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Assessment of Cermets Performance in Aggressive Media

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Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any other degree or examination

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The larger the island of knowledge, the longer the shoreline of wonder.
Saying by Ralph W. Sockman [1].

De omni rescibili et quibusdam aliis.
Concerning everything knowable and a few other things besides, Latin [2].

And the wind was blowing and the soil was about to fly away but the roots of plants that have gone it through were helping to hold it for ages. It looks like that the idea of composite structures, designed by nature to sustain erosion is well-tried.

INTRODUCTION

Wear and corrosion (usually acting together to some extent) are the prevailing modes of material degradation causing sufficient economic losses in industrial applications. Right material selection, surface engineering, reduction of process aggressiveness through the optimization of its parameters are applied for the reduction of direct and indirect losses.

The present study focuses on the performance of Cr_3C_2-based cermets and some other metal-ceramic composites and steel being the promising materials for applications requiring high wear, corrosion, oxidation and thermal shock resistance. Materials have been mostly studied in aggressive media.

The interplay of different factors and processes acting simultaneously is established with the help of proposed rationale. The maps for simplifying of selection and developing of composites are constructed. New pilot tester for evaluation of materials performance under erosive conditions at high temperature is created. The role of microstructural features and surface layer in cermets response to aggressive conditions is investigated.

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CONTENTS

LIST OF PUBLICATIONS

The present dissertation is based on the following papers, which are referred in the text by their Roman numerals I-V. As some of the resent research have not been published yet, this thesis was somewhat enlarged.

I. Hussainova, I., Antonov, M.
Elevated temperature wear of chromium carbide based cermets. Proceedings of the Estonian Academy of Sciences, Engineering, Vol. 9/4, pp. 261-271, 2003.

II. Antonov, M., Hussainova, I.
Erosion testing of refractory cermets at high temperature. Proceedings of 12th Nordic Symposium in Tribology, Nordtrib 2006, Helsingør, Denmark, June 7-9, 2006 (CD-ROM).

III. Hussainova, I., Antonov, M.
Assessment of cermets performance in erosive media. International Journal of Materials and Product Technology, 2006 (accepted-in press).

IV. Stack, M.M., Antonov, M., Hussainova, I.
Some views on the erosion-corrosion response of bulk chromium carbide based cermets. Journal of Physics D: Applied Physics, Vol. 39, pp. 3165-3174, 2006.

V. Antonov, M., Hussainova, I.
Thermo-physical properties and thermal shock resistance of chromium carbide based cermets. Proceedings of the Estonian Academy of Sciences, Engineering, Vol.12, pp. 4, 2006 (accepted-in press).

Other publications (not included in the thesis)

VI. Hussainova, I., Antonov, M., Volobujeva, O.
Microstructural aspects of ceramic-based composites performance in erosive media. Advances in Science and Technology, series "Ceramics and New Materials Forum", Vol. 45, pp. 10-12, 2006.

VII. Antonov, M., Stack, M,M., Hussainova, I.
Erosion-corrosion of Cr_3C_2-Ni cermets in salt water. Proceedings of the Estonian Academy of Sciences, Engineering, Vol. 12, 3-1, pp. 176-187, 2006.

VIII. Sergejev, F., Preis, I., Antonov, M., Kübarsepp, J.
Correlation between surface fatigue and microstructural defects of cemented carbides. Proceedings of 12th Nordic Symposium in Tribology, Nordtrib 2006, Helsingør, Denmark, June 7-9, 2006 (CD-ROM. Selected for publication in the Wear).

IX. Sergejev, F., Antonov, M.
Comparative study on indentation fracture toughness measurements of cemented carbides, Proceedings of the Estonian Academy of Sciences, Engineering, Vol. 12, 4, 2006 (accepted-in press).

X. Antonov, M., Hussainova, I., Pirso, J.
Chromium carbide based cermets as the wear resistant materials. Proceedings of DAAAM International Conference, Tallinn, Estonia, April 29-30, pp. 177-180, 2004.

XI. Zimakov, S., Pihl, T., Kulu, P., Antonov, M., Mikli, V.
Applications of recycled hardmetal powder. Proceedings of the Estonian Academy of Sciences, Engineering, Vol. 9/4, pp. 304-316, 2003.

XII. Hussainova, I, Antonov, M.
Thermo-mechanical properties and tribological behavior of ceramic-based composites. Report of the European research programme "Improving the Human Research Potential and Socio-Economic Knowledge Base". Available online at site of AMTT, http://www2.arcs.ac.at/AMTT/reports/reportII-90.pdf , 2003.

XIII. Antonov, M., Hussainova, I.
Erosion of Cr_3C_2*-based cermets at room and elevated temperatures*. Proceedings of DAAAM International Conference, Tallinn, Estonia, April 25-27, pp. 137-140, 2002.

XIV. Hussainova, I., Antonov, M.
High temperature erosion of Cr_3C_2*-based cermets.* Proceedings of 10th Nordic Symposium on Tribology, Nordtrib 2002, Stockholm, Sweden, June 9-12, 2002 (CD-ROM).

XV. Antonov, M., Hussainova, I., Pirso, J.
Solid particle erosion of Cr_3C_2*-Ni metal-matrix composites*, Proceedings of OST-01 Symposium on Machine Design, Tallinn, Estonia, October 4-5, pp. 233-243, 2001.

Approbation

International conferences

1. The 15th International Baltic Conference “Engineering Materials & Tribology” BALTMATTRIB-2006, Tallinn, Estonia, October 5-6, 2006.

2. The 12th Nordic Symposium in Tribology, Nordtrib 2006, Helsingør, Denmark, June 7-9, 2006.

3. The 14th International Baltic Conference “Materials Engineering 2005”, Kaunas, Lithuania, October 6-7, 2005.

4. The 4th International Conference "Industrial Engineering - Innovation As Competitive Edge for SME", DAAAM International Conference, Tallinn, Estonia, April 29-30, 2004.

5. The 10th Nordic Symposium on Tribology, Nordtrib 2002, Stockholm, Sweden, June 9-12, 2002.

6. The 3rd International Conference “Industrial engineering-new challenges to SME”, DAAAM International Conference, Tallinn, Estonia, April 25-27, 2002.

7. OST-01 Symposium on Machine Design, Tallinn, Estonia, October 4-5, 2001.

Authors contribution

The author of this thesis took part in sample preparation routine, was responsible for carrying out of the experiments, collecting, processing and further analysis of experimental data (Paper I-VII, X, XII-XV; XI-only experimental part). The author also took part in discussion on the content (Paper I-X, XII-XV) and have compiled several manuscripts (Paper II, V, VII, X, XIII, XV). However the intellectual merit which is the result of the framework where the contribution of every author should not be underestimated.

ABBREVIATIONS

AMTT - Aerospace Materials Technology Testhouse (Vienna)

CAD – Computer-Aided Design

CTE – Coefficient of Thermal Expansion

ECP – École Centrale Paris

ECx – Code of Equipment (x is the number)

EDS – Energy-Dispersive X-ray Spectroscopy

HT – High Temperature

MML – Mechanically Mixed Layer

PC – Personal Computer

PM – Powder Metallurgy

RH – Relative Humidity

SCE – Saturated Calomel Electrode

SHE - Standard Hydrogen Electrode

SEM – Scanning Electron Microscope

TUT – Tallinn University of Technology

UH – Universal Hardness

vol – volumetric (%)

wt – weight (%)

1 REVIEW OF THE LITERATURE

1.1 Cermets

The term **cermet** designates "a heterogeneous combination of **met**al(s) or alloy(s) with one or more **cer**amic phases" [3] with chemical bond formed at the phase borders [4]. The group of materials covered by this meaning could be broader or wider depending on the application area but in general the components of this composite material could be cobalt, nickel, iron, molybdenum, chromium, tungsten and carbides, nitrides, carbonitrides, oxides, borides, silicides. The basic concept of combining metal and ceramic on an intimate scale is incorporation of the desirable qualities of either species and suppression of the undesirable properties [5]. The first commercially successful metal-ceramic composite – cemented carbide on the base of tungsten carbide (WC) with the cobalt binder was developed in Germany in the early 1920's in response to demand for die materials having sufficient wear resistance for drawing tungsten incandescent filament wires to replace the expensive diamond wires then in use [5-7]. After this breakthrough the new grades of cermets were designed to serve as materials for machining and forming of metals, cutting and drilling of rocks, protection against wear, as material for brakes, as a machine components, as a nuclear fuel elements, electrodes, bearings, friction materials, as materials with superior refractoriness, in electronic components and for many other applications [8-15]. The main factor that constrain the further use (for example as gas-turbine engine materials) of cermets is referred as their very low impact strengths and low resistance to thermal shock [5, 16].

1.1.1 Basic features of cermets

The idea to use powder metallurgy techniques for the production of metal-ceramic composites was the starting point for the development of cermets in 1914 [17]. The pounding of components, blending of the powders, pressing and heating (sintering) of the compound close to the melting temperature of the component with lowest melting point are still in use and governing the microstructure and properties of cermets [18].

The schematic representation of important factors determining the properties of cermets are presented in Figure 1. They are divided into four groups. All four groups of factors are of great importance and in dependence one on the others. The choice of the components is dictated by the final application [3]. Little is known about the actual mechanisms of adherence between ceramic and metal phases although many theories are proposed for different cermet systems [3, 4, 19-23].

One of clearly stated difficulties is the fact that one cannot observe the interface during the interaction [24, 25]. It is recommended to seek for better wettability, selected chemical reactions and some solubility for good bonding. The microstructure can be technologically controlled to provide the optimal microstructure for chosen application [17, 22, 26]. Compatibility of phases is necessary to ensure the work of cermets in wide range of temperatures to avoid formation of strength decreasing microstructural features or inducing of excessive stresses [17, 20, 27].

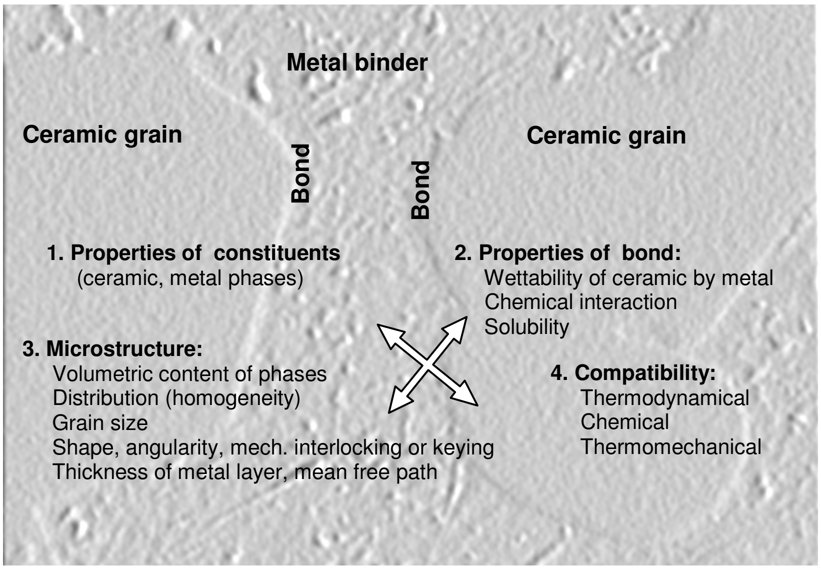


Figure 1. The main factors determining the properties of cermets.

The role of the bond strength inside the phase or between the phases is illustrated at Figure 2. If the composition of metal and ceramic phases is just the mechanical mixture (so is not the cermet) then the addition of one phase to the other leads to the sufficient drop in strength properties (curve 1). If the strength of the metal-ceramic bond is higher or lower than metal-metal (σ_M) or ceramic-ceramic (σ_C) bond then the curve will of convex or concave shape (curve 4 and 2 consequently). If the strength of mentioned bonds will be equal then the dependence will have linear tendency. If small additions of any phase to the other leads to the strengthening of the least then it will be the dependence similar to curve 5 [4]. It is rather difficult to offer reliable generalisation concerning the optimal structure of interfaces in composites. Nevertheless, in addition to the load bearing capacity, the interface should deflect propagation of cracks within the material and thus to promote energy absorption and rise the toughness. A further requirement concerning the interfacial region may be that it should be highly resistant to chemical attack from the environment [26].

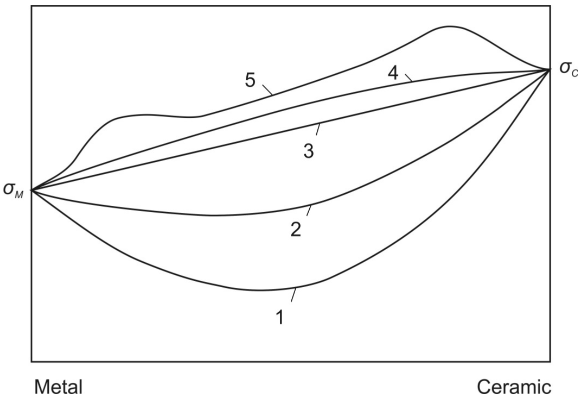


Figure 2. The effect of bond strength on strength of cermet. Explanations-see text. [4]

The ceramic phase in cermets is usually not fibrous, but consists of more ore less equiaxed fine grains (particulate reinforcement). The constituent that is continuous and is often but not always, present in greater quantity is termed the matrix. The normal view is that it is the properties of the matrix that are improved on incorporating another constituent [19]. It is not designated in formulation of cermets which phase is matrix. That is why part of cermets could be designated as metal matrix composites and the other one as ceramic matrix composites. However it is often stated that the most desirable microstructure of cermet is “a uniform dispersion of a fine particle-size hard phase in a matrix of metal binder” [3, 18]. The concentration of ceramic phase in cermet usually lies between 15 and 90 vol % [5, 16].

It often said that WC-Co is a versatile material with significance that still remains undiminished and that is no evidence of new materials that could achieve a wholesale replacement of them [28, 29]. However, according to the known deposits (supplies of raw materials) of tungsten and its consumption rate the lack of this important metal is approaching in the nearest decades [4, 29, 30]. That is the main stimulus for studies to get the substitution materials. An additional reason was also to find something as good as patented WC-Co hard metal but different in order to make it possible to produce without any obligations [17]. Some advantages of tungsten free materials are as follows. Friction coefficient of TiC-based cermets upon the steel is 1.5 – 2.0 times lower due to the more rounded carbide grains [31]. The adhesion of WC-Co to carbon steel is very strong that is crucial for machining [32]. The corrosion resistance of conventional hard metals in many environments is sufficiently lower than that of Cr_3C_2-based ones [33, 34]. It is not possible to use WC-Co materials at temperatures higher than 500-600 ºC due to their intensive oxidation, while other cermet grades can be used at temperatures up to 1000 ºC [5, 32, 34].

1.1.2 Surface

It is well known that the calculated strength of perfect crystals exceeds that of real ones by two or three orders of magnitude [35]. The crystalline solids do not and, in fact, cannot actually exist in nature as single crystals in which the positions of the atoms are perfectly ordered in space. In real solids at thermodynamic equilibrium, deviations from perfect order in the form of finite concentrations of defects such as vacancies and interstitial atoms will always be present depending on the quality of the crystal [36]. The surface itself is a kind of defect of material where the atoms or ions have different bonding than inside the bulk material. That is why the properties of the surface are of the same importance especially in applications where the bodies are contacting each other additionally modifying the surface layer [37- 41].

The definition of a "surface" or of a "thin film" varies considerably from person to person and with application area. The academic discipline of "Surface Science" is largely concerned with chemistry and physics at the atomic monolayer level, whereas the "surface region" in an engineering or applications sense can be much more extensive [41].

The main aspects that influence the behavior of material in surface area during the contact with the other body are summarized below [25, 34, 42-44]:

1. Nature of the solid (bulk) material and coating (if applied) (properties, production technology, internal stresses, ability to change properties under internal activity)
2. The difference in microstructure of bulk material and surface layer (surface treatment to change surface metallurgy or chemistry, ability to create protection layer)
3. History of applied surface engineering operations (machining) (applied processes, surface geometry, roughness, irregularities, additional layers of grease, contaminants etc., induced defects like cracks, corrosion, inclusions etc.)
4. Previous working conditions (parameters of contact events like counter body, velocity, angle, distance etc., failures, defects, wear debris, induced stresses, additional phases formed during the contact or transferred from the environment or counter body).
5. Parameters of the present contact (parameters of contact events, lubrication conditions, adhesion between contacting bodies, the presence of the third bodies, geometry and roughness of contacting areas, environmental aspects like the presence of liquids or gases, temperature, oxidizing ability etc.).

The surfaces contain irregularities of various orders ranging from shape deviations to irregularities of the order of interatomic distances. No machining method, however precise, can produce a molecularly flat surface on conventional materials [25]. In addition to surface deviations, the solid surface itself consists of several zones having physicochemical properties peculiar to the bulk material itself (see Figure 3). As a result of the forming process in metals and alloys, there is a zone of work-hardened or deformed material on top of which is a region of microcrystalline or amorphous structure that is called the Beilby layer. Deformed layers would also be present in ceramics and polymers. These layers are extremely important because their properties, from a surface chemistry point of view, can be entirely different from the annealed bulk material. Likewise, their mechanical behavior is influenced by the amount and depth of deformation of the surface layers [25].

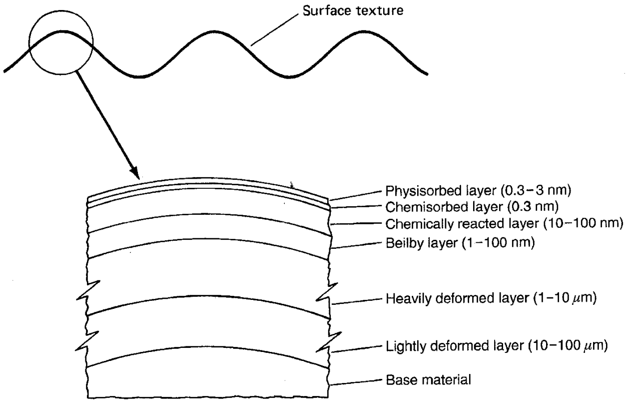


Figure 3. Solid surface details: surface texture (vertical axis magnified) and typical surface layers [25].

It was also observed that during the sliding of some (mainly ductile metals or alloys based composites) materials the mixing of elements that compose the surface layer and the counterbody could take place leading to the formation of the mechanically mixed layer (MML) or transfer layer [45-47]. The mechanism of MML is based on the formation and stretching of interlocked "tongues" (rough peaks) of contacting materials accompanied with extensive plastic deformations and large shear strains and final breakage of their roots [45] or in other words turbulent mixing of counterparts [48] and the oxides from the surface [49]. This layer is mostly considered to be a protective layer, and provides improved wear resistance [46, 48, 50] It was observed that the mechanically mixed layer (MML), rather than the bulk strength of the material, control the wear behavior of studied materials [47]. The hardness, stress-strain behavior and ductility of MML could differ from that of bulk material [51]. The stability of MML depends on the critical thickness of MML, applied load, sliding speed, sliding distance and frictional heating [52]. The correlation between the thickness or hardness of formed MML and specific wear rate was not found [53].

1.1.3 Scale effect

Materials response to loading or environment effects can be considered on different scales. Parameters and characteristic scientific approaches for one scale level may be remarkably different from the next or the previous scale level [54]. At the **macro**scale the material and its respond to the external impacts is often overlooked as homogeneous, having total elastic and plastic deformations in contact zone that results in total material degradation. This level is convenient for the material selection by designers. At the **micro**scale (1 μm and down to nm scale) fillers, matrices, filler-matrix interface are taken into account. The mechanisms of material degradation are described showing the stress and strain formation at an asperity-to-asperity level; the crack generation and propagation, material liberation, and formation of degradation products are also discussed. **Nano** scale is applied to describe the behavior of constituents at molecular level (nanophysical effects) [25, 55]. Illustration of the tribological scale levels from atomic to universal dimensions is shown in Figure 4.

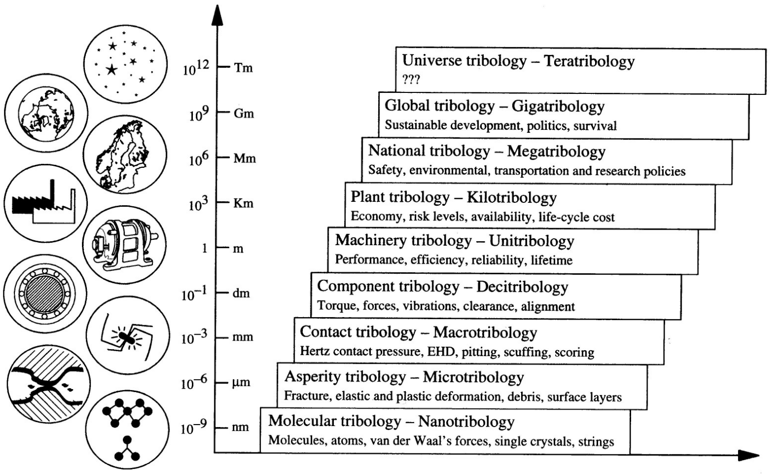


Figure 4. Scales of tribology [54]

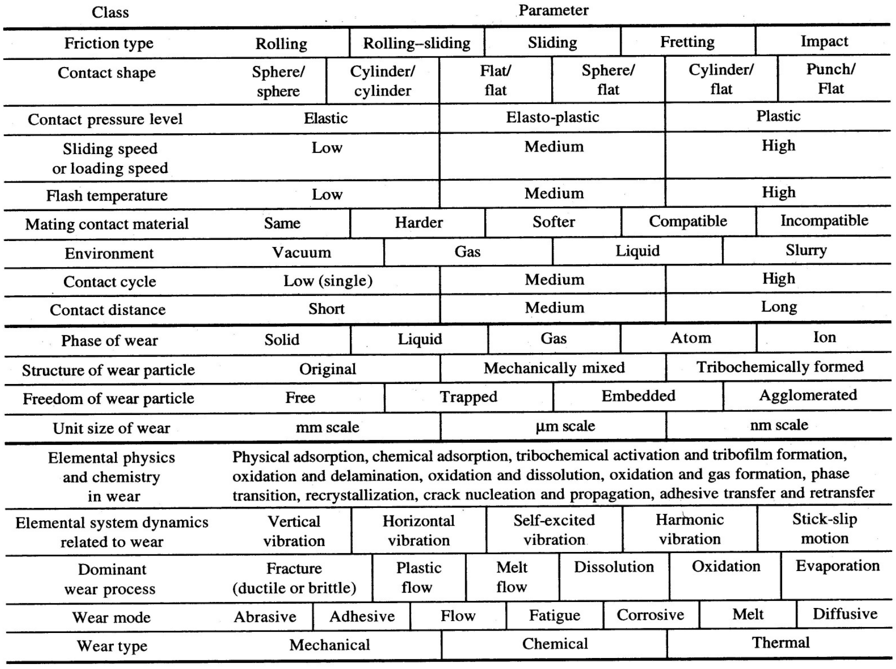
In a tribological context it is told that if the frictional work is dissipated over a large volume of composite material, compared with the scale of the secondary-phase domain size, then a material could be overlooked as homogeneous. However the energy is also dissipated at two different scales: in a large subsurface of the order of the contact dimensions and a very thin interface zone of the order of asperity dimensions [37].

The properties of composite materials itself are also influenced by the scale of the microstructural features [35, 56]. Nanoscale materials have the physics very different from the macroscale properties of the same substance and the different, often superior, properties [57].

1.2 Aggressive environments causing degradation of materials

1.2.1 Wear

Tribology (from the Greek τριβος – rubbing or attrition) is defined as “the science and technology of interacting surfaces in relative motion” [58]. In general, **wear** may be defined as “damage to a solid surface caused by the removal or displacement of material by the mechanical action of a contacting solid, liquid, or gas” [34]. The classification of wear parameters, along with descriptive terms of mechanisms is shown in Figure 5.



Class	Parameter						
Friction type	Rolling	Rolling–sliding	Sliding	Fretting	Impact		
Contact shape	Sphere/ sphere	Cylinder/ cylinder	Flat/ flat	Sphere/ flat	Cylinder/ flat	Punch/ Flat	
Contact pressure level	Elastic	Elasto-plastic	Plastic				
Sliding speed or loading speed	Low	Medium	High				
Flash temperature	Low	Medium	High				
Mating contact material	Same	Harder	Softer	Compatible	Incompatible		
Environment	Vacuum	Gas	Liquid	Slurry			
Contact cycle	Low (single)	Medium	High				
Contact distance	Short	Medium	Long				
Phase of wear	Solid	Liquid	Gas	Atom	Ion		
Structure of wear particle	Original	Mechanically mixed	Tribochemically formed				
Freedom of wear particle	Free	Trapped	Embedded	Agglomerated			
Unit size of wear	mm scale	μm scale	nm scale				
Elemental physics and chemistry in wear	Physical adsorption, chemical adsorption, tribochemical activation and tribofilm formation, oxidation and delamination, oxidation and dissolution, oxidation and gas formation, phase transition, recrystallization, crack nucleation and propagation, adhesive transfer and retransfer						
Elemental system dynamics related to wear	Vertical vibration	Horizontal vibration	Self-excited vibration	Harmonic vibration	Stick-slip motion		
Dominant wear process	Fracture (ductile or brittle)	Plastic flow	Melt flow	Dissolution	Oxidation	Evaporation	
Wear mode	Abrasive	Adhesive	Flow	Fatigue	Corrosive	Melt	Diffusive
Wear type	Mechanical	Chemical	Thermal				

Figure 5. Classification of wear parameters [59].

It is almost impossible to find the object that is not subjected in some way to the effect of wear. Even joints in human body are subjected to wear and are replaced if necessary [60].

The successful attempts to diminish the friction forces and the wear were stimulated by the necessity of people to transport goods and objects. So the lubricants (animal fat or tallow) were applied to reduce the friction forces in wheels and sleds [61-63]. Studies of sliding friction have a long history, going back to the time of Leonardo da Vinci. Luminaries of science such as Amontons, Coulomb and Euler were involved in friction studies, but there is still no simple model which could be used by a designer to calculate the frictional force for a given pair of materials in contact [43].

Wear related researches were started in Tallinn University of Technology in 1955 and are held up to date. The work was initially governed to diminish the wear of such disintegrator parts as impact elements, rotor rings as well as economiser tubes, cyclone collectors, draft fans and hammer mils for production of silicate concrete and in power station boilers. The standard GOST 23.201-78 “Gas abrasive wear testing of materials and coatings with a centrifugal accelerator” developed in 1978 has verified the importance of this work [64, 65].

On the basis given above, some ways to diminish the material losses during application may be suggested [43, 59, 61, 66-69]:

1. Change the design of parts to be subjected to wear (avoid the contact between parts, optimize shape, use exchangeable protection parts, bearings, try to diminish vibration caused by changing of parts dimensions due to wear).
2. Make conditions less severe (control the energy income during the contact, the contact area, impact angle, and temperature, diminish formation, income and the abrasiveness of abrasive, isolate from unwanted chemicals).
3. Change the material or make additional treatment (chose the material of high wear resistance, apply coating, treat a surface to change surface chemistry and/or properties).

Hardness of materials is usually considered as the main factor among the mechanical properties influencing the wear resistance of metal and ceramic based materials. The wear resistance generally increases as the material hardness increases [58, 70]. In metal matrix composites the hard ceramic constituents are responsible for wear resistance, while the soft matrix keeps the reinforcement in place and transfers the applied load to the reinforcement [20]. Increase in metal binder content of cermets leads to increase in erosion rate [71]. However, resent researches have pointed the importance of other properties of composites and, first of all, fracture toughness [25, 58, 72, 73].

1.2.2 Corrosion, oxidation

Corrosion is a chemical or electrochemical process in which surface atoms of a solid body react with a substance in contact with the exposed surface [34].

The chemical reactions taking place at the surfaces during sliding contact, and also during the periods between repeated contacts, change the composition of the outermost surface layer and its mechanical properties. The chemical reactions on the surfaces are strongly influenced by the high local pressures and the flash temperatures, which can be over 1000 °C, at spots where asperities collide [25, 73].

Usually the binder metal only corrodes during process of chemical interaction of cermet and substance. Binder metal is generally dissolved from the surface of the material leaving surface covered by ceramic grains. Loosing their support grains can be easily removed from the surface. The amount and rate of corrosion may change considerably with changes in such factors as concentration and temperature of the corrosive fluid and exposure time [10]. However ceramic can also corrode under some certain environments [74-76].

The resistance of Ni to corrosion is acceptable-to-good in sulfuric, hydrochloric, hydrofluoric, phosphoric and organic acids, alkalis, salts and sea water. The application in nitric acid environments is not recommended [77].

The scientific exploration and exploitation of the ocean depths is now proceeding at a greatly accelerated pace. Typical areas of interest can be roughly classified as off-shore mineral development (oil, gas, sulfur, salt, diamonds, and coal); food production (fish, shellfish, plants, etc.); seawater extraction (magnesium, bromine, salt, and fresh water); and off-shore meteorology (control of storms) [78, 79].

The corrosion rate of nickel in salt water is approximately 10 times lower than that of cobalt and at least 50 times lower than that of low alloyed steel. In case of Ni and Co some local attacks (pitting) may be expected where salt and deposits set up corrosion cells [78, 80]. The corrosion resistance of chromium carbide cermets with nickel binder in sea water is also 20-50 times higher than that of cermets with steel binder [81].

Methods of corrosion protection and prevention include alloying, changing the environment by desiccation or the use of inhibitors, controlling the electrochemical potential, applying coatings, taking into account installation methods and maintenance procedures, considering that each material is a part of a bigger identity [34, 75].

Oxidation is a special form of corrosion degradation of metals and alloys that occurs when the metals or alloys are exposed to air or oxygen. If the formed oxide scale is thin, slowgrowing, and adherent, it protects the substrate from further oxidation. However, if the scale spalls frequently, the metal is consumed continuously and the material ultimately fails [82].

It is well known that most metals, with exception of the noble metals, form layers of oxides, even at room temperature. Iron, nickel, cobalt form the group of transition elements, which have moderate oxidation resistance and are used mainly for intermediate temperatures but are the base elements for important alloys for high temperature applications [82]. The chromium carbide based cermets have the highest oxidation resistance among hard metals [83].

1.2.3 Effect of temperature

All properties of the materials (physical, mechanical, chemical, thermal, etc) are dependant on temperature. The increase in temperature leads usually to the decrease in hardness, strength, accelerated chemical reactions and diffusion processes etc [84-86]. The temperature changes (especially rapid) are leading to the development of temperature gradients consequently gradients of other properties, that may lead for example to the development of cracks due to thermal stresses [87-89]. The combining of phases with different properties in composites leads to additional effects that should be considered [21, 27]. The thermal stresses generated due to the difference in thermal expansion coefficients could have the positive effect in cermets since ceramic phase is under compression that leads to the improved strength properties [20].

1.3 Simultaneously acting processes

The materials in real conditions are subjected to several processes or mechanisms acting simultaneously. So, however corrosion can often occur in the absence of mechanical wear, the opposite is rarely true. Corrosion accompanies the wear process to some extent in all environments, except in vacuum and inert atmospheres [25, 34, 90, 91].

It is usually said that the erosion-corrosion is the acceleration of corrosion rate due to the impact of erodent [34, 38, 39, 75, 81, 92]. However it was shown that degradation rate could be decreased through the formation of oxide layer with better wear resistance than bulk material [93, 94].

The rationale involving the measuring of several output factors, the experimental procedures, defined borders and the mathematical instrumentation allows to define the wastage rate regimes and “synergistic” (corrosion enhances or impede wear), “additive” (wear enhances corrosion), and other modes of processes interplaying [95, 96].

The determination of the dominating mechanism of material destruction, the knowledge about the effect of process variables and the impact of each process leads to the better understanding of the material behavior and gives the ability to decrease the wastage rate [92, 97, 98].

1.4 Mapping of the data

The dependence on a large number of variables has been a significant barrier in achieving a comprehensive representation of such complicated processes as wear. Therefore, there is a strong need for a methodology to define and measure wear of a material in definitive terms [61, 68, 99-101]. The first simplified wear map was published in Japan in 1941. Later, the maps were completed by adding the information concerning the wastage regimes; the mathematical basis for charting the transitions between them was established by Lim and Ashby [102, 103].

Maps can provide valuable guidance to the designer in selecting materials and choosing operating conditions to minimize material wastage, and can also indicate how changes in these conditions will influence the rate, and more importantly - the dominant mechanism [104]. Maps can also be used to characterize interaction of different processes acting simultaneously as a function of the main process parameters [95]. A map is considered one of the best descriptions of tribological conditions and is useful in selecting and developing of materials in a wide range of operating conditions [99]. However there is much more work needed to fully develop this approach for practical applications [100].

2 AIMS OF THE STUDY

Cermets as well as hard metals during the last 80 years of service have proven their efficiency in different application areas where wear and corrosion resistance and the ability to work at high temperature are of the great importance. **The aim of this work is to study the behavior of perspective grade of cermets in order to make the assessment of its performance in aggressive media (1).** Chromium carbide cermet is chosen as the target material for investigation since the information concerning it was quite rare at the time of beginning of the present work. This tungsten free cermet is proposed as an alternative to conventional WC based hard metals and as material with superior properties in severe corrosion conditions and for high temperature applications. It is decided to make the variety of tests to show the application ability of this material (see Figure 6).

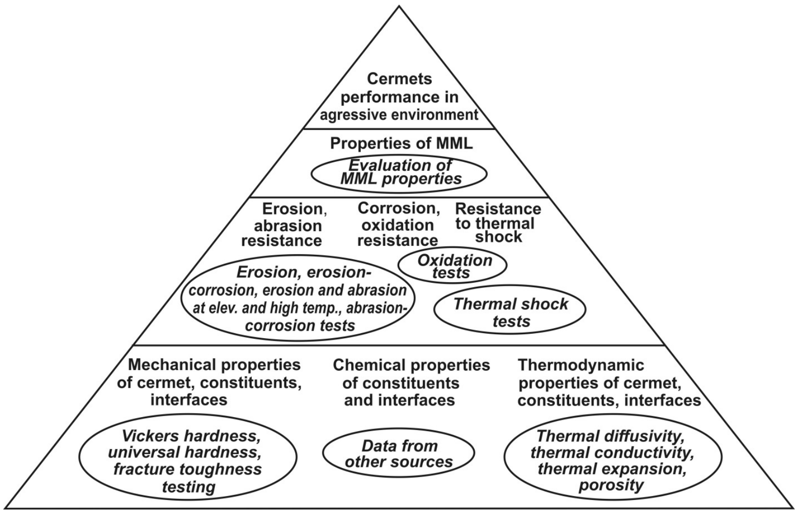


Figure 6. The schematic representations of the major factors relative to the cermets performance in aggressive conditions and the scope of the present work (shown in ellipses).

The special attention is given to the tests in interdisciplinary areas with several processes acting simultaneously. **It is important to test the existing rationale for calculation of impacts of each process and their interaction for the chosen cermet material (2).** Mechanisms of degradation of the tested material is important to evaluate as the way of understanding the behavior of the cermet material with combined ceramic and metal phases. **On the basis of the experimental data and the data obtained with the help of proposed rationale the maps should be build in order to simplify the selection and developing of cermet materials in a range of operating conditions (2).**

The two erosion testers used in TUT have different working features. **It is necessary to calculate the rotor rotating angle during the erosion of one specimen (3).** The effect of specimen's width should also be evaluated. This angle is used for calculation of erosion wear rate. The data and equations for the conversion of results into over units of erosive wear should also be evaluated.

The maximum test temperature of elevated temperature erosion tester is 700 ºC. Higher test temperatures are required in order to develop new materials for high temperature applications. **It is necessary to analyze the possibility of creating of HT erosion tester, to design it and to evaluate it performance (4).**

As it was previously shown the properties of surface layer are different from those of bulk material. The information concerning microstructural features of eroded surface and subsurface layer of cermets is quite rare. **It is the task to study the surface layer and MML in order to understand its effect on the material degradation rate (5).**

3 RESULTS AND DISCUSSION

The materials tested

The target materials tested were the chromium carbide cermets with different binder composition, binder content, grain size and porosity. The conventional hard metal as well as cermets, standard high temperature and wear resistant alloys (Haynes 25, 282, Ultimet, Hardox 400), steel (Steel 45 (normalized steel 0.45 % C, GOST1050-74), AISI316) were tested also for comparison. All the cermets were produced in TUT through the conventional PM procedure. Composition of cermets tested and some typical properties related to room temperature are listed in Table 1.

Table 1. List of cermets and hard metals tested.

Grade	**Hard phase content, wt %**	**Binder content, wt %**	**Density ρ, kg m^{-3}**	**Vickers hardness number HV**	**Fracture toughness K_{IC}, MPa m$^{1/2}$**	**Transverse rupture strength, MPa m^{-2}**
C10	90 Cr_3C_2	10 Ni	6900	1490	9.5	690
C15	85 Cr_3C_2	15 Ni	7000	1410	9.8	840
C20	80 Cr_3C_2	20 Ni	7100	1368	13.8	1050
C25	75 Cr_3C_2	25 Ni	7200	1128	14.0	1140
C30	70 Cr_3C_2	30 Ni	7300	995	18.3	1210
C40	60 Cr_3C_2	40 Ni	7500	900	19.0	1000
CK20	80 Cr_3C_2	16/4 Ni/Cr	7030	1500	9.2	1100
VK8	92 WC	8 Co	14500	1350	13.0	2100
VK15	85 WC	15 Co	13900	1200	18.0	2700
VK20	80 WC	20 Co	13700	1030	19.0	2500
TZC60	60 TiC	31.5/7/1.5 Fe/Cr/Si	5800	1360	13.0	2000
TZC40	40 TiC	49.5/9/1.5 Fe/Cr/Si	6100	1150	14.0	1830
TH20A	80 TiC	13/7 Ni/Mo	5500	1380	11.5	1080
TH40A	60 TiC	26/14 Ni/Mo	6000	1190	18.2	1320
TH50A	50 TiC	33/17 Ni/Mo	6420	1020	18.3	1610

In general, cermets with higher content of tough binder phase possess higher fracture toughness and transverse rupture strength and lower hardness.

Equipment

The list of main equipment used in the work is presented in Table 2. The equipment code is used to avoid the excess description later throughout the thesis.

Table 2. List of equipment involved into investigation of cermets performance in aggressive environments.

Code	Name	Producer	Important parameters / basic features
EC1	AB 204 electronic scales	Mettler Toledo	Accuracy 0.1mg. Maximum weight 200 g.
EC2	РН-10Ц13У (GOST 13882-68) mechanical scales	Tyumen	Accuracy 5 g. Maximum weight 10 kg.
EC3	Abrasive fraction sift analyzer	TUT	Vibratory, equipped with set of sieves Fritsch GMBH, Laborgerätebau.
EC4	Phoenix 4000 sample preparation system	Buehler	Polishing machine.
EC5	Prestopress-3 hot mounting press	Struers	Encapsulating of samples for further investigations.
EC6	Universal Hardness Tester BZ 2,5	Zwick	Personal computer controlled with Vickers indenter.
EC7	Surtronic 3+ profilometer	Rank Taylor Hobson Limited	Diamond stylus. Resolution 0.01µm.
EC8	Labotom disc cutting machine	Struers	Equipped with sample cooling system.
EC9	Supra 35 FESEM	LEO	Equipped with high resolution GEMINI column.
EC10	Stereoscan 360 SEM	Leica Cambridge Instruments	Able to detect secondary and backscattered electrons, x-rays spectra. Max magnification 50.000X.
EC11	CUK 5 erosion tester	TUT	For tests at room temperature. Max 15 samples simultaneously. Impact velocity 15-100m s^{-1}. Impact angle 20-90º. See Paper III for more details.

Code	Name	Producer	Important parameters / basic features
EC12	Elevated temperature erosion tester	TUT	For tests at room and elevated temperatures (up to 700 ºC). Max 20 samples simultaneously. Impact velocity 15-100 m s^{-1}. Impact angle 20-90º. See Paper I for more details.
EC13	High temperature erosion/abrasion tester	TUT	For tests from room to 1100 ºC. Impact velocity 0-5 m s^{-1}. Impact angle 0º. See Paper II for more details.
EC14	Electrical oven	SNOL	SNOL-1,6.2,5.1/9-И4 Maximum temperature 1100 ºC.
EC15	GILL AC potentiostat	ACM Instruments	For electrochemical measurements. PC controllable. Equipped with SCE. See http://www.potentiostat.com/ for more information.
EC16	Slurry Erosion-Corrosion test rig	Strathclyde University, UK	Impact velocity 0-5 m s^{-1}. Impact angle 0-90º. Abrasive particle concentration 3-15 wt % . Equipped with potentiostat.
EC17	Dilatometer DIL 402	Netzsch	Was applied for evaluation of CTE
EC18	Differential Scanning Calorimetry rig DSC 404C Pegasus	Netzsch	Was applied for evaluation of specific heat that was used for calculation of thermal conductivity
EC19	Laser flash apparatus LFA 427	Netzsch	Was applied for evaluation of thermal diffusivity that was used for calculation of thermal conductivity
EC20	Thermal shock testing facility	AMTT	Vertical electrical furnace equipped with PC controlled sample movement system. Heating temperature up to 1500 ºC. Cooling by air or in water.
EC21	Pin-On-Ring Tribometer	AMTT	Pin-on-ring and ball-on-ring modes are available. The pin and ring could be air heated up to 250 ºC or pin only up to 700 º C. Lubricated testing is available. Load up to 750 N can be applied. PC controllable.
EC22	Micromesure high resolution 3D microtopography measurement system	Stil	Equipped with Stil CHR 150-N high resolution optical sensor. Lateral resolution-1 µm, vertical resolution - 30 nm. PC controllable (Stil Surface Map).
EC23	Pin-On-Disk Tribometer	ECP	Equiped with Potentiostat/galvanostat for in-situ tribo-corrosion measurements. Maximum normal force – 50 N. Maximum rotation frequency – 150 min^{-1}.
EC24	273A Potentiostat/Galvanostat	EG&G Princeton Applied Research	Computer-controlled Potentiostat/Galvanostat. See http://www.princetonappliedresearch.com/ for more information.

3.1 Resistance of cermets to oxidation

The resistance of cermets to oxidation was evaluated in order to evaluate the contribution of oxidation to the erosion at elevated temperatures. The oxidation tests were conducted in electrical oven (EC14) under the same temperatures as the erosion testing (300 and 600 ºC). The specimens were cleaned in acetone prior to testing. Mass change was measured with the help of scales (EC1). The average mass gain of 3 samples tested simultaneously was evaluated. The mass gain is given in respect to area subjected to oxidation (Figure 7).

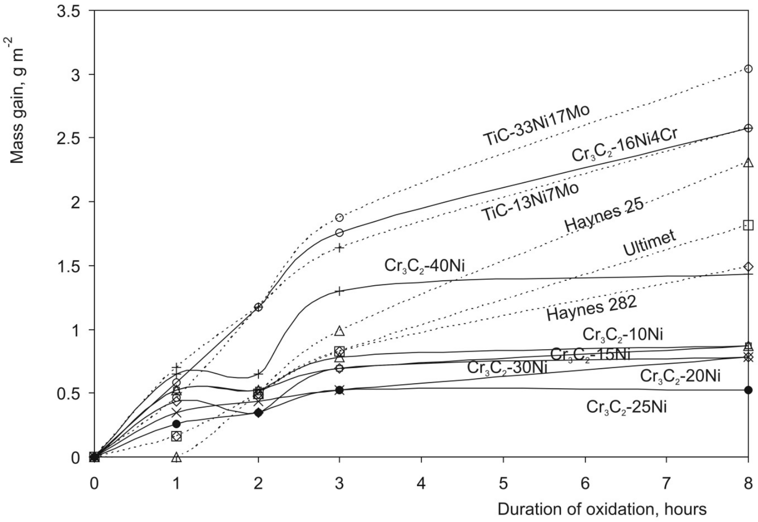


Figure 7. Mass gain of cermets and Haynes alloys during the oxidation at 600 ºC. Numbers in cermet grade designations are showing the weight percent of binder metal.

The experiments at 300 ºC have shown no measurable mass change. Oxidation of WC-Co based cermets was extremely high at 600 ºC followed by flaking of the oxide layer.

It is possible to say that during the first hour the mass gain was at the higher rate almost for all materials. During the following hours the rate of oxidation was decreasing. Only TiC based cermets, and Cr_3C_2-NiCr cermet has shown the continuing oxidation that was also growing within the next 5 hours. The mass gain of Cr_3C_2 cermets with Ni binder has reached the value of approximately 0.6 g m^{-2} and has stopped after 3 hours. The oxidation rate of chromium carbide cermet with nigh Ni content (40 wt %) was the highest.

During the erosion it is important to have the oxide layer that is hard to remove [38, 39]. The low mass gain of Haynes 25, Ultimet and Haynes 282 during the first hour could be favorable when oxide layer is constantly removed by erosive particles lowering the elevated temperature erosion rate.

3.2 Erosion resistance of cermets at different temperatures

3.2.1 Erosion resistance of cermets at room temperature

The erosion tests were done with the help of EC11 and EC12 testers. EC1 and EC2 scales were used for specimens and abrasive weighing consequently. EC3 abrasive fraction sift analyzer was used for the control of abrasive size.

Calculation of the erosion rate

Average material wastage during erosion (Δm, g) was determined through the mass measurement technique. For the calculation of volumetric erosion rate (E, mm^3 kg^{-1}) the mass of abrasive that has eroded one sample (θ_S) and the density of material (ρ, kg m^{-3}) are used:

$$E = \frac{\Delta m}{\theta_S \rho} \tag{1}$$

The mass of abrasive that has eroded one sample is determined as the total mass of abrasive used (θ, kg) reduced according to the angle during which the jet of abrasive particles erode the sample (γ, deg):

$$\theta_S = \theta \frac{\gamma}{360} \tag{2}$$

The scheme (see Figure 8) and the formulae (3-8) for calculation of γ angle are presented below.

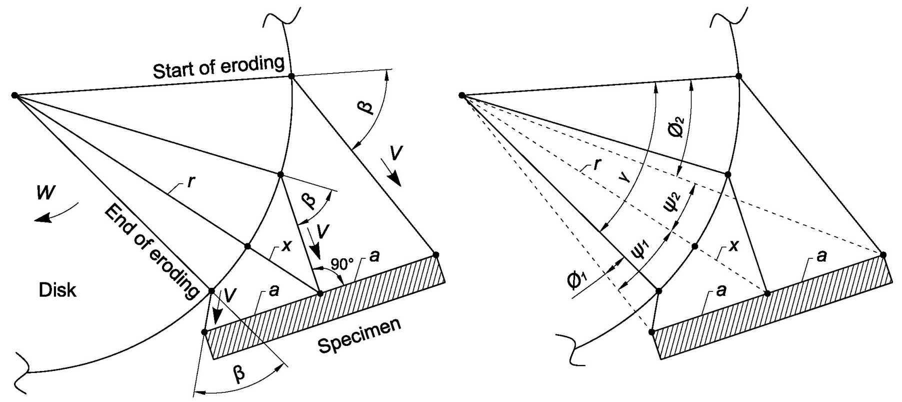


Figure 8. Scheme of single specimen eroding. Not in proportions.

$$\varepsilon = \arcsin\left(\frac{\sin(\beta)r}{r+x}\right) \tag{3}$$

$$\psi_1 = \arctan\left(\frac{a\cos(\varepsilon)}{r+x-a\sqrt{1-\cos^2(\varepsilon)}}\right) \tag{4}$$

$$\psi_1 = \arctan\left(\frac{a\cos(\varepsilon)}{r+x+a\sqrt{1-\cos^2(\varepsilon)}}\right) \tag{5}$$

$$\phi_1 = \beta - \arcsin\left(\frac{\sin(\beta)r}{\sqrt{((a\cos(\beta))^2+(r+x-a\sqrt{1-\cos^2(\varepsilon)})^2}}\right) \tag{6}$$

$$\phi_2 = \beta - \arcsin\left(\frac{\sin(\beta)r}{\sqrt{((a\cos(\beta))^2+(r+x+a\sqrt{1-\cos^2(\varepsilon)})^2}}\right) \tag{7}$$

$$\gamma = \psi_1 + \psi_2 - \phi_1 + \phi_2 \tag{8}$$

For the particular case of EC11 and EC12 testers the results are presented in Figure 9.

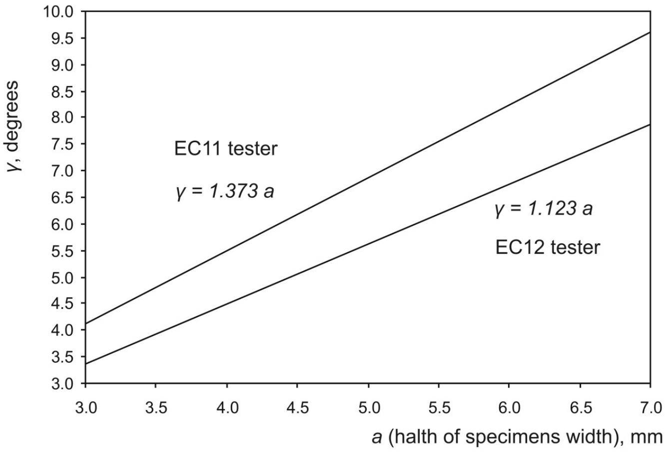


Figure 9. The effect of specimen's width on the γ angle.

Angle γ is approximately 8.5° for the EC11 tester and the width of sample of 12mm. The angle becomes smaller for EC12 tester and for the specimens with less width. The expressions for determination of the angle are placed near the graphs. The results were checked with the help of CAD program AutoCAD.

To represent the results with respect to area subjected to erosion (E_A, mm^3 kg^{-1} cm^{-2}) and as erosion rate per hour (E_H, mm^3 h^{-1}) the area of sample subjected to erosion (A, cm^2) and the abrasive feeding rate (F, kg h^{-1}) should be applied:

$$E_A = \frac{E}{A} \tag{9}$$

$$E_H = EF \tag{10}$$

The area subjected to erosion is limited in horizontal direction by protection bracket. The other size was determined experimentally with the help of traces of impacts left on soft specimens produced from aluminum. It was found that at impact velocity of 60 m s^{-1} and silica sand of 0.2 mm mean diameter, the size in vertical direction is approximately 8 and 12 mm for the erosion at 90° and 30° of impact angle consequently. That means that for the case of bracket with the opening of 12 mm width the A is 0.96 and 1.44 cm^2 consequently.

The feeding rate (F) determined at EC11 tester for impact velocity of 60m s^{-1} and silica sand of 0.2 mm mean diameter was 25 kg h^{-1}.

Incubation during erosion

It was found that the erosion rate during the run-in could be different from the constant rate that exhibit materials after some “starting” period. In some cases the erosion rate during the run-in was found to be lower or even mass gain was reported mainly for soft materials at high angle of impact [58]. At high velocity (55 m s^{-1}) and oblique impact angle (30°) chromium carbide cermets had shown stable results just from the beginning of erosion [105]. To have the data concerning the incubation of different grades of cermets and to see the difference in material behavior at different impact angles the series of tests were done (EC11 tester). The results are presented in Figure 10. The rate of erosion is given as a function of mass of abrasive particles impacted. It seems to be more convenient than “total material mass loss-mass of abrasive impacted”. Silica sand with mean diameter of 0.2 mm was used because of its involvement throughout this work. The speed of 60 m s^{-1} was chosen to produce sufficient mass lost. Tests were done at room temperature.

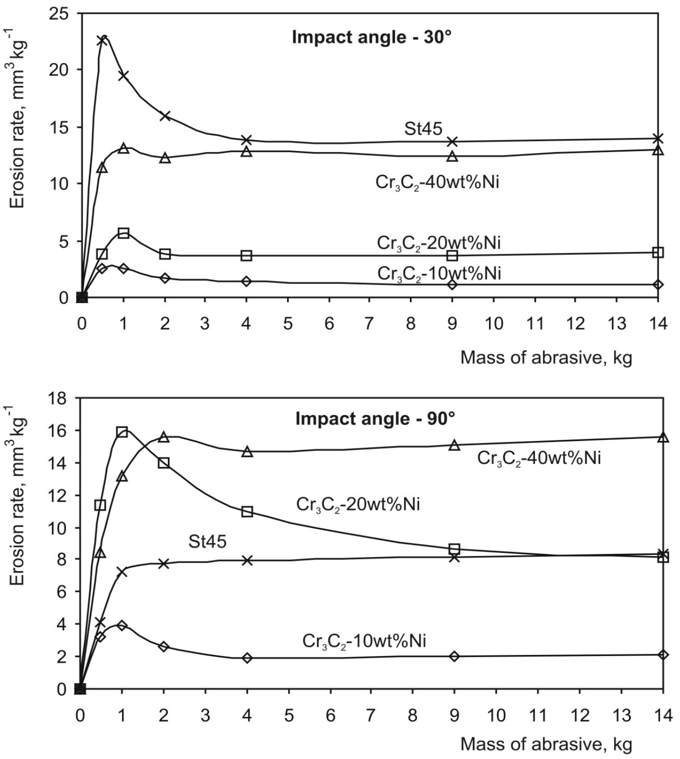


Figure 10. Incubation of erosion rate of cermets and steel at different impact angles.

In general it is possible to conclude that the mass of 3 kilograms of abrasive is sufficient to achieve the steady state erosion regime. In this work the steady state wear was studied (if not stated otherwise).

Repeatability and reproducibility of experiments

Accuracy of experimental results is influenced by the precisions of all test variables (factors). These factors could be categorized as following: materials related (inhomogeneity, structural defects), mass loss measurement accuracy (scales accuracy), impact velocity setting (calibration of motor controllers, the length of exchangeable channels and their wear), abrasive mass measurement accuracy (scales accuracy), temperature setting accuracy (thermopairs accuracy, regime of temperature holding), impact angle accuracy (specimen holder accuracy, its location accuracy, the wear of specimen and crater formation), accuracy of the sample's area subjected to wear (protecting bracket accuracy and its wear during test), abrasive feed rate accuracy (it is hampered in case of abrasives with higher size of grains, wear of channels). The human factor should be minimized.

In order to make the assessment of repeatability and reproducibility of erosion test results the set of ten tests under the same conditions was carried out at different angles. The tests were done at 60 m s^{-1} and at EC11 and EC12 conventional erosion testers. The silica sand with mean diameter of 0.2 mm was applied as an abrasive. The cermet with 15 wt % of Ni binder was used for this testing. Tests were done at room temperature.

The results have shown that the **repeatability** of both testers is almost the same at oblique and normal angles of impact. 7 out of 10 samples have shown the results within ±15 % deviation from the mean. During the erosion testing done throughout this work the tests that has shown the deviation grater than 25 % (or less depending on the requirements) from the mean where not taken into the account. The nature of extreme results was found to be caused mainly by the inhomogeneity of materials.

The **reproducibility** of erosion results at normal impact angle is quite satisfactory. However, in case of oblique impact the cermet has shown less resistance when eroded with EC11 than EC12 tester. As a conclusion it is possible to say that the difference in results obtained by two erosion testers do not exceed 15 %.

The effect of impact velocity

The damage that could be produced in material by abrasive is proportional to the kinetic energy of impacting particle. The kinetic energy itself is governed by the mass and velocity of erodent. However, the deviation of power (n) from the value of 2 in an empirical law describing the erosion (E) as: $E = kv^n$ where k is a coefficient depending on material and erodent properties and v is the impact velocity was observed. The value of n was varying in the range of 1.0-3.9 and was found to be dependant on material, impact angle as well as on abrasive. TiC based cermets with NiMo and steel binders have not revealed the effect of impact angle on n value that could be explained by their well known low (among the tool materials) adhesion to the sliding bodies. During the impact the initial kinetic energy is apportioned between particle and the surface. Rebounding and fracturing of particle, energy dissipation through the elastic deformations, emission of heat could cause the decrease of velocity effect. Cermets that absorb more energy have less erosion resistance. The high porosity of cermets leads to the sudden increase of n value at some threshold velocity (see Paper XV).

The effect of impact velocity on erosion rate of cermet is considered in the Paper I in details.

The effect of impact angle

The cermets have shown the maximum of erosion at impact angles between 60º and 90º. In case of tungsten carbide based cermets the maximum was observed at about 60º even for grades with low binder content that is showing that these materials are less prone to the cracking and the selective removing of the binder is the prevailing mechanism. Titanium carbide based ones with NiMo and steel binder has shown the maximum mainly at 75° that is showing that these materials exhibit more brittle behavior. The chromium carbide cermets have shown sufficient sensitivity to such variables as binder content, impact velocity and temperature exhibiting the maximum in the range of 60-90º. The hardness of cermet even among the compositions with the same phases but different content is not the indicator of erosion resistance. Cermets with HV 900 (40 wt % of Ni) have shown better erosion resistance at 75-90 angles than cermets with HV 995 (30 wt % of Ni). Such mechanical properties as fracture toughness, transverse rupture strength should also be taken into consideration. Also it could be explained by the formation of Mechanically Mixed Layer (see Paragraph 3.7).

The effect of impact angle on erosion rate of cermet is considered in the Paper I in details.

The effect of abrasive

The tests with different abrasives (silica sand, silicon carbide, electrocorundum and cast iron grit) has shown the presence of three regimes in erosion behavior of Cr_3C_2 based cermets:

- When hardness of abrasive is less than the hardness of cermet (cast iron grit) then the erosion rate of cermets is at least 10 (up to 100 at oblique impact angles) times lower than that of wear resistant alloy Hardox 400 and Steel 45.

- When hardness of abrasive is comparable to that of cermet (silica sand) then the erosion rate of cermet is only 2-3 times higher than that of less hard comparison materials (Steel 45, Hardox 400).

- When hardness of abrasive is higher than that of cermet (silicon carbide and electrocorundum) then their erosion resistance becomes lower than that of steel or wear resistant alloy. The advantage of less brittle materials is higher at normal impact angle reaching 5 times difference in erosion rates. The difference in erosion rates of cermets of different grades becomes less evident.

The use of abrasives with higher hardness was causing sufficiently higher erosion wastage to all materials tested. It should also be mentioned that such hard abrasives as silicon carbide and electrocorundum are having more pronounced sharp angles.

Microstructural aspects

SEM micrographs and 3D microtopography graphs enable to make conclusions concerning the microstructural aspects. In addition to the information presented in articles (Paper I-XV) and Paragraph 3.7 of this work, some resent information is to be presented.

The impact sites show some plastically deformed zones; however brittle fracture seems to be dominated (Figure 11 a-c). Material, extruded from the grove can be easily detached by the subsequent impacting particle (Figure 11 c). In some places the evaporation of the binder due to the flash of temperature during the impact were observed (Figure 11 d). 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 and propagate for a relatively long distance from the centre of the crater by brittle manner (Figure 11 e). The effect of difference in the coefficient of thermal expansion between two phases can stimulate crack nucleation and developing of thermo-cracks (Figure 11 f).

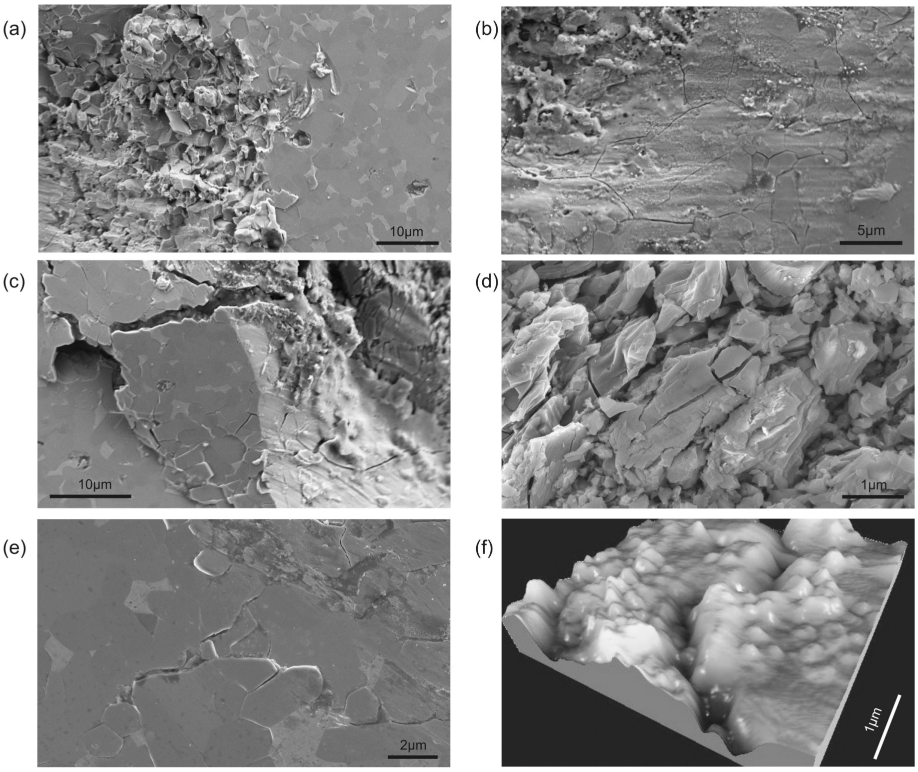


Figure 11. SEM micrographs of Cr_3C_2-Ni cermets eroded at room temperature, impact angle of 60° and impact velocity of 60 m s^{-1}: (a, b) edges of impact craters produced by SiC and SiO_2 particles consequently; (c) extruded material; (d) center of impact crater; (e) intergranular cracks; (f) 3D microtopography graph of thermo-crack.

3.2.2 Erosion resistance of cermets at elevated temperatures (up to 600 ºC)

The oxidation rate of chromium carbide cermets at 600 ºC (0.4 g m^{-2} h^{-1}) during the first hour is sufficiently low if compared with the erosion rate at this temperature (see Paper I). Only in the case of low velocities (below 10 m s^{-1}) and oblique impact angles is possible to apply the rationale to show the regimes of interaction between erosion and oxidation. Under the present conditions tested it is possible to say that materials possess superior oxidation resistance and the prevailing mechanism of degradation is erosion.

The erosion tests were done with the help of EC12 tester. The results are presented in the form of erosion wastage maps (see Figure 12) and compared with that obtained at room temperature. The erosion rate of cermets is usually higher at higher temperatures. It is caused by the softening of the metal binder phase and decreasing of the hardness of ceramic phase [94, 106, 107]. The fall of erosion resistance is less pronounced in case of cermets with higher binder content and at impact angles close to normal. The strength of ceramic phase at elevated temperatures is even higher than at room temperature [84].

Erosion rate below 1 mm^3 kg^{-1} was taken as low, 1-10 mm^3 kg^{-1} was taken as medium and erosion rate above 10 mm^3 kg^{-1} was taken as high erosion rate.

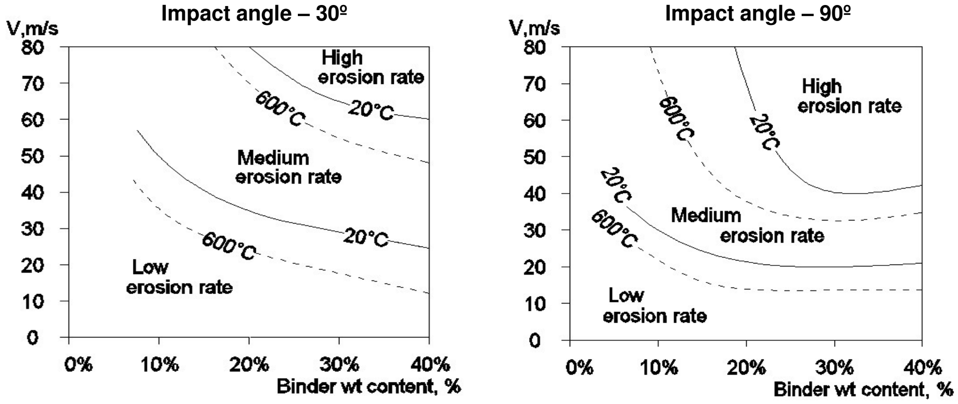


Figure 12. Erosion wastage maps of Cr_3C_2 cermets at different impact angles. Abrasive-silica sand with mean diameter of 0.3 mm.

The erosion resistance of cermets at elevated temperatures and microstructural aspects are considered in the Paper I in details.

3.2.3 Erosion resistance of cermets at high temperature (1000 ºC)

The advantage of chromium carbide cermets as erosion resistant materials is more pronounced at higher temperatures when oxidation conditions are severe. To test materials at temperature higher than 700 ºC the pilot erosion tester was designed. The estimation of its performance was carried out to have the experience for the future development of HT equipment.

The principle scheme of the test rig (EC13) is presented in Figure 13. The typical laboratory oven (EC14) with the opening in the door for additional thermometer was incorporated into the design. The specimen is oscillating horizontally for short distance. The movement of sample holder is actuated by the electrical motor. The one end of connection rod (16) is attached to the test holder and the other is connected eccentrically to the disk (14). The disk is constructed to allow adjusting the eccentricity (R in Figure 13) of connected rod.

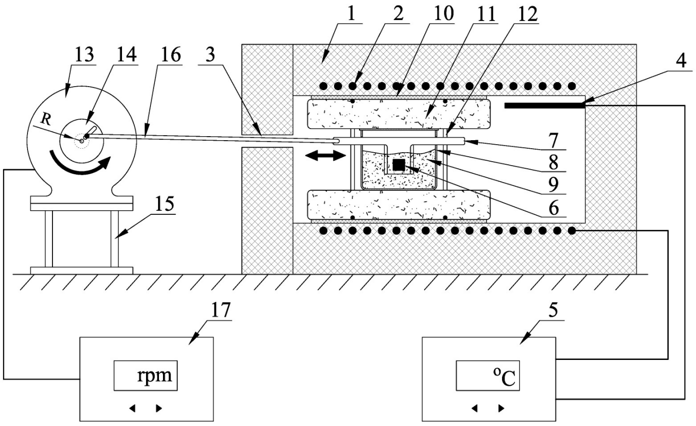


Figure 13. Scheme of experimental erosion tester: (1) electrical heating chamber; (2) heating elements; (3) opening in the door; (4) thermocouple; (5) temperature control unit; (6) specimen; (7) specimen holder; (8) case; (9) abrasive; (10) protection mats; (11) vibration damping bricks; (12) bricks clamp; (13) AC motor; (14) amplitude regulation disk; (15) motors support; (16) connection rod; (17) motor rotation frequency control unit.

The presented design allows keeping motor functioning at normal temperature and avoiding its overheating. Specimen, abrasive and environment are kept at the same temperature. The design allows making HT tests at affordable inputs if the number of tests is not high.

Chromium carbide cermets as well as Haynes 25 high temperature alloy were tested with the help of designed HT tester at different temperatures, velocities in silica and silicon carbide abrasive and the conclusions concerning materials behavior done.

The erosion resistance of cermets at high temperature and the designed erosion tester are presented in the Paper II in details.

3.3 Resistance of cermets to slurry erosion in corrosive media

The effect of material parameters such as composition and surface roughness, together with test conditions such as abrasive particle concentration, applied potential, temperature and time of experiment were studied in order to make the assessment of cermets performance under erosion-corrosion conditions. The possibility to control the corrosion process and the rationale used for calculation of the impacts of processes and their interaction has made it possible to develop the maps showing the performance of cermets under the interplay of material and process variables.

The rationale [93, 95, 97, 108] that allows assessing the interaction of erosion and corrosion components in quantitative manner is expressed as following:

$$K_{ec} = K_e + K_c \tag{11}$$

$$K_{ec} = K_{eo} + K_{co} + \Delta K_e + \Delta K_c \tag{12}$$

$$K_e = K_{eo} + \Delta K_e \tag{13}$$

$$K_c = K_{co} + \Delta K_c \tag{14}$$

where K_{ec} is the erosion-corrosion rate measured by mass change techniques, K_e and K_c are the erosion and corrosion rates, K_{eo} is the erosion rate in the absence of corrosion (i.e. in cathodic potential), K_{co} is the corrosion rate in the absence of particles, ΔK_e is the effect of corrosion on the erosion rate and ΔK_c is the effect of erosion on the corrosion rate. K_c and K_{co} are determined with the help of Faraday's law, i.e. through measurement of the current during experiment.

This methodology is well established for metals (Fe, Al, Cu) [97] but in the case of chromium carbide cermets exposed to the NaCl slurry solution there are several aspects which need to be considered. In this work, the corrosion rate (K_c) was higher than the wastage rate (K_{ec}). This tendency is prevailing for cermets with lower binder content and in case of experiments with lower abrasive particle concentration. Part of the dissolved nickel is not removed from the sample surface but attached to it in the form of chloride that in general leads to the increase in weight (see Figure 3 of Paper IV). In order to quantify the corrosion islands it is possible to scan the topography of corrosion islands or remove them (probably through the chemical mean).

SEM micrographs allow to conclude that the protective properties of corrosion islands could be established only in the case of cermets with low binder content. The formation of an overall protective layer is not possible due to the low adhesion between the chromium carbides and corrosion products. Besides, the layer of brittle corrosion products attached to the stiff carbide grain is easily removed due to the inability of the layer to absorb energy through deformation. The maximum size of corrosion products depends directly on the free surface of binder phase in the area of interaction and generally cannot be noticeably larger than the binder islands. Some islands can join each other but this is possible only if they are divided by small carbide grains.

A schematic representation of cermet material degradation is presented in Figure 14 and described below:

a) Surface of cermet before corrosion-erosion process.

b) Corrosion starts in the centre of the largest binder island. Due to the good adhesion to the binder the corrosion island is growing while it reaches the carbide grains.

c) Corrosion products are removed by the action of the slurry solution and the interface between the matrix of the carbide grains is weakened. Once the interface is weakened the particles of Cr_3C_2 are easily removed.

d) Several grains of cermet are removed as a consequence of the combined erosion-corrosion effect.

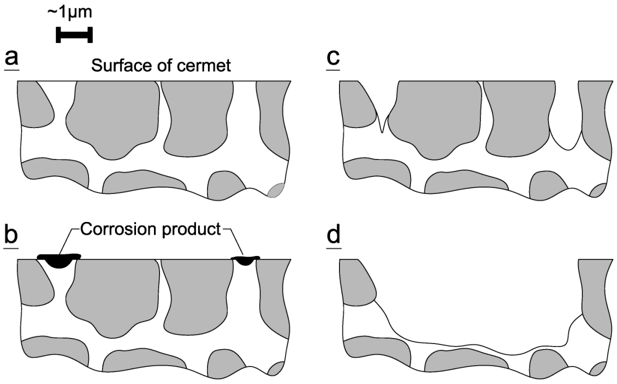


Figure 14. Schematic representation of cermet material degradation during the combined erosion-corrosion process. Dark phases indicate grains.

Unless the corrosion islands are not quantified it is possible to say that the presented rationale is valid mostly for construction of erosion-corrosion wastage maps and maps showing the transition between different additive regimes (see Figures 6, 7 and 9 of Paper IV).

The resistance of cermets to slurry erosion in corrosive media was studied with the help of EC1, EC10, EC15 and EC16 equipment and is considered in the Paper IV in details.

3.4 Resistance of cermets to sliding wear in corrosive media

Cermets have found their application as materials for valves and over parts in chemical and power industry where sliding wear resistance and the absence of cobalt is important [109-112]. The sliding tests with presence of corrosive media were done with the help of EC23 tester equipped with EC24 Potentiostat/Galvanostat in order to make the assessment of cermets performance in conditions (medium, normal pressure, velocity and frequency) close to those under which valves are operating. The scheme of specimens fastening is shown in Figure 15. The data presented here is taken from the project that is currently running. So, only some basic features available for presenting are shown.

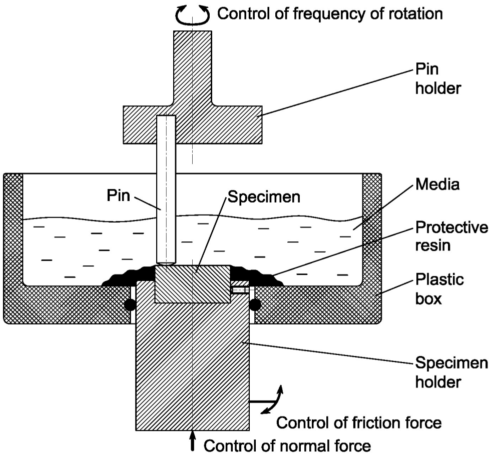


Figure 15. The scheme of specimen fastening during sliding wear in corrosive media.

The specimen was fixed to the current conductive specimen holder and only top side was subjected to corrosion (and wear). Pin holder was rotating at given speed. The normal force was applied to the specimen holder. Sintered corundum pin was 7 mm in diameter with a tip of a spherical shape with radius of 0.1 m. Corundum has high wear resistance, neither general corrosion nor galvanic coupling with the test material can take place. Saturated silver chloride reference electrode (Ag/AgCl, 199 vs. SHE) was used. A typical three electrode system was incorporated into the test rig to enable in situ electrochemical tests to be made, and to control the potential of the specimen. Titanium mesh covered with platinum was used as auxiliary electrode. All potentials were reported with respect to saturated silver chloride electrode throughout this work. Two solutions were applied. These are 1000 ppm H_3BO_3 with 130 ppm LiOH (pH 8.3) that is used in water reactors and 0.5 H_2SO_4 (pH 0.5) as reference medium.

Polarization curves (see Figure 16) were generated at potentials from -1000 mV to +1000 mV at a sweep rate of 1 mVs^{-1}.

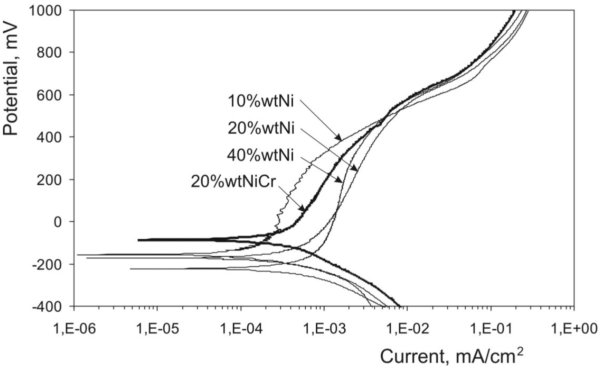


Figure 16. Potentiodynamic polarization behavior of the Cr_3C_2 based cermets. Medium was H_3BO_3/LiOH.

A study of these results has shown that the corrosion potential varied with change of cermet binder composition and content (from -90 to -220 mV). Cermets with higher binder content have lower corrosion potential. The corrosion potential of cermet with NiCr binder is higher than that of cermets with plain Ni binder. At most of the potentials the current of cermet with NiCr binder is lower than that of cermet with the same content of Ni binder. In order to see how fast the chromium carbide cermet can create the corrosion layer that leads to the decrease of current the materials were held at -4000 mV and then subjected to corrosion under different potentials. Some results are shown in Figure 17.

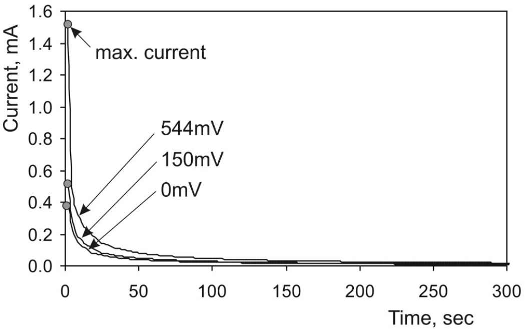


Figure 17. Passivation of chromium carbide based cermet (20 wt % of NiCr binder) depending on the applied potential. Medium was H_3BO_3/LiOH.

It is possible to see that after the application of the potential the current has the maximum after which it drops exponentially. Considerable drop is exhibited by cermets within the first 5-10 seconds after the application of potential.

In order to get the effect of rotation frequency and normal force on corrosion behavior of cermets the set of tests with varying parameters were carried out. The examples are presented in Figures 18 and 19. During the time of one turn of the pin's holder the track of abraded cermet has the possibility to create protective layer if the time is sufficient. If the time is insufficient then the material in track region will behave as active that will lead to increased corrosion rate.

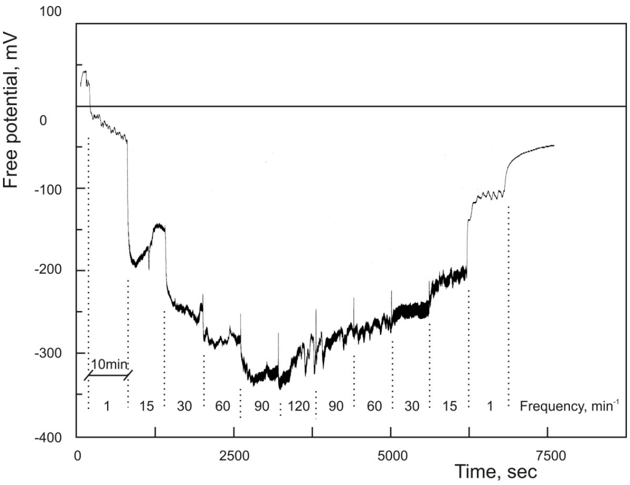


Figure 18. The effect of rotation frequency on free potential of chromium carbide cermet (20 wt % of NiCr binder). Normal force was 5 N. Medium was H_3BO_3/LiOH.

There is a drop of approximately 100 mA when the frequency was changed from 1 to 15 or back from 15 to 1 turn per minute (Figure 18). The low normal force of 5 N was chosen in order to make the effect of rotation frequency more pronounced. The frequency of 1 turn per minute (or 60 seconds for restoring of protective layer) seems to be most favorable for these materials. The decrease in time for restoring the layer is leading to the lower corrosion potential of cermets.

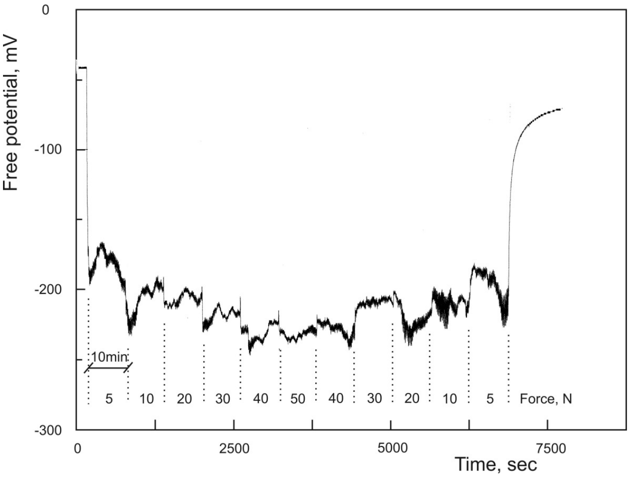


Figure 19. The effect of normal force on free potential of chromium carbide cermet (20 wt % of NiCr binder). Rotation frequency was 5 min^{-1}. Medium was H_3BO_3/LiOH.

The rotation frequency (5 min^{-1}) was chosen to be critical for the restoring of the protective layer to increase the effect of normal force. However, the normal force has less pronounced effect on corrosion behavior than rotation frequency (Figure 19).

The material wastage rate during sliding wear in corrosive conditions was measured with the help of EC22 microtopography scanning system able to determine the area of the cross section and the volume of the wear track. The results are presented in Figure 20.

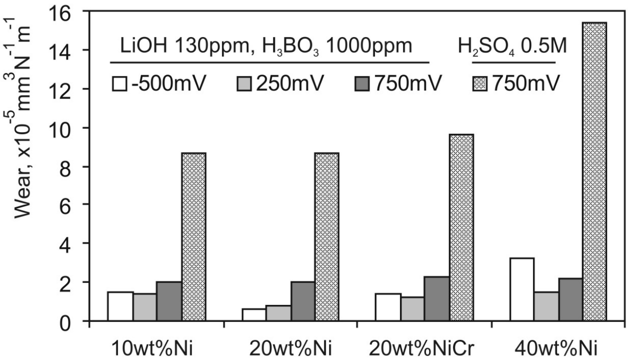


Figure 20. The effect of corrosion current and corrosive media on wear rate of Cr_3C_2-based cermets with different binder under sliding conditions. Rotation frequency 137 min^{-1} (0.05 m s^{-1}). Normal force 50N.

The wastage rate of chromium carbide cermet with 20 wt % of Ni binder is the least under mild corrosive or non-corrosive conditions (-500 and 250 mV). It is even lower than that of cermet with the same content of NiCr binder. At 750mV the wastage rate of cermets in H_3BO_3/LiOH environment is almost at the same level. Sulfuric acid has caused higher wear-corrosion rate. It is the most prevailing for materials with higher binder content. The wear rate is in the same order as during sliding wear in air conditions at room and elevated temperatures (see Figure 21).

3.5 Resistance of cermets to sliding wear at different temperatures

The friction coefficient and sliding wear of chromium carbide cermets were determined with the help of EC21 tester. The test parameters and conditions are presented in Table 3.

Table 3. Test parameters and conditions.

Pin		Ring		Load, N	Sliding Speed, m s^{-1}	Distance, m	Environment		
Material	Size, mm	Material	Radius, mm				type	% RH	°C
Cr_3C_2-Ni	4x5x20	WC-Co steel substrate	29	113	1	≈ 3070	Air	40	20 - 500

Cermets were tested against steel ring coated with WC-Co hard metal. The wear rate (W) was calculated from the mass loss measurements and expressed as a specific wear calculated according to the equation:

$$W = \frac{\Delta m}{\rho L F_N}, \tag{15}$$

where: Δm is the mass loss of the test specimen under the test conditions described (g), ρ is the density of the test specimen (kg m^{-3}), L is the sliding distance (m) and F_N - the normal load applied to the sample (N).

The variation of friction coefficient and wear rate depending on the cermet composition, and test temperature are presented in Figure 21.

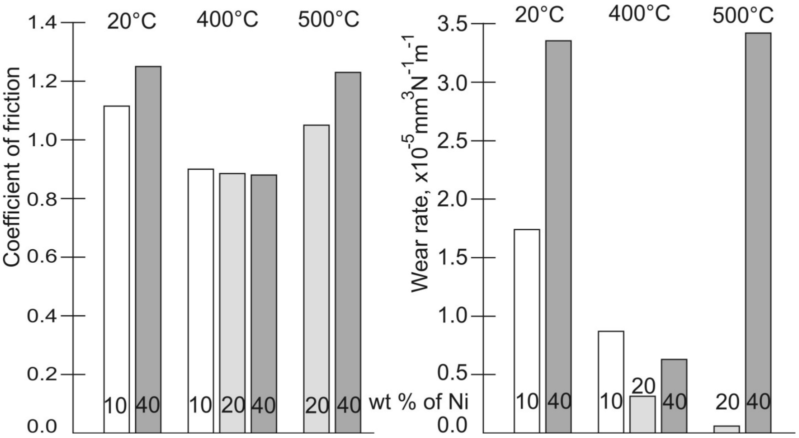


Figure 21. Mean coefficient of friction and mean wear rate under sliding conditions of Cr_3C_2-Ni cermets at different temperatures

Frictional behavior and wear rate of cermets is strongly dependent on the temperature and content of binder phase. The coefficient of friction of chromium carbide based cermets sliding against hard metal is very high and in a range of 1. The wear rate is linked to frictional behavior of cermet. The increase in friction coefficient is usually combined with higher wear rates. The minimum friction coefficient and material loss were recorded at 400 ºC. The cermet with 20 wt % of Ni binder has shown surprisingly low wear rate while the friction coefficient is not as low compared to other grades and temperatures tested. This grade has shown low friction coefficient and wear rate also under other conditions investigated. It seems that this material has optimum combination of such properties as fracture toughness, hardness, modulus of elasticity and thermo – mechanical ones.

3.6 Thermo-physical properties and thermal shock resistance of cermets

It was important to make the assessment of the effect of microstructure and thermal properties of constituents on resulting properties of cermets. The analysis of interfaces between carbide grains and/or grains and matrix metal were carried out on the basis of presented mathematical models. Thermal expansion and thermal conductivity were chosen due to their importance in process of generation of thermal gradients and thermal stresses inside the composites that in its turn has the effect on thermal shock resistance and overall performance of materials at HT.

All models for prediction of **coefficient of thermal expansion** are in good agreement with experimental results. In general, the representation of chromium carbide based cermets as a particular reinforced material is quite efficient. The CTE of cermets with lower binder content is overestimated that could be explained by formation of continuous carbide skeleton and the inability of Ni binder to deform it.

The models that do not take interfaces into account gives overestimated results of **thermal conductivity** of cermets. The Hasselman-Johnson-Benveniste model has showed very low conductivity of interfaces between Cr_3C_2 and Ni. The Cube model (proposed by the authors) that overlooks the cermets as a set of square columns where some of them consist of metal and ceramic phases (set to be non-conductive) and others only consist of metal phases (have the conductivity of metal) has shown its approachability. Low value (lower than that of Cr_3C_2 or Ni) of thermal conductivity of cermets with low nickel content is showing the presence of interfaces between carbides.

Thermal shock experiments had shown that the extension of cracks in materials with lower binder content is slightly greater. Partial immersion is found to be more effective to crack formation and may be used as fast way for determination of thermal shock/cycling properties.

Thermo-physical properties and thermal shock resistance of cermets were determined with the help of EC17, EC18, EC19 and EC20 equipment and is considered in the Paper V in details.

3.7 Properties of the surface layer formed during erosion of cermets at high temperature

WC, TiC, Cr_3C_2 – based cermets were selected for investigation. The binder volumetric content (12 vol %) was chosen to be at the same level for all grades to avoid the metal phase content effect on surface layer formation.

The main information concerning mechanical properties was obtained with the help of universal hardness testing technique (in accordance with DIN 50359-1 and EN 14577-1). The properties were measured before the test, after holding at test temperature, after testing at the surface and beneath it to the depth of 7 μm. Transverse SEM micrographs of samples obtained with the help of EC9 were used to give the additional information concerning mechanisms of material degradation under high temperature erosion. The slices of eroded material were removed with the help of polishing technique (EC4 machine) according to the rate measured previously and additionally controlled with the help of external micrometer. The erosion rate was evaluated in order to make the conclusions concerning the effect of surface layer properties on erosion rate. The samples were eroded under different velocities (20 and 80 m s^{-1}) and impact angles (30 and 90º) at temperature of 600 ºC with the help of EC12 tester, cut into parts (EC8 machine) and encapsulated (EC5 machine) for further investigations.

The universal hardness (UH) tests were repeated 9 times for every condition tested. The speed of load application and removal was 0.5 N s^{-1}. The test force of 10 N was held for 5 second for the stabilization of deformation. The creep data was recorded. Tests were conducted at room temperature.

The surface roughness value measured (EC7 profilometer) after erosion was in the range of 0.1-2.0 μm for the most severe conditions. This value is sufficiently small compared to the size of silica abrasive used for erosion (0.1-0.3 mm) that is showing that the main damage is induced mainly by abrasive dust created during the crushing of abrasive particles. The indentation force was chosen as 10 N since it was the minimum force with resulting set of measurements within ±10 % dispersion for as-received materials.

The UH testing of cermets revealed that TiC - based cermet is the hardest and has the highest indentation modulus and share of elastic work but the lowest creep rate. The hardness of all tested materials lowers (about 50HV for Cr_3C_2 and TiC based cermets and 250HV for WC based ones) after holding at 600 ºC as compared to as-received and polished ones. This can be attributed to the low hardness of oxide films formed at this temperature.

The distribution of the mean hardness in the outer layers of chromium carbide cermet tested at 600 ºC under the impact angles of 30º and 90º and the impact velocities of 20 and 80 m s^{-1} are plotted in Figure 22. The error bars show the whole range of hardness evaluated within 9 tests conducted for each point.

The erosion at 30º has less pronounced effect on modification of surface layer. After the erosion at impact angle of 90º the depth of the modified layer is deeper. The depth of layer within which the properties are changed, or in other words, the thickness of MML for Cr_3C_2 and TiC cermets is not larger than 4-5 μm while for WC grade it is at least 7 μm because of sufficient difference in hardness values of eroded WC cermet at depth of 7 μm and at surface.

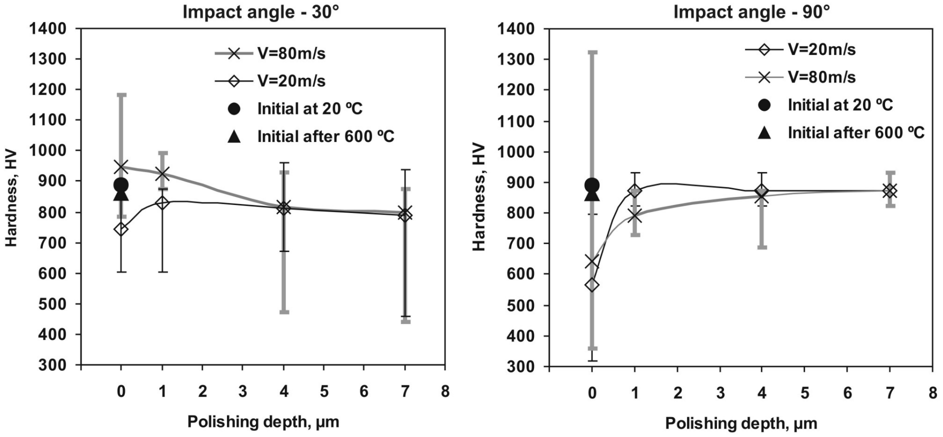


Figure 22. Distribution of hardness in the outer layers of chromium carbide cermet.

The investigation of SEM micrographs has shown that the oxidation resistance of binder is of high importance. So the WC cermets being the standard material for the room temperature application are loosing the binder in the MML leaving the carbide grains in direct contact that leads to their extensive cracking to as much as about 5 grains deep (15 µm – see Figure 23). The contact between carbide grains in case of Cr_3C_2 cermets also provoke the formation of crack due to the shifting of ceramic grains during the impact (Figure 24). The rim structure of TiC cermets with NiMo binder provide some damping ability or ability to deform elastically (Figure 25). This material has higher percent of elastic work during the indentation.

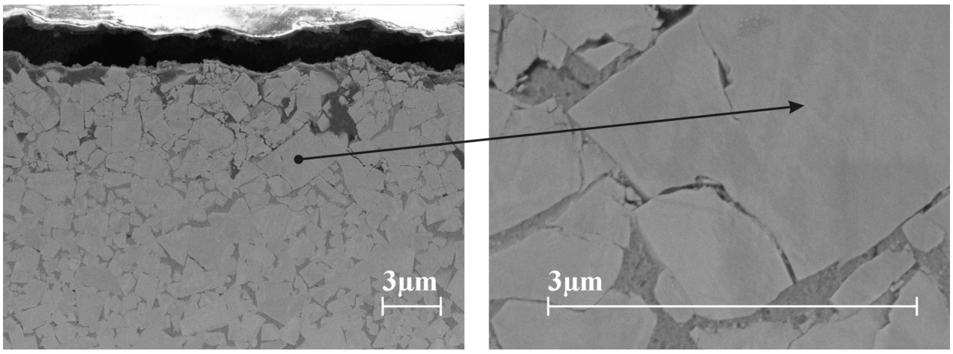


Figure 23. Cross section of the WC cermet eroded at impact angle of 90°, particle velocity of 80 m s^{-1} and temperature of 600 °C.

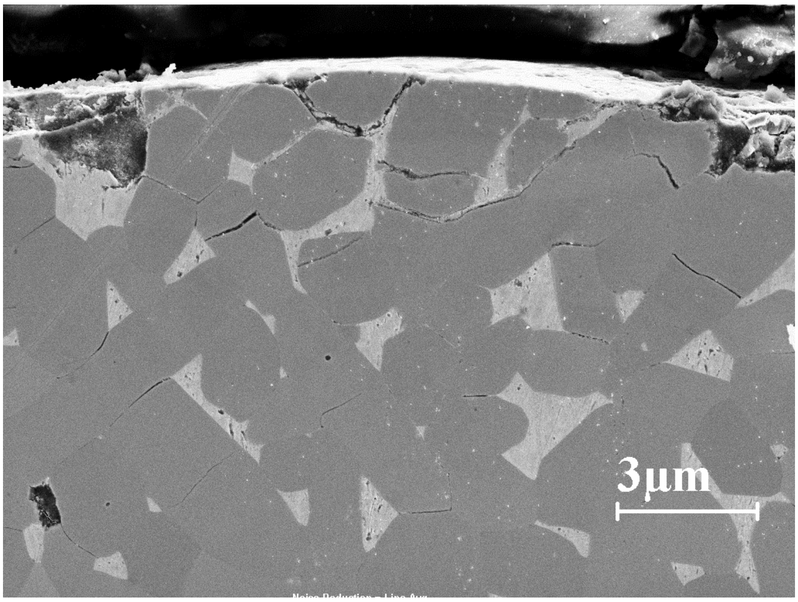


Figure 24. Cross section of the Cr_3C_2-based cermet eroded at impact angle of 90º, particle velocity of 80 m s^{-1} and temperature of 600 ºC.

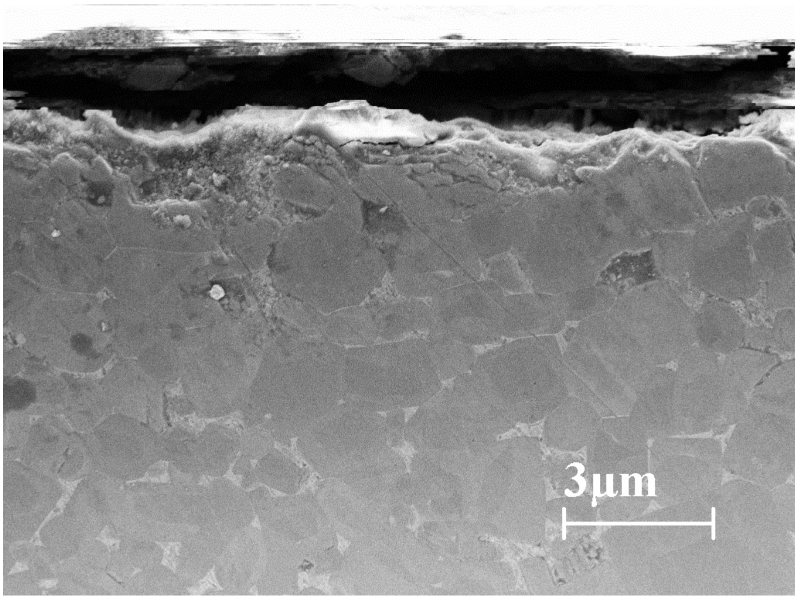


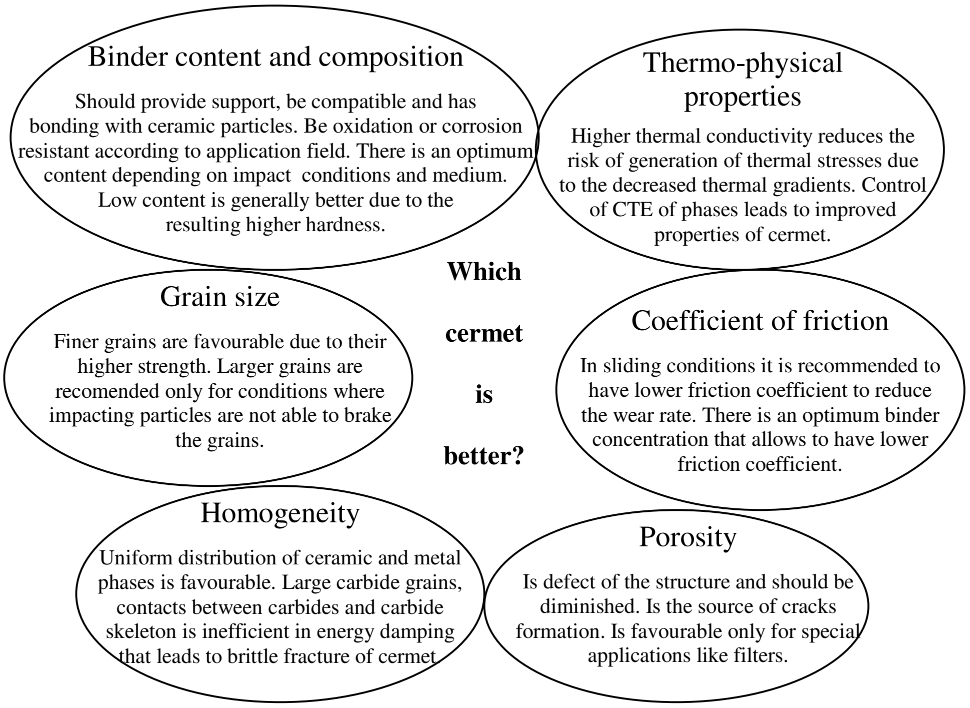
Figure 25. Cross section of the TiC-based cermet eroded at impact angle of 90º, particle velocity of 80 m s^{-1} and temperature of 600 ºC.

The formation of pronounced MML is possible only during the erosion at velocity higher than 20 m s^{-1}. The effectiveness of MML formation is higher at normal impact angles due to the more concentrated impact zone and the higher energy transferred. It is obvious that the cermets with higher binder content or the lower hardness of binder are more susceptible to the MML formation processes. Also the abrasives with higher hardness and more angular ones could cause more effective mixing in the surface zone.

Cermets have shown higher erosion rate at normal angle of impact that displays their brittleness. The MML having higher (compared to bulk material) part of plastic work can better accumulate stresses during the impact of abrasive particles leading to the lower erosion rates. So, probably, that is the reason why TiC cermet has shown the best performance in erosion testing.

3.8 What should be taken into account when selecting cermets for aggressive conditions?

The basic factors that should be taken into account are divided into material and process related ones and are represented in Figures 26 and 27. The presented are only conclusions concerned with the present work.



Binder content and composition

Should provide support, be compatible and has bonding with ceramic particles. Be oxidation or corrosion resistant according to application field. There is an optimum content depending on impact conditions and medium. Low content is generally better due to the resulting higher hardness.

Thermo-physical properties

Higher thermal conductivity reduces the risk of generation of thermal stresses due to the decreased thermal gradients. Control of CTE of phases leads to improved properties of cermet.

Which cermet is better?

Grain size

Finer grains are favourable due to their higher strength. Larger grains are recomended only for conditions where impacting particles are not able to brake the grains.

Coefficient of friction

In sliding conditions it is recommended to have lower friction coefficient to reduce the wear rate. There is an optimum binder concentration that allows to have lower friction coefficient.

Homogeneity

Uniform distribution of ceramic and metal phases is favourable. Large carbide grains, contacts between carbides and carbide skeleton is inefficient in energy damping that leads to brittle fracture of cermet

Porosity

Is defect of the structure and should be diminished. Is the source of cracks formation. Is favourable only for special applications like filters.

Figure 26. Some factors of material design and selection that should be taken into account in order to reduce cermets wastage rate in aggressive conditions.

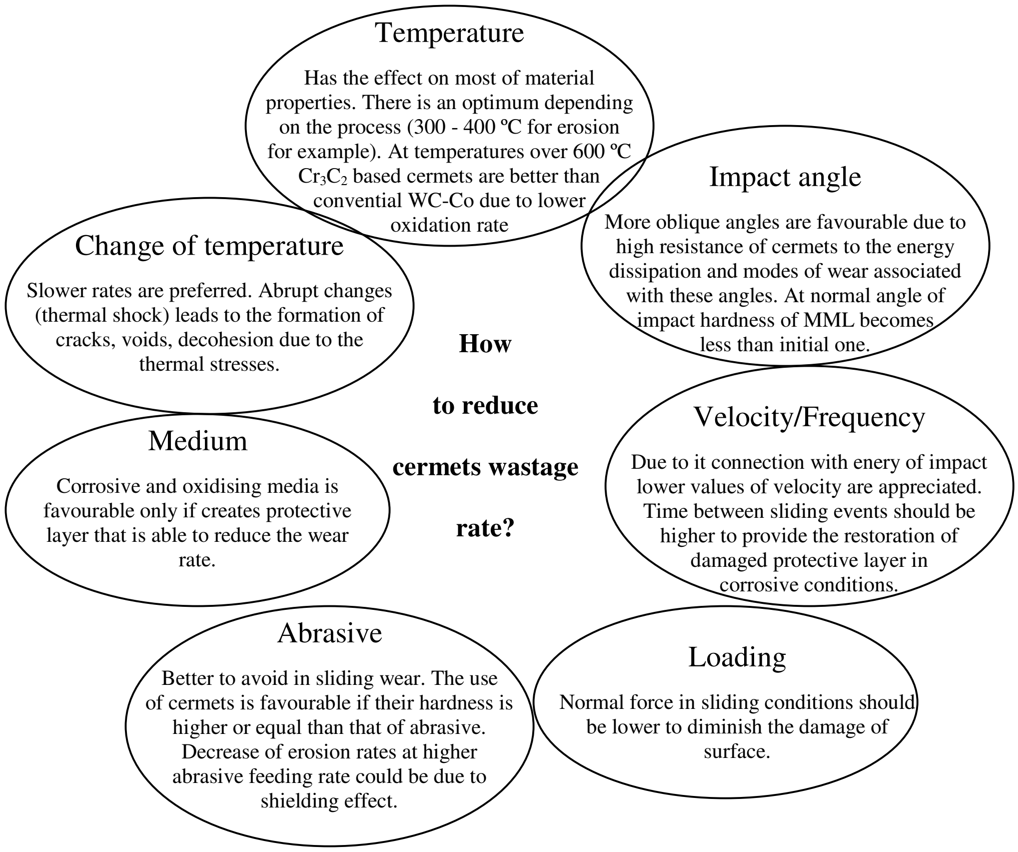


Figure 27. Some process related factors that could be modified in order to reduce the cermets wastage rate in aggressive conditions.

CONCLUSIONS

1. The behavior of Cr_3C_2-based cermets under various aggressive conditions was studied and the results were published. Some recently obtained data is in process at the moment.

   1.1. The use of Cr_3C_2-based cermets in wear applications is proved in the range of 600 – 900 ºC and in various corrosive conditions due to their high oxidation and corrosion resistance.

   1.2. The optimum binder content is 10-20 wt % depending on conditions.

   1.3. The hardness of cermet (even of the same grade) is not only the factor effecting erosion resistance. It was found that cermet with higher hardness can possess lower wear resistance. Such mechanical properties as fracture toughness (especially fracture toughness of carbide skeleton, if present), thermo-mechanical properties (especially coefficient of thermal expansion, thermal conductivity) should also be taken into consideration.

   1.4. Cr_3C_2 and TiC-based cermets exhibit the highest erosion rate at angle close to normal. Behavior of WC-Co hard metals may be attributed to more ductile with the poorest erosion resistance at impact angle of 60º.

   1.5. The grain boundaries of carbide skeleton and change in mechanism of heat transfer at interfaces lead to lowering of the cermets thermal conductivity.

   1.6. The extension of cracks induced through thermal shock is slightly greater in cermets with low binder content.

2. The rationale for the evaluation of the effects of different aggressive processes acting simultaneously and their interactions are presented and the assessment of chromium carbide based cermets is made on its basis.

   2.1. Different erosion and erosion-corrosion maps are constructed. They can be used for minimizing of material wastage rate under various working conditions.

   2.2. The erosion-corrosion of Cr_3C_2-Ni cermets in salt environment is governed by the removal of binder. The corrosion products found on the surface have to be quantified in order to improve the maps.

3. The principle of calculation of the rotor rotating angle during the erosion of one specimen is presented.

   3.1. Equations of wear rate calculation based on the applied tester working features are given.

4. Different high temperature erosion testers are overlooked and the most suitable design is chosen.

   4.1. The new rig for evaluation of materials response to erosive medium at temperatures up to 1000 ºC is designed and produced.

   4.2. The behavior of cermet and Haynes 25 high temperature alloy at 1000 ° C in erosive medium is influenced to great extent by sticking of abrasive grains or/and splitters to the surface.

5. The properties of surface layer and mechanically mixed layer (MML) formed during erosion at elevated temperatures as well as bulk properties are evaluated and discussed for three different cermet grades.

   5.1. The properties (hardness, indentation modulus, share of elastic work, creep rate) of surface layer and MML formed during erosion differ from those of bulk material.

   5.2. The thickness and the microstructure of MML are affected by such process parameters and conditions as impact velocity, impact angle and temperature.

   5.3. At normal angle of impact hardness of surface layer becomes less than initial one.

   5.4. Corroding cobalt binder in conventional WC-Co materials at 600 ºC leads to loosing of the protective metal matrix, contacting carbides and their cracking that is the reason of the extensive wastage rate of this metal-ceramic composite.

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KOKKUVÕTE

KERMISTE KÄITUMINE AGRESSIIVSETES KESKKONDADES

Looduse vaatlemisel ilmneb, et erinevate komposiitmaterjalide kasutamine loodusnähtuste kahjuliku mõju vähendamiseks pärineb juba ammusest ajast. Näiteks mulda läbivad taimejuured aitavad kaitsta pinnast lihete ja uhtumise (erodeerimise) vastu.

Kõvasulamid ehk kermised on komposiitmaterjalid, mis koosnevad kõvadest ja habrastest rasksulava ühendi osakestest (karbiidid, karbonitriidid, boriidid) ning suhteliselt plastilisest ja pehmest Fe-grupi metallist (Fe, Co, Ni). Sellistes materjalides on edukalt ühendatud keraamika kõrge kulumis- ja korrosioonikindlus ning termopüsivus metallmaatriksi võimega vähendada keraamika soodumust haprale purunemisele.

Materjalide korrosioon ja kulumine põhjustavad tööstuses suurt majanduslikku kahju. Õige materjali ja tehnoloogia valik ning pindade termotöötlemine võimaldavad tekkivaid kahjusid vähendada.

1. Töös on uuritud erinevate materjalide (kermised, kõvasulamid, kõrgtemperatuursed sulamid, kulumiskindlad sulamid ning terased) käitumist mõningates agressiivsetes keskkondades (erosioon- ja abrasiivkulumine erinevatel temperatuuridel; erosioon- ja abrasiivkulumine korrosiooni, oksüdeerimise tingimustes ning termilise löögi tingimustes). On leitud, et Cr_3C_2 baasil kermised on perspektiivsed materjalid töötamaks agressiivsetes ja abrasiivsetes tingimustes.

   1.1. Cr_3C_2 baasil kermiste kasutamine on õigustatud kulumiskindla materjalina või kaitsekihina kõrgematel temperatuuridel (600 - 900 ºC) ning korrosiooni tingimustes, tulenevalt nende kõrgest korrosiooni- ja kulumiskindlusest agressiivsetes keskkondades.

   1.2. On leitud, et Cr_3C_2 baasil kermiste optimaalne sideaine sisaldus on 10 - 20 mass % Ni. Antud sideaine sisalduse vahemikus on vastupanu agressiivse keskkonna mõjule suurim enamustes tingimustes.

   1.3. On leitud, et kermiste kulumiskindlus ei sõltu ainult kõvadusest. On leitud, et väiksema kõvadusega kermistel võib olla suurem erosioonkulumiskindlus võrreldes sama tüüpi, aga suurema kõvadusega kermistega, seetõttu tuleb kulumiskindluse hindamisel arvestada ka materjali löögisitkuse ning soojuslike omadustega (soojuspaisumine, soojusjuhtivus).

1.4. Cr_3C_2 ning TiC baasil kermiste maksimaalne erosioonkulumine oli täisnurgale lähedase kohtamisnurga korral. Plastsemate WC-Co kõvasulamite korral oli vähim erosioonikindlus 60º kohtamisnurga korral.

1.5. Karbiiditerade piirid ning soojuse ülekande mehhanismi muutus keraamilise ja metalse faasi vahel vähendavad kermiste soojusjuhtivust.

1.6. Termolöögist põhjustatud pragude pikkus on suurem väiksema sideaine sisaldusega kermiste korral.

2. Töös on toodud põhimõtted samaaegselt toimuvate kahjulike protsesside hindamiseks.

2.1. On loodud kaardid erosioon ning erosioon-korrosioon protsesside hindamiseks. Neid saab kasutada antud tingimustes töötavate materjalide loomiseks ja uurimiseks ning toimuvate triboloogiliste protsesside hindamiseks.

2.2 On leitud, et Cr_3C_2-Ni kermiste erosioon-korrosioonkulumise korral merevees on põhiline kulumise põhjus metallmaatriksi eemaldumine.

3. Töötati välja metoodika võrdlemaks erinevaid Tallinna Tehnikaülikoolis läbiviidud erosioonikatseid.

4. Loodi katseseade kõrgtemperatuuriliste (kuni 1000 ºC) erosiooniprotsesside uurimiseks, teostati katsed erinevate materjalide erosioonkulumise hindamiseks.

5. Teostati mikrostruktuuri uuringud, võrreldi erinevat tüüpi ja erineva sideaine sisaldusega kermiste kulumise ja korrosiooni mehhanisme.

5.1. Erosiooni toimel kahjustatud pinna paksus ning mikrostruktuur sõltuvad abrasiivosakeste kiirusest, kohtamisnurgast ning keskkonna temperatuurist.

5.2 WC-Co kermiste sideaine korrosioon kõrgetel temperatuuridel (600 ºC) põhjustab metallmaatriksi eemaldumist ja karbiiditerade pragunemist, mis on WC-Co kermiste madala erosioonikindluse põhjuseks.

6. Teostati materjali universaalkõvaduse uuringud. On näidatud, et eksisteerib erinevus erosioonkulumisel kahjustatud kihi ning põhimaterjali omaduste (kõvadus, elastsusmoodul, kõrgtemperatuurne roome) vahel. Kermiste pinna kõvadus väheneb peale kulutamist abrasiivijoas 90º nurga all. Pinna kõvadus abrasiivijoas kulutamisel 30º nurga all sõltub protsessi parameetritest.

PUBLICATIONS

Paper I

Hussainova, I., Antonov, M.
Elevated temperature wear of chromium carbide based cermets. Proceedings of the Estonian Academy of Sciences, Engineering, Vol. 9/4, pp. 261-271, 2003.

Paper II

Antonov, M., Hussainova, I.
Erosion testing of refractory cermets at high temperature. Proceedings of 12th Nordic Symposium in Tribology, Nordtrib 2006, Helsingør, Denmark, June 7-9, 2006 (CD-ROM).

Paper III

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Paper IV

Stack, M.M., Antonov, M., Hussainova, I.
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Paper V

Antonov, M., Hussainova, I.
Thermo-physical properties and thermal shock resistance of chromium carbide based cermets. Proceedings of the Estonian Academy of Sciences, Engineering, Vol.12, pp. 4, 2006 (accepted-in press).

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12. Teadustöö põhisuunad	Kermiste omadused, kulumine, korrosioon, termilised omadused, kõrgtemperatuused omadused.