SHOT-PEENING-BASED MECHANO-CHEMICAL SURFACE MODIFICATION FOR FRICTION AND WEAR REDUCTION IN CUTTING TOOLS

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SHOT-PEENING-BASED MECHANOCHEMICAL SURFACE MODIFICATION FOR FRICTION AND WEAR REDUCTION IN CUTTING TOOLS

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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>BUE</td>
<td>built-up edge</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat capacity</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>EDM</td>
<td>electrical discharge machining</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>$E_f$</td>
<td>energy barrier between two equilibrium states</td>
</tr>
<tr>
<td>$F$</td>
<td>external force</td>
</tr>
<tr>
<td>FEM</td>
<td>finite element method</td>
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<tr>
<td>HSS</td>
<td>high-speed steel</td>
</tr>
<tr>
<td>$I$</td>
<td>internal heat generation rate per unit volume</td>
</tr>
<tr>
<td>$K$</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate</td>
</tr>
<tr>
<td>$L$</td>
<td>typical length of reactant region</td>
</tr>
<tr>
<td>$m_1$, $m_2$</td>
<td>atomic mass</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>$R_a$</td>
<td>arithmetic mean deviation of linear roughness</td>
</tr>
<tr>
<td>Ref</td>
<td>reference</td>
</tr>
<tr>
<td>$S_a$</td>
<td>arithmetic mean deviation of areal roughness</td>
</tr>
<tr>
<td>$S_k$</td>
<td>core roughness depth of areal roughness</td>
</tr>
<tr>
<td>$S_{pk}$</td>
<td>reduced peak height of areal roughness</td>
</tr>
<tr>
<td>$S_{vk}$</td>
<td>reduced valley height of areal roughness</td>
</tr>
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</table>
SD  standard deviation

SEM  scanning electron microscope

SP  shot peening

$T$  absolute temperature

$T_i$  initial temperature

$T_m$  melting temperature

$T_r$  temperature above which lubrication is working at harsh conditions

TEM  transmission electron microscope

$t$  transient time

$\mu$  reduced mass representing the "effective" mass in the two-body problem

$v$  particle speed

WC  tungsten carbide

$w$  work of deformation per unit volume

$\Delta V$  activation volume, the activation length multiplied by the area over which the applied stress acts

$\Delta x$  activation length, a distance from the initial to the transition state during chemical reaction

$\varepsilon$  normal force per unit length

$\theta$  particle impact angle

$\rho$  density

$\sigma$  von Mises stress
SUMMARY

In machining processes, higher friction and wear can result in more frequent tool replacement, higher energy consumption, lower dimensional accuracy, and inferior surface quality. Therefore, methods to modify cutting tool surfaces to improve their tribological performance, thus leading to more sustainable and efficient machining, are of great importance to the manufacturing industry and to the research community. Here, a mechano-chemical surface modification was proposed to improve cutting tools’ performance. The approach consists of modifying the rake faces of cutting tools through localized plastic deformation of the near-surface region accompanied by a simultaneous exposure to a proper chemical precursor. Shot peening with a mixture of Al₂O₃ and Cu₂S particles, with the former serving as the mechanical agent that enhances the chemical reactivity of the surface through plastic deformation and the latter serving as a chemical precursor, was utilized to form a lubricious layer on the cutting tool surfaces.

The potential and capability of the shot-peening-based mechano-chemical surface modification of cutting tools were explored both theoretically and experimentally in the following way. 1) A deterministic model including stress, temperature, and reaction rate simulations was developed to estimate the kinetics of mechano-chemical reaction between Cu₂S and Fe thus providing theoretical support of the proposed modification technique. 2) The effects of critical surface modification parameters on the surface chemistry, topography, and hardness were studied and correlated to the machining performance of high-speed steel (HSS) cutting tools. 3) The effect of mechano-chemical surface modification of HSS cutting tools on the reduction of cutting forces was investigated and
supplemented with the analysis of surface chemistry and topography. 4) The wear resistance of mechano-chemically modified HSS tools was examined along with the corresponding changes in the surface properties. 5) Tungsten carbide (WC) inserts were mechano-chemically modified to examine cutting forces and tool wear with respect to the chemical composition, roughness and residual stresses of the tested tool surfaces.

The shot-peening-based mechanochemical modification was experimentally proved to be able to decrease cutting and thrust forces of HSS tools. Reaction kinetics of dissociation of Fe-Fe and Cu-S bonds prior to formation of FeₓSᵧ was successfully simulated by the reaction rate model with respect to particle speed and impact angle, demonstrating a local optimum impact angle around 75 deg that was validated by cutting experiments. The mechanochemically modified HSS tools were found to extend the tool wear life twofold compared to the reference tools; this explained by the hints of presence of iron sulfide known to improve oil-retaining ability. WC inserts demonstrated to be insensitive to the suggested mechanochemical surface modification but assisted in demonstrating the synergetic effects of surface topography and residual stresses on cutting forces and tool life.
CHAPTER 1.  INTRODUCTION

1.1 Motivation

Machining is defined as a process in which a cutting tool is used to remove material from the workpiece in order to achieve desired surface finish and dimensional accuracy. Machining processes are favorable and necessary in manufacturing operations since parts manufactured by primary shaping and deformation processes often require further processing to impart specific characteristics, such as certain dimensional accuracy, surface finish, and special geometric features, before the product is ready to use.

Cutting tools are indispensable in machining operations, and it shows in the global market volume of cutting tools, which, for instance, was equal to 16.33 billion US dollars in 2013 [1]. These costs are mainly determined by the requirement of frequent tool replacement due to wear and chipping. It is well known that cutting tools are subjected to high normal and frictional stresses when in operation and they are pushed to the limits by increasing productivity through increased cutting speeds. The mechanical energy dissipated in the cutting zone is transformed into heat, and rising temperature induces interface adhesion and facilitates tool wear. In addition, new structural materials with superior properties are continuously developed and extensively used in modern industry. These materials are characterized by high hardness and strength, and low thermal conductivity, which adversely affects the strength, hardness, and wear resistance of cutting tools during machining, while worn tools make control of dimensional accuracy difficult, and cause thermal damage to the machined surface. Therefore, studies on friction and wear of cutting
tools are highly needed to minimize tool replacement and energy consumption, while achieving higher dimensional accuracy, and better surface quality of machined parts.

1.2 Literature Review

1.2.1 Cutting tools

It is well known that modification of tribological properties of cutting tools could significantly improve the machining quality and efficiency. Surface texturing and coating have been demonstrated as reliable techniques to enhance the functional properties of cutting tools.

Texturing the tool rake face (defines the tool-chip interaction) is reported to be a successful approach for improving cutting performance, and it has been applied in a variety of cutting processes including turning [2, 3], drilling [4, 5], and milling [6, 7]. Regular surface textures generally feature micro-patterns based on dimples [8], and parallel or crossed grooves with various orientations [9] (Figure 1-1), which can be fabricated by electrical discharge machining (EDM) [10], laser machining [9] and electrochemical etching [11]. It was shown that a nanoscale texture oriented perpendicularly to the chip flow can decrease cutting force by altering the adhesion of an Aluminum alloy workpiece to cemented carbide tools (WC-Co) [8]. Similar behavior was found by 3D finite element modeling, indicating that perpendicular surface texture shows better stress and temperature distributions when machining Titanium alloy (Ti-6Al-4V) [12]. Surface textures fabricated on the flank faces (define the tool-workpiece interaction) of coated carbide tools exhibit lower flank wear and better surface finish compared to non-textured tools, due to reduced tool-workpiece contact area and lower temperature at the interface [13]. Tungsten carbide round inserts with
dimple textures on the rake face and square pyramidal textures on the flank face demonstrate the lowest flank wear compared to inserts textured with dimples or square pyramids alone, which increased tool life by approximately 30% over non-textured inserts [14]. Simpler irregular surface textures with stochastic topographies have been also fabricated on the tool rake surfaces by EDM [15] and shot peening (SP) [16], and they were shown to improve cutting tool performance as well. Furthermore, the irregular surface textures produced by EDM have been shown to reduce cutting forces more than the regular textures created by the same technique [15].

![Figure 1-1. Textures on tool rake faces with grooves of different orientations [8] (a-c), and textures of micro-dimples [9] (d).](image)

Cutting tools with hard coatings have been successfully employed in industry for almost 50 years. Fabrication of coatings using chemical vapor deposition (CVD) [17], physical vapor deposition (PVD) [18], or their combinations [19] can increase cutting performance
by supplementing the surface with a layer of higher hardness and wear resistance. The most widely used cemented carbide tools are generally coated with a material consisting of nitrides (TiN, TiAlN, CrN, etc.), carbides (TiC, CrC, W2C, WC/C), oxides (Al2O3) or combinations of these [20-22] (Figure 1-2). Al2O3-coated cemented carbides are very popular for turning operations [23], and their low adhesion tendency protects against adhesive wear; however, it also prevents good adhesion of the coating to the tool substrate. Another promising CVD coating is diamond, which is able to cut carbon fiber reinforced polymer (CFRP) [24] and ceramic. TiAlN was introduced 30 years ago and became the most important PVD coating system, and even today acts as the base of numerous PVD developments [25, 26]. To improve the resistance to wear and failure, multi-layered nano-structured or nanocomposite coatings were developed on carbide cutting tools [27] and high-speed steel tools [28]. Soft coatings in the form of solid lubricants have been also deposited on cutting tools to improve their performance by reducing friction. MoS2, which is well known for its lubrication properties [29], has been applied to cutting tools by magnetron sputtering [30] and by filling laser-machined grooves [31], which improved tool life in dry cutting applications. Deposition of WS2 films on the laser-textured rake surfaces using PVD [32, 33] has been also demonstrated to improve cutting tool performance.

Even though surface texturing and coating are reported as being effective for improving cutting performance and extend wear life of machining tools, they all have high manufacturing cost. Furthermore, surface textures fabricated by laser or EDM introduce detrimental tensile residual stress on the surface due to material re-melting [34]. In addition, surface coatings may suffer from binding problems to the tool substrate, which result in failure of the coating.
1.2.2 Lubrication

Except for surface modification of cutting tools, a widely applied methodology to improve cutting performance is lubrication. The purpose of lubrication is to introduce a low-shear-strength film between the moving surfaces, so the relative displacement is accommodated within this film, while the base material is not disturbed [36, 37]. Depending on the thickness of this film, it is possible to distinguish between (a) full film lubrication whose performance is determined by the internal friction of the lubricant due to complete separation between the surfaces, (b) boundary lubrication whose performance is determined by the physico-chemical interactions at the base material/lubricant interface.

Figure 1-2. Characteristic coating architectures on cutting tools [35].
due to contact between the surfaces, and (c) mixed lubrication whose performance is affected by both abovementioned modes of lubrication. It is well known that boundary lubrication, which is characterized by the highest friction, is unavoidable in many practical cases, so the surface performance in this regime is of great importance in engineering practice [38]. Cutting processes are typically under boundary lubrication due to high stresses and temperature at tool-chip interface.

Figure 1-3 presents stylized diagrams of the frictional behavior of various boundary films on metal surfaces [37, 39] under the conditions of temperature decrease, which corresponds to an increase in the Sommerfeld number (increase in lubricant viscosity at constant normal load and sliding speed). Curve I represents a system lubricated with nonpolar base oil. Curve II represents a system lubricated with oil having an oiliness additive, such as fatty acid, alcohol or ester, which forms a metal soap that is able to work below the melting temperature $T_m$. When the contact is subjected to extreme loading conditions, $T_m$ is exceeded and the bonds between oil molecules and the metal substrate break, so oil is removed and substrate materials are exposed to contact, which results in high friction. Curve III represents a system lubricated with an oil having an extreme conditions additive, such as sulfur, chlorine or phosphorus (among them—famous WS$_2$, MoS$_2$ and ZDDP), which reacts to form a stable low-shear-strength oil-retaining layer [40-42] on the surface after $T_r$ is exceeded at harsh working conditions. The extreme conditions additive, however, also stops functioning at a certain high temperature. The question of interest is whether a surface layer with a performance of an effective combination of II and III (curve IV) can be formed in a direct, simple and controlled way, as an alternative to the use of oil additives. An affirmative answer to this question may lead to a paradigm shift in surface
engineering. Thus, the ability to introduce tribologically beneficial metal-salt films during manufacturing instead of using their constituents as lubricant additives, which are expensive and environmentally hazardous [43], presents a significant interest. Utilizing mechanochemical processes may serve as a potentially useful approach that can be examined in this respect. There are also other possible techniques such as electrochemistry [44], but mechanochemical modification is probably the most flexible one.

![Figure 1-3. Schematic of unreduced Strubeck curve (constant load and speed) of boundary lubrication system. Curve I nonpolar base oil. Curve II oil having an oiliness additive. Curve III oil having an extreme condition additive. Curve IV ideal hypothetical oil. Redrawn from [37, 39].](image)

1.2.3 Mechanochemistry

Mechanochemical reaction is a process in which chemical interactions are assisted by mechanical activation, with rubbing pieces of wood to make fire being probably the first example of its technical use. Unlike the traditional way of dissolving, heating, stirring
chemicals in solutions, mechanochemistry does not rely on many solvents and allows to synthesize chemical products only through mechanical activation, which enables the chemical processes used by industry to be more environmentally friendly. Nowadays, it is widely employed in organic [45, 46] and inorganic [47, 48] chemical syntheses, and application of mechanochemistry is reported in various disciplines ranging from biology [49-51] to tribology [52, 53].

A few examples of this phenomenon can be mentioned. Solid-particle erosion is known to increase dramatically oxidation rates [54]. Ball milling leads to initiation and acceleration of displacement reactions [55]. Chemical reactions, which would normally require high temperatures can occur at low temperatures in a ball mill without any need for external heating [56]. Due to the process of particle deformation and fracture that accompanies repeated ball-powder collision events, nanoparticles whose properties differ substantially from those of bulk material can be synthesized [57].

Mechanochemical reactions are stress-induced processes in which the energy landscape is modified by an external force to reduce the energy barrier, where the transition over the modified energy barrier is thermally assisted and thus depends on temperature. Mechanochemical kinetics is often described by reaction rate theory where reaction rate exhibits an exponential relationship with respect to activation energy [58] which is reduced by work from an external force. It was first used to model crystal plasticity [59] and subsequently to explain material fracture [60], rubber friction [61], and atomic scale friction [62] and wear [63].
Reaction rate theory describing modification of the energy barrier between metastable chemical states has been successfully applied to explain mechanochemical reaction in removal as well as in growth of surface layers during normal and shear loading of nanoscale contacts [53, 64, 65]. The rate of mechanochemical decomposition of methyl thiolate species adsorbed on Cu (100) was found to correlate well to the energy dissipated in indentation experiments performed using an atomic force microscope (AFM) probe in ultrahigh vacuum [64]. In a combined normal and shear loading, a Si AFM probe sliding against a diamond substrate in a transmission electron microscope has exhibited wear rate corresponding to the rate of a stress-assisted chemical reaction shown in Figure 1-4(a) [53]. Sliding a DLC-coated Si AFM probe against an iron oxide surface in a ZDDP-containing lubricant resulted in the surface film growth with the rate that increased exponentially with either applied stress or temperature, also consistent with the reaction rate theory shown in Figure 1-4(b) [65].

![Figure 1-4](image.png)

**Figure 1-4.** Reaction rate due to wear loss as a function of average contact stress shown in (a) [53] and tribofilm growth rate as a function of contact pressure shown in (b) [65].
Considering that mechanochemistry is widely applied in industry, we should be able to find out an appropriate mechanical process through which tribologically beneficial metal salt films can be produced.

1.2.4 Shot peening

Shot peening is a cold working process used to produce a compressive residual stress layer and modify the mechanical properties of metals and composites by striking a surface with shots (metallic, glass, or ceramic particles) to create plastic deformation. As one of the most flexible mechanical surface treatments, shot peening has been widely used to improve the fatigue life of engineering components made of metals and alloys by refining the microstructure [66] and inducing the compressive residual stress [67] in the near-surface regions where fatigue failure usually initiates. At the same time, shot peening can harden the treated surface where the localized plastic deformation occurs as the shot balls impact on it [68]. These advantages improved the surface finish of workpiece after milling and turning and reduced cutting forces and tool wear [16].

As an effective way of inducing compressive residual stresses, shot peening is one of surface pretreatments such as PVD pre-coating process applied to carbide cutting tools. Rake faces of uncoated carbide cutting inserts were shot peened with two different shot media, S330 and SCCW14, and the compressive residual stress depth distribution was studied as a function of various shot peening parameters [34], as shown in Figure 1-5. Increasing the shot peening gas carrier pressure can further the compressive residual stress under the treated surface but little additional effects are observed after the pressure raises
over 3 bar. However, residual stresses and work hardening effect introduced by shot peening relax in many cases such as at high temperature or in cyclic loading environment.

Thermal stability of compressive residual stress and work hardening in the near-surface region of shot peened WC was evaluated at elevated temperatures to optimize the shot peening parameters employed in surface strengthening of cemented carbides [69]. Even though the compressive residual stresses and microhardness reduced sharply with increased temperature and annealing time, they gradually levelled to the stable state (Figure 1-6 and Figure 1-7). Interestingly, the residual stresses in WC and Co phases remained at compressive state under temperature of up to 850 °C suggesting that the shot peened WC-Co composite has good thermal stability when the shot peening parameters are optimized. It is of great importance to cutting tool fatigue life since machining processes are always under high stresses and temperature rise [70].

Figure 1-5. Residual stress depth distributions after shot peening with S330 (a) and SCCW14 (b) [34].
Figure 1-6. Residual stress relaxation in WC (a) and Co (b) phase as a function of heating temperature and annealing time [69].

Figure 1-7. Line profiles of microhardness at the surface with the increasing heating temperature and annealing time [69].

Shot peening is a good approach to eliminate the tensile stress of welding. It can also eliminate the surface defects and result in stain strengthening and fine grain strengthening. All these factors contributed to the significant improvement in mechanical properties of the Mg/Ti joints [71]. Nanostructured surface layers on low alloy steel can be achieved under severe shot peening and the grain refinement were observed under electron microscopy shown in Figure 1-8 [66]. The grain refinement evolution resulted from shot
peening is also accompanied with element diffusion and chemical kinetics. For example, nitriding kinetics in low-temperature plasma nitriding of Ti-6Al-4V was enhanced by a severe plastic deformation layer [72]. A 0.6 µm thick nanocrystalline TiN layer followed by a 0.5 µm thick layer of Ti$_2$N (grain size 0.1-0.5 µm) was formed and it was attributed to accelerated nitriding process due to the increased preferential nucleation sites in the severe plastic deformation. The thickness of nitrogen diffusion zone increased by 50% when compared to that of the untreated sample. Thus, shot peening has a good potential to accelerate diffusivity and chemical reactivity through plastic deformation, which makes it a reasonable choice to try tailoring surface chemistry towards improved tribological properties.

Developing a model to analyze the process of shot peening is useful to predict the material state after peening without having to conduct costly experiments and to be able to optimize peening processes. Shot peening can be seen as a multiple and progressively repeated elastic-plastic interaction between the surface and the shots. For a large and thin plate, a radial disturbance is propagated outwards after normal impulsive forces applied on the center which remains stationary until the return of the disturbance reflected from the boundary of the plate [73]. When impact occurs between two elastic bodies, the kinetic energy becomes elastic energy stored in the two bodies and energy for elastic wave to propagate. If the kinetic energy is high enough, plastic deformation occurs. For low velocity impact, the energy lost in plastic deformation and elastic wave is negligible. As impact velocity is increased, more energy lost in plastic deformation and elastic wave is expected. Assuming the effect of elastic wave propagating away from the contact is neglected, the lost kinetic energy is transformed into energy of plastic deformation. This
makes it possible to simulate the single impact by a loading model (impacting process to maximum deformation) and unloading model (detachment of the sphere from the surface). The elastic unloading model is based on the Hertz solution while the loading process can utilize an elasto-plastic contact model. Most of such models including Johnson model [74], Chang-Ling model [75], Tabor model [76], and Jackson-Green model [77] simulate the coefficient of the restitution (rebound velocity over incident velocity), contact interference, and elasto-plastic energy.

**Figure 1-8.** Cross section SEM and TEM micrographs taken at various depths of the treated specimens [66].
To simulate surface roughness, surface hardening, and stress and strain state from a single dynamic impact or multiple impact processes with random oblique angle, explicit module or solver of FEM software tools is a better choice for 3D models. ANSYS LS-DYNA has been used to simulate a single impact process with different impact angle to find the distribution of residual stress and plastic strain along the depth, and ANSYS APDL can generate the random coordinates of each shot to simulate the peening coverage and surface roughness of multiple impact processes [78]. ABAQUS/EXPLICIT was utilized to investigate effects of multiple impacts on residual stresses, surface work hardening, and formation of nanostructured layer based on equivalent plastic strain, predicting the shot peening conditions that lead to surface nanocrystallization.

Numerical simulation of shot peening proves that shot peening converts kinetic energy to energy of plastic deformation, which can lower the energy barrier of chemical reaction. The grain refinement resulted from shot peening demonstrates that the existence of dislocation or other lattice defects facilitates diffusion and chemical reactions.
1.3 Research Objectives

Shot peening results in extensive plastic deformation of the near-surface region, leading to an anomalous acceleration of diffusion activity and chemical kinetics. This happens through mechanical stimulation by heat and by the rupture of atomic bonds (or increase in interatomic distance). To this end, supported by an analysis of possible surface states [68], we hypothesize that, by introducing tribologically beneficial reactive compounds containing sulfur in the immediate environment while shot peening process is activating the treated surface, stable metal-salt films of $\text{Fe}_x\text{S}_y$ can be formed in advance. Due to chemical affinity of sulfur to oil molecules [79], sulfur is widely used as an oil additive that can form anti-oxidation and friction-lowering compounds. Hence, the mechanochemically modified surface layer is expected to perform as well as or better than the system shown in curve IV on Figure 1-3. This hypothesis has been partially proved by tribological testing in previous research work [69]. A cast iron surface peened with a mixture of $\text{Al}_2\text{O}_3$ and $\text{Cu}_2\text{S}$ particles showed a friction coefficient of 0.01 when lubricated with base oil, while the reference surface demonstrated a friction coefficient of 0.1. However, the contact pressures and temperatures in cutting are at least two and one orders of magnitude (respectively) higher than those of previous testing. It is still an open question whether mechano-chemically modified tools can operate properly in these harsh conditions.

Considering the success of the reaction rate theory at the nanoscale, an implementation of this approach for the analysis of the processes taking place at a larger scale represents a remarkable interest. Hence, it is desirable to simulate and study the shot-peening-based mechano-chemical surface modification using the reaction rate theory.
In light of the above, the research goal is to investigate the potential and capability of the shot-peening-based mechano-chemical surface modification for application in cutting tools. To achieve this goal, the following research objectives were defined.

(1) Estimating cutting performance of treated HSS tools in terms of reduction of cutting forces, which are known to be affected by the change of friction and lubricity at the tool-chip interface.

(2) Developing a theoretical model able to simulate the reaction kinetics of dissociation of Fe-Fe and Cu-S bonds prior to the chemical reaction between S and HSS substrate in terms of different particle speed and impact angle.

(3) Validating the model simulations through cutting experiments of HSS tools shot peened with three different parameters (particle volume ratio, stage speed, and impact angle).

(4) Experimentally estimating the extension of HSS tool wear life by the mechanochemical surface modification.

(5) Identifying the mechanism of mechanical and chemical transformations underlying the formation and preservation of S-containing surface layers of high lubricity needed to reduce friction, temperature, and wear.

(6) Exploring the applicability of the mechanochemical surface modification to WC inserts with respect to the chemical composition, roughness, residual stresses and hardness of the modified surfaces.
A mechanochemical reaction is a stress-assisted transition from one stable equilibrium state to another, in which an external force reduces the energy barrier between the two states and the transition is activated thermally. For a one-dimensional atom-transfer reaction, \( A + BC \rightarrow AB + C \) (in our case, \( Fe + Cu_2S \rightarrow FeS + 2Cu \)), the reaction rate is given by

\[
k = L^{-1} \left( \frac{2\pi \mu}{k_B T} \right)^{-\frac{1}{2}} \exp \left( \frac{-E_T}{k_B T} \right)
\]

(2-1)

where \( L \) is the typical length on the side of the reactant region, \( \mu \) is the reduced mass \((\mu^{-1} = m_1^{-1} + m_2^{-1})\), \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( E_T \) is the energy barrier \([58]\). An external force \( F \) reduces the energy barrier by \( F \Delta x \), with \( \Delta x \) being the activation length along the reaction coordinate, so the energy barrier becomes \( F \Delta x - E_T \). However, given that it is more convenient to work with stresses than with forces, Equation (2-1) is rewritten as

\[
k(\sigma) = L^{-1} \left( \frac{2\pi \mu}{k_B T} \right)^{-\frac{1}{2}} \exp \left( \frac{\sigma \Delta V - E_T}{k_B T} \right)
\]

(2-2)

where \( \sigma \) is the stress and \( \Delta V \) is the activation volume \([63]\).

To analyze the efficiency of the studied mechanochemical surface modification process, we compared the mechanochemical reaction rates obtained for different shot peening conditions characterized by various combinations of stress and temperature. In doing so, a higher reaction rate is considered to be more beneficial for generating a lubricious surface layer to reduce cutting forces and tool wear. The stresses and temperatures needed for
determining the reaction rate are derived as follows. Similar to previous works on modeling the shot peening process [78, 80], we use a finite element method to simulate the impact of a single spherical shot against a flat substrate to evaluate the maximum contact stress and plastic work. The plastic work is then interpreted as the internal heat source to find the maximum temperature on the contact surfaces.

2.1 Stresses

The Explicit Dynamics module of ANSYS (Ansys Inc., Canonsburg, PA) is used to develop a 3D model of impact between a spherical shot and a flat HSS surface, with a symmetry constraint applied as shown in Figure 2-1. Given large differences in material properties and sizes of Al₂O₃ and Cu₂S particles (see below for details), we model the peening shot as a single core-shell particle, with the Al₂O₃ core being 150 µm in diameter and the Cu₂S shell being 10 µm in thickness. The treated HSS surface is modeled as a cylinder of 200 µm in height and 450 µm in diameter, with a motion constraint applied to all surfaces except the one facing the shot. The effects of surface roughness of the HSS surface are neglected. An initial speed \( v \) is applied to the shot with a specific impact angle \( \theta \). The Explicit Dynamics module only requires the input of mesh size and then it meshes the model automatically. A finite element mesh refinement zone with diameter of 160 µm and element size of 4 µm (minimum size, below which the model does not work due to the “negative volume” error) encloses the contact area, which moves along the x axis according to the changes in the impact angle. The mesh is created using four-node tetrahedron finite elements. The minimum mesh size of 5-6 µm show very similar stress gradient distribution, so the solution is considered convergent. The Explicit Dynamics module detects all the possible contacts during impact so only friction coefficient needs to be provided for solving
the problem. The friction coefficient of the Al$_2$O$_3$/HSS interface is set to be 0.35 [81], and the friction coefficients of the Cu$_2$S/Al$_2$O$_3$ and Cu$_2$S/HSS interfaces are assumed to be equal to 0.15 based on values that can be expected in metal sulfides [82]. Al$_2$O$_3$ is considered to have an isotropic elasticity behavior, while Cu$_2$S and HSS are modeled to have a bilinear isotropic hardening behavior (the properties of all three materials used in the simulation are shown in Table 2-1). The impact angle $\theta$ is chosen to be either 30, 45, 60, 75 or 90 degrees and the particle speed is set to be either 90, 120 or 150 m $s^{-1}$. After the impact process is done, elastic wave propagation is not observed. The reason may be related to that the substrate size is comparable to the shot size so the wave propagation is not clear. We are interested in the maximum von Mises stress at the contact surface of HSS and Cu$_2$S where chemical reaction happens.

![3D finite element model of a single shot impact.](image)

**Figure 2-1.** 3D finite element model of a single shot impact.
Table 2-1. Material properties of Cu$_2$S [83-86], HSS [87, 88] and Al$_2$O$_3$ [89].

<table>
<thead>
<tr>
<th>Material</th>
<th>Density, kg m$^{-3}$</th>
<th>Yield strength, GPa</th>
<th>Young’s modulus, GPa</th>
<th>Poisson’s ratio</th>
<th>Tangent modulus, GPa</th>
<th>Thermal conductivity, W m$^{-1}$ K$^{-1}$</th>
<th>Specific heat capacity, J kg$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$S</td>
<td>5600</td>
<td>0.28</td>
<td>76</td>
<td>0.36</td>
<td>1.52</td>
<td>36</td>
<td>389</td>
</tr>
<tr>
<td>HSS</td>
<td>8138</td>
<td>3.25</td>
<td>210</td>
<td>0.3</td>
<td>98.7</td>
<td>41</td>
<td>460</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3960</td>
<td>N/A</td>
<td>300</td>
<td>0.21</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 2-2 demonstrates the effects of particle speed and impact angle on the time between the instant of initial contact and the moment at which indentation reaches its maximum. This time accounts for the impact duration needed to estimate the timeline of the mechanochemical reaction. We can see that higher impact speed and larger impact angle result in shorter impact duration, which represents an expected outcome.

Figure 2-2. Impact time as a function of particle speed and impact angle.

The maximum von Mises stresses on the contact surfaces of Cu$_2$S and HSS are shown in Figure 2-3 (a) and (b). The stresses increase with the particle speed, which is reasonable because a greater speed is associated with a higher kinetic energy leading to a stronger impact. The impact angle, however, demonstrates a non-monotonic effect on the maximum stresses, which exhibit a clear optimum for both HSS and Cu$_2$S. With the angle changing
from 30 to 90 degrees, the maximum stresses first increase and then drop down. The HSS shows a narrower maximum stress region at around 75 degrees, while the Cu$_2$S shows a much broader maximum stress region at about 60 degrees. This result somewhat resembles the effect of impact angle on the solid-particle erosion, in which more brittle materials show greater damage at high angles than more ductile materials [42].

![Figure 2-3](image.png)

**Figure 2-3.** Maximum stress and temperature at the contact surfaces of Cu$_2$S and HSS as a function of particle speed and impact angle.

### 2.2 Temperatures

Without an external heat supply, the plastic work of shot peening serves as the internal heat source; the corresponding temperature increase activates the chemical reaction between the HSS substrate and the Cu$_2$S. Based on Figure 2-2, we conclude that the impact lasts for less than 0.3 µs, so there is not enough time for heat exchange with the surrounding material.
The thermal diffusivity of steel is around 0.03 to 0.04 cm² s⁻¹ [91]. Multiplying the thermal diffusivity by the impact duration, we find that the heat diffusion takes place within 0.3 to 1.2 µm² during the impact, which is small compared to the area of one element (14 µm²) at the maximum temperature location. So the process is reasonable to be assumed adiabatic. In this case, the governing equation for the 2D transient heat transfer [92] is

\[
\left\{ \begin{array}{l}
\frac{ρC_p}{K} \frac{∂T}{∂t} = \frac{∂^2T}{∂x^2} + \frac{∂^2T}{∂z^2} + \frac{l(x,z,t)}{K} \\
T_i = 293 \, K
\end{array} \right. \tag{2-3}
\]

where \( ρ \) is the density, \( C_p \) is the specific heat capacity, \( K \) is the thermal conductivity, \( T \) is the temperature, \( T_i \) is the initial temperature (293 K), \( t \) is the transient time, and \( I \) is the rate of the internal heat generation per unit volume, arising from the dissipation of the plastic energy/work in our problem. A specific plastic work can be found using the equation [93]

\[
w = \int σ \, dε \tag{2-4}
\]

where \( w \) is the work of deformation per unit volume, and \( ε \) is the plastic strain.

Maximum temperatures are found by solving Equation (2-3) for the impact duration (the time between the instant of initial contact and the moment of maximum indentation) at the point of the maximum strain and stress at the interface between the HSS and the Cu₂S. This is done using a thermal module in the MATLAB numeric computing environment (MathWorks, Natick, MA), based on the material properties shown in Table 2-1. The rate of internal heat generation per unit volume needed for Equation (2-3) is estimated by finding the total specific plastic work (Equation (2-4)) and dividing it by the time needed to reach the indentation maximum. The simulations of the plastic work and temperature
are done at the $x$-$z$ contact interface (HSS/Cu$_2$S), at around the local point of maximum plastic deformation, so the effects of temperature and heat along the $y$ axis outside of the contact interface are neglected.

The maximum temperatures on the contact surfaces of the HSS and the Cu$_2$S are shown in Figure 2-3 (c) and (d). As expected, the temperatures behave similarly to stresses, rising monotonically with the particle speed and exhibiting an optimum when the impact angle is changed. Interestingly, 35NiCrMo15 steel peened by a rigid shot is modeled to have a maximum temperature as high as 473K [90]. In our case, the maximum temperature of the HSS peened under similar conditions is about 330K, which is reasonably lower due to the presence of the Cu$_2$S layer, which can serve as a solid lubricant or deform to create a larger contact area, with both actions reducing stresses generated at the impact zone.

### 2.3 Reaction Kinetics

To allow for the chemical reaction between the HSS, which consists mostly of Fe, and the Cu$_2$S particle, the Fe-Fe and Cu-S bonds must break first. To find the kinetics of dissociation of these bonds, we use the reaction rate model given by Equation (2-2), into which the maximum von Mises stresses and temperatures presented above are substituted. The energy barrier, $E_T$, is assumed to be equal to the bond dissociation energy, and the activation volume, $\Delta V$, is assumed to be equal to $\frac{4}{3} \pi L^3$, where $L$ is the length of the Fe-Fe or Cu-S bond, with all values being shown in Table 2-2.
Table 2-2. Dissociation energy and length of the Fe-Fe [94, 95] and Cu-S [94, 96] bonds at room temperature.

<table>
<thead>
<tr>
<th>Chemical bond</th>
<th>Fe-Fe</th>
<th>Cu-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond dissociation energy (kJ mol⁻¹)</td>
<td>100</td>
<td>285</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>2.85</td>
<td>2.14</td>
</tr>
</tbody>
</table>

Figure 2-4 exhibits the chemical reaction rate of breaking the Fe-Fe and Cu-S bonds under the modeled temperature and stress ranges. It is obvious that, under these conditions, the dissociation rate of the Fe-Fe bond is much higher than that of the Cu-S bond. Interestingly, while the reaction rate increases monotonically with increasing stress, increasing temperature can lead to slower reaction rate under high stresses (this is observed for the Fe-Fe bond above 2 GPa and for the Cu-S bond above 11 GPa), which can possibly be associated with concentration changes [34]. Consequently, increasing the contact stresses appears to be the most effective way to accelerate the reaction of Fe, while higher temperatures better promote the reaction of Cu₂S.

Figure 2-4. Reaction rate of dissociation of Fe-Fe and Cu-S bonds as a function of stress, shown for several characteristic temperatures.
A reciprocal of the product of the reaction rate and the impact time estimates the number of impacts needed to break the chemical bonds by shot peening. The required number of impacts is shown in Figure 2-5 for the Fe-Fe and Cu-S bonds as a function of the particle speed and the impact angle. The most important conclusion is that while one impact is enough to dissociate the Fe-Fe bond (and, hence, to promote the replacement reaction), tens of thousands of impacts are needed to dissociate the Cu-S bond even at the highest modeled particle speed, which may seem to be difficult to achieve. However, considering the approximate nature of the performed analysis as well as our previous experimental findings [97], we should take this result as a qualitative guide to controlling the chemical reaction kinetics. Along this line of thought, given that the particle speed demonstrates a (mostly) monotonic effect on the number of impacts needed to initiate chemical reaction, while the impact angle exhibits a clear optimum (narrow for the Fe-Fe bond and wide for the Cu-S bond), it is worth verifying the model prediction by testing experimentally the impact angle effect.

![Figure 2-5](image.png)

**Figure 2-5.** Number of mechanical impacts necessary to break Fe-Fe bonding and Cu-S bonding.
2.4 Concluding Remarks

A reaction rate model combined with solid mechanics simulations is successfully used to analyze the mechanochemical reaction during dual shot peening of the rake face of HSS tools with a mixture of Al₂O₃ and Cu₂S particles. The model predicts that the dissociation of both Fe-Fe and Cu-S bonds needed for the eventual formation of Fe-S bonds accelerates monotonically with the shot peening particle speed, whereas its rate reaches a local maximum at the impact angle of about 75 deg. The simulation finding will be validated by latter experimental study.
CHAPTER 3.  CUTTING OF HIGH-SPEED STEEL TOOLS

In this chapter, the Al₂O₃ and Cu₂S particles used as shot peening media, the customized dual shot peening device with controllable X-Y stage for moving the treated tools, and the machining setup are introduced. High speed steel tools are first shot peened with different combinations of particles (Al₂O₃ alone, Cu₂S alone, and mixture of Al₂O₃ and Cu₂S) to explore the influence of different media on cutting friction. After that, high speed steel tools are shot peened with the mixture of Al₂O₃ and Cu₂S particles only while varying shot peening parameters to study their influence on cutting performance.

3.1 Surface Modification

3.1.1 Shot peening media

Two different sizes of Al₂O₃ particles (hardness 2300 HV; Comco, Burbank) were used for shot peening: 50 µm and 100-200 µm, as shown in Figure 3-1(a) and (b). Cu₂S particles used in this research work had two different sizes as well, less than 44 µm (hardness 90 HV; Sigma-Aldrich, St. Louis, MO) and less than 75 µm (hardness 90 HV; Alfa Aesar, Ward Hill, MA) shown in Figure 3-1(c). To confirm the chemical composition of Al₂O₃ and Cu₂S, the crystal structures of Al₂O₃ and Cu₂S particles was characterized by an X-ray diffractometer (XRD), Empyrean (Malvern Panalytical, Malvern, UK) equipped with Cu Kα radiation and PIXcel hybrid line detector. The XRD analysis results are shown in Figure 3-2. The Al₂O₃ particles are mostly α-Al₂O₃ and a small amount of β-Al₂O₃. The Cu₂S particles includes three different compositions, Cu₁.⁹⁶S, Cu₁.₈₁S, and Cu₅S₉, overall they can be treated as Cu₂S.
Figure 3-1. Microscope images of Al₂O₃ particles in mean size of (a) 50 µm and (b) 100-200 µm, and (c) Cu₂S particles of less than 75 µm in mean size.

Figure 3-2. X-ray diffraction analysis of Al₂O₃ particles (a) and Cu₂S particles (b).
3.1.2 Shot peening setup

The mechano-chemical surface modification performed in this work is based on a shot peening process conducted using a dual-tank MicroBlaster MB1002 (Comco, Burbank, CA) customized to enable discharging of two types of particles simultaneously. Figure 3-3(a) shows the schematic of the apparatus. When the shut-off assembly is open, the modulator coil becomes energized, and the modulator opens and closes the entry of a dry pressurized N\(_2\) gas into the mixing chamber with a frequency of 50 Hz. During the open stage, the N\(_2\) gas is forced into the tank with particles, and, during the closed stage, the pressurized N\(_2\) gas pushes a small amount of particles into the mixing chamber, so the start/stop action of the modulator results in a constant stream of particles out through the nozzle. Figure 3-3(b) shows the interaction between the nozzle and the tool surface during shot peening. The impact angle of the shots with respect to the tool surface, and the distance between the nozzle and the tool surface along the nozzle axis can be seen in Figure 3-3(b). These and other parameters, such as tank orifice diameter, and gas pressure can be changed to test the effects of different shot peening parameter combinations.

The shot-peened tools were fixed on a custom X-Y table assembled on two linear stages, ET-100-11 (Newmark Systems, Rancho Santa Margarita, CA, USA), operated with stepper drives, SMD-7613 (National Instruments Co., Austin, Texas), using LabVIEW software (National Instruments Co., Austin, Texas). The rake surfaces of the tools were shot peened along a meandering path with a controllable linear velocity and a pitch of 0.4 or 0.6 mm to guarantee uniform coverage, as shown in Figure 3-3(c). After shot peening, the cutting tools were blown with compressed air to remove particles left on the surface.
Figure 3-3. Schematic of (a) custom dual-tank shot-peening device, (b) orientation of nozzle with respect to treated cutting tool, and (c) raster shot-peening path on the tool rake surface.

3.1.3 Shot peening conditions

The first controllable shot peening parameter is the volume ratio of Al₂O₃ and Cu₂S particles. The diameter of the orifice at the bottom of each tank from the shot peening device controls how much particles can be taken into the system by the pressured N₂. The diameter of the orifice can be 1.016 mm or 1.524 mm, that is the volume ratio Cu₂S/Al₂O₃ can be 0.44 or 2.25. It is also possible to use only one type of particles so we can discharge them selectively. The impact angle \( \theta \) is the orientation of the nozzle axis with respect to the tool rake face and it can be changed between 0 and 90 degrees. The N₂ gas pressure can be chosen between 1 and 5 bar. The outlet diameter of the nozzle cannot be smaller than the tank orifice diameter. The distance between the nozzle and the rake face along the axis of the nozzle was always 13 mm in this work. The cutting tool surfaces were shot peened along a raster path with a linear stage velocity between 1 and 50 mm s\(^{-1}\), a pitch of 0.4 or 0.6 mm, and a different coverage area (Figure 3-3(c)). The cutting edge was protected from rounding (by nearby-flying particles) with a special jig clamped to the tool
flank. The temperature and relative humidity in the laboratory were 21–23 °C and 45–55%, respectively.

3.2 Machining Tests

After surface treatments, we performed machining tests to investigate how the tool rake face modifications influence the cutting forces. Figure 3-4 shows a schematic of the setup used in the orthogonal cutting experiments. The tests were performed in a two-axis CNC turning center LB2000EX (Okuma America, Charlotte, NC) using 1018 steel tubes as a workpiece. The cutting speed and feed were controlled to adjust the required experimental conditions. An oil delivery system was configured to supply Americas Core 100 base oil (kinematic viscosity of 20.4 cSt @ 40 °C; ExxonMobil, Wellesley, MA) to the tool rake face at the rate of 20 drops (~0.4 ml) min⁻¹. The orthogonal cutting and thrust forces were measured by a piezoelectric multicomponent dynamometer 9257B (Kistler Instrument Corp., Amherst, NY) and were sampled by a data acquisition system cDAQ-9178 (National Instruments Co.) using LabVIEW software (National Instruments Co.). Only the steady state portion of the sampled data was analyzed. After each cutting test, the tube workpiece was pulled out of the chuck to have the same initial overhang length.

![Figure 3-4. Schematic of the orthogonal cutting experimental setup of high-speed steel tools.](image)
3.3 Cutting Analysis

3.3.1 Effect of shot peening media

The cutting tools used in this study were 0 deg rake angle, M2 high-speed steel uncoated turning tools (McMaster-Carr, Elmhurst, IL) with a hardness of $1007 \pm 78$ (mean±SD) HV 1 and an average rake face arithmetic surface roughness (Ra) of 0.2 µm. To find out whether the shot-peening-based mechano-chemical surface modification could improve the cutting tool performance experimentally, high-speed steel tools were treated by three different shot peening media: (i) Al$_2$O$_3$ particles (50 µm in mean size) alone, (ii) Cu$_2$S particles (less than 44 µm in mean size) alone, and (iii) a 1:1 mixture of Al$_2$O$_3$ and Cu$_2$S. Peening of the tool rake face with Al$_2$O$_3$ particles was performed to study the effect of surface plastic deformation only. Peening of the rake face with Cu$_2$S particles was performed to study the effect of the chemical interaction between Cu$_2$S and the ferrous tool surface. The surface peened with a blend of Cu$_2$S and Al$_2$O$_3$ particles was prepared to study the effect of accelerated chemical activation of the tool rake face due to intensive surface plastic deformation. Nontreated tools were used as a reference. After shot peening, the Al$_2$O$_3$-, Cu$_2$S-, and mixture-treated rake surfaces were measured to have a roughness average Ra of 1 µm, 0.3 µm, and 1 µm, and a hardness of $1036 \pm 72$ HV 1, $808 \pm 79$ HV 1, and $600 \pm 87$ HV 1, respectively. The surface topography and hardness were examined using a 3D optical profiler ContourGT-I (Bruker, San Jose, CA, USA), and a micro-hardness tester HM-220 (Mitutoyo, Kawasaki, Japan), respectively.

The shot peening parameters were as follows. The N$_2$ gas pressure was 3 bar, the nozzle had an outlet diameter of 1.17 mm, and the impact angle was 75 deg. The stage velocity
was 1 mm s$^{-1}$, the pitch of shot peening path was 0.4 mm, and a coverage area was 8 × 15 mm (Figure 3-3(c)).

During cutting processes, the workpiece tube was 36 mm in outer diameter with a wall thickness of 2 mm to ensure plane-strain conditions. The cutting speed and feed were 16.14 m min$^{-1}$ and 0.15 mm rev$^{-1}$ and represented rough machining conditions. Each tool was used for three cuts and each cut occupied a new location along the cutting edge. Three tools were employed for examining each of the four surface types and each combination of test conditions was repeated 9 times.

Illustrative examples and complete datasets of cutting and thrust forces measured for tools with different rake faces are shown in Figure 3-5. Interestingly, although all the treated tools demonstrated a visible reduction in cutting and thrust forces with respect to the reference tools, a statistically significant difference is observed only between the non-treated reference tools and the tools peened with a blend of Al$_2$O$_3$ and Cu$_2$S (Table 3-1), which undoubtedly points to a synergetic effect of the two peening materials.
Figure 3-5. Cutting and thrust forces measured with different tools. (a) and (b) Illustrative examples of the force evolution over time (stopped after reaching steady state). (c) and (d) Complete datasets of the mean steady state values. The data are presented using box-and-whisker diagrams, where the solid line inside the box is the median, the bottom and top of the box are the 25th and 75th percentiles, the ends of the whiskers are the 10th and 90th percentiles, and the dotted line is the mean.

The tools peened with Al₂O₃ particles behave similarly to the reference tools (Figure 3-5 (a, b)) and demonstrate the least reduction in forces (Figure 3-5 (c, d)). Given that the difference in hardness between the peened and reference tools is not statistically
significant, this reduction is associated with the peening-induced increase in surface roughness, which can lead to a reduced contact area in the tool-chip interface and, hence, to lower contact forces [8, 12].

Table 3-1. All pairwise multiple comparisons (one-way ANOVA, Holm-Sidak method) for overall significance level of 0.05.

<table>
<thead>
<tr>
<th>Comparison of surface treatments</th>
<th>Cutting force</th>
<th>Thrust force</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Difference of means (N)</td>
<td>P-value</td>
</tr>
<tr>
<td>None vs. Blend</td>
<td>143.8</td>
<td>0.012</td>
</tr>
<tr>
<td>None vs. Cu2S</td>
<td>86.9</td>
<td>0.217</td>
</tr>
<tr>
<td>None vs. Al2O3</td>
<td>59.8</td>
<td>0.450</td>
</tr>
<tr>
<td>Al2O3 vs. Blend</td>
<td>83.9</td>
<td>0.256</td>
</tr>
<tr>
<td>Cu2S vs. Blend</td>
<td>56.8</td>
<td>0.359</td>
</tr>
<tr>
<td>Al2O3 vs. Cu2S</td>
<td>27.1</td>
<td>0.550</td>
</tr>
</tbody>
</table>

The tools peened with Cu2S particles exhibit a slightly larger reduction in forces than the tools peened with Al2O3 (Figure 3-5 (c, d)). This result cannot be explained based on the tool surface deformation because of the inability of softer Cu2S to indent harder high-speed steel. However, the softer Cu2S particles can be smeared on the surface of the tool, while reacting chemically with it to form compounds of Fe and S [98], which are well known to reduce friction in boundary lubrication [42, 99]. Indeed, several observations allow us to confirm this hypothesis. First, the hardness measurements suggest the presence of a soft layer on the tool surface after shot peening. Next, the force evolution over time (Figure 3-5 (a, b)) demonstrates a transient period of high cutting and thrust forces, which can be associated with the removal of this soft layer during breaking-in of the tool surface. Last,
the energy-dispersive X-ray spectroscopy (EDS) maps (Section 3.4.2) show that a small amount of S is still present on the worked tool’s surface, while Cu is not observable.

The tools peened with the blend of Al$_2$O$_3$ and Cu$_2$S particles demonstrate the same behavior as the tools peened with Cu$_2$S particles alone (Figure 3-5 (a, b)) but show larger reduction in cutting and thrust forces (Figure 3-5 (c, d)) with respect to the reference tools. We attribute this result to a much more intensive interaction between Cu$_2$S particles and the tool surface, which is activated by Al$_2$O$_3$ particles through plastic deformation [100-102]. This conclusion is supported by a thicker Cu$_2$S layer on the tool surface, as follows from its lower hardness, and by the fact that, unlike in the case of Cu$_2$S-peened surface, this layer could not be removed from the tool by ultrasonic cleaning. It also follows from the EDS analysis (Section 3.4.2) that much more S is left on the tool surface after the cutting tests.

3.3.2 Effect of shot peening parameters

After proving that the shot-peening-based mechano-chemical surface modification allows to reduce the cutting forces significantly in HSS tools, the effects of the surface processing parameters on the performance of the modified tools were studied. The processing parameters included (1) the volume ratio of the two different types of particles (Cu$_2$S over Al$_2$O$_3$), (2) the shot peening stage velocity, and (3) the impact angle between the nozzle axis and the tool rake face, while each parameter was tested at two different levels, as shown in Table 3-2. The volume ratio of particles is related to the balance between the chemical precursor and the plastic deformation media, which determines the efficiency of synergy between the two. More Cu$_2$S provides an additional raw material for chemical reaction, while more Al$_2$O$_3$ induces more plastic deformation, facilitating the chemical
reaction. The peening stage velocity provides means for adjusting the time of shot peening a unit area, thus defining the surface treatment coverage. In addition, a longer shot peening time leads to a more extensive plastic deformation, thus leading to a more pronounced chemical reaction. The angle at which particles strike the surface is known to affect the material removal rate in solid-particle erosion of different materials [42], so adjusting this parameter should also influence the extent and balance of interaction between the shot peening media and the treated surface.

HSS tools were shot peened according to the eight different combinations shown in Table 3-2. We used Al₂O₃ particles with a mean size of 100-200 µm and Cu₂S particles with a mean size less than 75 µm. Two different diameters (1.016 mm and 1.524 mm) of the orifice were used and the ratio of the orifice cross area (2.25 or 0.44) was the volume ratio of the particles, therefore two different levels of the particle volume ratio were set. According to the instruction of the shot peening device, the diameter of the nozzle outlet should not be smaller than the diameter of the orifice. The diameter of nozzles we used was 1.524 mm, and, as a result, the pitch of shot peening path was increased to 0.6 mm. The stage velocity which controls the speed of shot peening path on the tool rake face was set to a high level of 50 mm s⁻¹ and a low level of 1 mm s⁻¹. The impact angle was examined at two different levels, 40 deg and 75 deg. After shot peening, the flank faces of the tools were ground to ensure a uniform sharpness of the cutting edge. The differently modified tool surfaces were characterized based on roughness and hardness measurements, as shown in Figure 3-6.
Table 3-2. Shot peening parameter combinations.

<table>
<thead>
<tr>
<th>Combination</th>
<th>Volume ratio</th>
<th>Stage velocity (mm s⁻¹)</th>
<th>Impact angle (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.44</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>0.44</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>0.44</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>2.25</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>2.25</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>2.25</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>2.25</td>
<td>1</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 3-6. Surface roughness and hardness of differently treated (including untreated reference) tools, with “+” and “−” representing the high and low levels of all process parameters.

The schematic of the setup used in the orthogonal cutting experiments is the same as Figure 3-4. The 1018 steel tubes of 38.1 mm in outer diameter as a workpiece. The tube wall thickness is 1.8 mm to ensure plane-strain conditions. The cutting speed and feed were set to 14.935 m min⁻¹ and 0.2 mm rev⁻¹, respectively. Same lubrication system was applied. The tube workpiece was pulled out of the chuck to have the same initial overhang length of 50.8 mm for each cutting test that removed 12.7 mm of the tube length. A total of two
cuts per tool was used, with two tools employed for examining each of the treated surface types.

The cutting and thrust forces were recorded and analyzed for each of the eight combinations of the tested variables and an untreated reference tool, as shown in Figure 3-7 and Table 3-3. The ANOVA results demonstrate that the impact angle is the most significant factor affecting the cutting and thrust forces, and it exhibits a negative correlation with both of them, as follows from Figure 3-7. The second important parameter is the stage speed, which shows a positive correlation with both types of forces, though its effect on the thrust force only is found to be statistically significant. The effect of the volume ratio of Cu$_2$S to Al$_2$O$_3$ particles appears to be statistically insignificant. Thus, a combination of the higher impact angle and the lower stage speed leads to the lowest forces generated in cutting (within the tested range).

![Figure 3-7](image)

**Figure 3-7.** Cutting and thrust forces of differently treated (including untreated reference) tools, with “+” and “–” representing the high and low levels of all process parameters.
Table 3-3. Three-way ANOVA results of the effects of the three process parameters on the treated surface characteristics and the tool performance at a significance level of 0.05.

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Surface Roughness</th>
<th>Surface Hardness</th>
<th>Cutting Force</th>
<th>Thrust Force</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P-value</td>
<td>Statistical difference</td>
<td>P-value</td>
<td>Statistical difference</td>
</tr>
<tr>
<td>Impact angle</td>
<td>0</td>
<td>Yes</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Volume ratio</td>
<td>0.161</td>
<td>No</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>Stage speed</td>
<td>0.461</td>
<td>No</td>
<td>0.025</td>
<td>Yes</td>
</tr>
<tr>
<td>Angle*Ratio</td>
<td>0.028</td>
<td>Yes</td>
<td>0.282</td>
<td>No</td>
</tr>
<tr>
<td>Angle*Speed</td>
<td>0.037</td>
<td>Yes</td>
<td>0.279</td>
<td>No</td>
</tr>
<tr>
<td>Ratio*Speed</td>
<td>0.229</td>
<td>No</td>
<td>0.336</td>
<td>No</td>
</tr>
<tr>
<td>Angle<em>Ratio</em>Speed</td>
<td>0.536</td>
<td>No</td>
<td>0</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The effects of the shot peening process parameters on the cutting forces can be explained as follows. Based on the reaction rate model presented above, the higher impact angle (of the two tested) leads to the higher surface stress and temperature, facilitating the replacement chemical reaction to form a beneficial layer that improves the surface lubricity and drives the cutting forces down. Thus, the experimental results are consistent with the model prediction. The effect of the stage speed can be understood along the same lines: lower speed results in an increased number of Al$_2$O$_3$ particle impacts per unit area, leading to a more extensive chemical reaction on the tool surface. Given that the thrust force represents friction in orthogonal cutting, it is therefore affected more extensively by this parameter than the cutting force, which acts in the normal direction to the treated rake face. Lack of the effect of the particle volume ratio may result from the Cu$_2$S saturation of the shot peening mixture at both tested levels.

It is also interesting to note that while the particle volume ratio affects the measured cutting forces less significantly and the stage speed affects them more significantly, the importance of these two process parameters is reversed when the tool roughness and hardness are
considered (see Table 3-3). This may indicate that the soft Cu$_2$S layer, which is left on the surface after treatment and whose roughness and hardness are actually characterized, is removed from the tool surface when the cutting operation starts, exposing the (chemically) modified substrate to the contact with the workpiece [97]. Though being less evident, this finding also supports our hypothesis that the dual shot peening with a mixture of hard and chemically potent particles is able to modify the peened surface chemically instead of just creating a soft low-friction coating on the surface [103].

3.4 Surface Characterization

3.4.1 Surface morphology

Post-test images of the rake surfaces were obtained with an optical stereo microscope M125 (Leica Camera AG, Wetzlar, Germany) and a scanning electron microscope (SEM) SU8230 (Hitachi, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) silicon drift detector X-Max 80 mm$^2$ (Oxford Instruments, Abingdon, UK).

Figure 3-8 shows representative post-test optical images of the tool rake face for each of the studied surface types. Comparing the shot peened surfaces to the non-peened reference, we see that while the Cu$_2$S-peened tool undergoes minimal alteration, the surface appearance changes for the Al$_2$O$_3$- and blend-peened tools. This change is reflected in different roughness values and is attributed to the use of Al$_2$O$_3$ particles, which can plastically deform the tool surface. Interestingly, similar to regular surface texturing [13], the increase of roughness as a result of the surface peening involving Al$_2$O$_3$ particles had a dampening effect on the built-up edge (BUE) formation. While the BUE was found in 5 and 3 out of 9 cuts performed with the non- and Cu$_2$S-peened tools, respectively, the Al$_2$O$_3$-
and blend-peened tools demonstrated the BUE in 0 and 1 out of 9 cuts, respectively. Therefore, in addition to a significant reduction of cutting forces, peening the rake face with the blend of Al$_2$O$_3$ and Cu$_2$S particles is thought to increase the tool life and to enable better dimensional control and surface quality of a workpiece by virtue of suppressing the BUE formation.

Figure 3-8. Representative low-magnification images of (a) non-peened, (b) Al$_2$O$_3$-peened, (c) Cu$_2$S-peened, and (d) blend-peened rake faces of the tested tools.

Figure 3-9. Representative high-magnification images of (a) non-peened, (b) Al$_2$O$_3$-peened, (c) Cu$_2$S-peened, and (d) blend-peened rake faces of the tested tools. Top row, non-contact region away from the cutting edge. Bottom row, contact region adjacent to the cutting edge shown on the right.

To compare the pre- and post-test appearance of the tool surfaces at the microscale, we imaged the contact and non-contact regions of the rake faces in SEM (Figure 3-9). Looking at the tool surfaces that did not participate in cutting (Figure 3-9, top row), we can clearly
distinguish between different surfaces. The reference non-treated tool features parallel scratch marks associated with surface grinding, the surface finishing process used in making the tool. The surface peened with hard Al₂O₃ particles exhibits a random irregular surface pattern associated with overlapping impact sites having raised crater rims and lips characteristic for solid-particle erosion, and no initial grinding marks are visible. This suggests extensive plastic deformation of the surface. The surface peened with soft Cu₂S particles demonstrates random irregular surface projections of much larger scale found at much greater distances from each other if compared to the Al₂O₃-peened surface, while initial grinding marks are occasionally visible. This supports the above hypothesis of smearing soft Cu₂S particles atop a practically undeformed tool surface. The surface peened with the blend of Al₂O₃ and Cu₂S particles appears to have a combination of features demonstrated by the other two peened surfaces and looks like a transition in between them.

The tool surfaces that participated in the cutting process (Figure 3-9, bottom row) stand in marked contrast to their initial states and have much more similarities with each other than previously. Doubtless signs of material transfer near the cutting edge are observed on the surface of the reference tool, which points to a high possibility of BUE formation. The cutting edge peened with Cu₂S particles appears to have a much more even surface than before, with the random projections being removed under heavy contact stress, original grinding marks being still visible, and the BUE being initiated, which makes this surface resemble the reference tool. The cutting edge peened with Al₂O₃ particles exhibits a newly obtained directionality consistent with the chip flow and a smoothed clean surface that seems to be very similar to the surface peened with the blend of Al₂O₃ and Cu₂S particles.
The latter also features a distinct and differently looking strip of about 50 μm in size (~1/3 of the depth of cut) at the very cutting edge. Given that the zone of about the same size on the surface of the reference tool is heavily covered with transferred material, this strip is associated with a sticking region [70]. Interestingly, the blend-peened cutting edge appears to be the least damaged among all tools, which can be related to the lowest measured cutting forces and, presumably, the smallest amount of heat generated at the tool-chip interface.

3.4.2 Surface composition

To perform chemical analysis of the studied surfaces, EDS measurements were taken for the non-contact and contact regions. Figure 3-10 shows the elemental spectra on the rake faces of the tested tools. Comparing the non-contact and contact spectra of the non-peened high-speed steel reference tool, we see moderate reduction in intensity of the alloying elements W, Mo, V, and Cr, which can be related to the presence of a transferred layer of low-carbon steel lacking these elements. The tool peened with Al₂O₃ particles exhibits an Al peak, which points to the presence of embedded particles or their fragments. The cutting region of this tool has much less Al, suggesting that it was partially worn during the operation. The tool peened with Cu₂S particles demonstrates a significant presence of Cu and S, with the former having the highest peak of about twice the intensity of that of the latter. It is also evident that Fe is not the dominating element on the surface, which may result from the presence of large patches of Cu₂S on top of it. However, the contact region of this tool lacks both Cu and S, which implies their removal during cutting. The tool peened with the blend of Al₂O₃ and Cu₂S particles displays more Cu and S than Fe and little of Al, which suggests that the surface is covered by a relatively thick layer of Cu₂S.
The cutting region of this tool still exhibits a significant amount of S, while Cu is almost gone, which may mean that S formed a compound with Fe due to a replacement reaction [98] accelerated by plastic deformation. This conclusion is also supported by the force measurement results discussed in Section 3.3.1.

![Figure 3-10. EDS spectra of (a) non-peened, (b) Al₂O₃-peened, (c) Cu₂S-peened, and (d) blend-peened rake faces of the tested tools. Top row, non-contact region away from the cutting edge. Bottom row, contact region adjacent to the cutting edge.](image)

Figure 3-10. EDS spectra of (a) non-peened, (b) Al₂O₃-peened, (c) Cu₂S-peened, and (d) blend-peened rake faces of the tested tools. Top row, non-contact region away from the cutting edge. Bottom row, contact region adjacent to the cutting edge.

In light of the above, it is very interesting to analyze the spatial distribution of the chemical elements on the tool surfaces that did not participate (Figure 3-11) and did participate (Figure 3-12) in cutting. Comparing the two regions on the reference tool, we see that the alloying elements W, Mo, V, and Cr are distributed uniformly in the non-contact region (Figure 3-11(a)) and are absent in the areas marked with asterisks in the contact region.
(Figure 3-12(a)). This supports the hypothesis of material transfer and proves that the asterisk-marked patches were torn from the workpiece during cutting.

Looking at the rake face of the tool peened with Al₂O₃ particles (Figure 3-11(b)), we see a uniform distribution of spatially matching islands of Al and O, which represent small fragments that were split off from the original, much larger and brittle Al₂O₃ particles. In the contact region (Figure 3-12(b)), these fragments are practically absent within the above-mentioned strip of about 50 µm in size at the very cutting edge, which suggests that they are worn out during cutting. Given that Al is not observed without corresponding O, we conclude that Al₂O₃ remains chemically inert, which also follows from the high position of Al in the electrochemical series [104].
Figure 3-11. EDS maps of (a) non-peened, (b) Al$_2$O$_3$-peened, (c) Cu$_2$S-peened, and (d) blend-peened rake faces of the tested tools in the non-contact region away from the cutting edge.
Figure 3-12. EDS maps of (a) non-peened, (b) Al₂O₃-peened, (c) Cu₂S-peened, and (d) blend-peened rake faces of the tested tools in the contact region adjacent to the cutting edge.

Looking at the rake face of the tool peened with Cu₂S particles (Figure 3-11(c)), we see spatially matching patches of Cu and S, which cover irregularly shaped areas and are larger than the original particles, suggesting that soft Cu₂S was indeed smeared on the tool
surface. The high-speed steel substrate is seen well, but it does not dominate the picture. In the contact region (Figure 3-12(c)), the high-speed steel substrate clearly dominates, while Cu is not visible at all and a much more uniformly distributed S is seen lightly. This observation supports the hypothesis of a replacement reaction between Cu$_2$S and Fe, leading to the formation of compounds of Fe and S, but it indicates that Cu$_2$S particles alone cannot react strongly with the substrate.

The rake face of the tool peened with the blend of Al$_2$O$_3$ and Cu$_2$S particles displays a nearly uniform layer of Cu and S with small islands of the substrate material seen through the openings (Figure 3-11(d)). Obviously, this layer is smeared on the tool surface, and its formation is undoubtedly assisted by Al$_2$O$_3$ particles, as becomes clear when comparing Figure 3-11(d) and (c). Al$_2$O$_3$ fragments are rare, while the surface exhibits a trace amount of O that is not associated with Al, which may suggest formation of copper sulfates due to a deformation-enhanced oxidation. Looking at the contact region (Figure 3-12(d)), we do not see either Al$_2$O$_3$ fragments or Cu within the strip of about 50 µm in size at the very cutting edge, which suggests that they are worn out during cutting. However, uniformly distributed S is detected throughout the whole tool-chip contact region. Considering that S is not stable under the high temperatures developed during cutting (it melts at 115 ºC), S is very likely to bond chemically to the substrate, forming iron sulfides (melting point of 1,194 ºC) known to enhance the oil retention and the tribological response of sliding interfaces [42, 99].

Given that the cutting tool surface is covered by a relatively thick Cu$_2$S layer after shot peening while it exhibits an iron sulfide layer after cutting experiments, we may ask the question of when the sulfides are formed – during shot peening or during cutting. In the
first case, the reaction should take place at the initial stages of shot peening, when Fe is still exposed to direct contact with Cu$_2$S. In the second case, the reaction should take place after most of the Cu$_2$S layer is worn, so tribological interaction with the workpiece material can facilitate it. Though the answer to this question is yet to be verified, we tend to believe that the replacement reaction takes place mostly during shot peening, because otherwise we would not see much difference between the surface peened with Cu$_2$S alone and the surface peened with the blend of Al$_2$O$_3$ and Cu$_2$S. Thus, Al$_2$O$_3$ is thought to act as an assisting agent, which activates the surface through plastic deformation and accelerates the chemical reaction to form iron sulfides.

3.5 Concluding Remarks

Lubricated plane-strain orthogonal cutting with mechano-chemically modified high-speed steel tools results in reduction of cutting and thrust forces, as well as in dampening of the BUE formation. These effects are obtained because of an increase in the lubricity and roughness of the tool caused by shot peening treatment of its rake face with a blend of Al$_2$O$_3$ and Cu$_2$S particles, leading to formation of iron sulfides on the tool’s steel surface. Further study on critical shot peening parameters demonstrates lower cutting and thrust forces with the tools peened at the angle of 75 deg compared to those peened at the angle of 40 deg. It validates the finding of reaction rate model in chapter 2 that the dissociation of both Fe-Fe and Cu-S bonds needed for the eventual formation of Fe-S bonds accelerates monotonically with the shot peening particle speed, whereas its rate reaches a local maximum at the impact angle of about 75 deg. Additional peening parameters, namely, the particle volume ratio and the stage speed are found to be much less statistically significant under the conditions tested. The developed approach may be instrumental in guiding the
optimization of processing parameters in order to improve the frictional performance of mechanochemically treated surfaces.
CHAPTER 4. SERVICE LIFE OF HIGH-SPEED STEEL TOOLS

This chapter presents the study of the wear resistance of mechanochemically modified HSS tools, with the flank wear being examined to estimate the wear life of the tools. Chemical characterization of the tool cross section is utilized to explain the performance of the mechanochemically modified tool.

4.1 Surface Modification

Before shot peening, the rake faces of the HSS tools were ground to have a surface roughness, Ra, of 0.35±0.10 (mean±SD) µm and a hardness of 962±43 HV 1. After a 15 min long ultrasonic cleaning with acetone, the tools were shot peened by a mixture of Al₂O₃ (100-200 µm in mean size, hardness 2300 HV; Comco, Burbank, CA) and Cu₂S particles (less than 75 µm in mean size, hardness 90 HV; Alfa Aesar, Ward Hill, MA).

During shot peening, the pressure of the carrier N₂ gas was 5 bar, the diameter of the nozzle was 1.524 mm, and the diameters of the Cu₂S and Al₂O₃ tank orifices were 1.524 and 1.016 mm, respectively, with the volume ratio of the discharged Cu₂S to Al₂O₃ being roughly equal to 2.25. The rake faces of the HSS tools were shot peened following the raster path with a pitch of 0.6 mm and a coverage area of 10 × 13 mm. The stage velocity was 1.25 mm s⁻¹. The angle between the tool rake face and the nozzle axis was 75 degrees. The cutting edge was shielded from rounding (by nearby-flying particles) with a special jig clamped to the tool flank. After shot peening the rake faces, the flank faces of the tools were ground to ensure a uniform sharpness of the cutting edge. The average surface roughness and hardness of the peened rake faces were 2.09±0.11 µm and 619±83 HV 1.
4.2 Machining Tests

The workpiece was 1018 steel tubes of 38.1 mm in outer diameter and 1.8 mm of tube wall thickness to ensure plane-strain conditions. The cutting speed and feed were set to 116.88 m min\(^{-1}\) and 0.2 mm rev\(^{-1}\), respectively, to accelerate the wear rate in order to see the difference between the tested tools. An oil delivery system was configured to supply Americas Core 100 base oil (kinematic viscosity of 20.4 cSt @ 40 °C; ExxonMobil, Wellesley, MA) to the tool rake face at the rate of 20 drops (~0.4 ml) min\(^{-1}\). For the wear test of each cutting tool, the tube workpiece was pulled out of the chuck to have the same initial overhang length of 50.8 mm of each cut. The first cut removed 25.4 mm of the tube length, then all the subsequent cuts removed 15.24 mm of the tube length until the tool failed catastrophically. After each cut, the tool rake and flank face topography were examined under an optical stereo microscope M125 (Leica Camera AG, Wetzlar, Germany). Average flank wear (wear land) was used to estimate the tool wear life according to ISO 3685. Each test was repeated 3 times. The temperature and relative humidity in the laboratory were 21–23 °C and 35–55%, respectively.

4.3 Wear Analysis

The average flank wear obtained in all repetitions for both the reference (Ref1-3) and modified (SP1-3) tools is presented in Figure 4-1 as a function of cutting distance. All curves suggest that the wear process begins with a relatively short running-in period (none of the curves crosses the origin) followed by a period of steady-state wear, which transforms into a catastrophic failure as the wear rate increases towards the end of the test. Interestingly, the projected y-intercept of the wear curves for the reference tools is on
average higher than that of the modified tools, which means that the running-in wear is larger in the reference case, pointing at another advantage of the mechano-chemical surface modification.

![Graph showing average flank wear of reference (Ref) and modified (SP) tools measured as a function of cutting distance.](image)

**Figure 4-1.** Average flank wear of reference (Ref) and modified (SP) tools measured as a function of cutting distance.

The tested tools failed during the cut performed after the last point shown on each curve, so there is some uncertainty about their exact end of life. However, if we disregard the data on their last cuts, for the three trials of the reference tools, the wear life ranged between 40.9 m and 58.4 m. As a comparison, the wear life of the modified tools ranged between 84.7 m and 128.6 m, which is more than twice the wear life of the reference tool on average. This result unequivocally proves that the mechanochemical modification is able to improve the wear resistance of high-speed steel tools significantly.

Figure 4-2 and Figure 4-3 show the appearance of the flank and rake faces, respectively, of the tested tools imaged at a continuously increasing cutting distance. We can see in
Figure 4-2 that the wear land of the reference tool grows much faster, leading the tool to approach failure more quickly than the modified tool, which exhibits slower wear and experiences longer service life. It is also possible to observe small cracks developing within the wear land during the last stages of the experiment, as marked in Figure 4-2. Obviously, their presence explains sudden failure of the tools at the end of their service lives. It is noteworthy that the mechanochemical modification of the rake face postponed the appearance of cracks on the flank face, which may be associated with the compressive residual stresses resulting from the plastic deformation involved in the process [105].

As shown in Figure 4-3, the contact area formed when chip slides against the tool rake face is visualized through temperature discoloration. The tool-chip contact area of the modified tools is smaller than that of the reference tool, which may result from the chip curling due to a lower temperature at the tool-chip interface [93] and from lower adhesion of the workpiece material to the rake face [9]. In addition, the build-up edge initiates earlier on the reference tool than on the modified tool. At the end of life of the reference tool, a large build-up edge can be observed, while a much smaller build-up edge is present on the modified tool at the comparable time, which can also be seen in Figure 4-3. The early developed and steadily increasing build-up edge clearly shows a consistent trend with the growth of the wear land. Interestingly, at the time of failure, the build-up edge on the modified tool is much larger than that on the reference tool, indicating that the former can withstand higher cutting loads than the latter.
Figure 4-2. Flank faces of reference (Ref) and modified (SP) tools imaged at progressively growing cutting distance.

Figure 4-3. Rake faces of reference (Ref) and modified (SP) tools imaged at progressively growing cutting distance.

4.4 Surface Characterization

An IsoMet 1000 precision cutter (Buehler, Lake Bluff, IL) equipped with a diamond saw was used to prepare cross sections of the tested tools. To avoid chemical contamination,
the process of sawing was lubricated using the same Americas Core 100 oil as in the wear testing. The cross sections were wiped with Acetone before examination. A scanning electron microscope (SEM) SU8230 (Hitachi, Tokyo, Japan) equipped with an 80 mm² energy-dispersive X-ray spectroscopy (EDS) silicon drift detector X-Max (Oxford Instruments, Abingdon, UK) was used to characterize the chemical composition of the studied cross sections.

![Figure 4-4. EDS map of the cross section prepared inside the cutting region of the reference tool, with (b) being the zoom-in image of the rectangular zone shown in (a).](image)

The EDS maps of the cross sections prepared inside and outside the cutting region of the reference tools are shown in Figure 4-4 and Figure 4-5. The high-speed steel tools are mainly composed of Fe and additionally contain small amounts of W, Cr, V, and Mo, with the latter being shown on a separate map for the discussion that will follow. The region marked by a white star in Figure 4-4(a) exhibits fewer solute elements, representing an example of the material transferred from the low carbon steel workpiece that does not
include the same constituents. Obviously, no material transfer is observed on the reference tool outside the cutting zone (Figure 4-5).

Figure 4-5. EDS map of the cross section prepared outside the cutting region of the reference tool, with (b) being the zoom-in image of the rectangular zone shown in (a).

Figure 4-6 presents the EDS map of the cross section prepared outside the cutting region of the modified tools, which corresponds to the treated surface before wear tests. Unfortunately, because the characteristic X-ray energies are very close for Mo (2.293 keV) and S (2.307 keV), the Mo and S maps look alike. Consequently, both maps exhibit a superposition of the Mo and S information. Comparing the EDS maps of the reference and modified tools, we can still identify a layer that consists of Cu and S located on the rake face after the treatment because Mo cannot be present there as a solute that is distributed uniformly within the Fe matrix. The corresponding presence of Al and O in the added surface layer in Figure 4-6 (a) and (b) demonstrates Al₂O₃ fragments embedded in the shot peening layer.
If we compare the distributions of Cu and S in Figure 4-6(b), we can see slight differences between the two at the interface between the added layer and the tool substrate, with S extending at certain locations deeper into the substrate than Cu. One explanation for this observation is the presence of Mo, which is not distinguishable from S. Alternatively, this may be due to the anticipated mechanochemical reaction between Cu$_2$S and Fe activated by shot peening, which draws S into the substrate.

Figure 4-6. EDS map of the cross section prepared outside the cutting region of the modified tool, with (b) being the zoom-in image of the rectangular zone shown in (a).
Figure 4-7. EDS map of the cross section prepared inside the cutting region of the modified tool, with (b) being the zoom-in image of the rectangular zone shown in (a).

The EDS maps of the cross section inside the cutting zone of the modified tools are shown in Figure 4-7. Similar to the above, the solute elements W, Cr, V and Mo are randomly distributed below the surface, the transferred material is found on the surface, as evidenced by the O map, the Cu map exhibits a background white noise, and S is indistinguishable from Mo in Figure 4-7(a). However, zooming into the region marked by a rectangle in Figure 4-7(a), we can clearly identify a horizontally elongated zone just below the surface on the left side of both the Mo and S maps in Figure 4-7(b), which is noted as “most likely
S”. This region has a different shape than the typical Mo inclusions below, it is adjacent to the surface along its whole length, and it is located immediately below the Al₂O₃ fragment, suggesting that it experienced heavy plastic deformation during shot peening. This makes us believe that it represents proof of the mechanochemical reaction between Cu₂S and Fe leading to the formation of the tribologically beneficial iron sulfide that allows the modified tool to perform better by retaining oil on the surface more efficiently. During the cutting process, the additional layer created by the shot peening particles being spread on the surface is easily removed, but the iron sulfide formed on the tool surface can maintain its integrity much longer. As a result, the iron sulfide layer consistently enables the cutting surface to maintain better lubrication and to substantially delay failure.

4.5 Concluding Remarks

Mechanochemical surface modification of the high-speed steel cutting tools using dual shot peening with a mixture of Al₂O₃ and Cu₂S particles enables to improve wear resistance and significantly extend the tool life under the base oil lubrication. This is attributed to a formation of iron sulfide and its ability to retain oil at the cutting interface, which results in lower stresses and temperature. This technique shows good potential to lower manufacturing cost, reduce energy consumption, and improve machining quality, while also being more environmentally friendly compared to the use of fully formulated cutting fluids.
CHAPTER 5. PERFORMANCE OF TUNGSTEN CARBIDE TOOLS

This chapter presents the study of the tungsten carbide (WC) inserts that were treated mechanochemically and then used in cutting to examine their frictional performance. Additionally, shot peening with Al₂O₃ particles alone and electrical discharge machining (EDM) were employed to further study the friction and wear of WC inserts to understand the effects of roughness, surface hardness and residual stresses.

5.1 Mechanochemical Treatment

5.1.1 Surface modification

The cutting inserts are 5 deg rake angle uncoated WC inserts, TPG321 Grade HT10 (Hertel, Essen, Germany), and shot peened by three different media, Al₂O₃ particles (100 µm in size, hardness 2300 HV; Comco, Burbank, CA, USA) alone, Cu₂S particles (less than 74 µm in size, hardness 90 HV; Sigma-Aldrich, St. Louis, MO, USA) alone, and a 1:1 mixture of Al₂O₃ and Cu₂S. Studying the cutting forces of inserts treated with different media could help us to find the influence and function of different media used in shot peening. The WC inserts were mounted on the X-Y stage and shot peened following a raster path with a linear velocity of 0.1 mm s⁻¹ and a pitch of 0.4 mm, shown in Figure 5-1(a). The impact angle between nozzle axis and tool surfaces was 75 deg, and the distance between nozzle and tool surface along nozzle axis was 13 mm. N₂ pressure was 3 bar.
5.1.2 Machining tests

Figure 5-1(b) shows a schematic of orthogonal tube turning experiments performed in an Okuma Spaceturn CNC lathe (LB2000EX). The workpiece is 1018 steel tubes with an outer diameter of 36 mm and wall thickness of 2 mm to ensure plane strain conditions. An emulsion created by mixing cutting fluid Trim MicroSol 690XT with water at 1:9 ratio was supplied to the tool rake face at the rate of 120 drops (~2.4 mL) min\(^{-1}\). The orthogonal cutting and thrust forces were measured by a piezoelectric multi-component dynamometer (Kistler Instrument Corp 9257B) and were sampled at a sampling rate of 1000 Hz (National Instruments Co cDAQ-9178). The turning speed was 85 m min\(^{-1}\) and the cutting feed is 203 µm rev\(^{-1}\). Each cutting test was repeated three times.

5.1.3 Cutting analysis

Figure 5-2 shows the cutting and thrust forces of differently modified WC inserts, each of which was tested twice. The inserts modified with the blend of Al\(_2\)O\(_3\) and Cu\(_2\)S did not show any advantage over the tools modified with Al\(_2\)O\(_3\) only. Furthermore, the tools
modified with Cu$_2$S only did not show statistical difference with respect to the reference tools and were significantly inferior to the inserts modified with Al$_2$O$_3$ only. These results suggest that pure mechanical surface treatment through shot peening should be responsible for the improved cutting performance of WC inserts, while the chemical aspect of the mechano-chemical surface modification is negligible. Given that shot peening is known to change surface topography, strength and residual stresses, the effects of these parameters were studied, as presented in the next section.

![Figure 5-2. Cutting force and thrust force of modified WC inserts.](image)

### 5.2 Shot Peening and EDM

#### 5.2.1 Surface modification

The rake faces of WC inserts are treated either by shot peening (SP) with Al$_2$O$_3$ alone or EDM aiming at achieving the same surface average roughness. Here we only used Al$_2$O$_3$ (100 μm in size, hardness 2300 HV; Comco, Burbank, CA, USA) to shot peen WC inserts. The WC inserts were mounted on the X-Y stage and shot peened following a raster path.
with a linear velocity of 0.1 mm s\(^{-1}\) and a pitch of 0.4 mm. The impact angle between nozzle axis and tool surfaces was 75 deg, and the distance between nozzle and tool surface along nozzle axis was 13 mm. N\(_2\) pressure was 3 bar. A ZNC EDM AccuteX sinker (Oscarmax, Taichung, Taiwan) was used to prepare the EDM-modified inserts, shown in Figure 5-3. A rectangular copper block EDM electrode polished using 4000 grit sandpaper was set to modify the surface area right at the cutting edge (uniform treatment named U-EDM) or at a distance of 3 times the cutting feed from the cutting edge (partial treatment named P-EDM), which was chosen according to a previously found optimum [15].

![Figure 5-3. Experimental setup of EDM.](image)

The inserts’ surface topography and hardness were examined using a 3D optical profiler, ContourGT-I (Bruker, San Jose, CA, USA), and a micro-hardness tester, HM-220 (Mitutoyo, Kawasaki, Japan), respectively. The residual stresses were measured using an X-ray diffractometer, Empyrean (Malvern Panalytical, Malvern, UK) equipped with Cu Ka radiation and PIXcel hybrid line detector. The determination of residual stresses was
done by successive $\sin^2 \varphi$ stress measurement at the WC 112 peak. The x-ray penetration depth was estimated to be 12.5 µm based on the calculation of Highscore software. Pre- and post-cutting images of the rake and flank surfaces were taken with an optical stereo microscope M125 (Leica Camera AG, Wetzlar, Germany) and a scanning electron microscope (SEM), Quanta 250 (Thermo Fisher Scientific Electron Microscopy, Hillsboro, OR, USA). In addition, after etching with Murakami Reagent (ES Laboratory, Glendora, CA, USA) for 3 minutes, the cross-sections of different treated inserts were imaged with SEM.

Studying the rake surface characteristics obtained by the SP and EDM treatments, as shown in Table 5-1, we see that the roughness averages, $S_a$ of treated surfaces, appear to be very similar, as adjusted in accord with our test plan. This similarity, however, is not preserved if a more detailed analysis is performed based on bearing ratio parameters. Comparing reduced peak height, $S_{pk}$, and reduced valley depth, $S_{vk}$, reveals that the SP-treated surface features more pronounced valleys, which presumably result from peening indentations, while the EDM-treated surface exhibits more pronounced peaks, which are supposedly induced by melting around electrical discharge sites. The surface hardness also changes differently after the studied treatments, with SP leading to surface hardening, and EDM leading to slight surface softening, most likely due to corresponding changes in the grain size. In line with the hardness test results, we see that the SP-based treatment dominated by plastic deformation leads to compressive residual stresses on the insert surface, while the EDM-based treatment dominated by thermal mechanisms of electrical spark erosion leads to tensile residual stresses.
Figure 5-4. Optical microscope (a) and SEM (b) images of the surface, and SEM images of the cross section (c) of the rake faces of reference, SP-treated, and EDM-treated inserts.
Table 5-1. Topography, hardness, residual stresses and edge radius (mean ± std. dev.).

<table>
<thead>
<tr>
<th></th>
<th>Sa (µm)</th>
<th>Bearing ratio parameters</th>
<th>Micro-hardness (HV 1)</th>
<th>Residual stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sc (µm)</td>
<td>Spk (µm)</td>
<td>Svk (µm)</td>
</tr>
<tr>
<td>Reference</td>
<td>0.061±0.006</td>
<td>0.184±0.024</td>
<td>0.086±0.010</td>
<td>0.154±0.019</td>
</tr>
<tr>
<td>SP</td>
<td>0.540±0.002</td>
<td>1.742±0.010</td>
<td>0.539±0.002</td>
<td>0.884±0.037</td>
</tr>
<tr>
<td>EDM</td>
<td>0.536±0.004</td>
<td>1.697±0.022</td>
<td>0.815±0.019</td>
<td>0.694±0.012</td>
</tr>
</tbody>
</table>

Optical microscope and SEM images of the studied inserts are shown in Figure 5-4. When observed under the optical microscope (Figure 5-4 (a)), the SP- and EDM-treated inserts seem to have similar surface texture. However, when examined under higher magnification (Figure 5-4 (b)), the treated surfaces exhibit clear differences in visual appearance, which are also consistent with the roughness measurements (Table 5-1). The SP-treated inserts demonstrate more uniform surface topography than the EDM-treated inserts that clearly show smooth patches and splashes of molten material associated with spark erosion. Comparing the appearance of the insert cross-sections shown in Figure 5-4 (c), we can also see that while the SP-treated surface features a layer of about 1 µm in thickness that consists of what appears to be smaller grains, the EDM-treated surface does not exhibit signs of the grain size reduction. In comparison, the EDM-treated surface shows the presence of surface cracks, which most likely appear due to the tensile residual stresses associated with spark erosion (Table 5-1).

5.2.2 Machining tests

Orthogonal cutting tests were performed by turning 1018 steel tubes having wall thickness of 2 mm and constrained to a stick-out of 76.2 mm, as shown in Figure 5-1(b). Cutting performance was tested over a cutting distance of 3.315 m under a cutting speed of 85 m min\(^{-1}\) with feeds of 100, 150, 200, and 250 µm rev\(^{-1}\), and under cutting speeds of 21, 53,
85, and 117 m min\(^{-1}\) with a feed of 200 \(\mu\)m rev\(^{-1}\). After each cutting test, a new location along the tool cutting edge was used for a total of 2 cuts per insert, and each combination of the test conditions was repeated twice. An emulsion created by mixing cutting fluid, Trim MicroSol 690XT (Master Chemical Co., Perrysburg, OH, USA), with water at a 1:9 ratio is supplied to the tool rake face at the rate of 120 drops (~2.4 mL) min\(^{-1}\). The cutting and thrust forces were measured by a piezoelectric multi-component dynamometer 9257B (Kistler Instrument Co., Winterthur, Switzerland), and were sampled at a rate of 1000 Hz with cDAQ-9178 (National Instruments Co., Austin, Texas).

To evaluate the life duration of the textured WC inserts, wear tests were conducted at a speed of 85 m min\(^{-1}\), and a feed of 200 \(\mu\)m rev\(^{-1}\), while all other conditions were identical to those used in the cutting force tests. Based on ISO 3685, end of tool life was defined as the time required to generate an average flank wear land width of 300 \(\mu\)m, at which point the test ended \[106\]. The temperature and relative humidity in the laboratory were 21-23 °C and 45-55%, respectively.

5.2.3 Cutting analysis

Comparing the performance of the studied inserts (Figure 5-5), we see that despite having the largest edge radius, the SP-treated inserts consistently demonstrate the lowest cutting and thrust forces for all but one cutting condition. The only combination of the speed and feed, at which a slight SP-induced reduction of cutting and thrust forces is statistically insignificant (at a confidence level of 0.05), is associated with the lowest cutting speed. In contrast, the EDM-treated inserts exhibit no statistically significant effect on cutting performance under all conditions except the same one associated with the lowest cutting speed.
speed, at which the U-EDM-treated inserts demonstrate significant reduction in cutting and thrust forces. Interestingly, P-EDM-textured high-speed-steel tools demonstrate a reduction in the cutting forces under similar conditions earlier [15], which can be associated with the different tool material.

The opposite behavior of the SP- and EDM-treated inserts can be attributed to the friction force, which is the product of the real contact area and the shear strength of the interface. These two parameters, which are different for the SP- and EDM-treated inserts, may dominate at different conditions.

Based on the values of the reduced peak height, $S_{pk}$, (lower for SP and higher for EDM), we can conclude that the SP-treated inserts should have larger real area of contact than the EDM-treated inserts. On the other hand, based on whether plasticity or thermal mechanisms are involved in the surface treatment, we can conclude that the SP-treated surfaces have smaller grains than the EDM-treated surfaces, which is also supported by the micro-hardness measurements. Since smaller grain size is reported to be associated with lower friction [107] and lower surface free energy [108], which suggests that the SP-treated inserts should have a smaller shear strength of the interface than the EDM-treated inserts. If the size of the contact area dominates the cutting behavior at lower cutting speeds, and the shear strength of the interface dominates is more important at higher cutting speeds, when increasing temperature amplifies the differences in mechanical properties, then we can expect to see the results demonstrated in Figure 5-5.
5.2.4 Wear analysis

Figure 5-6 demonstrates the flank wear and the tool-chip contact length measured as a function of the cutting distance. Comparing the flank wear development for different inserts, we see that while the P-EDM-treated inserts perform similarly to the reference inserts, the U-EDM-treated inserts reach the critical wear much faster and the SP-treated inserts reach the critical wear much slower than the reference inserts. These results are consistent with the tool-chip contact length measurements that demonstrate similar outcomes in the cases of the reference and P-EDM-treated inserts and a much shorter
contact length in the case of the SP-treated inserts. Interestingly, the U-EDM-treated inserts initially also show a shorter tool-chip contact length compared to the SP-treated inserts, but soon after it starts growing sharply. This can be associated with chipping of the cutting edge seen clearly in the optical images of the progressively worn rake and flank insert faces shown in Figure 5-7 and Figure 5-8.

![Graph showing flank wear and tool-chip contact length as a function of cutting distance at speed of 85 m min⁻¹ and feed of 200 µm rev⁻¹.](image)

**Figure 5-6.** Flank wear and tool-chip contact length measured as a function of cutting distance at speed of 85 m min⁻¹, and feed of 200 µm rev⁻¹.

Chipping of the cutting edge in the U-EDM-treated inserts is attributed to the tensile residual stresses generated on the tool rake face due to thermal effects associated with spark erosion. Given that the cutting edge is the most highly stressed region of the cutting tool [109], these tensile stresses result in catastrophic failure in the case of the U-EDM that extends to the very edge of the insert and are harmless in the case of the P-EDM that does not affect the stress state of the cutting edge.
It is also interesting to analyze the differences in the tool-chip contact area and their correlation with flank wear. It is well known that the use of cutting fluids lowers friction and cools the tool surface causing the chip to become more curled [109], which can be explained by changes in the residual stresses on the chip surface rubbing against the tool. Based on both the tool-chip contact length and direct chip measurements, chips are about 40% more curled in the case of the SP-treated inserts. To this end, given that the lowest cutting forces are measured in the SP-treated inserts as well, we can safely deduce that, similar to the observations made when using cutting fluids, the SP-treated insert must have the lowest surface temperature as well. The lower temperature of the SP-treated rake face inevitably results in better wear resistance of the flank face due to a less pronounced thermal weakening of the insert material. Comparing the tool-chip contact length in the initial stages of wear development in the U-EDM and P-EDM treated inserts, we can also note that leaving untreated the area adjacent to the cutting edge reduces the beneficial effect of lowering the rake face temperature.
Figure 5-7. Rake faces of differently treated inserts imaged at progressively growing sliding distance.
Figure 5-8. Flank faces of differently treated inserts imaged at progressively growing sliding distance.

5.3 Concluding Remarks

The mechanochemical surface treatment based on using Cu$_2$S particles is not able to modify WC inserts. WC inserts modified to have irregular surface texture on their rake faces can last either longer or shorter than the untreated inserts depending on the combination of roughness and residual stresses generated close to the cutting edge of the tool. Having compressive residual stresses and increased roughness close to the cutting edge leads to significantly increased tool life through reduction of friction and the tool-chip
contact length. Having tensile residual stresses close to the highly stressed cutting edge results in chipping of the tool and, hence, in shortening of the tool life even if friction force is lowered. Shifting the treated area away from the cutting edge causes the effect of texture on the tool life to be neutralized. In light of this, uniform shot peening treatment has better potential to become a practical and effective tool surface modification technique for WC inserts than electrical discharge machining.
CHAPTER 6. CONCLUSION

6.1 Research Resume

We explored the influence of a proposed mechanochemical surface modification on HSS and WC cutting tools. First, rake faces of HSS tools were shot peened with three different media: Al₂O₃ particles alone, Cu₂S particles alone, a mixture of Al₂O₃ and Cu₂S particles. Al₂O₃ particles served as plastic deformation media, and Cu₂S particles served as chemical precursor. Orthogonal cutting under base oil lubrication demonstrated that HSS tools shot peened by the mixture of Al₂O₃ and Cu₂S show a reduction of cutting and thrust forces compared to the other types of modified and reference tools. EDS characterization results suggest a chemical bonding of sulfur to the iron-based tool substrate. This helps to retain oil better at the cutting interface, hence reducing the cutting and thrust forces. The study also indicated that surface roughness is not the only factor affecting the cutting performance and that shot peening can assist chemical reaction.

To understand the mechanochemical mechanism better, a reaction kinetics model coupled with solid mechanics was developed to simulate the shot-peening-assisted reaction of S and Fe. The model predicts that the dissociation of the Fe-Fe and Cu-S bonds needed for the formation of Fe-S bonds accelerates monotonically with increase in the shot peening particle speed, whereas its rate reaches a local maximum at the impact angle of about 75 deg. The latter finding was validated by treating the rake faces of HSS cutting tools and performing orthogonal cutting experiments in which the tools peened at the impact angle of 75 deg exhibited lower cutting and thrust forces than those peened at 40 deg. Additional
peening parameters, namely, the particle volume ratio and the stage speed were found to be much less statistically significant under the conditions tested.

After proving that the mechanochemical surface modification was able to reduce cutting forces, we were interested in investigating its effects on tool wear. To pave the way for practical implementation of this technology, we studied wear of mechanochemically treated HSS tools. Wear land was examined to estimate the wear life of a HSS tool. Orthogonal cutting tests performed under base oil lubrication demonstrate at least a twofold increase of the wear life of the modified tools compared to the untreated references. This is attributed to a formation of iron sulfide and its ability to retain oil at the cutting interface, which results in lower stresses and temperature. This environmentally friendly technique shows good potential to lower manufacturing cost, reduce energy consumption, and improve machining quality.

Since the mechanochemical modification works well on HSS tools, we wanted to extend the study to WC inserts. Unfortunately, the inserts modified with the blend of Al₂O₃ and Cu₂S did not show any advantage over the tools modified with Al₂O₃ only though their cutting and thrust forces were lower compared to the reference inserts. Therefore, the mechanochemical modification could not affects the WC inserts. We furthered the study by texturing the WC inserts with shot peening and EDM. Lubricated orthogonal tube turning experiments demonstrated that the WC inserts with irregular surface texture of rake face exhibited either longer or shorter service lives than untreated inserts depending on the combination of surface roughness and residual stress. Higher roughness and compressive residual stress produced by SP led to significantly increased wear resistance and could increase tool life by approximately 30 percent through reduction of the tool-chip contact
area and the apparent tool-chip friction. Tensile surface residual stresses generated by EDM resulted in chipping of the tool and, hence, shorter tool life even when cutting forces were lowered. Moving the treated area away from the cutting edge neutralized the effect of texture on tool life. Based on the test results, surface modification of WC inserts through SP yielded better tool life performance than surface modification through EDM.

6.2 Research Contributions

The work presented in this dissertation makes the following original contributions:

1. We proposed a mechanochemical modification technique for improving the cutting performance of machining tools. This technique works well with HSS cutting tools by reducing the cutting/thrust forces and extending the tool wear life.

2. We developed a reaction kinetics model coupled with solid mechanics to simulate the shot-peening-assisted chemical reaction between S and Fe. The model is able to predict the effects of shot peening parameters on the HSS tool performance. The model is validated by experimental results under different shot peening parameters.

3. We found that the mechanochemical modification is not applicable to WC inserts. Pure shot peening with Al₂O₃ shots is proved to be able to lower the cutting/thrust forces of WC inserts and to extend the tool life due to surface topography change and induced residual stresses.
6.3 Recommendations for Future Work

The theoretical model we built simulates a single impact process. The real shot peening is characterized by multiple impacts, so developing a more realistic model can simulate the process better and help to find more accurate stress distribution at the interface. These results will yield a more accurate temperature rise obtained from the plastic work. Such enhanced model will help simulating the reaction rate closer and will provide more practical guidance for tool modification.

The main chemical characterization methodology used in this work was EDS. However, EDS is not good at differentiating S from Mo, which is a characteristic solute material in M2 HSS tools. It is necessary to find a better way for chemical characterization. One possible way is to work with materials that do not contain Mo. Without the interference of Mo, we should be able to find the change in distribution of S much more accurately. Another possible way is to try other characterization tools or methodology that can distinguish Mo from S. We tested the time of flight secondary ion mass spectroscopy (TOF-SIMS) which uses mass of atoms or atom groups to characterize different elements or chemical compositions. Due to the limited time and funding, we could not prepare better samples to get more conclusive results. It is worthwhile to prepare the sample in a more precise way to use this characterization tool in the future.

The formation of iron sulfide could retain oil better at the cutting interface. As we all know, better lubrication can lower the temperature. That is one of our explanations of why mechanochemical modification can extend the HSS tool life. However, we did not have any direct proof or measurement results to support this claim. In the future work, it would
be good to measure the temperature rise in the cutting zone. One possible way to do that is to apply an infrared camera to take images of the temperature distribution in the cutting zone during machining. Temperature rise is one of the main reasons for machining tools to wear and fail earlier. The extent to which the mechanochemical modification can prevent or slow the temperature rise can help estimating the effects of the proposed technique.
REFERENCES


