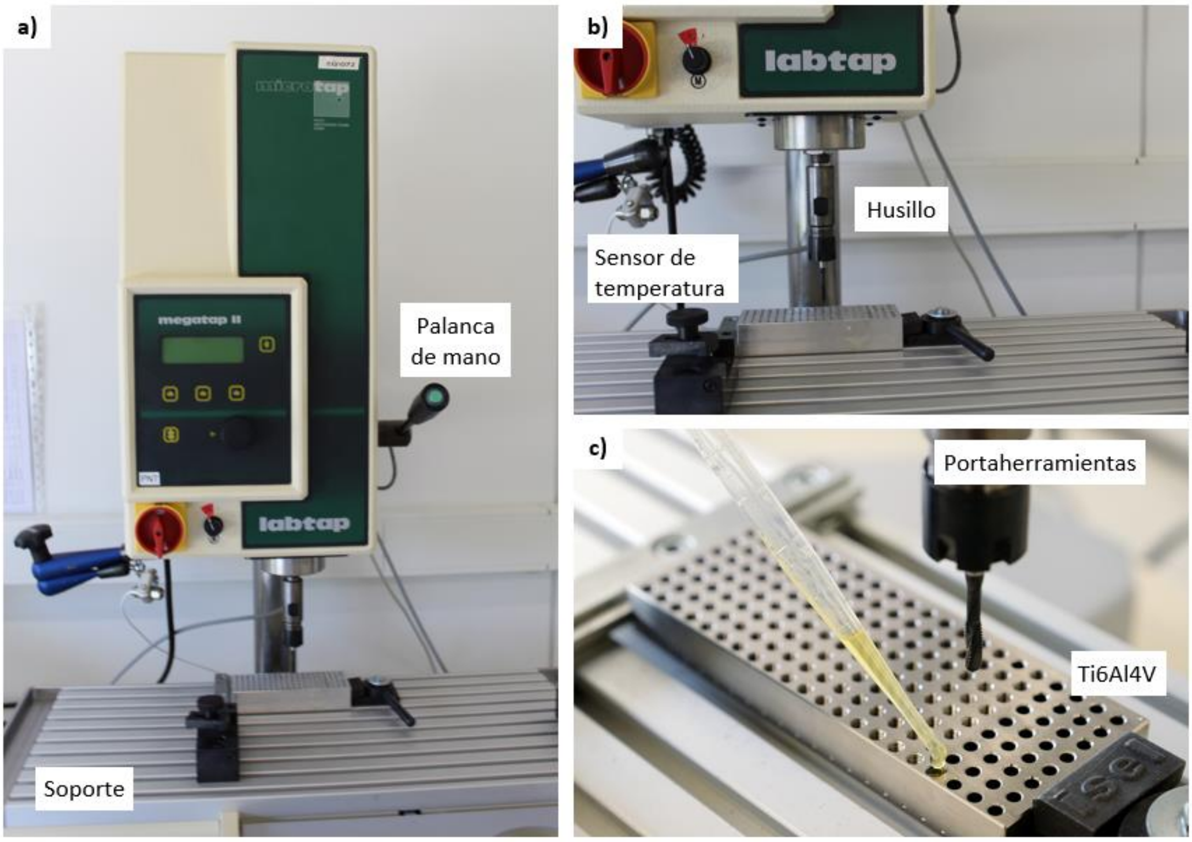


Figura 5. Operación de roscado con una pieza de Ti6Al4V: a) Microtap Labtap 8, b) montaje del sistema con sensor de temperatura y, c) adición del fluido de corte en la pieza de trabajo.

b) Corrosión

Debido al contenido de agua del fluido de corte, se debe evaluar la capacidad que tiene el fluido de corte para proteger las superficies expuestas (máquina-herramienta, equipos de distribución del fluido y la pieza de trabajo) contra la corrosión. Uno de los métodos más usados para su evaluación es el método estandarizado DIN 51360/2. Siguiendo esta norma, se añade el fluido de corte diluido con agua dura (20°dH) a unas virutas de acero sobre un papel de filtro. Transcurridas dos horas, se retiran las virutas y se observa el nivel de protección que proporciona el lubricante contra la corrosión del acero. Si las virutas se han oxidado, se aprecian unas manchas anaranjadas en el papel, que provienen del óxido del acero [90].

c) Espuma

La formación de espuma de los fluidos de corte puede: originar elevados costes de operación debido a la pérdida de fluido, reducir la vida útil de las bombas debido a la cavitación, y reducir el poder de lubricación y de refrigeración del fluido. Hay varios factores a tener en cuenta aparte de la propia composición del fluido de corte como, por ejemplo, la calidad del agua, la presión y la temperatura del fluido, los contaminantes y los sistemas de filtración [91]. Para el estudio de la formación de espuma, se sigue el estándar NFT 60-185:1992 [92]. Este estudio consiste en hacer recircular el fluido de corte por un circuito termostático a 25 °C (Figura 6). El fluido se bombea a 250 ml/h en una probeta graduada que permite medir la formación de espuma.

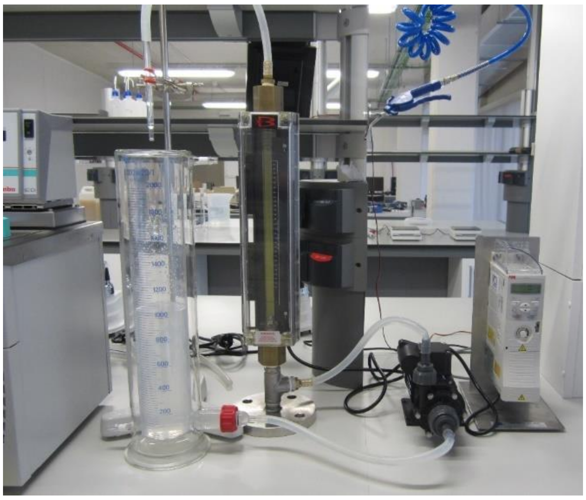


Figura 6. Montaje para el control de espuma según el estándar NFT 60-185:1992.

3.3. Investigación y desarrollo del fluido de corte para sistemas MQL

Los sistemas de lubricación y refrigeración de MQL utilizan fluidos de corte tipo aceites puros gracias a su gran capacidad de lubricación. Los aceites vegetales químicamente modificados y los alcoholes grasos son las alternativas a los aceites minerales más comunes para aplicaciones de MQL. A diferencia de las taladrinas, los aceites puros no necesitan tensoactivos, su tendencia a formar espuma es mucho menor y el propio aceite protege de la corrosión. Sin embargo, su capacidad de refrigeración es menor que las taladrinas.

Para el estudio se usan los ésteres de poliol por su elevada biodegradabilidad, estabilidad oxidativa y disponibilidad. Además, tienen una elevada capacidad de adsorberse en la superficie metálica y formar una película lubricante [70]. Se han elegido distintos ésteres de poliol (Tabla 5) obtenidos por reacción de diferentes alcoholes, para conseguir distintos grados de ramificación, con ácidos grasos de longitud de cadena comprendidas entre C12 y C18. Con las pruebas tribológicas realizadas con el equipo Microtap labtap 8, se selecciona el éster de poliol que tiene mayor capacidad de lubricar y de disminuir el desgaste de la herramienta y que servirá como fluido de corte diseñado para los sistemas de lubricación y refrigeración de MQL.

Tabla 5. Ésteres de poliol para aplicaciones de MQL suministrados por Industrial Química Lasem.

Producto	ALCOHOL	ÁCIDO GRASO
Oleato de isopropilo	Isopropanol	Ácido oleico (C18:1)
Dioleato de neopentil glicol	Neopentilglicol	Ácido oleico (C18:1)
Trioleato de trimetilolpropano	Trimetilolpropano	Ácido oleico (C18:1)
Oleato de pentaeritritol	Pentaeritritol	Ácido oleico (C18:1)
Laurato de isopropilo	Isopropanol	Ácido láurico (C12:0)
Miristato de isopropilo	Isopropanol	Ácido mirístico (C14:0)
Palmitato de isopropilo	Isopropanol	Ácido palmítico (C16:0)
Estearato de isopropilo	Isopropanol	Ácido esteárico (C18:0)

3.4. Sistema tribológico

Una vez desarrollados los fluidos de corte para inundación (EcoMWF) y para MQL, se inicia el estudio en un sistema tribológico. Se comparan los dos fluidos de corte desarrollados con un fluido de corte convencional comercial base aceite mineral, con el mecanizado en seco, con aire comprimido frío y con el mecanizado criogénico con nitrógeno. Todos los ensayos se realizan con un mismo torno paralelo (Pinacho moldeo L-1/200) para eliminar la influencia del tipo de máquina-herramienta. Se utiliza una barra cilíndrica de γ-TiAl para investigar la influencia de los sistemas de lubricación y refrigeración y los parámetros de mecanizado en una operación de torneado horizontal, concretamente de pequeña profundidad de corte como la utilizada en las operaciones de acabado, reparación y/o mantenimiento. La pieza de trabajo utilizada es la aleación Ti-43,5Al-4Nb-1Mo-0,1B de 45mm de diámetro y 250mm de longitud.

El proceso de mecanizado está controlado por una serie de parámetros de operación que tienen un claro efecto sobre el proceso. Por lo tanto, es importante controlar estos parámetros para que el proceso sea más eficiente. Los parámetros de corte se han seleccionado de acuerdo con estudios previos similares, referenciados en la última publicación derivada de esta Tesis Doctoral (“*Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry*”). Además, se describe con detalle la metodología empleada. Por un lado, la velocidad de giro del husillo, el avance y el tipo de herramienta son los parámetros de corte que se varían para estudiar los diferentes sistemas de lubricación y refrigeración. Por otro lado, se incluyen como parámetros de respuesta para analizar los resultados del proceso, la rugosidad superficial y la redondez de la pieza mecanizada, la temperatura de corte y el desgaste de la herramienta (Figura 7).

Figura 7. Operación de torneado como sistema tribológico.

Los experimentos se realizan a dos velocidades de avance (0,14 y 0,28 mm/rev), dos velocidades de giro del husillo (500 y 800 pm), mientras que la profundidad de corte (0,03 mm) y la longitud de mecanizado (120 mm) se mantienen constantes. Las herramientas utilizadas son de carburo cementado sin recubrimiento y de carburo cementado con recubrimiento por deposición física de vapor (PVD) de Seco Tools, con referencias de fabricante CNMG120408-M1-883 y CNMG120408-M1-TS2500 PVD respectivamente. Para cada experimento se utiliza un filo nuevo del inserto. Finalmente, una vez realizados todos los experimentos se lleva a cabo el análisis de datos. Para investigar el efecto de los parámetros de proceso en el resultado de la operación, se utiliza un software de diseño de experimentos (DOE). Este programa sirve tanto para evaluar los resultados del proceso como para comprender las relaciones con los parámetros de operación.

Capítulo 4. Publicaciones

Como resultado de las investigaciones desarrolladas en esta Tesis Doctoral por Compendio de publicaciones, se han realizado cuatro artículos publicados en revistas científicas cuyo índice de impacto se encuentra incluido en la relación de revistas del *"Journal citation reports"* (JCR). El conjunto de las publicaciones cumple con los requisitos definidos en:

- El documento regulador aprobado por el Comité de Dirección de la Escuela Internacional de Doctorado de la Universidad Nacional de Educación a Distancia (EIDUNED), en su reunión de 16 de enero de 2017, y por la Comisión de Investigación y Doctorado de la UNED, con fecha 21 de febrero de 2017.
- El Anexo del Programa de Doctorado en Tecnologías Industriales, a la regulación sobre Tesis por compendio de publicaciones, de la EIDUNED, aprobado por la Comisión Académica en reunión celebrada el 8 de abril de 2021.

El primer trabajo, "*A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification* ", define la metodología novedosa desarrollada que permite conocer la capacidad de distintas sustancias en formar una película lubricante. Gracias a ello, se ha estudiado la influencia de los tensoactivos y de los ésteres en las taladrinas, descrito en la segunda y tercera publicaciones: "*The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloy*" y "*Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys*".

Por último, recientemente se ha publicado el resultado del estudio de los fluidos de corte eco-eficientes desarrollados y otros sistemas de lubricación y refrigeración para el mecanizado de aleaciones de titanio, en el artículo "*Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry*".

En las siguientes secciones, se aporta un resumen de cada una de las publicaciones incluyendo el título de la publicación, los autores, la referencia completa de la revista, los indicios de calidad (factor de impacto y cuartil), las aportaciones de la doctoranda y la copia completa de la publicación.

4.1. A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification

A continuación, se presentan los detalles de la publicación (Tabla 6), las aportaciones de los autores y una copia completa de la publicación. Los indicios de calidad de este artículo pueden encontrarse en el Apéndice A.

Tabla 6. Datos de la publicación e indicios de calidad de *A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification.*

Título	**A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification**	
Autores	Elisabet Benedicto, Diego Carou, Eva María Rubio, Laura Batlle	
Revista	Tribology International	
ISSN	0301-679X	
Editorial	Elsevier Sci Ltd	
País	Reino Unido	
Volumen	128	
Páginas	155-160	
Fecha	2018	
doi	10.1016/j.triboint.2018.07.020	
Indicios de calidad	**Factor de impacto**	**3,517** (JCR-2018) 3,246 (JCR-2017)
	Posición en el ranking	**Q1** (18/133, Engineering, Mechanical, JCR-2018) Q1 (16/133, Engineering, Mechanical, JCR-2017)

En esta publicación se describe un nuevo método directo desarrollado, basado en la espectroscopia de reflexión-absorción en el infrarrojo (IRRAS) y en el análisis elemental de carbono para la determinación cuantitativa de ésteres de ácidos grasos en una superficie de Ti6Al4V. El nuevo método consiste en el análisis de los espectros infrarrojos y en la cuantificación de carbono orgánico de una placa de Ti6Al4V tratada con una emulsión de tensoactivos y ésteres ajustada a pH 9,2 con 2-aminoetanol. Los resultados muestran que la cantidad de éster que se adhiere a la superficie metálica depende de la concentración de éster y de tensoactivo. Las señales analíticas corresponden al valor de la integral de las señales CH_2 y CO de los espectros infrarrojo y al contenido de carbono. La principal ventaja del método propuesto es que el análisis realizado directamente sobre la superficie del metal permite conocer la capacidad de una emulsión para formar una película orgánica. El método puede ser útil para la investigación y el desarrollo de taladrinas más respetuosas con el medioambiente para la industria del metal.

Se trata de un trabajo de coautoría. Las aportaciones de cada uno de los autores son las siguientes:

- Elisabet Benedicto: conceptualización, metodología, validación, análisis formal, investigación, recursos, tratamiento de datos, redacción del borrador original, redacción de la revisión y edición.
- Diego Carou: conceptualización, análisis formal, redacción de la revisión y edición, supervisión.

- Eva María Rubio: conceptualización, análisis formal, redacción de la revisión y edición, supervisión, administración del proyecto, adquisición de fondos.
- Laura Batlle: metodología, validación, análisis formal, recursos y tratamiento de datos.

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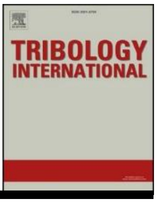

A novel method for the determination of fatty acid esters in aqueousemulsion on Ti6Al4V surface with IRRAS and carbon quantification

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ABSTRACT

A novel direct method based on infrared reflection absorption spectroscopy (IRRAS) and carbon elemental analysis has been developed for the quantitative determination of fatty acid ester on Ti6Al4V surface. The new approach involves the IR spectra and carbon analysis of a Ti6Al4V strip treated with a surfactant and ester emulsion adjusted to pH 9.2 with 2-aminoethanol. The results are dependent on the ester and surfactant concentration. The analytical signals are the integral value of the CH2 and CO signals of the IR spectra and the carbon content. The main advantage of the proposed method is that the analysis made directly on the metal surface allows knowing the film forming ability of the emulsion. The method may be useful for re- search and development of more environmentally friendly water-based metalworking fluids for the metal industry.

1. Introduction

The advantages of titanium, such as its high mechanical strength, low density and excellent corrosion resistance make it an attractive material for the aeronautical sector. Ti6Al4V constitutes the major part of the production of all currently available titanium alloys used, representing the 50% of all titanium alloys produced [1]. However, it is adifficult-to-cut-material. Its low machinability is associated with its inherent characteristics, such as low thermal conductivity, low modulus of elasticity compared to other high strength alloys, and high chemical reactivity at high temperatures [2]. Due to the thermal properties of titanium and its alloys, the application of lubrication/cooling systems is extremely important [3]. In titanium machining, water-based cutting fluids are generally used due to the excellent cooling effect of the water [4]; they are diluted at a concentration of 3–10% in water [5] for direct use in the machining operation. Challenges in the formulation of cutting fluids continues to increase as end users are demanding better performance over longer periods and under more severe conditions [6]. Efforts have been placed on replacing conventional mineral oil [7].

In metalworking, oil-in-water (O/W) emulsions are widely used to lubricate and remove heat from the cutting zone. Dispersion of oil droplets in water and their transport to the cutting surface controls lubricity [8]. Oil works as lubricant, reducing the friction coefficient, whereas water removes the heat generated in the cutting zone. Ester based fluids have attracted broader interests from both, academic re- searchers and from industrial users to replace mineral oil due to their high polarity and excellent lubricity in the boundary lubrication zone [9]. The most common esters in water-soluble cutting fluids are isopropyl oleate, isobutyl stearate, neopentyl glycol dioleate and trimethylolpropane derivatives, which are highly resistant to hydrolysis [10]. The ester is adsorbed to the metallic surface with the alcohol part located closer to the metal surface, whilst the fatty acid hydrocarbonchain is oriented away from the metallic, thus allowing a layer film formation. Therefore, the fatty acid chain offers a sliding surface that prevents direct metal-to-metal contact [11]. Under the extreme pressure condition, maximum load-bearing capacity has been found usingesters, by retaining quality without breakdown compared to mineral oil [12].

The composition of the metalworking fluid is clearly related to its lubricating performance, which is a topic of continuous development [13]. An effective O/W emulsion in terms of film formation should maximize the tendency of oil droplets to wet solid surfaces. The

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wettability is strongly linked to the type and concentration of the surfactant used and also to the pH value of the solutions [14]. Surfactants are used to stabilize ester droplets in the aqueous continuous phase due to its amphiphilic molecular structure with a hydrophobic tail and hydrophilic head [15]. As the surfactants have both hydrophobic and hydrophylic groups, the surfactant molecules tend to adsorb on the solid surface as the surface is immersed in surfactant aqueous solution [16]. The presence of surfactant and other polar compounds could reduce the adsorption of esters through natural competition [17].

Brinksmeier et al. [18] have studied some of the techniques that are used for the characterization of surface chemical composition and atomic and electronic structure. Some traditional methods for identifying the fatty acid ester adhered on a metal surface are Electron Spectroscopy for Chemical Analysis (ESCA) based on the photoelectric effect and Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). TOF-SIMS is a non-quantitative analysis where the main difficulty lies on the need of coupling with other complex techniques as X-ray Photoelectron Spectroscopy (XPS) [19]. However, these methods need high complex equipment with highly qualified workers and they are not quantitative.

In recent years, many researchers have focused on physical properties of ester such as viscosity index, viscosity, pour point, and oxidative stability, but there is little research on the tribochemical properties of esters [20]. In general, esters have a high wetting tendency resulting in reduced friction with at least equal and often higher tool life [21]. The results from these measurements are reported, and the correlation between thermal properties, molecular structure, and the test fluid rheological parameters are discussed [22]. However, more studies are needed to evaluate the performance of these esters when formulated with environmentally adapted compatible lubricants [23]. Other studies have been focused on the effect of emulsifier concentration on lubricating properties of O/W emulsions by surface and interfacial tension measurements, contact angle measurements and droplet size distribution, predicting the film forming ability of emulsions. These parameters have shown relationship with the lubricating behaviour [13].

To the best of our knowledge, the ester in O/W emulsions has been barely studied and no research publication is available on the quantification of ester adhered on titanium alloys. This research is aimed to fill this gap. In this paper, the fatty acid ester and the surfactant con- centration were investigated to understand the usefulness of the method in order to evaluate ester adhesion in Ti6Al4V. Trimethylolpropane trioleate and a blend of two surfactants were used in this study. Furthermore, quantitative measurement was done to investigate changes in the amount of ester adhered; varying the concentration of ester and surfactant and modifying the surfactant: ester ratio. Finally, the milligrams of carbon from ester and other organic compounds adhered on the Ti6Al4V strip are quantified. This method can be used to optimize the use of raw materials on environmentally friendly water-based metalworking fluids.

2. Experimental

2.1. Materials and mix proportions

A commercially available trimethylolpropane trioleate or TMP oleate (Weichol 3/134 W from Industrial Química Lasem), commonly used as environmentally compatible base fluid [24] was used as fatty acid ester in the study. 2-aminoethanol (MEA), non-ionic surfactant (Dehypon OCP502 from BASF) and anionic surfactant (Akypo LF2 from Kao Chemicals GmbH) were used to prepare the aqueous emulsions in distilled de-ionized water (DDW). All the potentially present species (ester, 2-aminoethanol and surfactants) have to be analysed with Infrared Reflection Absorption Spectroscopy (IRRAS) separately in order to build a list of characteristic peaks. These analyses are performed on the substrate of interest, Ti6Al4V.

The mix proportion (by mass) used to prepare the samples are specified in Table 1. It is needed a mixture of anionic and non-ionic surfactant to provide better emulsion stability [25]. Two different approaches were used in this research: (i) equivalent surfactant and ester proportion at three different concentrations, and (ii) same surfactant concentration but varying the ester amount. Different anionic and ester concentrations between 1 and 3 wt % were mixed and analysed with the base emulsion at pH 9.2. The representative additives and their concentrations were selected based on general metalworking fluid formulation used in previous studies [26,27].

2.2. Sample preparation and analysis

To obtain chemical information on the absorbed products at the surface of the metal strip, it was necessary to clean and remove previously the protective oil layer with hexane. The cleaned metal strips were dip in the test emulsion for 10 min at 25 °C with a magnetic stirrer. Metal strips were not rinsed with water after being in contact with the emulsion, as in metalworking industry, cutting fluids do not go through a rinsing process during machining process. Otherwise, the concentration on the surface would be diluted either cleaned and, at the same time, surfactant concentration would be modified. For each emulsion, five strips were used for carbon determination and three for IRRAS evaluation.

A multi-phase carbon and water determination instrument (RC612, Leco, Fig. 1) was used to measure the carbon content of the samples treated with the different emulsions. Immediately after the treatment of the strips, they were evaluated with RC612 at an isotherm at 550 °C with nitrogen as carrier gas. The readings were expressed in milligrams (mg) of C.

Spectra were taken by IRRAS (Vertex 70, Bruker, Fig. 2). The instrument is equipped with a specular reflectance accessory and the sample and detector chambers were purged with nitrogen gas before starting the experiments. The spectral analysis was carried out using OPUS 7.5 version software. Prior to the IRRAS evaluation, the incident

Table 1

Chemical composition of emulsions to treat the Ti6Al4V strip, in percentage of active matter and molar concentration.

AM (%)	1:0	1:1	2:0	2:1	2:2	3:0	3:1	3:2	3:3
DDW	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
TMP oleate	–	1.000	–	1.000	2.000	–	1.000	2.000	3.000
MEA	0.080	0.080	0.090	0.090	0.090	0.100	0.100	0.100	0.100
Dehypon OCP 502	0.400	0.400	0.800	0.800	0.800	1.200	1.200	1.200	1.200
Akypo LF2	0.600	0.600	1.200	1.200	1.200	1.800	1.800	1.800	1.800
Molar (M)									
TMP oleate	–	0.012	–	0.012	0.024	–	0.012	0.024	0.036
MEA	0.013	0.013	0.015	0.015	0.015	0.015	0.016	0.016	0.016
Dehypon OCP 502	0.008	0.008	0.016	0.016	0.016	0.024	0.024	0.024	0.024
Akypo LF2	0.011	0.011	0.022	0.022	0.022	0.033	0.033	0.033	0.033

Fig. 1. Multi-phase carbon determination instrument (RC612, Leco).

Fig. 2. Infrared reflection absorption spectroscopy (Vertex 70, Bruker).

angle for Ti6Al4V surface evaluation was optimized at 75° from the normal surface. Incident angles of 70°, 75° and 80° were compared, and spectrum at 75° showed the most enhanced intensity peaks.

Before sample measurements, a cleaned metal strip was taken as a reference. In addition, the prepared samples for IRRAS evaluation were dried in an oven for 2 h at 40 °C. During the drying process in the oven, metal strips were set vertically in order to remove the excess of ester and surfactant of the surface. Three measures of each sample were made at different strip points.

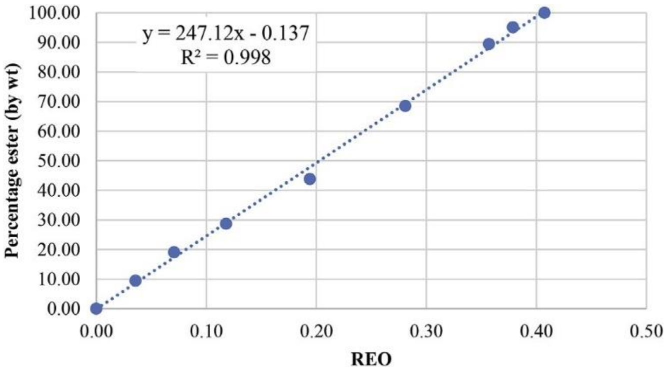

Fig. 4. Calibration Curve. REO (integrated area ratio between C=O and CH2 stretching vibration peaks) against the weight percentage of ester.

Machining performance was measured with the emulsions using a tapping torque test system (Microtap labtap G8) at a machining speed of 300 rpm on Ti6Al4V workpieces. The performances reported as tapping torque (N·cm), with higher values indicating lower metalworking performance.

3. Results and discussion

3.1. Characterization of IRRAS spectra

Fig. 3a shows the IRRAS spectra of a layer of TMP oleate adsorbed on a Ti6Al4V substrate. It shows absorption bands at 2925 and 2850 cm^{-1} which arise from the antisymmetric (d−) and the symmetric (d+) methylene (-CH2-) group stretching vibrational modes, respectively. Moreover, an absorption band appears at 1745 cm^{-1}, which can be attributed to the presence of ester (-C=O-) group on the metal strip, as it is proven when observing the IR spectrum of bulk TMP oleate (Fig. 3c).

A ratio (REO) is defined as the ratio between the integrated absorbance under C=O peak (1735-1750 cm^{-1}) and integrated absorbance under CH2 stretching vibration peaks (2850-2925 cm^{-1}). For the metal strip sample, the REO was calculated using IRRAS and the weight percentage of ester was evaluated through the calibration curve described in Fig. 4. For building up the calibration curve, solutions of known ester concentration were analysed using Fourier transform

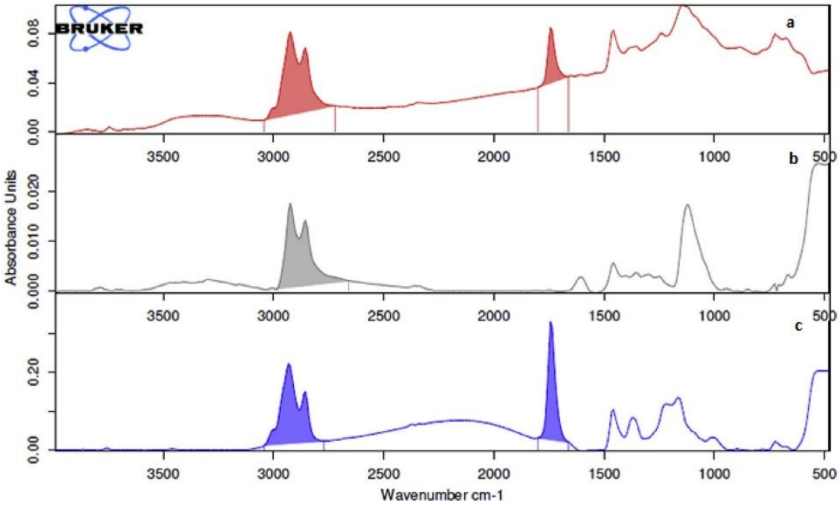

Fig. 3. IRRAS spectra of a Ti6Al4V strip treated with: a) surfactant system emulsion with ester at ratio 1: 2, b) surfactant system solution without ester, and c) 100% bulk TMP oleate.

Table 2
REO values measured by IRRAS and weight percentage of ester on the Ti6Al4V surface calculated from the calibration curve for different surfactant and ester concentration.

Formula	1:0	1:1	2:0	2:1	2:2	3:0	3:1	3:2	3:3
REO	0.002	0.168	0.031	0.172	0.272	0.019	0.149	0.155	0.197
% ester (w/w)	0.4	41.3	7.4	42.4	67.1	4.6	36.7	38.1	48.5

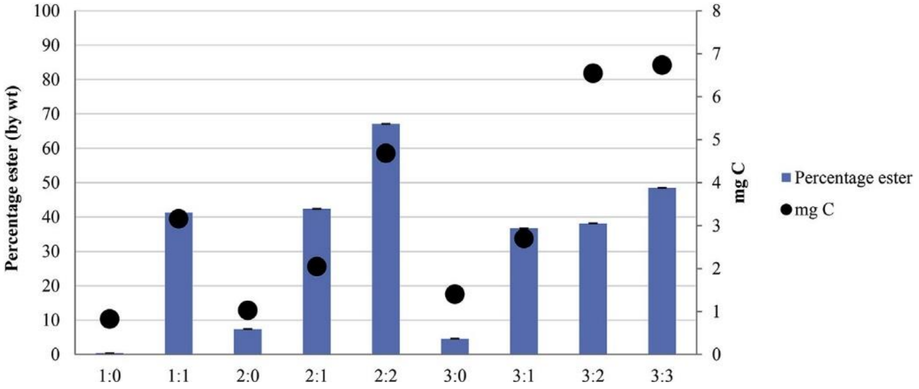

Fig. 5. Weight percentage of ester and total organic carbon (mg) adhered on the Ti6Al4V surface for different surfactant and ester concentration.

infrared spectrophotometry (FTIR). Measurements were done with FTIR (Shimadzu, Iraffinity-1S CE). Then, REO has been calculated and plotted against the percentage of ester in each solution. The equation of the regression line is given by: % ester = – 0.137 + 247.12 REO, with a correlation coefficient of 0.998, indicating that REO can provide a good estimation of ester concentration for these samples.

The REO with a solution without the presence of ester is 0, due to the lack of C=O bond in the other chemical compounds. The integrated absorbance value increases with increasing the analyte concentration in the sample. An increase of TMP oleate is observed on the Ti6Al4V strip when the ester concentration in the emulsion increases (Table 2). A maximum of TMP oleate adhered on the metal is reached in the formulation 2:2.

3.2. *Carbon quantification*

The tendency of oil droplets of an O/W emulsion to wet the surface was quantified using the total organic carbon. The organic carbon content adhered on the strip surface for each emulsion is shown in Fig. 5. It illustrates that the amount of carbon increases when the strips are treated at higher concentrations and at a constant surfactant:ester ratio. In addition, for the same surfactant concentration with increasing ester content, higher differences are observed due to the TMP oleate affinity with the metal surface.

3.3. *Determination of fatty acid ester on Ti6Al4V*

The combination of both analytical methods allows knowing the amount of carbon from TMP oleate adhered on the Ti6Al4V strip. Milligrams of ester are calculated multiplying the percentage of ester (from IRRAS measurements) by the milligrams of total organic matter calculated according to the molecular weight and number of carbons average of the organic layer for each experiment.

Fig. 6 shows a higher carbon content when the fatty acid ester is present in the emulsion. In the case of equivalent surfactant and ester proportion at the three different concentrations (1:1; 2:2; 3:3), the amount of organic carbon increases with the concentration. In the case of using a constant surfactant concentration with different ester amounts (2:0; 2:1; 2:2), a high fatty acid ester adhesion is observed, as expected.

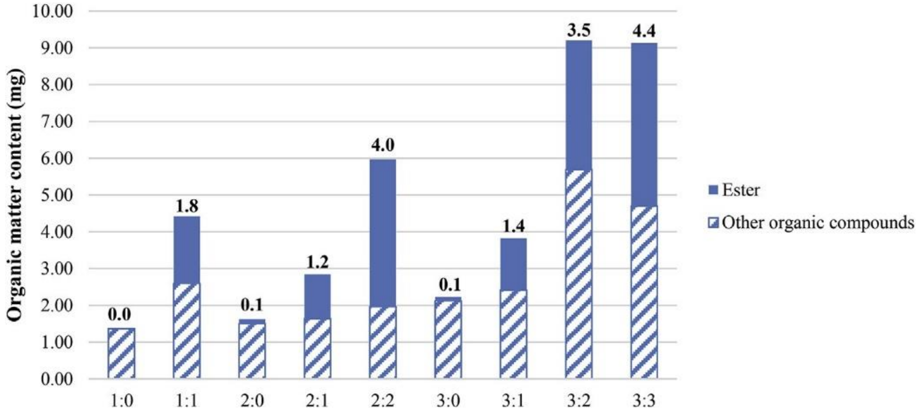

Fig. 6. Total organic matter of TMP oleate adhered on the Ti6Al4V strips treated with emulsion containing different ratios of surfactant and ester. Milligrams of ester are quantified.

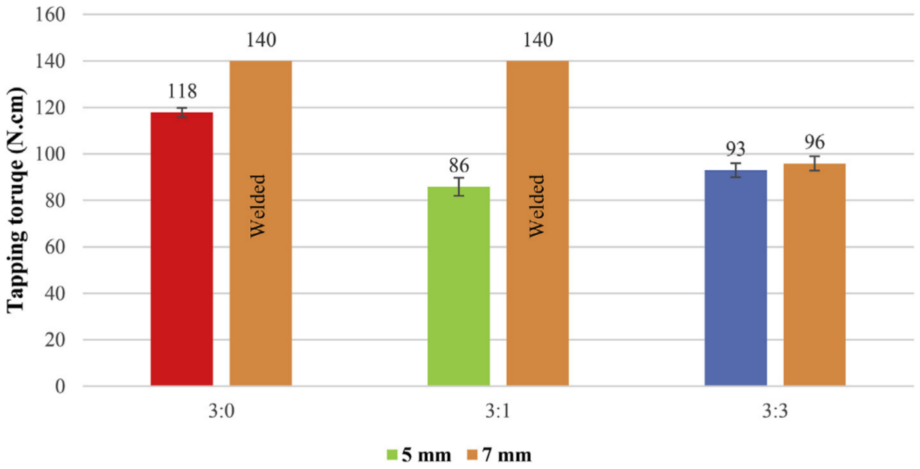

Fig. 7. Tapping torque of three samples with different ester amount using Ti6Al4V workpiece, and a machining speed of 300 rpm.

3.4. *Lubricity performance on Ti6Al4V*

In order to characterize the lubricity of the emulsions, machining performance was measured with three emulsions (3:0; 3:1, 3:3) using a tapping torque test system (Microtap labtap II, G8) at a machining speed of 300 rpm on Ti6Al4V workpieces. The performances, evaluated in terms of tapping torque (N·cm), with higher values indicating lower metalworking performance (Fig. 7).

The emulsion without ester (3:0) presents high values of tapping torque as compared to the emulsions with the same surfactant amount but with ester content (3:1; 3:3). No significant differences were found between 3:1 and 3:3 at a depth of 5 mm. However, when changing the parameters and making them more demanding, clear differences are found. When the test was run at 7 mm of depth, only the emulsion 3:3 containing high percentage of ester and surfactants, prevents the welding between the tool and the Ti6Al4V workpiece, meaning that it has better lubricity values.

4. Conclusion

In this paper, a method is presented to determine the amount of carbon from fatty acid ester adhered on Ti6Al4V strips. The metal surface treated with an oil-in-water (O/W) emulsion with different oil and surfactant concentrations has been studied. Several surfactant and ester concentrations have been analysed using this methodology. The method described is useful to assess the affinity of chemical compounds used in metalworking fluids with different metal surfaces, maximizing the film formation and, therefore, enhancing their lubricity performance. The test results indicate that this method is good to evaluate the amount of fatty acid esters and its interaction with other organic compounds as surfactants and amines, which play a key role in the lubrication performance. The investigation of the effect of fatty acid ester and surfactant concentration on film forming ability of O/W emulsions has been studied.

1. The ester is adsorbed to the metallic surface allowing a layer film formation, which offers a sliding surface that prevents direct metal-to-metal contact. The percentage of fatty acid ester adhered on the Ti6Al4V surface can be quantified by infrared reflection absorption spectroscopy (IRRAS), due to its characteristic C=O peak. The sensitivity and resolution of IRRAS have proved invaluable to detect and analyse the very thin layer films found on the metal surface.
2. The organic film formed on the metal strip can be quickly determined by the total organic carbon with Leco equipment. Based on the analysis, the ester concentration is the most important factor, while surfactant has less effect.
3. The combination of the analytical methods has enabled the ester concentration to be identified and also the influence of surfactant concentration on esters' adhesion to be studied. This shows the tendency of the ester of an O/W emulsion to wet the Ti6Al4V surfaces. Therefore, the method allows knowing the amount of ester adhered on the metal strip, for the development of an effective oil-in-water emulsion in metalworking.

Future work will include different surfactant types (anionic, cationic and non-ionic) to study the behaviour of surfactant charges as well as fatty acid ester of different chain length; using the method described in this paper as a tool to assess the affinity of the different esters to the metal surface. The ultimate target is to promote the optimal adhesion of the ester with the suitable fatty acid length onto the metal surface, so that the best lubricity and anti-wear properties are found using environmentally friendly water-based metalworking fluid. A relation will be established with the ester's load carrying capacity and tribological characteristics to investigate the properties of ester based O/W emulsion and make them technologically competitive as metalworking fluid.

Acknowledgment

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This development has been carried out under the guidance and with close collaboration of Laurent Aubouy and Jaume Josa from Leitat Technological Center.

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4.2. The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys

A continuación, se presentan los detalles de la publicación (Tabla 7), las aportaciones de los autores y una copia completa de la publicación. Los indicios de calidad de este artículo pueden encontrarse en el Apéndice B.

Tabla 7. Datos de la publicación e indicios de calidad de *The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloy.*

Título	**The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys**	
Autores	Elisabet Benedicto, Eva María Rubio, Diego Carou, Coral Santacruz	
Revista	Metals	
ISSN	2075-4701	
Editorial	MDPI (Multidisciplinary Digital Publishing Institute)	
País	Suiza	
Volumen	10	
Páginas	1388 (1-14)	
Fecha	2020	
doi	10.3390/met10101388	
Indicios de calidad	**Factor de impacto**	2,351 (JCR-2020) **2,117** (JCR-2019)
	Posición en el ranking	Q2 (24/80, Metallurgy & Metallurgical engineering, JCR-2020) **Q1** (18/79, Metallurgy & Metallurgical engineering, JCR-2019)

En las operaciones de mecanizado de aleaciones de titanio, la mayoría de los problemas están relacionados con el elevado consumo de las herramientas de corte debido al excesivo desgaste que sufren. La mejora de los fluidos de mecanizado (MWF) permite aumentar la productividad, la sostenibilidad y la calidad de los procesos de mecanizado mediante una lubricación y refrigeración adecuada. En este artículo, se presenta cómo afecta la estructura química de los tensoactivos en la capacidad de formar una película lubricante sobre un sustrato de Ti6Al4V. Por consiguiente, se han seleccionado tensoactivos de distinta carga (aniónicos y no-iónicos), de longitud de la cadena de hidrocarburos entre C8 y C18 y con un grado de etoxilación entre 2 y 10. Los tensoactivos se añaden a una concentración de 1,2 mM en una base acuosa de fluido de corte y trioleato de trimetilolpropano. Por un lado, para estudiar la capacidad de la emulsión para formar una película lubricante, se ha utilizado la espectroscopia de absorción por reflexión en infrarrojos y el análisis del carbono orgánico total. Por otro lado, se ha medido el esfuerzo de torsión durante el proceso de roscado para estudiar la capacidad de lubricación de estos fluidos. Los resultados del estudio muestran que, cambiando la estructura molecular del tensoactivo es posible variar la afinidad entre el éster y el sustrato y alcanzar una combinación óptima, que mejora la formación de la película lubricante. La mezcla con tensoactivos aniónicos tiene un buen rendimiento tribológico, mientras que los tensoactivos no-iónicos acortan la vida útil de la herramienta. Además, el aumento de la longitud de la cadena de hidrocarburos y del número de etoxilaciones de los tensoactivos favorece la adhesión del éster a la superficie del metal, mejorando las propiedades de lubricidad del EcoMWF.

Se trata de un trabajo de coautoría. Las aportaciones de cada uno de los autores son las siguientes:

- Elisabet Benedicto: metodología, validación, análisis formal, investigación, recursos, tratamiento de datos, redacción del borrador original, redacción de la revisión y edición.
- Eva María Rubio: conceptualización, metodología, análisis formal, redacción de la revisión y edición, supervisión, administración del proyecto y adquisición de fondos.
- Diego Carou: conceptualización, metodología, análisis formal, redacción de la revisión y edición.
- Coral Santacruz: metodología, validación, análisis formal, recursos y tratamiento de datos.

metals

MDPI

Article

The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys

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Abstract: In cutting operations of titanium alloys, most of the problems are related to the high consumption of cutting tools due to excessive wear. An improvement of metalworking fluid (MWF) technology would increase the productivity, sustainability, and quality of machining processes by lubricating and cooling. In this research article, the authors varied the surfactant's charge, the hydrocarbon chain length, and the ethoxylation degree. Surfactants were dispersed at 1.2 mM in water and trimethylolpropane oleate to produce water-based MWF. Infrared reflection absorption spectroscopy and total organic carbon analysis were used to study the influence of surfactant structure on the film forming ability of the emulsion and performance was studied on Ti6Al4V using tapping torque test. The results showed that by changing the molecular structure of the surfactant, it is possible to vary the affinity between the ester and the substrate and reach an optimal combination, which improves the formation of a tribofilm. The mixture with anionic surfactants has good tribology performance, while non-ionic surfactants shorten the tool's life. Moreover, the increase in the hydrocarbon chain length and the number of ethoxylations of surfactants promotes the adhesion of ester onto the metal surface, improving the lubricity properties of environmentally friendly MWF.

Keywords: metalworking fluid; tool wear; tool life; Ti6Al4V; surfactant

1. Introduction

Titanium and its alloys are considered difficult-to-cut materials due to their low thermal conductivity, high hardness, and high chemical reactivity at elevated temperatures. Most of the problems related to conventional machining of titanium alloys are associated with the high consumption of cutting tools due to excessive wear caused by the high temperature reached during the cutting process as well as the tendency of the chip to weld to the tool. Unfortunately, the lack of BUE (Built-up edge) also increases abrasion and chip welding. The combination of these characteristics and the relatively poor thermal conductivity of titanium causes unusually high temperatures at the tool's edge [1], causing premature tool failure and promoting corrosion, residual stress formation, and micro-cracks [2].

Wear mechanisms depend on the tool material type. Tungsten carbide (WC) cutting tools are the most suitable tool materials commercially available in almost all machining processes [3] due to their low cost and availability [4]. However, coating on carbide tools has no beneficial effect on their

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performance. Chemical vapor deposition (CVD) coated carbides and ceramic tools are not generally used in titanium machining due to their higher reactivity with titanium and their relatively low fracture toughness as well as the poor thermal conductivity of most ceramics [5].

In general, low machining speeds are used to lengthen the tool life. At increased cutting speeds, high compressive stresses and high temperatures are generated near the cutting edge [6]. Under these conditions, the dominant wear mechanisms are plastic deformation and crack development because of thermal shock. The variation of feed, cutting depth, or cutting speed modifies the degree of wear, but also it is greatly affected by the type of metalworking fluid (MWF) used [7]. Depending on the fluid type, tool life may be prolonged up to 30% [8]. MWF must be both a coolant and a lubricant to decrease the cutting forces and avoid chip welding. However, most formulations are developed for ferrous metals and aluminum alloys, and few efforts have been made to design an effective MWF for machining titanium alloys [9].

Conventional MWFs are, in general, derived from petroleum, which is heavily toxic and can have negative effects on the environment and especially on human health. New technologies that include dry machining, minimum quantity lubrication (MQL) [10], cryogenic and gaseous cooling, incorporation of nanofluids into polymer matrix [11] or in MWF [12], environmentally friendly lubricants [13], and combinations of them [14] have gained increasing interest within the sector and led to the exploration of even broader opportunities to reduce or to completely eliminate conventional MWFs [15]. As such, new sustainable MWFs from vegetable oil or raw material from renewable sources have been seriously considered [16] in the manufacturing industry as an alternative to petroleum-based oils [17]. Ester-based fluids have gained interest from both the research community and industrial users [18] because of their excellent lubricity over a wide temperature range in the boundary lubrication zone [19]. In addition, synthetic esters provide corrosion protection and, in contrast to neat vegetable oils, they have high oxidative stability [20].

The number of variables required to formulate a water-based MWF (e.g., workpiece material, cutting operation, and cutting parameters) is too large to describe all possible formulations. MWFs are most often sold as concentrates that are diluted between 3 and 20% in water. This MWF type can be classified according to DIN 51385 [21] concerning their oil content in emulsions and solutions. Due to its growing demand, the present work is focused on the study of emulsions, particularly oil in water (O/W) emulsions, which are widely used in cutting processes. The oil (dispersed phase) functions as a lubricant, reducing friction between the contact surfaces, while the water (continuous phase) helps to evacuate the heat generated, thanks to its greater heat capacity [22]. For the emulsion to help improve lubrication, the oil must reach the substrate and replace water. The oil droplet is attracted to the metal surface by Van der Waals forces, while the electrostatic interaction between the oil and the negatively charged surfaces is repulsive [23].

Surfactants are used to stabilize the oil drops in the water phase by their amphiphilic molecular structure [24]. Their adsorption at the solid–liquid interface is strongly dependent on [25] the nature of the solid substrate and the molecular structure of the surfactant and the aqueous phase properties—for example, pH, electrolyte content, and temperature. Surfactants modify surface properties, influencing the lubrication performance [26]. They can be classified according to their dissociation power in the presence of an electrolyte as ionic or non-ionic. Within the ions as a function of charge, they are classified as anionic, cationic, and amphoteric [27]. Cationic surfactants, such as quaternary ammonium salts, have anti-corrosive and bactericidal properties and can significantly improve water lubricity [28] by reducing surface tension and forming a durable lubricating film [29]. However, they are not typically used in MWF formulations as they are more expensive and non-compatible with anionic [30]. Non-ionic surfactants do not bear an electrical charge and therefore have the advantage that they do not interact with calcium and magnesium ions in the water used for dilution. Surface activity depends primarily on the hydrophilic and hydrophobic part [31]. Even though anionic surfactants are, in general, much more sensitive to water hardness, they improve the wettability of the cutting fluid on the metal surface due to the adsorption of surfactant monomers onto the surface [32] and they are considerably less expensive than non-ionic surfactants [33].

Previous work has shown that there are many phenomena involved in lubrication with O/W emulsions. It is a complex system in which the physicochemical interactions between oil, water, and the surface control the lubrication mechanisms [34]. Recently, new studies have been published confirming that more knowledge of the MWF composition is needed [35], that emulsion lubrication is still not fully understood [36], and that there is still no agreement on the influence of various parameters such as stability or droplet size of emulsions on tribological behavior [37].

The aim of this study is to provide valuable information relating to the formulation of a sustainable and effective MWF by assessing the lubricity performance on Ti6Al4V. It aims to formulate a new MWF formulation including a renewable ester as the base oil and a mixture of two surfactants. Previous studies have demonstrated that mixed surfactants are synergistic [24]; they have a greater solubilization capacity and higher emulsion stability by increasing the packing density of the surfactant around the oil droplet. Although mixtures of anionic and non-ionic surfactants are commonly used in the metallurgical industry, they are not well known at the molecular level [38]. Surfactants with different charge, hydrocarbon chain length, and ethoxylation degree were used to identify the optimum surfactant that promotes the adhesion of the ester onto the Ti6Al4V surface. Moreover, this study reports the performance of the MWF by tapping torque tests against the surfactants used in the emulsion.

2. Materials and Methods

To develop a sustainable and effective MWF that provides improved Ti6Al4V machining,the surfactant molecular structure was modified to study its interaction with the ester oil when building up a lubricant film on the titanium surface. Using water-based lubricant improves heat removal due to its very high thermal conductivity. However, it is also necessary to use other substances to reduce the friction coefficient, such as a biodegradable and renewable fatty acid ester.

This work aims to point out the benefits of using sustainable water-based lubricants as an alternative to mineral oil and to report the preliminary experimental investigations for a future comparison with other lubrication and cooling systems. The procedure includes two main phases: the ability of the MWF to form a tribofilm and the lubricity performance (Figure 1). Several emulsions were prepared (Section 2.1). With these MWFs, a surface analysis was conducted according to the method presented by Benedicto et al. [39] to quantify the amount of organic matter, specifically trimethylolpropane trioleate (TMP oleate) (Section 2.2). The film forming ability of the emulsion considering surfactant structure is then related to the lubricity performance by tapping torque test (Section 2.3).

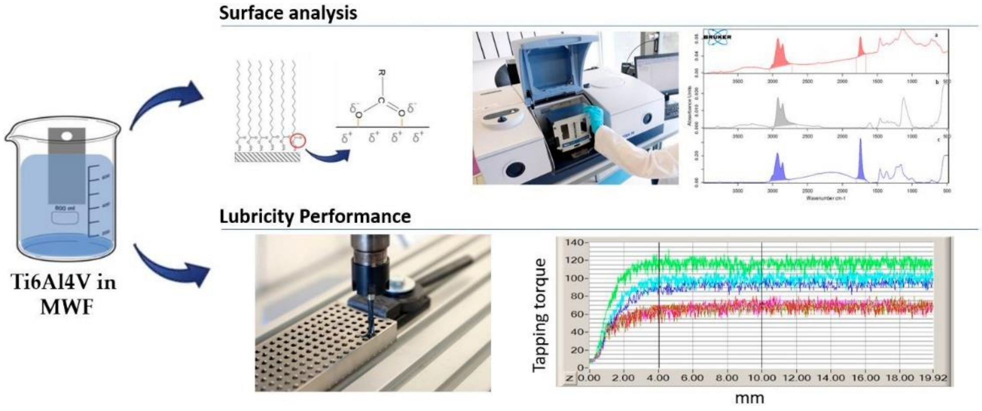

Figure 1. Test set-up diagram to study the role of surfactant structure on the ability to build up a lubricating film.

2.1. Materials and Mix Proportions: Preparation of Emulsion

Numerous specialty additives can be found in MWF formulations, such as anti-corrosive agents, foam stabilizers, bactericides, and fungicides. The products formulated in this work are simplified systems compared to commercial concentrates. Nevertheless, they contain the main raw materials: oil, water, pH buffer, and surfactants. The concentrations of the ingredients were selected based on the common MWF formulation used in Zhao et al.'s [40] previous study (Table 2):

- The oil phase: this is a fatty acid ester trimethylolpropane trioleate or TMP oleate, Weichol 3/134W from Industrial Química Lasem (IQL, Castellgalí, Spain), commercially used as environmentally adapted lubricant [41].
- The aqueous phase: this is a solution of 2-aminoethanol (MEA) (supplied by Across, Noisy Le Grans, France) in distilled deionized water to reach and maintain a pH above 9. The ideal pH of water-based MWF is within the range 8.5 to 9.5. At this condition, it prevents corrosion on ferrous metals, minimizes the potential for contact dermatitis, and controls biological growth [42,43].
- The surfactant blend: this is a mixture of a non-ionic surfactant oleyl/cetyl propoxylated alcohol with the trade name Dehypon OCP502 (BASF, Ludwigshafen, Germany) and the different surfactants under study (Kao Chemicals GmbH, Emmerich, Germany) (Table 1) with a 2:3 ratio. Adding a non-ionic surfactant allows closer packing at the interface and it contributes to stabilizing the emulsion. The oleyl/cetyl propoxylated alcohol was selected according to guidelines for formulating microemulsions from the experimental results of the study conducted by Zhao et al. [40], where the hydrocarbon chain length of the non-ionic surfactant should be equal to or greater than the hydrocarbon chain length of the oil fatty acids.

Table 1. Properties of surfactants under study from Kao Chemicals GmbH.

Charge	Abbreviation	Chain	Ethoxylation Degree (EO)	Chemical Name
Anionic	AC8E8	C8	8 EO	Capryleth-9 carboxylic acid
	AC12E4.5	C12	4.5 EO	Laureth-6 carboxylic acid
	AC12E10	C12	10 EO	Laureth-11 carboxylic acid
	AC18E2	C18	2 EO	Oleth-3 carboxylic acid
	AC18E5	C18	5 EO	Oleth-6 carboxylic acid
	AC18E9	C18	9 EO	Oleth-10 carboxylic acid
Non-ionic	NC8E8	C8	8 EO	Octyl alcohol, ethoxylated
	NC12E4.5	C12	4.5 EO	Lauryl alcohol, ethoxylated
	NC12E10	C12	10 EO	Lauryl alcohol, ethoxylated
	NC18E2	C18	2 EO	Oleyl alcohol, ethoxylated
	NC18E5	C18	5 EO	Oleyl alcohol, ethoxylated
	NC18E10	C18	9 EO	Oleyl alcohol, ethoxylated

Table 2. Chemical composition of emulsions, in molar concentration.

Product	Molar
TMP Oleate	0.0010
Dehypon OCP 502	0.0008
Surfactant under study	0.0012

From a fundamental research point of view, pure substances should be used as surfactants. Considering the final use of the results obtained, the authors tried to ensure that the lubricating substance had adequate performance characteristics and was commercially available. Therefore, the surfactants under investigation have some polydispersity in the ethoxylation degree (EO) and the hydrocarbon chain distribution.

2.2. *Determination of Fatty Acid Ester Content on Ti6Al4V Surface*

In these experiments, it is important to know the composition at the metal surface, as it could differ from the composition in the bulk, i.e., the original composition of the emulsion. The ester adhered on the Ti6Al4V surface was quantified according to Benedicto et al. [39] by the use of infrared reflection absorption spectroscopy (IRRAS) with Vertex 70 (Bruker, Ettlingen, Germany) and total organic carbon (TOC) quantification with Leco RC612 (Leco, St Joseph, MI, US).

Following the method, calibration curves were built for each surfactant, varying the concentration of TMP oleate in the surfactant blend and using a Fourier transform infrared spectrophotometer Iraffinity-1S (Shimadzu, Nagoya, Japan). The ratio between the integrated absorbance under C=O peak and under CH2 stretching vibration peaks (REO) was calculated for each mixture using OPUS software. The equation from each regression line allowed us to determine the percentage of ester (w/w) given a REO value from a spectrum (Figure 2).

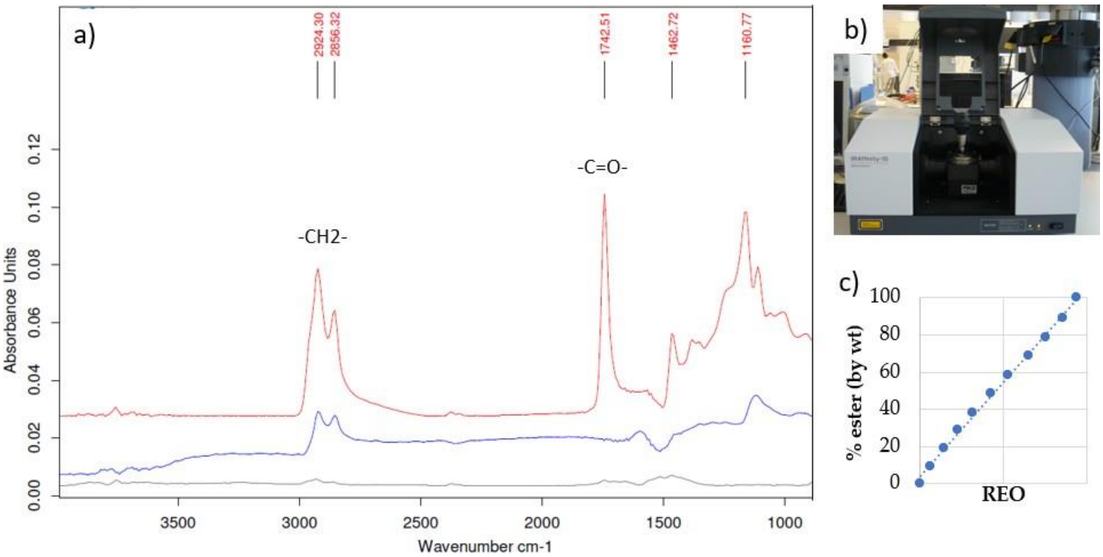

Figure 2. Determination of fatty acid ester on metal surface: (a) spectrum of an emulsion with the C=O characteristic peak of an esters; (b) Iraffinity-1S (Shimadzu, Nagoya, Japan); (c) calibration curve.

Ti6Al4V strips are pretreated with hexane to clean the surface and, after, they are dipped in the MWF formulation for 10 min at room temperature. On the one hand, TOC was measured to quantify the amount of organic matter on the strip surface, calculated according to the molecular weight and the number of carbon atoms. On the other hand, strips were evaluated with IRRAS and spectra were analyzed to calculate the REO and determine the percentage of ester adhered on the metal through the calibration curves. From both analytical techniques, the amount of ester and the total organic matter of the lubrication layer were determined.

2.3. *Tapping Torque Test for Tribological Study*

The tapping torque test was used to determine the role of the surfactant's molecular structure in MWFs as it is very sensitive to lubrication condition [44,45]. Formulations were evaluated based on the standard ASTM D5619 for comparing metal removal fluids [46]. Tribological test was conducted using the taping torque test Labtap G8 (Microtap, Munich, Germany) (Figure 3) and Ti6Al4V workpiece material. Cutting parameters were mostly determined by the material that was being machined. Spindle speed and depth of cut were selected at 300 rpm and 6 mm, respectively, as presented in Table 3.

In the tapping process, taps were filled with the test formulation. A rotating torque (cutting torque) was produced, and the performance was reported as tapping torque (N·cm) mean value, as an average of the generated work performance. Tapping torque lower values indicate better MWF performance.

In Figure 4, during the tapping process, a graphical measurement of the torque is shown: beginning of cut to full contact of all chamfer teeth (tap entrance) and cutting torque of the tap that is now cutting with all its chamfer teeth [47]. Due to due to the high tool wear when machining titanium alloys, a new tool was used for each product under study. As the tool wear rate progresses in each tapping process, the microtap mean value increases. The taps were made until the tool broke or reached a maximum of 15 cuttings.

Figure 3. Experimental setup: tribological test using a tapping torque test system with Ti6Al4V workpiece.

Table 3. Machining conditions.

Parameter	Value
Spindle speed (rpm)	300
Depth of cut (mm)	6
Hole diameter (mm)	3.3
Tapping tool	TTT_M4C
Workpiece material	Ti6Al4V pre-drilled

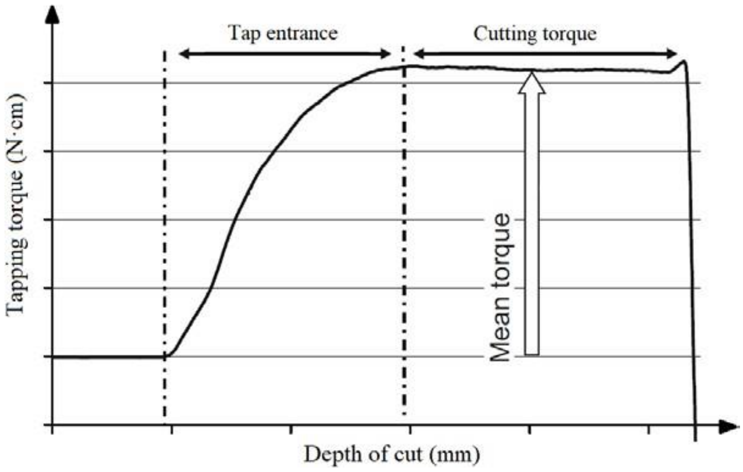

Figure 4. Measurement of the tapping torque during cutting.

3. Results and Discussion

3.1. *Effect of Surfactant Charge on the Lubricity Performance of Emulsions*

To study the impact of anionic and non-ionic surfactant molecular structure on the lubricity performance of MWF products, a surfactant system was generated for each substance listed in Table 1. An amine balance was added to maintain the pH at 9.2. Moreover, the total molar concentration of fatty acid ester and surfactant was kept constant.

For comparison between surfactant charges, equivalent anionic and non-ionic surfactants with different hydrocarbon chain lengths and ethoxylation numbers were tested. Results are plotted in Figure 5, where the bars represent the amount of ester adhered on the Ti6Al4V strips (in µmol) after being treated with the several MWF emulsions containing the surfactant under study and points show the tapping torque mean value (TTT) from each formulation.

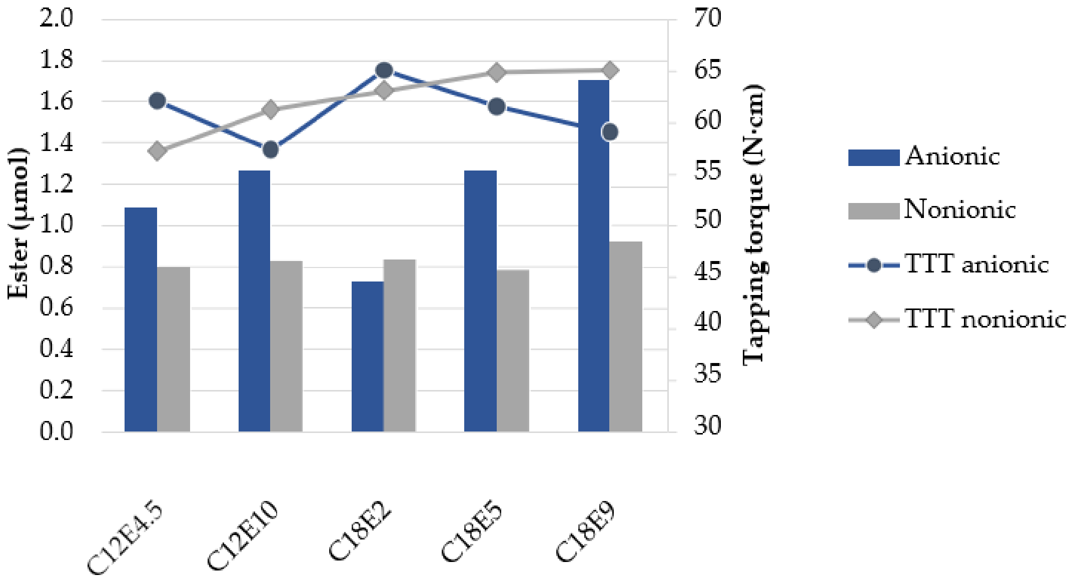

Figure 5. Amount of fatty acid ester adhered on titanium alloy strips after treatment with several emulsions. Points correspond to the first tapping torque value (TTT) for each emulsion.

Results show that all the MWFs formulated with the non-ionic surfactants have similar amounts of ester adhered on the metal surface, meaning that their structures have little impact on the adherence of TMP oleate regardless of the hydrocarbon chain length and ethoxylation degree. Compared to non-ionic surfactants, anionic surfactants promote the adhesion of ester on the Ti6Al4V strips. Data also indicate that the molecular structure of anionic surfactants has an influence on the amount of ester on the titanium alloy surface. Moreover, the ester adhered on the strip is plotted against the lubricity performance (TTT). For MWFs containing anionic surfactants, the more ester is adhered to the metal surface, lower the tapping torque values are.

To further explore the lubricity performance for each emulsion, tapping was run until 15 taps were achieved or until the tool broke, meaning that the tool and the workpiece were welded (Figure 6). After each tap, there was an increase in the tapping torque, due to tool wear. This increment depends on the anti-wear properties of the MWF and its ability to form a tribofilm.

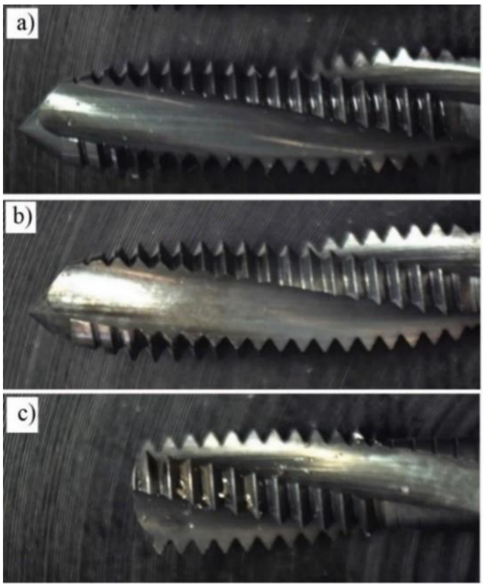

Figure 6. Tool life: (a) new cutting tool; (b) cutting tool after 15 cuts with an anionic surfactant emulsion; (c) broken tool after tapping with a non-ionic surfactant emulsion.

It was observed that the tools used with the combination of non-ionic surfactants welded at the tenth cut and, for one surfactant (NC18E5), before reaching the seventh cut. However, anionic surfactants have greater anti-wear properties, prolonging the tool life (Figure 7). None of the tools used with the negatively charged surfactants were broken during the study. This behavior could be explained by the fact that the anionic surfactant tends to promote the ester adsorption onto sliding surfaces, thus forming a lubricating film that prevents direct metal contact. Consequently, the increase in the tapping torque values with each consecutive cut is lower compared to non-ionic surfactant.

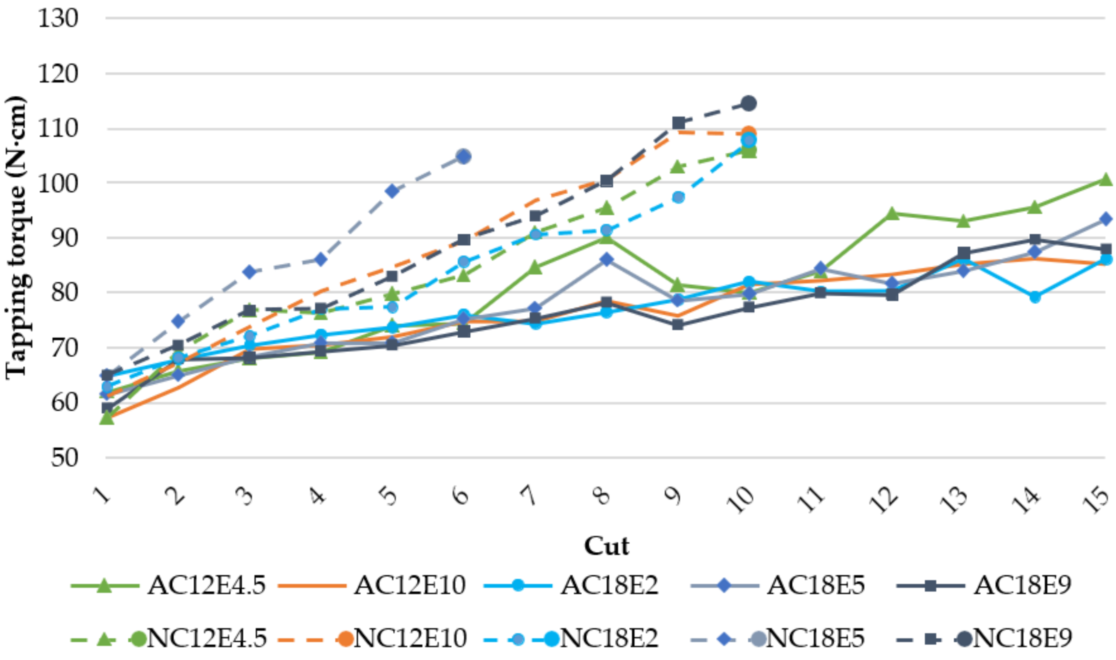

Figure 7. Evolution of the tapping torque with machining of consecutive cuttings: anionic with continuous line and non-ionic with dashed line.

3.2. *Effect of Surfactant's Hydrocarbon Chain Length on the Tribological Performance of Emulsions*

In order to study the influence of surfactant's hydrocarbon chain length on the emulsion system, tests were performed for surfactants with similar numbers of ethoxylations and varying the number of carbons of the lipophilic part from 8 to 18. The analysis of the Ti6Al4V surface, treated with the different emulsions, is presented in Figure 8. Bars represent the total organic matter adhered onto the titanium alloy surface. The upper part indicates the amount of ester (also noted with a number), while the lower part shows the other organic compounds such as amine and the surfactant mixture. Moreover, the tapping torque mean value (TTT) for each formulation is represented as points. The distance between different markers denotes the tool wear after the first and fifth cut with the MWF; lower distance means less tool wear.

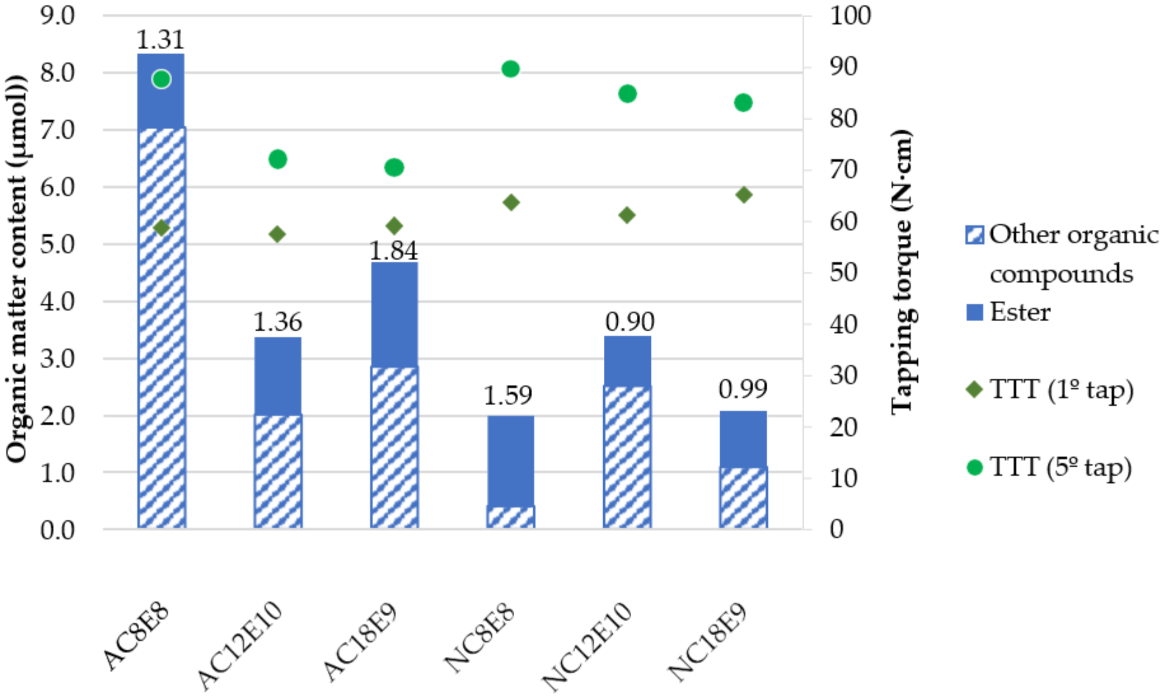

Figure 8. Evolution of the tapping torque with machining of consecutive cuttings: anionic with continuous line and non-ionic with dashed line.

Results pointed out that the concentration of ester increases with the length of the hydrocarbon chain of the anionic surfactant, making it more lipophilic. As other researchers have also demonstrated [48], the MWF with more lipophilic surfactant is found to form a stronger tribofilm, reducing the tapping torque values. Shorter hydrocarbon chain length has greater distance between the first and the fifth tap values, meaning higher tool wear. Similar trend in the anti-wear performance is observed when increasing the lipophobicity of non-ionic surfactants. However, the amount of organic matter is lower than the anionic surfactant and, thus, the highest TTT values are achieved.

The high amount of organic matter in the AC8E8 emulsion can be explained by its instability. Surfactants with a hydrocarbon chain of eight carbons are very unstable, as the study by Zhao et al. [40] predicted. This suggests that the difference between the chain lengths of the mixed surfactants should be less than six to maximize the range of stable emulsions.

The difference between the first and the fifth tapping torque mean value (Δ) was adopted as the measure of tool wear. The results presented in Figure 9 show that as the surfactant's hydrocarbon length chain increases (more lipophilic) as it forms a more robust tribofilm that allows for decreasing the wear, regardless of whether it is anionic or non-ionic.

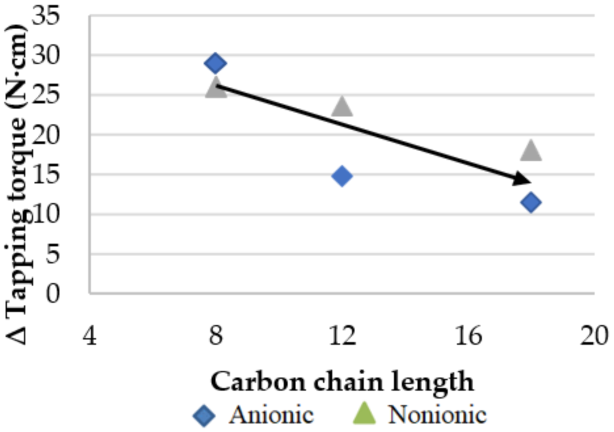

Figure 9. Difference in tapping torque between the first and fifth cut versus carbon chain length.

3.3. *Effect of Anionic Surfactant's Ethoxylation Degree on the Tribological Performance of Emulsions*

The influence of the number of ethoxylations (EO) in the surfactant has been studied with surfactants of 12 and 18 carbons in their lipophilic chain. Although the charge and hydrocarbon chain length of the surfactant have significant effects, the number of ethoxylations also plays an important role. On the one hand, with increasing ethoxylation degree within the same hydrocarbon chain length, a smaller amount of organic matter is adhered on the surface. MWF is more soluble due to the number of EO groups increasing the hydrophilic/lipophilic balance (HLB).

On the other hand, Figure 10 shows that even though there is less surfactant on the surface, the amount of ester increases, forming a more resistant layer and therefore improving the lubricity performance. This is in line with another study that revealed that higher ethoxy group content was found to improve anti-wear properties [49]. As a result, a surfactant with a higher number of ethoxylate groups is preferred.

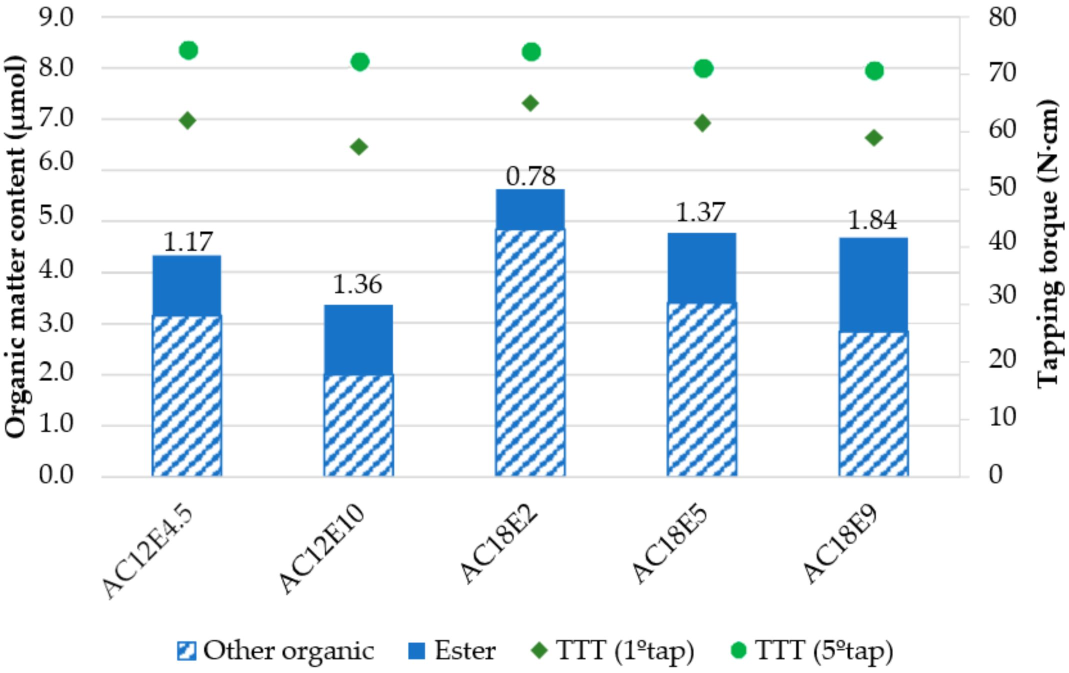

Figure 10. Organic matter adhered on Ti4Al4V strips treated with formulations containing different anionic surfactants with different ethoxylations against its lubricity performance.

4. Conclusions

The surfactant used to disperse the oil in water and stabilize the emulsion controlled the ester adhered onto the metal substrate. By changing the molecular structure of the surfactant, it is then possible to vary the affinity between the ester and the substrate and to reach an optimal combination, which enables easy adherence onto the contact zone and improves the formation of a tribofilm. In this paper, the authors varied the surfactant's charge (anionic and non-ionic), the hydrocarbon chain length, and the ethoxylation degree. The surfactants were dispersed at 1.2 mM molar concentration in water to study the emulsion behavior with the Ti6Al4V surface. Moreover, tribological experiments with tapping torque machine were conducted in O/W emulsion. The main conclusions drawn from this study are listed below:

- It was found that, from the surfactants tested, non-ionic surfactants are less promising and their structures have little impact on the adherence of TMP oleate. The application of surfactants bearing an anionic group can be successful, as they not only promote TMP oleate adhesion, but also, they improve the anti-wear.
- The data also indicate that the molecular structure of anionic surfactants has a high impact on the amount of ester adhered on the titanium alloy surface, forming a lubricating film that prevents direct metal contact. The more ester is adhered, the lower the tapping torque values are, indicating less wear.
- The concentration of ester increases with the hydrocarbon chain length of the anionic surfactant, as it becomes more lipophilic. However, surfactants with a hydrocarbon chain below eight carbons show high emulsion instability.
- It was apparent that the longer the hydrocarbon chain of the surfactant is, the higher the wear reduction is, regardless of surfactant type, whether it is anionic or non-ionic.
- In the tested anionic surfactants, the higher the number of ethoxylations, the more significant the increase in lubricity observed. Even though there is less surfactant on the surface, due to higher solubility increases, the amount of ester increases, forming a more resistant layer.

The obtained results showed the suitability of a water-based MWF of fatty acid ester for titanium alloy machining. The interactions among the surfactant molecules, the ester, and metal surface play a key role in the lubricity and tool wear protection. Using an anionic surfactant with oleic hydrocarbon chain and a high number of ethoxy groups, such as AC18E9, can lead to better lubricity and tool protection as well as to environmental advantages of ester-based cutting fluids over mineral-based fluids. The research group has also been exploring other fatty acid esters to be used in machining processes with titanium alloys, which are typically applied in the aerospace industry. For further technology evaluation analysis, a comparison of a sustainable water-based MWFs with other lubrication and cooling systems for machining titanium and its alloys is needed.

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4.3. Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys

A continuación, se presentan los detalles de la publicación (Tabla 8), las aportaciones de los autores y una copia completa de la publicación. Los indicios de calidad de este artículo pueden encontrarse en el Apéndice C.

Tabla 8. Datos de la publicación e indicios de calidad de *Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys.*

Título	**Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys**	
Autores	Elisabet Benedicto, Eva María Rubio, Laurent Aubouy, María Ana Sáenz-Nuño	
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Indicios de calidad	**Factor de impacto**	2,351 (JCR-2020)
		2,117 (JCR-2019)
	Posición en el ranking	Q2 (24/79, Metallurgy & Metallurgical engineering, JCR-2020)
		Q1 (18/79, Metallurgy & Metallurgical engineering, JCR-2019)

El mecanizado de las aleaciones de titanio sigue siendo un reto exigente y es imprescindible el desarrollo de nuevas tecnologías sostenibles que permitan lubricar y refrigerar el sistema tribológico. Como alternativa sostenible al aceite mineral, los ésteres han demostrado un excelente rendimiento durante el mecanizado. El objetivo de este trabajo es investigar la influencia de la estructura molecular de los ésteres en las emulsiones de aceite en agua y su interacción con la superficie para formar una película lubricante, mejorando, así, la eficacia del fluido de corte. Para estudiar el rendimiento de los fluidos de corte y la protección contra el desgaste de la herramienta se ha analizado la formación de la película lubricante, así como el esfuerzo de torsión necesario para el proceso de roscado en Ti6Al4V. Los resultados muestran que el rendimiento del fluido mejora al aumentar la formación de la película orgánica en la superficie del metal, lo que depende de la estructura molecular del éster y de su capacidad de adsorción en la superficie frente a otros compuestos tensoactivos. De los fluidos de corte probados, cabe destacar los resultados obtenidos con el trioleato de trimetilolpropano. Este fluido de corte aumenta la formación de la película lubricante (contiene un 62% de éster), mejorando así la lubricidad hasta en un 12% y reduciendo el incremento del esfuerzo de torsión por desgaste de la herramienta en un 26,8%. Este trabajo puede ser muy útil para sectores en los que frecuentemente se utilizan materiales difíciles de mecanizar -como el Ti6Al4V o el γ-TiAl- que requieren grandes cantidades de fluidos de corte, ya que la formulación desarrollada permite que los procesos sean más eficientes y sostenibles.

Se trata de un trabajo de coautoría. Las aportaciones de cada uno de los autores son las siguientes:

- Elisabet Benedicto: conceptualización, metodología, validación, análisis formal, investigación, recursos, tratamiento de datos, redacción del borrador original, redacción de la revisión y edición.
- Eva María Rubio: conceptualización, análisis formal, redacción de la revisión y edición, supervisión, administración del proyecto y adquisición de fondos.
- Laurent Aubouy: conceptualización, metodología, validación, análisis formal, redacción de la revisión y edición.
- María Ana Sáenz-Nuño: análisis formal.

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Article

Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys

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Abstract: The machinability of titanium alloys still represents a demanding challenge and the development of new clean technologies to lubricate and cool is greatly needed. As a sustainable alternative to mineral oil, esters have shown excellent performance during machining. Herein, the aim of this work is to investigate the influence of esters' molecular structure in oil-in-water emulsions and their interaction with the surface to form a lubricating film, thus improving the efficiency of the cutting fluid. The lubricity performance and tool wear protection are studied through film formation analysis and the tapping process on Ti6Al4V. The results show that the lubricity performance is improved by increasing the formation of the organic film on the metal surface, which depends on the ester's molecular structure and its ability to adsorb on the surface against other surface-active compounds. Among the cutting fluids, noteworthy results are obtained using trimethylolpropane trioleate, which increases the lubricating film formation (containing 62% ester), thus improving the lubricity by up to 12% and reducing the torque increase due to tool wear by 26.8%. This work could be very useful for fields where often use difficult-to-machine materials—such as Ti6Al4V or γ-TiAl—which require large amounts of cutting fluids, since the formulation developed will allow the processes to be more efficient and sustainable.

Keywords: cutting fluid; esters; lubrication; tool wear; titanium alloys

1. Introduction

Titanium alloys, particularly Ti6Al4V, are used extensively in the aeronautic, aerospace, automotive, chemical, and biomedical industries due to their unique mechanical properties (Table 1), such as high specific strength, hardness, corrosion resistance at high temperatures, and biocompatibility [1]. Despite these exceptional properties, Ti6Al4V is classified as a difficult-to-cut material because of its high chemical affinity, low thermal conductivity, and work hardening. The poor machinability of these alloys leads to excessive tool wear and catastrophic tool failure, resulting in decreased tool life and low productivity.

Due to the low conductivity of Ti6Al4V, the heat generated during machining cannot be dissipated throughout the workpiece and chips effectively. Therefore, the application of lubrication/cooling systems is extremely important. In most difficult-to-machine alloys, cutting fluids are employed in the machining process by providing lubrication under boundary friction at the workpiece-tool interface, or, more specifically, at the chip-tool interface, eliminating heat from the cutting zone and removing abrasive particles from the contact area [2]. The creation of the lubricating film depends on the media composition, particularly the absorption and chemisorption of polar or metal-active additives on the surface of the workpiece, while the coolant and cleaning capacity depends on the physical properties of the cutting fluids (e.g., specific heat capacity, vaporization heat, viscosity, and surface tension) [3]. Additionally, the cutting fluid protects the workpiece, the tool, the machine tool, and other metal surfaces from corrosion.

Table 1. The main properties of the Ti6Al4V alloy [4–6].

Property	Ti6Al4V
Density (g/cm3)	4.42
Young's modulus at RT (GPa)	120± 10
Yield Strength (MPa)	800–1100
Tensile strength (MPa)	900–1200
Ductility at RT (%)	13–16
Creep limit (◦ C)	385
Oxidation limit (◦ C)	400
Hardness (HV10)	360 ± 30
Thermal conductivity (W·mK)	7.5–8.6

However, the use of conventional mineral oil-based cutting fluids has been thoroughly reviewed because of their environmental and health hazards [7]. Many investigations have aimed to improve the machinability of titanium alloys using sustainable lubrication/cooling systems. The advantages and drawbacks of the most common systems are summarized in Table 2.

Table 2. The advantages and drawbacks of sustainable lubrication/cooling systems used in titanium alloy machining [1,8,9].

Lubrication/ cooling systems	Advantages	Drawbacks
Dry cutting	No need for cutting fluid Easier chip collection for recycling Minimal environmental impact	High cutting temperature generation High tendency of workpiece microstructural alterations Reliable results for limited cutting parameters Poor tool life and surface finish Problematic chip evacuation
MQL	Reduction in cutting fluid Less costly method in comparison to other systems Good results in terms of cutting forces, tool wear, surface roughness are noted	Poor chip evacuation Poor cooling capacity Mist formation Very sensitive to MQL supply system
Cryogenic cooling	Eliminate the use of cutting fluid No need to clean the chips and improved chip breakability Promote improvements in surface integrity Improved tool life	Highly sensitive to tool–material pairs. The production cost of the cryogen is very high compared to cutting fluids Special Dewar is needed for cryogenic supply Overcooling lead to embrittlement of workpiece
Cold compressed air	Absence of cutting fluid Chips can be collected in dry form	Additional energy is required to produce compressed air
Sustainable cutting fluids	Can be totally biodegradable and renewable Less costly compared to cryogenic cooling Chip evacuation Effective removal of heat	Vegetable oils have low oxidation stability Formulation difficulties

A great improvement in the machining of titanium alloys is observed when different lubrication/cooling systems are combined. Noteworthy results were obtained with a minimum-quantity lubrication (MQL) and a cryogenic cooling hybrid system. The poor cooling capacity and lack of chip evacuation in the MQL system can be enhanced using compressed air or cryogenic cooling [10]. Moreover, vegetable oils or even recycled oils can be used as MQL fluid, thus increasing not only its efficiency but also reducing its environmental impact [11].

In order to ensure high levels of productivity whilst meeting the surface integrity of the machined parts, industrial companies still employ cutting fluids, especially in the most demanding operations. More than 2,000,000 m^3 of cutting fluids are used globally each year, the majority of which (85%) are petroleum-based [12]. Hence, these cutting fluids are non-renewable and toxic. Therefore, introducing new sustainable materials for the formulation of environmentally friendly cutting fluids as an alternative to mineral oil-based fluids is one of the main future trends in the machining of titanium alloys [10].

When selecting the type of cutting fluid to use, there are several aspects to consider, such as the machining operation, the workpiece material, the cutting tool material, the mode of application, the cutting fluid, and the environment friendliness [13]. The excellent heat dissipating properties of water and its cleaning capacity to remove chips of water- based cutting fluid, make it suitable for machining titanium alloys [14]. Moreover, the components of the cutting fluid and its physico-chemical properties determine the wetting and adsorption properties on the metal surface, which further affect the quality and performance of the machined surface. Chemical reactions can result in the loss of effective alloying elements thus damaging the surface [15].

Sustainable cutting fluids is a commonly used term for products that meet the following characteristics: good biodegradability; low eco-toxicity; risk of low contamination for water, air. and soil; low consumption; a long shelf life; recyclable; an ability to produce less waste; and an ability to promote energy saving [16]. There is a trend towards the use of vegetable or synthetic based oils and against the formulation of environmentally hazardous mineral oils [17], as well as the elimination or reduction in hazardous substances in the formulation of cutting fluids.

The most commonly used sustainable base fluids as alternatives to mineral bases are low molecular weight polyalphaolefins, polyalkylene glycols, vegetable oils, and synthetic esters [18]. This research addresses synthetic esters, which have attracted wider interest from both academic researchers and industrial users due to their high polarity and excellent lubricity in the boundary lubrication [19]. Synthetic esters perform well over a large temperature range, have a high viscosity index, possess a high lubricity, provide corrosion protection, and have a high oxidative stability [20]. In general, synthetic esters meet the requirements for aquatic biodegradability and toxicity, although they tend to be less readily biodegradable than vegetable oil-based lubricants.

There is a wide range of synthetic esters with properties that vary greatly depending on their chemical structure. A synthetic ester in its simplest form consists of an alcohol and a fatty acid. In lubricants, esters are usually made with two or more carboxylate groups. Due to the large number of different alcohols and fatty acids available for ester formulation, esters can be synthesized to suit a specific application [21]. In particular, this study is focused on polyol esters obtained from the reaction of fatty acids and polyhydric alcohols, also known as polyol, which are less susceptible to hydrolysis [22]. The fatty acids most commonly considered in the synthesis of polyol esters are caprylic acid, oleic acid, rapeseed oil, olive oil, animal fats, and palm oil. Examples of commonly used polyols are trimethylolpropane, neopentylglycol, and pentaerythritol [23].

The challenges in formulating water-based cutting fluids continue to increase as end users demand a better performance over longer periods of time and under harsh conditions [24]. Currently, vegetable oils and the synthetic esters obtained from them are emulsified as additives in water-based cutting fluids [25]. However, there are few studies that describe the lubrication/cooling results obtained in the machining of difficult-to-cut materials [26].

In contrast to oils, water has many unique properties due to its polarity, which makes aqueous lubrication much more complicated than traditional oil lubrication. Water-based lubrication mechanisms are not yet well known due to the diversity and complexity of aqueous solutions. In addition, some traditional lubrication theories are not applicable to aqueous lubrication due to the complex physical and chemical properties of water [27]. In the case of water-soluble cutting fluids, the effect of hydrolysis must be considered. Emulsions contain significant amounts of water, which can cause ester hydrolysis and variation of the chemical composition in the lubrication film, resulting in a completely different tribochemical mechanism between the water-based emulsion and the ester [28].

The aim of this work was to study the influence of the polyol ester on the development of a sustainable cutting fluid for titanium alloys. Oil-in-water (O/W) emulsions were formulated with several polyol esters and the ability to form a lubrication film was analyzed on Ti6Al4V strips. Finally, the lubricity performance was tested using a tapping process and evaluated with design of experiments (DOE) software.

2. **Materials and Methods**

2.1. Materials and Sample Preparation

To carry out the study, five cutting fluids were prepared by adding a mixture of non-ionic and anionic surfactants to stabilize the O/W emulsions. Oleyl/cetyl propoxylated alcohol (BASF, Ludwigshafen, Germany) and oleth-10 carboxylic acid (Kao Chemicals GmbH, Emmerich, Germany) were mixed in deionized water at 0.8 mmol/L and 1.2 mmol/L, respectively. The mixture was adjusted to the recommended pH 9.2 with monoethanolamine. Four commercial esters synthetized by Industrial Química Lasem (IQL, Castellgalí, Spain) were used to formulate the cutting fluids. All of them were commercialized as environmentally adapted lubricants [29] and were recommended for the formulation of lubricants. The esters were obtained from a reaction of oleic acid and the number of ramifications were varied, modifying the alcohol group. The esters were added in a concentration of 1.0 mmol/L and stirred in order to obtain a homogeneous mixture.

The same molar concentration for all esters was used to easily compare the effect of the molecular structure of the polyol esters. The cutting fluids prepared were:

- without an ester;
- C18:1 × 1 using isopropyl oleate;
- C18:1 × 2 using neopentylglycol dioleate;
- C18:1 × 3 using trimethylolpropane trioleate;
- C18:1 × 4 using pentaerythrityl tetraoleate.

Moreover, the cutting fluids were prepared without the addition of anti-wear and extreme pressure chemical additives to prevent interference with the lubricity performance of the mixtures.

2.2. Determination of Lubricating Film on Ti6Al4V Surface

The lubricity performance is related to the capability to form a lubricating film on the surface, providing a layer that protects the surface from wear. The schematic diagram of the experimental setup is shown in Figure 1. Tests were conducted with Ti6Al4V (grade 5) panels (special metals and products, Spain) with dimensions of 17 75 0.8 mm3, and the chemical composition shown in Table 3. Panels were immersed in the cutting fluid at room temperature and stirred for 10 min. The film formation was determined according to the method developed by Benedicto et al. [30]: (1) measuring the total organic carbon (TOC) with RC612 (Leco, St. Joseph, MI, USA) to quantify the milligrams of carbon adhered to the Ti6Al4V panel and (2) calculating the ratio of the ester, analyzed by infrared reflection absorption spectroscopy (IRRAS) (Vertex 70 Bruker, Ettlingen, Germany).

Table 3. The chemical composition of Ti6Al4V (grade 5) (wt%).

Ti	Al	V	Fe	O
89.75%	6%	4%	0.25% max.	0.2% max

Following this method, four calibration curves were built for each ester, varying its concentration in the O/W emulsion and using a Fourier Transform infrared spectrophotometer (Iraffinity-1S Shimadzu, Nagoya, Japan). The regression line provided the ratio (REO) between the integrated absorbance under the C=O peak (1735–1750 cm^{-1}) and under the CH2 stretching vibration peaks (2850–2925 cm^{-1}). The following regression equation allowed the percentage of ester (wt%) to be given a REO value from a spectrum and the correlation coefficient (R^2) measured the strength of the relationship between them:

$$\% \text{ ester} = A + B \cdot \text{REO}, \quad (1)$$

Finally, the amount of ester adhered to the Ti6Al4V panels was calculated by multiplying the percentage of ester by the milligrams of TOC, taking into account the molecular weight and the average of number of carbons on the organic layer for each cutting fluid.

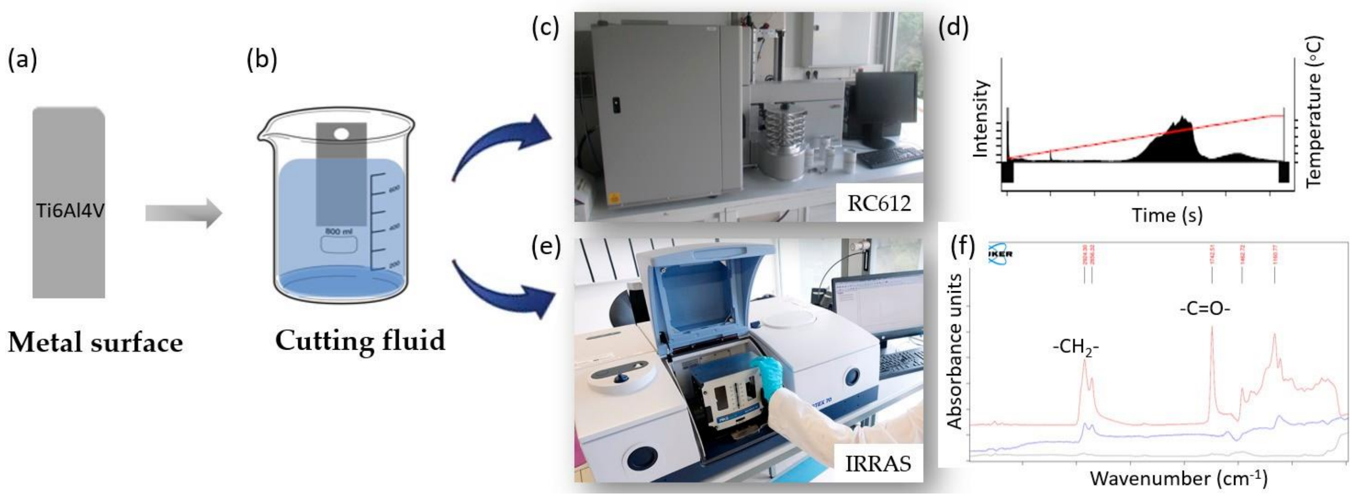


Figure 1. The experimental setup to study the lubrication film formed on the panel surface: (**a**)Ti6Al4V panel, (**b**) cutting fluid, (**c**) RC612 equipment, (**d**) the total carbon rate of evolution as a function of temperature, (**e**) IRRAS equipment and, (**f**) IRRAS spectra with C=O and CH2 stretching vibration peaks.

2.3. *Lubricity Performance of Polyol Ester Cutting Fluids*

To gain a better understanding of the behavior of the polyol ester in water-based cutting fluids, a tapping torque test was conducted in Labtap G8 (Microtap, Munich, Germany). This cutting operation is highly sensitive to lubrication [31]. The material used for the machining was a Ti6Al4V with pre-drilled holes (Figure 2). A TTT_M4C coated tool, size M4 (0.7 mm pitch, 3.3 mm tapping diameter) with helical channels was used for each cutting fluid.

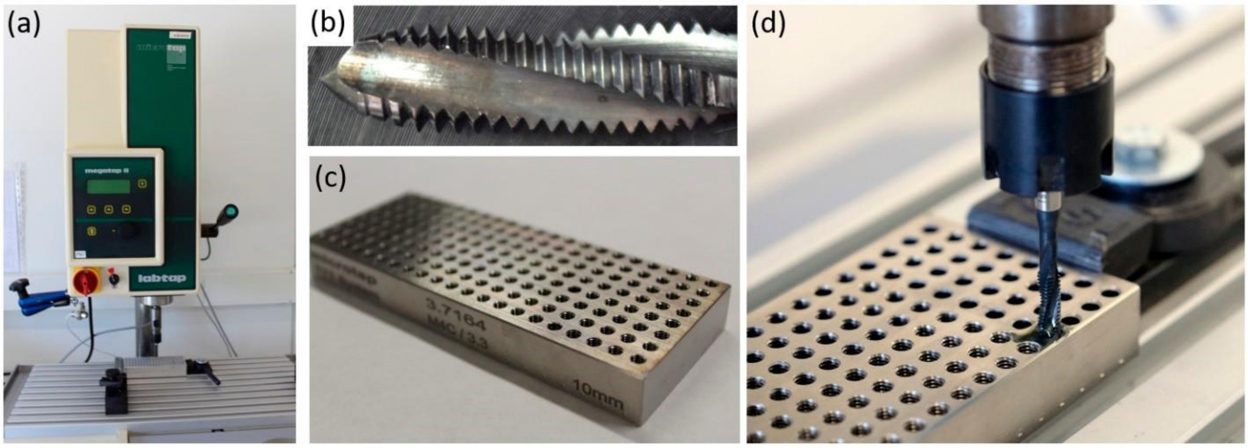


Figure 2. The experimental setup to study the lubricity performance using the Labtap G8: (**a**) Labtap G8 equipment, (**b**) TTT_M4C coated tool, (**c**) Ti6Al4V workpiece and, (**d**) cutting process.

The cutting fluid was poured in the holes to lubricate them during the tapping process at 300 rpm, with a 6 mm length of thread, as shown in Table 4 each tapping process was repeated 15 times or until the tool broke. Figure 3 shows the tapping procedure graphically where: (1) shows the beginning of the cut; (2) shows the tool penetrating the workpiece and the torque increasing due to the increasing contact surface between the workpiece and the tool; (3) shows the tool cutting with all its chamber teeth until the length's thread is achieved and (4) shows the beginning of the reversal of the spindle to bring the tool to the initial position [32]. Finally, the results were reported averaging the tapping torque values (N·cm) in the 1 mm to 6 mm range of cut.

Table 4. Cutting operation conditions.

Parameter	Value
Workpiece material	Ti6Al4V (grade 5) pre-drilled
Spindle speed (rpm)	300
Length of the thread (mm)	6
Hole diameter (mm)	3.3
Tapping tool	TTT_M4C coated tool. Size M4
Tap mode	Cutting

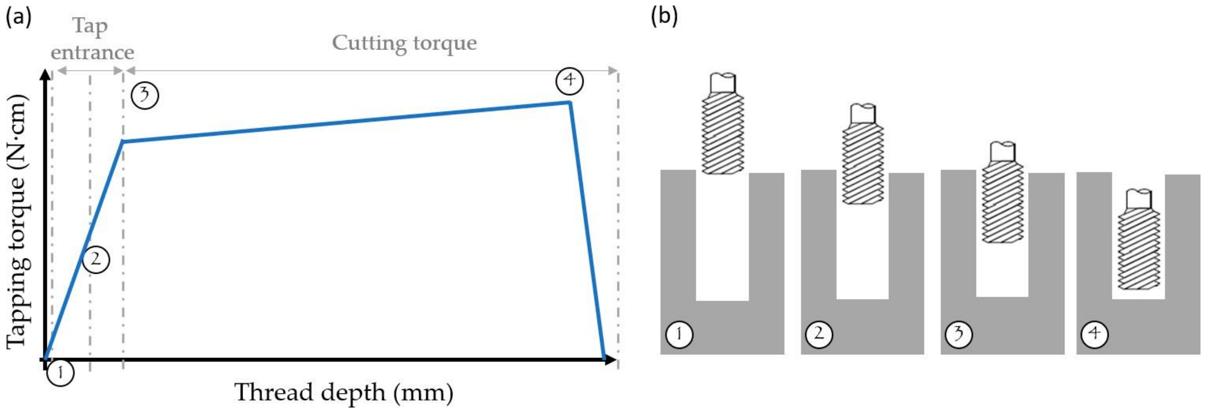


Figure 3. The tapping process: (**a**) graphical measurement of the tapping torque, (**b**) different positions of the tap during processing. (1) beginning of the cut, (2) tool penetrating the workpiece, (3) complete chamber teeth and (4) beginning of the reversal of the spindle.

3. Results and Discussion

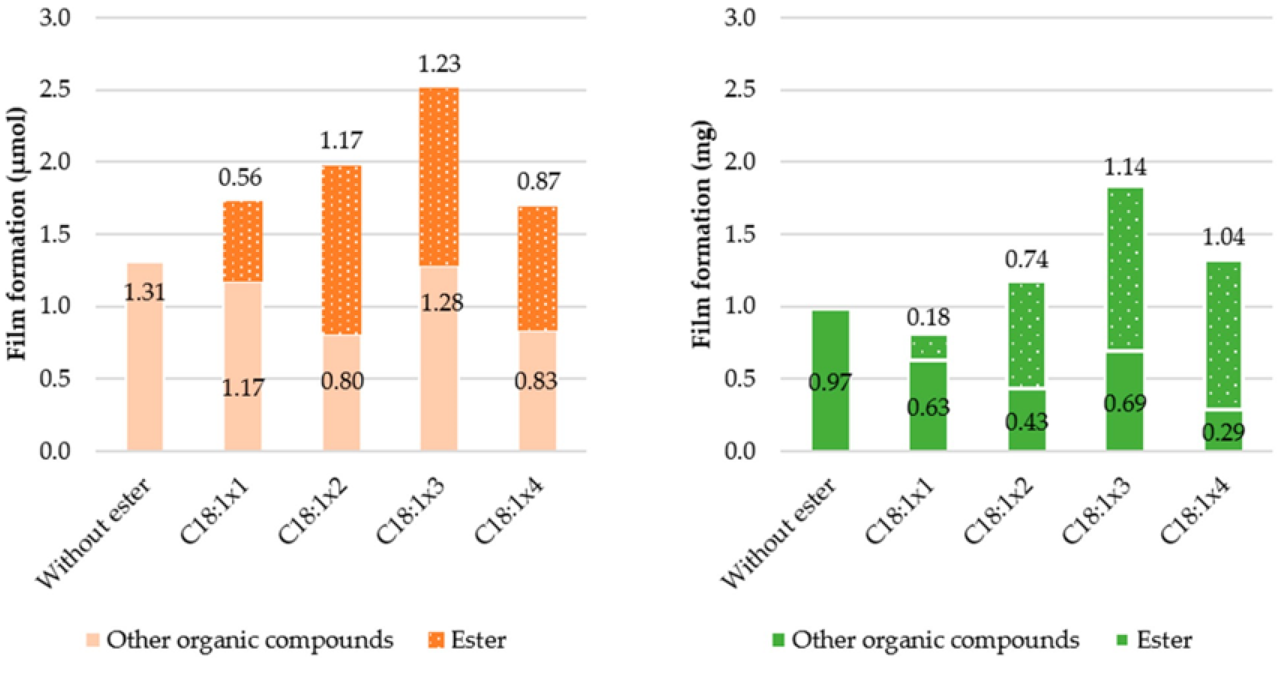
3.1. Film Formation on Ti6Al4V

The formation of the lubrication layer was calculated according to the equations of the regression line abstracted from the calibration curve of each polyol ester cutting fluid under study (Table 5). The REO values were calculated with the IRRAS spectra on the Ti6Al4V panels and the total organic matter adhered to the surface, allowing the quantification of the lubrication layer formation.

Table 5. The REO, TOC, and equations of the regression line results of the cutting fluid formulated with polyol esters.

MWF	***REO***	***TOC* (mg C)**	**Equations of the Regression Line % ester = *A* + *REO* · *B***			**% ester (w/w)**	**Organic Matter (µmol)**	**Ester (µmol)**
			A	**B**	**R²**			
C18:1x1	0.074	0.557	1.523	284.966	1.000	22.564	1.17	0.56
C18:1x2	0.219	0.860	2.077	279.079	0.999	63.166	0.80	1.17
C18:1x3	0.231	1.344	2.403	259.594	0.995	62.481	1.28	1.23
C18:1x4	0.304	1.200	2.474	250.050	0.999	78.408	0.83	0.87

Figure 4 shows the results of the organic film formed on the Ti6Al4V surface and the corresponding amount of ester after the panel was dipped in the O/W emulsions. The addition of esters in the cutting fluid resulted in lubrication layer growth. The ability to increase the film formation can be attributed to the stronger adsorption of polar functional groups on the metal surface. The molecular structure of such esters has a clear influence on the layer formed. Noteworthy results were obtained with C18:1x3. When the strip was dipped in the trimethylolpropane trioleate emulsion, a higher amount of organic matter was adhered, including both ester and surfactants.



(a) (b)

Figure 4. The film formation on the metal strips after the immersion of the panels in the cutting fluid: (**a**) in micromoles and (**b**) in milligrams.

At the same time, the presence of the ester interfered with the ability of other additives to attach to the metal surface. The results suggest that there is an adsorption competition on the surface between the surfactant and the ester molecules. The large molecular volume and polarity of pentaerythrityl tetraoleate prevents other molecules from being deposited on the metal, reducing the total organic matter. Therefore, it can be considered that the molecular structure of an ester in O/W emulsions has a substantial influence on its ability to form a lubricating film and on its conformation. The influence of the physico–chemical properties and the chemical composition, such as the branching structure and the polar functional groups on the film thickness has been observed by several authors [33], but unlike this study, they used neat esters.

When the Ti6Al4V strip was treated with C18:1x1 cutting fluid, the amount of ester that adhered to the surface was lower. This result can be attributed to the high stability of oil droplets in the emulsion, which are too stable to form a film. This relation between the oil droplet's stability and the film formation observed in this work was described by Ratoi-Salagean et al. [34], who correlated its incidence with a different emulsifier concentration.

3.2. *Influence of Polyol Esters in the Lubricity of Cutting Fluids*

To evaluate the lubricity of the cutting fluids, a tapping torque machine was used for experimental investigation. With this equipment, experiments are conducted by performing a tapping operation of a tool inside a hole with the cutting fluid and the torque is measured in situ. During the first tap, using deionized water as the cutting fluid, the tool welds in the Ti6Al4V workpiece. Comparing these results to the results from the cutting fluid without an ester, which showed that even after 15 taps the tool was not broken, it must be noticed that surfactants not only help to stabilize the emulsion, but they can also reduce the tapping torque. The lubricity properties of the surfactants observed in the present work were described by Benedicto et al. [35] who correlated their performance to the molecular structure of surfactants. Moreover, the addition of a polyol ester in the cutting fluid increases its lubricity and can reduce the tool wear by up to 37%.

The effect of the fatty acid ester in O/W emulsions on lubricity and wear is depicted in Figure 5. By comparing tapping torque values in the first tap, the ability of cutting fluids to lubricate can be studied. After the first tap, it is noted that the torque values increase with each tap due to tool wear.

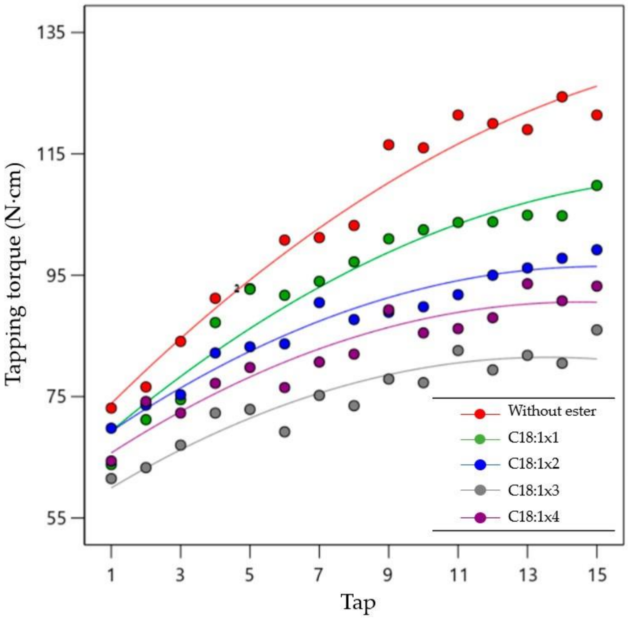


Figure 5. The effect of the addition of esters into an O/W emulsion on the tapping torque.

In order to analyze the effect of the cutting fluid on the tapping torque, a mathematical model was predicted by the design of experiments method (DOE). For each cutting fluid, a second order polynomial response has been fitted into the following equation:

$$Y = a + b \cdot X + c \cdot X2, \qquad (2)$$

where Y is the corresponding response (tapping torque) and X is the tap number.

The regression equations that have been obtained are collected in Table 6. The terms of these equations can be correlated with the lubricity performance (coefficient a) and the increase in tapping torque values in each consecutive tap due to the tool wear (coefficient b).

Table 6. The regression equations for a quadratic model.

Cutting fluid	Regression Line
Without ester	$68.07 + 5.91\,X - 0.14\,X^2$
C18:1x1	$64.41 + 5.04\,X - 0.14\,X^2$
C18:1x2	$65.31 + 4.11\,X - 0.14\,X^2$
C18:1x3	$56.40 + 3.69\,X - 0.14\,X^2$
C18:1x4	$61.90 + 3.94\,X - 0.14\,X^2$

The analysis of variance (ANOVA) with a *F*-value of 202.82 implies that the model is significant and there is only a 0.01% chance that an *F*-value this large could occur due to noise. *p*-values less than 0.0500 indicate the model terms are significant. Additionally, the verification of the model was analyzed by R2, whose value is 0.969, very near to 1.

The results show a positive correlation between the lubricity and the total organic matter adhered and the amount of ester in the film layer. The ester was adsorbed to the metal surface with the fatty acid hydrocarbon end facing away from the metal surface, thus allowing a monolayer film formation. This is in accordance with the lubrication mechanism of the castor oil-in-water fluid described by Ni et al. [36]. Therefore, the fatty acid chain provided a sliding surface that reduced friction and facilitated chip evacuation through the tool's channels.

The wear protection was improved by increasing the ester, which resulted in stronger adsorption on the metal surface [37]. Remarkable results were obtained using C18:1x3. This can be attributed to the higher lubrication film that was formed on the metal surface, thus increasing lubricity and protecting the tool from wear. On the contrary, from the esters tested, C18:1 1 had the highest tool wear, corresponding to the polyol ester with the lowest ability to adhere on the Ti6Al4V surface. C18:1x3 improved the lubricity performance by 12.4% and decreased the tapping torque of consecutive taps by reducing the tool wear by 26.8% compared to the cutting fluid C18:1x1.

In comparison with C18:1x2, a slight decrease in the tapping values was detected using the cutting fluid C18:1x4. The molecule packing of C18:1 4 improves the deposition of the ester on the surface (1.04 mg of pentaerythrityl tetraoleate), increasing the lubricity properties of the cutting fluid. In terms of tool wear, the lowest indices were achieved with C18:1x4 fluid.

The results in this work demonstrate considerable potential for the introduction of the polyol ester as an alternative to mineral oil in water-based cutting fluids. Moreover, the associated environmental and health benefits of polyol esters make them more attractive substitutes. The characteristics of esters, such as their high biodegradability and the reduction in fossil carbon sources, reduces their contribution to global warming compared to mineral oil by approximately four times [38].

4. Conclusions

This study provides an evaluation of the influence of polyol esters in oil-in-water (O/W) emulsions on titanium alloys to overcome the challenges in formulating sustainable water-based cutting fluids. The emulsions were formulated by adding polyol esters with different molecular structures and surfactants to stabilize the O/W emulsion. The film formation on the surface and the tapping torque were measured to identify the factors that have a significant effect on lubricity performance.

Based on the results of the present experimental and analytical investigations, the following conclusions can be drawn:

- The molecular structure of esters influences the amount of the ester that adheres to the surface forming a lubricant film, which protects the tool from wear. By the addition of 1 mmol/L of ester in the water-based cutting fluid, trimethylolpropane trioleate ester can double the amount of ester adhered on the panel surface compared to isopropyl oleate.
- There is an adsorption competition on the surface between the ester and other additives. The molecular structure of esters has a high impact on the conformation of the lubricant film which, in turn, also has an impact on the lubricity properties of the cutting fluid.
- The increase in ester in the lubrication film improves the tribological performance and prolongs the tool life. The addition of a polyol ester in the cutting fluid increases the lubricity by up to 17% and can reduce the tool wear by up to 37%.
- From the polyol esters under study, C18:1x3 is preferred as a water-based cutting fluid for machining titanium alloys. It can double the amount of lubrication film

formed compared to the rest of the cutting fluids. The best lubricity results were obtained with C18:1 3. In terms of tool wear, the lowest rate was achieved with the trimethylolpropane trioleate O/W emulsion.

This study may be used to develop new sustainable and environmentally friendly cutting fluids for titanium alloys to replace conventional mineral oil water-based cutting fluids. However, further work needs to be conducted to investigate the industrial potential of these cutting fluids for titanium alloys, comparing them with other lubrication and cooling systems, such as cryogenic cooling.

Author Contributions: Conceptualization, E.B., E.M.R. and L.A.; methodology, E.B. and L.A.; validation, E.B. and L.A.; formal analysis, E.B., E.M.R., L.A. and M.A.S.-N.; investigation, E.B.; resources, E.B.; data curation, E.B.; writing—original draft preparation, E.B.; writing—review and editing, E.B., E.M.R. and L.A.; supervision, E.M.R.; project administration, E.M.R.; funding acquisition, E.M.R. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Not applicable.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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4.4. Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry

A continuación, se presentan los detalles de la publicación (Tabla 9), las aportaciones de los autores y una copia completa de la publicación. Los indicios de calidad de este artículo pueden encontrarse en el Apéndice D.

Tabla 9. Datos de la publicación y e indicios de calidad de *Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry.*

Título	**Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry**	
Autores	Elisabet Benedicto, Eva María Rubio, Laurent Aubouy, María Ana Sáenz-Nuño	
Revista	International Journal of Precision Engineering and Manufacturing-Green Technology	
ISSN	2288-6206	
Editorial	Springer Nature and Korean Society for Precision Engineering	
País	Alemania y Corea del Sur	
Fecha	2022	
doi	https://doi.org/10.1007/s40684-022-00435-x	
Indicios de calidad	**Factor de impacto**	**5,671** (JCR-2020)
		4,171 (JCR-2019)
	Posición en el ranking	**Q1** (11/50, Engineering Manufacturing, JCR-2020)
		Q1 (12/50, Engineering Manufacturing, JCR-2019)

Este trabajo presenta el estudio del torneado para procesos de acabado, reparación y mantenimiento en la industria aeronáutica, de piezas de aluminuro de titanio gamma (γ-TiAl), una aleación de titanio nueva y relativamente poco explorada. El objetivo principal es evaluar diferentes sistemas de lubricación y refrigeración sostenibles, incluyendo un fluido de corte desarrollado con un éster sintético (EcoMWF) para sustituir al fluido de corte tradicional de base mineral (MWF). Los sistemas considerados en este trabajo son el mecanizado en seco, con aire comprimido frío, con mínima cantidad de lubricante (MQL), criogénico y mediante inundación. Por consiguiente, se ha investigado la influencia de los parámetros de mecanizado y del tipo de inserto en el desgaste de la herramienta, la rugosidad superficial, la redondez y la temperatura de corte para cada sistema de lubricación/refrigeración. Los resultados detallados en este trabajo muestran una influencia significativa de estos sistemas en el mecanizado de las aleaciones γ-TiAl. El menor desgaste de herramienta se ha obtenido al mecanizar con el sistema MQL. El estudio también concluye que la sostenibilidad del proceso de torneado de γ-TiAl puede mejorarse con el nuevo EcoMWF desarrollado, manteniendo el mismo rendimiento de mecanizado que los fluidos de corte base aceite mineral comúnmente usados.

Se trata de un trabajo de coautoría. Las aportaciones de cada uno de los autores son las siguientes:

- Elisabet Benedicto: conceptualización, metodología, validación, análisis formal, investigación, recursos, tratamiento de datos, redacción del borrador original, redacción de la revisión y edición.

- Eva María Rubio: conceptualización, metodología, validación, análisis formal, redacción de la revisión y edición, supervisión, administración del proyecto, adquisición de fondos.
- Laurent Aubouy: conceptualización, análisis formal, redacción de la revisión y edición.
- María Ana Sáenz-Nuño: análisis formal.

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REGULAR PAPER

Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry

Elisabet Benedicto[1,2,4] · Eva María Rubio[1] · Laurent Aubouy[2] · María Ana Sáenz-Nuño[3]

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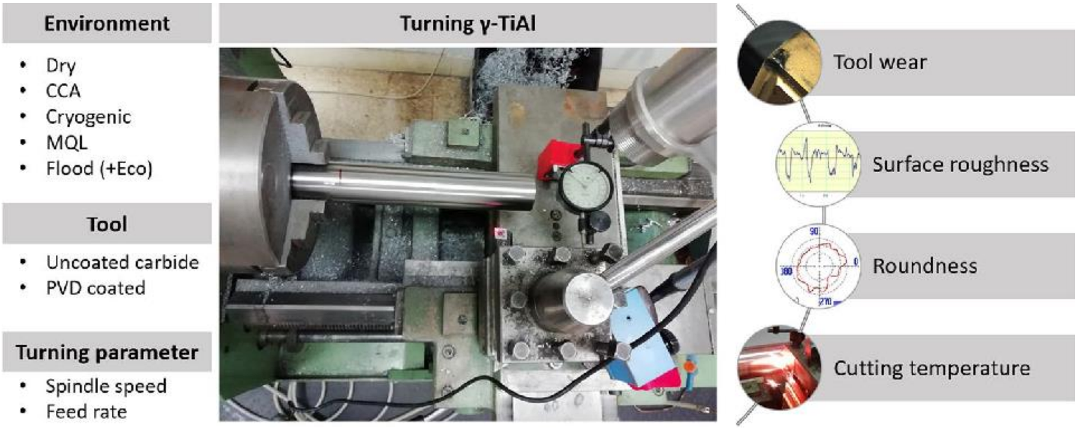
Abstract

This paper presents the study of the finishing, repair, and maintenance turning operations of gamma titanium aluminide (γ-TiAl) parts from the aeronautic industry, with the aim to evaluate different sustainable lubrication/cooling environments, including a newly developed synthetic ester water-based metalworking fluid (EcoMWF) to replace mineral-based MWF (MWF). The systems considered in this work are dry, cold-compressed air, minimum quantity lubrication (MQL), cryogenic, and flood on turning of a new and relatively low explored titanium alloy, γ-TiAl. Therefore, the influence of machining parameters and insert type on tool wear, surface roughness, roundness, and cutting temperature have been investigated for each environment. Results detailed in this study showed a significant influence of the lubrication/cooling systems on the machinability of γ-TiAl. The study also revealed that the sustainability of turning γ-TiAl could be improved under the cryogenic system and the new EcoMWF, keeping the same machining performance as common mineral-based MWF.

Graphical abstract



Keywords Metalworking fluid; γ-TiAl; Lubrication/cooling systems; Environmentally sustainable manufacturing; Turning operations; Aeronautic industry

1. Introduction

Gamma titanium aluminide (γ-TiAl), due to its excellent characteristics such as high elevated temperature strength and good oxidation resistance, has advanced applications in the automotive, aeronautic, and aerospace industries. The difference in the working temperature could be 50 % higher compared to other titanium alloys used, such as Ti6Al4V [1]. Moreover, titanium aluminides have become an alternative to replace heavy materials such as nickel-based superalloy to allow mass saving [2], and during the last years, several industries are introducing and qualifying this new alloy to produce their components [3]. Nevertheless, this new lightweight alloy is considered a difficult-to-machine material because of its low machinability rating [4]. The machining cost can

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represent as much as 40 % of the total cost of manufacturing the component [5].

The third generation γ-TiAl materials, including Ti-43.5Al-4Nb-1Mo-0.1B (TNM-B1) with three phases γ+α2+β/βo (Fig.1), have high fatigue properties compared to the second generation Ti-48Al-2Cr-2Nb [6]. β-phase is stabilized by Nb and Mo addition, increasing the hardening effect of γ-TiAl but reducing diffusivity [7]. The manufacturing of γ -TiAl TNM-B1 parts is achieved via vacuum arc remelted (VAR skull melting) and subsequent centrifugal casting in permanent molds. After, pieces are subjected to hot-isostatically pressed (HIP) thermal treatment and mechanical machining.

Reducing the rapid tool wear is essential to decrease manufacturing costs. The machining conditions for γ-TiAl are significantly lower than conventional Ti6Al4V alloy, with a typical cutting speed below 30 m/min, a feed rate between 0.05 to 0.10 mm/rev, and a depth of cut between 0.3 to 0.7 mm even in finishing processes [4]. Metalworking fluid (MWF) is used to enhance the metal machining processes by providing boundary lubrication, dissipating heat, and removing chips from the cutting zone [9]. Due to its numerous advantages, the demand for MWF, mostly mineral-oil based, is constantly growing in the machining industry [10], reaching a global consumption of more than 13,700 million tons with an annual increment of 1% in 2016 [11]. Nevertheless, MWFs have been criticized due to their negative environmental impact and potential health hazards [12].

New approaches have been reported to overcome the drawbacks related to MWF. This includes, cryogenic cooling, gaseous lubrication, dry machining, environmentally friendly MWF (EcoMWF), minimum quantity lubrication (MQL), and combinations of them [13]. There is a trend to reduce the MWF amount by dry machining or MQL, which has been demonstrated to have significant advantages in cutting operations of aluminum and steel alloys. However, several studies have shown that when machining titanium alloys in dry conditions, the absence of cutting fluid results in a higher temperature increase, which causes severe and premature tool wear and poor surface roughness of the workpiece [14]. Moreover, chips or parts of the workpiece material remain adhered to the tool.

In MQL, a minimum amount of fluid is supplied as oil droplets or air-oil mist into the cutting zone. Cutting fluids for MQL machining are commonly based on mineral oils, fatty alcohols, vegetable oils, or synthetic esters (chemically modified vegetable oils). Recent studies have shown that the addition of nanoparticles in the cutting fluid, such as molybdenum disulfide, boron nitride, graphite, metal nanoparticles, or carbon nanotubes, significantly reduces the tool wear and improves surface roughness by increasing the heat transfer due to an increase in the thermal conductivity of the fluid [15]. However, for difficult-to-machine materials, this lubrication/cooling system has a reduced performance to remove heat from the cutting zone, resulting in excessive tool wear. Therefore, the usage of MWF is still required [16].

There are very few investigations studying the effect of gaseous cooling in machining operations [17], none of

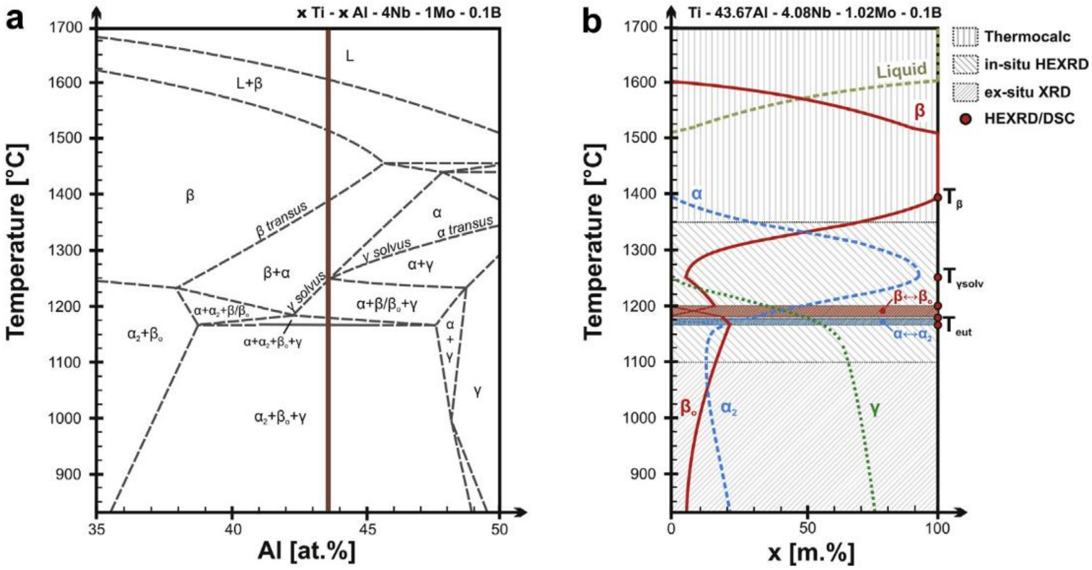


Fig. 1 Phase equilibria of γ-TiAl: a) quasi-binary section, and b) course of phase fractions with temperature [8].

which are related to the machining of γ-TiAl. Cold-compressed air (CCA) has a high cooling ability compared to other lubricating systems, and its flow helps break the chips, remove them from the cutting zone, and collect them in dry form. However, they do not have any lubricating capacity [18]. Therefore, CCA is commonly applied along with MQL in the form of spray or mist.

For difficult-to-machine materials, such as Ti6Al4V, cryogenic cooling has proved to be a successful alternative to MWF, thanks to the low temperature of the medium [19]. Liquid nitrogen (LN2) at -196ºC or liquid carbon dioxide (CO2) at -78ºC applied in the cutting zone, absorb the heat generated during cutting, and evaporates, providing no pollutant residue on the workpiece, chips, and machine tool. Moreover, it is considered a clean and environmentally friendly lubrication/cooling system with lubrication capacity by forming a gas layer between interfaces and providing significant benefits such as chip breakability, increased tool life, and surface quality improvement [20].

Regarding EcoMWF, vegetable oils and synthetic esters are considered potential alternatives to replace mineral oil-based fluids due to their high biodegradability, low toxicity, and high performance [21]. For turning titanium alloys, the use of water-based MWF is preferred due to its excellent heat dissipating properties, the ability to provide a thin lubricant film, and its cleaning capacity to remove chips [22]. However, there is relatively limited literature accessible describing lubrication and cooling performance obtained with vegetable oil or ester-based water-soluble MWF in the machining of difficult-to-machine materials.

Most of these alternative lubrication/cooling systems on machining titanium alloys have been conducted on Ti6Al4V, so additional research is needed on other commercial and experimental alloys. There is little literature found on the work related to turning γ-TiAl. According to previous research achievements, when machining γ-TiAl alloy, the workpiece can suffer several surface damages and microstructural alterations, such as microcracks, redeposited materials, plastic deformation, cavities, and heat-affected zones [23]. Priarione et al. [24] studied the surface integrity and tool life when machining Ti-43.5Al-4Nb-1Mo-0.1B (TNM) with cubic boron nitride and polycrystalline diamond (PCD) coated inserts under conventional MWF cutting (6% emulsion) and cryogenic cooling with LN2. Results showed that under cryogenic cooling, PCD tool life was increased compared to conventional MWF.

The significant influence of lubrication/cooling systems on the machinability of γ-TiAl alloys is shown by Kockle et al. [25]. The authors studied the effect of conventional MWF (6% mineral oil emulsion), MQL (vegetable oil with compressed air), dry, and LN2 cooling on the surface integrity and tool wear when turning Ti-45Al-2Nb-2Mn+0.8 with uncoated cemented carbide tools. Results confirm that dry condition is not appropriate for machining γ-TiAl. Compared to conventional MWF, with MQL, a slight decrease of the tool wear and a reduction of approximately 30% of surface roughness is achieved. However, the best results were obtained using cryogenic cooling.

To overcome these challenges of the machinability of γ-TiAl, this study responds to the need of replacing mineral-based MWF in turning γ-TiAl by introducing a formulation of a new sustainable ester-based water-soluble MWF (EcoMWF). It includes the evaluation of the performance obtained with an EcoMWF in comparison with conventional mineral oil-based water-soluble MWF and other green lubrication/cooling systems such as dry, CCA, MQL, and cryogenic; under different cutting parameters during finishing, repair, and/or maintenance turning processes in workpieces of the aeronautic industry. The effects of the lubrication/cooling systems, tool type (coated/uncoated carbide insert), and cutting parameters on the quality of the machined part (surface roughness and roundness), tool temperature, and tool wear have been studied with analysis of variance (ANOVA).

2. Experimental

2.1 Workpiece, tools, and equipment

A cylindrical bar of γ-TiAl was used to investigate the influence of lubrication/cooling systems and machining parameters on the horizontal turning, in particular, with a small depth of cut as the used in finishing, repair, and/or maintenance operations. The workpiece used was a Ti-43.5Al-4Nb-1Mo-0.1B alloy with 45 mm diameter and 250 mm in length. The turning tests were conducted on a parallel lathe (Pinacho model L-1/200). The selection of the cutting parameters for turning γ-TiAl is based on similar studies in the literature, referenced in Table 1.

Spindle speed, feed rate, and insert type were selected as input machining parameters in different conditions of lubrication/cooling systems, while surface roughness, temperature, roundness, and tool wear were selected as response parameters. The experiments were carried out at two feed rates (0.14 and 0.28 mm/rev) and two spindle speeds (500 and 800 rpm), whereas the other two cutting parameters were kept constant (depth of cut = 0.03 mm and machining length = 120 mm). The tools used in the research were uncoated cemented carbide (883) and physical vapor deposition (PVD) coated carbide tools (TS2500) from Seco Tools (CNMG120408-M1-883 and CNMG120408-M1-TS2500 PVD manufacturer codes, respectively Fig. 2). A new insert cutting edge was used for each experimental run.

The influence of cutting parameters and different conditions of lubrication/cooling systems on the cutting

Table 1 Cutting conditions for turning γ-TiAl alloy [v_c: cutting speed; a_p: depth of cut; f: feed]

References	Alloy	Machining parameters	Tool	Environment
Settineri et al. [26]	Ti-48Al-2Cr-2Nb, Ti-43.5Al-4Nb-1-Mo-0.1B, Ti-45Al-2Nb-2Mn+0.8	v_c: 80 m/min; a_p: 0.25 mm; f: 0.1 mm.	Uncoated cemented carbide	MWF
Kocke et al. [25]	Ti-45Al-2Nb-2Mn+0.8	v_c: 80 m/min; a_p: 0.25 mm; f: 0.1 mm	Uncoated cemented carbide	MWF, cryogenic, dry, MQL
Cheng et al. [27]	Ti-47.5Al-2.5V-1Cr	v_c: 25 – 100 m/min; a_p: 0.15 - 0.35 mm; f: 0.05 – 0.2 mm/rev	Uncoated cemented carbide	MWF
Sharman et al. [23]	Ti-45Al-2Nb-2Mn+0.8	v_c: 25 – 40 m/min; a_p: 0.05 – 0.1 mm; f: 0.05 mm/rev	Uncoated cemented carbide	MWF
Yao et al. [28]	γ-TiAl	v_c: 30 – 50 m/min; a_p: 0.2 – 1 mm; f: 0.06 – 0.1 mm/rev	PVD-coated carbide inserts	-
Priarone et al. [24]	Ti-43.5Al-4Nb-1Mo-0.1B	v_c: 80 m/min; a_p: 0.25 mm; f: 0.1 mm	Cubic boron nitride and polycrystalline diamond (PCD)	MWF, cryogenic
Beranoagirre and López de la Calle [1]	Ti-44Al-6Nb-0.2C	v_c: 40 – 60 m/min; a_p: 0.5 – 2 mm; f: 0.05 – 0.15 mm/rev	Tungsten carbide	MWF

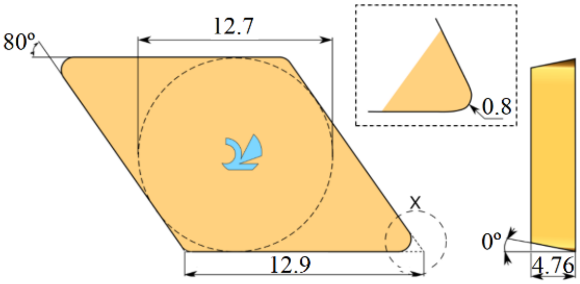


Fig. 2 Geometry of the tested tools

temperature, surface quality, and tool were studied. Temperature at the tool interface was measured using an Optris CT model LT pyrometer, and the approximate cutting temperature was recorded. After the experiment, the surface roughness of each cut was measured Mitutoyo Surftest SJ 401 profilometer. The arithmetic averaged surface roughness (Ra) was measured at 15 mm, 67 mm, and 110 mm.

The workpiece's roundness affects the dimension accuracy, the quality, and the suitability of the piece for assembly [29]. Roundness is the difference between the maximum and minimum radius. Based on the literature review, few studies report on the effect of cutting conditions on roundness in the turning of titanium alloys. In this study, the roundness was measured in the middle of the machined workpiece (60 mm) using Mitutoyo Roundtest RA-10.

The tool wear (Fig. 3) was analyzed using an optical microscope Euromex model ST, while the wear on the rake and flank faces of the inserts were measured using Tesa Visio DCC300. A detailed investigation of the worn tool to determine the main wear mechanisms during γ-TiAl turning under different lubrication/cooling systems was

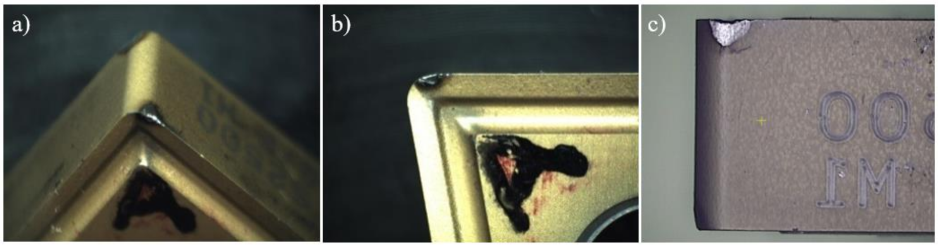


Fig. 3 Microscopic image of TS2500 insert when machining at 0.14 mm/rev and 500 rpm: **a** tool wear, **b** rake, and **c** flank face

carried out using Scanning Electron Microscope (SEM, model JEOL JSM-6010LV). Finally, the software of design of experiments was used to analyze the responses and determine the effect of the cutting parameters and the lubrication/cooling system, as well as the interactions among other factors.

2.2 Lubrication/cooling systems

The different cutting environments considered in this study include dry, cold-compressed air system (CCA), cryogenic, flood (12 l/min with EcoMWF and commercial MWF), and MQL (0.9 ml/min) (Fig. 4). For the CCA system, a Cold Air Gun Vortex system was used to achieve a cooling medium of -16.7 ºC, measured at the injector exit point with Multimetrix DMM220. In cryogenic cooling trials, liquid nitrogen has been conditioned in a 180-liter ranger at low pressure, and an LN2 jet was applied on the insert.

EcoMWF for this study was formulated using a magnetic stirrer. A mixture of monoethanolamine (5.76 g), triethanolamine (5.64 g), and isononanoic acid (7.09 g) was added in deionized water and stirred for one hour. These raw materials have pH buffering capacity and are used to protect the workpiece and machine surface against corrosion. After, non-ionic surfactant (oleyl/cetyl propoxylated alcohol, 13.12 g) and anionic surfactant (oleth-10 carboxylic acid, 10.20 g) were used to reduce the surface tension of the fluid, to emulsify the ester in water, and to improve the lubricity of the cutting fluid [30]. A highly biodegradable trimethylolpropane trioleate ester (provided by Industrial Química Lasem, 6.44 g) and an eco-friendly phosphate ester (provided by Solvay, 12.14 g) were added to provide lubricity and anti-wear properties. Finally, 8.25 g of glycol was added to stabilize the mixture. The fluid was magnetically stirred at room temperature for two hours.

Before conducting experiments, the formulated EcoMWF and a commercial MWF (trade name Servol 634) containing mineral oil supplied by Brugarolas (Spain) were tested in Labtap G8 (Microtap, Munich, Germany) with Ti6Al4V workpiece at 300 rpm spindle speed and 6 mm depth of cut. In the experiments, the MWFs were diluted at 10% in deionized water. Observing the results shown in Fig. 5, the tapping torque of the formulated MWF remains below the commercial. The increase in tapping torque is attributed to the increase in tool wear for each consecutive run. Therefore, the formulated EcoMWF was expected to provide better anti-wear performance than the commercial mineral-based lube in titanium alloys.

Chemically modified vegetable oils and fatty alcohols are the most common products for machining with the MQL system [31]. In this study, for the MQL environment, a trimethylolpropane trioleate was used as the same ester oil to formulate the EcoMWF. Fig. 4b shows the MQL externally connected setup with a flow of 0.9 ml/min.

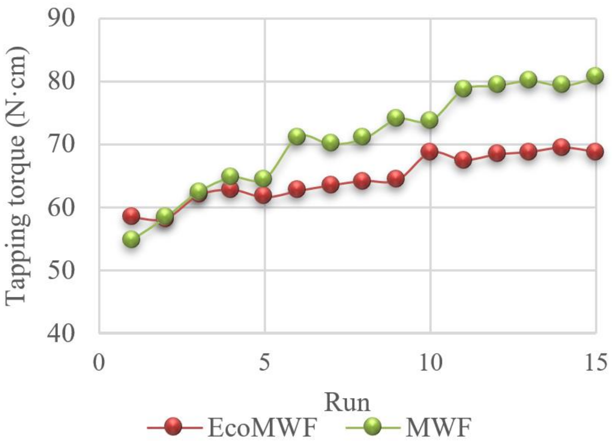


Fig. 5 Tapping torque results with machining consecutive taps with the formulated EcoMWF and commercial MWF

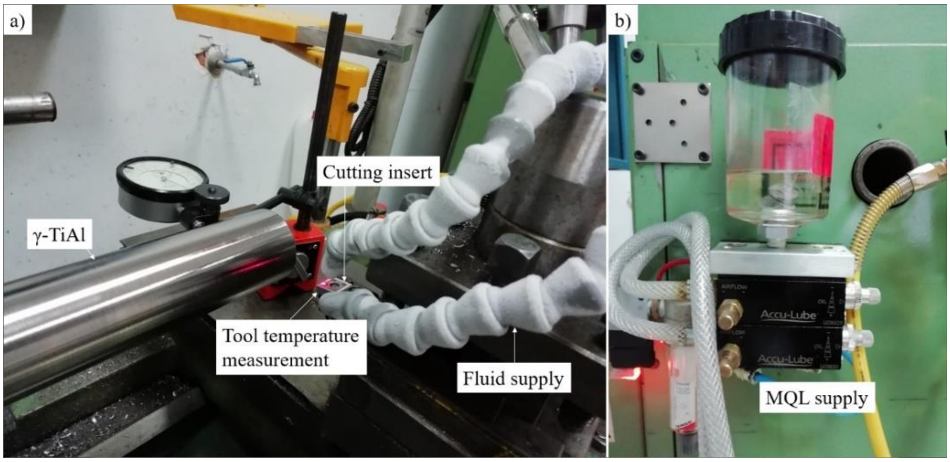


Fig. 4 Experimental configurations under different environments: **a** CCA, cryogenic and MWF fluid supply, and **b** MQL

3 Results

The objective of this work was to investigate the effects of input parameters on the surface roughness and the roundness of the γ-TiAl workpieces as well as the temperature at the tip of the tool, under different environments produced by dissimilar lubrication/cooling systems. The experimental data of the 2 (feed rate levels) x 2 (spindle speed levels) x 2 (insert type levels) x 6 (environment levels) = 48 cutting conditions are presented in the Appendix.

Regarding the chips formed during machining, neither dry condition nor MQL systems could remove chips from the cutting zone, leading to an agglomeration of fine titanium chips that are highly combustible, and even in some experiments, sparks occurred. This danger is present with high cutting temperatures as the chips retain the heat and, worse yet, when oil-based lubricants are used in the machining [10]. Using water-based MWF eliminates the danger of ignition while it removes the chips. In the case of CCA and cryogenic cooling cutting, chips become brittle and easy to break. Furthermore, they offer the advantage that chips can be collected in dry and clean form.

3.1 Tool wear

Tool wear leads to decrease productivity while increasing machining costs. The inserts depicted in Fig. 6 and 7 show the microscopic images of the flank of the uncoated and PVD-coated insert, respectively, used in turning γ-TiAl at different cutting parameters with several lubrication/cooling systems. The examination of the inserts used for machining reveals that the lubrication/system and the insert type are the main parameters determining the tool life. Weather coated or uncoated, the cutting edge is characterized by clearly defined cracks.

At first glance, it is noticeable that the highest tool wear is achieved in dry conditions. Moreover, Fig. 8 shows the excessive wear on the rake face accompanied by discoloration of the uncoated carbide tool and temperature contours of the PVD tool due to the elevated temperatures associated with dry lubrication. The results confirm that dry machining is not appropriate for turning γ-TiAl due to the extreme tool wear.

Table 2 shows the results of the statistical analysis of the flank wear for the linear model. The model F-values of 6.25 implies that the model is significant. Spindle speed, insert type, and environment are significant model terms with p-values below 0.0500.

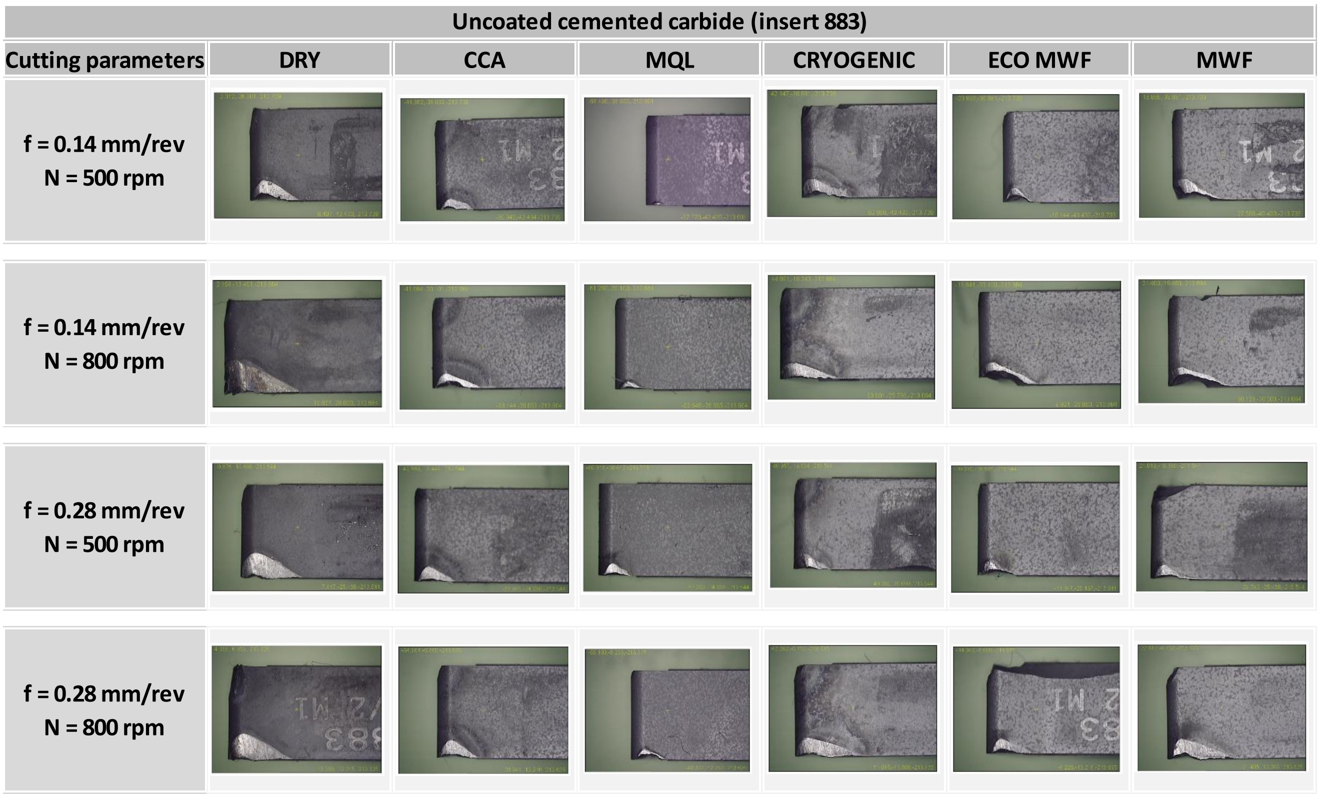


Fig. 6 Microscopic images (objective x0.75) of the flank of the uncoated insert used in turning γ-TiAl at different cutting parameters with different lubrication/cooling systems

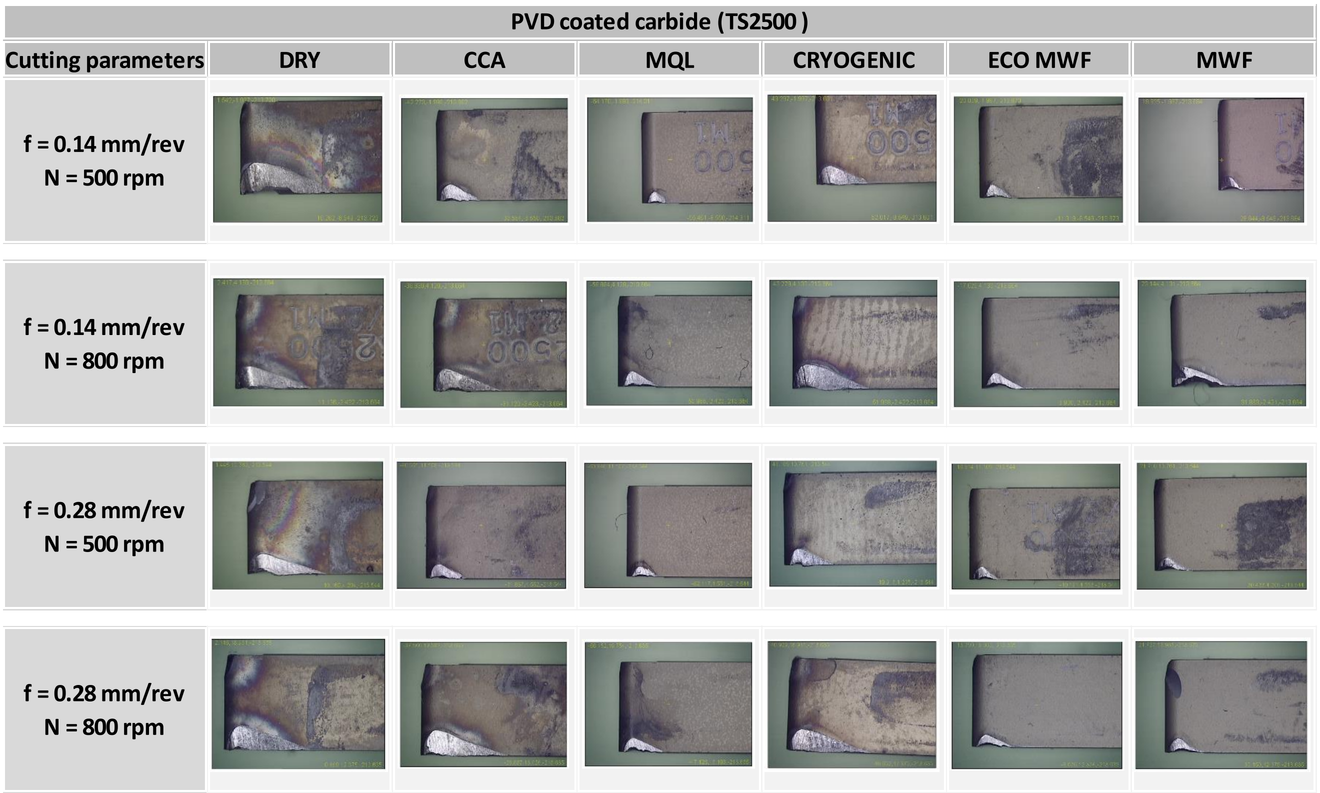


Fig. 7 Microscopic images (objective x0.75) of the flank of the PVD coated insert used in turning γ-TiAl at different cutting parameters with different lubrication/cooling systems

Fig. 8 Microscopic image of the insert during dry turning at 500 rpm and 0.28 mm/rev: **a** uncoated insert (883) and **b** with PVD coated insert (TS2500)

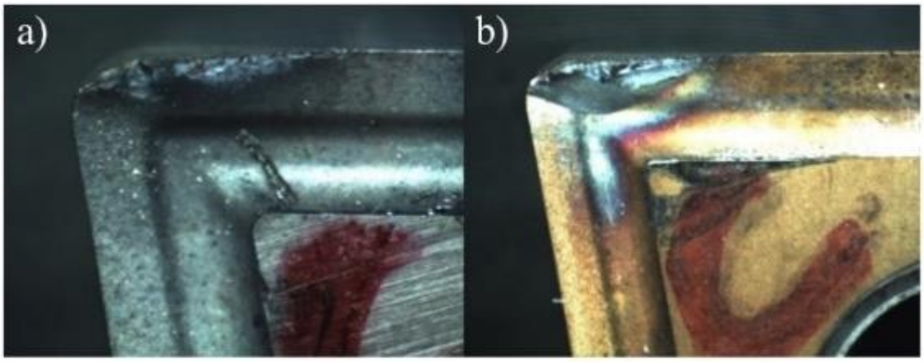


Table 2 Linear ANOVA model for flank wear after turning process

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4.12	8	0.5150	6.25	< 0.0001	significant
A-feed rate	0.1796	1	0.1796	2.18	0.1480	
B-Spindle speed	0.9565	1	0.9565	11.60	0.0015	
C-Insert	1.00	1	1.00	12.14	0.0012	
D-Environment	1.98	5	0.3966	4.81	0.0016	
Residual	3.22	39	0.0824			
Cor Total	7.33	47				

Fig. 9 shows the tool wear using two different tools. Each bar represents a different combination of feed rate and spindle speed, with bars grouped according to the lubrication/cooling system. The wear is more pronounced on the flank face rather than the rake face. The analysis shown in Fig. 9a indicates that the uncoated carbide inserts used during machining with MQL systems prolong the tool life. The high capability of the ester to form a lubricating film protects the surface from flank wear.

At low spindle speed (500rpm), MQL, cryogenic, and EcoMWF are the lubrication/cooling systems that prevent further tool wear. Based on the experimental results, an increase in spindle speed tends to accelerate the flank wear. At these severe conditions, lubrication predominates over cooling capacity, with the lowest tool wear using MQL. The flank wear of uncoated carbide tools (883) is reduced using MQL. With this lubrication/cooling system, rake wear values of approximately 0.1 mm can be achieved.

The coating of the tool has a significant influence on its lifetime, especially in the case of flood systems, where the flank wear of the uncoated carbide tool is, in general, higher than PVD coated tool. The results indicate the benefits of MQL and flood systems in terms of tool life. At the lowest spindle speed of 500 rpm, the results for low (0.14 mm/rev) and high (0.28 mm/rev) feed rates are nearly identical for MQL and flood systems. When turning γ-TiAl with EcoMWF, the TS2500 insert shows reduced flank and rake wear, especially for 500 rpm and 0.28 rev/min, where 0.5 mm2 and 0.03 mm values are achieved, respectively. This empathizes the effectiveness of liquid fluid in reducing the tool wear due to its lubrication film formation, which improves the tool performance and hence, productivity.

In addition to the quantification analysis of the tool wear, the type of wear was studied using SEM. Due to the relatively large number of variables considered in this research, the tools observed belong to a fixed cutting condition of spindle speed of 500 rpm and feed rate of 0.28 mm/rev. This was considered to be sufficient to study the impact of lubrication/cooling systems on tool wear. The wear on cutting tools occurred on the flank face and rake face, although significant wear was produced in the region of the tool nose when turning under dry, cryogenic, and CCA systems. A lack of lubrication effect causes an increase of tool nose wear due to higher friction at the tool-chip interface [32]. CCA shows similar wear characteristics as cryogenic system. It is also observed that between flood systems, EcoMWF and MWF, there are no significant changes in the wear type.

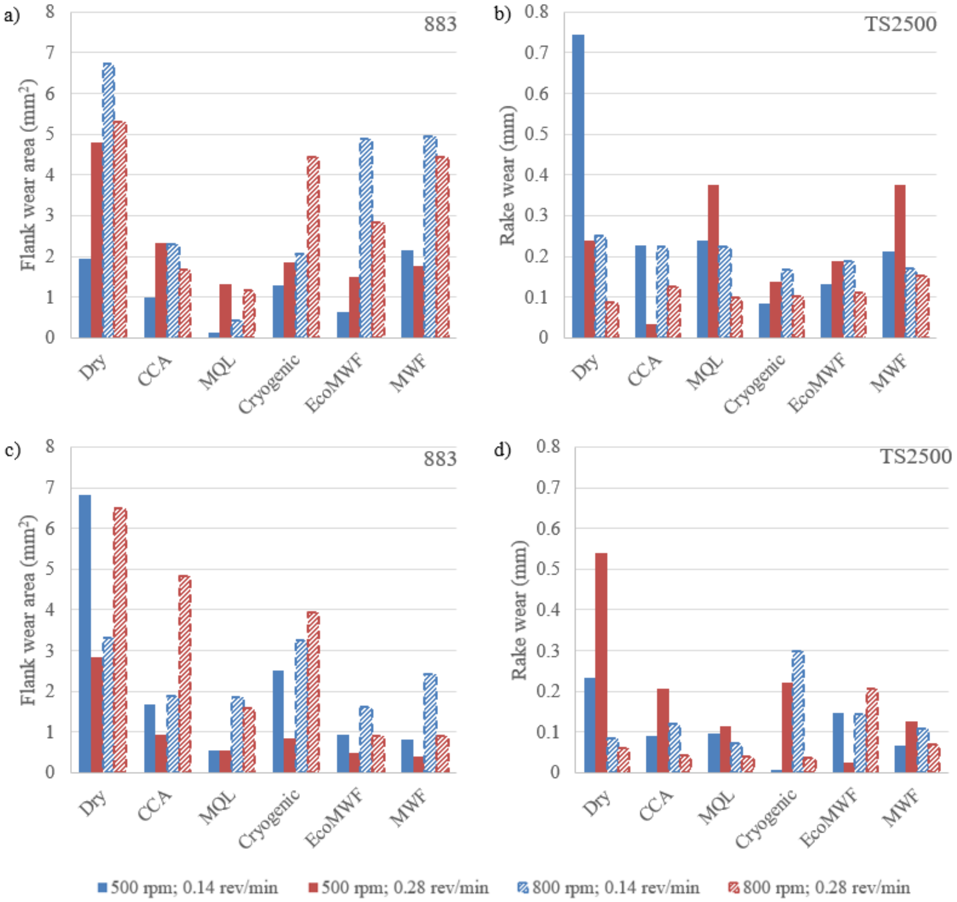


Fig. 9 Tool wear at different cutting parameters with different lubrication/cooling systems: **a** flank wear area of uncoated insert (883), **b** rake wear of uncoated insert (883), **c** flank wear area of PVD coated insert (TS2500), and **d** rake wear of PVD coated insert (TS2500)

Fig. 10 shows the wear types that occurred when turning γ-TiAl using uncoated carbide tools. The severity of tool wear caused catastrophic failure through edge fracture was noticed in all the tests. SEM observations of the damaged tools indicate that there is a high amount of adhered material onto the flank face. Compared to MQL, a smoother adherent layer is formed with flood systems.

Flank wear occurs on the flank face of the tool as a result of the friction between the newly cut surface of the workpiece and the tool flank. The wear initiates at the cutting edge and grows perpendicular to the flank face. Moreover, hard particles are observed on the flank face. These particles may originate from the tool either by the chip formation or the workpiece. The high temperature and the high pressure during machining cause the welding of these particles to the adherent layers of the flank face. Due to the problematic chip evacuation and low cooling effect of MQL, more hard particles weld to the cutting tool. During turning, chips rub in these adherent layers, yielding abrasive mechanisms. Abrasion could also have happened before adhesion, but, in most cases, it was not possible to observe it on the flank face.

From Fig. 11, the cutting edge crack is less for PVD coated carbide tools, although a high amount of adhered material is also observed in the flank face. Abrasive particles stick onto the tool surface and the adherent later. Examination of the worn coated tools revealed that the coating was removed from the substrate. Such delamination occurred with all lubrication/cooling systems used.

Adhesive wear takes place on both coating and substrate surfaces (Fig. 12). A possible explanation for this observable fact is that the workpiece material is adhered to the coating, followed by flaking. As turning progresses, the material continues to adhere to the uncoated substrate. When the coating is removed, the worn tool presents similar wear behaviors to uncoated carbide tools.

A lost of material on the tool rake face and the formation of craters is observed in all cases. Crater wear is a common type of wear when turning titanium alloys, due to the chemical affinity between the workpiece and the cutting tool material [33]. Abrasive particles easily weld to the cutting edge and rake face leading through different wear types, especially with uncoated carbide tools. Fig. 13 shows SEM images of uncoated and PVD coated tools after machining with MWF. Adhesion of workpiece material can be clearly seen on the worn area of the insert and that the coating has been flaking off.

3.2 Surface roughness

The surface roughness of the workpiece was measured at 110, 67, and 15 mm (Ra1, Ra2, Ra3, respectively). Fig. 14 represents the surface roughness average obtained at different cutting parameters with coated and uncoated carbide tools for each length with each lubrication/cooling system. The surface roughness values obtained at the beginning of the turning operation (Ra3) are the highest. As the turning progresses, the surface roughness improves. In terms of workpiece quality, it is undesirable to obtain very different roughness along the workpiece length, which would require an additional finishing operation. When machining with the coated carbide tool, these increments are more prominent in the case of CCA, MQL, and MWF.

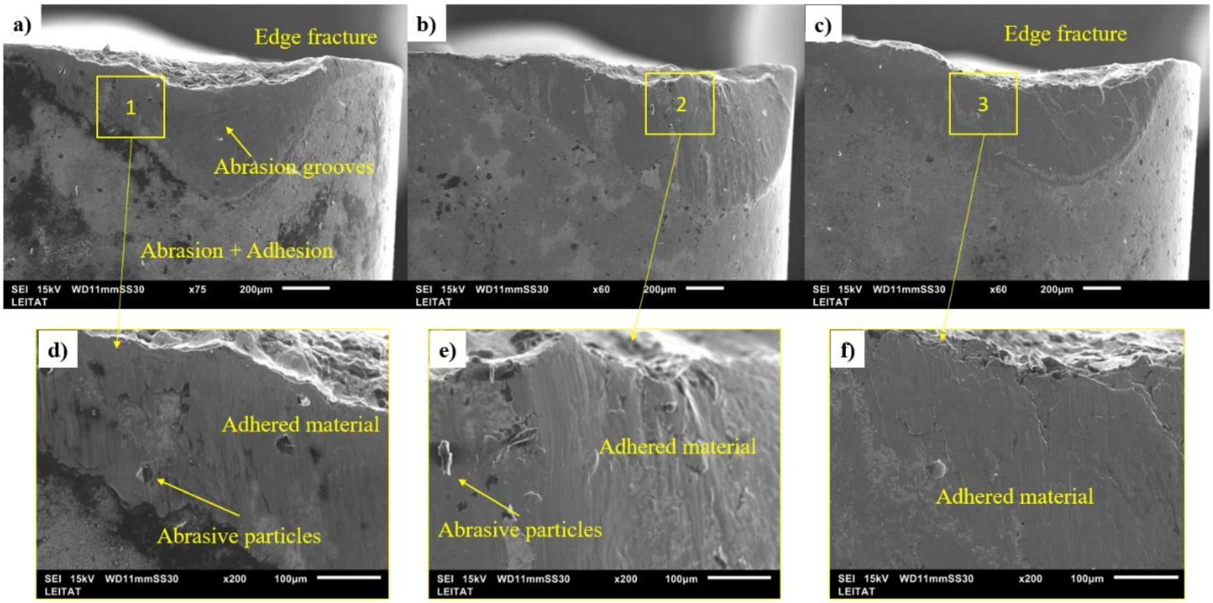


Fig. 10 SEM images of the flank face uncoated carbide tool (883): **a** under MQL, **b** under cryogenic, **c**) under MWF, **d** magnification of area 1, **e** magnification of area 2, and **f** magnification of area 3

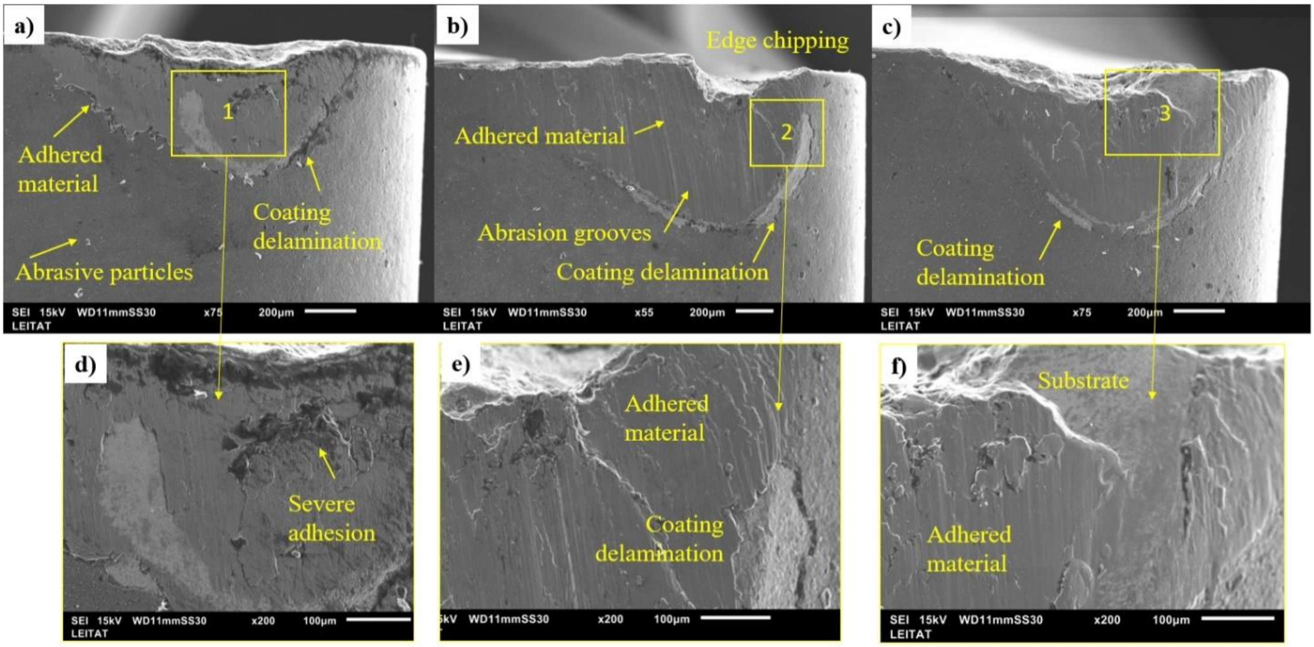


Fig. 11 SEM images of the flank face coated carbide tool (TS2500): **a** under MQL, **b** under cryogenic, **c** under EcoMWF, **d** magnification of area 1, **e** magnification of area 2, and **f** magnification of area 3

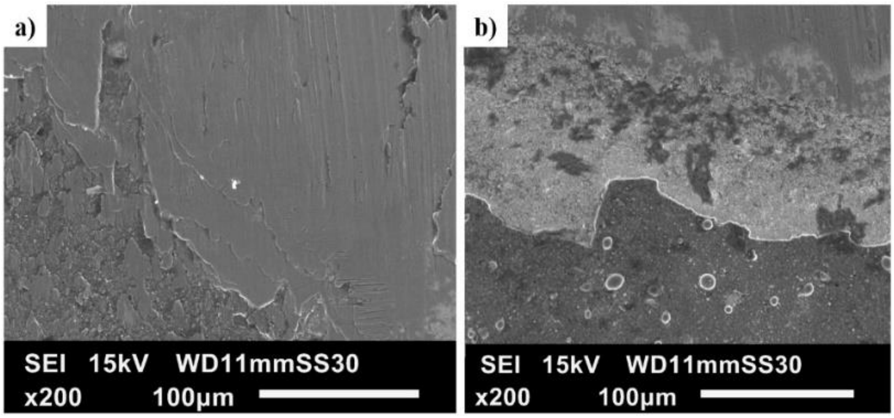


Fig. 12 Flank face areas of the PVD tool with adhered material: **a** on the coating and **b** on the substrates

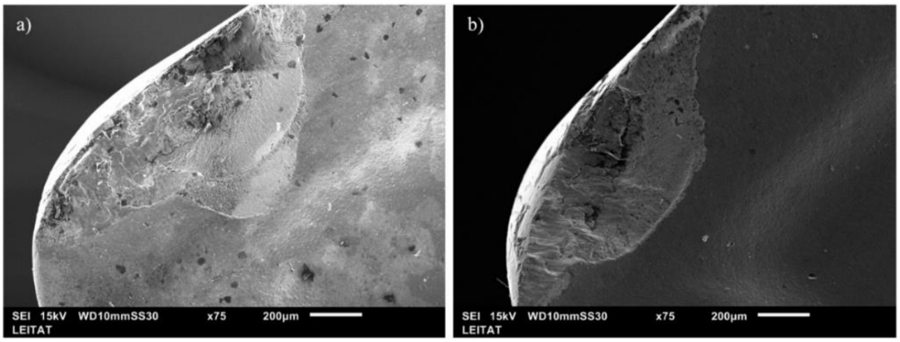


Fig. 13 Rake face of the tool: **a** uncoated (883) and **b** PVD coated insert (TS2500)

The surface roughness average of Ra1, Ra2, and Ra3 (Ra) is used hereafter in the data post-analysis. The influence of varying the insert and environment on surface roughness average at different machining parameters is shown Fig. 15. It can be observed that using EcoMWF, the surface roughness obtained is inside the aeronautic

Fig. 14 Surface roughness values measured at different lengths versus environment with **a** insert 883 and **b** insert TS2500

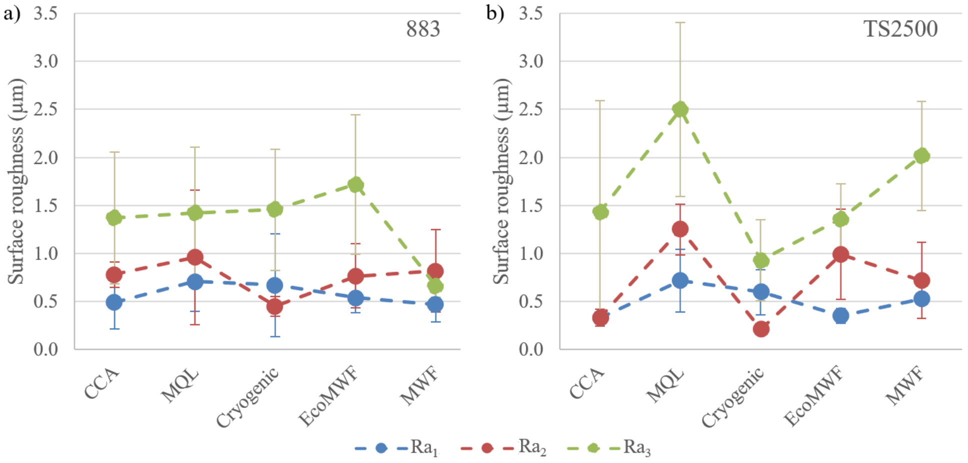
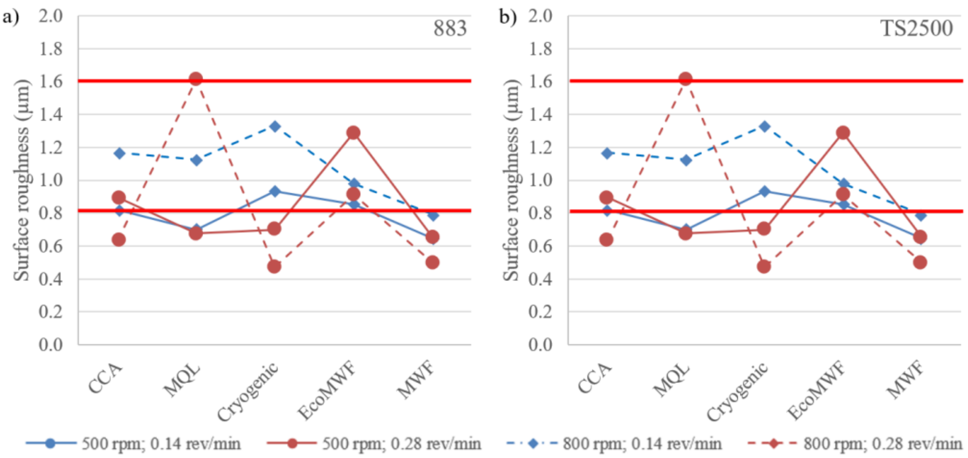


Fig. 15 Surface roughness values, Ra, obtained at different cutting conditions for the different lubrication/cooling systems tested: **a** uncoated insert 883 and **b** coated insert TS2500. The red lines represent the range of the Ra values usually required in the aeronautic sector 0.8 mm<Ra<1.6 mm



requirements (between the range 0.8 µm to 1.6 µm), according to the general criteria of the aeronautic industry [34]. In this case, only at the lowest cutting speed (500 rpm and 0.14 mm/rev) with the coated tool, the surface roughness is slightly below the desired values.

In general, when machining at 800 rpm, the surface roughness values are lower by increasing the feed rate. Whereas, at 500 rpm, slight differences among results can be seen when varying feed rates. Surface roughness varies significantly over the lubrication/cooling system used during machining without any apparent relation to tool wear.

Main differences among lubrication/cooling systems are observed when machining with the uncoated carbide insert (883) at high cutting speed (800 rpm and 0.28 mm/rev). Based on the results obtained, 0.14 mm/rev appears to be the optimum feed rate, where most of the surface roughness values are in the aeronautic requirements range. Compared to 883, after turning γ-TiAl with TS2500 insert, the lubrication/cooling systems influence is more significant. The use of MQL resulted in increased surface roughness.

3.3 Roundness

Roundness is a critical quality parameter during turning, influenced by radial force and elasticity of the material, and is indirectly associated with localized softening caused by localized heat generation [35]. Table 3 shows the ANOVA for the reduced two-factor model interaction (2FI) for roundness. An F-value of 10.35 implies that the model is significant. In this case, the feed rate, the environment, and its relationship with the insert type are the most significant model terms.

Figure 16 presents the influence of using various lubrication/cooling systems on roundness. By analyzing the results for roundness, different trends to those in surface roughness can be observed. When turning γ-TiAl with the uncoated carbide inserts (883), the roundness of the workpiece tends to vary depending on the machining parameters. The PVD-coated tool (TS2500) achieved the best results, and they also show a workpiece quality increase by increasing the feed rate. By comparing flood systems,

Table 3 Reduced 2FI ANOVA model for roundness after turning operation

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4811.65	18	267.31	10.35	< 0.0001	significant
A-Feed rate	368.02	1	368.02	14.25	0.0007	
B-Spindle speed	125.68	1	125.68	4.87	0.0355	
C-Insert	3.09	1	3.09	0.1195	0.7321	
D-Environment	1830.86	5	366.17	14.18	< 0.0001	
BD	310.47	5	62.09	2.40	0.0610	
CD	2173.53	5	434.71	16.83	< 0.0001	
Residual	748.93	29	25.83			
Cor Total	5560.58	47				

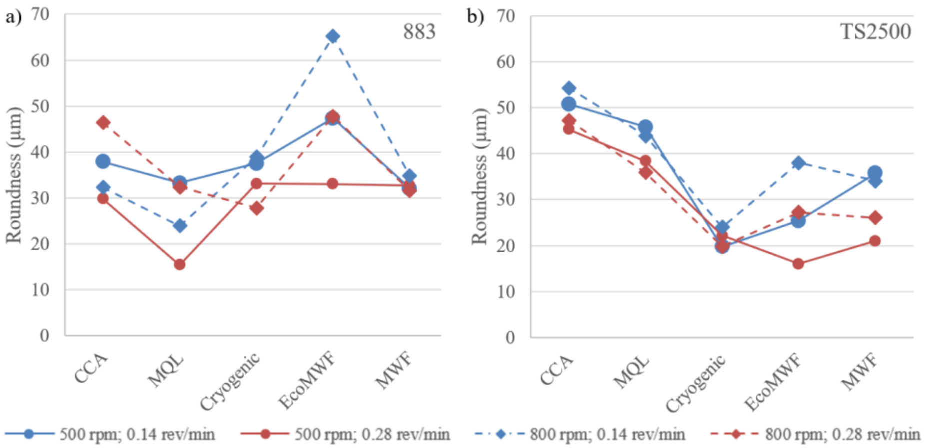


Fig. 16 Influence of insert and environment on the roundness: **a** insert 883 and **b** insert TS2500

roundness values do not show significant changes between the commercial mineral-based MWF and the EcoMWF.

3.4 Temperature

The temperature of the cutting tool depends on the heat generated during turning and the ability of the lubrication/cooling system to dissipate heat. Figure 17 shows the cutting temperatures measured for each lubricating and machining condition. The bar chart indicates the increasing temperature during the turning process, with a maximum temperature of 654 ºC in dry machining and a minimum of 11 ºC with the cryogenic system. As feed rate and spindle speed increase, machining times are reduced (shortened bars).

The temperature sensor cannot measure in MWF environment conditions due to the liquid blocks the measurement. However, the heat-affected zone on the coated tool and the white interface layer on the carbide tool, generated due to heat accumulation, is shown in dry, MQL, and CCA systems, but not on cryogenic and flood systems. The high-water content in EcoMWF and MWF allows removing heat from the machining operation, thus reducing the temperature.

The results of ANOVA for the linear model (Table 4) show the strong influence of the environment on the maximum temperature. The cryogenic system shows the lowest cutting temperatures measured. LN2 absorbs the heat generated during the metal cutting and evaporates rapidly. In this media, the machining conditions where the tool temperature achieves the highest values (348 ºC) is at 0.14 mm/rev, 800 rpm, and using the PVD coated insert.

The temperature of the tool, under CCA and MQL conditions, stood at the lowest compared to dry ones. In dry conditions, the absence of fluid neither lubricates nor removes heat from the cutting zone, increasing the temperature during turning and achieving maximum values of 654ºC at 500 rpm and 0.28 mm/rev with the PVD coated insert. Compared to cryogenic, the MQL system has a reduced cooling capacity due to the low amount of fluid that reached the cutting zone and the low thermal conductivity of ester compared to water, causing the temperature to increase substantially.

4 Discussion

From the results shown above, the lubrication/cooling system used on the machinability of gamma titanium aluminides alloy has shown a high impact on tool wear, surface roughness, and roundness. The wear types

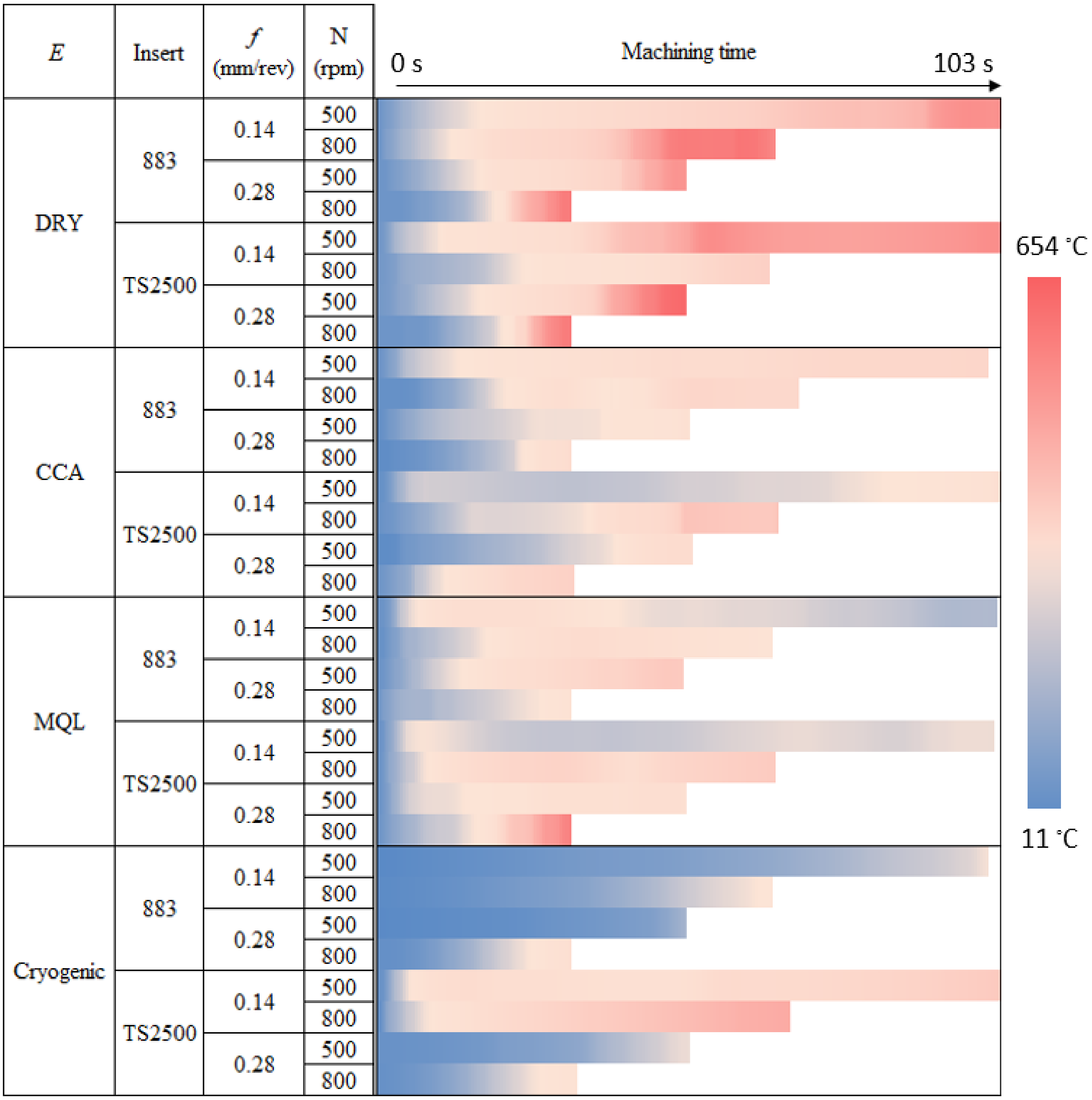


Fig. 17 Influence of the lubrication/cooling system, tool, and machining parameters on the temperature of the tool

Table 4 Linear ANOVA model for maximum temperature achieved during the turning operation

Source	Sum of Squares	ff	Mean Square	F-value	p-value	
Model	12.02	6	2.00	7.42	0.0001	significant
A-Feed rate	0.0097	1	0.0097	0.0358	0.8514	
B-Spindle speed	0.5507	1	0.5507	2.04	0.1655	
C-Insert	0.4911	1	0.4911	1.82	0.1894	
D-Environment	10.97	3	3.66	13.55	< 0.0001	
Residual	6.75	25	0.2698			
Cor Total	18.76	31				

usually observed when machining titanium aluminides include flank wear, crater wear, chipping, and fracture of the cutting edge [4]. The cutting tool presents different wear mechanisms depending on the tool areas. SEM observations indicate that the predominant tool wear mechanism is adhesion, followed by attrition of workpiece material on the flank and rake surface, which cause severe tool wear. Under all cutting conditions, the removal of tool material by the adherent material (attrition) was observed on the cutting edge.

In most cases, the adhered layer was found mainly on the flank face rather than on the rake face. This suggests that the adhered material on the rake face had been removed, causing chipping of tool material. As wear increases, the tool is subjected to more force and heat, leading to a higher temperature in the cutting zone and higher vibrations Many sparks are produced when flood systems are not used. Coated carbide tools show a low beneficial impact on the tool's wear due to the severe crater wear that rapidly removes the coating, leading to an exposed substrate. However, the coating delays various wear types and helps increase tool life.

There is no clear relationship between surface roughness and tool wear. This performance can be explained, in part, by the increased edge radius, which can improve surface roughness [36]. According to the study of Derani and Ratnam [37], a decrease in Ra is often interpreted as an improvement in surface roughness. However, as the authors explained, Ra can decrease due to gradual tool wear. During finish turning, the nose region of the tool engages the workpiece and shapes the surface profile. The theoretical surface roughness can be estimated by the following equation [9]:

$$R_a = 0.032\frac{f^2}{r} \quad (1)$$

where f is the feed rate and r is the tool nose radius.

There are two main reasons why surface roughness varies during machining for a fixed feed rate. On one hand, the wear, chipping, or fracture at the nose region, changes the effective nose radius. On the other hand, the increase of the tool wear flank causes tool chatter and vibration that affects the surface quality of the workpiece [37]. During machining, the surface roughness values decreased. Initially, when the tool is new and, the nose radius is 0.8mm, Ra values are close to the theoretical Ra. As cutting progresses, the insert tends to suffer excessive nose wear. The nose radius increases, and following equation 1, Ra decreases.

This also explains why the surface roughness values using cryogenic and CCA systems are lower than MQL and flood systems, especially when machining with the coated carbide tool. It is observed from Fig. 18 that the nose region of the tool is seriously damaged under cryogenic machining, those reducing the effective nose radius. However, it cannot be dismissed that other types of tool wear, the temperature on the cutting zone, chip flushing capability, and vibration, can affect the surface roughness of the workpiece. For instance, due to the lack of chip evacuation of MQL systems and the low plasticity of γ-TiAl alloy, the chip can scratch the workpiece surface, leading to an increase of Ra values [28].

Considering both tool wear and surface roughness, when turning with TS2500 tool, EcoMWF offered the best performance at 500 rpm and 0.28 rev/min. With 883 tool, the best alternative is the use of MQL at 800 rpm and 0.28 rev/min, flowed by CCA and EcoMWF at 500 rpm and 0.14 rev/min. The absence of lubrication and cooling functions during dry machining leads to higher friction and higher cutting temperature, which results in severe tool wear and catastrophic failure. Under flood machining, metalworking fluids reduce the heat generated and remove abrasive particles from the cutting zone. Moreover, metalworking fluids form an organic film on the metal surface, thus reducing the cutting forces and tool wear [38]. Comparing the two metalworking fluids, EcoMWF showed lower tapping torque values than conventional MWF (Fig. 4). When using MWF, the rapid tool wear increases the cutting forces measured during tapping, which is highly sensitive to lubrication [39].

During finish turning with MQL, an ester is supplied in the cutting zone. The ester adheres to the surface, forming a lubricant film, which reduces friction forces and tool wear. The high viscosity of the ester, compared to metalworking fluids, tends to resist the flow, thus providing a more effective lubricating at the tool-chip interface, which reduces friction

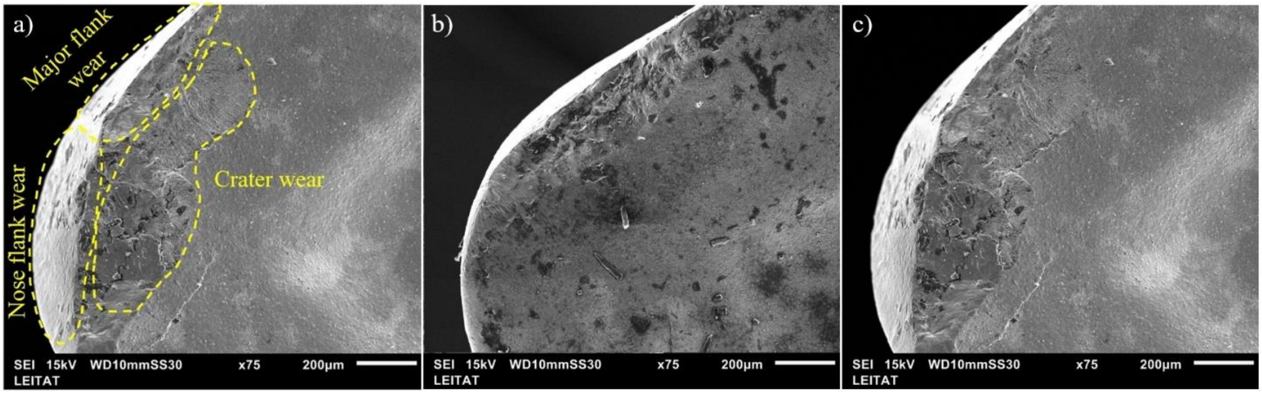


Fig. 18 SEM images of tool rake face when turning γ-TiAl with uncoated carbide tool at 500 rpm and 0.28 mm/rev: **a** tool wear types, **b** under MQL and **c** under cryogenic

and prevents rapid tool wear [40]. However, the poor chip evacuation and low cooling capacity cause higher surface roughness values.

On the contrary, the use of LN2 and CCA improves the effective cooling action due to the extremely low temperatures. The fluid supply pressure removes the abrasive particles, although it is less efficient than flood systems. Compared to MQL, when turning with cryogenic and CCA systems, the flank wear increases, particularly with PVD coated carbide tools. This may be attributed to the lack of lubrication and the abrasive mechanism, which leads to flank and nose wear. The coating of the insert is removed and followed by an abrasion of the base tool material and adhesion of workpiece.

The evaluation of the eco-efficiency of the lubrication/cooling systems considers the technical and environmental impacts for each lubrication/cooling system. Additionally, some features should be considered, as the ability to remove chips, fire prevention, and its economic and environmental aspects. All the features of the generated data are rescaled within the range of 1 (worst) to 5 (best). All the indices in the radar chart (Fig. 19) have been considered of equal importance. From Fig. 19, the eco-efficiency of each lubrication/cooling system can be easily established.

Eliminating the lubrication/cooling system, as in dry machining, has shown a reduced capacity to remove heat from the cutting zone, resulting excessive tool wear and catastrophic tool failure. Moreover, its low chip evacuation causes fire due to the agglomeration of metal particles and the high temperature in the cutting zone. In addition, although it is advantageous in terms of environmental impact because there is no fluid consumption and no fluid residue on the workpiece or chips to be treated, there is a high cost of tools due to their short life. Therefore, this analysis confirms that dry machining is not suited for turning γ-TiAl.

The application of cold-compressed air in turning γ-TiAl improves the cooling capacity, but not enough to avoid spark. Additionally, in terms of roundness and surface roughness, the workpiece quality is highly dependent on the cutting speed. CCA is considered one of the cleanest lubrication/cooling systems.

Using cryogenic not only can reduce tool temperature but also enhance the workpiece quality. LN2 absorbs the heat generated during cutting and evaporates without leaving a harmful residue. However, its reduced lubricating capacity results in excessive tool wear, regardless of the tool used. Despite the high electrical energy consumption to produce LN2 [41], it is an alternative that may be of particular interest in special operations.

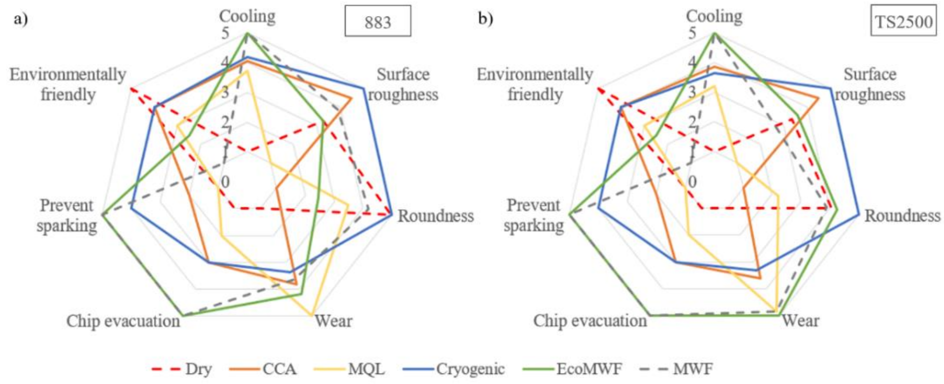
To make a remarkable reduction in the MWF consumption, MQL was studied. Due to its high affinity with the surface, it forms a lubricating film resulting in a reduction of tool wear. The biodegradable ester used as a lubricating fluid is consumed entirely during the turning operation, eliminating the need for fluid disposal. Nevertheless, like dry machining, there is a problematic chip evacuation which, together with the organic ester, increases the probability of fire hazard.

Flood system can effectively remove heat and chips from the cutting zone, resulting in longer tool life and prevents sparking. The use of EcoMWF and MWF resulted in reduced surface roughness. Using EcoMWF, surface roughness values are within the parameters of the aeronautic industry (0.8 mm < Ra<1.6 mm). The presence of the tool coating appears to have a beneficial effect on tool wear and surface quality. Comparing the two flood systems, EcoMWF formulation leads to reduced tool wear, enhancing the use of this system as an alternative to mineral-based MWF. Moreover, the properties of EcoMWF based on esters reduce the contribution to global warming compared to fossil carbon sources by nearly four times [42].

5 Conclusions

This work compares different sustainable lubrication/cooling systems that can be employed in repair and maintenance turning operations of aeronautic industry workpieces made of γ-TiAl. In particular, the feasibility of using the EcoMWF

Fig. 19 Radar chart with the general perspective of the technical and environmental impact for each lubrication/cooling system with **a** uncoated carbide tool (883) and **b** PVD coated carbide tool (TS2500)



developed ad hoc for this study. Tool wear, surface roughness (in terms of Ra), roundness and cutting temperature have been analyzed as response variables. Following are the main conclusion drawn from this study:

- From the observations using SEM on the worn tools, it can be concluded that the tools failed primarily on the flank and rake faces of the insert. Crater, nose wear, and adhesion of material were observed. The underlying wear mechanisms responsible for these types of wear were characterized mainly as abrasive and adhesive, giving rise to attrition. Furthermore, due to the removal of the coating material, TS2500 fails similar to the uncoated tool 883.
- Tool wear could be a key performance indicator to compare different lubrication/cooling systems, while surface roughness data could lead to incorrect conclusions if other changes on the profile topography are ignored. Further work should include the study of the subsurface deformation and microstructure alteration of the workpiece.
- The PVD-coated tool also shows promising results in the machinability of γ-TiAl. After turning γ-TiAl with TS2500 insert, flank wear is significantly lower than with the uncoated carbide tool (883), especially under MQL and flood systems.
- The statistical analysis showed that the lubrication/cooling system is the most influential parameter in the turning process of γ-TiAl. Also, the interaction of environment and tool types has a significant influence on surface roughness and roundness.
- At all the cutting speeds, MQL has outperformed in terms of tool wear (flank and rake) compared to dry, cryogenic, and CCA machining conditions. Hence, flood systems (EcoMWF and MWF) performed the best machining for the turning of γ-TiAl within the selected range of cutting parameters and the TS2500 tool.
- Considering both tool wear and surface roughness, when turning with TS2500 tool, EcoMWF offered the best performance at 500 rpm and 0.28 rev/min. With 883 tool, the best alternative is the use of MQL at 800 rpm and 0.28 rev/min, flowed by CCA and EcoMWF at 500 rpm and 0.14 rev/min.
- Overall, the formulated water-based MWF with a synthetic ester (EcoMWF) can be identified as a lubrication/cooling system to potentially enhance cutting performance through tool wear reduction and surface quality enhancement, as at the same time the environmental and health are reduced.

The novelty of this work depends upon exploring some green lubrication/cooling systems to improve the machinability of third-generation γ-TiAl and the formulation of a newly eco-efficient water-based MWF. Future research may focus on the machinability of hybrid lubricating/cooling systems such as MQL together with cold-compressed air or cryogenic cooling for gamma titanium aluminides.

Appendix. Experimental data for the turning process of γ-TiAl

Run	Insert	*f* (mm/rev)	*N* (rpm)	Environment	Ra at 110 mm Ra_1 (μm)	Ra at 67 mm Ra_2 (μm)	Ra at 15 mm Ra_3 (μm)	Roundness (μm)	Temperature (ºC)
1	883	0.14	500	MQL	0.64	0.64	0.82	33.26	108.1
2	883	0.14	800	MQL	0.61	0.50	2.27	23.96	115.6
3	883	0.28	500	MQL	0.43	0.70	0.90	15.44	206.2
4	883	0.28	800	MQL	1.15	2.00	1.69	32.37	88.7
5	TS2500	0.14	500	MQL	1.18	1.50	1.53	45.81	74.5
6	TS2500	0.14	800	MQL	0.41	1.39	3.66	43.89	195.7
7	TS2500	0.28	500	MQL	0.63	1.22	2.70	38.42	105.8
8	TS2500	0.28	800	MQL	0.66	0.89	2.11	35.89	533.4
9	883	0.14	500	DRY	0.29	1.18	1.20	19.17	480.1
10	883	0.14	800	DRY	0.47	0.19	2.71	18.77	598.5
11	883	0.28	500	DRY	0.42	0.34	1.86	20.64	452.9
12	883	0.28	800	DRY	0.66	0.56	1.54	22.81	566.2
13	883	0.14	500	CCA	0.49	0.77	1.20	37.92	145.3
14	883	0.14	800	CCA	0.26	0.86	2.38	32.30	145.5
15	883	0.28	500	CCA	0.87	0.89	0.93	29.80	98.8
16	883	0.28	800	CCA	0.33	0.60	0.97	46.40	116.2
17	TS2500	0.14	500	DRY	0.52	0.39	0.42	29.79	487.4
18	TS2500	0.14	800	DRY	0.64	0.27	0.57	32.59	173.0

19	TS2500	0.28	500	DRY	0.35	0.22	0.89	27.67	654.0
20	TS2500	0.28	800	DRY	0.46	0.33	0.43	21.83	565.2
21	TS2500	0.14	500	CCA	0.28	0.40	0.48	50.80	104.3
22	TS2500	0.14	800	CCA	0.34	0.20	3.03	54.26	231.8
23	TS2500	0.28	500	CCA	0.33	0.36	1.54	45.27	115.3
24	TS2500	0.28	800	CCA	0.37	0.36	0.66	47.22	166.1
25	883	0.14	500	Cryogenic	0.34	0.55	1.91	37.50	73.4
26	883	0.14	800	Cryogenic	1.47	0.48	2.04	38.93	81.3
27	883	0.28	500	Cryogenic	0.46	0.46	1.18	33.10	40.6
28	883	0.28	800	Cryogenic	0.41	0.31	0.70	27.84	101.5
29	TS2500	0.14	500	Cryogenic	0.29	0.23	0.68	19.71	205.7
30	TS2500	0.14	800	Cryogenic	0.72	0.17	1.28	23.98	347.9
31	TS2500	0.28	500	Cryogenic	0.83	0.22	1.29	22.20	69.4
32	TS2500	0.28	800	Cryogenic	0.55	0.23	0.46	19.82	89.8
33	883	0.14	500	EcoMWF	0.48	1.25	0.83	47.31	-
34	883	0.14	800	EcoMWF	0.35	0.54	2.05	65.20	-
35	883	0.28	500	EcoMWF	0.64	0.72	2.51	33.08	-
36	883	0.28	800	EcoMWF	0.70	0.55	1.49	47.79	-
37	TS2500	0.14	500	EcoMWF	0.33	0.57	0.84	25.42	-
38	TS2500	0.14	800	EcoMWF	0.27	1.17	1.43	38.00	-
39	TS2500	0.28	500	EcoMWF	0.45	0.65	1.47	16.03	-
40	TS2500	0.28	800	EcoMWF	0.35	1.57	1.70	27.25	-
41	883	0.14	500	MWF	0.72	0.61	0.61	32.11	-
42	883	0.14	800	MWF	0.43	1.36	0.59	34.78	-
43	883	0.28	500	MWF	0.42	0.94	0.61	32.74	-
44	883	0.28	800	MWF	0.30	0.37	0.83	31.61	-
45	TS2500	0.14	500	MWF	0.46	0.46	2.83	35.70	-
46	TS2500	0.14	800	MWF	0.57	0.74	1.70	34.04	-
47	TS2500	0.28	500	MWF	0.55	0.41	1.57	21.02	-
48	TS2500	0.28	800	MWF	0.54	1.27	1.96	26.05	-

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Author Contributions EB Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing—original draft preparation, Writing—review and editing. EMR Conceptualization, Methodology, Validation, Formal analysis, Writing—review and editing, Supervision, Project administration, Funding acquisition. LA Conceptualization, Formal analysis, Writing—review and editing. MAS-N: Formal analysis.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Capítulo 5. Otras aportaciones científicas derivadas de la Tesis Doctoral

Participación en el congreso internacional “*Tribology International Conference 2022*” con la comunicación oral que se detalla a continuación:

Congreso: **Tribology International Conference 2022** (TRIBOLOGY2022)
Entidad organizadora: Setcor Media FZ-LLC
Carácter: Internacional
Lugar celebración: Barcelona
Fecha: 27-29 de abril de 2022
Título: Development of sustainable and effective water-based metalworking fluid for titanium machining
Autores: E. Benedicto, E.M. Rubio, L. Aubouy, M.M. Marín
Tipo de participación: comunicación oral
Publicación: Book of abstracts (ver Apéndice E)

Participación en el congreso internacional “*The International Conference on Advances in Material & Processing Technologies 2016*” con el póster que se detalla a continuación:

Congreso: **The International Conference on Advances in Materials & Processing Technologies** (AMPT2016)
Entidad organizadora: Institute of Metals and Technology (IMT)
Carácter: Internacional
Lugar celebración: Kuala Lumpur (Malasia)
Fecha: 15-18 de noviembre de 2016
Título: Technical, economic and environmental review of the lubrication/ cooling systems used in machining processes
Autores: E. Benedicto, D. Carou, E.M. Rubio
Tipo de participación: póster (ver Apéndice F)
Publicación: Benedicto, E., Carou, D., Rubio, E.M., Technical, economic and environmental review of the lubrication/cooling systems used in machining processes, Procedia Engineering, 184, 2017, 99-116. doi: 10.1016/j.proeng.2017.04.075).

A continuación, se presentan los detalles de la publicación (Tabla 10) relacionada con la participación en el congreso internacional "*The International Conference on Advances in Material & Processing Technologies 2016*". La copia completa de la publicación y los indicios de calidad de este artículo pueden encontrarse en el Apéndice G.

Tabla 10. Datos de la publicación e indicios de calidad de *Technical, economic and environmental review of the lubrication/ cooling systems used in machining processes.*

Título	**Technical, economic and environmental review of the lubrication/ cooling systems used in machining processes**	
Autores	Elisabet Benedicto, Diego Carou, Eva María Rubio	
Revista	Procedia Engineering	
ISSN	18777058	
Editorial	Elsevier BV	
País	Países Bajos	
Volumen	184	
Páginas	99-166	
Fecha	2017	
doi	10.1016/j.proeng.2017.04.075	
Indicios de calidad	**Factor de impacto**	0,282 (SJR-2017)
		0,286 (SJR-2016)
	H index	88 (SJR-2017)
		88 (SJR-2017)
	Nº de citas	**122 (18 autocitas)**

Capítulo 6. Conclusiones y desarrollos futuros

Los fluidos de corte tienen un rol muy significativo durante el mecanizado, pero su uso presenta algunos inconvenientes, como sus efectos negativos sobre el medioambiente y la salud de los trabajadores, así como los costes asociados a los equipos del sistema de lubricación, la compra del fluido de corte y el tratamiento del residuo. Todo ello, sumado a la regulación gubernamental, está animando a las empresas a implantar sistemas de lubricación y refrigeración más eficientes y sostenibles. Las técnicas alternativas como el mecanizado en seco, el MQL, la refrigeración criogénica y gaseosa se han implementado en algunos procesos de mecanizado, incluso pueden llegar a ser más eficientes que la lubricación/refrigeración convencional. Sin embargo, todavía hay aplicaciones en las que no se pueden eliminar los fluidos de corte, como es el caso del mecanizado de aleaciones de titanio, más concretamente de γ-TiAl.

En esta Tesis Doctoral se han investigado y desarrollado nuevos fluidos de corte eco-eficientes para superar las dificultades del mecanizado de aleaciones de titanio. Este estudio aborda algunas de las necesidades relacionadas con los sistemas de lubricación y refrigeración que se habían detectado en anteriores trabajos: 1) investigación y desarrollo de fluidos de corte sostenibles para materiales no ferrosos (titanio, aluminio, magnesio, cobre, latón) y superaleaciones (níquel, cobalto) y, 2) sustitución de compuestos peligrosos y no renovables de los fluidos de corte, como el ácido bórico o las aminas secundarias, por compuestos renovables y biodegradables [93,94].

Además, esta Tesis Doctoral contribuye al conocimiento actual:

- Este estudio aborda la necesidad de investigación de sistemas de lubricación y refrigeración durante el mecanizado de aleaciones, concretamente de los aluminuros de titanio.
- El conocimiento adquirido durante este estudio sobre la operación de torneado de γ-TiAl en relación con la herramienta, los parámetros de corte y los sistemas de lubricación y refrigeración sostenibles en el desgaste de la herramienta y la calidad de la pieza, puede constituir una base sólida para mejorar tanto la sostenibilidad como superar los retos técnicos del mecanizado de otras aleaciones difíciles de mecanizar.
- La principal contribución en el desarrollo del fluido de corte es el nuevo método establecido para poder diseñar y optimizar los fluidos de corte específicos teniendo en cuenta el material de la pieza de trabajo.

6.1. Conclusiones generales

De los artículos publicados que constituyen esta Tesis Doctoral, se pueden extraer las siguientes conclusiones generales:

- El fluido de corte O/W, al estar en contacto con la pieza de trabajo, forma una película orgánica que lubrica la superficie metálica y protege la herramienta del desgate [95]. Las interacciones entre los tensoactivos y el éster (usados para formular taladrinas) y su capacidad de adherirse a la superficie metálica, tienen un impacto muy significativo en la formación de la película lubricante y, por lo tanto, en la eficiencia del fluido de corte [96].
- Se ha establecido un método para evaluar la afinidad entre los compuestos químicos utilizados en los fluidos de corte con diferentes superficies metálicas. Esto permite diseñar un fluido de corte que optimice la formación de la película y, por tanto, mejorar su eficiencia en términos de lubricidad y proteger la herramienta del desgaste [95].
- El método desarrollado es una herramienta que permite optimizar la concentración de éster de la taladrina y conocer su interacción con otros compuestos orgánicos como los tensoactivos y las aminas, que desempeñan un papel clave en el rendimiento de la lubricación [95].
- En la superficie metálica, existe un fenómeno de competencia de adsorción entre el éster, el tensoactivo y otros aditivos. La estructura química de los ésteres tiene un gran impacto en la conformación de la película lubricante que, a su vez, también tiene un efecto en las propiedades lubricantes del fluido de corte y en la vida útil de la herramienta [97].
- Es posible variar la afinidad entre el éster y la superficie, modificando la estructura química del tensoactivo. Es decir, variando el tipo de tensoactivo y con la misma cantidad de éster, se puede incrementar la adherencia del éster en la superficie metálica y mejorar la formación de la película lubricante [96].
- Los ésteres de poliol son un candidato potencial para sustituir los aceites minerales de las taladrinas usadas durante el mecanizado de aleaciones de titanio. Variando la estructura química del éster, se puede mejorar la lubricidad y alargar la vida de la herramienta [97].
- Para mejorar la eficiencia y sostenibilidad de los fluidos de corte se ha reemplazado el aceite mineral con éster de poliol y se han eliminado las sustancias peligrosas de los fluidos de corte convencionales. Además, como fluido para el sistema MQL, se ha utilizado el mismo éster de poliol (trioleato de trimetilolpropano) por su origen de fuentes renovables, elevada biodegradabilidad y buena capacidad de lubricación [98].
- Se ha comprobado la viabilidad de utilizar el nuevo fluido de corte formulado con un éster sintético (EcoMWF), desarrollado *ad-hoc* para este estudio. Para el torneado de γ-TiAl, se ha identificado el EcoMWF como un sistema de lubricación/refrigeración que mejora el rendimiento del fluido de corte a través de la reducción del desgaste de la herramienta y la mejora de la calidad superficial de la pieza, al mismo tiempo que se reduce el impacto medioambiental y sobre la salud de los trabajadores [98].
- Los sistemas de lubricación y refrigeración tienen un rol muy importante en la eficiencia del torneado para operaciones de reparación y mantenimiento de piezas de γ-TiAl para la industria

aeronáutica [98]. Por un lado, el menor desgaste de herramienta se obtiene al mecanizar con el sistema MQL. Por otro lado, los mejores acabados superficiales de la pieza se consiguen con los sistemas de inundación (EcoMWF y MWF) y la herramienta con recubrimiento [98].

6.2. Conclusiones particulares

De los artículos publicados que conforman esta Tesis Doctoral, se pueden extraer las siguientes conclusiones particulares:

- Gracias al pico característico C=O de los ésteres de poliol, se puede determinar el porcentaje de éster que queda adherido a la superficie de Ti6Al4V al estar en contacto con el fluido de corte, mediante espectroscopía de absorción por reflexión de infrarrojos. La película orgánica formada sobre la superficie de metal puede ser cuantificada rápidamente mediante el análisis de carbono orgánico total. La sensibilidad del método permite detectar y analizar la película orgánica que se encuentra en la superficie del metal [95].
- Cuando se incrementa la concentración del tensoactivo en el fluido de corte, se forma una mayor película lubricante en la superficie de Ti6Al4V. Este efecto es más significativo cuando se incrementa la concentración del éster [95].
- En comparación con los tensoactivos no-iónicos, los aniónicos promueven la adhesión de éster trioleato de trimetilolpropano. Cuanto más se adhiere el éster, menores son los valores del esfuerzo de torsión, lo que indica un menor desgaste [96].
- Independientemente del tipo de tensoactivo, ya sea aniónico o no-iónico, cuanto más larga es la cadena de hidrocarburos del tensoactivo, mayor es la reducción del desgaste. Al incrementar la longitud de la cadena de hidrocarburos del tensoactivo aniónico, la concentración de éster en la película orgánica aumenta [96].
- La lubricidad mejora al aumentar el número de etoxilaciones de los tensoactivos aniónicos. Aunque haya menos tensoactivo en la superficie, debido al aumento de la solubilidad, la cantidad de ésteres aumenta, formando una capa más resistente [96].
- La combinación de un tensoactivo no-iónico y un aniónico con cadena de hidrocarburo C18 (ácido oleico) y 8 grupos etoxilados, como el AC18E9, mejora la lubricidad y alarga la vida de las herramientas [96].
- El aumento de la concentración de éster en la película lubricante mejora el rendimiento tribológico y prolonga la vida útil de la herramienta. La adición de un éster de poliol en el fluido de corte aumenta la lubricidad hasta un 17% y puede reducir el desgaste de la herramienta hasta un 37% [97].
- Mediante la adición de 1 mmol/L de éster en una taladrina, el éster trioleato de trimetilolpropano puede duplicar la cantidad de éster adherido a la superficie de Ti6Al4V en comparación con el oleato de isopropilo [97].
- En el torneado de piezas de γ-TiAl, el fallo de la herramienta se produce principalmente en la cara de incidencia y de desprendimiento. Se observan cráteres, desgaste del radio de la nariz y adhesión de material. Los mecanismos de desgaste subyacentes responsables de estos tipos de desgaste se atribuyen principalmente al desgaste abrasivo y adhesivo [98].

- No se ha encontrado ninguna relación significativa entre la rugosidad superficial media aritmética (*Ra*) y el desgaste de la herramienta. Una disminución de *Ra* puede interpretarse como una mejora de la rugosidad superficial. Sin embargo, la *Ra* puede disminuir por un aumento del radio del filo de corte debido al desgaste gradual de la herramienta [98].
- El desgaste de la herramienta es un indicador de rendimiento clave para comparar diferentes sistemas de lubricación y refrigeración, mientras que los datos de rugosidad superficial pueden llevar a conclusiones incorrectas si se ignoran otros cambios en la topografía del perfil de la pieza [98].
- En el torneado de γ-TiAl, el desgaste del flanco de la herramienta con recubrimiento de PVD es significativamente menor que el de la herramienta sin recubrimiento, especialmente bajo sistemas MQL y de inundación. Sin embargo, con todos los sistemas de lubricación y refrigeración usados, se observa desprendimiento del recubrimiento [98].
- En el torneado de γ-TiAl usando la herramienta con recubrimiento, los mejores resultados, considerando tanto el desgaste de la herramienta como la rugosidad superficial, se obtienen con el EcoMWF a 500 rpm y 0,28 rev/min. Con la herramienta sin recubrimiento, la mejor alternativa es el uso de MQL a 800 rpm y 0,28 rev/min, seguido por el CCA y el EcoMWF a 500 rpm y 0,14 rev/min [98].
- La eliminación de los sistemas de lubricación y refrigeración no es adecuada para el torneado de γ-TiAl. El mecanizado en seco da lugar a un desgaste excesivo de la herramienta y al fallo catastrófico de la misma. Además, su escasa capacidad para evacuar las virutas provoca chispas debido a la aglomeración de partículas metálicas y a la elevada temperatura en la zona de corte [98].
- El CCA se considera uno de los sistemas de lubricación y refrigeración más limpios. Su aplicación en el torneado de γ-TiAl mejora la capacidad de refrigeración. Sin embargo, la calidad de la pieza depende en gran medida de la velocidad de corte [98].
- El uso de LN2 permite reducir la temperatura en la zona de corte, mejora la calidad de la pieza y además, se evapora sin dejar residuos perjudiciales. Es una alternativa que puede resultar especialmente interesante en operaciones especiales. Sin embargo, en el torneado de γ-TiAl, su reducida capacidad de lubricación provoca un desgaste excesivo de la herramienta [98].
- El éster biodegradable utilizado como fluido lubricante para MQL, reduce notablemente el consumo de MWF. Debido a su gran afinidad con la superficie, forma una película lubricante que da lugar a una reducción del desgaste de la herramienta. Se consume en su totalidad durante la operación de torneado, suprimiéndose la necesidad de eliminar el fluido. No obstante, al igual que el mecanizado en seco, existe una problemática evacuación de virutas que, junto con el éster orgánico, aumenta la probabilidad de riesgo de incendio [98].
- Las taladrinas pueden eliminar eficazmente el calor y las virutas de la zona de corte, lo que prolonga la vida útil de la herramienta y evita las chispas. La formulación de EcoMWF protege mejor la herramienta del desgaste, lo que potencia el uso de este sistema como alternativa al fluido de corte convencional [98].

- El EcoMWF desarrollado, basado en ésteres, reduce casi cuatro veces la contribución al calentamiento global en comparación con los fluidos de corte convencionales basados en aceites minerales [98].

6.3. Desarrollos futuros

Esta Tesis Doctoral sirve como herramienta de diseño para desarrollar nuevos fluidos de corte sostenibles y respetuosos con el medioambiente para el torneado de aleaciones de titanio. Sin embargo, aún hay escasa información disponible. A continuación, se muestras algunas líneas de investigación expuestas en esta Tesis Doctoral que podrían ampliarse como desarrollos futuros:

- El método experimental desarrollado para investigar la formación de la película lubricante puede emplearse para encontrar correlaciones entre otras sustancias y sustratos. Dicha correlación puede permitir la predicción del rendimiento del fluido de corte sobre un material en concreto. De este modo, se puede ahorrar tiempo y recursos en la selección de los fluidos de corte y conseguir un fluido de corte tecnológicamente competitivo.
- El análisis realizado en la Tesis Doctoral ha demostrado que la rugosidad superficial, en términos de *Ra*, puede llevar a conclusiones incorrectas si se ignoran otros cambios en la topografía del perfil de la pieza. En consecuencia, se sugiere un estudio de la superficie mecanizada más profundo y detallado para observar daños superficiales y alteraciones microestructurales, como micro-fisuras, redeposición de materiales y zonas afectadas por el calor.
- La dificultad que conlleva el mecanizado de las aleaciones de γ-TiAl hace que se produzcan vibraciones indeseables durante el mismo que contribuyen a un mayor y más rápido desgaste de las herramientas de corte. Por ello, podría ser interesante repetir los ensayos en máquinas-herramienta más robustas, esto es, en las que se produzcan menores vibraciones y, a ser posible, de control numérico para minimizar la influencia de la pericia del operario. Además, sería interesante que se utilizaran distintas combinaciones de sistemas de lubricación y refrigeración y tipos de herramientas (con distintos materiales base y recubrimientos) para poder analizar las mejores combinaciones de ellas en el mecanizado de este tipo de aleaciones de titanio.
- El fluido eco-eficiente y el fluido para MQL se ha diseñado específico para las aleaciones de titanio. Asimismo, los fluidos se han probado con una operación de torneado horizontal, concretamente de pequeña profundidad de corte como la utilizada en las operaciones de acabado, reparación y/o mantenimiento. Sería interesante realizar ensayos con parámetros de corte más elevados, propios de producción y no solo de reparación y mantenimiento, para otros procesos y operaciones de mecanizado y empleando diversas aleaciones de titanio, así como otros procesos de mecanizado.

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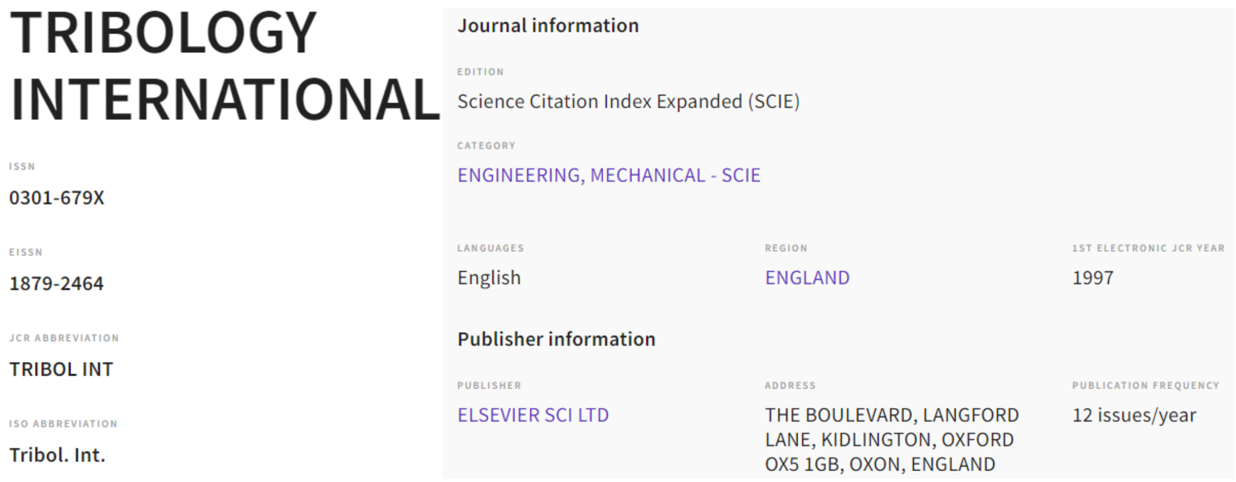
Apéndices

Apéndice A. Indicios de calidad del artículo “A novel method for the determination of fatty acid esters in aqueous emulsion on Ti6Al4V surface with IRRAS and carbon quantification”



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ENGINEERING, MECHANICAL - SCIE

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Key Indicators 2018

Impact metrics	
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Journal Impact Factor	3.517
5 Year Journal Impact Factor	3.440
Immediacy Index	1.099
Impact factor without Journal Self Cites	2.722
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Normalized Eigenfactor	2.04315
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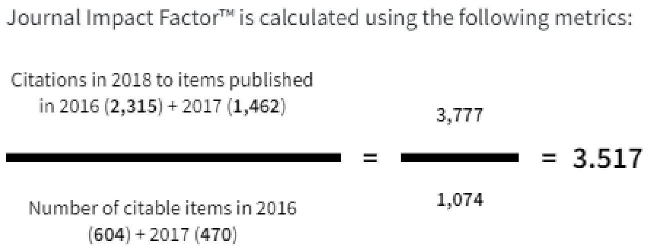

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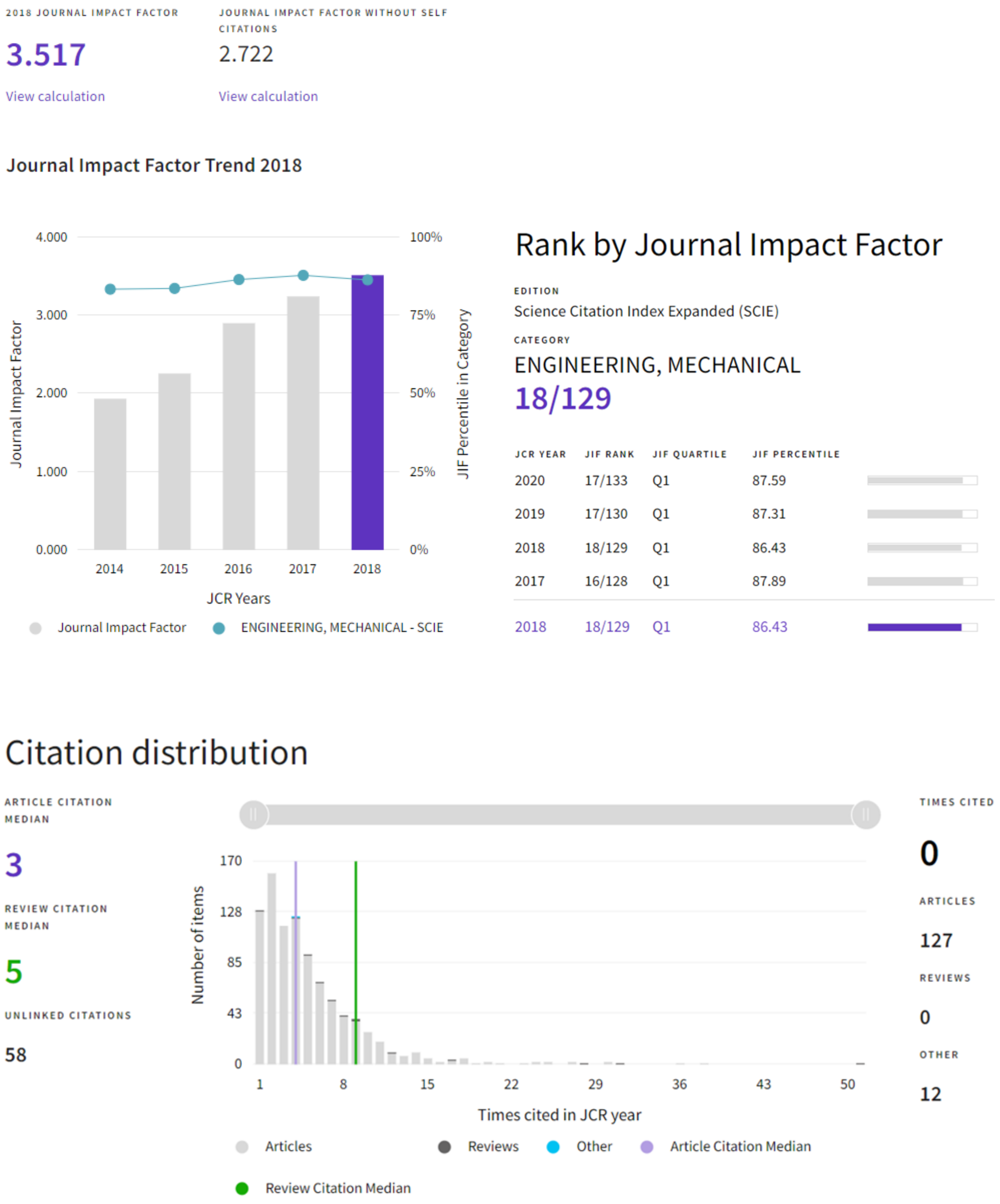

2018 JOURNAL IMPACT FACTOR

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JOURNAL IMPACT FACTOR WITHOUT SELF CITATIONS

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View calculation

Journal Impact Factor Trend 2018

Rank by Journal Impact Factor

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2019	17/130	Q1	87.31
2018	18/129	Q1	86.43
2017	16/128	Q1	87.89
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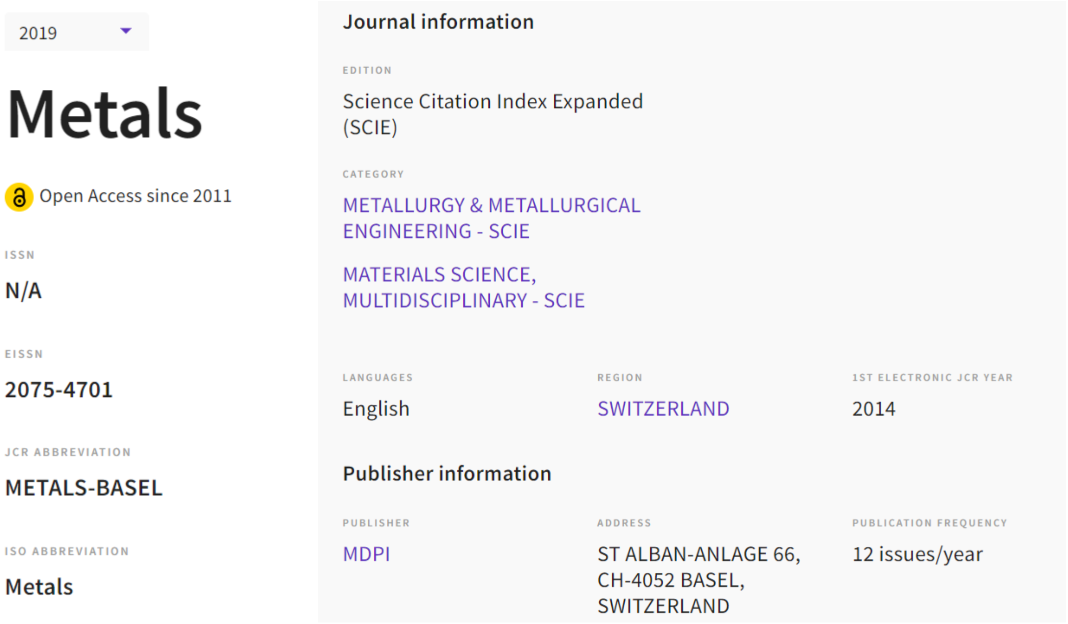
Apéndice B. Indicios de calidad del artículo "The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys"



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MATERIALS SCIENCE, MULTIDISCIPLINARY - SCIE

LANGUAGES	REGION	1ST ELECTRONIC JCR YEAR
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Key Indicators 2019

Impact metrics	
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5 Year Journal Impact Factor	2.244
Immediacy Index	0.594
Impact factor without Journal Self Cites	1.633
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Source metrics	
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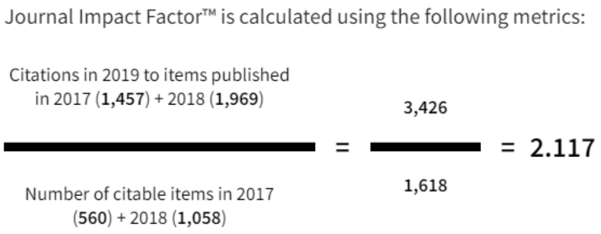

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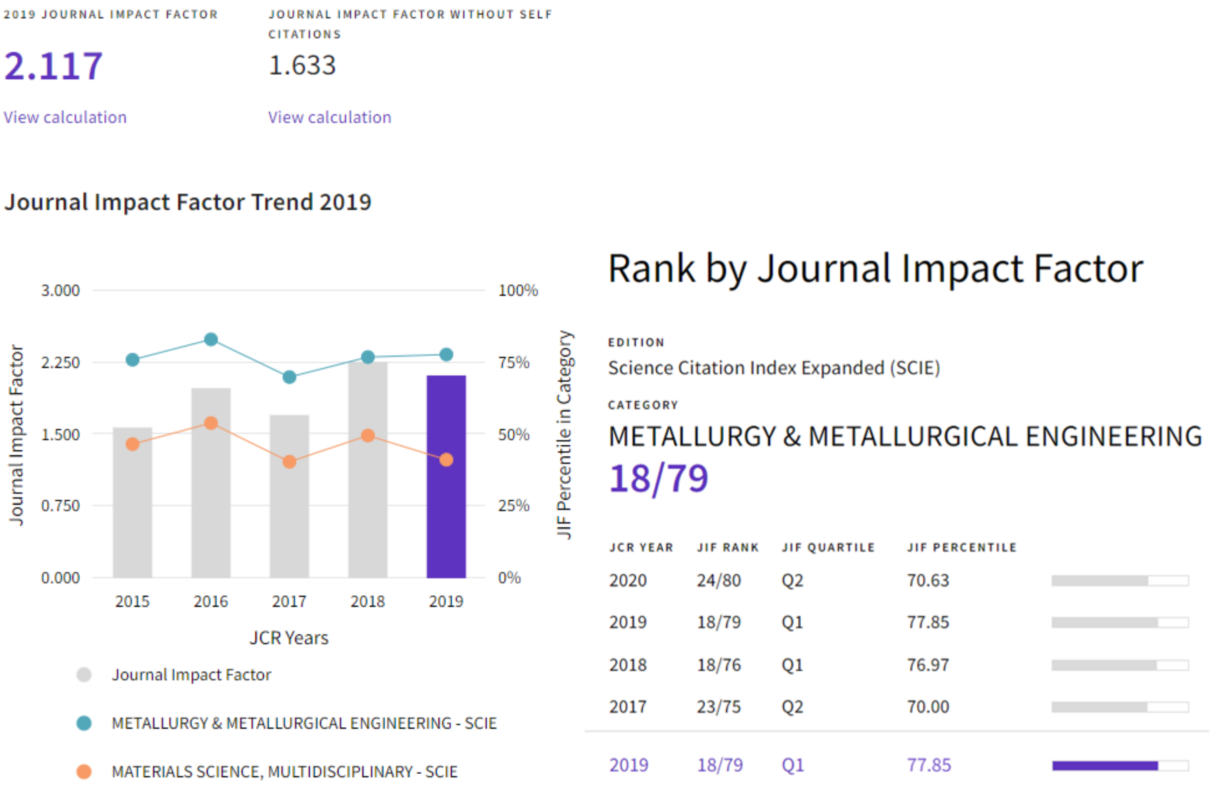

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View calculation

JOURNAL IMPACT FACTOR WITHOUT SELF CITATIONS

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View calculation

Journal Impact Factor Trend 2019

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METALLURGY & METALLURGICAL ENGINEERING

18/79

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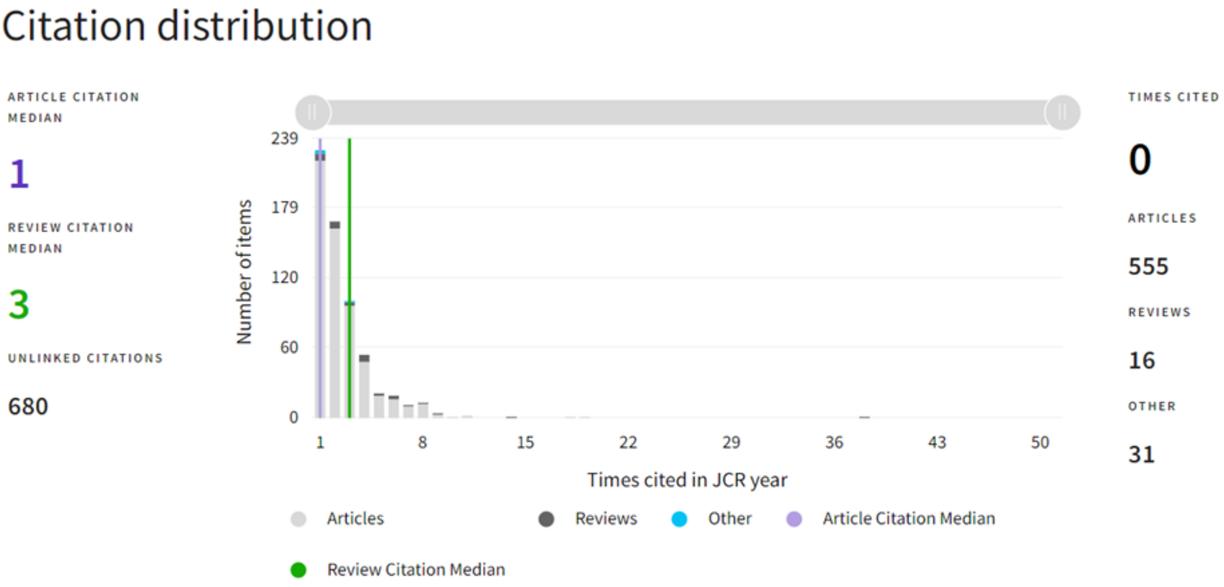

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ARTICLES

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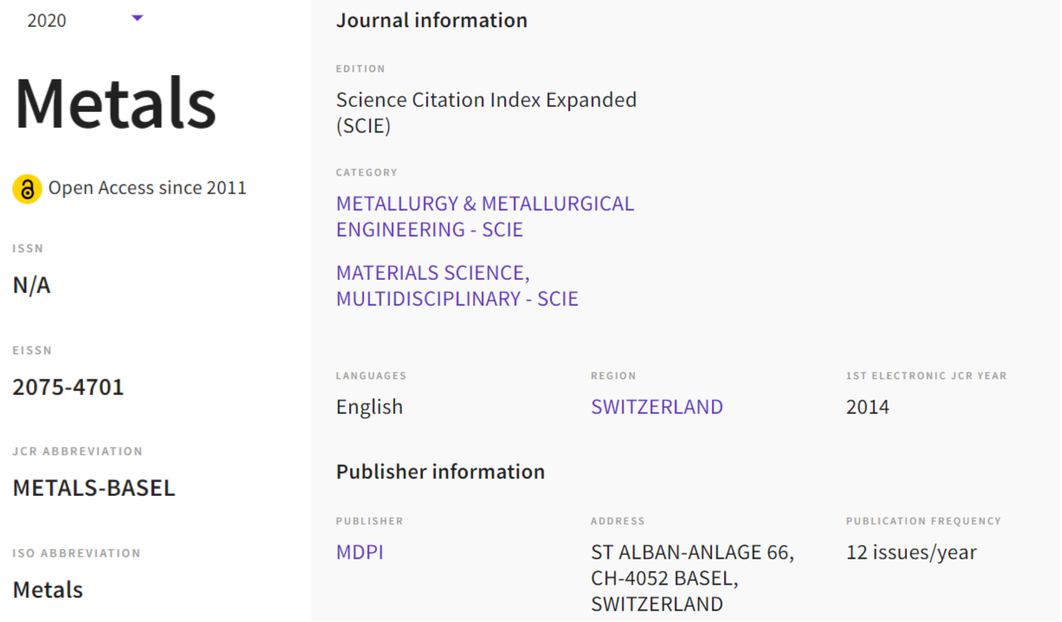
Apéndice C. Indicios de calidad del artículo “Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys”



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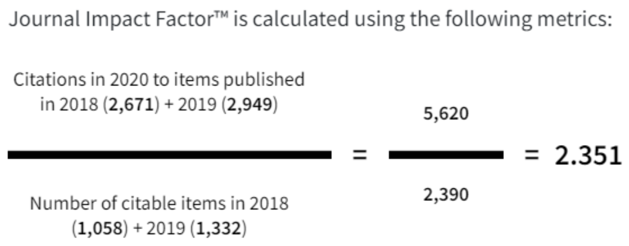
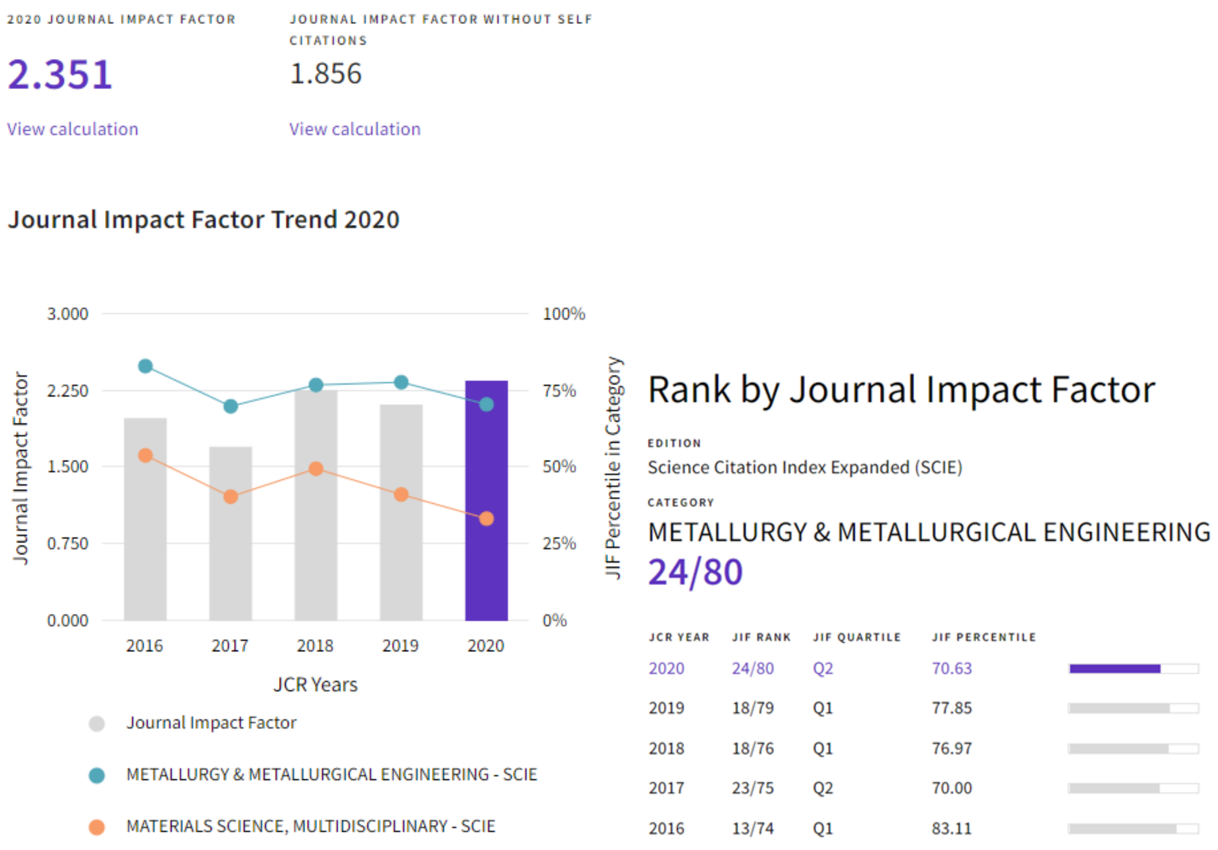
Immediacy Index	0.969
Impact factor without Journal Self Cites	1.856
Influence metrics	
Eigenfactor Score	0.01352
Normalized Eigenfactor	2.83544
Article influence score	0.384
Source metrics	
Citable items	1,657
% Articles in Citable items	98%
Average JIF Percentile	52.00
Cited Half-Life (years)	2.3
Citing Half-Life (years)	7.5



Journal Impact Factor™ is calculated using the following metrics:

$$\frac{\text{Citations in 2020 to items published in 2018 } (\mathbf{2{,}671}) + 2019\ (\mathbf{2{,}949})}{\text{Number of citable items in 2018 } (\mathbf{1{,}058}) + 2019\ (\mathbf{1{,}332})} = \frac{5{,}620}{2{,}390} = 2.351$$



2020 JOURNAL IMPACT FACTOR

2.351

View calculation

JOURNAL IMPACT FACTOR WITHOUT SELF CITATIONS

1.856

View calculation

Journal Impact Factor Trend 2020

Rank by Journal Impact Factor

EDITION

Science Citation Index Expanded (SCIE)

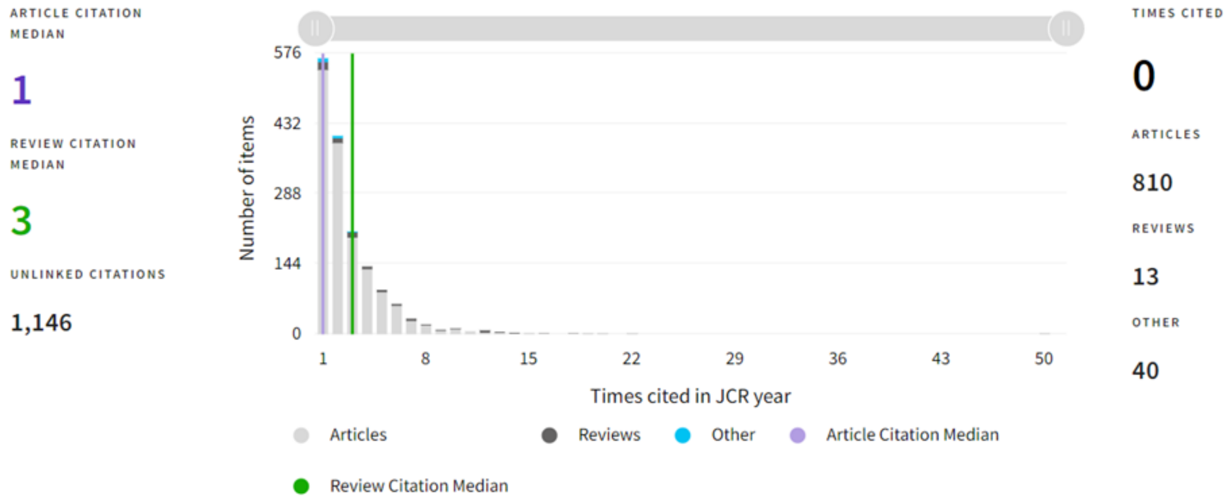
CATEGORY

METALLURGY & METALLURGICAL ENGINEERING

24/80

JCR YEAR	JIF RANK	JIF QUARTILE	JIF PERCENTILE
2020	24/80	Q2	70.63
2019	18/79	Q1	77.85
2018	18/76	Q1	76.97
2017	23/75	Q2	70.00
2016	13/74	Q1	83.11

Citation distribution



ARTICLE CITATION MEDIAN

1

REVIEW CITATION MEDIAN

3

UNLINKED CITATIONS

1,146

TIMES CITED

0

ARTICLES

810

REVIEWS

13

OTHER

40

Apéndice D. Indicios de calidad del artículo “Sustainable lubrication/cooling systems for efficient turning operations of γ-TiAl parts from the aeronautic industry”

International Journal of Precision Engineering and Manufacturing-Green Technology

ISSN
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EISSN
2198-0810

JCR ABBREVIATION
INT J PR ENG MAN-GT

ISO ABBREVIATION
Int. J. Precis Eng Manuf-Green Technol.

Science Citation Index Expanded (SCIE)

CATEGORY
GREEN & SUSTAINABLE SCIENCE & TECHNOLOGY - SCIE
ENGINEERING, MECHANICAL - SCIE
ENGINEERING, MANUFACTURING - SCIE

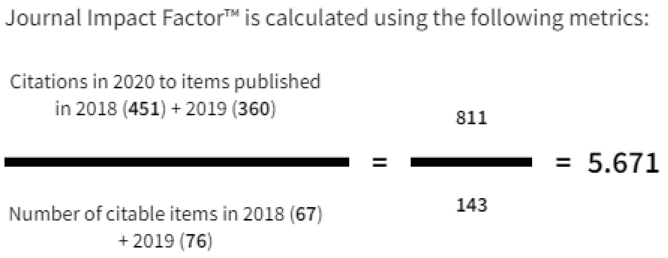
LANGUAGES	REGION	1ST ELECTRONIC JCR YEAR
English	SOUTH KOREA	2014

Publisher information

PUBLISHER	ADDRESS	PUBLICATION FREQUENCY
KOREAN SOC PRECISION ENG	RM 306, KWANGMYUNG BLDG, 5-4 NONHYUN-DONG, KANGNAM-GU, SEOUL 135-010, SOUTH KOREA	4 issues/year

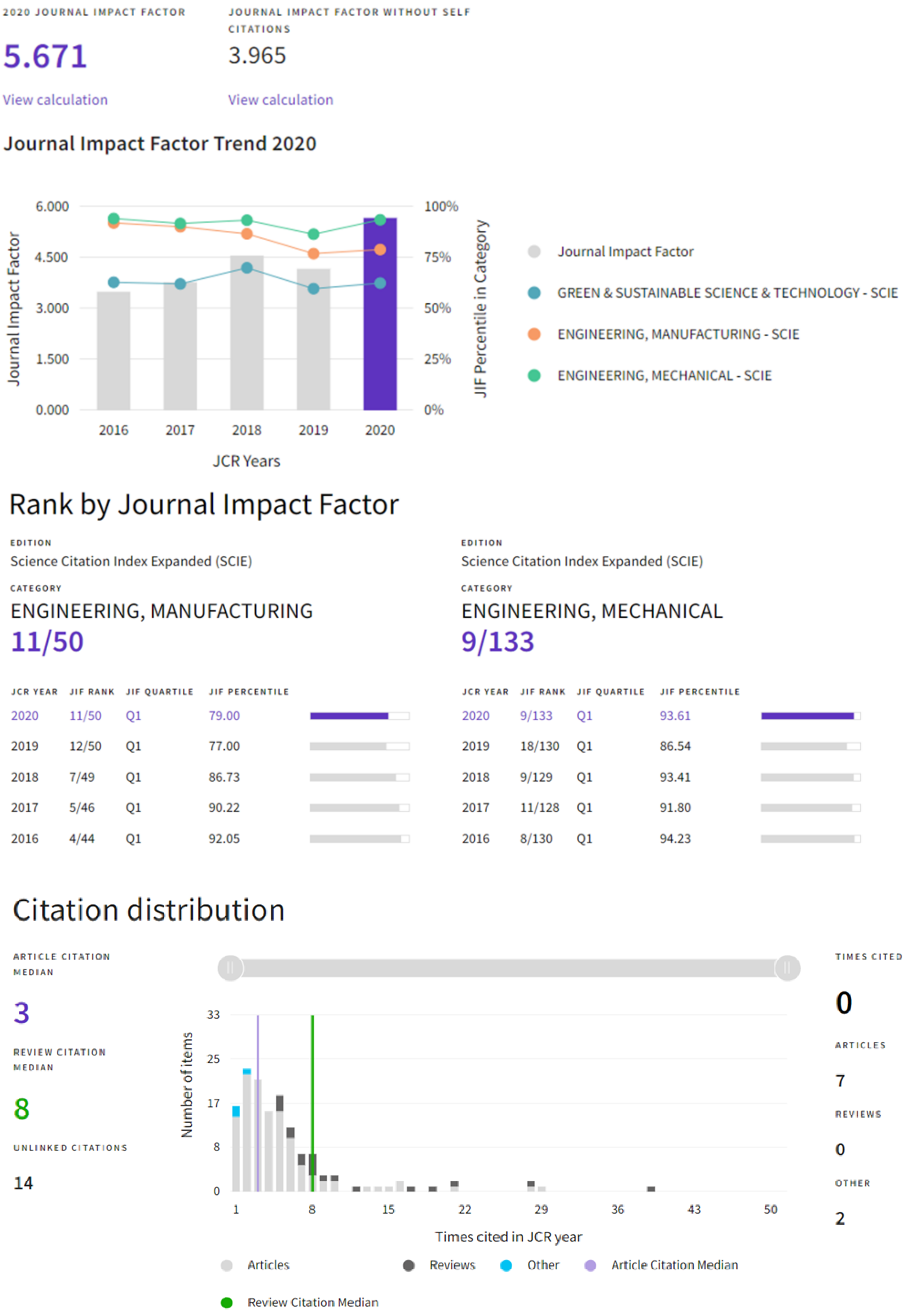
Key Indicators 2020

Impact metrics	
Total citations	2,223
Journal Impact Factor	5.671
5 Year Journal Impact Factor	6.112
Immediacy Index	1.365
Impact factor without Journal Self Cites	3.965
Influence metrics	
Eigenfactor Score	0.00241
Normalized Eigenfactor	0.50519
Article influence score	0.819
Source metrics	
Citable items	170
% Articles in Citable items	98%
Average JIF Percentile	78.37
Cited Half-Life (years)	3.1
Citing Half-Life (years)	6.0



Journal Impact Factor™ is calculated using the following metrics:

$$\frac{\text{Citations in 2020 to items published in 2018 (451) + 2019 (360)}}{\text{Number of citable items in 2018 (67) + 2019 (76)}} = \frac{811}{143} = 5.671$$



2020 JOURNAL IMPACT FACTOR

5.671

View calculation

JOURNAL IMPACT FACTOR WITHOUT SELF CITATIONS

3.965

View calculation

Journal Impact Factor Trend 2020

Rank by Journal Impact Factor

EDITION
Science Citation Index Expanded (SCIE)

CATEGORY
ENGINEERING, MANUFACTURING

11/50

JCR YEAR	JIF RANK	JIF QUARTILE	JIF PERCENTILE
2020	11/50	Q1	79.00
2019	12/50	Q1	77.00
2018	7/49	Q1	86.73
2017	5/46	Q1	90.22
2016	4/44	Q1	92.05

EDITION
Science Citation Index Expanded (SCIE)

CATEGORY
ENGINEERING, MECHANICAL

9/133

JCR YEAR	JIF RANK	JIF QUARTILE	JIF PERCENTILE
2020	9/133	Q1	93.61
2019	18/130	Q1	86.54
2018	9/129	Q1	93.41
2017	11/128	Q1	91.80
2016	8/130	Q1	94.23

Citation distribution

ARTICLE CITATION MEDIAN

3

REVIEW CITATION MEDIAN

8

UNLINKED CITATIONS

14

TIMES CITED

0

ARTICLES

7

REVIEWS

0

OTHER

2

Apéndice E. Extracto del programa y resumen del congreso “Tribology 2022”

SURFACES, INTERFACES AND COATINGS TECHNOLOGIES

SICT 2022

PLASMA PROCESSING AND TECHNOLOGY

PLASMA TECH 2022

TRIBOLOGY INTERNATIONAL CONFERENCE

Tribology 2022

SICT 2022 / PLASMA TECH 2022 / TRIBOLOGY 2022
HYBRID JOINT CONFERENCES

27-29 Avril, 2022 - Barcelona, Spain

Book of Abstracts

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SICT 2022 / Plasma Tech 2022 / Tribology 2022 Joint Hybrid Conferences Book of Abstracts

Development of sustainable and effective water-based metalworking fluid for titanium machining

E. Benedicto [1,2,*], E.M. Rubio [1], L. Aubouy [2], M.M. Marín [1]
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*Programa de Doctorado en Tecnologías Industriales

Abstract:

Metalworking fluids (MWF) can increase the productivity, sustainability, and quality of machining processes, especially for difficult-to-cut materials, such as titanium alloys, where most of the problems are related to the high consumption of cutting tools due to excessive wear. Cutting fluids are used to improve the machining process by providing lubrication, dissipating heat, and removing chips from the cutting zone. However, MWFs are under review due to their environmental impact and health risks to workers. There is an urgent need for the development of new sustainable MWFs, and it still represents a demanding challenge.

Herein, we study the influence of surfactant and esters' molecular structure in oil-in-water emulsions and its interaction with the metal surface to form a lubricating layer, thus improving the performance of the MWF. Lubrication and tool wear protection are studied through film formation analysis and the tapping process on Ti6Al4V (Figure 1). By modifying the molecular structure of the surfactant, it is possible to enhance the affinity between the ester and the substrate and reach an optimal mixture, which enhances the formation of a tribofilm [1]. Polyol esters show promising results to replace mineral oils. Specifically, a higher lubricating film is formed with trimethylolpropane trioleate, thus improving the lubricity by up to 12% and reducing tool wear by 26.8% [2]. The applied technology of this work may be helpful for the development of new environmentally friendly MWF, not only for titanium machining but also for the design of MWF for conventional and advanced alloys.

Keywords: metalworking fluid, cutting fluid, surfactant, ester, lubrication, tool wear, tool life, difficult-to-cut materials, titanium alloys, Ti6Al4V.

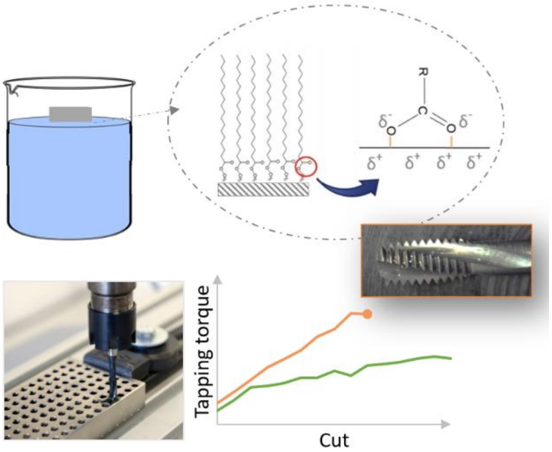


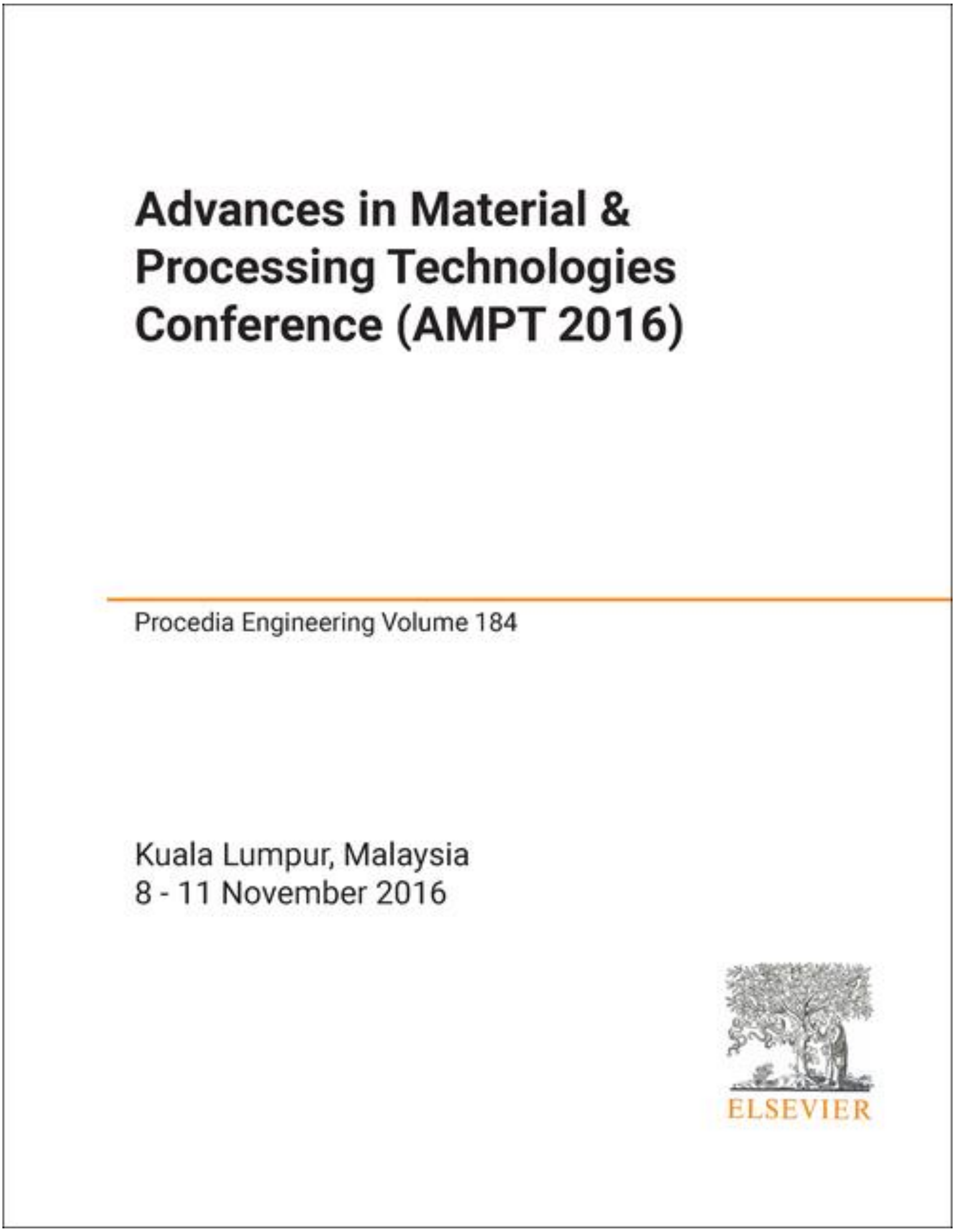
Figure 1: Test set-up diagram of the analysis of tribofilm and the tool wear during tapping to study the role of surfactants and esters on the development of sustainable and effective MWF.

References:

[1] Benedicto E, Rubio EM, Carou D, Santacruz C. The Role of Surfactant Structure on the Development of a Sustainable and Effective Cutting Fluid for Machining Titanium Alloys. Metals (Basel) 2020;10:1388. doi:10.3390/met10101388.

[2] Benedicto E, Rubio EM, Aubouy L, Sáenz-Nuño MA. Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys. Metals (Basel) 2021;11:773. doi:10.3390/met11050773

Apéndice F. Extracto del programa y póster del congreso “AMPT2016”



Advances in Material & Processing Technologies Conference (AMPT 2016)

Procedia Engineering Volume 184

Kuala Lumpur, Malaysia
8 - 11 November 2016

ELSEVIER

Advances in Materials & Processing Technologies Conference
November 8th - 11th, 2016, Kuala Lumpur, Malaysia

Technical, economic and environmental review of the lubrication/cooling systems used in machining processes

E.Benedicto[a,b], D. Carou[c,d], E.M. Rubio[a]

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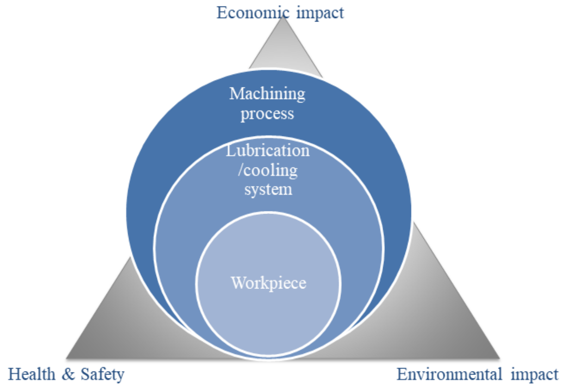
[b]Department of Tribology and Metal Processing, Leitat Technological Center, C/ Innovació, 2, E08225 Terrassa, Spain
[c]School of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Dublin, Ireland
[d]Centre for Mechanical Technology and Automation (TEMA), University of Aveiro, Campus Santiago, 3810-193, Aveiro, Portugal

The use of cutting fluids in machining processes is a serious concern because their cost, and environmental and health effects. In the last decades, efforts have been developed to come up with alternatives to overcome their main drawbacks. The ultimate goal is the complete suppression of cutting fluids. However, because of the demanding requirements of the machining processes, in some cases it is not possible to use dry machining conditions. Reasons can be found in the excessive heat generated in the process, the increase of the friction between the tool and the workpiece or the need to evacuate the chips generated. The pull for sustainable products is also encouraging the developing of new cutting fluid formulations. In the present paper, a comprehensive analysis of the use of cutting fluids and main alternatives in machining is carried out. Particularly, the analysis was done focusing on the technical, economic and environmental points.



TECHNICAL REVIEW

Cutting fluids its main function is to cool, lubricate and transport the chips. Moreover, they allow increasing the cutting speed, prolonging the tool life, reducing the workpiece damage, improving the surface quality and meeting with the dimensional specifications. Therefore, they increase productivity, improve efficiency, help to ensure the process safety and guarantee and enhance the machining quality.

Dry machining. For a right implementation it should be considered an adequate selection of the tool material. Generally, it is possible at lower cutting speeds and when the workpiece does not require great dimensional and shape precision.

MQL advantages are: reduction of cutting fluid consumption, cost and tool wear; improvement of surface roughness, diminution decrease of the environmental and worker health hazards and improve lubrication than that of the of conventional lubrication/cooling system .

Solid lubricants, such as graphite, MoS_2 and WS_2, have high heat dissipation and thermal conductivity and are more effective than cutting fluids in machining processes that operate discontinuously under high loads and speeds. Moreover, they are able to lubricate at extreme temperatures and pressures.

Cryogenic cooling like LN_2 or CO_2. The liquid absorbs the heat and evaporates quickly, forming a gas layer between the chip and the tool face, acting as a lubricant. It may be of special interest in operations where the tool cost is high.

Gaseous coolants. Air is one of the most commonly used gases, though it has a low cooling capacity that can be increased by its cooling, preserving its gaseous state. Other usual gases are argon, helium and nitrogen.

Sustainable cutting fluids

Performance	Canola oil	TMPTO	Sat/Complex	PAG	Mineral oil
Biodegradability	*****	****	***	***	*
Toxicity	****	****	****	****	*
Lubrication	*****	****	****	****	***
Oxidative stability	*	**	****	***	****
Thermal stability	**	***	****	***	***
Hydrolytic stability	*	**	***	***	****
Viscosity index	****	****	****	****	**
Low temperature	*	***	***	***	***
Seal compatibility	**	**	**	***	****
Relative cost[(1)]	2	4	6-8	4	1

(*) Poor; (**) Moderate; (***) Good; (****) Very good; (*****) Excellent
(1) Cost compared to mineral oil cost

Nanofluids can easily penetrate the surface, increase the heat transfer capacity and improve the tribological properties of the fluid.

ECONOMIC REVIEW

	Raw material	Fluid consumption	Equipment costs	Tool costs	Cleaning costs	Disposal costs
Cutting fluids	**	*****	****	***	*****	*****
Dry machining	*	*	*	*****	*	*
MQL	**	**	***	**	**	**
Solid lubricant	****	***	***	***	***	****
Cryogenic	***	***	*****	***	*	*
Gaseous	***	***	****	****	*	*
Sustainable	***	****	****	**	****	***
Nanofluids	*****	****	****	***	****	*****

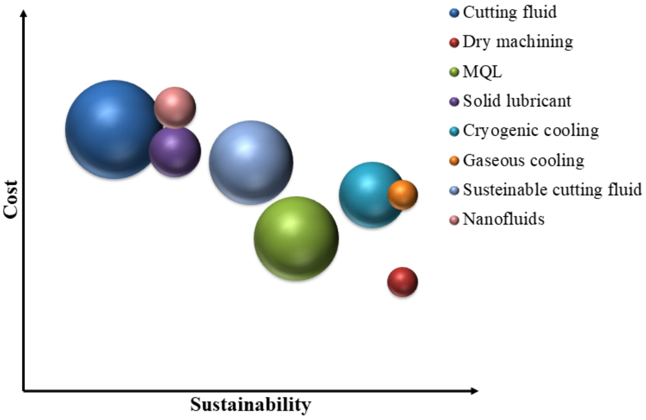
(*) Very low; (**) Low; (***) Medium; (****) High; (*****) Very high

ENVIRONMENTAL REVIEW

	Residue	Fluid drag out	Dangerous substances	Mist and emissions	Health hazards
Cutting fluid	*****	*****	****	*****	*****
Dry machining	*	*	*	*	*
MQL	**	**	**	***	***
Solid lubricant	*****	*****	***	****	****
Cryogenic	*	*	*	**(1)	*
Gaseous	*	*	*	*	*
Sustainable	****	*****	***	****	***
Nanofluids	****	*****	Unknown	****	Unknown

(*) Very low; (**) Low; (***) Medium; (****) High; (*****) Very high
(1) Very low for liquid nitrogen

Comparison among different lubrication/cooling systems. Cost and sustainability values are represented taking into account the qualitative estimations and the diameter considers the industrial potential use according to the technical feasibility.

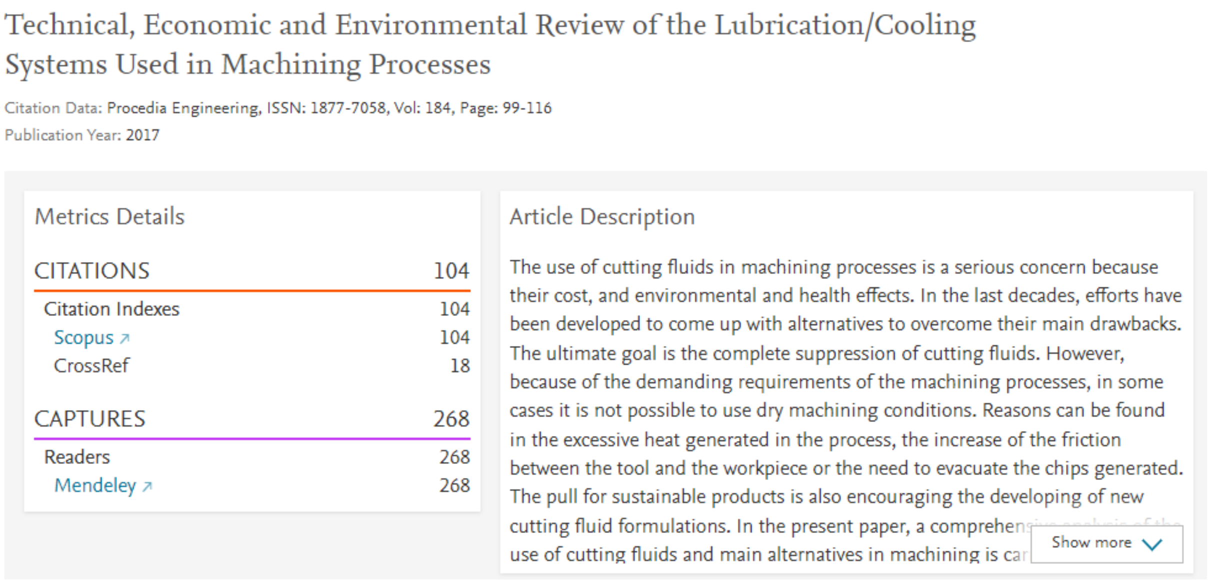


Acknowledgement
The authors thank to the Research Group of the UNED "Industrial Production and Manufacturing Engineering (IPME)" the given support during the development of this work. The study was funding by the Spanish Ministry of Science and Innovation, and the Industrial Engineering School-UNED by the funding of the projects DPI2014-58007-R and REF2016-ICF05, respectively.

Apéndice G. Indicios de calidad y copia del artículo "Technical, Economic and Environmental Review of the Lubrication/Cooling Systems used in Machining Processes"

Key Indicators 2017

SCImago Journal Rank (SJR)	0.282
H Index	88
Total cites	11,266
Self cites	741



Technical, Economic and Environmental Review of the Lubrication/Cooling Systems Used in Machining Processes

Citation Data: Procedia Engineering, ISSN: 1877-7058, Vol: 184, Page: 99-116

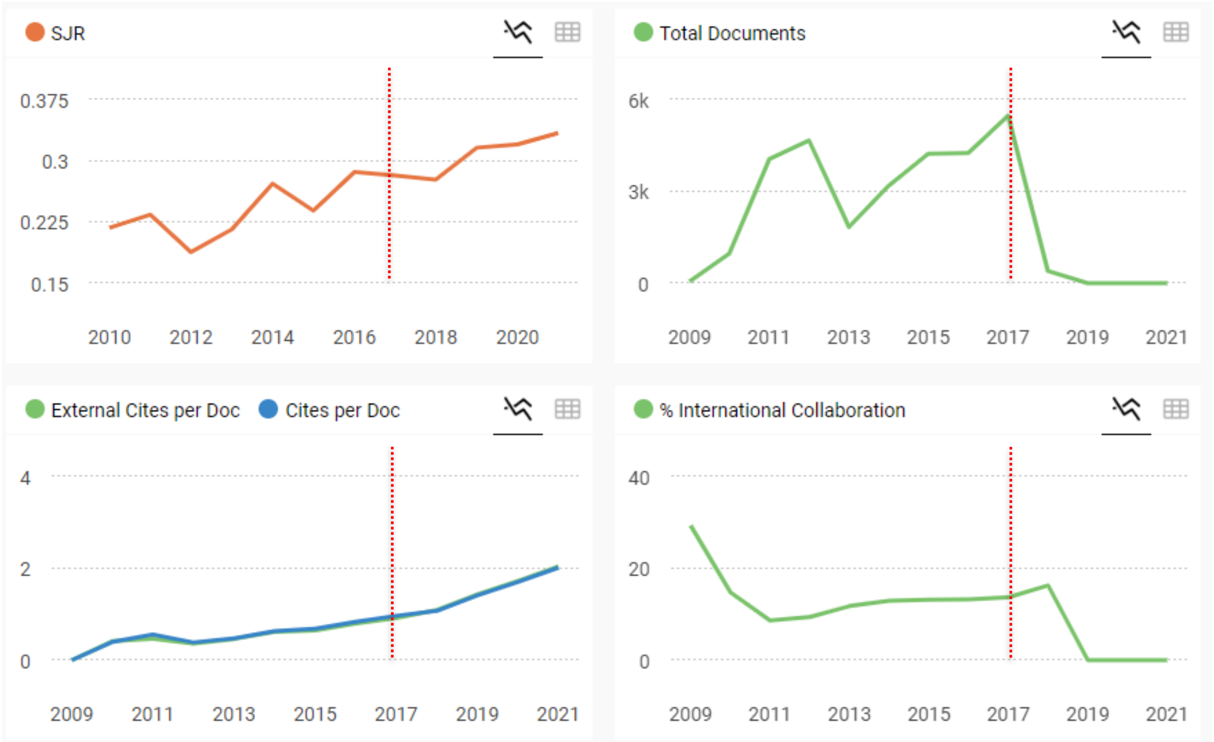
Publication Year: 2017

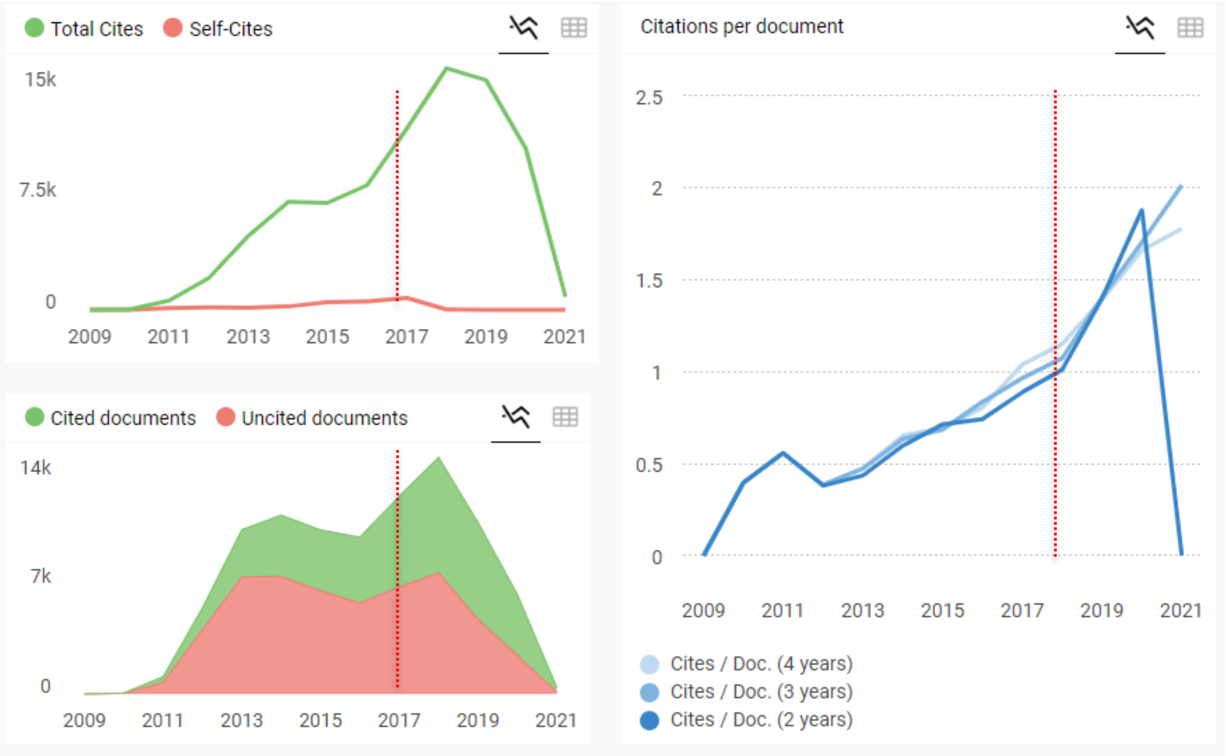
Metrics Details

CITATIONS	104
Citation Indexes	104
Scopus ↗	104
CrossRef	18
CAPTURES	268
Readers	268
Mendeley ↗	268

Article Description

The use of cutting fluids in machining processes is a serious concern because their cost, and environmental and health effects. In the last decades, efforts have been developed to come up with alternatives to overcome their main drawbacks. The ultimate goal is the complete suppression of cutting fluids. However, because of the demanding requirements of the machining processes, in some cases it is not possible to use dry machining conditions. Reasons can be found in the excessive heat generated in the process, the increase of the friction between the tool and the workpiece or the need to evacuate the chips generated. The pull for sustainable products is also encouraging the developing of new cutting fluid formulations. In the present paper, a comprehen use of cutting fluids and main alternatives in machining is ca




Total Cites
Self-Cites
15k
7.5k
0
2009
2011
2013
2015
2017
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2021
Cited documents
Uncited documents
14k
7k
0
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Advances in Material & Processing Technologies Conference

Technical, Economic and Environmental Review of the Lubrication/Cooling Systems used in Machining Processes

E.Benedicto[a,b], D. Carou[c,d], E.M. Rubio[a*]

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[b]*Departmentof Tribology and Metal Processing, Leitat Technological Center, C/ Innovació, 2, E08225 Terrassa, Spain*

[c]*Schoolof Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Dublin, Ireland*

[d]*Centre for Mechanical Technology and Automation (TEMA), University of Aveiro, Campus Santiago, 3810-193, Aveiro, Portugal*

Abstract

The use of cutting fluids in machining processes is a serious concern because their cost, and environmental and health effects. In the last decades, efforts have been developed to come up with alternatives to overcome their main drawbacks. The ultimate goal is the complete suppression of cutting fluids. However, because of the demanding requirements of the machining processes, in some cases it is not possible to use dry machining conditions. Reasons can be found in the excessive heat generated in the process, the increase of the friction between the tool and the workpiece or the need to evacuate the chips generated. The pull for sustainable products is also encouraging the developing of new cutting fluid formulations. In the present paper, a comprehensive analysis of the use of cutting fluids and main alternatives in machining is carried out. Particularly, the analysis was done focusing on the economic, environmental and technical points.

Keywords:cost; cryogenic machining; dry machining; environmental impact; machining; MQL system; solid lubricants

1. Introduction

The global lubricant demand was 39.4 million tons in 2015 [1] and it is expected to reach 43.9 million tons in 2022. The industrial lubricant market can be segmented into several categories taking into account their applications. Some of the most used lubricants are gear oils, hydraulic lubricants and engine oils. Cutting fluids represent about 5%

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E-mail address: erubio@ind.uned.es

doi:10.1016/j.proeng.2017.04.075

of the global lubricant market, with Asia as the largest consumer [2]. Approximately, 85% of the cutting fluids used are mineral based. However, the estimated values deviate significantly because of the processes diversity [3].

Cutting fluids are widely used in machining processes. The main cutting fluid roles are cooling, reducing friction, removing metal particles, and protecting the workpiece, the tool and the machine tool from corrosion [4]. However, the use of cutting fluids has also associated some disadvantages such as their cost, environmental impact and health hazards to workers (Fig.2) [5]. In machining processes, sustainable manufacturing can be addressed for example, by reducing the consume of electric energy [6], improving the tool life and the surface quality of the workpiece [7].

In the last decades, new alternatives have been developed to overcome the main drawbacks of cutting fluids. The main alternatives include dry machining, minimum quantity lubrication (MQL), solid lubrication, cryogenic cooling, gaseous cooling, sustainable cutting fluids and nanofluids. Some of these alternatives, such as dry machining and minimum quantity lubrication, have been widely evaluated from the technical point of view. However, the study of other alternatives such as gaseous cooling has received less attention. Besides, further efforts in the analysis of these alternatives in both economic and environmental aspects are clearly needed.

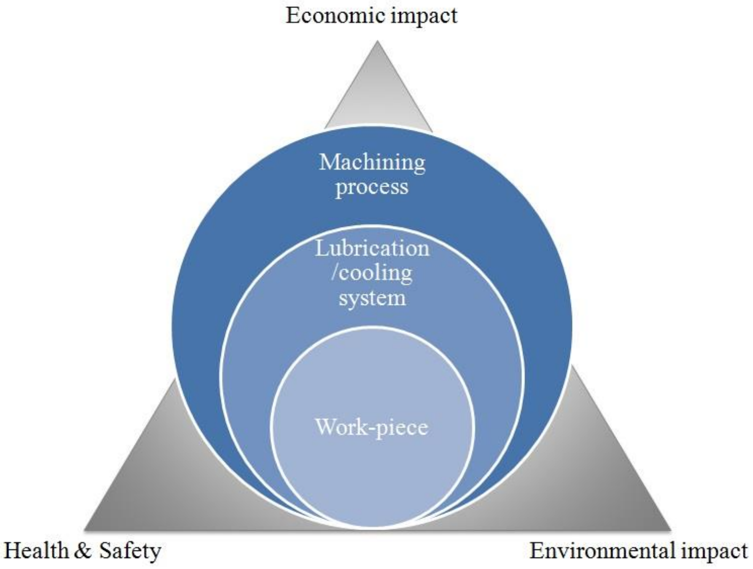

Fig.2. Economic, environmental, and health & safety impacts in sustainable manufacturing.

2. Technical review

2.1 Conventional lubrication/cooling systems

Cutting fluids are mixtures formulated with oil (base) and additives to enhance various properties depending on the machining process. They have been commonly used to enhance productivity and quality in the machining processes. They play an important role in the machining along with machining parameters such as cutting speed, depth of cut and feed rate [8]. The main function of the cutting fluids is to cool and lubricate. So, the use of cutting fluids helps reducing power consumption and protecting from corrosion the machined surface as well as tools and machine tools parts [9]. Moreover, cutting fluids cool down and transport the chips out of the cutting area, carrying away contaminants and debris in liquid instead of being suspended in the air. The ability to evacuate the chips will strongly depend on the viscosity and surface tension [10]. They allow increasing the cutting speed, prolonging the tool life, reducing the workpiece damage, improving the surface quality and meeting with the dimensional specifications. Therefore, cutting fluids increase productivity, improve efficiency by reducing the number of defects, help to ensure the process safety and guarantee and enhance the machining quality [11].

Low speed machining processes benefit more of the lubrication than of the cooling. Cutting fluids minimize friction creating a lubrication film that varies depending on the lubrication regime [12]. When friction is reduced, lower heat is generated and wear is decreased. As the cutting speed increases, the wear by built-up-edge (BUE) decreases and the cutting forces are lower, but the heat generated increases. In these cases, the use of cutting fluids is important to reduce the temperature of the tool the workpiece and the chip [13]. It provides thermal stability to the cutting zone allowing a greater dimensional control. The tool heat release depends on the tool form and its thermal conductivity, the cutting speed and the cooling system used [14]. For example, at a cutting speed of 150 m/min, 75-80% of the heat is conducted by the chips, 10-15% is transferred into the tool and the residual 5-10% is transported by the workpiece [15].

Cutting fluids are classified according to their chemical formulation in straight oils and water soluble oils [16]. Straight oils or neat oils are non-water-soluble fluids formulated to reduce the friction between the tool and both the chips and workpiece. They can be mineral (petroleum based), vegetable or animal oil [3, 17]. Straight oils have excellent lubrication and corrosion resistance properties but poor cooling capacity and they may create mist, which is harmful to the workers health [16]. They have a specific heat capacity close to 2.10 J/(g·K), around half the water's capacity, and a thermal conductivity approximately one-third of the water. Straight oils are more effective in low cutting speed operations and tend to lose their effectiveness at high speeds. One of the reasons is due to the chip movement at high speeds that prevents the fluid to reach the tool interface. Another reason is that, at high speeds, high cutting temperatures are generated and oils vaporize before they can lubricate [18].

Water soluble oils, contrary to neat oils, are more effective at relatively high cutting speeds, where heat generation and high temperatures are a problem [18]. They are usually supplied as concentrates and the end-user dilutes them in water before use. Water content increases the specific heat and thermal conductivity and allows the coolant to remove heat from the machining process, thus reducing the temperature [3]. However, water content induce corrosion, bacteria growth and evaporation losses [16]. These fluids generally contain emulsifiers which provide good cleaning properties, although they may have foam tendencies, which can inhibit heat transfer. In addition, water soluble oils are non-flammable and its tendency to form aerosols is lower than that of neat oils [19].

Water soluble oils can be classified according to the oil content in [12, 20]: emulsions, semi-synthetic fluids and synthetic fluids (Table 1). Emulsions and microemulsions with oil content greater than 40% provide lubricity and better corrosion protection than fluids with higher water content. They are more effective at high speeds machining. Semi-synthetic fluids are emulsions with less than 40% of oil and additives, emulsified in water. Synthetic fluids are oil free cutting fluids that have the greater cooling effect. Different from emulsions and semi-synthetic, they are not sensitive to water hardness and they are transparent, that allows good visibility during machining.

Table 1. Cutting fluid properties[3, 16]

	Straight oils	**Emulsions**	**Semi-synthetic**	**Synthetic**
Aspect	Oily	Milky	Translucent	Transparent
Lubricity	Excellent	Good	Good	Poor
Cooling	Low	Good	Good	Excellent
Corrosion control	Excellent	Poor	Good	Good
Microbial control	Excellent	Poor	Good	Excellent
Fire	Hazard	Non-flammable	Non-flammable	Non-flammable
Other disadvantages	Limited to low-speed operation Create mist	Evaporation losses Foam tendencies	Hard water influence Foam tendencies	Easily contaminated by other processing fluids

Cutting fluids can be applied by different methods, the most common is by flood. This method provides a continuous cutting fluid flow to the tool and the workpiece. It needs several components in the system, mainly filters, a recirculation system, pipes and nozzles and oil recovery device [19]. Other application methods are by mist, where the fluid is applied by pressurized air stream at high speed mist; and high pressure system, where the fluid is supplied at 5.5 to 35 MPa, which allows increasing heat removal and chip transport [3].

2.2 Alternatives to conventional lubrication/cooling systems

Dry machining

Dry machining eliminates completely the use of cutting fluid. Therefore, the heat removed decreases, resulting in a temperature increase on the tool and workpiece [14]. To implement dry machining it should be considered an adequate selection of the tool material to improve wear resistance [21]. The tool should have high hardness and resistance to pressure and temperature, high toughness, high thermal fatigue limit and chemical stability [22, 23].

Generally, dry machining operations are possible at lower cutting speeds [24] and when the workpiece does not require great dimensional and shape precision, which depends on the temperature. Thus, it is required to take special measures to ensure that hot chips are drawn quickly and efficiently from the cutting area, and that the heat introduced into the elements of the machine-tool is removed [25]. The main advantage of dry machining is that there is no atmosphere and water contamination. Moreover, there are no fluid residues in the workpiece neither in the chips. As a result, there is a cost and energy reduction due to the elimination of the cleaning process and the waste fluid treatment. However, dry machining has several disadvantages like material adhesion on the cutting tool, heat generation, friction increase between the tool and the workpiece, and poor chip removal [9].

In interrupted machining processes such as milling with ceramic tools, dry machining could prolong the tool life compared to conventional lubrication/cooling systems, because of the reduction of thermal shock effects [16, 26, 27]. Another application of dry machining is when machining magnesium to avoid ignition and fire hazards caused by the hydrogen formation due to magnesium and water reaction [28].

Although dry machining has been successfully implemented in numerous machining processes such as the drilling of aluminum [29, 30], nowadays there are still several challenges such as the drilling and turning of titanium that still require the use of cutting fluids [31, 32, 33].

Minimum Quantity Lubrication

Minimum Quantity Lubrication (MQL) uses a mix of compressed air with a reduced amount of oil in form of drops, producing a spray that is pulverized on the cutting zone [34]. The oil flow used is in the range between 0.01 and 2 l/h [10], instead of the 50-1000 l/h in the case of conventional lubrication/cooling systems [3, 35]. Most commonly products for machining with MQL system are fatty alcohols and synthetic esters (vegetable oils chemically modified). However, fatty alcohols are used in machining operations where it is more important the cooling than the lubrication effect [23].

Some MQL advantages against other lubrication/cooling systems are: reduction of cutting fluid consumption, cost and tool wear; improvement of surface roughness, diminution decrease of the environmental and worker health hazards and improve lubrication than that of the of conventional lubrication/cooling system [36, 37, 38, 39]. The cutting fluid is used in such small quantities that it is practically consumed in the process, eliminating the fluid disposal problems. In addition, chips produced are nearly clean from cutting fluid, which are easily recyclable [35].

Sharma et al. [40] have presented a review on the MQL system in different machining processes, showing that the MQL system can be a promising alternative to the use of cutting fluids. MQL is used focusing on the lubricant properties rather than coolant properties, heat removal is achieved mainly by the compressed air [41]. Due to its poor cooling capacity, some conditions of the machining process like MQL feed system, cutting parameters, workpiece material, and secondary operations should be studied before reducing the flow of cutting fluid without compromising the workpiece quality [23, 42]. However, some authors have studied minimum quantity lubrication technique in combination with cooled air can improve cooling and lubricating performance during machining steel [43] and difficult-to-machine materials [41].

Solid lubrication

Solid lubricants are materials that are in solid phase, such as graphite and its allotropic structures (fullerene, nanotubes, graphene, diamond), molybdenum disulfide (MoS2) and tungsten disulfide (WS2) [44]. They have high heat dissipation and thermal conductivity and are more effective than cutting fluids in machining processes that operate discontinuously under high loads and speeds [45]. Moreover, solid lubricants are able to lubricate at higher temperatures than oil-based lubricants. These materials are highly stable at extreme temperatures and pressures. They can be used up to 350°C in an oxidizing media and even at higher temperatures in a reducing or non-oxidizing media (molybdenum disulfide up to 1100 °C) [46]. The lubricity of these solids is attributed to their layered structure with weak Van der Waals bonds. Their layers are capable of sliding on each other with very small forces, which gives them the properties of low friction [44] and wear resistance [47].

They are mostly used in aerospace and automobile industry, though they are being also used in machining industry [45]. They are required in applications where it is necessary to avoid contaminating the product or environment, to maintain or to lubricate inaccessible or difficult-to access areas or to provide prolonged storage [45].

Solid lubricant can be applied as an additive in lubricating oils but they may have undesirable color [48] or directly applied [49, 50]. The combination of graphite with MQL system is a good alternative to conventional cutting fluids in the grinding [51] and turning [52] processes. With low concentrations of solid lubricants, the cutting temperature can be reduced, which improves the tool-chip interaction and the tool life is increased, allowing higher cutting speed and feed rate [53].

Cryogenic cooling

Cryogenic cooling uses materials like liquid nitrogen (LN2) at - 196 °C or carbon dioxide (CO2) at - 78 °C, as support during machining. Liquid nitrogen absorbs the heat and evaporates quickly, forming a gas layer between the chip and the tool face, acting as a lubricant [19]. In the case of LN2 cryogenic cooling, it is a system that leaves no harmful residues to the environment. LN2 absorbs the machining process heat, the fluid evaporates as nitrogen gas and becomes part of the air (taking into account that the 79% of the air is nitrogen) [5].

In general, cryogenic cooling is an expensive system. Both the LN2and the CO2 are basic products, but it is needed special equipments to reach the temperatures of -196 °C and -78 °C for the LN2 and the CO2, respectively [19]. However, despite the high cost of the equipment and the challenges to implement this technique in industrial applications, it is an alternative that may be of particular interest in special operations and, particularly, when the tool cost is high. For example, the use of the CO2 liquid is very effective to reduce the crater wear on the carbide tools in the machining of titanium alloys, austenitic nickel-based superalloys, and other materials difficult-to-machine [12].

Gaseous cooling

Gaseous coolants are substances which are in a gaseous state at room temperature. Air is one of the most commonly used gas, though it has a low cooling capacity that can be increased by its cooling, preserving its gaseous state. Other usual gases are argon, helium and nitrogen used to prevent workpiece and tool oxidation [54]. However, as cryogenic cooling, the high cost of these gases makes them not advisable for common applications [55].

Compressed air in combination with cutting fluids reduces the consumption of fluid and can ameliorate the heat transfer problems in superalloy machining [56]. Moreover, the simultaneous use of the spray mode of a vegetable cutting fluid, compressed air and inserting liquid nitrogen to the cutting zone, not only can reduce the cutting forces and temperature, but also makes possible to achieve high cutting speeds and feed rates [57].

Sustainable cutting fluids

Sustainable cutting fluids are one of the main growth areas for the lubricants market due to restrictions and individual pressures and environmental concerns, which is opening multiple research lines. On the one hand, the market is exploring the use of biodegradable vegetable or synthetic oils to replace petroleum products [58]. The rapid increase in the petroleum products prices, the higher dependence on offshore sources, the declining rate of production and the decreasing rate of finding new reserves are some of the reasons to remove mineral based oils [45]. On the other hand, there is a tendency to eliminate or reduce the use of dangerous substances in the cutting fluids formulation. For example, the removal of sodium nitrite and aromatic compounds, the use of more biodegradable additives and an efficient use of biocides in water based fluids [59].

There is a wide range of base fluids that can be used as alternative to mineral oil based like poly-alkylene glycols, vegetable oil, poly-alphaolefins, dibasic acid esters, polyol esters [60], and polymer based fluids [61]. Table 2 compares the properties of different base fluids: canola oil with a 60% oleic acid, a commonly used polyol ester such as trimethylol propane trioleate (TMPTO), a fully saturated or complex synthetic ester, a polyalkylene glycol and a mineral oil. Several studies show that vegetable oil based cutting fluids can be a good alternative to conventional fluids [8, 62, 63, 64]. Vegetable oils have excellent lubricity, biodegradability, viscosity-temperature properties and low volatility. Their main disadvantage is their low thermal and oxidative stability, but it can be improved by using a combination of chemical additives, olefin and high oleic vegetable oils [62].

Table 2. Typical base fluid for sustainable lubricants compared to mineral oil. Based on [45]

Performance	**Canola oil (vegetable oil)**	**TMPTO (polyol ester)**	**Sat/Complex (synthetic ester)**	**PAG (petroleum synthesized)**	**Mineral oil (petroleum)**
Biodegradability	Excellent	Very good	Good-Very good	Good	Poor
Toxicity	Low	Low	Low	Low*	High
Lubrication	Excellent	Very good	Very good	Very good	Good
Oxidative stability	Poor	Moderate	Very good	Good	Very good
Thermal stability	Moderate	Good	Very good	Good	Good
Hydrolytic stability	Poor	Moderate	Good	Good	Very good
Viscosity index	Very good	Very good	Very good	Very good	Moderate
Low temperature	Poor	Good	Good	Good	Good
Seal compatibility	Moderate	Moderate	Moderate	Good	Very good
Relative cost**	2	4	6-8	4	1

*Solubility may increase the toxicity of some PAGs

**Cost compared to mineral oil cost (1)

Nanofluids

Nanofluids are fluids obtained by suspending nanoparticles (nanographene or nanoparticles prepared from materials like copper oxide, molybdenum disulphide or titanium) in a base fluid like water, ethylene glycol or oil. Nanofluids physical analysis show that these dispersions can easily penetrate the surface, increase the heat transfer capacity and improve the tribological properties of the fluid [65, 66]. Many lubricants containing nanoparticles are considered advantageous in new technology, as they can provide lubricity over a wide range of temperatures [66].

Water with oxide graphene nanosheets show better friction and wear properties than pure water and water with oxide multiwall nanotubes [47]. Nanoparticles synergism in terms of the lubrication film stability have been found mixing MoS2 and SiO2 [67] or alumina and colloidal solution of silver [68].

Recently, an extensive number of studies combine nanofluids with MQL system as alternative to conventional lubrication/cooling systems. For example, nanographene particles in combination with vegetable oil in MQL milling [69], turning [52, 70, 71], and grinding decreases the tool wear and exhibits better performance in terms of surface roughness [72] than MQL. One barrier for the industrial use of the nanofluids is the viscosity. By adding nanoparticles to the base fluid both thermal conductivity and viscosity are increased. Another barrier is the special condition required for nanofluids, such as uniform and stable suspension or low clustering of particles [73].

3. Economic review

3.1 Conventional lubrication/cooling systems

Machining process cost depends strongly on the Material Removal Rate (MRR), but increasing the MRR results in shorter tool life due to the increase of friction and heat generation in the cutting edge [14]. Winter et al. [61] have studied grinding process, identifying the influence of the cutting fluid composition on the MRR, the energy consumption and the surface quality reached. Besides, the cutting parameters and workpiece properties, there are three other factors to improve the technological requirements, and the environmental and economic impact, which are: tool, machine tool and cutting fluids [74].

These fluids provide numerous advantages in the manufacturing process, but there are also several disadvantages that suppose a machining cost overrun (Table 3) [75]. In addition to these considerations, environmental legislation is becoming more severe, increasing disposal costs and arising the need to develop new lubrication/cooling systems and new cutting tools.

Table 3. Cutting fluids advantages and disadvantages in machining operations

Advantages	**Disadvantages**
Increase tool life	Costs related to fluid purchase, storage, maintenance, waste fluid disposal
Lower cutting forces and power required	As time passes it can cause workpiece and machine tool damages due to a bad maintenance
Higher cutting speeds and feed rates	Environmental impact
Reduce post-process heat treatments	Worker health hazards
Better workpiece quality	

Heine (1998) [76] noted that the cost of lubrication/cooling systems represents between 7.5 and 17% of the total manufacturing costs, compared with 4% of the tool costs. Later, Sreejith et al. (2000) [77] estimated that the lubrication costs ascend to 16-20% of the manufacturing costs. More recent studies showed that the lubrication/cooling costs in the automotive industry achieves the 16-18% versus the 7-8% of the tool costs [78]. Moreover, in machining of difficult-to-cut materials, the coolant acquisition, use, disposal and the cleaning of the pieces lead to major costs, four times more expensive than that of other machining materials [24]. For the evaluation of the cost of the cutting fluids system should be taken into account the following factors [75]:

- Cutting fluid purchase cost.
- Workpiece cleaning and secondary operations costs to remove the lubricant film from the surface and avoid contamination between different manufacturing process [10].
- Water cost to dilute the concentrated emulsifiable cutting fluids and added to offset losses by evaporation. The water amount may vary between 5 and 20% of the tank volume per day. Moreover, water used for cleaning the workpiece and the system itself should also be considered [79]. This cost can vary greatly depending on the water quality required.
- Energy costs. Recent studies indicate that the use of cutting fluids has a significant influence on up to 50% of the total energy demand. Therefore, it is very important the proper selection of the lubrication/cooling system to improve the energy demand of the manufacturing process [10].
- Costs associated with the fluid replacement due to the drag out of fluid with chips and workpiece. Fluid must be added to reach the concentration and the level required [11].
- Fluid supply system costs like fluid recirculation and filtration.

- Maintenance costs associated with the additives used to prolong the fluids life. Additives, such as bactericides or pH buffers, may be controlled and added when necessary.
- Maintenance tasks costs associated with pumping, cleaning and refilling.
- Costs of treatment and fluid disposal. They can cause air and soil pollution, and surface water and ground contamination [80].

Additionally, to comply with environmental regulations there are other costs associated to reduce and maintain a low level of workers exposure to cutting fluids [75].

3.2 Alternatives to conventional lubrication/cooling systems

When using dry machining, both cost of the cutting fluid and subsequent waste treatment costs are suppressed. Moreover, not using cutting fluids reduces the workpiece cleaning and maintenance operations. However, in general there is a higher tool wear. It should be noted that a higher tool wear leads to higher costs due to the need of changing tools more often [54]. This system requires specific studies and involves tools and materials technology development, opening new application possibilities.

A growing number of companies are making the transition to the MQL systems to reduce costs, the environmental impact and health hazards, that it is going on in U.S according to Skerlos et al. [31]. Although, it should be considered that there is a power consumption to produce compressed air, costs savings are mainly due to a lower infrastructure required and less cutting fluid consume which could be reduced down to 95%. Moreover, MQL system enhance the tool life [81] and the chips are released in a practically dry condition, thus avoiding cutting fluid recycling costs [82]. However, if costs related with the health and the environment are not considered, many manufacturers consider that the costs for changing the technology are too high [31].

Solid lubricant applied directly as lubricant, reduces friction in machining, resulting in better material removal rates without affecting the quality of surface produced and thus increasing product reliability, enhancing productivity, and reducing costs. However due to the high cost and the difficulty to clean and apply the lubricant, it is only found in specific machining applications [83]. Solid lubricants in combination with MQL system reduces the tool wear, improving the tool life and enhancing the productivity [51].

The cryogenic machining equipment cost is much higher than that of conventional lubrication/cooling system [7]. The nitrogen liquid storage needs special pressure tanks. Cryogenic gas transport to the cutting zone is one of the main challenges of these systems. Hong and Broomer [5] and Lu and Jawahir [84, 85] make an economic analysis of cryogenic machining. These studies show that, contrary to the general perception, the cost of liquid nitrogen is competitive against the conventional fluids, due to a lower flow, the high cost of cutting fluids treatment and that liquid nitrogen can be used only when machining. Cryogenic cooling is significantly less expensive than conventional machining when high efficiency and high productivity are required [7].

Gaseous cooling is more environmentally friendly than conventional lubrication/cooling systems. However, they require additional equipment, which normally is not provided with the machine tools, although it is not needed special equipments to achieve cryogenic temperatures. Moreover, the high cost of some of these gases, like helium, usually does not make them profitable for manufacturing processes [86].

Price is a major barrier in the sustainable lubricants development as the vegetable oil prices are not competitive in comparison with the world market prices for many mineral oils [57]. They are between 1 to 8 times more expensive than a mineral based fluid [45]. In addition, the use of sustainable cutting fluids can help improving machining performance and increasing the tool life. Moreover, it may lead to cost decreasing to ensure competitiveness and meet the demands of cleaner production [87].

Nanofluids are transported to the cutting zone through nozzles like the conventional lubrication/cooling system, but the higher manufacturing costs of nanofluids and waste treatment during the machining is a barrier for its use [88]. The cost of nanoparticles and the prevention of the sedimentation are the major challenges for the application of nanofluids in machining processes [73, 89]. Among a variety of nanoparticles, nano-SiO2 are identified as a material easily acquired on the market in a wide range of sizes at affordable prices [90] compared to nano-MoS2 [67]. Despite their costs, in the last decade, they have been combined with MQL system to increase the energy savings and reduce costs, gaining interest as an alternative to cutting fluids [55].

In order to evaluate machining costs for conventional lubrication/cooling systems alternatives, all the costs should be included, beginning with the raw material until the final workpiece and disposal costs. Therefore, raw materials costs, fluids consumption, equipment costs, tools costs and disposal costs are included. Moreover, costs for cleaning the final part and chips are also considered because of they are time consuming and so costly [7]. Table 4 shows a comparison for different lubrication/cooling systems of the costs.

Table 4. Qualitative estimation of lubrication/cooling system costs[31, 37, 88]

	Raw material cost	**Fluid consumption**	**Equipment costs**	**Tool cost**	**Cleaning costs**	**Disposal costs**
Cutting fluids	**	*****	****	***	*****	*****
Dry machining	*	*	*	*****	*	*
MQL	**	**	***	**	**	**
Solid lubricant	****	***	***	***	***	****
Cryogenic cooling	***	***	*****	***	*	*
Gaseous cooling	***	***	****	****	*	*
Sustainable cutting fluids	***	****	****	**	****	***
Nanofluids	*****	****	****	***	****	*****

(*) Very low; (**) Low; (***) Medium; (****) High; (*****) Very high

4. Environmental review

4.1 Conventional lubrication/cooling systems

Cutting fluids are used worldwide in large quantities. In 2010, the consumption in Europe, including Russia, was approximately 610,000 tones [59], that means a risk for many workers but also a high environmental impact [91]. The environmental impact minimization of manufacturing processes has become an important research topic. Cutting fluids are one of the main causes of environmental pollution during the machining [92].

The selection of the product cannot be based only on its primary properties (cooling, lubrication and chip evacuation), it should also considered secondary properties such as biodegradability and stability [9]. Cutting fluids must meet the governmental regulations for the environmental protection, and voluntary international ISO 14000 standards for environmental management system [78]. Law restrictions not only establish limitations in the manufacturing processes and provoke undesirable costs; they also encourage developing and finding new technological alternatives. Some countries have promulgated an Ecomark, for instance the European Ecolabel [58] or the German “Blue Angel” [17], to give security to the users of environmentally compatible products.

At the end of its useful life, cutting fluids are considered dangerous and, therefore, non-environmentally friendly fluids. Four major environmental problems related to cutting fluids can be distinguished in the machining process: cutting fluid disposal, fluid drag in workpiece and chips, the use of hazardous substances and mist.

Cutting fluid disposal

It is considered a waste cutting fluid when it is degraded and cannot meet the required functions. The fluid is recirculated; so throughout its use, it suffers chemical, physical and biological changes that affect its composition. Wasted cutting fluid residues depend on the physicochemical nature of the product, which will determine the fluid life as well as the waste treatment type. The deterioration of water-based cutting fluids is the result of several causes [4, 93]:

- Oil and water incompatibility, from the accumulation of oils, hydraulic fluids and other external to the cutting fluid lubricants.
- Metal particles and chips, dirt and debris accumulation.
- Susceptibility to microbial growth.
- Water evaporation and additives depletion.
- Hard water ions capacity to destabilize the emulsion and losing the capacity of lubrication and cooling
- Surfactants susceptibility to generate foam when they are agitated mechanically.

Some of the problems associated with the bad condition of the fluid are corrosion or oxidation of the tool or workpieces, tool failure due to the loss of functionality, rancid smell due to microbial growth and fluid properties changes, for example in pH.

Fluids must periodically be replaced. The replacement period can vary from weeks to months depending on the process requirements and the cutting fluid maintenance. Life can be enlarged by increasing the resistance to micro-organisms growth and to fluctuations in the concentration of active ingredients that are consumed during the process. It should be also taken into account the cutting fluid robustness to contaminants such as oil drip and the accumulation of ions and metal particles generated from the machined parts [31]. Cutting fluids replacement involves a high volume of waste to treat. In order to recycle the water, first the water is separated from the oil. Then, the water goes to a waste fluid treatment and oil can be send to energy recovery [11].

Fluid drag in workpiece and chips

A relevant amount of cutting fluid is lost due to drag-out via workpiece and chips. This loss depends mainly on the workpiece' shape and cavities [94]. Resulting pieces should be cleaned to remove all fluid traces and it is necessary to clean the chips before managing them as a solid residue. Cutting fluids drag causes a high cutting fluid consumption and a reduction of the cleaner bath efficiency due to an excessive accumulation of fluid in the workpiece [31].

Hazardous substances

There is a wide variety of chemical substances on the market, some of them with risk to human health or environment. Cutting fluids substances with major concern are: secondary amines, sodium nitrite, phenols, chlorinated paraffin, boric compounds, polycyclic aromatic hydrocarbons (PAHs) and biocide products [95].

One of the main problems of cutting fluids that has recently been decreased is the amount of nitrosamines, which are carcinogenic; produced by the reaction of nitrite with secondary amines (such as the diethanolamine) [96]. On the one hand, sodium nitrite is a compound used as a corrosion inhibitor, very toxic to aquatic life and harmful to the workers. On the other hand, secondary amines are used to neutralize the acids from the cutting fluids and provide corrosion protection. Currently, these amines are replaced by other primary and tertiary amines, as monoethanolamine and triethanolamine, respectively [96].

The use of chlorine additives, such as chlorinated paraffin which had been used as extreme pressure additives, poses threat to ecology and the workers health. In addition, chlorinated additives are not suitable for the titanium machining because they can cause corrosion on the workpiece surface [54]. Treatment of cutting fluids disposal with chlorinated content is classified as hazardous waste and it is expensive [11].

Boric compounds, such as boric acid, are substances that provide multiple functions including corrosion protection, pH buffer capacity and bacterial growth inhibition [64]. However, boric acid is classified as substance that may cause problems for reproduction and is included as a candidate on the list of substances of very high concern from the ECHA (European Chemicals Agency) [97]. Other compounds that have been banned or restricted because of their toxicity are PAHs. PAHs are present in the mildly refined base oils and as a product of thermal degradation at very high temperatures. These compounds are carcinogens, mutagens and teratogens. The exposure risk has decreased and currently, the formation during the machining is very low [96].

Bacteria and fungi may grow in water miscible cutting fluids, the most common Comamonas and Pseudomonas testosteronei [98]. These organisms feed on corrosion inhibitors, emulsifiers and contaminants from the system. The uncontrolled microorganisms growth can cause the premature loss of fluid functional characteristics [11] and adverse economic charges. Biocides can be used to control the microbial and bacterial activity and increase the fluid lifetime. Some of the most commonly used biocides are triazine, the oxazoline, the dicyclohexylamine or phenoxyethanol.

However, maintaining the optimum concentration of biocides in the cutting fluid can be difficult due to the fluid evaporation. On the one hand, high concentrations of biocides can affect the workers health and cause dermatitis through cutting fluids contact. On the other hand, an insufficient concentration of biocides does not inhibit the bacteria growth and may even promote the formation of biofilms. When there is microorganisms growth and biofilm, even if there are biocides, only a thorough cleaning and a disinfection process prior to the system filling, are effective for inhibiting the microorganism regrowth [98].

Many of the biocides used in the lubricants industry, as the HTHT (hexahydro-1, 3, 5-tris(2-hidroxietil)-triazine) are formaldehyde releasers [99]. Formaldehyde is a highly volatile and extremely flammable chemical compound that has been classified by the International Agency for Research on Cancer (IARC) in Group I, carcinogenic to humans. The use of biocides is literally forbidden by some manufacturers, regardless of whether they are legally certified or that there is a demonstrated microbiological need. There is no consensus of the bactericide or fungicide level, each lubricant manufacturer may make a recommendation to the user to determine the best prophylactic level [11]. Pasteurization and UV irradiation have been proposed as biocide alternative; however their use is not extended due to economic reasons [59].

Mist

Mist is one of the environmental concerns with greater impact in the workers' health. The typical particle size of an aerosol is 0.1 to 10 μm, with 75% of particles (mass concentration) size enough to be inhaled by the human body. In the one hand, high cutting speeds results in smaller particle sizes of oil mist, therefore the oil mist concentration is higher. In the other hand, higher cutting fluid flow contributes larger diameter of oil mist and higher concentration [100]. The main mechanisms through which the cutting fluid produces mist in the environment are [59]:

- Evaporation due to the high temperature of the cutting zone. The compounds more volatile vaporize and then are condensed forming small particles of size less than 1 μm, with a composition different from cutting fluid and tend to migrate throughout the environment.
- Atomization occurs by mechanical movement due to the fluid impact against the tool or workpiece, forming particles of a size from 1 to 10 μm, with the same composition as the cutting fluid and do not migrate far from the cutting zone.
- Splash caused by the cutting fluid under pressure against tool, workpiece or machine-tool.
- Fluid aeration, either by its foam tendency or due to an excessive agitation.

Mist inhalation risk is due to the exposure of three agents: fluid process, microbial contaminants and other chemical contaminants accumulated in the cutting fluids during the process as, toxic elements (mineral oils, alkanolamines, nitrosamines, volatile organic compounds) or metal workpiece allergens (such as Cr, Pb, Ni, Cd) [22]. Mist can cause serious problems in the workers' health: eye, nose and throat complaints, irritation of the respiratory tract, pulmonary dysfunction, bronchitis and asthma, and also in less frequent circumstances pneumonitis, lipoid pneumonia and fibrosis [96].

4.2 Alternatives to conventional lubrication/cooling systems

Dry machining reduces the environmental impact and the workers' health risks. Moreover there is no fluid residue in the workpiece or chips, which reduces the costs and energy in the cleaning process.

MQL systems reduces drastically the use of cutting fluids [37]. The amounts used are so low that the cutting fluid is consumed almost completely in the process, eliminating the problems of fluid disposal. In addition, chips produced during machining are almost clean of fluids, which are easily recyclable [35]. Although, the environmental effects that should be considered in the MQL systems are related to the power consumption of the gas compressor and the pressure required for the supply, it can be an intermediate strategy for reducing direct electrical energy requirements and global warming potential compared to conventional machining [81]. However, the main disadvantage of using MQL is mist generation, which is harmful to workers [101]. An excess of MQL fluid flow can produce aerosols, although at a level much lower than cutting fluids, even at levels below the detection limits [31].

Cryogenic cooling with liquid nitrogen is a system that leaves no harmful residue to the environment. Liquid nitrogen absorbs the heat generated during the manufacturing process and evaporates quickly becoming part of the air [19]. In the cryogenic cooling with carbon dioxide, the fluid also evaporates and although the amount of carbon dioxide evaporated is low, it is a greenhouse gas. Workpieces and chips resulting from machining are clean of cutting fluid residues; so further treatment costs are reduced. Moreover, the used substances are not harmful and do not produce mist [86]. Besides, gaseous cooling has the same advantages as cryogenic cooling, being both techniques considered as some of the most eco-friendly cleanest methods for machining of various engineering alloys, after dry machining [102].

Another alternative is the use of sustainable cutting fluids. On the one hand, they eliminate those additives considered dangerous substances, as sodium nitrite or biocides. On the other hand, they replace the mineral oil base by vegetable or synthetic oil, such as rapeseed oil and palm oil. These oils are organic, renewable, less toxic and more easily biodegradable than those of the conventional fluids [64].

The biodegradability is the main measure to determine the environmental compatibility. The plant oils, also used in MQL applications, are highly biodegradable, and the synthetic esters possess a broad range of biodegradability [23]. Currently, there are five major groups of biodegradable products applied as base fluids [60]:

- High oleic vegetable oils, mainly triglycerides.
- Low viscosity olefin.
- Polyalkylene glycols.
- Dibasic acid esters.
- Polyol esters.

Besides the biodegradability, in a sustainable cutting fluid, it must be taken into account the additives. Many of them such as biocides, can be potentially toxic and hazardous to the environment and health [103].

While nanomaterials are a topic of research due to their potential in advanced technologies, little is known about their environmental impact and their effects on human health [104]. Handling the nanoparticles themselves without mixing with fluid is dangerous to human's health. They can be toxic because they would become as airborne nanoparticle in the air and represent a potential source of environmental damage. By mixing them with lubricant oil is hardly to become as airborne nanoparticle in the air [105]. However, limited investigations have been conducted on environmental, safety and health aspects of application of nanofluids in machining processes. Further research should be emphasized in mist generation of the nanofluids, as the fluids have metallic inclusions, the mist might hazards to the workers' health [106].

Table 5 presents a qualitative estimation of the environmental impact of various lubrication/cooling systems used in the machining, taking into account the above considerations.

Table 5. Qualitative estimation of lubrication/cooling environmental impact

	Residue	Fluid drag out	Dangerous substances	Mist and emissions	Workers health hazards
Cutting fluid	*****	*****	****	*****	*****
Dry machining	*	*	*	*	*
MQL	**	**	**	***	***
Solid lubricant	*****	*****	***	****	****
Cryogenic cooling	*	*	*	**(1)	*
Gaseous cooling	*	*	*	*	*
Sustainable cutting fluids	****	*****	***	****	***
Nanofluids	****	*****	Unknown	****	Unknown

(*) Very low; (**) Low; (***) Medium; (****) High; (*****) Very high

(1)Very low for liquid nitrogen.

5. Discussion

Fig.3 shows a comparison among eight different lubrication/cooling systems used in machining processes. In the one hand, cost and sustainability values are represented taking into account the qualitative estimation of Table 4 and Table 5, respectively. In the other hand, the diameter considers the industrial potential use according to the technical feasibility.

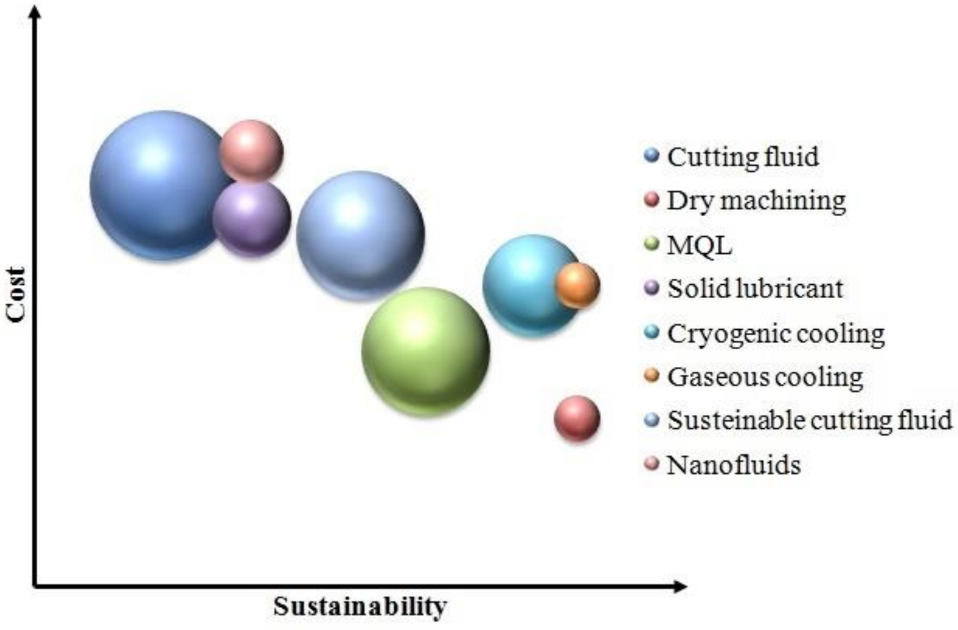

Fig.3. Cost of lubrication/cooling systems in machining as a function of sustainability.

This comparison is based on the type of lubricant/coolant system and the appropriate method of application. However, this is not the only possible classification. It could also be grouped according to the type of lubricant or the type of system separately [10, 107]. Table 6 shows the relationship between the type of application system (i.e. dry machining, flood) and the lubricant type (i.e. neat cutting oil, water soluble fluid, gases).

Table 6. Relation between the type of lubricant and the strategy application methods [10, 107].

	Dry machining	Flood	Cooling	Cryogenic	High pressure	MQL
Neat cutting oil	None	Common	Not common	None	Not common	Mixed with gas
Water soluble fluid	None	Common	Not common	None	Not common	Mixed with gas
Solid lubricant	None	Mixed with fluid	None	None	None	Mixed with fluid
Gases	None	None	Common	Common	Common	Mixed with fluid

While this classification or combination of possible strategies is theoretically possible, some of the resulting combinations are not use in practice. The focus of the work is expected to be eminently practical and applicative. Consequently, even in a qualitative way, efforts have been made in the combinations used in the machining industry, intended to be of assistance to all those persons related to this type of processes, both researchers and manufacturers.

6. Conclusions

Cutting fluids play an important role during machining but they use have some drawbacks such as their negative effects over the environment and workers health as by costs associated such as the equipment, fluids purchase and waste fluid treatment. All of these plus governmental regulations are encouraging companies to implement lubrication/cooling systems more efficient and sustainable. The alternative techniques such as dry machining, MQL, solid lubricants, cryogenic and gaseous cooling have been implemented in some machining processes, even may become more efficient than conventional lubrication/cooling. However, there are still applications where cutting fluids cannot be removed.

- The best environmental alternative is dry machining since completely removes the cutting fluid and ensures a clean atmosphere and workers safety, though it has many application limitations. To implement this alternative is necessary to have an exhaustive control of the cutting parameters and a suitable tool selection.
- MQL system reduces the fluids use and is a more viable alternative taking into account not only the economic and environmental impact, but also the performance.
- Solid lubricants are mostly used in aerospace industry although, for machining process mixed with a base fluid and in combination with MQL, can increase the lubrication performance.
- Cryogenic cooling can lengthen the tool life, especially in difficult-to-machine materials. Its environmental impact is lower than cutting fluids, but the initial cost is high.
- Gaseous cooling are systems with very low environmental impact, but they have limitations in their cooling and lubrication performance.
- Sustainable lubricants are potential substitutes for mineral based cutting fluids. Vegetable base oils are readily biodegradable, environmentally friendly and may have the same or even superior tribological properties. In general terms, their cost is frequently higher than the mineral-oil-based products. Although its use is growing, is proceeding more slowly than expected and currently represents a small part of the overall lubricants market.

7. Future research

Further investigation is needed to overcome the drawbacks of lubrication/cooling conventional systems:

- Research on dry machining with other metal alloys different from aluminum in drilling process.
- Investigate on MQL with materials as aluminum and magnesium to reduce the material adhesion over tool surface and with difficult-to-machine materials.
- Explore further solid particles as additives able to improve lubricity properties.
- Research and development of cryogenic cooling equipments to improve industrial application implementation.

- Research and development of sustainable cutting fluids in applications for non ferrous materials (titanium, aluminum, magnesium, copper, brass) and superalloys (nickel, cobalt).
- Enhance vegetable based fluids characteristics to overcome their disadvantages, such as its low thermal and oxidative stability, without impairing their tribological and environmentally properties.
- Replace dangerous and non-renewable cutting fluids components such as boric acid or secondary amines, conventionally employed due to their low cost as pH-buffers and corrosion inhibitors, with ingredients that are renewable and biodegradable.
- Research and development of the environmental impact and health hazard of nanofluids, which are growing as alternative lubrication/cooling systems.

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