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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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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 research 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 a difficult-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 researchers 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 hydrocarbon chain 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 using esters, 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 concentration 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).

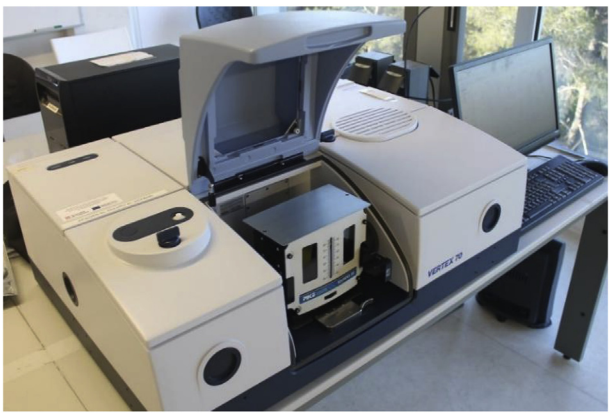

Fig. 2. Infrared reflection absorption spectroscopy (Vertex 70, Bruker).

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.

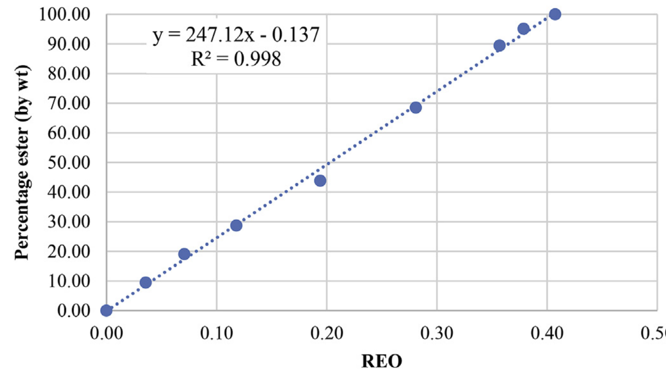

Fig. 4. Calibration Curve. REO (integrated area ratio between C = O and CH2 stretching vibration peaks) against the weight percentage of ester.

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

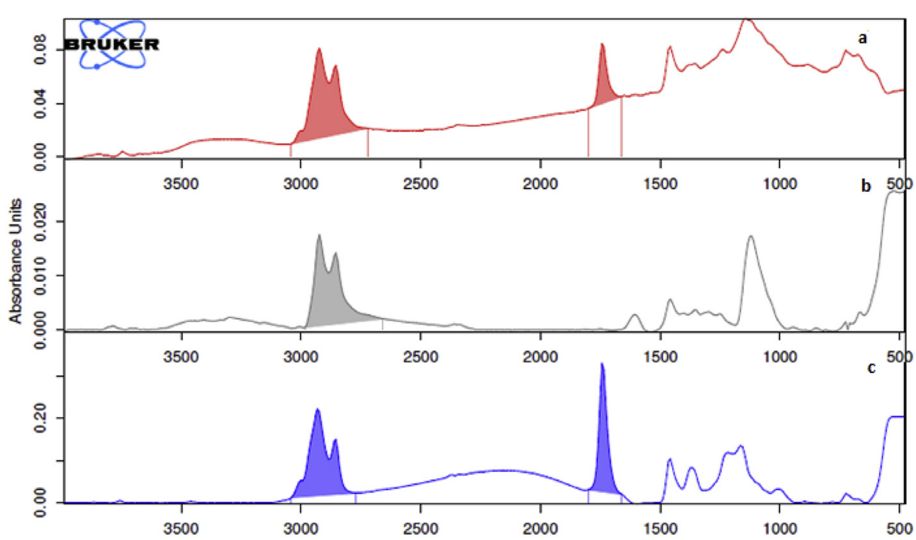

Fig. 3. IRRAS spectra of a Ti6Al4V strip treated with: a) surfactant system emulsion with ester at ratio 1: 2, b) surfactant system solution without ester, and c) 100% bulk TMP oleate.

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

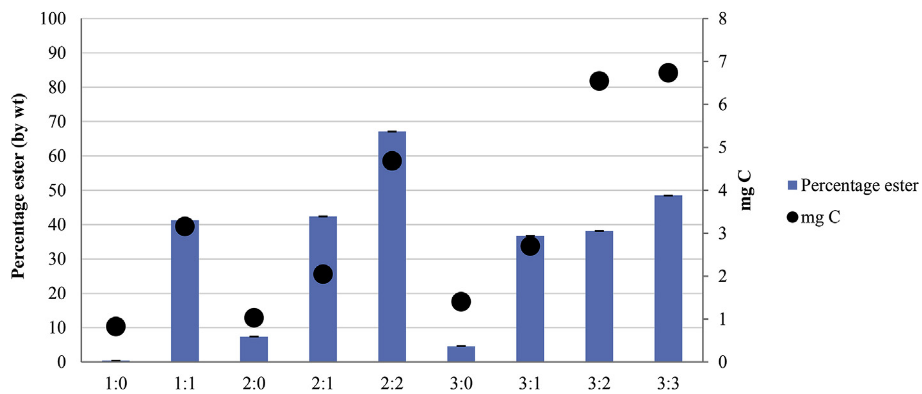

Fig. 5. Weight percentage of ester and total organic carbon (mg) adhered on the Ti6Al4V surface for different surfactant and ester concentration.

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.

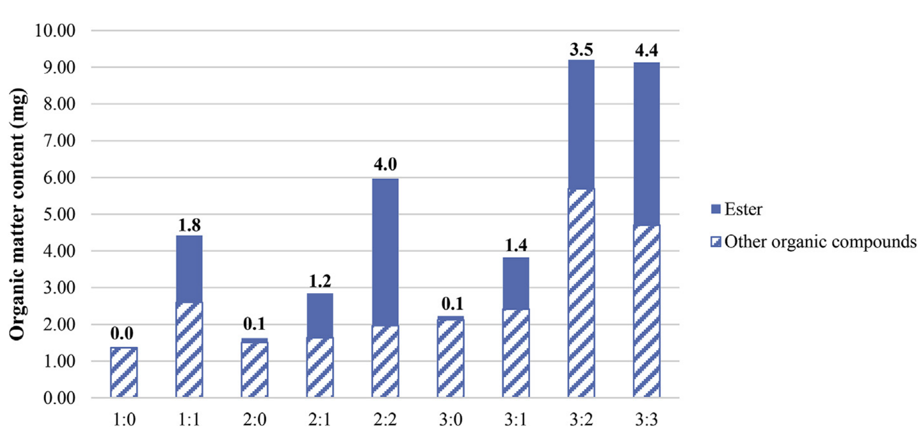

Fig. 6. Total organic matter of TMP oleate adhered on the Ti6Al4V strips treated with emulsion containing different ratios of surfactant and ester. Milligrams of ester are quantified.

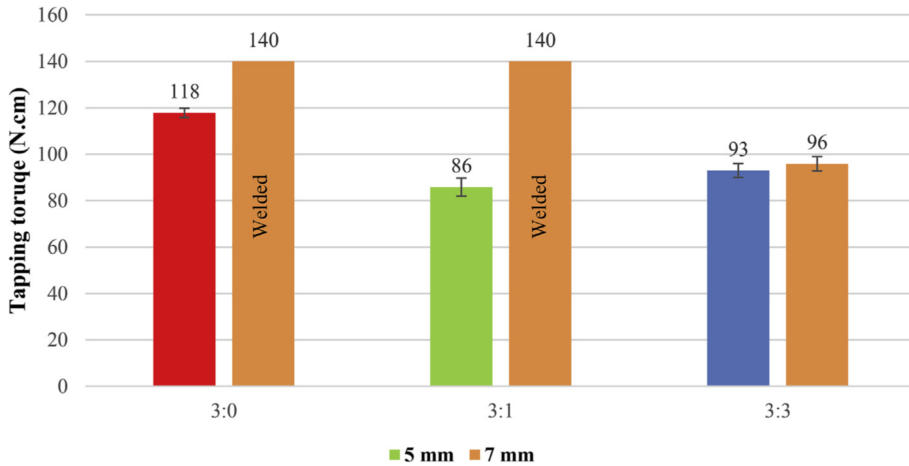

Fig. 7. Tapping torque of three samples with different ester amount using Ti6Al4V workpiece, and a machining speed of 300 rpm.

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.

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