Microstructural Aspects of Ceramic-Metal Composites
Performance in Erosive Media.

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Abstract. Solid particle erosion tests were conducted on WC-, TiC-, and Cr3C2 - based ceramic-metal composites (cermets) to study their performance in erosive media. The overall objectives of this study are: (i) to improve our current understanding with regards to the influence of intrinsic properties on wear behavior of cermets, (ii) to estimate an influence of metallurgical features during cermets fabrication on resistance to fracture; (iii) to consider micromechanical aspects of cermets durability; and (iv) to offer the criteria of material reliability in different erosive conditions. For this reasons, microstructure of multiphase materials, fracture mechanisms, ability of energy dissipation and thermo-mechanical parameters and erosion resistance were analyzed.

Introduction
Ceramic – metal composites are materials systems composed of two or more constituents that differ in chemical composition and are essentially insoluble in each other. Cermets are widely used in industry because of their unique combination of properties such as high hardness over a wide range of temperatures, high elastic modulus and thermal conductivity, low thermal expansion and oxidation rate. Moreover, these materials are usually wear resistant ones [1-3]. Tungsten carbide (WC) based cermets consist of WC particles bonded together in a cobalt matrix. Titanium carbide (TiC) based composites usually have a nickel-molybdenum alloy as the matrix. As compare with conventional WC-Co cermets, TiC-NiMo composites are promising light-weight and wear resistant at elevated temperatures materials [4]. Chromium carbide based and nickel bonded cermets are good material candidates to be used in corrosive, abrasive and aggressive environments [5,6].

Although there are a lot of works concerning erosion of WC- based hard metals and steels [2,5,7], there are not so many studies on cermets. Moreover, almost no studies except some [1,8] are concerning the comparative analysis of erosion resistance of different ceramic-metal composites.

It is well known that there is a dramatic difference for ductile and brittle materials when the weight loss in erosion is measured as a function of the angle of impact [7]. Various mechanisms have been proposed to explain these erosion phenomena of material removal. There is general agreement that the materials can be characterised as responding in either a ductile or brittle mode. But only limited number of fundamentally inclined papers have been published on the erosion of ceramic-metal composites [1-3,5,8]. It was reported [8] that a large volume percent of the hard phase is necessary to obtain the optimum erosion resistance. However, in [9] decrease in erosion resistance with an increase in volume fraction of oxide particles in Al2O3-Ni cermet was described.

The amount of metal binder significantly affects the properties of cermet tools. Commonly, as the metal content increases, the strength, hardness and wear resistance of cermets decreases, while their toughness increases because of the higher toughness of metals. The erosive behaviour of cobalt based tungsten carbide was investigated in [2,10] and various mechanisms of material removal were proposed. Ball and Patetson [11] observed that if cobalt content was below 10 wt. % the erosion rate is controlled by WC skeleton. Above 10 wt.%, the erosion is controlled by the strength and toughness of the binder. For high binder levels, erosion appears to occur mainly by preferential removal of the binder phase, while the WC grains undergo only minor erosion that
results in blunting of sharp corners or edges. The type of erosion response for high binder levels is characterised as ductile mode. The type of erosion for low binder types is characterised as a brittle mode. As well, the effect of relative hardness values of the erodent particles and the target was also observed to be important in [8]. In [3] it was suggested that the low toughness of the hard constituencies resulted in a loss of erosion resistance that explained the poor performance of brittle TiC and the possible benefit of the tougher WC. However, it was shown [1,12] that behaviour of multiphase materials cannot be evaluated by only a measured mechanical characteristic or by complex of bulk properties. The internal stress state plays the most important role in composites performance and strongly depends on the microstructural characteristics of materials.

The present study considers the microstructural aspects related to erosion resistance in order to improve our current understanding of wear behaviour of cerments; to consider micromechanical aspects of cerments durability; and to make a comparative analysis of materials performance in erosive media. To achieve these goals wear behaviour of 3 grades of cerments was studied at identical test conditions.

Experimental details

Materials. It is well known that binder metal content influence the material properties to a great extend. Because of above, composites consisted of similar weight percent of metals were prepared for the comparative analysis. The content of hard carbide particles in the cerments was 80 wt.%. Cermet materials tested in this study were produced by conventional press and sinter powder metallurgy. Powders were mixed, milled together, pressed to a green bodies and liquid phase sintered during 30 minutes at temperatures from 1320°C in the case of Cr3C2-Ni and 1420°C in the case of WC-Co hard metals to 1480°C in the case of TiC-Ni(Mo) or TiC-steel.

Overview of the composition and mechanical properties of the materials examined in this study are listed in Table 1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Carbide content, wt.%(%)</th>
<th>Composition and structure of binder</th>
<th>Vickers hardness number, HV</th>
<th>Density $\rho$, [kgm$^{-3}$]</th>
<th>Elastic modulus $E$, [GPa]</th>
<th>Fracture toughness $K_{IC}$, [MPa m$^{-1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>80 WC</td>
<td>Co</td>
<td>1030</td>
<td>13700</td>
<td>550</td>
<td>19.0</td>
</tr>
<tr>
<td>TS</td>
<td>80 TiC</td>
<td>Austenite steel</td>
<td>1410</td>
<td>5400</td>
<td>410</td>
<td>14.0</td>
</tr>
<tr>
<td>TN</td>
<td>80 TiC</td>
<td>Ni Mo</td>
<td>1380</td>
<td>5500</td>
<td>400</td>
<td>11.5</td>
</tr>
<tr>
<td>CR</td>
<td>80 Cr$_3$C$_2$</td>
<td>Ni</td>
<td>1400</td>
<td>6970</td>
<td>340</td>
<td>9.8</td>
</tr>
</tbody>
</table>

The carbide grains in each material have an anisotropic shape with some size distribution. Since the grain size and porosity are important factors in determining the erosion resistance of multiphase materials, the processing parameters were chosen in such a way as to produce cerments similar grain size. Size distribution was conveniently measured with SEM using the black scattered electron mode. Carbide grain size exhibited a range in size of approximately 1.0 – 4.0 μm. Porosity was of 0.2 - 0.5 vol.% for all materials tested with exception of tungsten carbide based ones. The porosity of WC-Co composites was about 0.1 vol.%. 

Experimental procedure. The erosion tests were conducted in a conventional centrifugal four-channel accelerator that has been described in details in [3,12]. The device allows testing all materials simultaneously, thus all materials were examined at identical conditions. The samples to be eroded were chosen on the basis of a full factorial experimental design with factors consisting of target materials size, impact angle, initial particle velocity, and abrasive particles. The tests conditions are given in Table 2. At least four runs were completed for each sample. The erosion rate was determined as volume loss of the target sample per mass of erodent particles (mm$^3$/kg) to allow for the comparison of target materials with different densities. An
accuracy of 0.1 mg was obtained for the target mass loss measurements, and the erosion rate was calculated from average mass loss divided by sample density.

**Table 2.** Erosion test data.

<table>
<thead>
<tr>
<th>Samples size, [mm]</th>
<th>20 x 12 x 4</th>
<th>Before and after being eroded, samples were ultrasonically cleaned and weighed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact angle, [deg]</td>
<td>30, 45, 60, 75, 90</td>
<td></td>
</tr>
<tr>
<td>Initial particle velocity, [m s⁻¹]</td>
<td>20, 30, 45, 60, 80</td>
<td></td>
</tr>
<tr>
<td>Abrasive particles</td>
<td>SiO₂, SiC</td>
<td>Silica hardness $HV = 1100$ and silicon carbide hardness $HV = 3000$. Abrasive particles size of 0.1 - 0.3 mm.</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

Some samples were polished and then impacted with only a few particles to examine single impact sites on the surface of the materials. Scanning electron microscope (SEM) Gemini, LEO, Supra 35 was used to characterize the as-received materials and worn surfaces.

The particle accelerator [3,12] and a special test facility equipped with a digital video camera [13] and software for the results interpretation were used for the precise determination of impact variables and energy absorbed by surface during particle – target collision.

**Results and discussion**

**Erosive wear.** Figures 1 and 2 demonstrate the steady-state erosion rates of the cermet as functions of the impact angle at constant particle velocity of 30 m/s. Usually dependence of erosion rate (E) on angle of incident indicates the nature of the dominant erosion mechanism.

![Figure 1](image_url)

**Figure 1.** Effect of impact angle on the erosion rates of the cermet. Erodent – silica; impact velocity – 30 m/s.

TiC- based cermet exhibit the maximum erosion rate at impact angle of 75°, while Cr₃C₂- based ones have poorer erosion resistance at 90° and exhibit brittle behavior. The tungsten carbide - cobalt cermet, on the other hand, exhibit a maximum erosion rate at 60° in the case of being impacted by silica and 75° in the case of SiC. The mode of cermet erosion is associated with a combination of ductile and brittle modes of wear. The ductile extrusion mechanism is dominant for the erosion process of the binder. This leads the grain uplift of carbides and displacement which are subsequently fractured by successive impacts with erodent. The higher the hardness of erodent particles, the more efficient cracks are initiated in the target by erodent.
Figure 2. Effect of impact angle on the erosion rates of the cerments. Erodent – SiC; impact velocity – 30 m/s.

Figures 3 and 4 show the manner in which the erosion rate increases as the particle velocity increases. Velocity is a critical test variable in erosion of cerments. Independently on their hardness, at low velocity erodent can hardly cause a local destruction of carbide grains and damage may have a though nature across the binder material. Under this test conditions the selective erosion prevails when the failure starts in the binder as the weakest phase. Some fatigue cracks may be developed.

Figure 3. Effect of particle velocity on the erosion rates of the cerments. Erodent – silica; impact angle – 90°.

In the conditions of high velocity of abrasive particles a low-cycle fatigue failure of the carbide skeleton and large carbide grains and microcutting occur depending on the ratio of material and abrasive hardness.

The erosion rate has been shown elsewhere to follow an empirical power law relationship with velocity: \( E = k v^n \), where \( k \) is a coefficient depending on material and erodent properties, \( v \) is a particle velocity. The empirical relationships for \( E \) of cerments tested as a function of the particle velocity at the impact angle of 90° are shown in Table 3. An \( n \) value of 2 would be expected based on the impacting particle kinetic energy, given by \( \frac{1}{2}mv^2 \). A satisfactory explanation for the deviation of \( n \) from 2 has not yet been given in the literature. Values of \( n \) less than 2 may be caused by target material properties that affect rebound, or by particle variables, such as possibility to fracture that dissipates energy, or by embedment of the parts of abrasive particles. The erodents striking cerments are themselves prone to deformation and fracture on impact and the initial kinetic energy is apportioned between the target and the abrasive particles so that less energy is available for erosion. Surprisingly low values of \( n \) were obtained even in the case when erosion is caused by very hard (HV = 3000) SiC particles.
Figure 4. Effect of particle velocity on the erosion rates of the cermets. Erodent – SiC; impact angle – 90°.

Table 3. Erosion rate of the cermets as a function of particle velocity.

<table>
<thead>
<tr>
<th>Grade</th>
<th>$E$, erodent - silica</th>
<th>$E$, erodent - SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC</td>
<td>$E \propto v^{1.52}$ ($R^2=0.97$)</td>
<td>$E \propto v^{1.87}$ ($R^2=0.93$)</td>
</tr>
<tr>
<td>TN</td>
<td>$E \propto v^{1.53}$ ($R^2=0.98$)</td>
<td>$E \propto v^{1.56}$ ($R^2=0.96$)</td>
</tr>
<tr>
<td>TS</td>
<td>$E \propto v^{2.44}$ ($R^2=0.98$)</td>
<td>$E \propto v^{1.82}$ ($R^2=0.94$)</td>
</tr>
<tr>
<td>CR</td>
<td>$E \propto v^{1.1}$ ($R^2=0.986$)</td>
<td>$E \propto v^{1.81}$ ($R^2=0.96$)</td>
</tr>
</tbody>
</table>

One of the most useful models of brittle fracture [14] proposes the following relationship for the erosion rate and widely used materials properties: $E = C K_{IC}^m H^n$, where the exponents $m$ and $n$ have negative value and $C$ is a constant of proportionality. Evans et al. [11] proposed $m = -1.3$ and $n = -0.25$. Assuming that all environmental factors are constant, the volume wear of the various grades should be controlled by the overall magnitude of product $K_{IC}^m H^n$. Figure 5 shows inapplicability of this approach for the cermets evaluation in erosive media.

Figures 1-5 give evidence that no one mechanical property or their product can be useful for the assessment of the erosion resistance of cermets. This fact may be explained through examination of the microstructures, studying energy absorbed by surfaces and by evaluation the mechanisms by which material is removed from the surface during erosion.

**Microstructure and damage mechanism.** SEM micrographs in Figures 6 -10 show the single impact crater generated be abrasive particles during the erosion test. The microstructure of the unworn surfaces can be seen from those pictures, as well.

Figure 5. Erosion rate of the cermets as a function of product $K_{IC}^m H^n$. 

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**Figure 5.** Erosion rate of the cermets as a function of product $K_{IC}^m H^n$. 

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Figure 6. SEM micrographs of edges of single impact crater produced in CR cermet by (a) – SiC, and (b) – silica particle at impact angle of 60° and impact velocity of 60 m/s.

Figure 7. SEM micrographs of single impact crater produced in TS cermet by (a) – SiC, and (b) – silica particle at impact angle of 60° and impact velocity of 60 m/s.

Figure 8. SEM micrographs of single impact crater produced in WC cermet by (a) – SiC, and (b) – silica particle at impact angle of 60° and impact velocity of 60 m/s.

The impact sites in all cermets show some plastically deformed zones; however, brittle fracture seems to be dominating. Material is extruded from the groove by impacting particle (Figure 10a) and subsequent impact can easily detach this extruded material.
Figure 9. SEM micrographs of single impact crater produced in TN cermet by (a) – SiC, and (b) – silica particle at impact angle of 60° and impact velocity of 60 m/s.

Moreover, many grains in the crater surroundings are displaced that accumulates the additive grain boundary strain. If bond between grain and matrix and/or grain and grain is weak, intergranular cracks develop enough easily to propagate for a relatively long distance from the center of crater by brittle manner (Figure 10b). At the same time metal binder metal deforms to a great extent loosing its bonding effect and leaving carbides unconnected with the bulk material.

Figure 10. SEM micrographs of worn surfaces of cermets (a) – CR grade, and (b) – TS grade.

On the other hand, examination of the crater produced by abrasive particle reveals some distinctive features. There are two types of chromium carbide grains in Cr₃C₂-based cermet. In Figure 6 different grey color level indicates Ni phase as the lightest area, Cr₃C₂ particles as the middle grey area, and Cr₇C₃ grains as the darkest area. Being very brittle in nature and possessing hardness half as great as hardness of SiC particle, the grains are fractured at the impact site as well as beneath the eroded surface (Figure 11a, b). Like most ceramics, they are intrinsically brittle. This brittleness of carbides is related on the atomic level to their strong hybrid ionic-covalent bonds that prevent plastic deformation such as occurs in ductile metals. In the case of silica abrasive particles, the microstructural features play the most important role. The dihedral angels are large and extend of Ni penetration into the grain boundary is insignificant. In addition, there are a lot of coalescences grains and grain – grain interfacial energy may be twice greater than that of grain-binder energy. It results in reduced strength if intergranular surfaces and improvement in conditions for intergranular cracks propagation (Figure 11c). Moreover, the effect of difference in the coefficients of thermal
expansion between two phases can stimulate cracks nucleation. High temperature at impact site causes thermo-cracks developing (Figure 11d).

![Figure 11](image1.png)

**Figure 11.** SEM micrographs of CR cermet (a) – center of impact crater; (b) – subsurface cracks; (c) – intergranular cracks; (d) – thermo- cracks.

Titanium carbide grains themselves have a very high hardness of 3000 – 3500 HV [15] while low fracture toughness. Silica abrasive particle can hardly cause direct fracture of carbides and process of erosion starts with deforming, melting and extrusion of binder metal. Mean flash temperature under impact of solid particle onto cermet surface in many cases excesses the melting point of binder metal. Figure 12a presents the melted and solidified metal “gluing” carbide grains together. However, unprotected grains may be easily detached by subsequent impact. In this case binder microhardness and other mechanical characteristics have to be taken into account. Some advantage of mechanical properties of steel over nickel gives some preference to TS cermet over TN at low velocity of impact. However, the erosion rate of TS depends much stronger on impact velocity and it is mostly due to metallurgical aspects of cermets sintering such as residual stresses at the boundaries cause by crystallization, segregation of solute elements or impurities to interfaces.

Impact of SiC particle can cause a direct fracture of carbides and there is no significant difference between two grades of titanium carbide based cermets at least up to 80 m/s. In all probability, erosion at higher velocity eliminates any advantage of TiC-steel composite. It may be caused by some features of TiC-NiMo microstructure. Replacing 10 wt% of nickel binder with Mo results in complete wetting and (Ti,Mo)C complex carbides are formed. Core – rim structured hard grains are surrounded by a tough metallic phase. The outer and inner layers of the rim contain also some amount of Mo. The grain boundaries contain approximately half a monolayer of Ni.
segregation [16]. Properties gradients influence the crack propagation and its decelerating motion and damping in tougher phases. However, this statement has to be accurately proved in future work.

Figure 12. Centers of the impact craters produced by SiC particle in a surface of (a) – TS grade; and (b) – TN grade.

The cobalt binder contracts during cooling leaving the WC grains under compression and it undergoes a transformation from metastable to stable phase during deformation and consequently has a high stacking fault level. Although toughness of the composites mainly attributed to the presence of tough metal binder, the tungsten carbides contribute the high toughness themselves. Hexagonal structure of WC allows dislocation movement, especially taking into account high temperature at impact site under collision. Being impacted by silica particles, material behaves enough ductile (Figure 8b). The undamaged grains can be seen in the center of impact crater. Different reaction can be recognized when material is impacted by hard SiC. Plural splitting of carbide grains is responsible for the material removal.

Energy absorbed. Cermets CR, TN and TS mostly show brittle fracture with relatively low resistance to crack extension originating at pre-existing defects. Energy release is more likely achieved through the formation of fracture surfaces rather than through plastic or viscoplastic processes, as compared to the more ductile materials of similar strength level.

The energy transmitted to the surface of a material during impact can be estimated as following [13, 17]:

\[
K^* = (1-k)^2 \sin^2 \alpha_i + \frac{2}{\eta} \left( 2 - f_c \right) \cos^2 \alpha_i = K^*_n + K^*_f, \]

where \( \alpha_i \) is an angle before collision or impact angle. The coefficients of the velocity restitution \( k \) and the dynamic friction \( f \) can be determined from experiment; and \( f_c \) represents a boundary friction coefficient [13, 17]. This equation presents the energy that is normalized by dividing the full particle energy by the initial kinetic energy and, therefore, \( K^* \) is non-dimensional. Figure 13 shows the normalized energy absorbed by the cermets. Figure 13 allows concluding that energy transmitted to the surface and absorbed by materials influence the erosion rate of composites. TS grade, for example, has the highest erosion resistance while consume the less energy. Some additional energy needs to be applied for the creation of numerous new surfaces (micro-cracks). Any imperfections will take their parts in energy release. A common tendency to increase in erosion rate with increase in the amount of energy absorbed can be clearly observed.

Conclusions.
Erosion testing was conducted on powder processed WC-Co, TiC-NiMo, TiC-steel and Cr3C2-Ni composites using silica and silicon carbide abrasive particles at impact angles from 30 to 90° and particle velocity from 20 ms\(^{-1}\) to 80 ms\(^{-1}\). The following can be concluded from this study.
Figure 13. Normalised energy absorbed by the cerments and their erosion rate at abrasive particle velocity of 30 m/s.

The erosion rate of materials investigated depends on impact angle: the Cr$_3$C$_2$-based composites show a brittle response to the changes in impact angle with maximum material removal occurring at impact angle of 90$^\circ$; TiC-based cerments show the minimum erosion resistance at the impact angle of 75$^\circ$ and WC-Co grade has a poorer erosion resistance between impact angle in between 60 to 75$^\circ$. Materials behavior is ascribed to microstructural effects and is strongly system dependent. Limited plasticity is observed in all materials; however, the main failure mechanism is brittle fracture.

Velocity is a critical test variable in erosion. The velocity exponent $n$ is less than 2 for any cerments with exception of TS grade eroded by silica particles. Partially it may be explained by processes of deformation and fracture taking place in abrasive particles. Frictional heating may also contribute into energy release under collision.

Microstructure of the cerments determines the materials behavior under conditions of erosive wear while mechanical properties and/or their product may lead to the wrong conclusion concerning ceramic – metal composites performance in erosive media. Some insight into cerments evaluation can be obtained from the examination of energy transmitted into the surface by impacting particle.

References