

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 (scCO₂). 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 scCO₂ 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-CO₂ 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 CO₂ 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 scCO₂ performs significantly better than straight soybean oil, even when less oil is applied, meaning that scCO₂ provides additional benefit to the tapping process. This soybean oil-in-scCO₂ 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 (scCO₂) 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 CO₂ ($T_c =$

超临界二氧化碳输送金属加工液的可行性研究

(提交至《制造过程杂志》的技术说明)

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摘要

本文提出了一种利用超临界二氧化碳 ($scCO_2$) 在金属加工过程中润滑、冷却和排出切屑的新方法。尽管水基和直油金属加工液 (MWFs) 具有较高的经济成本、职业健康风险和环境代价, 目前仍被用于实现这些功能。高于临界温度和压力的二氧化碳是一种可精细调节的溶剂, 能够溶解特定油类, 这为使用 $scCO_2$ 以最小且精确的量将润滑剂输送到切削区域提供了可能, 同时显著降低了与 MWF 系统相关的职业健康和环境风险。在所提出的工艺中, 油包 CO_2 分散液通过喷嘴以高速高压喷射, 将油液和干冰输送至切削区域附近。 CO_2 的快速膨胀导致低温冷却, 而高压与低表面张力的结合使得传统 MWF 油水喷射无法触及的间隙空间得以进入。通过挤榨扭矩测试进行的研究表明, 溶解在 $scCO_2$ 中的大豆油性能显著优于纯大豆油, 即使使用较少油量时也是如此, 这意味着 $scCO_2$ 对榨榨工艺具有额外增效作用。这种 $scCO_2$ 中的大豆油 MWF 也优于纯矿物石油油以及大豆油或石油油乳液。通过扫描电子显微镜观察榨榨实验产生的油片表面图像可以发现, 较高的榨榨扭矩效率与较低的摩擦磨损程度呈现良好相关性。

引言

金属加工液 (MWFs) 作为润滑剂和冷却剂被广泛应用于金属切削工艺中。这类液体通常采用水包油乳化体系, 其中油相起到润滑作用, 水相则对切削区域进行冷却。 MWF 油水乳化体系会引发环境与职业健康问题, 这些问题主要源于微生物滋生、用于抑制微生物生长的杀菌剂、控制泡沫与腐蚀的添加剂, 以及使用过程中混入流体中的金属成分及其他有机物质。 MWF 维护系统不仅成本高昂且能耗巨大, 通常无法有效防止 MWF 劣化与处置, 这与微生物侵蚀、硬水离子积聚等因素密切相关[1,2]。若能采用无需水作为输送介质、以最小化且精准剂量实现润滑的生产工艺, 这些环境与健康隐患便可彻底消除。虽然直链油类可作为替代方案, 但其导热性能不足以满足高速切削加工需求, 且众所周知这类油品本身存在健康安全与环境方面的潜在风险[3,4]。

超临界二氧化碳 ($scCO_2$) 正越来越多地被用于工业应用, 作为传统有机溶剂、卤代溶剂和水性溶剂的替代品[5,6]。二氧化碳的超临界温度和压力为 CO_2 ($T_c=$

31.1 °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°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

31.1 °C和 $P_c = 72.8 \text{ atm}$) 在工业环境中很容易实现，且在超临界条件下 CO_2 是许多材料的良好溶剂，某些植物油具有高度溶解性[7]。近期研究重点集中在超临界溶液在涂层和喷涂应用中的快速膨胀[8]，并发现 CO_2 的快速膨胀溶液可达到低于 -80 °C 的温度，同时在喷雾表面形成均匀的溶解材料涂层。研究还表明，植物油在超临界溶液中的表面张力显著降低[9]，这在实际应用中可使油更易渗透至切削区域。此外，溶解油的高压输送将促进润滑剂向切削区域的输送，而润滑剂周围形成的干冰相较于水能提供最佳的冷却效果。出口喷嘴处 CO_2 的极高压力还可实现有效的切屑排出功能。所有这些特性使得 scCO_2 成为微囊化药物 (MWFs) 的理想递送介质，这促使本研究探讨基于 scCO_2 的MWFs开发可行性。

对于这项基于 scCO_2 的金属加工液 (MWFs) 研究，大豆油被选作 MWF 润滑剂。选择大豆油进行本研究的主要原因在于：其在 scCO_2 中的溶解度已在食品工业文献中得到充分证实[10,11]，且作者先前已证明大豆油在金属加工应用中是一种可行的润滑剂[122]。实践中也报道了基于大豆的MWFs近期取得的成功[13]。从环境角度来看，植物油适用于 MWF 应用，因其源自可再生原料，且在使用及报废处理过程中毒性较低[14]。此外 CO_2 会在植物原料种植过程中被封存。将可再生大豆油与从其他工业流程中捕获的废弃 CO_2 作为 MWF 结合使用，有望提供一种环境友好型有效工艺解决方案，同时降低对人类健康的风险。

采用**敲击扭矩试验**进行性能评估的方法

本研究开发的MWFs性能通过**攻丝扭矩测试**进行评估，测试设备为MicroTap Mega G8 (美国密歇根州罗切斯特山市) 机床，切割速度为1000转/分钟，试件为1018钢材质且预先钻孔并攻制了240 M6规格孔 (马拉斯工具公司，美国伊利诺伊州绍姆堡市)。为统一水性 MWF 评估标准，实验中将1mL MWF 注入空白孔内，并通过固定在工件底面的胶带保持位置。研究发现该 MWF 施加方法操作简便且能获得稳定的攻丝性能数据。

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° 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 scCO₂-based MWFs

An experimental testbed was developed as shown in Figure 2 to produce scCO₂-based MWFs and deliver them to the cutting region of a tapping machine. To start, the CO₂ 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 scCO₂ via a 6-way valve, with solubility of the soybean oil in scCO₂ 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 scCO₂ 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 scCO₂-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°C 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 CO₂ 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

扭矩效率测试结果与工业标准压力（如1.4个大气压）下采用10毫升/次切割喷雾施药量时的数值无显著差异（如图1所示）。攻丝作业采用未经涂层的高速钢丝锥，其螺距为60°、具有3条直槽（EMUGE公司，马萨诸塞州诺斯伯勒）。MWF性能评估依据ASTM D 5619标准进行，该标准采用攻丝扭矩试验机对金属去除液进行比对[15]，并根据 Zimmerman 等人（2002年）提出的方案[166]对 MWF 评估试验台进行了若干改进，该试验台可实现单工件多次切割测试。本文中 MWF 性能以攻丝操作中的百分比效率表示，该数值通过将测试 MWF 在完全工具啮合状态下测得的平均扭矩与参考 MWF 在相同条件下测得的平均扭矩之比进行归一化计算得出。较高的起钻扭矩效率表明起钻扭矩测试中性能的改善，并且先前已证明，如果在选择起钻条件时谨慎行事，其与现场性能的改善具有良好的相关性[16]。

基于scCO₂的MWF评估测试平台

如图2所示，开发了一个实验测试平台，用于生产基于scCO₂的MWFs并将其输送至打孔机的切割区域。首先，将CO₂从47.6 atm加压至超临界压力>72.8 atm，并转移至高压容器中。随后通过六通阀将大豆油加入scCO₂中，通过压力容器上设计的两个蓝宝石窗口进行目视检查，以确认大豆油在scCO₂中的溶解度。压力容器的出口端口连接至自动电磁阀，该电磁阀通过喷嘴控制scCO₂与润滑剂向打孔操作的切割区域喷射。计算机用于监测高压容器内的运行条件、控制电磁阀的驱动动作，并记录打孔过程中的扭矩数据。

在本研究开发的方法中，通过将大豆油注入高压容器以达到10%w/w的浓度，制备了基于scCO₂的配方。容器内维持102 atm压力和35 °C温度，并在将 MWF 混合物释放至切割区域前使用磁力搅拌棒进行混合。该混合物在整个抽拔工具啮合时间（约2秒）内持续作用于切割区域。每次切割后，容器内压力会降至约61.2 atm。每次切割后向容器中补充额外的CO₂以使压力恢复至102 atm。每隔六次抽拔后，压力容器中会添加额外的油液。

experiments to maintain approximately equal concentrations of soybean oil throughout the 30 scCO₂ tapping operations performed during this investigation. Approximately 2 grams of CO₂ 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 scCO₂-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 scCO₂ (without oil) has a statistically indistinguishable performance relative to the mineral oil

在本研究期间进行的30次scCO₂采收操作中，为维持大豆油浓度大致相等而进行的实验。每次采收操作时，切割区域会施加约2克CO₂和0.2克油。图1展示了使用水基和scCO₂基微波水力破碎器（MWFs）进行切割过程的对比照片。

用于性能比较的基准 MWF 制剂

为便于对比研究，实验还测试了纯油基和水基矿物油基液态润滑剂（MWF）。配方中使用的基础油包括石油基环烷油（D.A. Stuart公司，美国伊利诺伊州沃伦维尔）和植物基大豆油（碱精炼大豆油，嘉吉公司，美国明尼苏达州明尼阿波利斯）。配方体系参照商业 MWF 供应商提供的技术建议制定。MWF首先以浓缩形式制备，随后用去离子水稀释至工作浓度。各配方的具体配比详见表1。通过阴离子表面活性剂、非离子表面活性剂与偶联剂的组合，将油类（0.75% w/w）在水中实现稳定。与既往研究结果一致，矿物油与植物油基液态润滑剂需采用不同的乳化体系[13]。如表1所示，这些差异相对较小。所有流体组分均直接采用制造商原厂产品，并遵循相同的操作与储存条件。

实验结果与讨论

图3展示了针对每种 MWF 进行的30项独立随机试验所计算的平均抽吸扭矩效率及95%置信区间值。100%对应于以市售可溶性油作为参考流体时观测到的平均抽吸扭矩[16]。

正如文献先前所述，数据表明大豆油无论是纯油形式还是乳化形式，其润滑性能均优于矿物油。此外，数据进一步证实了一个广为人知的事实：纯油相较于水包油型乳液具有显著的润滑优势[17]。令作者感到意外的是，大豆油微乳液（水包油比例为0.75%w/w）的润滑性能略优于纯矿物油，而纯scCO₂（不含油）的润滑性能与矿物油相比在统计学上无显著差异。

microemulsion (0.75%w/w oil-in-water). The naphthenic mineral oil microemulsion is similar to base semi-synthetic MWFs used widely in industry [17].

Figure 3 also demonstrates the performance advantage of combining scCO₂ and soybean oil in MWF applications. It is observed that the soybean oil / scCO₂ system performs on average approximately 10% better than straight soybean oil, 20% better than the soybean oil microemulsion, and 30% better than straight scCO₂. This confirms that the combination of soybean oil and scCO₂ performs better than either can alone, and that soybean oil and scCO₂ have complimentary roles when formulated together as a MWF. The performance of scCO₂ alone can be improved by adding soybean oil for lubricity, and the performance of straight soybean oil can be improved by using scCO₂ for enhanced delivery of the dissolved oil to the cutting zone. Dissolving soybean oil in scCO₂ 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 scCO₂, 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 scCO₂ and soybean oil).

For instance, the scCO₂ (Fig. 4a) and the naphthenic 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 naphthenic oil and soybean oil microemulsion. These fluids have both similar tapping torque efficiencies (Fig. 3c and 3d) and similar chip

微乳液（0.75%w/w 油包水型）。环烷基矿物油微乳液与工业中广泛使用的基础半合成矿物油基润滑剂（MWFs）相似[17]。

图3还展示了在 MWF 应用中结合scCO₂与大豆油的性能优势。观察发现，大豆油/scCO₂体系的平均性能比纯大豆油高出约10%，比大豆油微乳液高出20%，比纯scCO₂高出30%。这证实了大豆油与scCO₂的组合效果优于单独使用任一成分，并且当作为 MWF 共同配制时，大豆油与scCO₂具有互补作用。通过添加大豆油以提升润滑性可改善scCO₂的单独性能，而使用scCO₂可增强溶解油向切削区的输送能力，从而提升纯大豆油的性能。将大豆油溶解于scCO₂中还能使每次切削过程中所需大豆油用量减少至少5倍，同时实现性能提升。

为验证**敲击扭矩测试**结果，并进一步提供基于溶解于scCO₂中的大豆油制备的金属水基润滑剂（MWFs）具有增强润滑性能的直接证据，我们对敲击过程中产生的芯片进行了扫描电子显微镜图像分析。图4展示了不同 MWF 系统制备的芯片表面代表性图像，每张图像对应图3中提供的敲击扭矩数据。图4中的电子显微镜图像清晰显示：与敲击扭矩效率较高（如of scCO₂与大豆油混合物）的实验相比，以较低扭矩效率为特征的敲击实验（如矿物油微乳液）中金属间接触面积显著增加。

例如，scCO₂（图4a）和环烷基微乳液（图4b）在切削过程中形成了磨损痕迹，这些痕迹被磨削成与工件表面平齐的形态。图像还显示工件表面存在条纹状划痕和划痕痕迹，表明润滑效果不佳且刀具与工件接触面积过大。这种摩擦现象意味着进行攻丝操作时需要施加更大的扭矩，如图3a和3b所示，导致攻丝扭矩效率值降低。这一趋势同样适用于直链环烷基油和大豆油微乳液。这两种流体不仅具有相近的攻丝扭矩效率（图3c和3d），其工件表面形貌也表现出相似特征。

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 scCO₂. 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 scCO₂, 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-CO₂ 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 scCO₂ 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 CO₂ (scCO₂). Tapping torque tests for machining performance indicated that the scCO₂ 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 scCO₂. 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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表面（图4c和4d）。其攻丝扭矩效率高于图3a和3b所示数值，且显微图像中观察到的切屑与刀具接触面积较图4a和4b更小。

切屑表面与攻丝扭矩效率之间的相关性同样适用于本研究中观察到的最佳两种MWF：直链大豆油和scCO₂中的大豆油。这些显微图像（图4e和4f）表明，与其它实验（图4a-4d）相比，切屑与工件之间的接触面积要小得多。scCO₂中的大豆油接触区域仅限于切屑表面少数未被研磨的凸起区域，这得益于有效边界润滑的存在。由于CO₂中的大豆油实验结果（图3f和4f）与单独使用大豆油的情况（图3e和4e）明显不同，可以合理推断：scCO₂的压力与其降低大豆油表面张力的能力相结合，能够有效将大豆油带入切削过程的深层。这有助于最小化切屑与工件之间的接触，从而降低摩擦力并减少攻丝操作中观察到的扭矩。

摘要与结论

在本研究中，我们采用大豆油开发了一种新型金属加工液（MWF）配方，并将其输送至超临界CO₂（scCO₂）中。切削扭矩测试表明，scCO₂ MWF 的加工性能显著优于纯油大豆油和石油基金属加工液，也优于基于这些油类的水基 MWF 乳液。对实验产生的切屑表面扫描电子显微镜图像分析显示，观测到的切削扭矩值与切屑-工件摩擦证据高度相关。综合数据表明，基于溶解或分散于scCO₂中的油类开发新型金属加工液具有可行性。此类流体凭借其废弃物或可再生成分基础且无法支持微生物生长的特点，有望大幅降低现有纯油和水基 MWF 配方带来的环境及职业健康风险。

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References

1. Zimmerman, J., Hayes, K., Skerlos, S.J., "Influence of Ion Type and Concentration on the Emulsion Stability and Machining Performance of Two Semi-Synthetic Metalworking Fluids", *Environmental Science and Technology*, 2003, Vol. 38, pp. 2482-2490.
2. Skerlos, S.J. and Zhao, F., "Economic Considerations in the Implementation of Microfiltration for Metalworking Fluid Biological Control", *Journal of Manufacturing Systems*, 22(3) 2003, pp. 202-219.
3. Bennett, E., "Minimizing Human Exposure to Chemicals in Metalworking Fluids". *Lubrication Engineering*, 1987: pp. 12-16.
4. Gorny, R.L., Szponar, B., Larsson, L., Pehrson, C., Prazmo, Z., Dutkiewicz, J., "Metalworking fluid bioaerosols at selected workplaces in a steelworks." *American Journal of Industrial Medicine*. 46 (4) 2004. pp. 400-403
5. Wells, S.L. and DeSimone, J., "CO₂ Technology Platform: An Important Tool for Environmental Problem Solving." *Angew. Chem. Int. Ed.*, 2001. 40: pp. 518-527.
6. DeSimone, J.M. and J.S. Keiper, "Surfactants and self-assembly in carbon dioxide. *Current Opinion in Solid State and Materials Science*." 2001. 5: pp. 333-341.
7. Yin, J. -Z, et al. "Experimental study on supercritical carbon dioxide fluid extraction of seed oil." *Huagong Xiandai/Modern Chemical Industry*. 2001. pp. 26-27
8. Diefenbacher, A. and M. Turk, "Phase equilibria of organic solid solutes and supercritical fluids with respect to the RESS process." *J. of Supercritical Fluids*, 2002. 22: pp. 175-184.
9. Simoes, P.C., Eggers, R., Jaeger, P.T., "Interfacial tension of edible oils in supercritical carbon dioxide." *European Journal of Lipid Science and Technology*. 102 (4): pp. 263-265
10. Reverchon, E.; Sesti Osseo, L., "Comparison of processes for the supercritical carbon dioxide extraction of oil from soybean seeds." *Journal of the American Oil Chemists' Society*, 1994, pp. 1007-1012
11. DeSimone, J.M., "Practical Approaches to Green Solvents." *Science*, 2002. 297: pp. 799-803.
12. Clarens, A.F., Zimmerman, J.B., Landis, H.R., Hayes, K.F., Skerlos, S.J., "Experimental Comparison of Vegetable and Petroleum Base Oils in Metalworking Fluids using the Tapping Torque Test." *Proceedings of the Japan/USA Symposium on Flexible Manufacturing*, Denver, Colorado, July 19-21, 2004.
13. James, Wes, "Soy Lubes: No. 1 With a Bullet", *Lubes and Greases*, 11(5), 2005, pp. 40-44.
14. Zimmerman, J. B., Clarens, A. F., Hayes, K.F., Skerlos, S.J., "Design of hard water stable emulsifier systems for petroleum and bio-based semi-synthetic metalworking fluids." *Environmental Science & Technology*, 2003, Vol. 37, pp. 5278-5288.
15. ANSI, ASTM D 5619: Standard Test Method for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine. 2000.
16. Zimmerman, J., Takahashi, S., Hayes, K.F., Skerlos, S.J., "Experimental and Statistical Design Considerations for Economical Evaluation of Metalworking Fluids Using the Tapping Torque Test." *Lubrication Engineering*, 2003. 59(3): pp. 17-24.
17. Childers, J., *The Chemistry of Metalworking Fluids*, in *Metalworking Fluids*. 1994, Marcel Dekker: New York. pp. 165-190.

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参考文献

1. Zimmerman, J., Hayes, K., Skerlos, S.J., 《离子类型与浓度对两种半合成金属加工液乳化稳定性及加工性能的影响》，《环境科学与技术》，2003年，第38卷，第2482-2490页。
2. Skerlos, S.J. 与 Zhao, F., 《微滤技术在金属加工液生物控制中的经济考量》，《制造系统杂志》，2003年第22卷第3期，第202-219页。
3. Bennett, E., 《降低金属加工液中化学物质对人体暴露量》。《润滑工程》，1987年：第12-16页。
4. Gorny, R.L., Szponar, B., Larsson, L., Pehrson, C., Prazmo, Z., Dutkiewicz, J. “钢铁厂特定工作场所中的金属加工液生物气溶胶研究”。美国工业医学杂志. 46(4): 2004. 第400-403页。
5. Wells, S.L. 和 DeSimone, J., 《CO₂技术平台：解决环境问题的重要工具》。《德国应用化学国际版》，2001年，第40卷：第518-527页。
6. DeSimone, J.M. 与 J.S. Keiper, “二氧化碳中的表面活性剂与自组装现象. 固体与材料科学前沿观点.” 2001. 5: 第333-341页。
7. Yin, J. -Z., 等. “超临界二氧化碳流体萃取种子油的实验研究.” 华工现代/现代化工. 2001. 第26-27页。
8. Diefenbacher, A. 与 M. Turk, “有机固溶质与超临界流体在RESS过程中的相平衡研究.” 超临界流体杂志, 2002. 22: 第175-184页。
9. Simoes, P.C., Eggers, R., Jaeger, P.T., “食用油在超临界二氧化碳中的界面张力.” 《欧洲脂质科学与技术杂志》102卷第4期：第263-265页
10. Reverchon, E.; Sesti Osseo, L., 《大豆种子中超临界二氧化碳萃取油脂工艺的比较研究》。美国油脂化学家学会杂志, 1994年, 第1007-1012页。
11. DeSimone, J.M., 《Practical Approaches to Green Solvents》。《科学》，2002年，第297卷：第799-803页。
12. Clarens, A.F., Zimmerman, J.B., Landis, H.R., Hayes, K.F., Skerlos, S.J., “采用拧紧扭矩试验对金属加工液中植物油与石油基油的实验比较。” 日美柔性制造研讨会论文集, 科罗拉多州丹佛市, 2004年7月19-21日。
13. 詹姆斯·韦斯, 《Soy Lubes : 一枪夺魁》，《润滑油与润滑脂》，2005年第11卷第5期，第40-44页。
14. Zimmerman, J. B., Clarens, A. F., Hayes, K.F., Skerlos, S.J., 《石油及生物基半合成金属加工液用硬水稳定乳化剂系统设计》，《环境科学与技术》，2003年，第37卷，第5278-5288页。
15. ANSI, ASTM D 5619: 采用转矩测试机比较金属去除液的标准试验方法。2000年。
16. Zimmerman, J., Takahashi, S., Hayes, K.F., Skerlos, S.J., 《采用扭矩测试法对金属加工液进行经济性评估的实验与统计设计考量》，《润滑工程》，2003年第59卷第3期，第17-24页。
17. Childers, J., 《金属加工液 The Chemistry》，载于《金属加工液》1994年版, Marcel Dekker出版社: 纽约, 第165-190页。

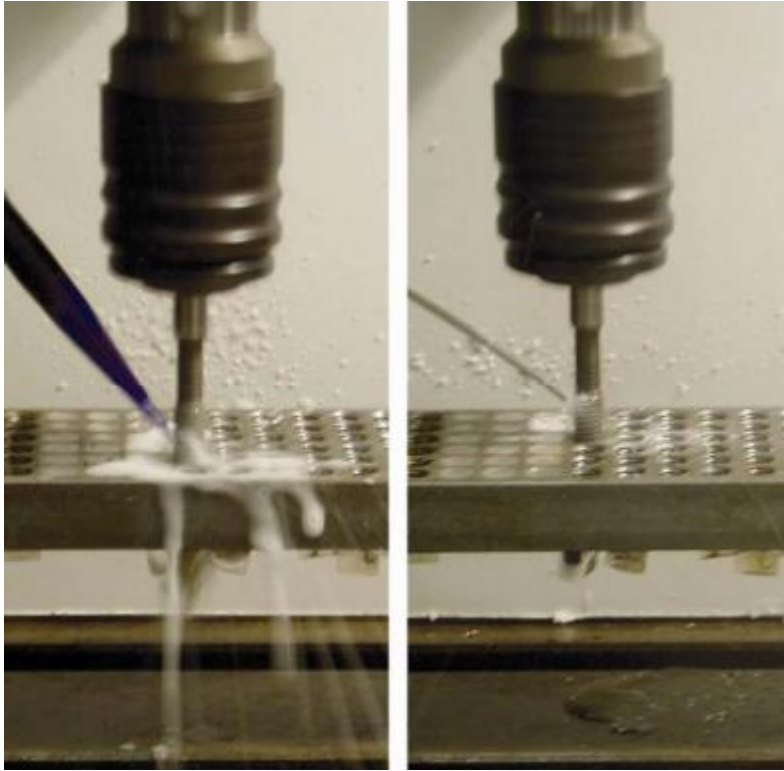


Figure 1. Images of tapping experiments using spray application of MWF microemulsion (left) and rapidly expanding supercritical carbon dioxide (scCO₂) solution (right).

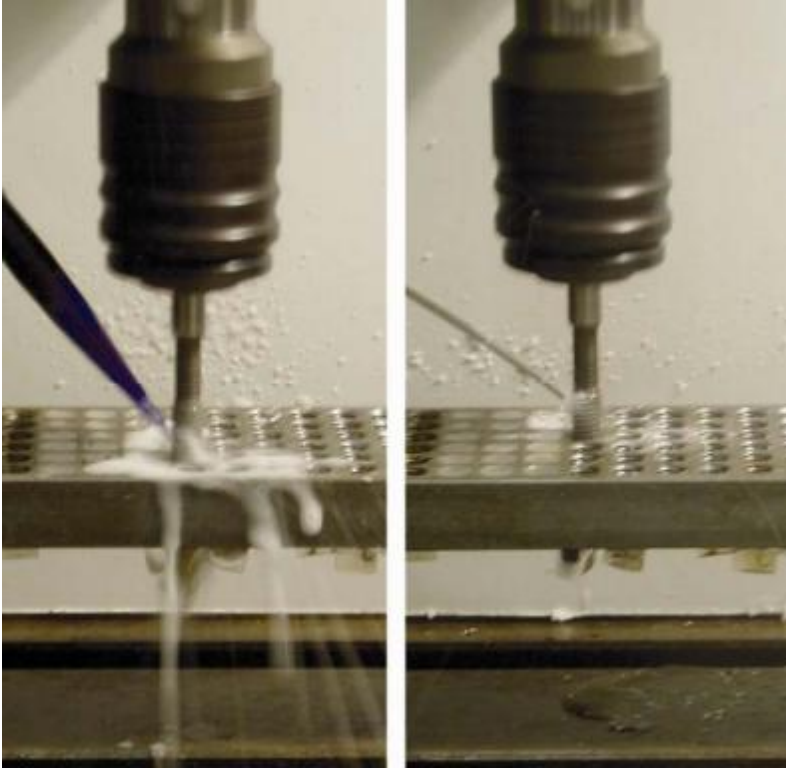


图1. 使用喷雾施加 MWF 微乳液（左）和快速膨胀的超临界二氧化碳（scCO₂）溶液（右）进行敲击实验的图像。

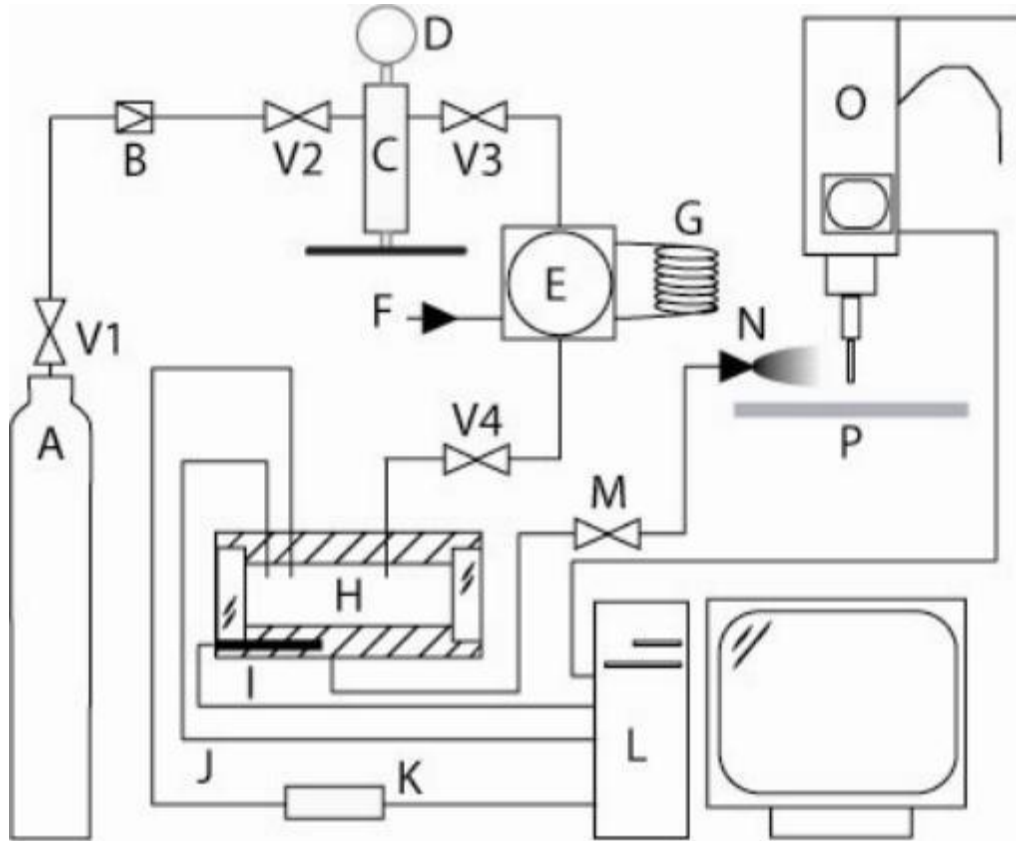


Figure 2. scCO_2 testbed: A. Tank of food-grade carbon dioxide; B. Check valve; C. Pressure booster; D. Pressure gauge; E. Six-way valve; F. Oil inlet; G. Fixed volume coil; H. High-pressure vessel; I. Heating element; J. Thermocouple; K. Pressure transducer; L. Computer; M. Solenoid valve; N. Nozzle;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

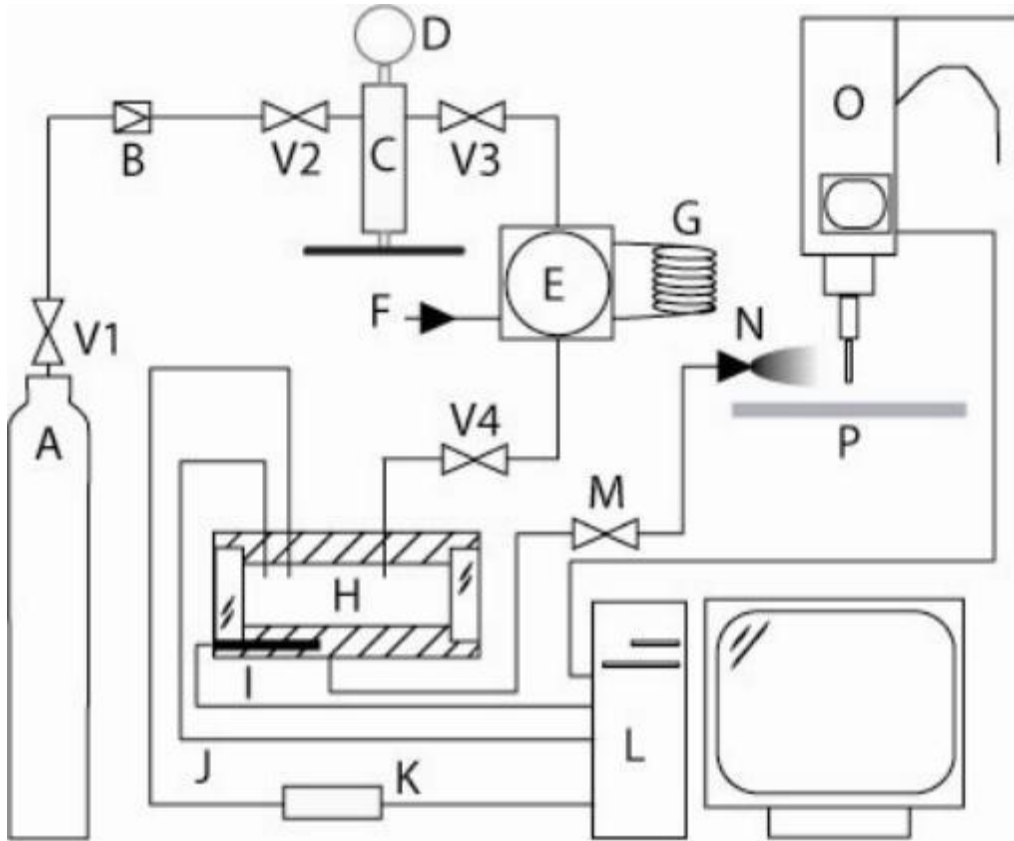


图2.scCO₂测试平台：A. 食品级二氧化碳储罐；B. 止回阀；C. 压力增压器；D. 压力表；E. 六通阀；F. 油液入口；G. 固定容积线圈；H. 高压容器；I. 加热元件；J. 热电偶；K. 压力传感器；L. 计算机；M. 电磁阀；N. 喷嘴；O. 扭矩攻丝机床；P. 工件；V1-3. 钉阀。

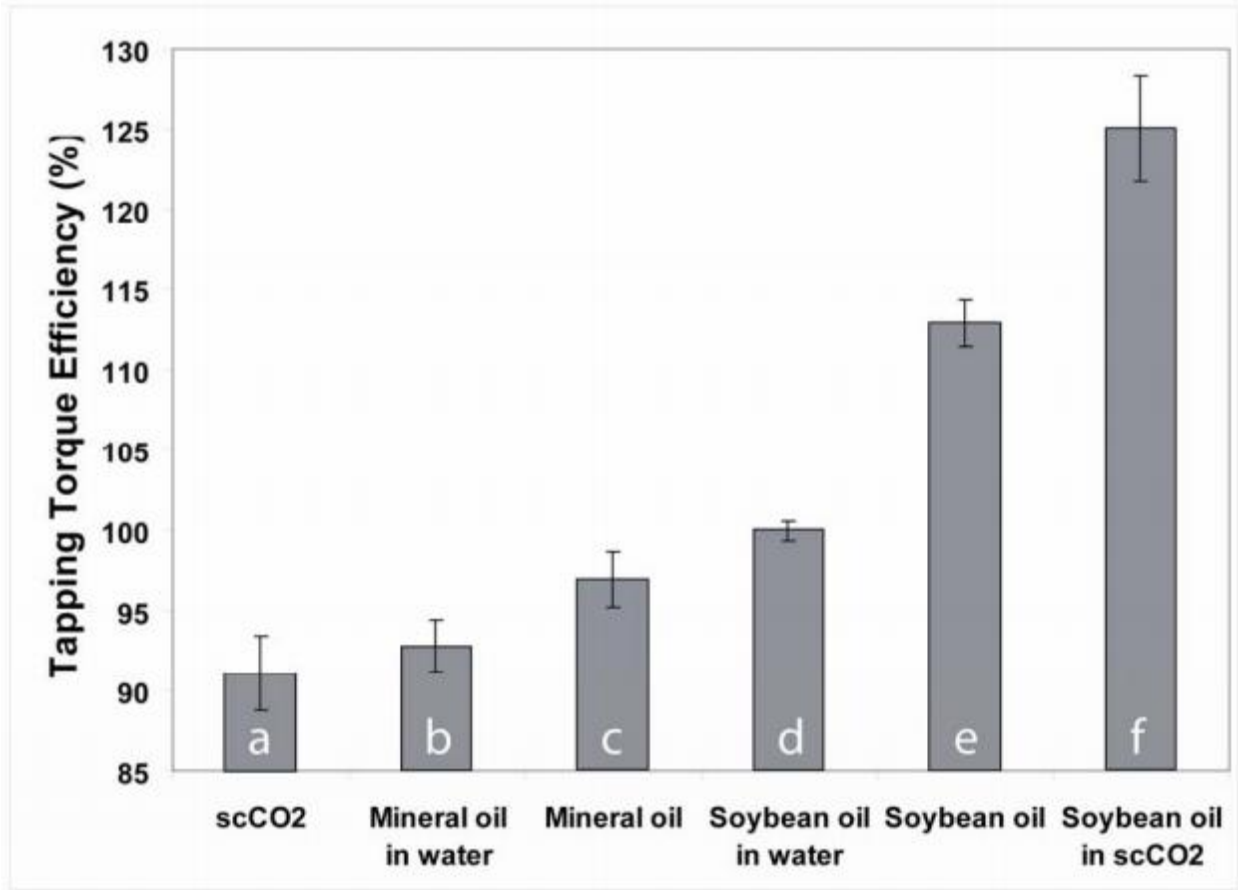


Figure 3. Tapping torque efficiency for straight oil, water-, and scCO₂-based MWFs. Letters correspond to electron microscopy images in Figure 4.

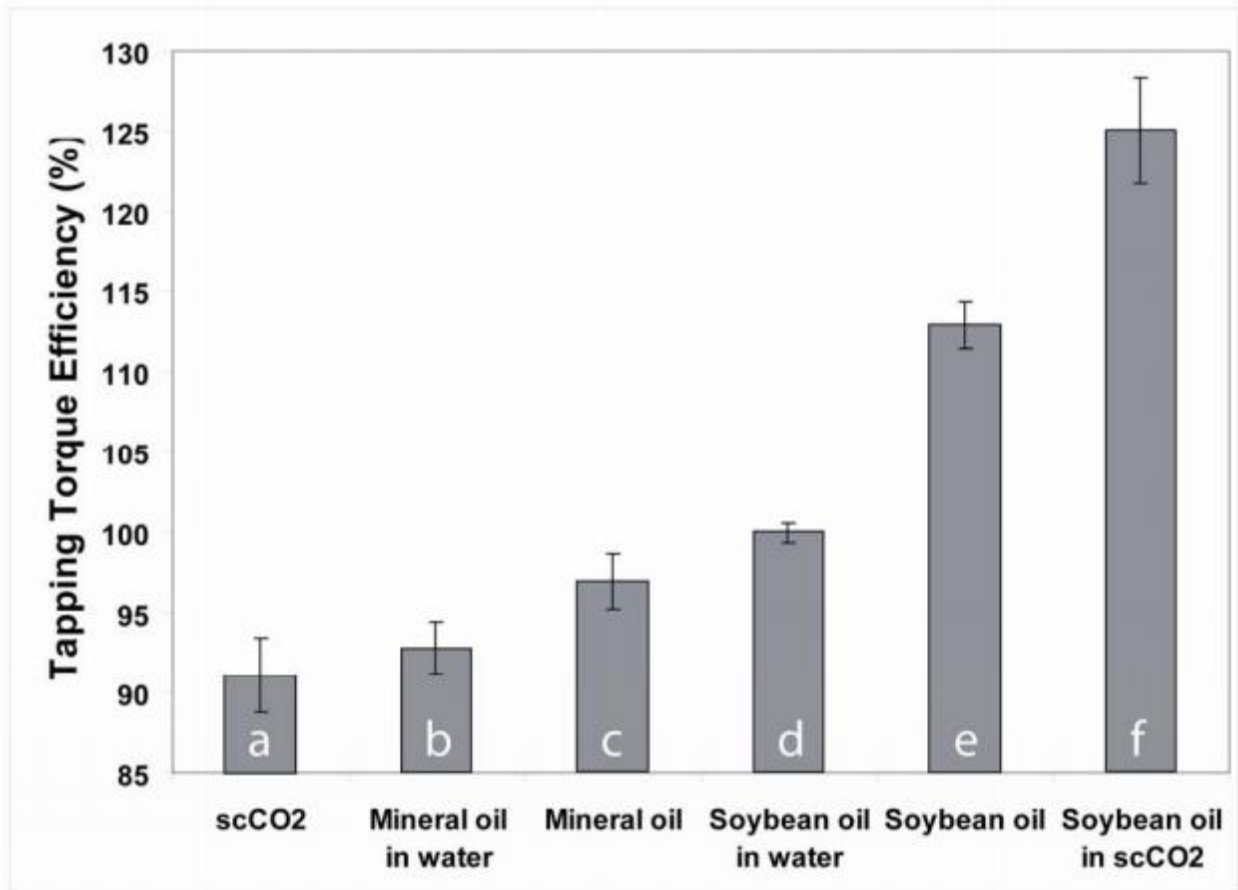


图3. 直接油基、水基及scCO₂基混合水基燃料（MWFs）的抽吸扭矩效率。字母对应图4中的电子显微镜图像。

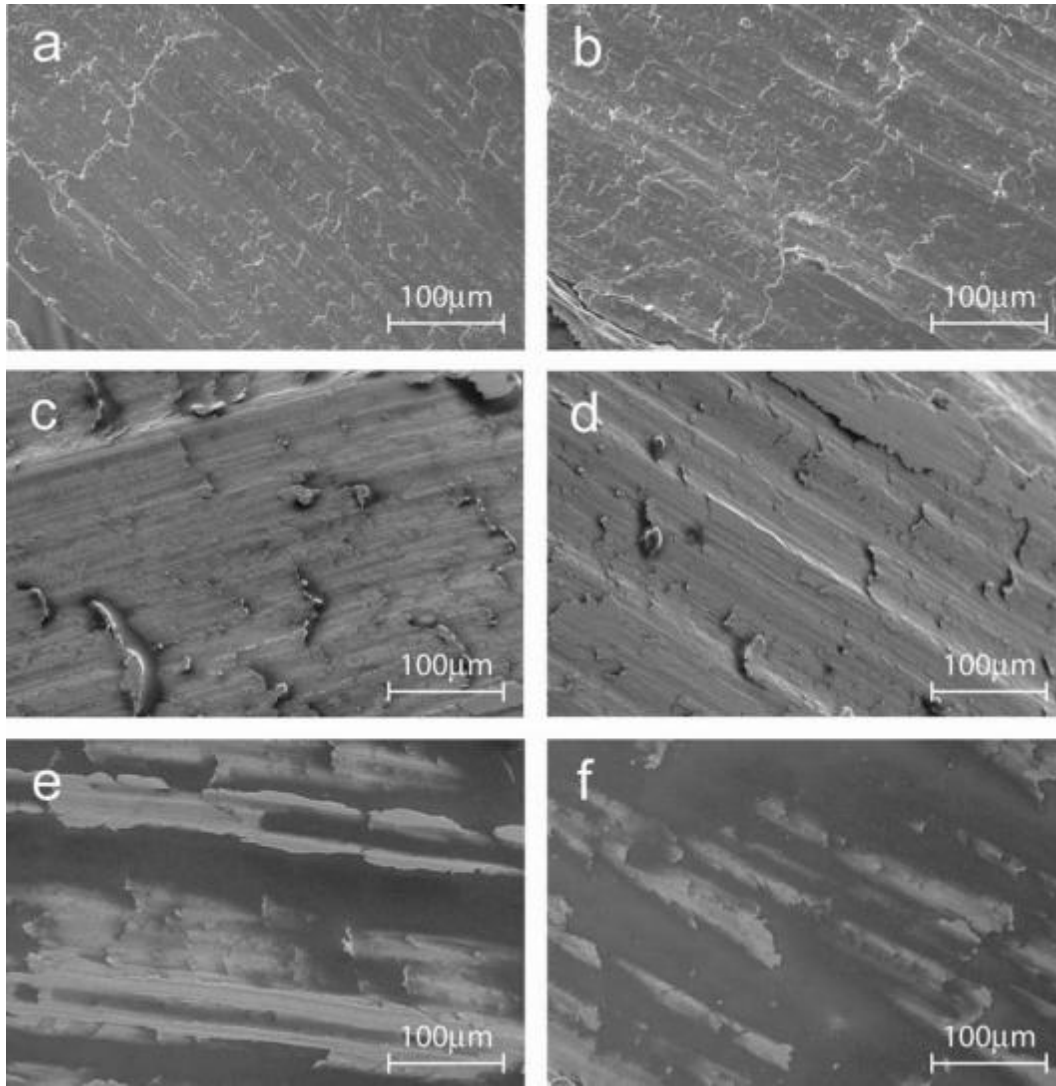


Figure 4. Magnified images of chip surfaces cut from 1018 cold rolled steel during tapping using a) scCO_2 alone, b) mineral oil in H_2O , c) straight mineral oil, d) soybean oil in H_2O , e) soybean oil alone, and f) soybean oil in scCO_2 .

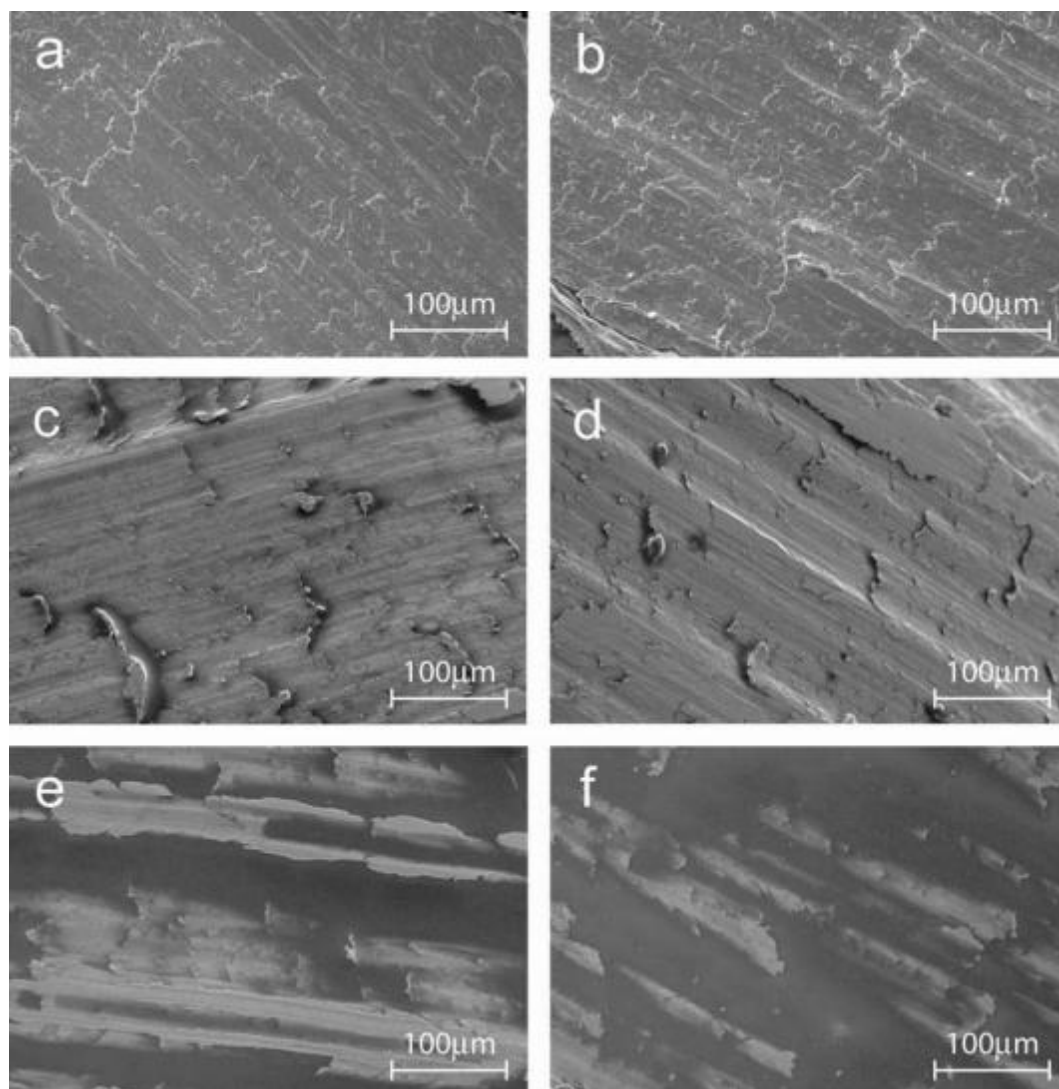


图4. 1018冷轧钢在攻丝过程中切割的芯片表面放大图像，分别采用以下处理方式：a)仅scCO₂；b)矿物油在H₂O中；c)普通矿物油；d)大豆油在H₂O中；e)仅大豆油；f)大豆油在scCO₂中。

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).

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%		

表1. MWF 配方（所有百分比均为重量百分比）。所列表面活性剂包括TagatV20非离子表面活性剂（德国赛-戈尔施密特化学公司，美国弗吉尼亚州霍普韦尔）、Tomadol91-6非离子表面活性剂（Tomah公司，美国威斯康星州米尔顿）以及Dowfax3B2阴离子表面活性剂（陶氏化学公司，美国密歇根州米德兰）。