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MACHINING OF TiAl6V4 USING LUBRICANTS CONTAINING RENEWABLE MICROALGAE-BORN PERFORMANCE ADDITIVES

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Abstract: Titanium and its alloys represent a special class of materials. A density of 4.81 g/cm³, a tensile strength of over 1,200 MPa, a fatigue strength greater than that of steel, a low modulus of elasticity and its self-passivating, inert surface make titanium an ideal material for lightweight structures in aerospace, marine applications, the chemical industry and medical implants. Although titanium is inert in its oxidised state, its nascent surface created in machining reacts with almost everything in its environment, including the tool. Moreover, its poor thermal conductivity results in high thermal stress on the tools. Overall, these properties lead to high wear rates and result in the requirement for finding a particularised solution for processes such as milling that involve the need to overcome such challenges. Such processes therefore require lubricants with well-selected performance additives. However, most of these performance additives are based on mineral oil and thus come from a non-renewable resource. In the presented work, environmental-friendly alternatives to conventional mineral oil-based performance additives were investigated. Due to the working mechanisms of performance additives in machining, this work focusses on sulphur- and phosphorus-containing polysaccharides and proteins from microalgae. It has been successfully shown that lubricants using extracts from microalgae as performance additives can be used for high-speed milling (HSC) of TiAl6V4. The investigated extracts were able to reach the performance level of conventional additives in terms of tool lifetime and wear. The results obtained show that appropriate alternatives to mineral oil-based additives exist from renewable raw-material sources.

Key words: titanium, TiAl6V4, high-speed milling, metalworking fluid, additives

1. INTRODUCTION

In metalworking processes, metalworking fluids (MWF) are used in various applications. In machining or forming processes, MWF are used to cool the process and enhance the tribological conditions between the workpiece and the tool. In general, MWF are based on mineral oils, synthetic base fluids, vegetable oils or even water and supplemented with specific additives. The additives improve and adjust, e.g. performance in machining and protection against wear and corrosion. Sulphur- and phosphorus-containing, esterified or ethoxylated hydrocarbons, fatty alcohols and fatty acid esters are typically used as performance additives. These performance additives interact electrochemically with the workpiece surface and provide the desired technical properties (Fig. 1). The type and strength of the interaction depend in particular on the kind of application, the workpiece material (quantity and type of alloying constituents and oxide structure of the metal surface) and the chemical-structural characteristics of the additives. The effects of additives occur in its adjacent surfaces and within the workpiece material itself and are caused by physical and chemical mechanisms in the MWF (Fig. 2). A substantial proportion of additives is made up of mineral oils and is therefore unsustainable. Manufacturers of lubricants and MWF are challenged to find suitable alternatives to offer to their customers, due to the increasing legal requirements, and the demand from civil society and industry to act more sustainably [1–3]. The research project ALBINA presented here has focused on the development of alternative performance additives based on microalgae as a resource for a new class of sustainable additives. Several microalgae produce substances that, due to their chemical structure, can be used as analogues to conventional additives in metal working processes. The results obtained in HSC milling of TiAl6V4 show the potential of algae-born substance to supplement conventional performance additives [4–5].

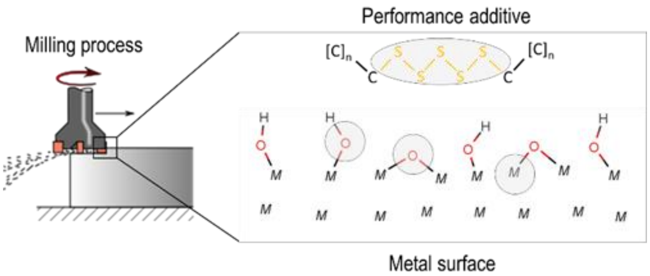

Fig. 1. Milling process as an example for metal cutting and working site of metalworking fluids. Scheme of a conventional performance additive and metal surface. The areas relevant to a potential interaction are highlighted in grey

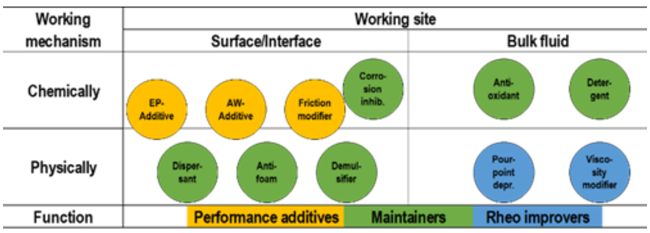

Fig. 2. Working sites and mechanisms of action for exemplary groups of additives (acc. [3], modified). AW, anti-wear; EP, extreme pressure

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2. OBJECTIVE

The overall objective of the work presented is to replace conventional MWF additives with components from microalgae. Many algae species are capable of synthesising substances that can work as equivalents to the common additives used in MWF. These include, in particular, sulphur- and phosphorus-containing polysaccharides and protein components. It is known that several polysaccharides and protein structures have naturally incorporated sulphur or phosphorus atoms. Therefore, they represent an ideal partner for interactions with the metal surface. These structural analogues are intended to replace conventional additives in tribological applications and ideally surpass them in their technical impact.

2.1. Titanium

Titanium is one of the most common elements in the Earth's crust. Alloys of titanium represent a special class of materials. Titanium has a density of 4.81 g/cm³, a tensile strength of over 1,200 MPa, a fatigue strength greater than the one of steel and a low modulus of elasticity. In addition to its specific mechanical properties, titanium is extremely corrosion-resistant due to the self-passivation of the surface with an oxide layer. Therefore, it is an ideal material for lightweight structures in aerospace and marine applications, the chemical industry and medical implants. In machining processes, the high strength and low thermal conductivity lead to a high thermal load and thus wear on the tool. Furthermore, the increasing spring-back effect with increasing cutting speed leads to a larger contact zone at the flank face of the tool, which also manifests itself in increased wear rates. Nascent titanium surfaces have a high affinity for oxygen, carbon and nitrogen. The surface created in machining processes can react with the tool and the components of the MWF. Due to this, specific additives are required for an efficient machining process [6–8].

2.2. Why microalgae

Microalgae are microscopic, mostly unicellular, phototrophic organisms. They colonise marine as well as limnic and terrestrial habitats. Numerous species have adapted to particularly extreme conditions. The estimated approximately 100,000 species of algae offer a high potential for substances of interest [9]. Applications can be found in biotechnology and the food and feed industry, as well as in technical industries. Due to their high surface-to-volume ratio, microalgae are highly productive and therefore suitable candidates for the production of renewable bio-based resources. So far, microalgal biomass production is being researched and commercialised, especially for food technology (pigments, lipids) and biofuel industries [10, 11].

The cultivation and harvesting of about 20 industrially used microalgae species are technically mastered. This creates an important prerequisite for the sustainable production of algae biomass for the development of new areas of application. The cultivation of microalgae is not tied to the use of agricultural land. Therefore, the need to consider the tank-plate conflict, which would require discussion in the case of other energy crops, is negligible.

2.3. Process data and material

The tests were carried out as a counter-face milling process on a five-axis high-speed milling machine shop Röders RXP 601 DS from Röders GmbH, Soltau. A sensory tool holder Spike V1.2 HSKE50 PG25 L100 C from pro-micron GmbH, Kaufbeuren, was applied for the recording of the resulting bending moment *M*, calculated from the individual moments *Mx* and *My*, the torsion *T* and the tensile/compressive force *F* during machining. Data analysis was performed post-process. The used cutting tool was a modular milling cutter equipped with two uncoated, round indexable inserts RDHT10T3M0-8-E04 H25 from Seco Tools GmbH, Erkrath, Germany. For tool wear measurements, the machine-integrated LTS35.60-40 laser-tool-measuring system from m&h Inprocess Messtechnik GmbH, Waldburg was applied. It enables automatic length correction, diameter and contour measurement, wear monitoring and breakage control of the milling tools. The accuracy is ±1.0 µm. The cutting-edge offset is integrated at 5° sections over a projected 50° arc on the insert and the worn area of the tool is calculated (Fig. 3).

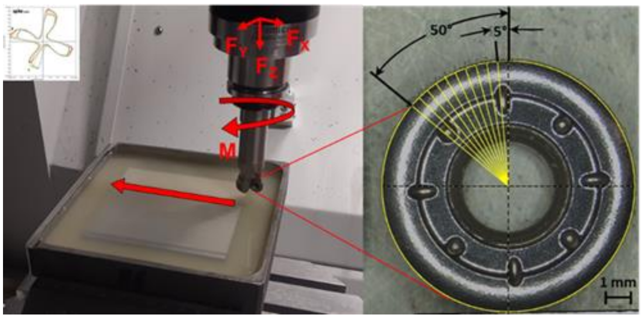

Fig. 3. Left: Work area of the five-axis high-speed milling machine Röders RXP 601 DS with tool and workpiece. Right: Top view of an indexable insert with segmentation of the 5° measuring locations where the deviation from the pristine tool geometry was measured by a laser-tool-measuring system of the machine

The workpiece was titanium grade 5 (TiAl6V4, 3.71649) with the following content of alloys:
- Al = 5.5%–6.75%,
- V = 3.5%–4.5%,
- Fe = ≤0.3%,
- O = ≤0.2%.

TiAl6V4 is the most common titanium alloy and is used in aerospace and medical applications. Tab. 1 documents the material and process data of the milling process.

A mineral oil-free water-miscible MWF concentrate (internal abbreviation: DBG_ohne) was used as the base fluid for the experiments. It was formulated without performance additives so as not to cover the effect of the tested substances in the milling process. The concentration of the MWF emulsion used was set up to 5% (v/v), and that of the reference substances and algae extracts was 0.05% (w/v) in the mixtures. As references, the following substances were incorporated into the MWF emulsion:
- Iota-carrageenan (CAS 9062-07-1) as a reference for sulphated polysaccharide,
- Gelita Novotec CL800 (CAS 68410-45-7), a gelatine hydrolysate as a reference for proteins,

– TPS20 and TPS32 (CAS 68425-15-0), a tertiary dodecyl polysulphide, as reference for commercial performance additives, and
– RC 2526, a sulphurised vegetable fatty acid ester, as a reference for commercial performance additives.

Tab. 1. Material and process data of the HSC milling process

Process	HSC face milling
Workpiece	TiAl6V4
Hardness (HRC)	33 ± 2
Tensile strength (N/mm^2)	>895
Diam. tool (mm)	20/eff. 16
No. of cutting edges	2
Diam. insert (mm)	10
Cutting microstructure	Fine grain
Grain size (µm)	<1
Cobalt (%)	~5
Microstructure hardness (HV10)	1,750
Rake angle (°)	20
Coating	None
Rotational speed, n (min^{-1})	7,958
Cutting speed, v_c (m/min)	400
Feed/tooth, f_{th} (mm/th)	0.025
Feed rate, v_f (mm/min)	398
Depth of cut, a_p (mm)	1.0
Width of cut, a_e (mm)	6.0
MWF concentration (%)	5.0
Additive concentration (%)	0.05

HSC, high-speed milling; MWF, metalworking fluid

The reviewed algae extracts are lyophilised biomass of the commercially available microalgae strains *Nannochloropsis salina* and *Porphyridium purpureum*. The lyophilizates were rehydrated at a concentration of 0.05% (w/v) in warm tap water for 15 min. Two batches were prepared from this stock solution:
– To the first batch 5% (v/v) of the above-described MWF, concentrate was added to obtain the emulsions Nanno BBT and Porph BBT (both internal abbreviations).
– In the second batch, the fluid was homogenised using a CAT X1740 homogeniser at 17,000 min^{-1} for 2 min. After resting it for 2 min, a second homogenisation step was performed at 17,000 min^{-1} for 2 min. Afterwards, 5% (v/v) of the above-described MWF concentrate was added to obtain the emulsions Nanno hom (abbr.) and Porph hom (abbr.). This processing approach was used to release the target substances' polysaccharides and proteins from the inner cellular material.

The HSC milling process was performed in triplicate for each of the described MWF compositions. The deviation bars reflect the minimum, mean and maximum of the respective values.

3. RESEARCH RESULTS

While comparing the performance of the respective MWF formulations, the HSC milling process of TiAl6V4 was stopped after a milling distance time of 1,000 mm. The addition of the reference substances, as well as the microalgae extracts, led to a significant reduction in tool wear, ranging about 50%, compared to the basic MWF without performance additives. However, the wear reduction effect is related to the individual additives. In particular, the addition of the extracts obtained from the microalgae N. salina shows a noticeable reduction in tool wear. The worn area is even less compared to one of the commercial additives. The homogenised extract of the microalgae P. purpureum led to a less pronounced reduction in tool wear, accompanied by a large scattering. Its positive effect on tool wear is smaller compared to the reference substances. Of the commercially available additives, the best results were obtained with the addition of TPS32 (Fig. 4).

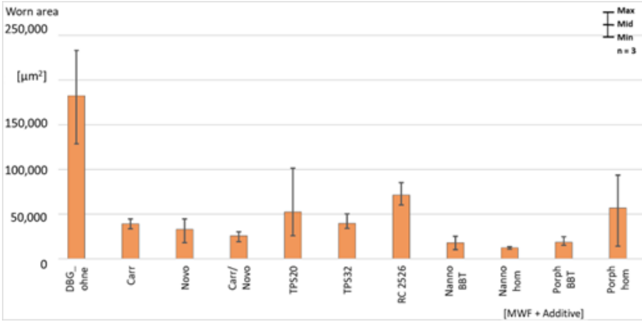

Fig. 4. Tool wear displayed as a worn area after a tool lifetime of 1,000 mm in the HSC milling process. HSC, high-speed milling; MWF, metalworking fluid

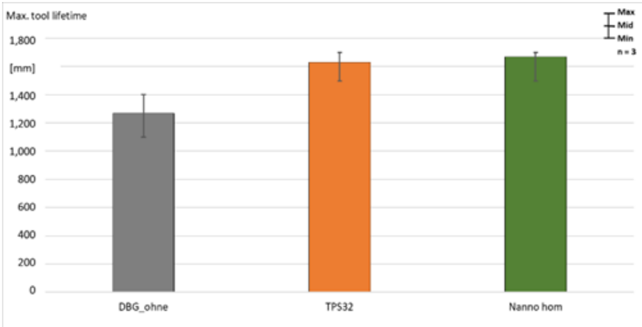

Fig. 5. Maximum tool lifetime of the MWF without performance additives and the MWF formulated with each 0.05% TPS32 and the homogenised N. salina biomass, respectively. MWF, metalworking fluid

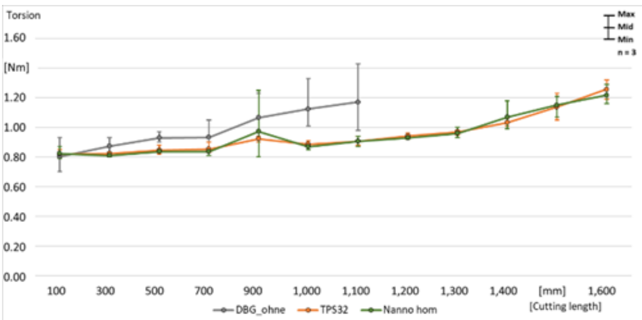

Fig. 6. Measured resulting bending moment in the tool during milling using the MWF without performance additives and the MWF formulated with each 0.05% TPS32 and the homogenised N. salina biomass, respectively. MWF, metalworking fluid

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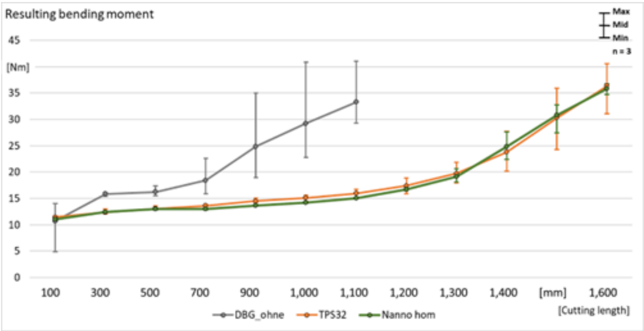

Fig. 7. Measured torsion in the tool during milling using the MWF without performance additives and the MWF formulated with each 0.05% TPS32 and the homogenised N. salina biomass, respectively. MWF, metalworking fluid

To determine the maximum tool lifetime, the homogenised extract of the microalgae *N. salina* was compared with the commercial performance additive TPS32. The non-additive MWF served as a reference. The results of the maximum tool lifetime determination in the milling of TiAl6V4 show that the homogenised extract of the microalgae *N. salina* has the same performance as the additive TPS32. The maximum achievable tool lifetime (Fig. 5), the measured resulting bending moment (Fig. 6) and torsion (Fig. 7) suffered by the tool, while working with the microalgae extract, are similar to those observed corresponding to the use of the conventional additive TPS32.

4. DISCUSSION

The subject of the investigations presented is to prove the potential of algae-based substances to work as a performance additive for MWF in a milling process of TiAl6V4. These are intended to replace the mineral oil-based conventional additives as sustainable active substances. The results obtained can be summarised as follows. Considering the values of the reference substances and commercial additives, TPS32 led to the best results regarding the worn area after a milling distance of 1,000 mm compared to the non-additive MWF. The tool wear of the algae substances was the lowest of all tested additives except for the homogenised *P. purpureum*. Compared to the conventional additive TPS32, the substances of the algae *N. salina* reached the same level regarding the anti-wear and performance properties. Concerning the process criteria maximum tool lifetime, the resulting bending moment and the measured torsion, it reached values similar to those involved in usage of the conventional additive TPS32.

The reason underlying the remarkable results obtained resultant to using the *N. salina* extract can be explained in terms of the chemical composition of the algae material. The protein fraction contains, among others, the amino acid hydroxyproline, for which a high affinity to metallic surfaces has been demonstrated. Similarly, the oximes from the polysaccharides, which also have a high intramolecular local charge density, can cause these interactions between the metal surface and the additive molecules. In milling, the cutting process is periodically interrupted, whereupon the influence of the MWF is obtaining a higher significance. During one revolution in face milling as conducted here, the cutting edge is wetted by the MWF for most of the time. The hot edge leaving the workpiece readily reacts with MWF constituents, which can lead to the formation of a protective film on its surface. The above-mentioned molecules can build up a tribological active surface layer on the tool and thus led to the reduction in wear observed in the milling experiments of titanium [4–6, 12, 13].

The anti-wear behaviour of the algae-born additives observed here is related to the high cutting speed in the HSC milling process. Titanium is a weak heat conductor [6, 14]. As a result, at lower cutting speeds, the temperatures at the cutting edge are not high enough to allow a chemical reaction between the tool surface and the additive molecules. This dependence was also observed by Ma et al. [15] whilst performing drilling processes under different process parameters.

Benedicto et al. [16] used the Tapping Torque Test for their tribological experiments. They assessed the surfactant's charge, the hydrocarbon chain length and the ethoxylation degree on machining TiAl6V4. One result they found is the context between the molecular structure of surfactants and the tool wear: the wear rate decreased with increasing chain length of the tested surfactants, independent of their ionic character. In addition, they found that the higher the number of ethoxylation on the hydrocarbon chain, the more significant was the observed increase in lubricity [16].

The subject of the research of Ma et al. [15] was to investigate the effect of polyalkylene glycol polymer-ester-based additives and phosphorus-based additives on the machining performance during the drilling of TiAl6V4. The tool wear and energy-dispersive spectrometry (EDS) were evaluated to assess the performance of the additives in the process. The drilling process was carried out with a constant material removal rate under varying feed rates and spindle speeds. The performance of the additives was dependent on the conditions of the drilling process. The MWF containing phosphorus led to a higher lubricity at lower spindle speeds compared to the polymer-based MWF. In addition, at higher spindle speeds, both phosphorus-rich and carbon-rich tribological layers were observed on the flank surface, depending on the MWF used [15].

Research dealing with the effect of additives in titanium machining in more detail is rare. The papers cited here support the approach that additives with a local charge density can improve the machining process of titanium. As mentioned above, additives with charge carriers such as phosphates and ethoxylates can lead to reduced wear and better performance.

5. SUMMARY AND OUTLOOK

The presented investigation focusses on algae-based substances as a sustainable substitute for conventional mineral oil-based performance additives in metalworking processes. The obtained results show the potential of the microalgae extracts to work as anti-wear additives in high-speed milling of TiAl6V4. Compared to the commercial additive TPS32, the extracts of the microalgae *N. salina* reached the same performance level regarding the tool wear and lifetime as well as the torsion and the resulting bending moment. The findings reveal that microalgae-based additives will be a first step to a new type of MWF additive. In combination with plant-based base oil, a fully sustainable and CO_2 neutral MWF will be achieved.

REFERENCES

1. Byers JP. Metalworking Fluids. Third Edition, Boca Raton, Taylor & Francis, CRC Press. 2017.
2. Czichos H, Habig KH. Tribologie-Handbuch, Springer Vieweg, Wiesbaden. 4. Edition. 2015.
3. Minami I. Molecular Science of Lubricant Additives. Applied Sciences, 2017, 7(5): 445. https://doi.org/10.3390/app7050445
4. Koch T, Gläbe R, Wenzel D, Siol A. Köser J. Thoeming J. Mesing S. Larek R. Gavalás-Olea A. Lang I. Nachhaltige Schmierstoff-Additive auf Basis von Mikroalgen in der Umformung und Zerspanung. Teil 1. Tribologie und Schmierungstechnik. 2022; 69(3): 18-26. DOI:10.24053/TuS-2022-0014
5. Koch T, Gläbe R, Wenzel D, Mesing S, Wilke K, Larek R. Nachhaltige Schmierstoff-Additive auf Basis von Mikroalgen in der Umformung und Zerspanung. Teil 2. Tribologie und Schmierungstechnik. 2022; 69(3): 18-26. DOI:10.24053/TuS-2022-0015
6. Meier L. Developing Metalworking Fluids for Titanium Cutting. ETH Zürich, PhD-Thesis. 2020. https://doi.org/10.3929/ethz-b-000413413
7. Schaal N, Kustera F, Wegenera K. Springback in metal cutting with high cutting speeds. Procedia CIRP. 2015, 31: 24-28. https://doi.org/10.1016/j.procir.2015.03.065
8. Thieme Römpp Lexikon: Titan - RÖMPP, Thieme Gruppe (cited 2022 Apr 08).
9. www.algaebase.org. (cited 2022 Apr 08).
10. D'Alessandro EB, Nelson RAF. Concepts and studies on lipid and pigments of microalgae: A review. Renewable and Sustainable Energy Reviews. 2016; 58: 832-841. https://doi.org/10.1016/j.rser.2015.12.162
11. Roux JM, Lamotte H, Achard JL. An Overview of Microalgae Lipid Extraction in a Biorefinery Framework. Energy Procedia. 2017; 112: 680-688. https://doi.org/10.1016/j.egypro.2017.03.1137
12. Murmu M, Sengupta S, Pal R, Mandal S, Murmu N.C. Banerjee P. Efficient tribological properties of azomethine functionalized chitosan as a bio-lubricant additive in paraffin oil: experimental and theoretical analysis. RSC Advances. 2020; 10(55): 33401-33416. DOI:10.1039/D0RA07011D
13. Reihmann M, Köhler B, Rittereiser N, Yüce C. New Properties of Metalworking Fluids by Introducing Hydrophilic Protein Protection Layers. OilDoc Conference & Exhibition Nov. 17^{th}-19^{th} 2021.
14. Krishnaraj V, Samsudeensadham S, Sindhumathi R, Kuppan PA. Study on high speed end milling of titanium alloy. Procedia Engineering. 2014, 97: 251-257.
15. Ma J, Mohammadi J, Zhou Y, Larsh J, Januszkiewicz K, Ewans R, Zhao Y, Gali OA, Riahi RA. An investigation into cutting fluid additives performance during machining processing of Ti-Al6-V4. Int J Adv Manuf Technol. 2021; 112: 977–987. doi.org/10.1007/s00170-020-06403-6
16. 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. 2020; 10(10): 1388. https://doi.org/10.3390/met10101388

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