The International Journal of Advanced Manufacturing Technology (2023) 126:2323–2336
https://doi.org/10.1007/s00170-023-11283-7

ORIGINAL ARTICLE

Development and testing of novel mineral oil- and biocide-free glycerol- and propanediol-based fluids for drilling and tapping aluminium alloys

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Received: 23 November 2022 / Accepted: 14 March 2023 / Published online: 21 March 2023

Abstract

This research covers the development of novel metalworking fluids for machining of aluminium alloys which are based on renewable raw materials and do not contain mineral oil and conventional biocides. Glycerol/water and propanediol/water solutions were used as base fluids. The formulations were systematically optimized by the addition of performance enhancing additives. Thereby, the optimization steps were guided through laboratory investigations, like determinations of viscosities, corrosion protection properties, foaming characteristics, and microbiological stabilities. Furthermore, the fluids were investigated using tribological Brugger and tapping-torque tests. Finally, the metalworking fluids were applied in experiments on an industrial production machine with the processing routines deep drilling and thread forming. Two Al-alloys were used for the investigations: EN AW 6060 as a soft and EN AW 7075 as a hard alloy. For comparison purposes, a commercially available metalworking fluid for Al-machining, a mineral oil emulsion, was tested in parallel. As a result, a glycerol/water-based metalworking fluid was obtained that had a similar performance to the reference fluid. It is therefore already well suited for machining the Al-alloys. The propanediol/water-based metalworking fluid however was superior to the reference, especially concerning the surface qualities of the workpieces. No toxicological relevant emissions from the novel metalworking fluids were found by air samplings and measurements at the test machine. The concentrations of some identified carbonylic compounds were significantly below the occupational limit values, at least by a factor of 800.

Keywords Metalworking fluid · Tribological test · Glycerol · Propanediol · Aluminium processing · Tapping and drilling

1 Introduction

Today, metalworking fluids (MWFs) are still mainly based on mineral oil which implies well-known disadvantages like the dependency on a finite resource, the limited compatibility to human health and environment, the legal restrictions on additive applications, the laborious deoiling of workpieces and swarf, and the costly residue disposal [1]. These drawbacks combined with the general demand for a decarbonization of industrial production processes directly lead to research and development work aiming at novel MWF concepts based on renewable resources [2, 3]. In this context, the use of renewable resources and here especially glycerol was found to be a promising approach because of its lubricating, viscosity increasing, solubilizing, and antimicrobial effects. Further advantages in this relation are its water solubility, its easy removability and disposal, and its harmlessness to human health and to the environment. Glycerol mainly results from ester oil production as a by-product [4]. Furthermore, propanediol was included into the investigations. It represents an alternative to glycerol in the MWF formulation. Propanediol can for example be directly produced from crude glycerol through a biotechnological process [5].

On the way to the development of a product family of glycerol-based lubricants, milestones have already been reached concerning grinding of steel [6, 7] and hydraulic applications [8]. In this paper, the investigation and development of a glycerol- and a propanediol-based fluid suitable for cutting and tapping of aluminium alloys are described

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to extend existing material and machining processes as well as the chemical composition of the set of these novel types of MWFs.

In practice, MWF formulations with high-performance additives were accordingly produced and chemically, physically, and tribologically tested in laboratory. Tribological investigations according to the Brugger test as well as to the tapping-torque test were applied. Further investigations aimed at foaming behaviour, pH development, viscosity, stability against microbial attack, and solubility of the components. A comparably soft and a hard aluminium alloy were used throughout the tribological investigations.

Subsequently, application tests were performed with the fluid variants and the two alloys resulting from the laboratory work by using an industrial-scale five-axis machining centre. Thus, it was possible to simulate industrial production conditions realistically. During all development work in laboratory and in the technology centre, a commercial mineral oil–based emulsion MWF was used as reference. Air sampling was performed at the metal working machine in order to ensure that no emission of toxicologically relevant chemicals occurred.

2 Material and methods

2.1 Laboratory tests

The determination of the investigations on laboratory scale was already described in detail by Gelinski et al. [8]. Therefore, an overview is given here:

The *kinematic viscosity* was measured with Ubbelohde Viscometers (Schott Instruments, Germany) at a temperature of 40 °C. In principle, the time was determined by a semi-automatic device (Viscoclock, Schott Instruments, Germany) in which the fluid needed to flow from an upper to a lower mark in a glass capillary.

For testing *corrosion protection* properties according to DIN 51360–2 [9], 2 g cast iron chips (Riegger Industriehandel, Germany) were placed on a paper filter in a petri dish, wettened with 2 mL test fluid and covered with a lid. After 2 h storage at 20 °C, the chips were removed and the filter was rinsed with water and acetone and dried thereafter. The corrosion degree was visually determined by observing brown or gray discolorations of the filter paper. In case of good corrosion protection, no discolorations occurred.

For a comparative study of *foaming characteristics*, 190 mL of a fluid sample was tempered at 25 °C and a bubbling nitrogen stream of 94 mL/min was passed through it. After 5 min, the gas flow was stopped and the foam volume on top of the liquid was determined. This was repeated after a period of 10 min without gas supply.

For testing the long-term *microbiological stability* of the fluid variants, the determination of the biological oxygen demand (BOD) over 20 days according to DIN EN ISO 5815–1 [10] was applied. The test mixtures were filled into BOD-flasks. Measuring heads (Oxitop-Messsystem, WTW GmbH, Germany) were screwed on the flasks, and the devices were placed in thermostatic containers at 20 °C. The double determined data were converted into BOD-values.

2.2 Tribological experiments

Throughout all the tribological and the machining tests, two industry-relevant aluminium alloys were applied, namely EN AW 6060, AlMgSi (soft alloy) and EN AW 7075, AlZnMgCu (hard alloy, often applied in car manufacturing). While the first alloy shows a high corrosion resistance and is easy to weld, the latter alloy can be machined easier due to its higher hardness. Furthermore, a mineral oil-based emulsion, recognized in the market for the machining of aluminium alloys, was used as the benchmark. The applied tests for the tribological experiments are introduced in Table 1.

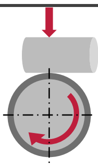
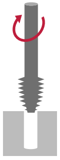
2.2.1 Brugger tests

A Brugger rubbing wear test device (Triboproof T100, NOLD Hydraulik & Pneumatik GmbH, Germany) was used to investigate the tribological impacts of fluid components with regard to dynamic friction. Within the Brugger test, a cylindrical specimen was pressed with a constant load onto a rotating steel-ring (100Cr6). The test cylinders, consisting of the Al alloys named above, were manufactured by cutting them from strands with 18 mm diameter (Bikar-Metalle GmbH, Germany). Different from DIN 51347 [11], the rotating ring was constantly wettened by the fluid that was supplied by a syringe pump with a flow rate of 5 mL/min. The aluminium specimen were pressed onto the ring with a defined load of 2500 g. During the experiments, the ring rotated with constant speed of 960 rpm. The test was stopped after a running time of 30 s and a running distance of 75 m. The procedure was repeated three times, respectively, for mean value determination. After each run, the rotating ring was polished and cleaned with water, cyclohexane, and acetone. For cleaning the test cylinders, the same solvents were used. From the wear ellipse, the load-bearing capacity after Brugger was calculated as follows:

$$B = \frac{4 \cdot 400}{a \cdot b \cdot \pi}$$

B load-bearing capacity after Brugger (N/mm^2)

Table 1 Applied tribological test systems

Test device		
Test	Brugger Test	Tapping-Torque-Test
Kinematics		
Result	wear surface	max/Ø/progression of torque, Δ temperature
Standard	in accordance with DIN 51347 part 1 and 2	ASTM D 5619
Lubricant volume (total)	10 mL	0.5 mL
Time effort (total)	3 min	7 min
Transferability of results to industrial applications	moderate	high

a longitudinal axis of the wear ellipse (mm)

b transverse axis of the wear ellipse (mm)

Good lubricating properties are indicated by small wear areas (high *B*-values), low surface roughness, and a smooth rim of the ellipses.

2.2.2 Tapping-torque tests

The tapping-torque test (microtap GmbH, Germany) enables the measurement of the torque during forming threads into previously prepared holes. The torque was monitored continuously during the forming process. As they are widely applied, M4 or M6 threads are used for this test. For experiments with M4 threads, test specimen with pre-drilled holes with a diameter of 5.55 mm and a depth of 23 mm were manufactured. The holes were filled with the MWF before the experiments started. The thread was formed at a speed of 600 rpm and a thread depth of 20 mm. A low torque and low fluctuations in the torque progression indicated a good performance of the MWF. Performance indicators were the mean torque in Ncm, the standard deviation as well as histograms that visualize the distribution of the torques during the forming process. The totally required energy for forming the thread was calculated by the integral of the torque progression. In addition, the temperature of the forming tool was measured with an integrated infrared thermometer directly before and after thread forming. Low-temperature differences were an indicator for low friction and high cooling performance during the experiments. Three repetitions were carried out for each fluid-specimen combination and evaluated using the mean values of the performance indicators.

2.3 Experiments on machine level

2.3.1 Machining process chain

A three-step machining process chain to manufacture tapped holes was applied to investigate the effect of the novel MWF variants. An overview of the three steps is given in Table 2.

Table 2 Tools and process parameters for the experiments on machine level

	Drilling	Chamfering	Thread forming
Tool material	Solid carbide	HSS-E	HSS-E
Tool coating	Diamond-like carbon	Titanium aluminium nitride	Titanium nitride
Tool standard	DIN 6537	Manufacturer-specific	DIN 2174
Depth	32 mm	0.3 mm	30 mm
Diameter	5.55 mm	45°	M6
Feedrate	0.25 mm/R		
Cutting speed	120 m/s		
Tolerance	h7		
MWF supply	Internal plus external nozzle	External	External

All three experimental steps were carried out with a DMU 100 monoBlock five axis machining centre. A 300-L MWF tank with a high and low pressure supply was used. The fluid was conditioned with metallic filters prior to use.

First, the holes were cut with a solid carbide drill with a diamond-like carbon coating. This drill allowed cutting aluminium at high speed and precision. The holes had a depth of 32 mm and a diameter of 5.55 mm as basis for a stand M6 thread. An additional reaming of the holes was not required to meet the h7 tolerance class. The MWF was supplied internally through the tool with a high pressure pump and externally for chip evacuation. After drilling, the holes were chamfered by 45° and 0.3 mm to enable the thread former to have a smooth start. The chamfering process was not considered for a more detailed investigation as the tool wear was negligible and no relevant quality criterion could be defined. The thread was formed with a cobalt-alloyed high-speed steel and titanium nitride coated thread former. Basically, the thread formers were the same as for the tapping-torque test. The thread followed the M6 standard and had a depth of 30 mm.

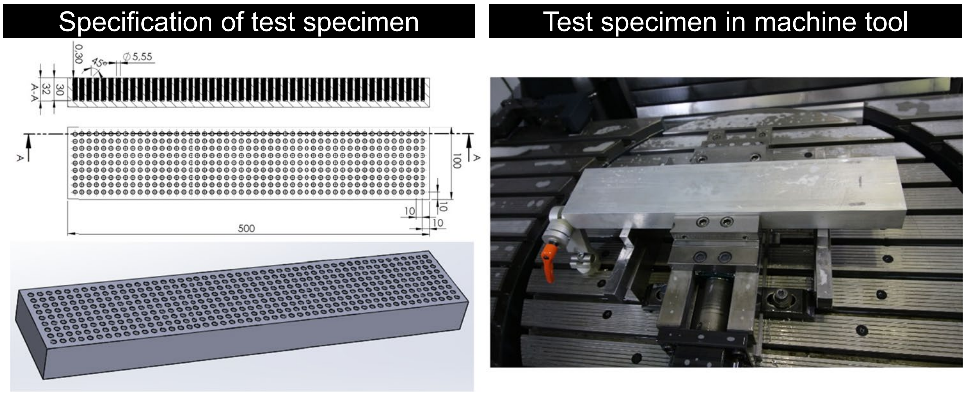
2.3.2 Machining tests

Test specimens (500 × 100 × 40 mm) with 441 holes/threads were used for the experiments (Fig. 1). The distances between the holes were chosen in a way that the holes/threads had no influence on the neighbouring holes/threads. The first and the last columns were not formed with threads in order to assess the drilling quality after the experiments. First, the specimens were fixed in the machine. Before the drilling experiments, the specimens were face turned to obtain a plain surface and the same surface conditions for all holes.

The dimensional accuracy of the holes and the threads was ensured with specifically manufactured gauges. The holes were required to be within an h7 class tolerance (max. + 12 µm). The surface roughness was measured at four different positions in the holes with a Jenoptic Hommel-Etamic W10 surface measuring device with results being evaluated by mean values. Images of the hole surfaces and the threads were taken using the digital optical microscope Keyence VW9000.

2.4 Control of operations-related emissions

Air sampling was performed during the experiments on machine level in order to investigate the probable formation and release of decomposition products and pollutants from the MWF variants while machining. Samples were taken in front of the machine, at the work area of the operating personnel as well as above the exhaust of the machine's air


Specification of test specimen

Test specimen in machine tool

Fig. 1 Test specimen for machining experiments extraction system. Air blank values were determined in a distance of 20 m from the test machine at a time when no other machines were operated in the hall. The samplings and the analytical procedures were conceptualized in a way that a broad range of nonpolar to polar volatile substances could be captured. Additionally, a particular analytical focus was set on aldehyde- and ketone-like compounds.

2.4.1 Screening of nonpolar to polar volatile compounds

Activated carbon adsorbers (ORBO™-32 Standard Charcoal Tubes, Supelco, Bellefonte, PA, USA) were used to collect nonpolar substances. For capturing the spectrum of weakly polar to polar volatile compounds, sampling tubes filled with XAD-7 (ORBO™-615 Adsorbent Tubes, 60/30 mg, Supelco, Bellefonte, PA, USA) were applied. Each time, two tubes, used as collection and control phases, were connected in line with a gas sampling device (Desaga GS 312, Sarstedt AG & Co, Germany). Air (60 L) were drawn in with a rate of 0.5 L/min, respectively. After the sampling, the tubes were sealed airtight, stored at 5 °C, and analysed within 5 days. For the latter, the adsorption materials were removed from the tubes and filled in glasses with screw caps and 2.0 mL carbon disulphide (activated carbon) or 2.5 mL ethyl acetate (XAD-7) were added. Subsequently, the samples were treated in an ultrasonic bath for 1 h. After a membrane filtration, the extracts were directly analysed with GC/MS (Table 3). For control purposes, unapplied sampling tubes were extracted and analysed as well.

2.4.2 Determination of volatile carbonyl compounds

For the enrichment of volatile carbonyl compounds, two sampling tubes (Sep-Pak® dinitrophenylhydrazon(DNPH)-silica cartridges, Waters, Ireland), used as collection and control phases, were connected in line with a gas sampling device (Desaga GS 312, Sarstedt AG & Co, Germany). With a sampling rate of 1 L/min, 120 L of air were sucked through the cartridges. After the sampling, the tubes were sealed airtight, stored at 5 °C, and analysed within 5 days. For the HPLC-analyses (Table 4), the cartridge's fillings were eluted with 5 mL acetonitrile and the eluates were directly transferred to measurement. For control purposes, unapplied cartridges were eluted and analysed as well.

A 5-point calibration line was determined in order to quantify the carbonyl compounds. Therefore, a so-called aldehyde-DNPH mixed standard (Air Monitoring Aldehyde, DNPH Mix 1, TechLab, France) was appropriately diluted with acetonitrile. For formaldehyde, the calibration range was 0.4–2.0 mg/L; for all other aldehydes and ketones, it was

Table 3 GC/MS-settings for screening analyses

Gaschromatograph	GC 7890B, Agilent Technologies (Santa Clara, CA, USA)
Mass selective detector	5977A MSD, Agilent Technologies (Santa Clara, CA, USA)
Chromatographic column	DB-1301, 60 m, inner diameter: 0.32 mm, film thickness: 1 µm, Agilent Technologies (Santa Clara, CA, USA)
Carrier gas	He, 1 mL/min
Injection mode	Splitless
Injection volume	1 µL
Temperature program	50 °C, 2 min, 10 °C/min to 280 °C, 15 min
Measuring mode	EI: 70 eV, full-scan-mode, m/z: 45–600

Table 4 HPLC-settings for the analysis of carbonyl compounds

Instrument	HPLC Series 1260 Infinity, autosampler, diode-array-detector, Agilent Technologies (Santa Clara, CA, USA)
Chromatographic column	Pursuit XRs 5 C18, 250×4.6 mm, 5 µm, Agilent Technologies (Santa Clara, CA, USA)
Column temperature	40 °C
Eluent	Eluent A: water/acetonitrile (40/60; v/v) Eluent B: acetonitrile
Gradient	Time (min) B (%) 0, 0 5, 0 20, 100
Flow rate	1.5 mL/min
Injection volume	10 µL
Detection wavelength	360 nm

0.2–1.0 mg/L. These namely were acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, 2-butanone, butyraldehyde, benzaldehyde, valeraldehyde, p-tolualdehyde, and hexaldehyde (DIN ISO 16000–3 [12]).

3 Results and discussion

3.1 Chemical development of the novel metal working fluids for aluminium machining

Based on former experiences, the starting point was a glycerol-water-mixture with 40 vol.-% of glycerol [6, 7]. This mixture already showed a good lubrication performance, and because of its antimicrobial effects, the addition of a common biocide could be omitted. Throughout first experiments performed as tribological tests as well as on machine level for processing aluminium alloys, it was recognized that glycerol could be replaced by propanediol in the base fluid. Concerning this application, propanediol had similar positive tribological characteristics and it allowed to waive the addition of conventional biocides as well. For increase in performance and for property settings, these base fluids were experimentally additive enhanced by adding components that are specified as alcohols, amines, and other nitrogen carriers, carbonic acids, fatty acid esters, glycol ethers, ionic liquids, nanoparticles, polydimethylsiloxanes, and other polymers like polyethylenglycols as well as phosphoric acid esters and sulphur carriers. The fluids were iteratively optimized in stages of physico-chemical laboratory tests (Section 2.1), tribological experiments (Section 2.2), and experiments on machine level (Section 2.3). In the following, information is provided about the final formulations of the glycerol/water-based and the propanediol/water-based MWFs (Table 5 “glycerol MWF” and Table 6 “propanediol MWF”) as well as about some important properties that were determined in laboratory tests. Subsequently, their performances are described and compared to that of the reference fluid.

In the *corrosion protection tests*, no brown or gray discolorations were visible on the filter papers for all three fluids. They all revealed very good corrosion protection.

The *defoamer* amounts specified in Tables 5 and 6 resulted from laboratory tests as described in Section 2.1 and from experience gained by the machine trials.

The *microbiological stability* of the glycerol MWF and the propanediol MWF was tested by determining the biological oxygen demand over 20 days. The results are depicted in Fig. 2. For both fluids, a very low oxygen consumption

Table 5 Formulation of the glycerol/water-based MWF (“glycerol MWF”)

Component	Concentration (mass-%)	Function
Water	44.43	Base fluid, cooling effect
Glycerol	45.60	Lubricity enhancement, thickening agent, preventing microbial attack
Alkanoic acids	3.00	Lubricity enhancement
Amine compounds	4.00	Neutralization, pH value adjustment, corrosion protection, complexing agent
Polyglycol ethers	2.80	Lubricity enhancement, defoamer
Ether	0.15	Defoamer
Triazole derivative	0.02	Non-ferrous metal inhibitor

Table 6 Formulation of the propanediol/water-based MWF (“propanediol MWF”)

Compound	Concentration (mass-%)	Function
Water	45.64	base fluid, cooling effect
1,3-Propanediol	22.50	lubricity enhancement, thickening agent, preventing microbial attack
Polyglycol ethers	12.50	lubricity enhancement, defoamer
Alkanoic acids	12.50	lubricity enhancement
Amine compounds	6.80	neutralization, pH value adjustment, corrosion protection, complexing agent
Ether	0.04	defoamer
Triazole derivative	0.02	non-ferrous metal inhibitor

The *kinematic viscosity* at 40 °C was determined for the fluids as:

Glycerol MWF: 9.7 mm^2/s

Propanediol MWF: 10.6 mm^2/s

Reference fluid: 1.5 mm^2/s

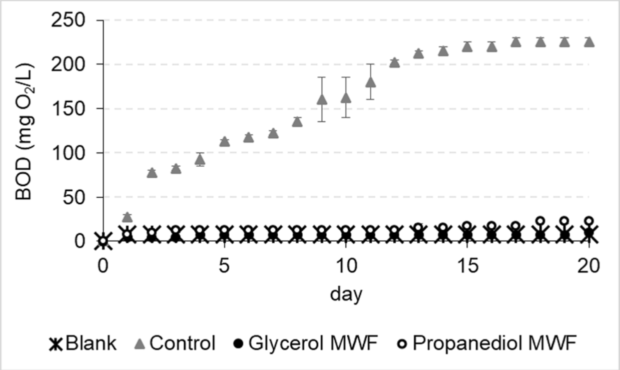


Fig. 2 Determination of the biological oxygen demand with the glycerol- and the propanediol-based MWFs. BOD approaches: Blank: without any C-source, control: with C-sources (glucose and glutaminic acid), glycerol MWF: s. Table 5, with C-sources, propanediol MWF: s. Table 6, with C-sources, **I** mean value deviation, (*n*: 2)

and thus a tolerable low metabolic activity of microbes was indicated in the period considered. Obviously, the polyvalent alcohols glycerol and propanediol as part of the base fluids are suitable for the protection of the MWFs against microbiological attack.

3.2 Tribological experiments

In Fig. 3 and in Table 7 results of tribological tests are introduced.

In the tapping-torque tests with thread forming (see Section 2.2.2 for setup), where temperature differences of the tool and torque values were considered, almost always better results were obtained with the novel MWFs compared to the reference fluid (Table 7). Only during application of the glycerol MWF on the hard Al-alloy, the torque value was slightly higher than the reference one, although the measured temperature difference was lower.

Table 7 Results of tapping-torque and Brugger tests with Al-alloys EN AW-6060 (soft) and EN AW-7075 (hard)

Metalworking fluid	Tapping-torque test		Brugger test
	ΔT (°C)	$Mz_{\max}$ (Ncm)	B (N/mm^2)
Alloy EN AW-6060			
Reference fluid	2.7	70.0	33.9
Glycerol MWF	1.5	65.0	19.3
Propanediol MWF	1.3	50.0	23.8
Alloy EN AW-7075			
Reference fluid	5.9	135.0	28.7
Glycerol MWF	4.4	141.7	24.3
Propanediol MWF	5.1	111.7	27.8

ΔT temperature difference during test, Mz_{max} maximum torque, B load-bearing capacity

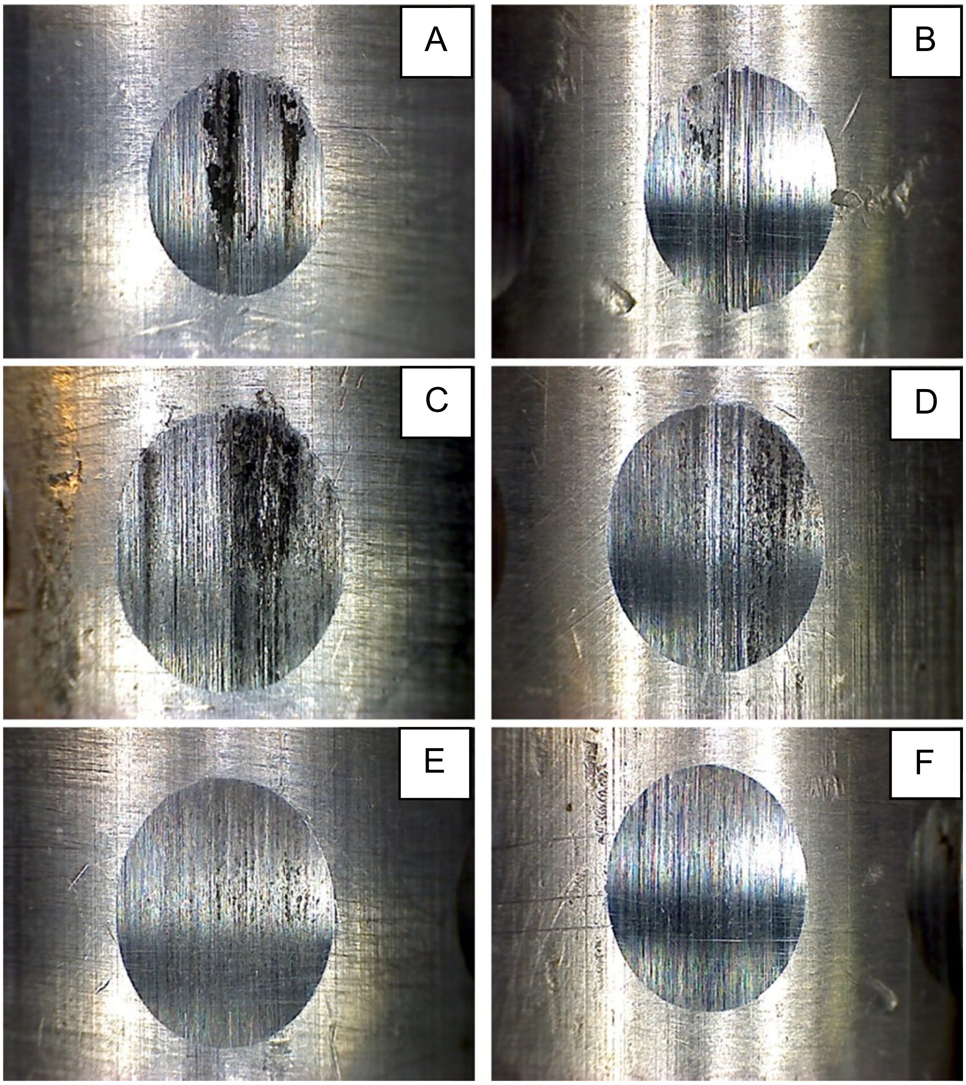


Fig. 3 Brugger test, wear ellipses in cylinders made from alloy EN AW-6060/soft (**A**, **C**, **E**) and alloy EN AW-7075/hard (**B**, **D**, **F**), lubricated with reference fluid (**A**, **B**), glycerol MWF (**C**, **D**), and propanediol MWF (**E**, **F**)

Considering the Brugger test results (Fig. 3), it was striking that the grinding ellipses were always smaller using the reference fluid (Fig. 3A, B), which means that this fluid had the biggest load bearing capacity. In this context, the differences compared to the novel fluids were bigger for the soft Al-alloy (Fig. 3, left) than for the hard Al-alloy (Fig. 3, right). Black deposits were visible both after application of the reference fluid (Fig. 3A, B) and the glycerol MWF (Fig. 3C, D). In case of the propanediol MWF, these deposits were only slightly visible on the soft alloy (Fig. 3E). The roughnesses of the surfaces and the edges of the ellipses were comparable when testing the reference and the glycerol MWF (Fig. 3A–D), and they were smaller/better after Brugger test with the propanediol MWF (Fig. 3E, F). After consideration of all these evaluation criteria, it can be stated that the Brugger test performance compared to the reference was slightly worse for the glycerol MWF and slightly better for the propanediol MWF. At least, all three MWFs revealed a good or very good load bearing capacity.

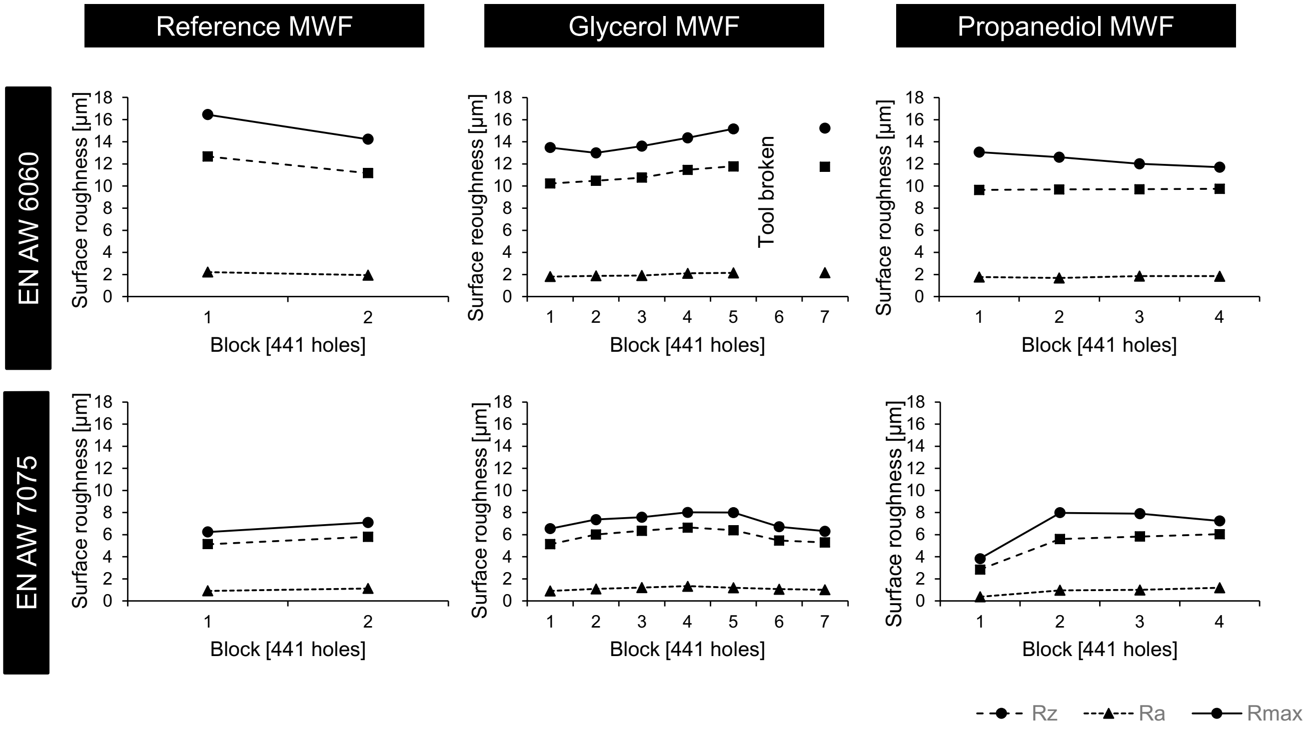
3.3 Experiments on machine level

The presentation of the results of the experiments on machine level is separated into the two topics cutting/drilling process, followed by the thread forming process. The chamfering process was not separately evaluated due to its low relevance and no detected challenges during chamfering. Generally, all the three MWFs showed a good performance in these machining experiments which were conducted according to industrial processes.

3.3.1 Drilling

a) Surface roughness

In Fig. 4, the results of the surface roughness measurements after the drilling operations are summarized. For these measurements, the blocks were cut at three positions to enable the surface roughness measurements of mean roughness



Standard deviations for the surface roughness [µm]						
	EN AW 6060			EN AW 7075		
	Rz	Ra	Rmax	Rz	Ra	Rmax
Reference MWF	2.1	0.4	4.0	1.0	0.3	1.5
Glycerol MWF	2.5	0.6	3.9	1.1	0.3	1.5
Propanediol MWF	1.7	0.4	2.6	1.9	0.5	2.8

Rz: mean roughness, Ra: average roughness, Rmax: maximum roughness

Fig. 4 Surface roughness for the two aluminium alloys and the three MWFs

Rz, average roughness Ra, and maximum roughness Rmax with a tactile surface roughness measurement device as already described by Winter et al. [13]. For each hole, the measurements were repeated four times at different positions in order to calculate an average value. For each block, 18 holes were investigated, so the given values in Fig. 4 represent the mean values of 72 measurements.

The reference fluid is widely used in the industry for this machining process chain, and thus, only two blocks were processed. The roughness values Rz, Ra, and Rmax slightly decreased from the first to the second block in case of the soft Al-alloy EN AW 6060 (Fig. 4, left, top). An opposite course was found for the harder alloy (Fig. 4, left, bottom).

The glycerol MWF showed similar roughness values compared to the reference fluid for both materials (Fig. 4, middle). However, while cutting the soft alloy AN AW 6060, the drilling tool broke during machining block 6 which could have reasons like a manufacturing defect of the tool, a material fatigue after its long-term use, or a deficient quality of the MWF-formulation. This could be clarified by extended time tests which are scheduled later. It was striking that the surface roughness values decreased from block six for the harder aluminium alloy EN AW 7075 (Fig. 4, middle, bottom).

The surface roughness achieved after processing with the propanediol MWF slightly decreased from machining block one to four (Fig. 4, right, top). With an exception of the second block, machining the harder alloy EN AW 7075 initially led to significantly lower surface roughness than machining with the reference and glycerol fluid (Fig. 4, right, bottom).

The surfaces of the drilled holes are shown in Fig. 5. The images confirm the results from the surface roughness measurements. The smoothest drilling holes with quite regular drilling holes were clearly seen after applying the propanediol MWF (Fig. 5, bottom). Using the reference-fluid (Fig. 5, top) or the glycerol MWF (Fig. 5, middle), the drilling

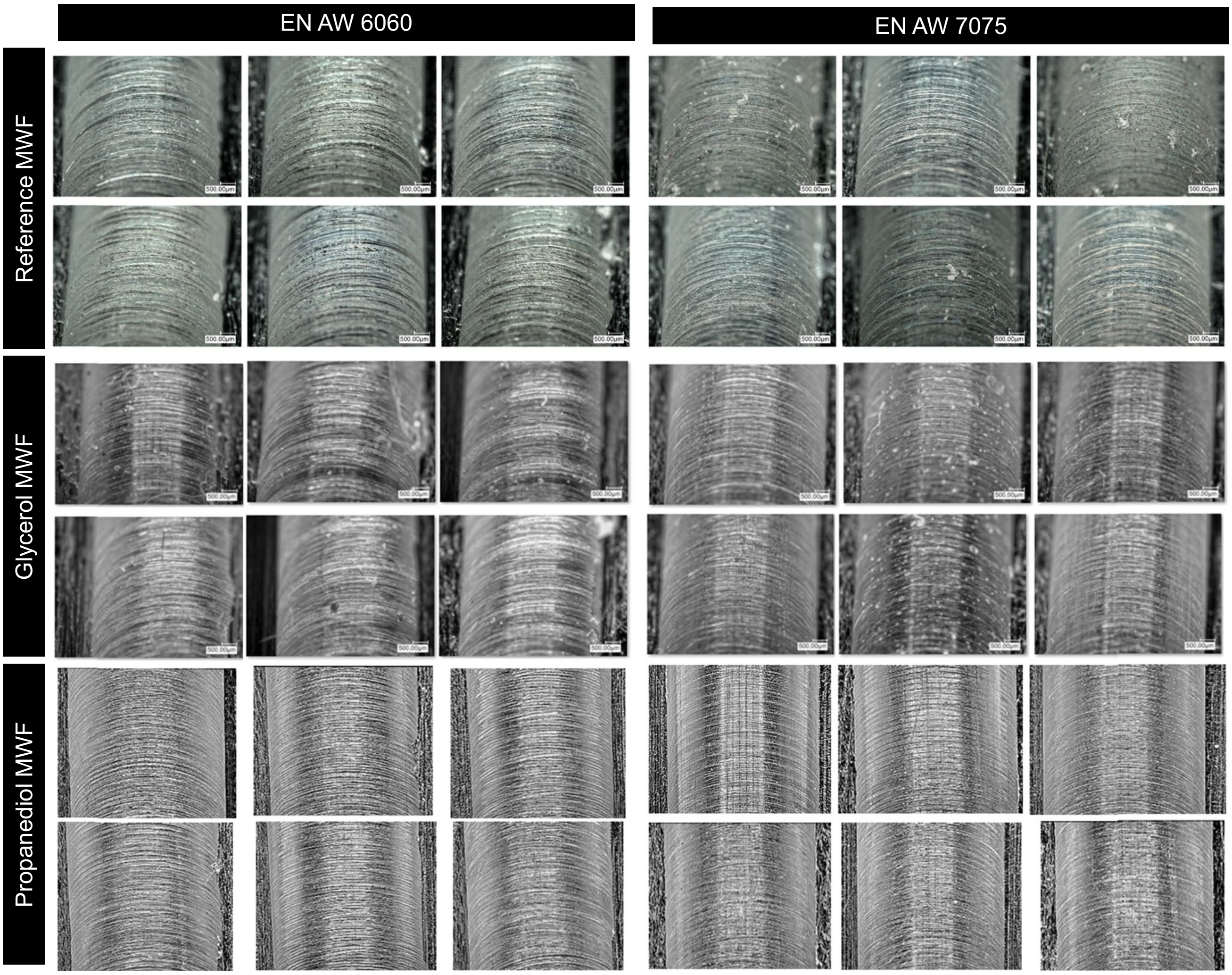


Fig. 5 Surfaces of six holes from block 1 prior to tapping for all materials and fluids

scratches were irregular in shape and depth, although these results could be considered as good. Based on these results, the propanediol MWF was rated as the best fluid for drilling amongst the three fluids under the given conditions.

b) Chip formation

The chips from the drilling processes of both Al-alloys with the three different MWFs are shown in Fig. 6.

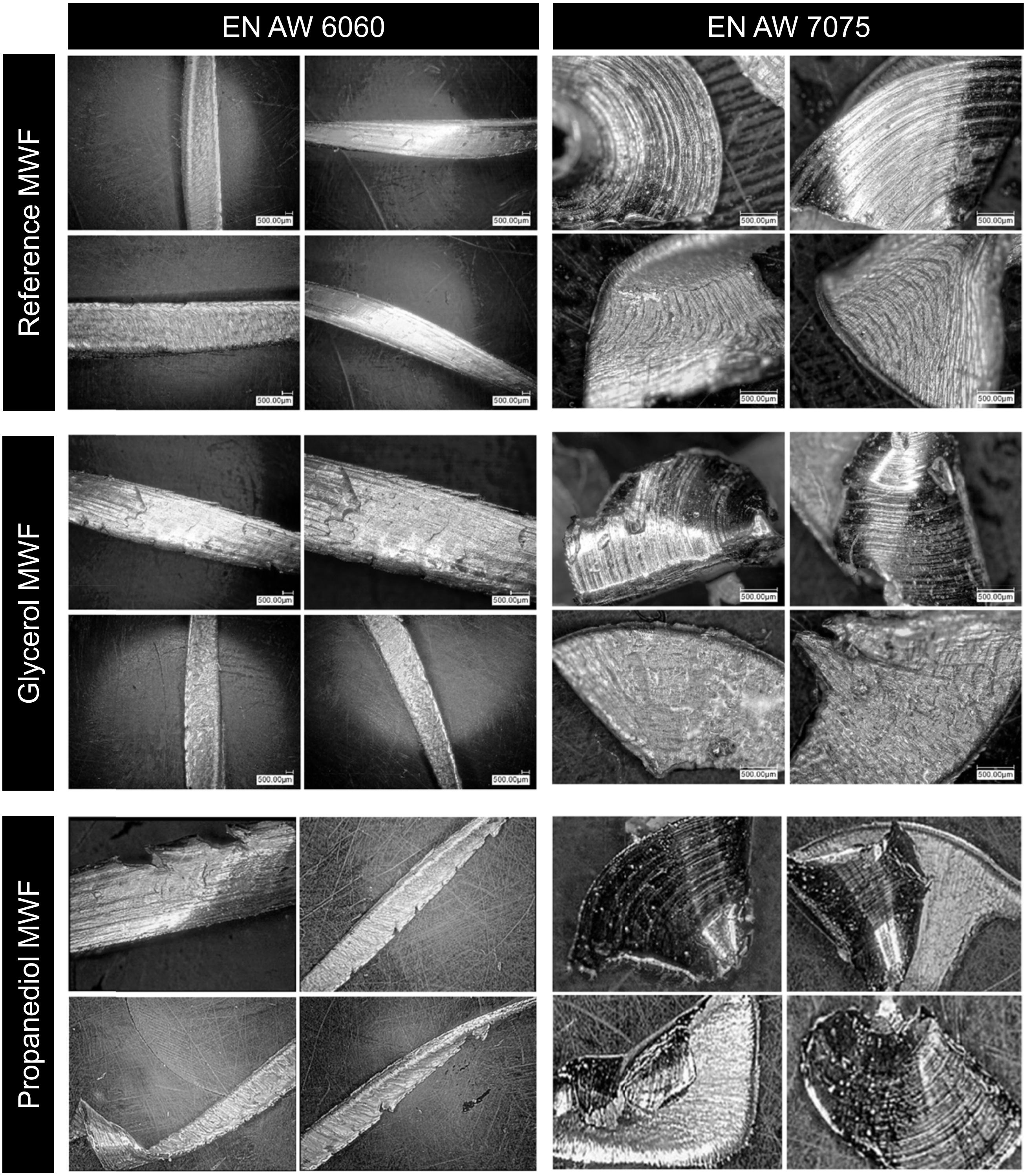


Fig. 6 Chips resulting from drilling processes with the different Al-alloys and the three different MWFs

Generally, the chips from drilling holes into the soft alloy EN AW 6060 (Fig. 6, left) were significantly longer and thicker than the chips obtained by drilling the harder alloy EN AW 7075 (Fig. 6, right). The long chips from EN AW 6060 were so-called ribbon chips with length of up to 100 mm. The chips left the hole at high speed so that a housing of the machine tool was required. In contrast, the short chips after machining the EN AW 7075 were so-called elemental chips and were not longer than 5 mm, with smoothest surface observed when the propanediol MWF was used (Fig. 6, right, bottom). In this case, the chips left the hole with low speed. Thus, a flood lubrication was required to remove the chips from the surface of the specimen. The influence of the selected MWF on the chip formation was significantly lower than that of the material to be drilled. Although especially the surfaces of the long ribbon chips from the drilling process with the reference fluid appeared slightly smoother (Fig. 6, top, left), the resulting inner surfaces of the holes did not have lower surface roughness than the others (Fig. 5, top, left). As the chip formation during application of the novel MWFs was quite similar to that of the established reference fluid, it could be concluded that no adjustments regarding chip capture and removal were necessary.

3.3.2 Thread forming

All threads were tested with a plug gauge and followed the DIN ISO 13–1 [14] and DIN 2279 [15] standards for M6 threads. In Fig. 7, images of the threads are given. For all investigated fluids and materials, no critical damages were found for the thread crests as well as for the thread roots. It could therefore be concluded that all fluids were well suited to be used in thread forming of both soft and hard aluminium alloys. However, comparing the fluids, the threads that were machined using the propanediol MWF (Fig. 7, bottom) appeared to have a more regular shape compared to those of

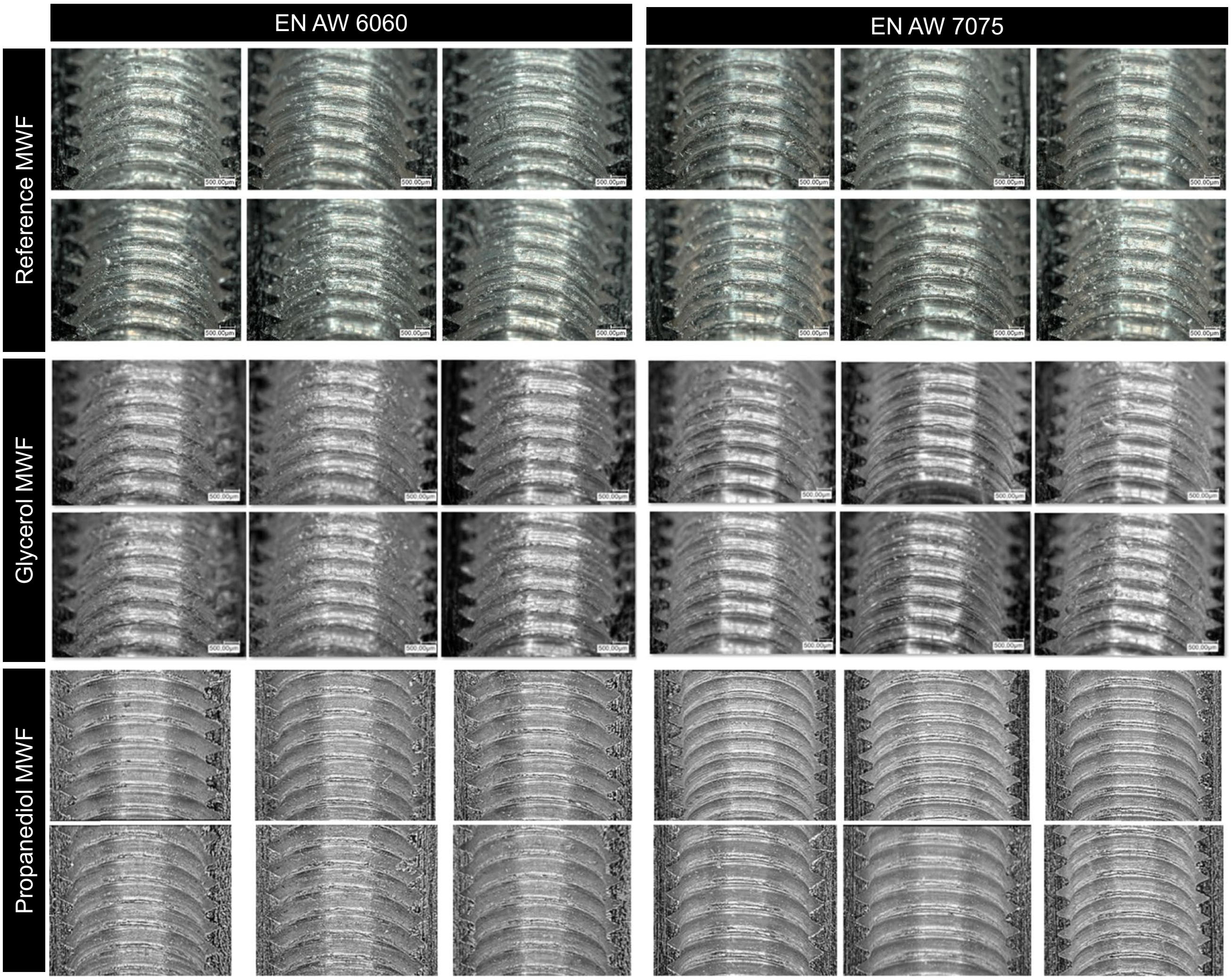


Fig. 7 Surfaces of six threads from the first machined block, respectively, for all materials and fluids

Table 8 Maximum air pollution with carbonylic compounds at the machine during Al-working with the novel MWFs

Compound	Max. air pollution at the machine (mg/m^3)	Occupational limit value according to TRGS 900 (mg/m^3)	Under-cutting factor
Acetaldehyde	0.084	91	1083
Acetone	1.5	1200	800
Butyraldehyde	0.071	64	901

the glycerol MWF (Fig. 7, middle) and the reference MWF (Fig. 7, top). The propanediol MWF was therefore considered as the best fluid for thread forming under the given conditions.

3.4 Analytical monitoring of airborne pollutants emitted from the MWF formulations in use

Novel MWFs with chemical compositions were developed that had not been known before for technical fluids in these application areas. In this context, an emission control during practical use with regard to human compatibility is important. During investigations on machine level, the fluids are temporarily exposed to elevated pressures and temperatures as well as to newly generated, reactive surfaces in this case of Al-alloys. The fluids are in contact with atmospheric oxygen which could cause oxidative decomposition processes. Furthermore, in practice, components of the fluids are partly added in technical quality, which allows chemical impurities to enter the lubricant formulations. All this could result in the formation and release of decomposition products or the emission of volatile impurities that the technical staff would be exposed to. In order to exclude those hazards, air samplings and measurements were performed as described in Section 2.4 that were qualified to record a wide range of substances. Thereby, special attention was paid to carbonylic compounds because it is known that especially from glycerol even in aqueous solution compounds like acrolein, acetaldehyde, and formaldehyde can be formed under thermal stress or with catalytically active surfaces present [16, 17]. These compounds have different adverse toxicological effects on humans.

The air sampling with nonpolar activated carbon and XAD-7, a polar resin based on an acrylic ester, as adsorbents (see Section 2.4.1) in principle allowed to measure analytes with a detection limit for GC/MS in the range of 0.4 mg/m^3. As a result, in all chromatograms of samples taken in the machine hall, a couple of small signals were visible. According to the mass spectra, they were identified as aliphatic hydrocarbons which were not present in the glycerol MWF and the propanediol MWF. It was assumed that these aliphatics had been emitted from mineral oil-based products used in the technology centre in other applications.

For the investigation of carbonylic compounds, aldehydes and ketones, a different analytical procedure according to the standard DIN ISO 16000–3 [12] was used (Section 2.4.2). In this case, the detection limit for each analyte was 0.02 mg/m^3. In the air samples that had been taken during the experiments on machine level of the glycerol MWF and the propanediol MWF, the substances acetaldehyde, acetone, and butyraldehyde were partly detected. In Table 8, the maximum air pollution measured at the machine is compared with the currently valid occupational limit values according to TRGS 900 [18].

As can be seen from Table 8, the maximum air pollution with the three identified carbonylic compounds, measured during the application of the novel MWFs, was distinctly below the occupational limit values. Therefore, a risk for the technical staff could be excluded. Nevertheless, laboratory investigations, not described in detail here, were done in order to clarify the origin of the carbonylic compounds. It was found that they were present in the additives named “polyglycol ethers” and “ether” (compare Tables 5 and 6) as contaminations, and thus, they got into the glycerol MWF and the propanediol MWF. Furthermore, acetone, as a common solvent, was used in the technology centre as well as in laboratory. Therefore, a contamination during air sampling or during the following analytical work cannot be completely excluded.

4 Conclusions

For the cutting and forming processing of aluminium alloys, novel MWFs were developed that are free of mineral oil as well as conventional biocides. The novel MWFs are mainly based on renewable materials and water. For this, a systematic research and development was done. Positive results have already been obtained with the base mixture glycerol/water during earlier steel manufacturing experiments, whereas the propanediol/water mixture was newly identified as particularly well usable for Al-processing. These base mixtures were continuously optimized by additivation on the basis of chemical-physical, tribological, and finally industrial-scale tests with an industrial machine. Additionally, the performances of the novel fluids were compared to that of a conventional reference fluid in all test phases.

It was demonstrated that the performance of the glycerol MWF during Al-working was almost as good as that of the reference. The propanediol MWF was even superior to the reference fluid in several aspects, especially concerning the surface qualities of the workpieces. It has to be considered that the task of the R&D-project was to design novel MWFs and to demonstrate their applicability in the field of aluminium processing. A finetuning, which means an exact conditioning of the novel fluids to a defined machining process for a defined Al-alloy, will be the task of industrial practitioners when taking up these innovations. In this context, an odour pollution and a light irritation effect were determined during the application of the propanediol MWF in experimental investigations on machine level. This could be traced back to the additive "alkanoic acid" (Table 6). Consequently, the acid was replaced by another, its share in the fluid was reduced, and a further additive was included. Subsequently, laboratory tests and tribological experiments indicated that the problem could be solved. Nevertheless, the proof by a test on machine level is still pending. In general, there is a demand for the development of novel, polar soluble high performance additives. This would extend the chemical basis of the novel MWFs and it would improve the options for their finetuning. This will be one of the challenges ahead.

Author contribution Alexander Leiden: conceptualization, data curation, methodology, visualization, writing — original draft. Robar Arafat: writing — review and editing. Marcel Callegari: data curation, methodology. Marit Kolb: writing — review and editing. Christoph Herrmann: supervision, conceptualization, writing — review and editing. Hubertus Wichmann: supervision, conceptualization, funding acquisition, methodology, writing — writing original draft.

Funding Open Access funding enabled and organized by Projekt DEAL. This project "Glycerin II – Entwicklung und Herstellung eines gesamtprozessorientierten, glycerinbasierten, biozidfreien Bearbeitungsmediums in industriellen Zerspanungs- und Umformungsprozessen für verschiedene metallische Werkstoffe" (grant ID: 22021814) was funded by the Agency of Renewable Resources (FNR) on behalf of the German Ministry of Food and Agriculture.

Declarations

Conflict of interest The authors declare no competing interests.

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