Feasibility of Metalworking Fluids Delivered in Supercritical Carbon Dioxide

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Abstract

This paper presents a new method to lubricate, cool, and evacuate chips in metalworking operations using supercritical carbon dioxide (scCO$_2$). Water-based and straight oil metalworking fluids (MWFs) are currently being used to perform these functions even though they are characterized by high economic, occupational health, and environmental costs. Carbon dioxide above its critical temperature and pressure is a finely tunable solvent that dissolves certain oils, creating the possibility of using scCO$_2$ to carry lubricants to the cutting zone in minimal and precise quantities, while significantly reducing the occupational health and environmental risks associated with MWF systems. In the proposed process, an oil-in-CO$_2$ dispersion is sprayed out of a nozzle at high speed and pressure to deliver oil and form dry ice near to the cutting zone. The rapid expansion of the CO$_2$ leads to cooling at cryogenic temperatures, and the combination of high pressure and low surface tension provides access to interstitial spaces that are inaccessible to conventional MWF oil and water jets. Research with the tapping torque test shows that soybean oil dissolved in scCO$_2$ performs significantly better than straight soybean oil, even when less oil is applied, meaning that scCO$_2$ provides additional benefit to the tapping process. This soybean oil-in-scCO$_2$ MWF also performed better than straight petroleum mineral oil and emulsions of soybean oil or petroleum oil. Scanning electron microscopy images of the chip surfaces produced by the tapping experiments illustrate that higher tapping torque efficiency correlates well with less frictional wear.

Introduction

Metalworking fluids (MWFs) are used extensively in metal cutting processes as lubricants and coolants. They are typically oil-in-water emulsions where the oil lubricates and the water cools the cutting zone. MWF emulsions of oil and water create environmental and occupational health problems that result from microbial growth, biocides used to control microbial growth, additives used to control foam and corrosion, and from the metals and other organic constituents that become entrained in the fluids during use. MWF maintenance systems are expensive, energy consuming, and typically cannot prevent MWF degradation and disposal due to factors such as microbial attack and hardwater ion accumulation [1,2]. These environmental and health concerns could be eliminated if manufacturing process lubrication could be provided in minimal and precise quantities without using water as the delivery medium. While straight oils are a possible alternative, they do not have adequate thermal conductivity for high speed machining applications and are well-known to possess their own health, safety, and environmental concerns [3,4].

Supercritical carbon dioxide (scCO$_2$) is being used increasingly in industrial applications as an alternative to traditional organic, halogenated, and aqueous solvents [5,6]. The supercritical temperature and pressure of CO$_2$ (T_c =

31.1 ^{o}C and P_c = 72.8 atm) is easily achieved in industrial environments, and under supercritical conditions CO_2 is a good solvent for many materials, with some vegetable-based oils being highly soluble [7]. Recent research efforts have focused on the rapid expansion of supercritical solutions in coating and spraying applications [8] and have found that rapidly expanding solutions of CO_2 can reach temperatures below -80^{o}C with a uniform coating of the solubilized material forming on the spray surface. It has also been demonstrated that there exists a significant decrease in the surface tension of vegetable oils in supercritical solutions [9], which in practice would permit the oil to penetrate into the cutting zone more readily. In addition, the high pressure delivery of dissolved oil would facilitate transport of lubricant to the cutting region, and the dry ice that forms around the lubricant would provide improved cooling relative to water. The intense pressure of CO_2 at the exit nozzle would also provide a viable chip evacuation function. All these characteristics make $scCO_2$ a promising delivery medium for MWFs, motivating this research investigation to examine the feasibility of developing $scCO_2$-based MWFs.

For this examination of $scCO_2$-based MWFs, soybean oil was selected as the MWF lubricant. Soybean oil was selected for this study primarily because its solubility in $scCO_2$ is well documented in the food industry literature [10,11] and because the authors have previously shown that soybean oil is a viable lubricant in metalworking applications [122]. Recent success with soybean-based MWFs has also been reported in practice [13]. From the environmental perspective, vegetable oils are desirable for use in MWF applications because they are derived from renewable feedstocks and because they are less toxic during use and end-of-life treatment [14]. In addition CO_2 is sequestered when the vegetable feedstocks are grown. Using renewable soybean oil in combination with waste CO_2 captured from other industrial processes as a MWF has the potential to offer an effective process solution that is environmentally benign while posing reduced risks to human health.

Method of Performance Evaluation using the Tapping Torque Test

The performance of the MWFs developed during this research was measured via the tapping torque test using a MicroTap Mega G8 (Rochester Hills, MI) machine tool at a cutting speed of 1000 RPM on 1018 steel workpieces that were pre-drilled and pre-reamed with 240 M6-sized holes (Maras Tool, Schaumburg, IL). To standardize the aqueous MWF evaluations, 1 mL of MWF was placed inside blank holes and held there by tape fixed to the underside of the workpiece. It was found that this method of applying MWF was simpler and produced tapping torque efficiency results indistinguishable from 10mL/cut spray application at standard pressures used in industry (e.g., 1.4 atm) as shown in Figure 1. Tapping was performed using uncoated high-speed steel taps with 60^o pitch and 3 straight flutes (EMUGE, Northborough, MA). MWF evaluations were carried out according to ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine [15], with several modifications made to account for the use of a MWF evaluation testbed that permits multiple cutting tests on a single workpiece as proposed by Zimmerman et al. (2002) [166]. MWF performance is reported here as percentage efficiency in the tapping operation, which is calculated by the ratio of the average torque measured during full tool engagement for the test MWF normalized to the average torque measured during full tool engagement for a reference MWF. Higher tapping torque efficiency indicates improved performance in the tapping torque test, and has been previously shown to be well-correlated with improved field performance if care is taken in selecting the tapping conditions [16].

Testbed for Evaluating scCO_2-based MWFs

An experimental testbed was developed as shown in Figure 2 to produce scCO_2-based MWFs and deliver them to the cutting region of a tapping machine. To start, the CO_2 is boosted from 47.6 atm to supercritical pressures >72.8 atm and transferred to a high-pressure vessel. Soybean oil is then added to the scCO_2 via a 6-way valve, with solubility of the soybean oil in scCO_2 being confirmed by visual inspection through two sapphire windows designed into the pressure vessel. The outlet port from the pressure vessel is connected to an automated solenoid valve which controls the spray of scCO_2 and lubricant through a nozzle toward the cutting region of the tapping operation. A computer is used to monitor the operating conditions in the high-pressure vessel, to control the actuation of the solenoid valve, and to record torque data from the tapping process.

In the method developed during this research, the scCO_2-based formulation was made by injecting soybean oil into the high-pressure vessel to achieve a concentration of 10%w/w. The contents of the vessel were maintained at 102 atm and 35^oC and mixed using a magnetic stir bar prior to the release of the MWF mixture to the cutting region. The mixture was applied to the cutting zone throughout the engagement time of the tapping tool (about 2 seconds). After each cut the pressure in the vessel would drop to about 61.2 atm. Additional CO_2 was fed into the vessel after each cut to return the pressure to 102 atm. Additional oil was added to the pressure-vessel after every six tapping experiments to maintain approximately equal concentrations of soybean oil throughout the 30 $scCO_2$ tapping operations performed during this investigation. Approximately 2 grams of CO_2 and 0.2 grams of oil were applied to the cutting zone during each tapping operation. Comparative photographs of the cutting process using water- and $scCO_2$-based MWFs are shown in Figure 1.

Benchmark MWF Formulations for Performance Comparison

For comparative purposes, straight oil and water-based MWFs were also investigated. The base oils used in the formulations were a petroleum-based naphthenic oil (D.A. Stuart, Warrenville, Illinois) and a vegetable-based soybean oil (Alkali Refined Soybean Oil, Cargill Inc., Minneapolis, MN). The formulations were based on recommendations provided by a commercial MWF supplier. The MWFs were first produced in concentrated form, and then were diluted to a working concentration in deionized water. The recipe used for each formulation is listed in Table 1. The oils (0.75% w/w) were stabilized in water using the combination of an anionic surfactant, a nonionic surfactant, and a coupler. As expected from previous research, it was necessary to utilize a different emulsification package for the mineral oil and the vegetable oil metalworking fluids [13]. These differences were relatively minor as shown in Table 1. All of the fluid components were used as delivered from the manufacturer and were subject to the same handling and storage conditions.

Experimental Results and Discussion

Figure 3 provides average tapping torque efficiency and 95% confidence interval values calculated for the 30 independent and randomized trials performed for each MWF. 100% corresponds to the average tapping torque observed for a commercially produced soluble oil that was utilized as a reference fluid [16].

As previously noted in the literature, the data reveal that soybean oil is a better lubricant than mineral oil, either in straight oil or emulsified form. In addition, the data corroborate the well known fact that straight oils provide a significant lubricity advantage with respect to oil-in-water emulsions [17]. It was surprising to the authors that the soybean oil microemulsion (0.75%w/w oil-in-water) performs slightly better than straight mineral oil, and that straight $scCO_2$ (without oil) has a statistically indistinguishable performance relative to the mineral oil microemulsion (0.75%w/w oil-in-water). The napthenic mineral oil microemulsion is similar to base semi-synthetic MWFs used widely in industry [17].

Figure 3 also demonstrates the performance advantage of combining $scCO_2$ and soybean oil in MWF applications. It is observed that the soybean oil / $scCO_2$ system performs on average approximately 10% better than straight soybean oil, 20% better than the soybean oil microemulsion, and 30% better than straight $scCO_2$. This confirms that the combination of soybean oil and $scCO_2$ performs better than either can alone, and that soybean oil and $scCO_2$ have complimentary roles when formulated together as a MWF. The performance of $scCO_2$ alone can be improved by adding soybean oil for lubricity, and the performance of straight soybean oil can be improved by using $scCO_2$ for enhanced delivery of the dissolved oil to the cutting zone. Dissolving soybean oil in $scCO_2$ also allows at least 5 times less soybean oil to be applied during each cut while achieving improved performance.

To corroborate these results from the tapping torque test and to provide more direct evidence of enhanced lubrication properties offered by MWFs based upon soybean oil dissolved in $scCO_2$, scanning electron microscopy images of the chips produced during the tapping process were analyzed. Figure 4 provides representative images of the chip surfaces produced by the different MWF systems, with each image corresponding to the tapping torque data provided in Figure 3. The electron microscopy images provided in Figure 4 show clearly that there is much more metal-to-metal contact in the tapping experiments characterized by lower values of tapping torque efficiency (e.g., mineral oil microemulsion) than experiments characterized by higher values of tapping torque efficiency (e.g., mixture of $scCO_2$ and soybean oil).

For instance, the $scCO_2$ (Fig. 4a) and the napthenic microemulsion (Fig. 4b) show wear scars from the cutting process that have been ground down flat into the surface of the chip. These images also indicate striations and scratch marks on the chips that are indicative of poor lubrication and significant tool-to-chip contact. This friction means that more torque must be supplied to perform the tapping operation, resulting in a lower value of tapping torque efficiency as indicated by Figures 3a and 3b. This trend also holds for the straight napthenic oil and soybean oil microemulsion. These fluids have both similar tapping torque efficiencies (Fig. 3c and 3d) and similar chip surfaces (Fig. 4c and 4d). Their tapping torque efficiencies are higher than observed in Figs. 3a and 3b, and there is less chip-to-tool contact observed in the microscopy images relative to Figs. 4a and 4b.

The correlation of chip surfaces and tapping torque efficiency also holds for the best two MWFs observed in this investigation: straight soybean oil and soybean oil in $scCO_2$. These microscopy images (Fig. 4e and 4f) indicate much less contact between the chip and workpiece than the other experiments (Figs 4a-4d). For soybean oil in $scCO_2$, the contact area is isolated to only a few elevated relief zones on the chip surface that have not been ground down due to the presence of effective boundarylubrication. Since the soybean oil-in-CO_2 results (Figures 3f and 4f) are readily distinguishable from the use of soybean oil alone (Figures 3e and 4e), it is plausible to conclude that the pressure of the $scCO_2$ coupled with its ability to lower the surface tension of soybean oil can effectively carry soybean oil deep into the cutting process. This serves to minimize contact between chip and workpiece and results in lower friction and lower observed torque in the tapping operation.

Summary and Conclusions

In this investigation, a novel metalworking fluid (MWF) formulation was developed using soybean oil and was delivered in supercritical CO_2 ($scCO_2$). Tapping torque tests for machining performance indicated that the $scCO_2$ MWF performs significantly better than straight oil soybean and petroleum MWFs, and better than water-based MWF emulsions based on these oils. An analysis of scanning electron microscopy images of chip surfaces produced from these experiments demonstrated that observed tapping torque values were highly correlated with evidence of chip-workpiece friction. Taken together, the data indicate the feasibility of developing a new class of MWFs based upon oils dissolved or dispersed in $scCO_2$. Such fluids hold potential to greatly reduce environmental and occupational health concerns associated with existing straight-oil and water-based MWF formulations, as they are based on waste or renewable components and are incapable of supporting microbiological growth.

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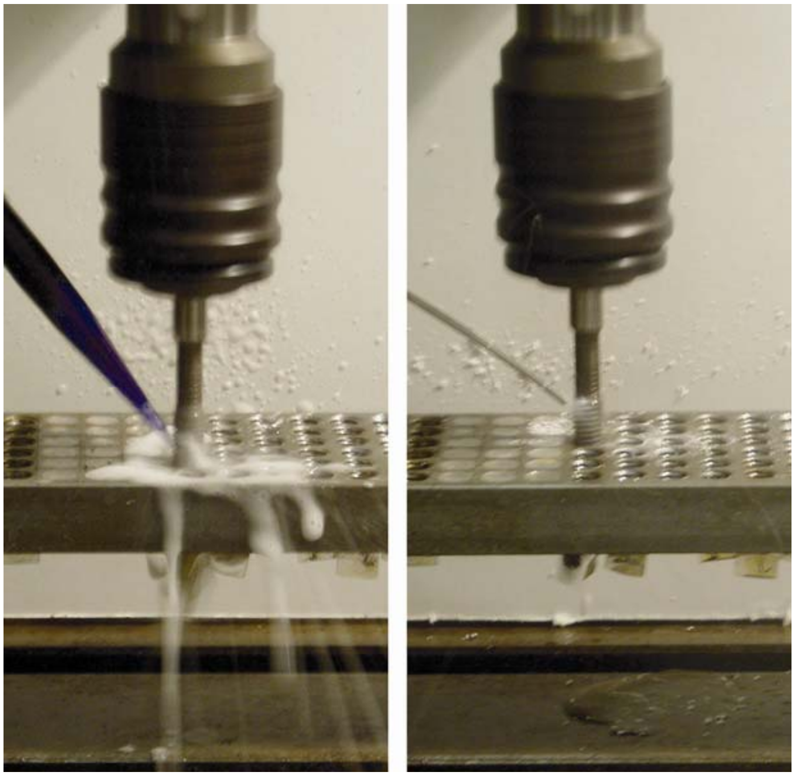

Figure 1. Images of tapping experiments using spray application of MWF microemulsion (left) and rapidly expanding supercritical carbon dioxide ($scCO_2$) solution (right).

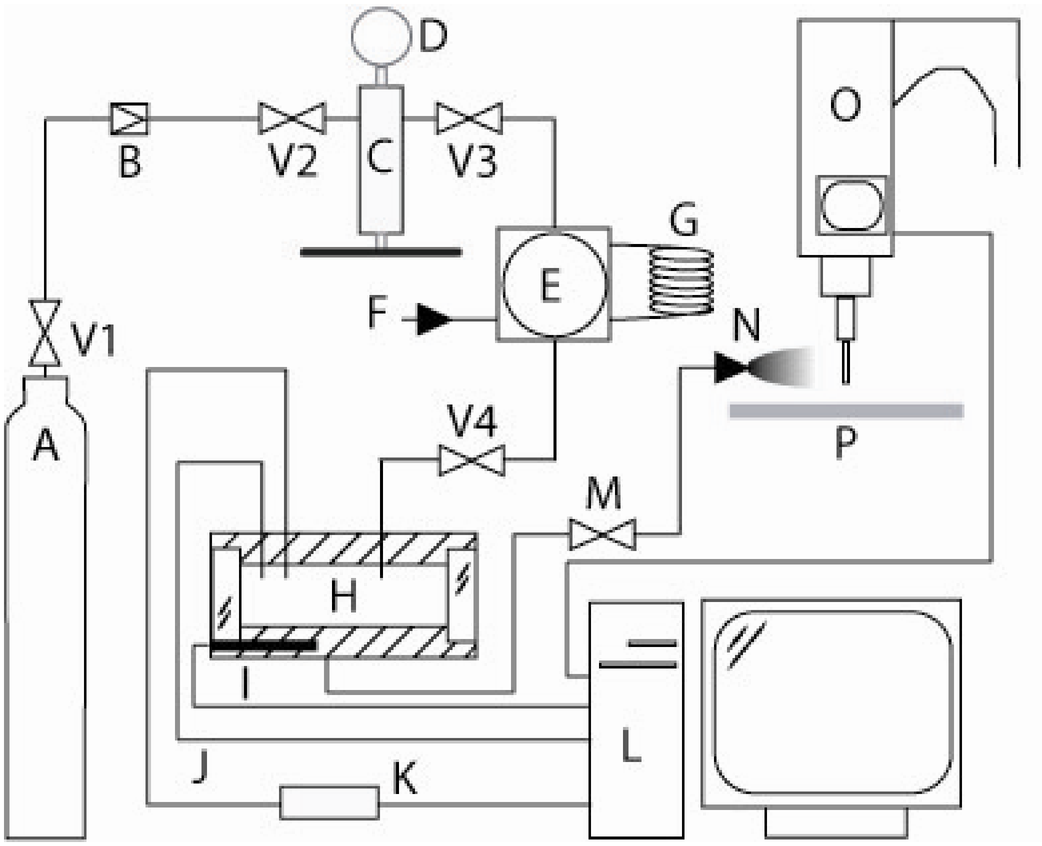

Figure 2. $scCO_2$ testbed: A. Tank of food-grade carbon dioxide; B. Check valve; C. Pressure booster; D. Pressure gauge; E. Six-way valve; F. Oil inlet; G. Fixed volume coil; H. High-pressure vessel; I. Heating element; J. Thermocouple; K. Pressure transducer; L. Computer; M. Solenoid valve; N. Nozzle; O. Tapping torque machine tool; P. Workpiece; V1-3. Pin valves.

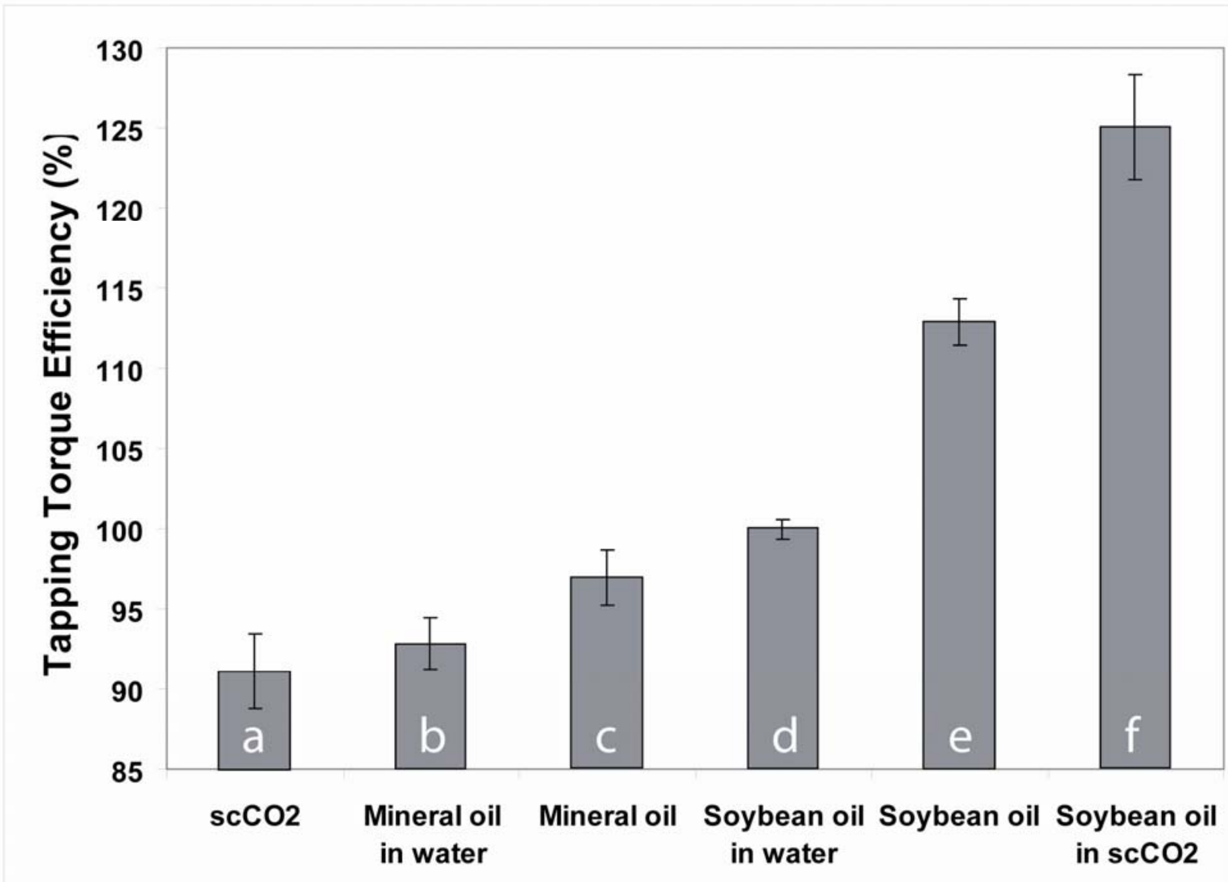

Figure 3. Tapping torque efficiency for straight oil, water-, and $scCO_2$-based MWFs. Letters correspond to electron microscopy images in Figure 4.

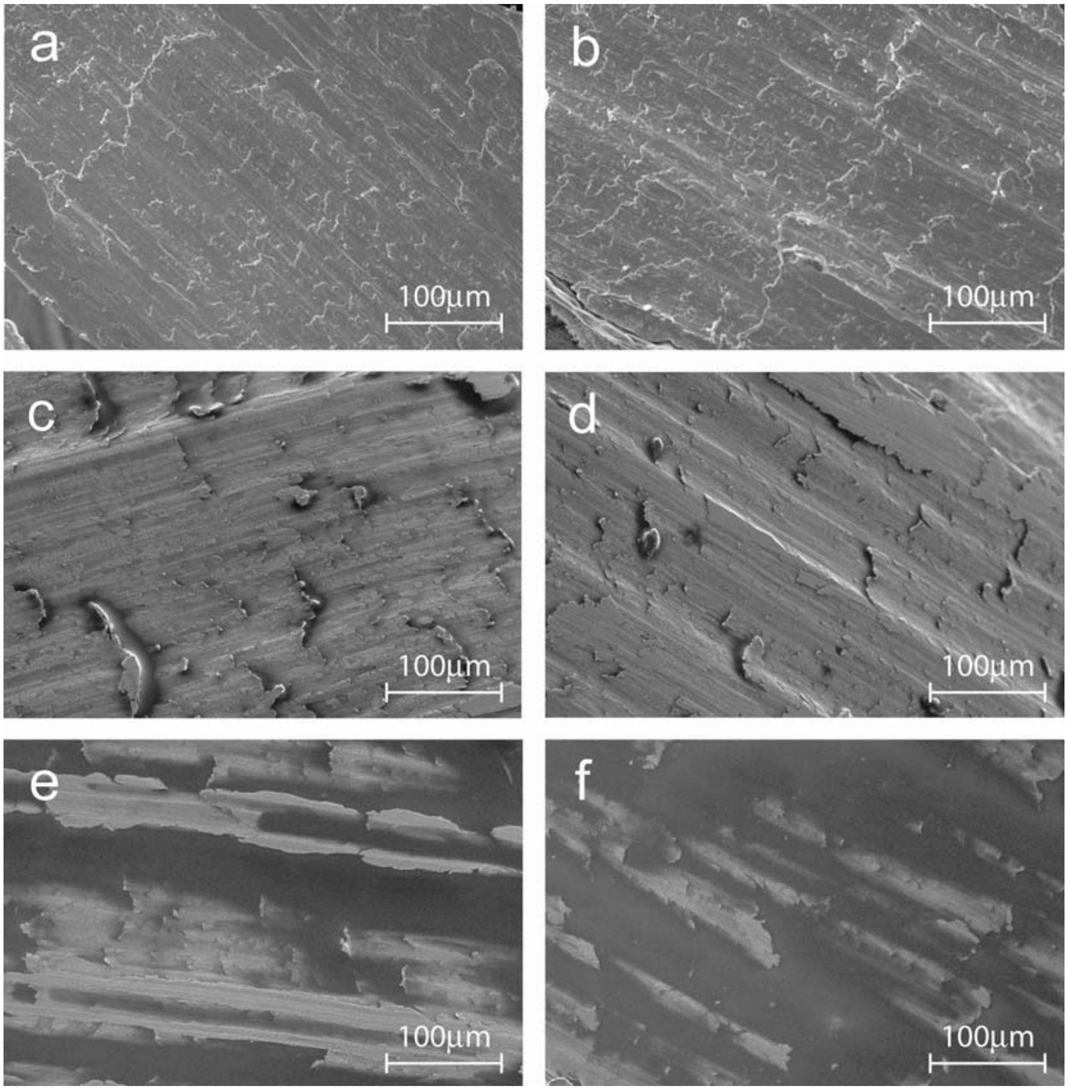

Figure 4. Magnified images of chip surfaces cut from 1018 cold rolled steel during tapping using a) $scCO_2$ alone, b) mineral oil in H_2O, c) straight mineral oil, d) soybean oil in H_2O, e) soybean oil alone, and f) soybean oil in $scCO_2$.

Component	$scCO_2$	Mineral Oil in Water	Mineral Oil	Soybean Oil in Water	Soybean Oil	Soybean Oil in $scCO_2$
Soybean Oil				0.72%	100%	10%
Mineral Oil		0.72%	100%			
Tomadol 91		1.56%				
Tagat V20				1.38%		
Dowfax 3B2		0.14%		0.21%		
Coupler		0.07%		0.10%		
$scCO_2$	100%					90%
Water		97.50%		97.59%		

Table 1. MWF formulations (all percentages are by weight). The listed surfactants were Tagat V20 nonionic surfactant (Degussa-Goldschmidt Chemical Corporation, Hopewell, VA), Tomadol 91-6 nonionic surfactant (Tomah Corporation, Milton, WI), and Dowfax 3B2 anionic surfactant (Dow Chemical, Midland, MI).