IMPACT OF NATURAL NANOADDITIVES SiO_2 AND TiO_2 ON THE QUALITY OF MACHINING PROCESS FLUIDS AND BACTERICIDAL PROPERTIES

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Abstract

An understanding of machining process fluids (types, compositions, operational conditions, lubricating and cleaning effect) is important for maximizing machining process efficiency by reducing heat generation, improving surface roughness, stabilizing the machining process, and increasing the operating life. Contamination by bacteria or even fungi is the weak point of these liquids. The uninhibited growth of bacteria may lead to poor lubricating properties and higher material oxidization; moreover, the presence of endotoxins in a shop floor atmosphere is the consequence of bacterial activity. Thus, biocide chemicals are added to process fluids in order to prevent the bacterial growth. The biocides maintain the efficiency of the process fluids; however, they are injurious to the operators (potential carcinogenic compounds). Natural nanoadditives are a modern way of increasing the biocidal effects. Nanoadditives added to the process fluids have a positive effect on the machining process by reducing the friction coefficient resulting in a reduction of wear of the cutting tool. Nanoadditives can also enhance the bactericidal effect by reducing bacterial respiratory rates and viability.

Keywords: natural nanoadditives; machining process fluids; tool wear reduction; bactericidal properties.

1. INTRODUCTION

Process fluids are important for effective machine cutting as they improve heat transfer away from the cutting surface, stabilize the machining process, extend the life of the cutting tool and improve product surface quality. Another problem that must be solved is the resistance to bacterial attack (bacteria or fungi), which may produce spores or endotoxins [1]. Biocidal components are frequently classified as hazardous, can produce highly unpleasant odours and cause allergic reactions and/or induce respiratory and skin problems [2], and have a huge ecotoxicological impact on the environment [3].

The use of nanoadditives in the form of nanoparticles (NPs) is highly efficient due to their high chemical and biological activity [4, 5]. Nanomaterial toxicity can be caused by a range of factors. It has been shown that their physicochemical properties (small size, shape, charge, and chemical composition) could lead to unique toxic effects in living systems that are difficult to predict [4, 6]. The biocide attributes of metal NPs, especially NPs based on SiO_2 or TiO_2, with dimensions smaller than 100 nm can interact easily and in a high rate (due to their large surface area) with biological material [7–10].

The aim of our work was to enhance machining process efficiency, especially by stabilizing the machining process, and increase the operating life and biological resistance (especially against bacterial attack) of process fluids during metalworking. Our goal was to introduce nanoadditives (SiO_2 or TiO_2) to reduce the friction coefficient and enhance the bactericidal effect by reducing bacterial activity.

2. MATERIALS AND METHODS

2.1. Chemical composition of the process fluids

The chemical composition of the process fluids was measured in the Mass Spectrometry laboratory of the Institute of Chemical Technology in Prague, Central Laboratories. Qualitative analysis of the fluids was performed using static headspace gas chromatography-mass spectrometry at elevated temperatures.

2.2. Characterization, size, morphology and application of the nanoparticles

Both of the tested NPs, titanium oxide (TiO_2, anatase, 99.5%, product #: 7910DL) and silicon oxide (SiO_2, 99.5%, product #: 6807NM) were supplied by 'SkySpring Nanomaterials', Inc., Houston, USA. The size of the particles was determined using a Zeiss Ultra Plus ultra-high-resolution field emission scanning electron microscope equipped with an Oxford Instruments EDS + WDS + EBSD microanalytic system, resolution: 1 nm @ 15 kV, 1.7 nm @ 1 kV, magnification 12x to 1000000x, with the possibility of 3D-imaging using a four-quadrant AsB detector. Samples were deposited with a thin layer of gold.

Energy dispersive X-ray spectrum analysis is an analytic technique used for elementary analysis or chemical characterization of the sample. The primary electron interact with surface of the sample create several emitted signals including x-ray spectrum. The spectrum observed by EDS – detector is characterized for each element. Distribution of elements was measured by SEM – EDS analysis whit line mode (parameters of scanning were voltage15kV, distance 7 – 7.5 mm).

The NPs were added in powder form at a concentration of 100 mg/L to a 5% solution of the cutting fluid. It was necessary to mix the suspension (5% solution of the cutting fluid + NPs) while preparing and it was agitated by shaking. A total of 25 L of the suspension was prepared.

2.3. Semi-industrials testing of milling

Semi-industrial testing of milling (pilot tests) was carried out in the Laboratory of Particle Technologies and Processes at the Technical University of Liberec. Conventional face milling has been selected as the machining process type. The experiments were carried out on an FNG 32 milling machine using a single workpiece. A Narex 2460.12 cutter tool was used, with a diameter of 63 mm, carbide indexable inserts ISO SNUN 120412; 8230 milling indexable cutting insert. The substrate material (8230) is cemented carbide produced from fine-grained tungsten carbide with 10% cobalt content. Physical vapour deposition coating forms multilayer (the coating consists of multilayers based on TiN [lower internal stresses] with a layer based on TiAlN [characterized by higher abrasion resistance]). A material of steel 16MnCr5 was used during machining process, EN 10084-94 chemical composition (hm. %) steel 16MnCr5 (C 0.14 – 0.19; Mn 1.10 – 1.40; Si 0.17 – 0.37; Cr 0.80 – 1.10; P max 0.035; S max 0.035).

2.4. Microorganism respiratory rate

No foreign bacteria were added to the samples of process fluids, only the natural presence of bacteria due to the milling was tested. Substrate utilization by microorganisms was estimated from their respiratory rate using a Micro-Oxymax respirometer (Columbus Instruments, USA). Consumption of O_2 was measured in hermetically sealed 250 mL flasks containing 100 mL of media cultivated at 40 ± 2 °C, to simulate elevated temperatures when processing, under aerobic conditions and shaken continuously for two days.

3. RESULTS

3.1. Chemical composition of the process fluids

Basic measurements were taken to determinate the chemical composition of the process fluids. Process fluid (PF 1) composed of one oxygen molecule and various amines (19 substances; pH 9.04) which can be toxic to the human body with proven carcinogenic effects, and can reduce the capacity of the blood to carry oxygen leading to respiratory distress, headache and dizziness. Process fluid (PF 2) is mainly composed of oxygenated organic compounds comprising glycols and higher alcohols (4 substances; pH 9.58); PF 2 does not contain substances that have carcinogenic or mutagenic properties and has no major negative impacts on the human body.

3.2. Size and morphology of the nanoparticles

TiO_2 NPs (**Fig. 1a**), size 10 – 25 nm, white nanopowder, specific surface area 50 – 150 m^2 / g, morphology: flat texture of the surface with smooth edges. SiO_2 NPs (**Fig. 1b**), size 15 – 20 nm, porous white nanopowder, specific surface area 640 m^2 / g, morphology: porous and nearly spherical (SkySpring Nanomaterials, Inc., Houston, USA).

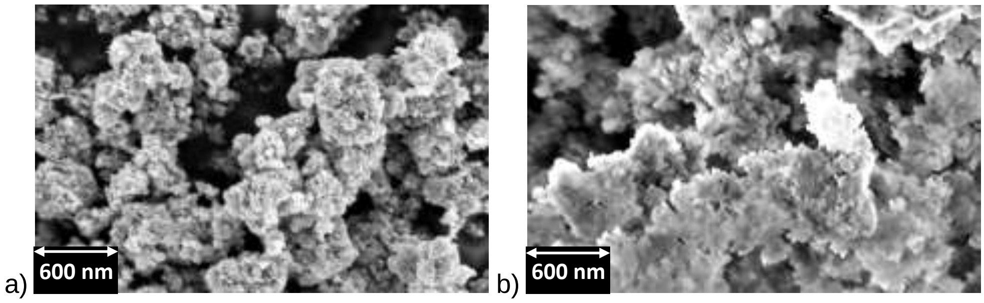

Fig. 1 SEM images of (a) titanium dioxide (TiO_2) NPs; (b) silicon dioxide (SiO_2) NPs.

3.3. Semi-industrial testing of milling

The experiment was conducted for duration of 3 hours, with the milling indexable cutting insert being replaced every hour. The milling was carried out on a machine where the continuous mixing of NPs was not ensured; moreover, the 3rd hour of milling was conducted the next day (i.e. after 24 hours; this was to simulate a situation where the machine stops and starts after a specific time).

Fig. 2 – 4 show the effects of the semi-industrial testing of milling on replaceable milling indexable cutting insert using a 5 % solution of pure PF1 (with no NPs), with NPs of SiO_2 or TiO_2. **Fig. 5 – 7** shows the same effect using a 5 % solution of PF2 (pure, with SiO_2 or TiO_2).

The graphs below show the measurements of the distribution of elements on the surface of the milling indexable cutting insert using a process fluid with and without NPs. The initial distribution of elements is shown in **Fig. 2 – 7** (left on the graph), where the functional coating mainly consists of elements of titanium (yellow line) and aluminium (green line) and the substrate is formed by elements of wolfram (blue line), carbon (red line) and silicon (purple line).

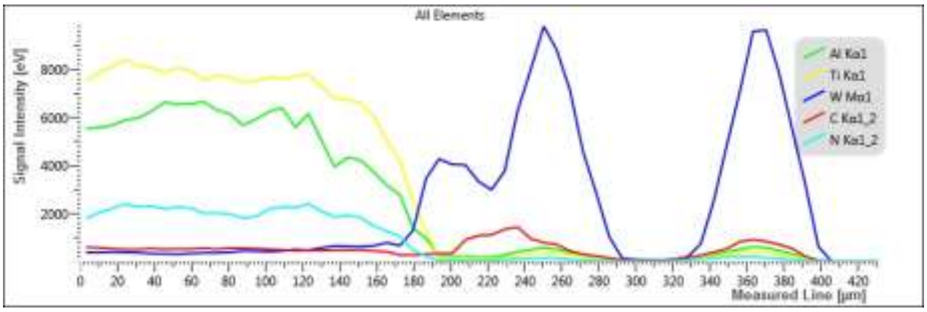

Fig. 2 The distribution of elements, PF1 with no NPs, the impact on milling indexable cutting insert.

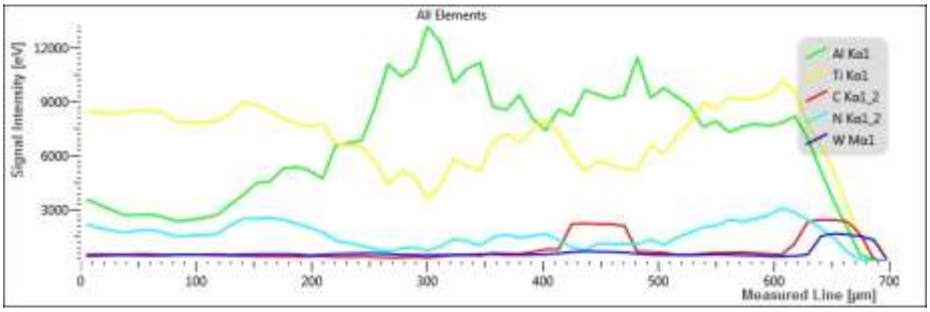

Fig. 3 The distribution of elements, PF1 with NPs of SiO_2, the impact on milling indexable cutting insert.

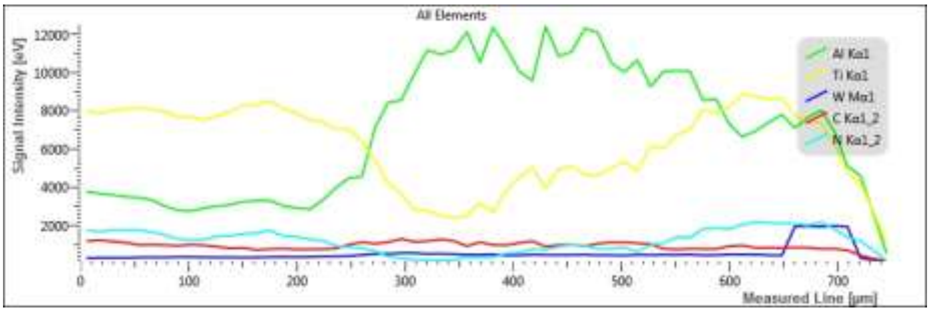

Fig. 4 The distribution of elements, PF1 with NPs of TiO_2, the impact on milling indexable cutting insert.

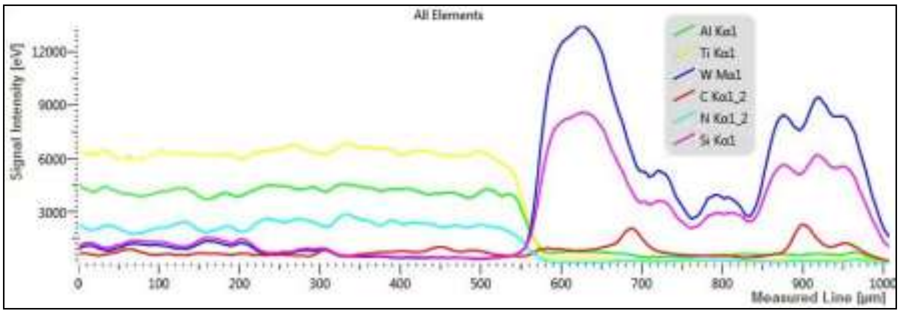

Fig. 5 The distribution of elements, PF2 with no NPs, the impact on milling indexable cutting insert.

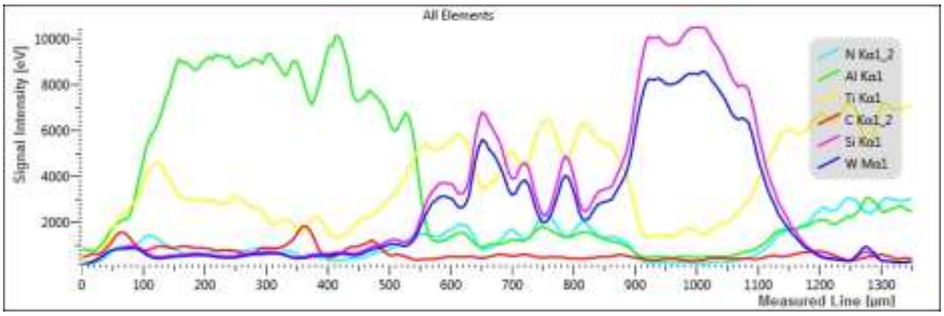

Fig. 6 The distribution of elements, PF2 with NPs of SiO_2, the impact on milling indexable cutting insert.

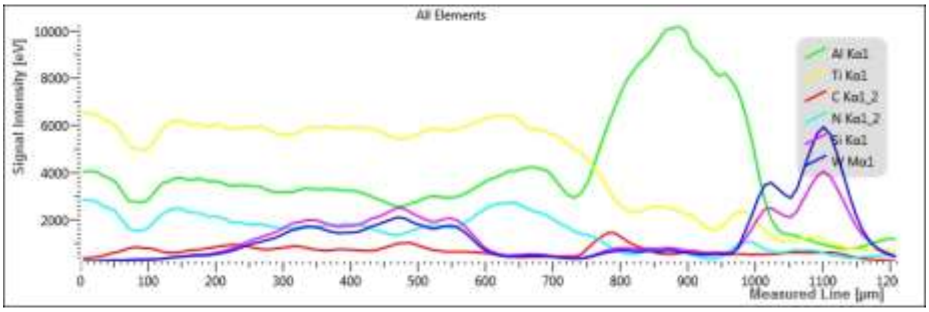

Fig. 7 The distribution of elements, PF2 with NPs of TiO_2, the impact on milling indexable cutting insert.

The milling indexable cutting insert are worn during the milling, resulting in a change in the distribution of elements on the surface of the milling indexable cutting insert i.e. elements under the coating are revealed as shown in **Fig. 2 – 7** on the right of the graph. There is significant change in the surface modification for the pure process fluid (without NPs); elements of wolfram and (carbon or silicon) appear abundantly on the graph and they form the core of the milling indexable cutting insert. Material loss of the milling indexable cutting insert (surface modification) is minimal when using SiO_2 and TiO_2 NPs and the distribution of elements is unchanged throughout the graph. As regards to the comparison of process fluids, the PF1 has better machining properties (in the presence of NPs has more stable mechanical properties).

3.4. Microorganism respiratory rate

The pH and specific conductivity of the process fluids with and without NPs was almost constant during the measurements, with a change in the range of 2 % for pH and 5 % for conductivity; and so these parameters did not influence the biocidal properties. **Table 1** summarizes the data obtained from the respiratory measurements (O_2 consumption). The data are recalculated separately for each hour and process fluid type in order to compare with the control sample with no NPs (indicated in the table in italics).

Table 1 Comparison of total O_2 consumption (%) in process fluids after milling separately for each process fluids type, with respect to samples with no NPs indicated in italics.

PF1			
Length of experiment [hours]	No NPs [% of control]	SiO_2 [% of control]	TiO_2 [% of control]
0	*100.00*	46.59	87.50
1	*100.00*	42.04	73.40
2	*100.00*	81.14	74.44
3	*100.00*	99.00	105.50
PF2			
Length of experiment [hours]	No NPs [% of control]	SiO_2 [% of control]	TiO_2 [% of control]
0	*100.00*	39.85	75.38
1	*100.00*	75.18	44.97
2	*100.00*	81.01	61.00
3	*100.00*	97.42	107.84

The addition of SiO_2 or TiO_2 to the process fluids caused a reduction in bacterial activity during the first few minutes of exposure to the NPs (i.e. 0 hours of the experiment). The SiO_2 NPs have a higher biocidal effect (reduction of 53.4 % for PF1; reduction of 60.1 % for PF2) than TiO_2 NPs (reduction of 12.5 % for PF1; reduction of 24.6 % for PF2).

However, the biocidal effects of both NPs decrease with increasing time of milling in both process fluids (PF1 and PF2). Moreover, no effect was measured after 3 hours of the experiment. Neither of the NPs have any biocidal effect on reducing bacterial activity in the semi-industrial testing of milling on the machine where the continuous mixing of NPs was not ensured or when the machine is stopped and started after a specific time (no agitation leads to significant aggregation and sedimentation of NPs, which in turn leads to significant loss of biocidal properties).

4. CONCLUSION

The addition of nanoadditives (SiO_2 or TiO_2 in a size of 10 – 25 nm) to the process fluids has a positive effect on the machining process, resulting in an increase in operating life. Nanoparticles reduce the friction coefficient leading to a significant reduction of wear of the milling tool; material loss of the surface modification of the milling indexable cutting insert is minimal.

The addition of SiO_2 or TiO_2 to process fluids caused a reduction in bacterial activity during the first few hours of the experiment, with a significant reduction for SiO_2 of up to 60.1 %. However, no differences were measured after 3 hours of the experiment as a consequence of no agitation of the process fluids with NPs. Ensuring consistent agitation during real milling is a major challenge that must be overcome if high efficiency of the NPs is required.

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