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Reactive Sintered Chromium and Titanium Carbide- Based Cermets

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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 academic degree.

/töö autori nimi ja allkiri/

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Finally I would like to thank my mother and my wife Airi for their help and encouragement.

CONTENTS

LIST OF PUBLICATIONS

The present dissertation is based on the following publications, which are reffered in the text by the Roman numerals I – IV.

I K. Juhani, J. Pirso, S. Letunovitš, M. Viljus, Phase evolution, microstructure characteristics and properties of Cr_3C_2-Ni cermets prepared by reactive sintering, Int. J. of Materials and Product Technology (in print).

II J. Pirso, M. Viljus, S. Letunovitš, K. Juhani, Reactive carburizing sintering- : A novel production method for high quality chromium carbide-nickel cermets, International Journal of Refractory Metals & Hard Materials, 24 (2006) 263-270.

III K. Juhani, J. Pirso, M. Viljus, S. Letunovitš, Abrasive wear of chromium carbide based cermets. In Proc. of 13th Nordic Symposium in Tribology, Nordtrib 2008, Tampere, Finland (2008) CD-ROM.

IV K. Juhani, J. Pirso, M. Viljus, S. Letunovitš, Microstructure and properties of reactive sintered TiC-based cermets, In: Proc. of European Powder Met. Conference PM2008, Mannheim, Germany, 3 (2008) 89-94.

APPROBATION

International conferences

1. The 15th International Baltic Conference “Materials Engineering & Tribology” BALTMATTRIB-2006, Tallinn, Estonia, October 5-6, 2006;
2. European Powder Metallurgy Conference & Exhibition Euro PM2007, Toulouse, France, October, 15-17, 2007;
3. The 16th International Baltic Conference of “Materials Engineering & Tribology” BALTTRIB-2007, Riga, Latvia, October 25-26, 2007;
4. The 6th International DAAAM Conference "INDUSTRIAL ENGINEERING” Tallinn, ESTONIA, April 24-25, 2008;
5. The 13th International symposium „Nordtrib 2008”, Tampere, Finland, June 10-13, 2008;
6. European Powder Metallurgy Conference & Exhibition Euro PM2008, Mannheim, Germany, 28.09-1.10.2008;
7. The 17th International Baltic Conference “Materials Engineering 2008”, Kaunas, Lithuania, November 06-07, 2008.

AUTHOR'S CONTRIBUTION

The list of publications not included in the present work is added to the references. The author of this thesis took part in the sample preparation routine, was responsible for carrying out of the experiments, collecting and processing the data, performing the further analysis of these experimental data (Paper I-XVII). The author also took part in the discussion on the content (of the current thesis) (Paper I-XVII) and compiled several manuscripts (Paper II-IV, VI, VIII, XII, XVI). However, the intellectual merit resulting in this framework with a contribution of each author should not be underestimated.

ABBREVIATIONS AND SYMBOLS

ASTM – American Society for Testing and Materials
BPR – Ball to Powder Ratio
CAK – centrifugal accelerator of Kleis
COV – Coefficient of Variation
F – normal load
HV – Vickers hardness
K – erosion rate
k – wear coefficient
MAS – Mechanically Activated Synthesis
s – sliding distance
SEM – Scanning Electron Microscopy
Sinter/HIP – pressure assisted sintering
TRS – Transverse Rupture Strength
XRD – X-ray diffraction

1 INTRODUCTION

1.1 Cermet materials and their producing technologies

An increasing use of the materials with special properties and the introduction of new cost-efficient manufacturing processes have had a decisive influence on the further development of cermet materials. Cermets are ceramic - metal composites which consist of the ceramic phase and metal binder phase [1]. Cermets are the materials which combine the optimal properties of a ceramic (like high-temperature stability and hardness) and those of a metal (like the ability to undergo plastic deformation).

It is well known that the mechanical properties of cemented carbides can be improved by the reduction of a carbide grain size up to the nano-size scale [2-4]. The best known material in this group is the WC-Co cermets, widely known as hard metals. The nanograin and sub-micron WC-Co composites have superior properties and a more homogeneous microstructure than those of the conventional WC-Co composites. They have potential to replace the standard materials for tools, dies and wear parts because of their increased hardness and wear resistance. WC is conventionally synthesized through a solid/solid reaction by heating a mixture of the tungsten powder and carbon black at temperatures in the range of 1400-1800 °C under a hydrogen atmosphere [5]. For fabricating the sub-micron or nanocrystalline WC-Co composites, the nanosized WC powder is used as a starting powder [6].

There are many ways to produce the nanocrystalline WC and WC-Co powders, such as the spray conversion process [7, 8], electric discharge machining [9], chemical vapour condensation [10, 11], thermal plasma process [12], high energy milling [13] and an integrated mechanical and thermal activation [14]. High-energy ball- milling, a well-known process for preparing amorphous alloys, intermetallides, metal nitrides, metal carbides and nanocrystalline materials, has been considered as a powerful technique due to its simplicity and relatively inexpensive equipment for synthesizing numerous nanocrystalline materials [13]. The ball- milled nanocrystalline powders have some unique characteristics compared to the other nanocrystalline powders, prepared by various techniques [14]. These powders are heavily work hardened with a high density of lattice defects and an excess- stored enthalpy [15]. The advantage of the method is that it can be used to synthesize the designed compound at the nano-size scale level at room temperature, a method also known as reactive milling [16].

The Cr_3C_2-Ni cermets are prospective materials to operate in the corrosive and abrasive environments [17-24]. The main disadvantages of these cermets are relatively low mechanical properties and wear resistance mainly caused by their coarse-grained structure (the carbide grain size is usually over 4 µm). Cr_3C_2 is usually produced by high temperature processes, such as the displacement reaction of chromium oxide or chromium and carbon [25, 26]. The chromium carbide powders are industrially produced mainly by two different methods – the direct and indirect syntheses (Fig. 1). In case of the direct synthesis, the Cr_2O_3 and graphite powders are mixed and then heated in a H_2 environment at 1600 ^oC [26]. In the indirect carbide synthesis, Cr and graphite powders are mixed and heated in a hydrogen environment at 1400 ^oC for 0.5–1 hours [27].

$3Cr_2O_3 + 13C = 2Cr_3C_2 + 9CO$ (direct carbidization)

$3Cr + 2C = Cr_3C_2$ (indirect carbidization)

For the industrial production of Cr_3C_2-Ni alloy, 5–30 wt% Ni powder is added to Cr_3C_2 and additionally milled in a ball- mill, pressed to the compacts, and sintered at 1250–1300 ^oC.

TiC - based cermets are known for their outstanding corrosion and high-temperature wear resistance; they are most commonly used in metal cutting tools, but their unique combination of properties offers wide scope to the materials design engineer [1]. However, the TiC-based cermets present some disadvantages, such as low toughness and bending strength compared with those of the cemented carbides [28]. Even today the best TiC-based cermets still possess poor erosive and wear resistance compared with that of the WC-Co cemented carbides [29, 30].

Titanium carbide (TiC) is the material of commercial interest because it possesses a range of desirable properties. It is extremely hard, being one of the hardest known metal carbides. TiC exhibits an excellent thermal stability and has a very high melting temperature of approximately 3100 ^oC [31]. This combination of very high hardness, a high melting temperature and an excellent thermal and chemical stability makes TiC suited to the TiC-NiMo cermets. However, one of the disadvantages of using TiC for commercial applications is that it is difficult to produce. Most of the industrial TiC powders are produced through the reduction of TiO_2 with carbon at temperatures of 1900 – 2100 ^oC for 10 to 20 hours [32]. This method has serious disadvantages due to the high cost of equipment and high power consumption because of the very high synthesis temperature (Fig. 2).

The method of high-energy milling or reactive milling has received considerable attention during the recent years. It has also been used to synthesize various carbides [13]. High-energy ball- milling is a simple and efficient way of manufacturing ultra-fine powders. The studies of the synthesis of compounds indicate that the structures developing during the milling are determined by the milling conditions and the collision energy in particular. High-energy milling has a number of potential advantages compared to the existing processes used. High-energy milling is performed at room temperature, so there is no need for the expensive high- temperature reaction equipment, which could result in a significant saving of capital expenditure. Another advantage of this synthesis technique is that the final product is a fine, homogeneous nanocrystalline powder, which can then be easily shaped and consolidated by using the conventional powder metallurgy processes. Such nanocrystalline materials have attracted much interest recently as the advanced engineering materials due to their unique, improved physical and mechanical properties.

Reactive milling cannot be solely applied to the synthesis of carbide, if the reaction has small negative free energy of formation. The synthesis of the tungsten carbide at room temperature by high- energy milling is also not reasonable, needing too long a milling time and a considerable amount of mechanical activation.

The mechanically activated synthesis (MAS) can be described as a modification of high-energy reactive milling. The basic form of the MAS process involves the mechanical activation of the reactants at room temperature through high-energy ball- milling, followed by the completion of a synthetic reaction at higher temperatures. The reactive ball- milling cannot be solely applied because a solid-state reaction between Cr and C is characterized by a small negative Gibbs energy variation. According to Huang and McCormik, [33] the synthesis of Cr_3C_2 by mechanical alloying is possible, but will need a considerable amount of mechanical activation. Most probably there is a certain critical energy concentration, below which the chromium carbide cannot be generated. The MAS is not limited by this and thus is suitable for the reactions with large positive free energies of formation at ambient temperature. The results of the current study have confirmed that it is quite difficult to produce the chromium carbide by mechanical alloying. Most critical is the capability of the milling device to provide enough collision energy. The synthesis of the chromium carbide at room temperature by mechanical alloying is not reasonable, needing a long milling time and a considerable amount of mechanical activation.

The Tungsten carbide powder, which is manufactured by high-energy ball-milling and follows the annealing, may behave unpredictably during heat-treatment because of the different amounts of absorbed energy and the structural micro-defects, oxidation, and a loss of carbon. It has been shown recently that the TiC powder can be produced during the high-energy milling of the titanium and carbon powders [13, 34-37]. However, the formation of TiC *in situ*, during milling needs a long time. High- energy milling of the Cr and graphite powders does not generate chromium carbide, but the chromium and graphite powders are so activated that the formation of chromium carbide during the following heat treatment takes place at much lower temperatures than in case of conventional methods. High- energy ball-milling significantly reduces the reaction temperatures between metals and carbon at which a series of reactions occurred during the subsequent low- temperature heating – the mechanically activated synthesis (MAS) [38-40]. Thus, the advantage of the MAS is shorter milling times than those required for the formation *in situ* in high- energy reaction milling.

The techniques *in situ* involve a chemical reaction resulting in the formation of a very fine and thermodynamically stable ceramic phase within a metal matrix. As a result, the reinforced surfaces are likely to be free from gas absorption, oxidation or other detrimental surface reactions to contamination.

During the investigation conducted at Tallinn University of Technology, the high- energy milling process was employed for the low- temperature synthesis of the carbide powder. High- energy ball-milling significantly reduces the reaction temperatures between the metals and carbon at which a series of reactions occurred during the heating, which followed it (Fig. 1, 2). The elemental powder mixtures of

Ti-C-Ni-Mo and Cr-C-Ni are mechanically activated during the milling in a high-energy ball- mill (attritor). The activated powder mixture with the nanocrystalline particles size was compacted and then reactive- sintered, the formation of the carbide phase is taking place in the same cycle with the liquid phase sintering of the cermet material. The sintering temperature and the time are the two most important factors determining the structure and properties of carbide cermets. For example, active growth in carbide grains during the sintering is characteristic of the Cr_3C_2-Ni cermets. As a rule, the longer and more intensive the previous milling of powders is (i.e. the finer the powder is), the faster the carbide grains tend to grow during the sintering.

1.2 Tribological properties

Wear is one of the most common reasons for a failure of engineering materials [41].

Abrasive erosion of Cr_3C_2-Ni cermets is investigated in works [42-49] and VII (not included in this thesis). It is found that the erosion resistance of Cr_3C_2-Ni cermets depends mainly on the carbide to-binder ratio and the carbide grain size.

Sliding wear of Cr_3C_2-Ni cermets is investigated in works [50-52]. These materials could be successfully used for the production of sleeve bearings and gaskets, due to their high hardness, good polishing qualities, and a thermal expansion close to that of steel, as well as a good corrosion resistance in aggressive environments and at high temperatures, especially if intended for operation in the corrosive media at elevated temperatures [21].

Abrasive wear is a detachment of the material from the surfaces in relative motion, caused by the sliding and rotating hard particles between the opposing surfaces; it is the most important one due to its destructive character [53]. The situation where only two bodies are involved in the interaction is known as a two-body abrasion. Two-body abrasive wear is a complex process often involving high strain and a strain-rate plastic deformation and a fracture of the micro volumes of the material that might be described as a removal of the discrete surface by a harder substance, which tends to be a gouge, score, or a scratch [54]. The situation where an abrasive particle can freely slide and rotate between the two surfaces is known as a three-body abrasion [55].

In the abrasive conditions, the multiphase materials are usually used. The multiphase materials, such as cermets, combine a softer matrix dispersed with the extremely hard grains. The chromium carbide- based cermets are prospective materials for special applications, such as high temperature or corrosive environments and in situations where a high corrosion-abrasive resistance is required simultaneously [56, 57].

There is no single universal view on the abrasive wear mechanism of the chromium carbide- based cermets. It was found that a two-body abrasive wear mechanism depends on the hardness ratio between the abrasive and the alloy [57-59]. If the hardness of abrasive particles is higher than that of the material, they could penetrate into the surface and then the deformed surface will consist of grooves and scratches. A three-body abrasive wear mechanism usually includes the following: the high-stress grinding abrasion, i.e. the abrasive particle is crushed during the wear interaction, and the low-stress scratching abrasion, i.e. the abrasive particle remains intact as it slides or rotates freely across the wear surface [59-62].

1.3 Aims of the study

Since the chromium and titanium carbide- based cermets have not been produced via reactive sintering before, the aims of the present work are: (1) to study the influence of different amounts of the carbide phase, containing various amounts of Cr and C or Ti and C, on the microstructure and properties of the chromium carbide and titanium carbide- based cermets, produced via reactive sintering; (2) to find out the suitable alloying additives (grain growth inhibitors); their optimal quantities and effects on the properties of the chromium carbide- based cermets; (3) to study the influence of technological factors (the sintering temperature and the time) on the microstructure and the mechanical and tribological properties of the reactive- sintered chromium carbide- based cermets.

2 EXPERIMENTAL

2.1 Investigated materials

The pure chromium (Cr), carbon black (C), and nickel (Ni) powders were used as the starting materials. The milling experiments were performed in the attritor with a vial reinforced with the WC-Co alloy. The Cr_3C_2-20%Ni balls (diameter 6 mm) were used as the milling media to minimize contamination. The charge ratio (the ball-to-powder mass ratio) was 5:1. The rotation speed of the impellers was 800 min^{-1} for all the tests. Petrol was used as the milling environment. Milling in petrol allows adding the plasticizer (paraffin) solution during the initial stage of milling; the said solution forms a thin film on the powder particles, thus preventing additional access of air to the ultra-fine active powder particles. Commonly plasticizers burn out (vaporize) completely during the first stadium of sintering (at temperature below 600 ^oC).

To perform reactive sintering, the as-milled powders were sieved (80 mesh/180 µm) and uniaxially pressed at 80 MPa to form the compacts with dimensions of 28 x 18 x 6 mm (for wear tests) and 22 x 6 x 6 mm (for transverse rupture strength tests). The compacts were then heated in a furnace with the graphite heaters. The sintering of the compacted samples was performed in vacuum for 30 min at 600, 900, 1100, 1200, and 1300 ^oC.

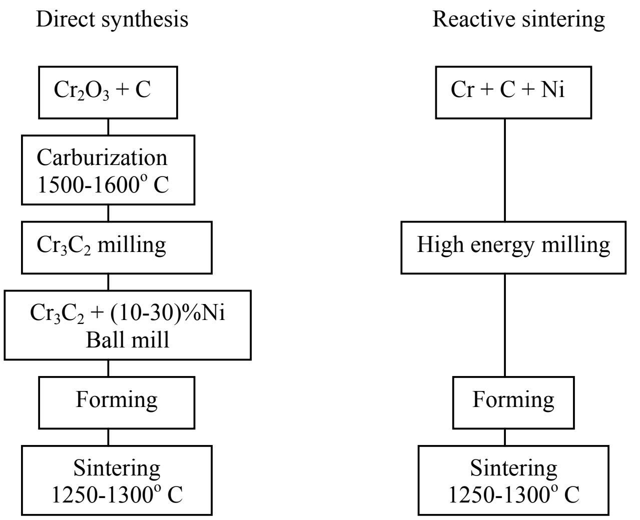


Figure 1. Chromium carbide based cermets producing routes [paper II]

To investigate the influence of the chromium to carbon ratio, different chromium to carbon ratios were used (paper I). The influence of alloying additives (TiO_2; Ne_2O_3; Ce_2O_3; Y_2O_3; B or Si_3N_4) was investigated; the chromium to carbon ratio of the investigated compositions was 6:1 (paper I). Sintering was carried out by two different routines: the vacuum sintering and the sinter/HIP technology. The sintering parameters for the vacuum sintering were the temperature – 1275 °C, the sintering time – 30 min, and for the sinter/HIP 1250 °C – the sintering time was 40 (15+10+15) minutes and the gas pressure was 60 bars. The binder content was 20 wt% of nickel for all the investigated cermets.

The referred chromium carbide- based cermets were produced via the conventional producing route of cermets [63].

For producing the titanium carbide- based cermets via reactive sintering the elemental powders of titanium, molybdenum, nickel and carbon black were milled in a high-energy ball- mill (attritor) for 6 hours. To investigate the influence of the carbon content in TiC, different carbon contents were used (15, 17, 19, 20 wt% of carbon). NiMo ratio was 4:1 for all the investigated materials. The WC-Co balls and gasoline and paraffin as plasticizers were used in high- energy milling. The mixture of the milled powder of the nanocrystalline particles size was compacted and sintered in the vacuum furnace at 1000, 1300 and 1430 °C for 30 minutes to investigate the evolution of microstructure. The referred TiC-50%NiMo cermets were produced by using the conventional powder metallurgy routine [63].

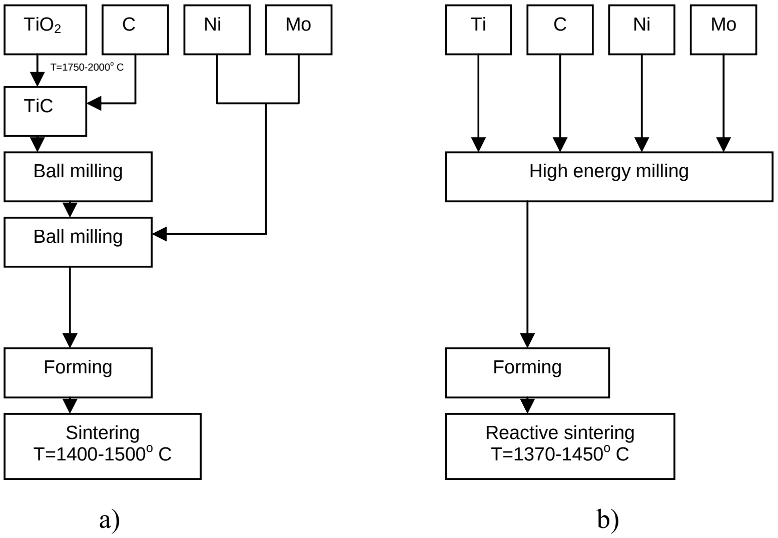


Figure 2. Producing routes of TiC-NiMo cermets [paper IV] by a) conventional technology b) reactive sintering

2.2 Test methods

2.2.1 Microstructure analysis

The phase identification of the milled powder was carried out using X-ray diffraction (XRD) methods with CuKa radiation (Bruker AXS D5005). The particle size of the powders all through the milling process was measured using the BET method (sorbtometer Kelvin 1040).

The size of crystallites was determined by the XRD peak broadening using Scherrer formula. The morphology and grain size of the sintered samples were characterized by using the scanning electron microscope (SEM) JEOL-JSM840A and the Image Pro Plus analysis system.

2.2.2 Determination of hardness and transverse rupture strength

The Vickers hardness was measured in accordance with ASTM Standard E384. Transverse rupture strength (TRS) was determined by the three- point bending tests in accordance with ASTM Standard B406-95 using device ”Instron 8616”. Each test point indicates the average value of six measured results.

2.2.3 Determination of tribological properties

Abrasive erosion test method

Abrasive erosion tests were obtained in centrifugal accelerator CAK-3m in accordance with the standard test method [64] at room temperature using a quartz sand stream with a velocity of 80 m/s at 30 ° impact angle. The wear was estimated as the specific volumetric wear in mm^3/kg as $K = \Delta G/G_a \cdot \rho$ (ΔG – weight loss of specimen, G_a – mass of abrasive per specimen, ρ - density of alloy).

Sliding wear test methods

Sliding wear tests were conducted on a modified block-on- ring test- device according to ASTM B611-85 [65]. The specimens with a size of 23x14x5 mm were clamped in a holder and held rigidly against the rotating steel wheel under normal loads of 20, 180 or 320 N. The rotation speed of the steel wheel was 235 min^{-1} (linear speed 2.2 m/s). The sliding distance was 4000 m for each test. The sliding wear results were averaged over three samples for each material. The standard deviation and coefficient of variation (COV) were calculated on ten tests of some cermets under the same conditions. The COV of wear coefficient of all cermets falls in between 10 and 15 %, decreasing with an increase in the binder content. The wear coefficient of materials is predicted by the Archard equation [66].

Abrasive wear test methods

Abrasive wear tests were carried out in the modified test device according to the materials testing standard ASTM B611-85 [65]. In case of the two-body abrasive, the steel wheel was replaced with an abrasive grinding wheel [paper VI]. Alumina used in these tests as the abrasive has a hardness of 1940 [67]. The structure of a vitrified grinding wheel is composed of the sharp abrasive grits, a bonding system, and a large number of pores. The size of the abrasive grits was 0.2–0.4mm (average 0.3 mm).

The rotation speed of the abrasive wheel was 235 min^{-1}, which gave a linear speed of 2.8 m/s. The sliding distance was 100 m and the normal load was 20 N. Prior to each wear testing, the abrasive wheel was sharpened, and each specimen ran on a fresh abrasive wheel.

In case of the three-body abrasive wear tests, a rotating steel wheel was used as a bed for the abrasive that was carried up out of a bath of slurry and onto the test piece at the wear interface. The silica sand particles of grit size 0.1-0.3 mm were used as abrasives, as it is the abrasive most commonly found in nature. 1500 g. silica sand was added to 940 g distilled water [63].

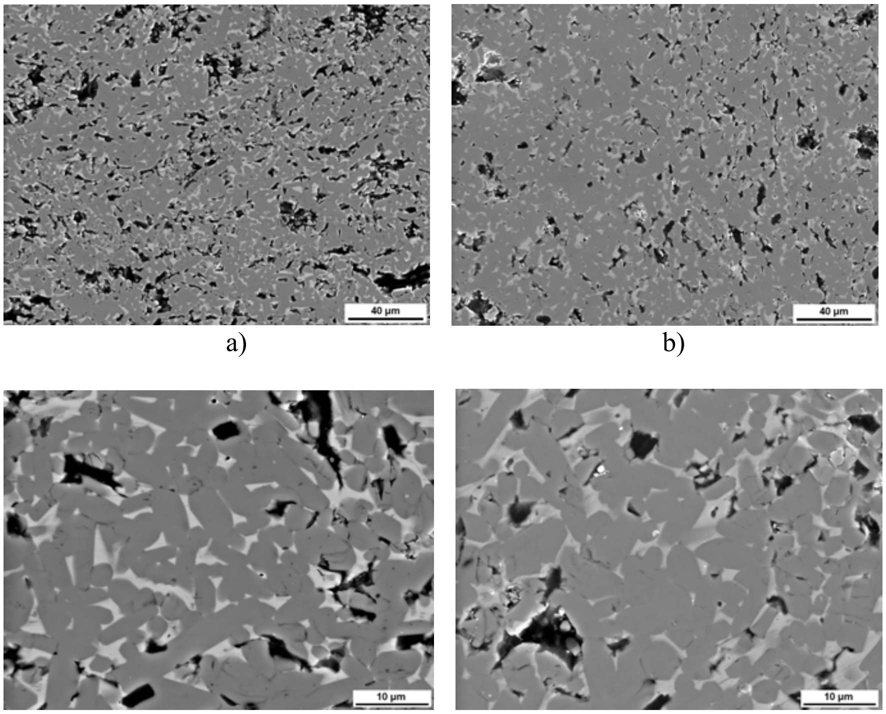
Each specimen was weighed before and after testing to an accuracy of 0.1mg. Weight loss was converted into volume loss. The results of abrasion were averaged over the three samples for each material. COV was calculated on ten tests of some cermets under the same conditions. The COV of the wear coefficient of all cermets falls in between 10 and 15 %, decreasing with an increase in the binder content.

3 RESULTS AND DISCUSSION

3.1 Developement of the chemical composition of the chromium and titanium carbide- based cermets

3.1.1 Development of the optimal chromium to carbon ratios

The influence of the chromium to carbon ratio on the microstructure evolution and properties of the chromium carbide- based cermets is studied in paper I. The microstructures of Cr_3C_2-20%Ni cermets with different chromium to carbide ratios, made by two different sintering routes are exhibited in Figures 3-5. The microstructures of the investigated cermets depend on the chromium to carbide ratio. The carbide grain size of the cermets sintered under gas pressure is somewhat higher than that in the cermets sintered in vacuum. It can be explained by a higher solubility of Cr_3C_2 in nickel and thus by a higher carbide grain growth under pressure.

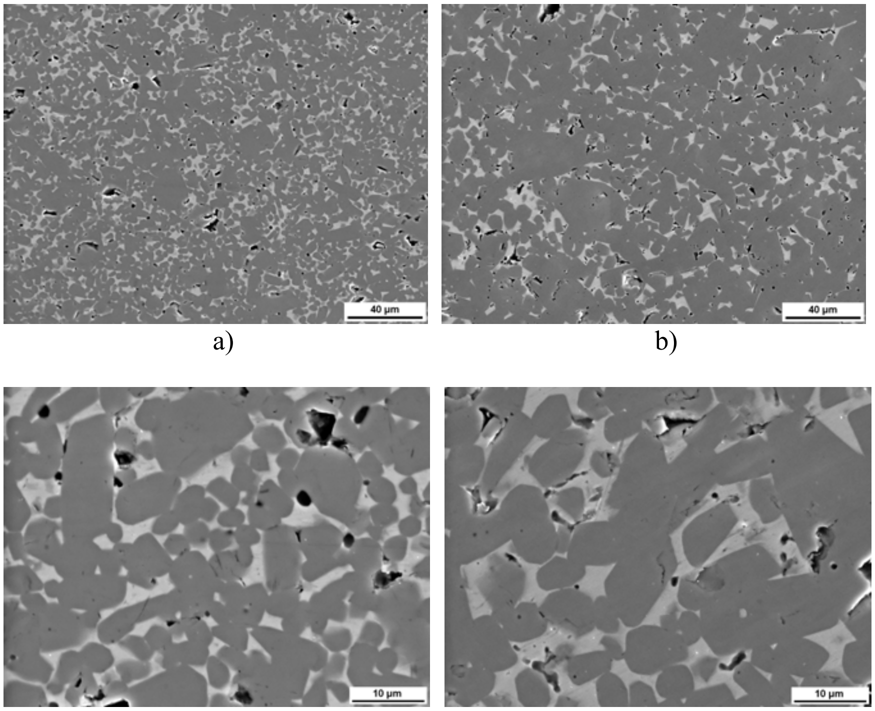


a) b)

c) d)

Figure 3. Microstructures of Cr_3C_2-Ni cermets with chromium to carbide ratio 4:1:
a, c – vacuum sintering; b, d – sinter/HIP

The XRD investigation (paper I) shows that in case of chromium to carbide ratio 8:1, the microstructure will contain mainly Cr_7C_3, the microstructures of other ratios will contain Cr_3C_2 with a small amount of Cr_7C_3; in case of chromium to carbide ratio 4:1, there will be an amount of free carbon in the microstructure, due to a bigger amount of graphite in the mixture. Comparing vacuum sintering and sinter/HIP exhibits that sinter/HIP causes an increase in the porosity rate of the investigated materials. The mechanism of the pores formation during the sintering under gas pressure is unknown.

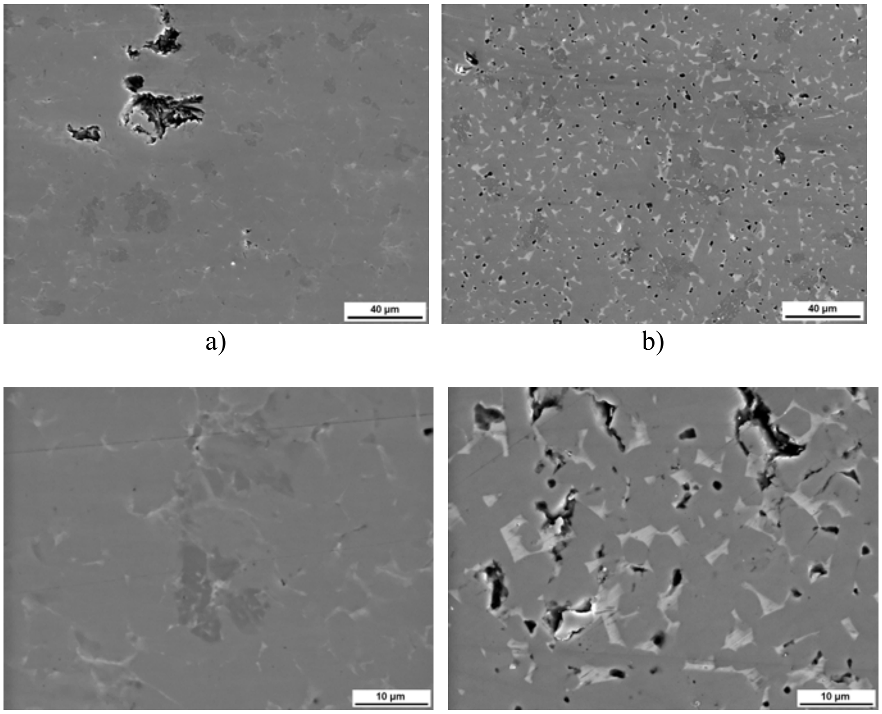


a) b)

c) d)

Figure 4. Microstructures of Cr_3C_2-Ni cermets with chromium to carbide ratio 6:1:
a, c – vacuum sintering; b, d – sinter/HIP

In Figure 6 there is exhibited the hardness of Cr_3C_2-20%Ni cermets vs. the chromium to carbide ratio depending on different sintering techniques. Hardness exhibits its highest value for chromium to carbon ratio 6:1. It can be explained by the minimum porosity of this alloy compared with other alloys. Hardness shows its lower value for chromium to carbon ratio 4:1, in which case an amount of free carbon is remained in the microstructure of the cermet.



a) b)

b) d)

Figure 5. Microstructures of Cr_3C_2-Ni cermets with chromium to carbide ratio 8:1:
a, c – vacuum sintering; b, d – sinter/HIP

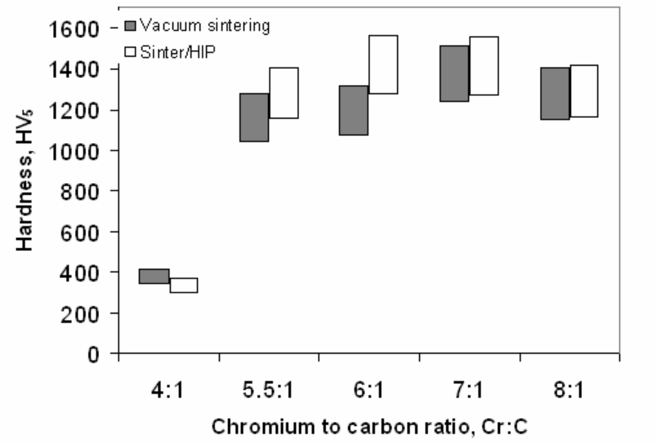


Figure 6. Hardness of Cr_3C_2-20%Ni cermets *vs*. chromium to carbide ratio depending on different sintering techniques

Figure 7 indicates the transverse rupture strength values of Cr_3C_2-20%Ni cermets dependent on the chromium to carbon ratio. In most cases the effect of the chromium to carbon ratio on the transverse rupture strength is not considerable, only the material with chromium to carbon ratio 4:1 shows a lower TRS value comparing to other chromium to carbon ratios. This alloy contains free graphite in structure, which reduces TRS. The cermets made by the sinter/HIP technology exhibited lower strength values of transverse rupture compared to the cermets sintered in a vacuum furnace. The TRS value of cermets with Cr:C ratio 8:1 is low because the Ni solubility in Cr_7C_3 is high and as result, the binder phase will reduce or disappear.

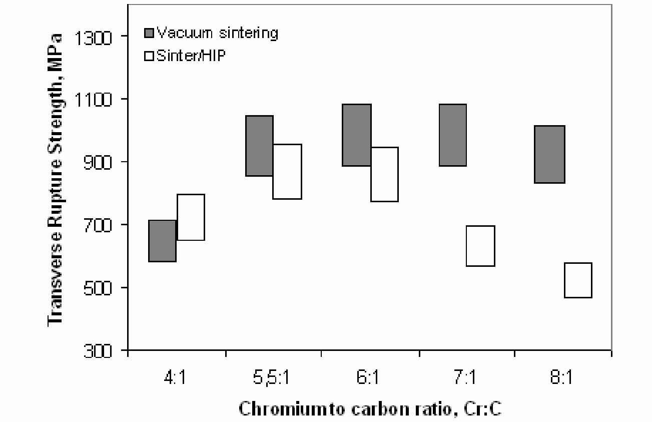


Figure 7. Transverse Rupture Strength of Cr_3C_2-20%Ni cermets *vs*. chromium to carbide ratio depending on different sintering techniques

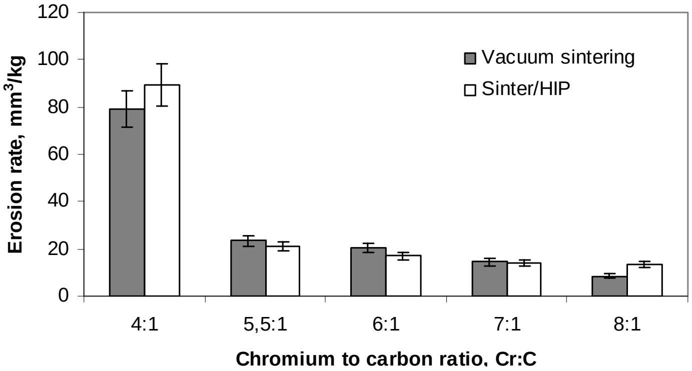
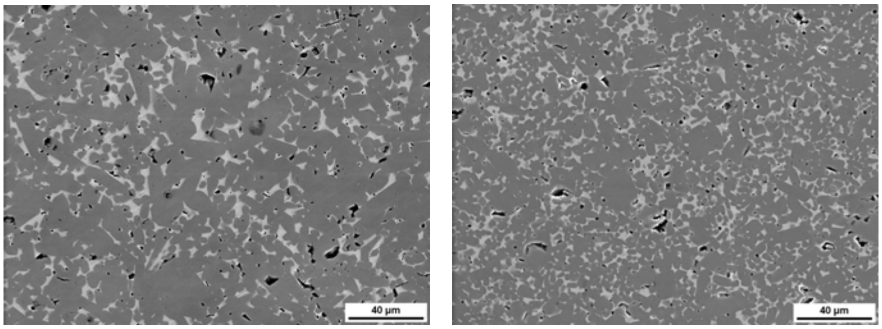


Figure 8. Erosion rates of Cr_3C_2-20%Ni cermets *vs*. chromium to carbide ratio depending on different sintering techniques

Figure 8 illustrates the dependence of the erosion rate on the chromium to carbide ratio. The erosion rate decreases when the chromium to carbon ratio increases. The highest erosion resistance shows the materials with chromium to carbon ratio 8:1. These cermets contain less of the soft binder phase because part of Ni dissolved in Cr_7C_3. There is no significant difference between the erosion resistance of the materials produced by vacuum sintering and sinter/HIP. The highest erosion rate shows the materials with chromium to carbon ratio 4:1. This can be explained by a higher free- graphite content in the material.

3.1.2 Influence of alloying elements on the properties of chromium carbide- based cermets

The microstructures of Cr_3C_2-20%Ni cermets with different alloying additives are exhibited in paper I. In Figure 9, there are compared the microstructures of Cr_3C_2-20%Ni cermet alloyed with 0.25 % Si_3N_4 (Fig. 9a) and without alloying (Fig. 9b). It shows that alloying does not inhibit the grain growth, but at the same time causes a bigger porosity rate of the investigated materials. The influence of alloying additives on the microstructure and properties of the reactive sintered chromium carbide- based cermets is exhibited in paper I.



a) b)

Figure 9. Microstructures of Cr_3C_2-20%Ni cermet alloyed with 0.25 % Si_3N_4 (a) and without alloying (b)

3.2 Development of optimal technological parameters

3.2.1 High energy milling of Cr – C – Ni powder mixtures

The high energy milling of Cr – C – Ni powders is investigated in paper II.

The X-ray diffraction patterns of the Cr and graphite powders with different milling times are shown in Figure 10.

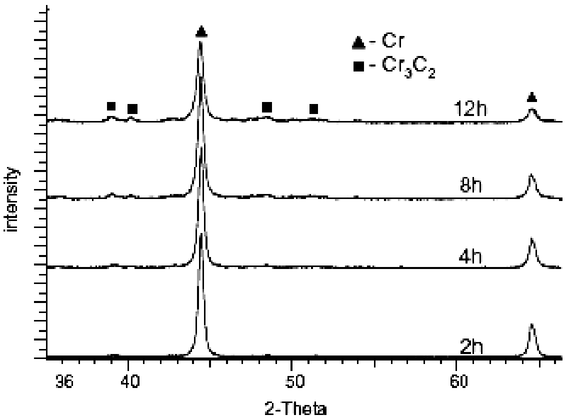


Figure 10. XRD patterns of mechanically activated Cr-C powder mixtures vs. milling time

Two essential features of the milling process can be recognized. Firstly, with an increasing milling time, the chromium peaks were broadened due to a reduction of the grain size and an increase in the internal strain, but the position of Cr peaks has not shifted (the patterns of 4, 8, and 12 h samples in the figure are shifted vertically for a better overview). Secondly, no carbide formation occurred during milling. Some weak traces of Cr_3C_2 can be noticed on the milled samples, but the carbide most likely originates from the milling media. During high-energy milling, the graphite is smeared onto the particles of Cr. Meanwhile, C atoms first segregate in the crystal interfaces of Cr, then diffuse gradually and during heat-treatment react completely with Cr to form chromium carbides. After high-energy milling (mechanical activation) the powder particles are nanosized (60–90 nm) with internal crystallites of 10–15 nm.

3.2.2 Reactive sintering of the chromium and titanium carbide- based cermets

The reactive sintering of chromium carbide- based cermets is investigated in paper II. It is expected that after mechanical activation the powder mixture will have a higher free energy, and thus a higher chemical reactivity than the powder mixtures without activation [13].

The XRD patterns of the mechanically activated Cr–C–Ni powder mixtures after heating at 600, 900, 1100, 1200, and 1300° C are presented in Figure 11. According to the XRD analysis, no reaction between chromium and carbon was detected below 600 °C and the synthesis reaction of Cr_3C_2 took place at temperatures between 600 and 1100 °C. For some reason, the Cr_3C_2 peaks disappeared at 1200 °C and returned at 1300 °C with a lower intensity. The reasons for that phenomenon are unclear, but are probably related to the formation of Cr_3C_2-Ni liquid eutectic at around 1200 °C.

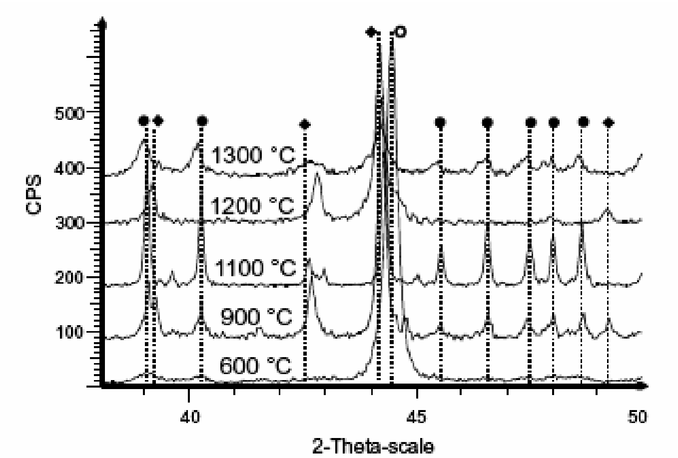


Figure 11. The XRD patterns of the mechanically activated Cr–C–Ni powder mixtures after heating: ● – Cr_3C_2, ♦ - Cr_7C_3, ○ – Cr

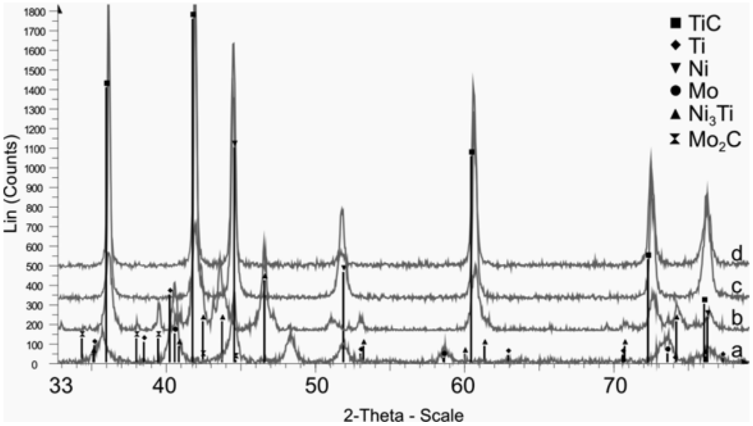
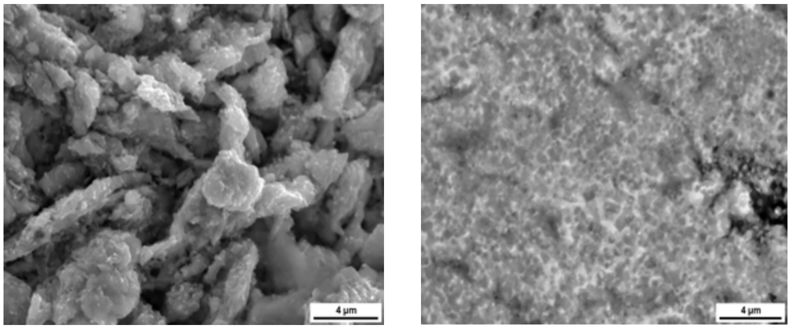


Figure 12. XRD patterns of 50(Ti -15%C)-50(NiMo) powders:
a - high energy milling (6 hours), b – 1000 °C, c – 1300 °C, d – 1430 °C

The reactive sintering of TiC-NiMo cermets is investigated in paper IV. Figure 12 covers the XRD patterns for 50(Ti-20%C)–50(NiMo) after 6h milling and heat treatment at 1000, 1300 and 1430 ^{o}C. The XRD patterns for the milled powder exhibited weak TiC peaks. The synthesis reaction between Ti and C took place during heat treatment at a temperature lower than 1000 ^{o}C; also some transition phases of Ni_3Ti appeared. After heat treatment at 1300 ^{o}C the transition phases disappeared.

After heat treatment at temperature 1000 ^{o}C (Fig. 13a), the necks appear between some particles. They are well crystallized and the average crystallite size in these necks is ranging between 7 and 15 nm. The crystallite size inside the particles is ranging between 20 and 30 nm. The situation is radically different after annealing at 1300 ^{o}C. The particles are now sintered and their size is in the micrometric range (Fig. 13b).



a) b)

Figure 13. The microstructure of 50 (Ti -20 %C)–50 (NiMo) cermets sintered at a different temperature: a – 1000 ^{o}C; b – 1300 ^{o}C

3.2.3 Carbide grain growth and microstructure

The carbide grain growth and the microstructure of chromium carbide- based cermets are investigated in paper II. The microstructures of the reactive sintered Cr_3C_2-20%Ni cermets are exhibited in Figure 14. The cermets sintered at 1250 ^{o}C for 30 or 60 min have a fine microstructure - the average carbide grain size is between 1.5 and 2 µm in both cases. The microstructure of cermets, sintered at 1300 ^{o}C is more irregular and has some coarse carbide grains. The carbide grain size in Cr_3C_2-Ni cermets is determined by the sintering parameters and by the particle size of the green powder in particular. High-energy milling can reduce the particle size to nanoscale. A rapid grain growth during the solid and liquid phase sintering is one of the main disadvantages of chromium carbide- based cermets [68]. The carbide grain growth also occurs during reactive sintering, but is somewhat retarded when compared to traditional processing. The synthesized chromium carbide *in situ* is indeed fine-grained and more homogeneous (Fig. 15). The carbide grain size in case of the reactive-sintered cermets is lower and also less sensitive to longer sintering times (Fig. 16).

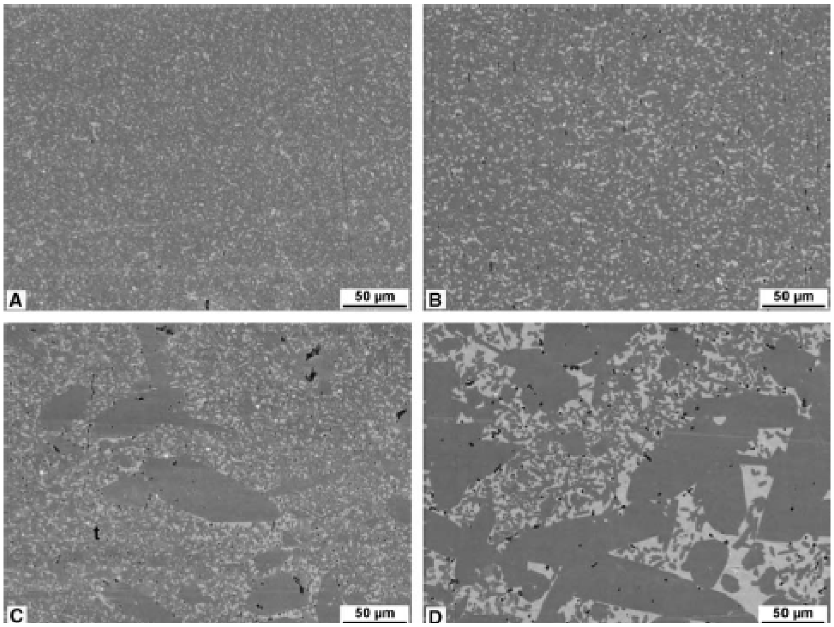


Figure 14. The microstructure of reactive sintered Cr_3C_2-20%Ni cermets at 1250 °C (A – 30 min, B – 60 min) and 1300 °C (C – 30 min, D – 60 min)

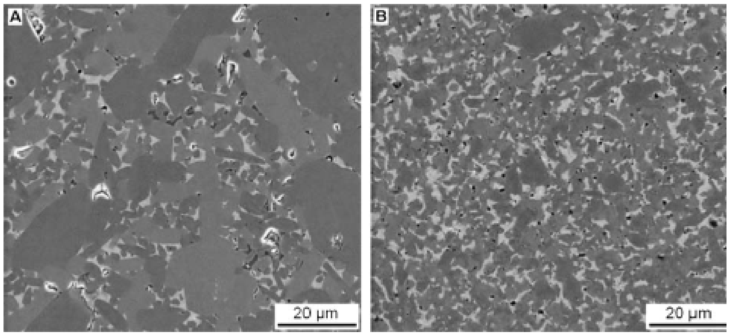


Figure 15. Microstructures of Cr_3C_2-Ni cermets produced by conventional routine (A) and reactive sintering (B)

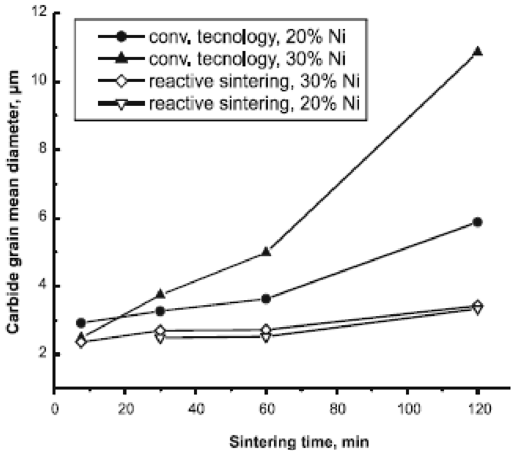
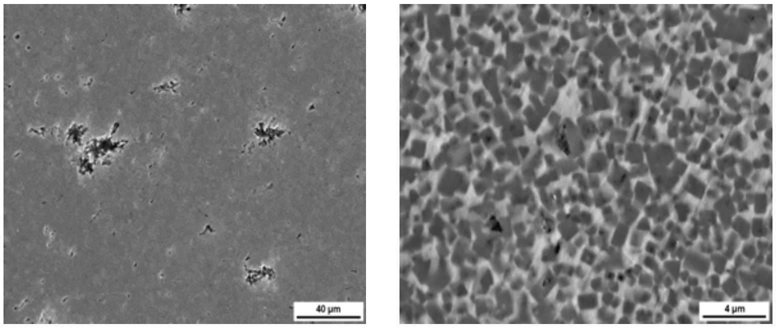
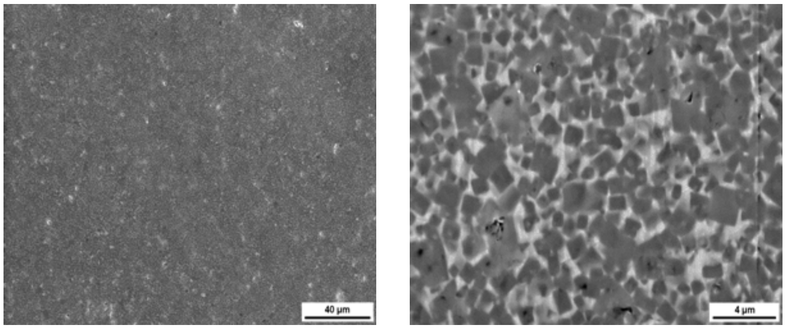


Figure 16. Mean diameter of carbide grains *vs*. sintering time and production technology (sintering temperature 1300 ^{o}C)



a) b)

Figure 17. Microstructure of 50 (Ti-20%C)–50(NiMo) cermets



a) b)

Figure 18. Microstructure of 50 (Ti-15% C)–50 (NiMo) cermets

The microstructure of the reactive sintered titanium carbide- based cermets is investigated in paper IV. In Figures 17 and 18, there are exhibited the microstructures of 50(Ti-20%C)–50(NiMo) and 50(Ti-15%C)–50(NiMo) cermets sintered at 1430 ^{o}C for 30 minutes. The cermets with the higher carbon content exhibited a more fine- grained structure and the porosity was lower for the materials with the lower carbon content.

The final density of the sintered samples of the reactive sintered TiC-50%NiMo cermets depends on the carbon content (Fig. 19). A higher density occurred in the cermets with the lower carbon content. In case of the higher carbon content there is free carbon remaining in the microstructure (Fig. 17a). The density of the cermets with 15 wt% of carbon in TiC is comparable with that of the industrial material (Fig. 19, specimen 20s).

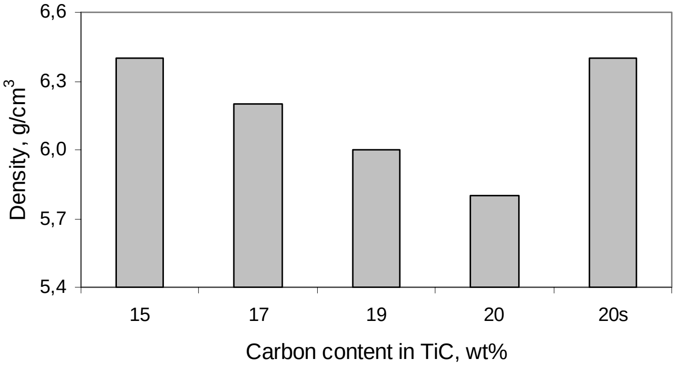
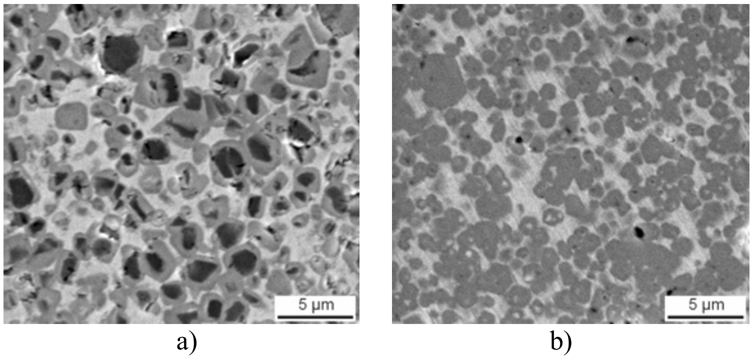


Figure 19. Density *vs*. carbon content in TiC



a) b)

Figure 20. Microstructure of TiC-NiMo cermets produced by different methods:
a – conventional technology; b – reactive sintering

The microstructure of the reactive sintered TiC-50%NiMo cermets (Fig. 20b) is without a core-rim structure, it is more fine- grained (the average size of the carbide grain is below 1 µm) and is more homogeneous than that of the cermets produced by conventional technology (Fig. 20a).

3.4 Mechanical properties

The mechanical properties of the reactive sintered Cr_3C_2-Ni cermets depend on their final composition and microstructure. The mechanical properties of the chromium carbide- based cermets are studied in papers I, II.

3.4.1 Hardness of chromium carbide- based cermets

In Figure 21, there is exhibited the Vickers hardness of the Cr_3C_2-Ni cermets depending on the sintering parameters and the carbide/binder ratio. As seen before, the hardness of the Cr_3C_2-Ni cermets depends mainly on the binder content and only slightly on the carbide synthesis method, being between HV 750 and 1400. It shows that the hardness decreases with the binder content due to an increase in the amount of the soft binder phase. The specimens sintered at 1300 ^{o}C are slightly softer than those sintered at 1250 ^{o}C because the carbide grains are finer, when sintered at 1300 ^{o}C. The hardness of the reactive sintered cermets is 15–30 % higher than that of the cermets produced via conventional technology.

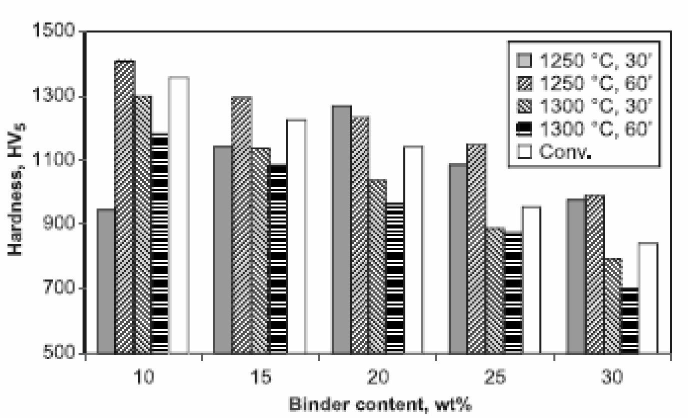


Figure 21. Hardness of the chromium carbide- based cermets *vs.* the chemical composition, sintering parameters and producing technology

3.4.2 Transverse rupture strength of chromium carbide- based cermets

The transverse rupture strength of the Cr_3C_2-Ni cermets depends on the carbide grain size in spite of the chemical composition. As seen from Figure 22, the TRS will decrease as the carbide content and sintering temperature and time are increasing. The reason for a decline in strength can be associated with a decrease in the binder content and an increase in the carbide grain size. The TRS of the reactive sintered cermets is somewhat higher than that of the cermets fabricated by conventional methods.

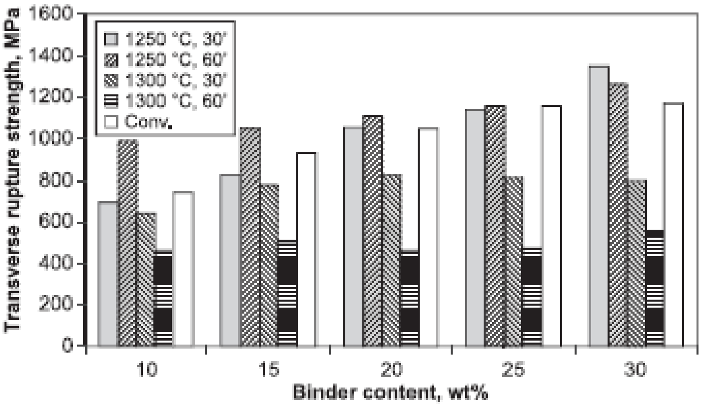


Figure 22. Transverse rupture strength of the chromium carbide- based cermets *vs*. the chemical composition, sintering parameters and producing technology

3.4.3 Hardness and transverse rupture strength of titanium carbide-based cermets

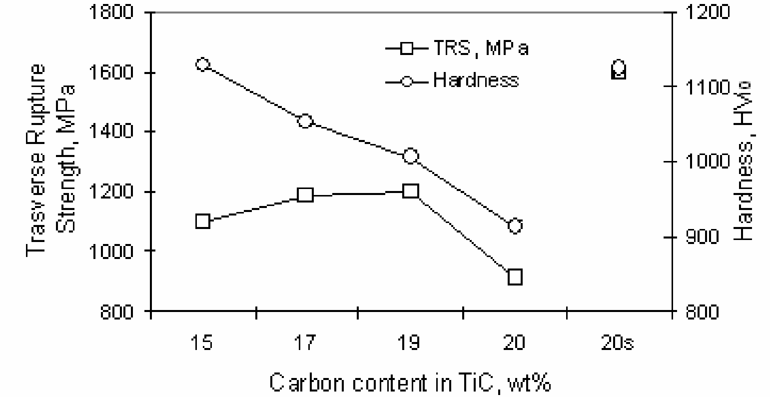


Figure 23. Transverse rupture strength and hardness of TiC-50%NiMo cermets *vs*. carbon content in TiC

The hardness and transverse rupture strength of the titanium carbide- based cermets are investigated in paper IV. Figure 23 exhibits the hardness and transverse rupture strength of TiC-50%NiMo cermets depending on the carbon content in TiC. Both the hardness and TRS decreased in case of an increase in the carbon content; the highest value of hardness is exhibited in the cermets with the carbon content 15 wt%. Compared to the conventional TiC-50%NiMo cermets (specimen 20s), the TRS values for the reactive sintered materials are lower due to the remaining microporosity; the hardness of the material with 15 wt% C is similar to that of the cermets produced by conventional technology.

3.5 Tribological properties

3.5.1 Abrasive wear of chromium carbide- based cermets

Abrasive erosion wear is studied in paper II. Figure 24 exhibits the abrasive erosion rate of the chromium carbide- based cermets depending on their chemical composition and the producing technology of the cermets. As seen above, the erosion rate of Cr_3C_2-Ni cermets depends on the carbide-to-binder ratio and the sintering parameters (the temperature and time). Sintering at 1250 ^{o}C for 60 minutes will give the best erosion resistance for the reactive sintered cermets. Most probably, sintering for 30 min would be insufficient for the formation of a strong bond between the carbide grains and the binder phase. The coarse-grain cermets, produced by sintering at 1300 ^{o}C have the lowest erosion resistance. Large grains are fragmented by brittle or low-cycle fatigue. The lateral cracking mechanism of erosion leads to much higher rates of erosion than the crumble of small carbide grains. When compared to the cermets produced by conventional technology, the erosion rate of the more fine- grained reactive-sintered cermets is 15–50 % lower if sintered at the optimal parameters. The abrasive erosion mechanism of the chromium carbide- based cermets is investigated in paper VII (not included in the thesis).

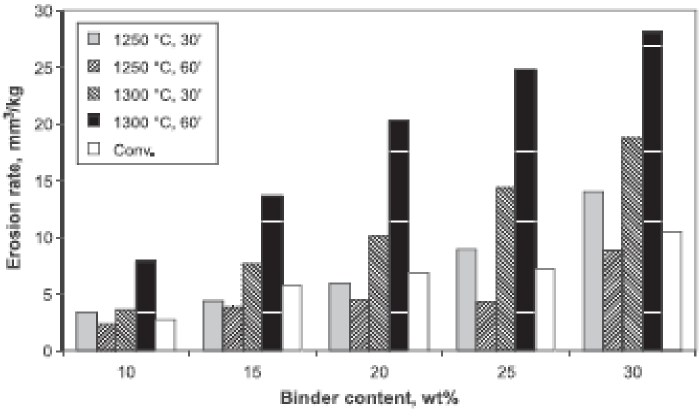


Figure 24. Abrasive erosion rate of chromium carbide- based cermets *vs*. chemical composition, sintering parameters and producing technology

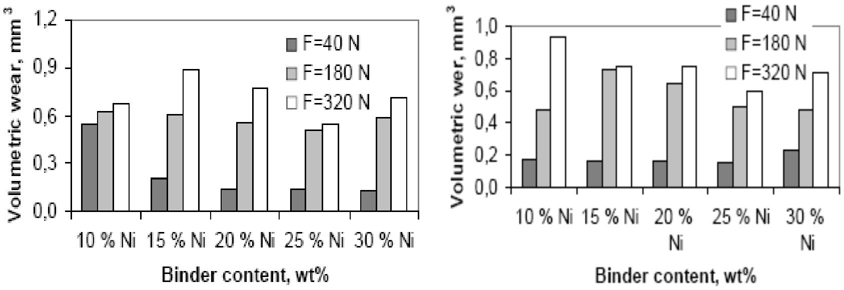
3.5.2 Sliding wear of chromium carbide- based cermets

The sliding wear properties of the reactive sintered chromium carbide- based cermets are investigated in paper II.

The sliding wear resistance of the chromium carbide- based cermets is shown in figure 25. The sliding wear of Cr_3C_2-Ni cermets is surprising, because in the normal load of 40 N, the cermets with a lower binder content and higher hardness exhibited a lower wear resistance than the cermets with a high binder content and lower hardness. As the examination of the wear mechanism is demonstrated in

[20], the brittle rupture of the surface of Cr_3C_2-10%Ni cermets takes place, for which the wear rate is rather high. An increase in the binder content results in a reduced brittleness and lower wear. Volumetric wear will increase in case there is an increase in the normal load. Under higher normal loads, the influence of the binder content decreases, but the main trend will preserve.

An increased wear resistance of the coarse-grain Cr_3C_2-Ni cermets, sintered at 1300 ^{o}C for 30 or 60 min is attributed to the bigger chromium carbide grains (see paper I). The large carbide grains first endure the external load and thus prevent the removal of the binder and the small carbide grains and thus raise the wear resistance of cermets. The fine carbide grains located in the surface layer are torn out from the material by friction forces, yet they are not crushed in the process. In such a case, the detached carbide grains behave as abrasive particles, able to penetrate the hard metal and scratch its surface, causing the formation of grooves. This way, the carbide grains torn out of the cermet, exert a negative influence on wear resistance. The wear resistance of the cermets produced by reactive sintering is about 1.2–1.4 times higher than that of the cermets produced by conventional technology (except the Cr_3C_2-10%Ni cermets).



a) b)

Figure 25. Volume wear of chromium carbide based cermets *vs*. chemical composition, normal load and cermets producing technology: a – reactive sintering; b – conventional technology

3.5.3 Abrasive wear of chromium carbide- based cermets

The abrasive wear of chromium carbide- based cermets is investigated in papers II, III. The two- body abrasive wear rate depending on the carbide/binder ratio is shown in Figure 26. The wear coefficient increased with an increase in the Ni volume fraction in the cermets. The wear coefficient increases approximately linearly while increasing the binder content from 10 to 30 wt% Ni. The wear coefficient of the cermets with 50 % Ni is very high. However, the wear coefficient for all alloys is lower for the fine-grained reactive-sintered cermets.

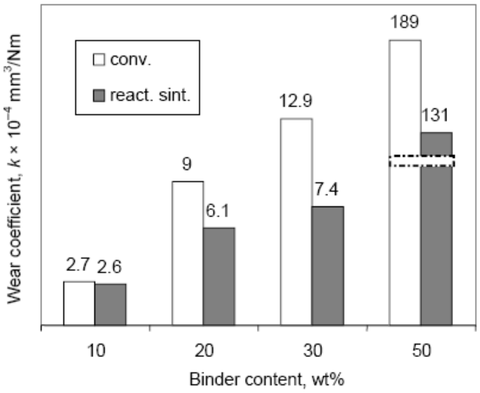
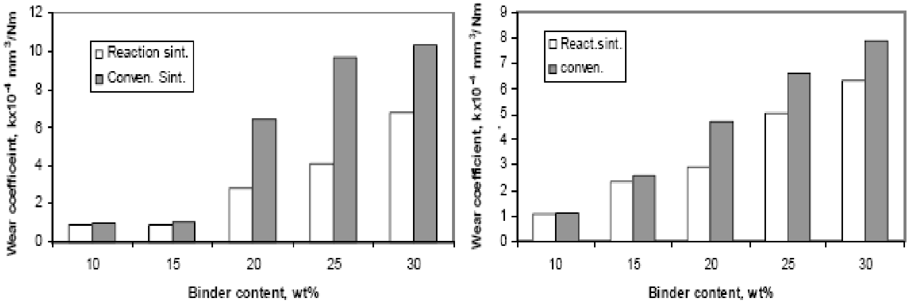


Figure 26. Two- body abrasive wear coefficient of chromium carbide based cermets *vs*. chemical composition and cermets producing technology



a) b)

Figure 27. The three- body abrasive wear coefficient of chromium carbide- based cermets *vs*. the chemical composition and cermets producing technology: a – F=40 N, s=50 m; b – F=222 N, s=260 m

The three- body abrasive wear coefficient of chromium carbide cermets is predicted by using the Lancaster model [69]. Figure 27 exhibits the three-body abrasive wear coefficient of the chromium carbide- based cermets for low and high stress conditions. The wear coefficient increases approximately linearly while increasing the binder content from 10 to 30 wt% Ni. However, the wear coefficient of all alloys is lower than that of the fine- grained reactive-sintered cermets. The wear coefficient k practically does not depend on the stress conditions (low or high-stress abrasion), which affirms the rightness of the Lancaster equation on wide wear conditions.

The abrasive wear mechanism is studied in paper III.

3.5.4 Abrasive erosion and sliding wear of titanium carbide- based cermets

The wear resistance of the titanium carbide- based cermets is investigated in paper IV.

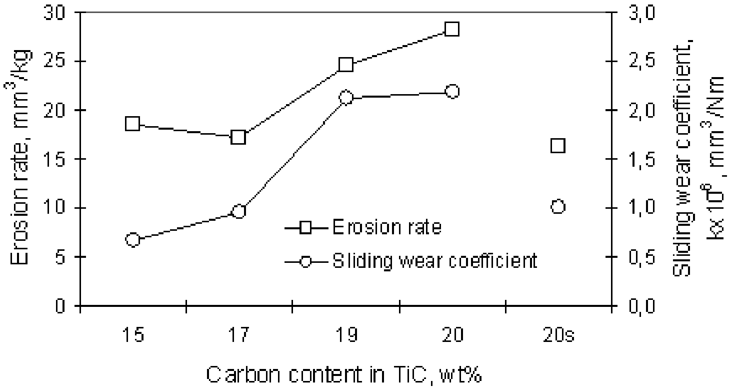


Figure 28. Erosion rate (v=80 m/s, $\alpha=30\ ^{o}$) and sliding wear coefficient (P=40 N, s=4000 m) of TiC-50%NiMo cermets *vs*. carbon content in TiC

Figure 28 shows the abrasive erosion and sliding wear resistance of the investigated TiC-50%NiMo materials. The abrasive erosion and sliding wear resistance will decrease in case there is an increase in the carbon content of TiC; a better wear resistance is observed in the cermets with the carbon content of 15 and 17 wt%, whose values for erosion resistance are comparable and those for the coefficient of sliding wear exceed those of the conventional material (20s), due to a higher hardness rate of the composition.

CONCLUSIONS

The main conclusions of the present thesis are as follows:
While conventionally chromium carbide and titanium carbide are produced via processes at a very high temperature, the current thesis demonstrates a simple and economical process - high-energy milling followed by reactive sintering - to produce the chromium carbide and titanium carbide- based cermets.

1. A novel technology – reactive sintering - to produce the fine- grained chromium carbide and titanium carbide- based cermets was developed;

2. The microstructure of reactive sintered chromium carbide based cermets with different amounts of the carbide phase containing various amounts of Cr and C depends on carbon content. It contains Cr_3C_2 in case of chromium to carbide ratio 6:1; Cr_7C_3 mainly in case of Cr:C ratio 8:1 and there is amount of free carbon in microstructure in case of Cr:C ratio 4:1. The most promising mechanical and tribological properties exhibited cermets with Cr:C ratio 6:1;

3. The microstructure of the chromium carbide based cermets with the alloying additives exhibited a less homogeneous microstructure with a bigger porosity;

4. In comparison to the conventional TiC-NiMo cermets the microstructure of reactive sintered (Ti,Mo)C-Ni cermets was more homogeneous and has finer carbides. The average carbide particle size is below 1 μm;

5. The optimal sintering parameters to produce the chromium carbide- based cermets via reactive sintering were developed, the optimal sintering parameters are: sintering temperature 1250 ^{o}C and sintering time 60 minutes;

6. The microstructure of the reactive- sintered chromium carbide based cermets is more fine- grained (average carbide grain size is between 1.5 and 2 μm), more homogeneous and less porous than that of the cermets produced by conventional technologies; they have the superior mechanical properties and wear resistance (in case of the same chemical composition) compared to the materials produced via conventional technologies;

7. The mechanical (hardness, transverse rupture strength) and tribological (abrasive erosion and sliding wear resistance) properties of reactive sintered (Ti,Mo)C-Ni cermets depend on carbon content on carbide phase. The most promising mechanical and tribological properties exhibited material with carbon content 15 wt%;

8. The investigation of wear mechanism exhibited that the material removal process was similar to the cermets made by reactive sintering and by conventional technology.

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ABSTRACT

“Reactive Sintered Chromium and Titanium Carbide- Based Cermets”

The chromium carbide- based cermets are prospective materials to operate in the corrosive and abrasive environments. The main disadvantages of these cermets are relatively low mechanical properties and wear resistance mainly because of their coarse-grained structure (the carbide grain size is usually over 4 µm).

TiC - based cermets are known for their outstanding corrosion- and high-temperature wear resistance; they are most commonly used in metal cutting tools, but their unique combination of properties offers wide scope to the materials design engineer. Even today the best TiC-base cermets still possess a poor erosive and wear resistance compared with the WC-Co cemented carbides. However, one of the disadvantages of using TiC for commercial applications is that it is difficult to produce.

The current thesis studies the methods of producing chromium carbide and titanium carbide- based cermets via reactive sintering. In case of reactive sintering the elements, which form the chemical compound during sintering are chosen. Reactive sintering preceded by mechanical activation allows to simplify the routine of producing cermets and produce the fine- grained cermets, which have the superior mechanical properties and wear resistance compared to the materials produced via conventional technologies.

The influence of different amounts of the carbide phase, containing various amounts of Cr and C or Ti and C, on the microstructure and properties of the chromium carbide and titanium carbide- based cermets, produced via reactive sintering were studied. The optimal graphite contents to produce those cermets via reactive sintering were developed.

The microstructure of the reactive- sintered cermets is more fine- grained, homogeneous and less porous than for the cermets produced by conventional technologies, they have the superior mechanical properties and wear resistance (in case of the same chemical compositions) compared to the materials produced via conventional technologies.

The influence of the sintering parameters on the properties of the reactive-sintered chromium carbide- based cermets with different chemical compositions was investigated; the optimal sintering parameters to produce the chromium carbide- based cermets via reactive sintering were developed.

The wear mechanism of the reactive sintered chromium carbide- based cermets under different wear conditions was studied; the material removal process was similar to the cermets made by reactive sintering and by conventional technology.

Keywords: Chromium and titanium carbide- based cermets, reactive sintering**,** mechanical and tribological properties

KOKKUVÕTE

“Reaktsioonpaagutatud kroom- ja titaankarbiidsed kermised”

Kroomkarbiidsed kermised on eriti perspektiivsed töötamaks abrasiivses ja agressiivses keskkonnas või kõrgel temperatuuril (kuni 1000 °C), eriti kui need faktorid mõjuvad samaaegselt. Samas tulenevalt nende suurest terasuurusest (kuni 4 µm) on nende mehaanilised omadused (tugevus, löögisitkus), võrreldes näiteks WC-Co kermistega madalad, mistõttu kasutatakse neid seni veel vähe.

Titaankarbiidsed kermised on tuntud oma suure korrosioonikindluse ja kulumiskindlusega kõrgetel temperatuuridel. Peamiselt kasutatakse neid metallilõikeriistade materjalina, kuid nende omadused võimaldavad kasutada neid laias valikus insenerimaterjalina. Samas jääb parimate omadustega titaankarbiidsete kermiste kulumiskindlus normaaltingimustes praegu veel alla WC-Co kermiste kulumiskindlusele; samuti on titaankarbiidi puuduseks tema valmistamise keerukus.

Antud töös uuriti kroomkarbiidsete ning titaankarbiidsete kermiste valmistamist reaktsioonpaagutamise teel. Reaktsioonpaagutamise korral valitakse sellised elemendid, mis moodustavad paagutamise käigus põhimetalliga keemilise ühendi. Reaktsioonpaagutamine eelneva mehaanilise aktiveerimisega võimaldab tunduvalt lihtsustada kermiste valmistamise tehnoloogiat ja valmistada peeneteralisi kermiseid, millel on tavatehnoloogiate teel valmistatud materjalidega kõrgemad mehaanilised omadused ja suurem kulumiskindlus.

Käesolevas töös uuriti erinevate Cr ja C ning Ti ja C sisalduste mõju algpulbrites reaktsioonpaagutatud kroomkarbiidsete ja titaankarbiidste kermiste omadustele, leiti optimaalsed süsiniku sisaldused valmistamaks antud kermiseid reaktsioonpaagutuse teel.

Reaktsioonpaagutatud kermiste mikrostruktuur on tunduvalt peeneteralisem, homogeensem ja väiksema poorsusega võrreldes tavatehnoloogiate teel saadud materjalidega, samuti on nad (sama keemilise koostise korral) kõrgemate mehaaniliste omadustega ja suurema kulumiskindlusega.

Uuriti paagutusrežiimide mõju erineva keemilise koostisega reaktsioonpaagutatud kroomkarbiidsete kermiste omadustele, töötati välja optimaalsed paagutusrežiimid kroomkarbiidsete kermiste valmistamiseks reaktsioonpaagutuse teel.

Uuriti kroomkarbiidsete kermiste kulumise mehhanismi erinevate kulumisliikide korral, leiti, et kulumise mehhanism reaktsioonpaagutuse ja tavatehnoloogia teel valmistatud materjalidel ei erine.

Märksõnad: kroom- ja titaankarbiidsed kermised, reaktsioonpaagutamine, mehaanilised ja triboloogilised omadused

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Paper I. K. Juhani, J. Pirso, S. Letunovitš, M. Viljus, Phase evolution, microstructure characteristics and properties of Cr_3C_2-Ni cermets prepared by reactive sintering, Int. J. Materials and Product Technology (in press)

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ETF6758, WC-Co jäätmeist ülipeene- ja nanostruktuuriga kõvasulamite valmistamine. 2006-2009

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8. Other research project

V361, Cermets for wear parts. 2007-2008;

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DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *MECHANICAL AND INSTRUMENTAL ENGINEERING*

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8. **Roberto Carmona Davila**. Some contributions to the quality control in motor car industry. 1999.
9. **Harri Annuka**. Characterization and application of TiC-based iron alloys bonded cermets. 1999.
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11. **Edi Kulderknup**. Reliability and uncertainty of quality measurement. 2000.
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14. **Martin Eerme**. Structural modelling of engineering products and realisation of computer-based environment for product development. 2001.
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21. **Sergei Zimakov**. Novel wear resistant WC-based thermal sprayed coatings. 2004.
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23. **Medhat Hussainov**. Effect of solid particles on turbulence of gas in two-phase flows. 2005.

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27. **Sergei Tisler**. Deposition of solid particles from aerosol flow in laminar flat-plate boundary layer. 2006.

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29. **Maksim Antonov**. Assessment of cermets performance in aggressive media. 2006.

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33. **Hans Rämmal**. Experimental methods for sound propagation studies in automotive duct systems. 2007.

34. **Meelis Pohlak**. Rapid prototyping of sheet metal components with incremental sheet forming technology. 2007.

35. **Priidu Peetsalu**. Microstructural aspects of thermal sprayed WC-Co coatings and Ni-Cr coated steels. 2007.

36. **Lauri Kollo**. Sinter/HIP technology of TiC-based cermets. 2007.

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