Sinter/HIP Technology of TiC-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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The author's contribution

The author of this thesis took part in the sample preparation routine, was responsible for carrying out of the experiments, collecting, processing and further analysis of experimental data. The aouthor also took part in discussion of the content. The intellectual merit which is the result of the framework where the contribution of every author of related papers should not be underestimated.

Contents

List of symbols and abbreviations

Abbreviations

HIP	hot isostatic pressing,
Sinter/HIP	concurrent vacuum sintering and HIP process,
TRS	transverse rupture strength,
HV	Vickers hardness number,

Symbols

d_0	initial average grain size of powder particulates,
d	final average grain size after sintering,
V_0	original volume of material,
ΔV	change of volume of the material,
R	gas constant,
T	absolute temperature, K,
t	time,
r_p	average pore radius,
γ_{LV}	tension between liquid and vapour phases,
L_0	initial length of material,
ΔL	change in length of the material,
k	constant for solution reprecipitation process,
δ	thickness of the boundary layer,
D	diffusion coefficient of solid in the liquid phase,
C_0	equilibrium solubility of solid in the liquid,
σ	yield stress of material,
σ_0	materials constant for the starting stress for dislocation movement,
B	constant for grain growth dependency of initial grain size,
Q	activation energy, J
ρ	density, g/cm^3,
DP	dew point, ^{o}C,
L_l	adhesive wear resistance, m/mm
C	contiguity
P	argon gas pressure, Bar,
p	vacuum, mBar,
$t_{milling}$	time of milling, h
T_{sint}	sintering temperature, ^{o}C,
$k_{1A}\ldots k_{16A}$	grain growth constant dependent of attritor milling time, μm/h,
k_{72B}	grain growth constant dependent of ball milling time, μm/h,
K	wear rate in abrasive erosion media, mm^3/kg,

1 Introduction

The losses resulting from wear in life cycle costs of equipment and components may be tremendous. In some industries such as mining, metallurgy, building materials production etc, recycling of wear parts and consumables may compose up to 40% of life cycle costs. Therefore challenge for the next years is to develop new reliable wear resistant materials and related technologies. Fundamental understanding of the correlations between processing, microstructure and material properties is the core of materials science and engineering.

The author of present study focuses on TiC-based cermets for metalworking industry (alloys TiC-FeNi) and for applications with prevalence of erosion wear (mining, oil refinery, wood and paper industry) – alloys TiC-NiMo.

The thesis consists of four main chapters. In introduction the theoretical background of the structure development mechanisms of the cermets will be reviewed. The structure – property relations and technological processes for better performance characteristics will be outlined.

The second chapter is about the materials selection and the employed mechanical, wear and microstructure property characterization methods.

The third chapter consists of five sections. The first section is dedicated to the effect of pre-sintering techniques on TiC-based cermets.

The second section of the third chapter is a study about sinter/HIP effect in conjunction with pre-sintering technologies.

In the third section of the third chapter the functional properties of the improved TiC-FeNi steel cermets will be revealed.

In the fourth section of the third chapter possibilities of employing sinter/HIP for TiC-NiMo cermets will be studied.

The fifth section of third chapter is dedicated to the effect of the sinter/HIP and reactive sinter/HIP of different (up to nanosized) initial average grain size materials

The last chapter presents general conclusions and suggestions for the research in the future.

The main results of present research have been published in 3 pre-reviewed journals and presented in 4 international conferences.

1.1 Titanium carbide-based cermets – an overview

In hard metal industry throughout the history strenuous attempts have been made to displace tungsten as a basic constituent for hard metals. The most auspicious carbide, carbo-nitride or boride forming metals for this has found to be titanium.

Titanium carbide based cermets came to the market in the mid-1960s. Since around 1968-1970, after systematic investigation by Kieffer and co-workers [1] most research efforts in this field have been subjected to development of titanium carbonitride based cermets as being perspective metal cutting tool material [2, 3].

Although having higher strength and toughness properties compared to TiC-based cermets, the inferior hardness, more demanding sintering parameters and elastic modulus [4] are not favorable for wear applications involving abrasion and erosion. For these applications titanium carbide based cermets have found most interest among the tungsten free cermets [5-18].

Titanium carbide – nickel molybdenum ceramic – metal composites (designated in literature usually as TiC-NiMo, TiC-MoNi, TiC-Mo-Ni, TiC-Ni-Mo or TiC-Mo_2C-Ni) have shown implications of the abrasive erosion wear properties amounting and even superior properties in some circumstances to the ones of common WC-Co hard metals [8, 18]. Due to trends of using tailored material properties in industry the TiC based cermets could be one attractive solution for specific applications.

Although nickel alloy with added molybdenum or tungsten as sintering aid being the mostly used binder materials for these materials, iron alloys are more attractive in respect to their raw materials availability, price, environmental friendliness, health prevention during powder handling, martensitic behavior etc. The martensitic behavior occurring at considerably lower temperatures and stress levels compared to plain steels with similar composition [19] allows transformation toughening of high nickel alloyed materials during crack propagation [8, 20, 21] or at the surface area during grinding [22]. Lower nickel content materials have found to obtain martensitic, martensitic-bainitic or martensitic-austenitic binder phase already during cooling in furnace after sintering [23].

Due to martensitic behavior and transformation toughening titanium carbide cermets with steel binder are used as materials withstanding high-cycle fatigue - stamping, blanking or drawing die materials [24, 25]. Additionally, high carbide fraction alloys can be used in applications similar to TiC-NiMo cermets such as valves, seals or bearings which are exposed to severely erosive fluids in mining, geothermal drilling and coal liquefaction industries [8].

Although steel-binder cermets having extraordinary properties due to martensitic behavior, many microstructure related aspects to technological parameters are still unclear.

1.2 Mechanisms of cermet structure development during sintering

In order to choose and design technological parameters for cermet production the driving forces and mechanisms for densification must be understood.

The main driving force for sintering is the reduction of total surface energy by the formation of interparticle bonds and reduction of chemical potential by dissolving of original and growth of equilibrium solid phase [26, 27]. The basic mechanisms, which lead to a change of particle size, shape and contiguity, are all connected to the dissolution of solid material in liquid phase, transport via the melt and reprecipitation on particles on other sites [28].

Prior to liquid phase sintering there is always solid state sintering present. During this state there are four mechanisms leading to changes in physical structure – evaporation-condensation, surface diffusion, viscous or plastic creep and volume diffusion. The major roles of these are playing viscous flow and volume diffusion [26]. For crystalline solids the rate of volumetric shrinkage $\Delta V/V_0$ is given by [29]

$$\frac{\Delta V}{V_0} = \left(\frac{20\gamma V_0 D_v}{\sqrt{2}RT} \right)^{2/5} r^{-6/5} t^{2/5}$$

where V_0 is the molar volume, D_v is the diffusion coefficient, R is the gas constant, T is the absolute temperature, ΔV the volume change, r is the particle radius and t is the time. In this case the important variables are the surface energy, diffusion coefficient and the particle size.

During liquid phase sintering in the densification process three steps have been observed – first, formation of a liquid phase and liquid flow to rearrange solid particles (rearrangement process); second, increase of density by solution and reprecipitation of solid (solid reprecipitation process) and third, coalescence of the solid particles to form a skeleton.

When liquid phase has appeared, pores are formed consisting of a negative pressure in each pore, given by the relation [27],

$$P^0 = \frac{-2\gamma_{LV}}{r_p},$$

where γ_{LV} is tension between liquid and vapor phases and r_p is pore radius.

During rearrangement process this pressure, together with stresses acting at particle-particle contact points are overcome with positive pressure from capillary forces.

During rearrangement process the densification corresponds approximately to viscous flow and follows a relation [27],

$$\frac{\Delta L}{L_0} = \frac{1}{3}\frac{\Delta V}{V_0} \approx t^{1+y}$$

where the exponent 1+y is close to unity, as the pore size is decreasing and the driving force is increasing during the process, and at the same time rearrangement increases from the initial pure viscous flow.

Solution reprecipitation, being the most important densification process, has found to be most adequate for cermets and hard metals with mechanism of diffusion in the liquid film between particles controlling the densification [28]:

$$\frac{\Delta L}{L_0} = \frac{1}{3}\frac{\Delta V}{V_0} = \left(\frac{2k_2 \delta D C_0 \gamma_{LV} V_0}{k_1 RT} \right)^{1/2} r^{-1} t^{1/2},$$

where k_2 and k_1 are the constants of the order of unity, δ is the thickness of the boundary layer, D is diffusion coefficient in the liquid phase, C_0 is the equilibrium solubility.

In the case when grain boundary energy of carbide grains is smaller than twice of the solid-liquid interface energy the liquid will not penetrate completely between grains. During this mechanism rapid densification will be stopped and material is transferred through the solid phase.

Aforementioned models of sintering mechanisms are highly simplified compared with real systems. Those mechanisms are acting as parallel processes, involving also secondary phenomena, which include chemical reactions, oxidation, phase transitions, effects of gas trapped in closed pores, gas evolution from solution, effects of non-uniform mixing and so forth [29]. Nevertheless, implications contained in sintering theories are beneficial for designing specific materials and materials technologies.

1.3 Structure – property relations of cermets

In powder metallurgy technological processes of compaction and sintering are complex processes, where many mechanisms can operate concurrently to influence the final properties of the material.

The problem of predicting material properties through functional connection with technology is also complicated [5]. The connecting link between technology and properties is structure of materials, having taken important role in materials science during later stages of its evolution. It is important that structure would not be just a theoretical abstraction but – like technological parameters and properties – is experimentally controlled.

First estimation in material selection of hard metals and cermets for specific wear condition can be done using strength-hardness plot (Figure 1. – [30 - 32,]). It is well known that the common cermets have considerably lower strength characteristics compared to WC based hard metals making them not applicable for many wear applications. Although FeNi steel bonded cermets having somewhat higher strength properties compared to TiC-NiMo cermets, they are noticeably inferior to WC-Co, and especially to WC-FeNi binder alloy hard metals, not exceeding 2500 MPa of transverse rupture strength [23].

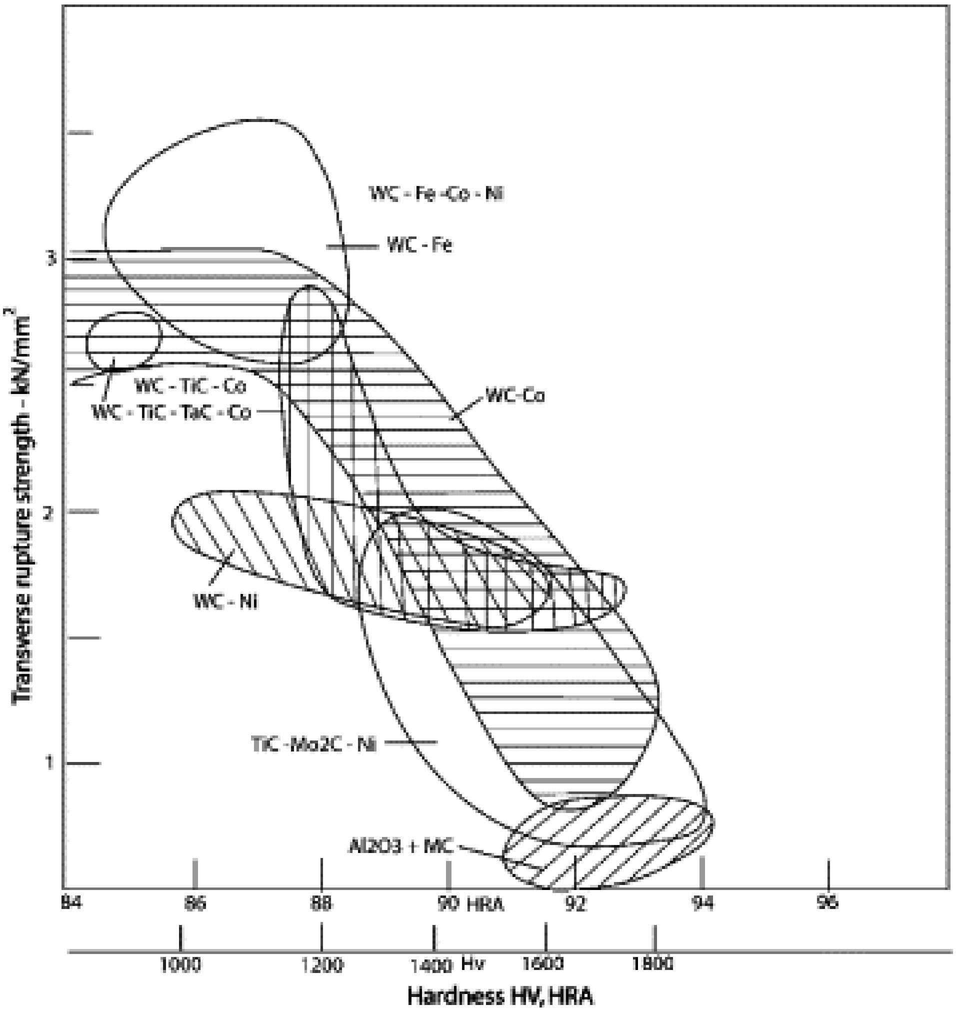


Figure.1. Typical transverse rupture strength and hardness ranges for hard metals and cermets with different compositions. [30-32]

The strength properties of cermets with core-rim structure have found to be dependent on grain size ([15] – Figure 2), binder microcomposition ([33], Figure 3) porosity and contiguity of the carbide particles. Additionally, there are influences from difficult to quantifiable grain size distribution, grain morphology, stress situation in the material, interphase bond strength, etc [10, 11].

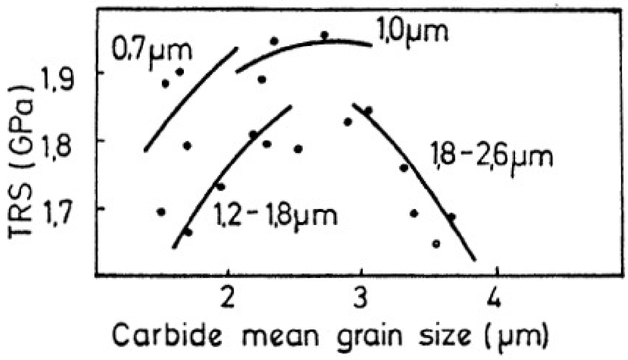


Figure 2. Variation of TRS of TiC-NiMo cermets with mean grain size of carbide. The grain size of TiC core, shown in the figure [15]

As seen from Figure 2 the strength values in the case of coaxial structured alloys are dependent on both, the core and the rim sizes. In general, strength has found to increase with increased thickness of surrounding structure for fine-grain alloys and inversely for large-grained alloys (Figure 2, left and right sides respectively).

Relying on the observed results the desired rim-core size ratio for the fine grained TiC-NiMo cermets is to have minimum core size possible.

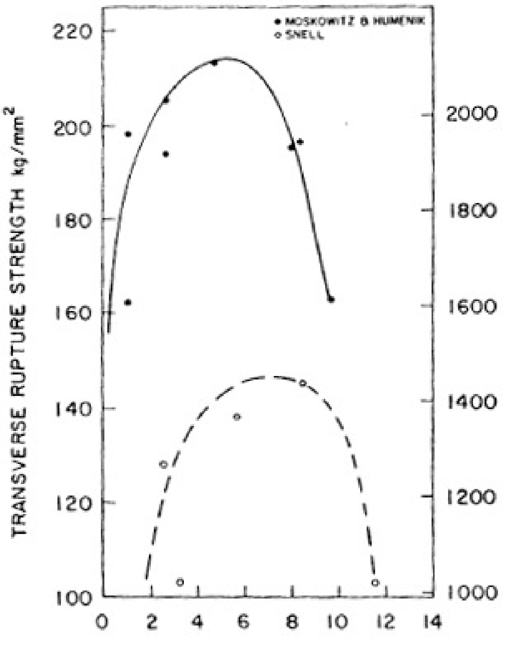


Figure 3. Transverse rupture strength versus binder titanium content of TiC-NiMo alloys [33]

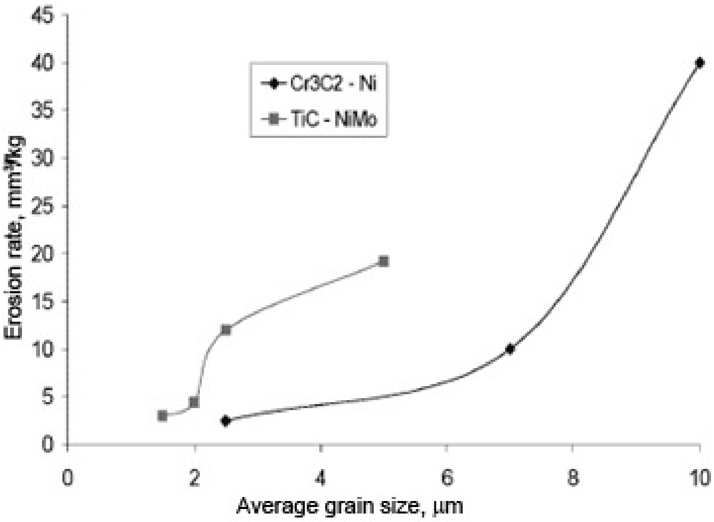


Figure 4. Erosion rate versus average grain size of tungsten-free cermets [17]

For the performance characteristics in metal forming applications it is known the sensitivity of microstructural features to be considerably higher due to the tension stresses prevailing in the adhesive wear situation, whereas in erosive and abrasion shear stresses are most important factor of degradation. Abrasive-erosion wear is much less dependent on microstructural effects of contiguity and grain size morphology, but highly dependent on average grain size (Figure 4 [17]).

Controlling the main structure properties for better performance in wear conditions can be done through evaluating the requirements for cermet production technologies. The principal requirement for pore-free, contiguous material is sufficient interfacial forces and diffusion forces during sintering in order to overcome gas pressure from the pores and fully densify the material.

For microstructure homogeneity of composite the most crucial is appropriate initial powder grain morphology and size distribution. Also wetting of the carbide phase by liquid metal phase must be adequate. Technological parameters during powder production, handling, milling, pressing and sintering are crucial for cermet quality.

Taking into account the economical point of view material composition and technological parameters must be adjusted to produce competitive material.

Grain refinement is another objective in materials science and also in development of ceramic and metal composites materials. The reason can be deduced from Hall-Petch relation that represents the relationship between the grain size, or crystallite size, and the yield stress σ of material by equation:

$$\sigma = \sigma_0 + k\frac{1}{\sqrt{d}},$$

where k is the fitting parameter, σ_o is a materials constant for the starting stress for dislocation movement, d is the grain diameter. Consequently smaller grain size materials behave less grain boundary slip motions and the mechanical properties are higher.

It has been proved that carbide particle size is influencing the abrasive and erosive wear rate [34, 35]. Fine particles provide increased wear resistance at equivalent carbide particle volume fractions as compared with the coarse particles.

1.4 Technologies for cermet production

As stated in previous paragraph, the main issue in liquid state sintering for defect-free material is to overcome the gas pressure trapped inside the material (O_2, CO, Ar, etc.). One possibility is purifying or regulation chemical composition of the raw materials. Also technological parameters can be adjusted and new sintering methods can be developed for this reason.

1.4.1 Oxidation prevention during powder processing and sintering

For titanium carbide cermets one important issue for adequate wetting is influenced by presence of oxygen in powder constituents. Especially for steel binder materials it is important because of the high reactivity of iron powder.

It is known that during milling the steel binder cermet powder mixtures oxidize in a certain content [23]. Oxygen in cermet composition vastly deteriorates the wettability of Fe- group metals on carbide particles, elucidating low contiguity and porosity in the microstructure, or even binder outflow and insufficient shrinkage of the material.

During conventional low-energetic ball milling of steel-binder alloys the oxygen pick-up is increased with the milling time and reduction of the grain size. Already after 40 … 60 hours of milling the oxygen content can be above 2% [23, 36]. As oxidation is dependent on surface area of the powder, powders milled with higher intensity oxidize more readily [37] and in such cases oxidation can take place even during handling in atmospheric environment [23].

Deduction of oxygen contamination during wet milling can be controlled by using proper, non-oxygen containing solvent. Addition of certain percentage of plasticizer during milling [38] can reduce the oxygen pick-up by providing a thin protective film on the surface of the particles [39].

The pre-sintering widely used for cermets is usually conducted in hydrogen [40, 41]. Results presented in [15, 16] refer to the possibility of substituting hydrogen by argon or nitrogen. One-step pre-sintering-sintering in vacuum is also possible with furnaces equipped with vacuum- or controlled atmosphere de-binding module [42].

During sintering part of the oxygen is absorbed from the powder through reaction with free and combined carbon. Sintering atmosphere has found to have its significance on wetting [6]. Vacuum has found to be the most appropriate sintering medium, showing the lowest contact wetting angle compared to hydrogen or helium [43].

1.4.2 Hot consolidation technologies and Sinter/HIP

In engineering applications where high performance of advanced materials is needed full density processing of metal and ceramic powders is becoming dominant. The main hot consolidation technologies today applied in industry for powder consolidation are Hot Pressing (HP), Hot Isostatic Pressing (HIP), Powder Extrusion and Powder Forging [44]. Another technique that has gained commercial significance, especially in the case of hard metal industry is Sinter/HIP (In the literature different nominations as Sinter-HIP, Pressure Assisted Sintering-PAS, Overpressure Sintering, Gas Pressure Sintering, Sinterhipping or High Pressure Sintering can be found).

During Sinter/HIP process a shaped compact is sintered to theoretical density greater than 92% (or up to the state of closed porosity) and isostatic gas pressure in the range of 30 to 150 Bar is applied.

The process of Sinter/HIP, compared to ordinary HIP technology eliminates containerization and separate sintering cycles. The applied pressure during sintering of Sinter/HIP is at order of magnitude less compared to HIP.

Sinter/HIP technology has found its application for the consolidation of hard metals, tool steels, stainless steels, rare earth magnets, titanium alloys of the type Ti-6Al-4V, silicon nitride etc. [44]. For tungsten carbide based cermets the technology has found extensive research interest [25, 45-60] due to the fact that the strength properties can be increased up to 100% and compared to HIP process there are no binder lakes in the microstructure.

Concluding from literature comparing HIP and Sinter/HIP it seems that Sinter/HIP works better in the case of medium grain size and medium binder contents of hard metals. Nevertheless, in the case of low-binder materials the strength increase of Sinter/HIP alloys compared to vacuum sintered materials is remarkable.

General conditions for strength increase of WC-based hard metals would be:

a) low cubic carbide materials;
b) high hardness, low Co mean free path materials;
c) materials which have excessive porosity levels after regular sintering;
d) applications not entailing the product to be heated during use at temperature sufficient to plastic deformation (e.a. CVD coating, heavy grinding) [60].

Titanium carbide and carbo-nitride cermets are much less investigated for Sinter/HIP. General understanding is that Sinter/HIP for this type of materials is not perspective as the strength properties can be enhanced only up to 10-20% [50].

Nevertheless there are results showing improved strength properties for Ti(C,N) cermets with Ni/Co alloy binder by HIP [47,52] or Sinter/HIP technology [61 - 63]. The improvements in Ti(C,N) cermet properties has been explained to be caused by the hindering nickel evaporation during sintering and lower porosity [62].

Low-carbide (volume fraction below 50%) steel-binder cermets (frequently designated as Ferro-TiC) are frequently densified by hot isostatic pressing [62] in order to eliminate the residual porosity. High carbide fraction alloys are less intensively investigated. In order to obtain satisfying porosity level also these types of materials have been sometimes HIP-ed [8, 19, 37].

1.4.3 Fine-grained cermets.

Grain growth during heating has found to depend on initial grain size of materials. According to relationship [64]:

$$d^{g} - d_{0}^{g} = B\exp\left(\frac{-Q}{RT}\right)t,$$

where d and d_o are the final and initial grain sizes, respectively, B is a constant, Q is the activation energy which is usually close to that for diffusion, and g is a constant, the small grain materials have higher tendency for grain coarsening.

Grain coarsening of nanostructured powders is believed to occur during the formation of liquid phase. Mainly the ultra-fine and nanostructured ceramic-metal composites have been densified by solid state sintering in the case of WC- based materials [65]. Recently ultra-fine titanium carbonitride based cermets have been processed also by liquid phase sintering by carefully choosing the initial grain size for the materials [66].

The options for obtaining finer-grained cermets would be optimizing initial powder grain size for sintering, decreasing the liquid phase formation temperature of binder material or introducing grain growth inhibitors.

Another possibility for obtaining ultra-fine structured titanium carbide based cermets with Ni binder alloy has found to be through reactive milling and sintering [67, 68]. These types of alloys are showing fine grain sizes sintering even at high temperatures up to 1510^{o}C [67]. The microstructure is consisting of (Ti,M)C hard grains in Ni binder alloy matrix (M = Mo, W). The properties are promising for fracture toughness. Another advantage of reactive processing is lower cost of technological processes.

Production of steel bonded titanium carbide through reactive processing has also been previously investigated [69-71], showing the possibility to produce nanocrystalline or ultra-fine grained bulk materials by combining high-energy milling and HIP [70].

Reactive sintering combined with high-energy milling has been performed with cermets based on chromium carbide resulting in fine-grained, homogeneous microstructures [72]. This process is believed to be preferential compared to reactive milling process for materials prone to oxidation, as the formation of thin oxide layer around chromium carbide particle is prevented before sintering increasing wettability of carbide particles.

1.5 Aims of this work. Setting of study objectives.

Two types of TiC base cermets are investigated – TiC-FeNi binder cermets for sheet metal blanking and TiC-NiMo cermets for erosion wear resistance applications.

The aim of the work is to develop technological parameters for vacuum sintering and sinter/HIP sintering for these materials in conformity with pre-sintering and powder preparation techniques (ball milling, high-energy milling) for the best performance characteristics.

In conformity with pre-sintering technologies oxidation behaviour and the ability of gas pressure for oxidation defect minimization will be studied.

In order to explain the effect of technological parameters on change in properties structure evolution and mechanisms of microstructure formation will be studied.

For studying initial powder grain size effect and possibilities for densified materials grain size minimization high-energy milling at different periods will be used and concept of high-energy milling – reactive sintering will be studied.

The objective is to propose materials and general recommendations for technological parameters of milling, pre-sintering, and sintering for the best performance characteristics in sheet metal stamping (TiC-FeNi steel cermets) and abrasive erosion wear resistance applications (TiC-NiMo cermets)

2 Experimental procedures. Materials, test methods

2.1 Materials tested

All materials were produced in the powder metallurgy laboratory of Tallinn University of Technology. The TiC-NiMo cermets were chosen for mapping the sinter/HIP sintered materials for strength and wear resistance in abrasive-erosive environment.

TiC cermets with a steel binder were chosen in order to comply with general requirements for using cermets as metal forming tool materials [25] - hardness HRA ≥ 87 and transverse rupture strength TRS ≥ 1.8 GPa.

The composition and main characteristics of conventional TiC-FeNi steel and TiC-NiMo cermets are provided in Table 1 and Table 2 respectively.

Table 1. Composition and the main characteristics of TiC-FeNi cermets

Grade	Powder composition, wt%	Binder structure	Hardness, HRA	Density ρ, g/cm^3	Transverse rupture strength TRS, MPa
T60/8	TiC-40(Fe-8Ni-1.5Si)	martensite-bainite	88.7	5.85	2300
T70/14	TiC-30(Fe-14Ni-1.5Si)	austenite-martensite	89.0	5.65	2100
T75/14	TiC-25(Fe-14Ni-1.5Si)	austenite-martensite	90.2	5.55	1800
T80/14	TiC-20(Fe-14Ni-1.5Si)	austenite-martensite	91.3	5.45	1400

Table 2. Composition and the main characteristics of TiC-NiMo cermets

Grade	Composition, wt. %	Hardness, HV	Density ρ, g/cm^3	Transverse rupture strength TRS, MPa
TN20	TiC-20(Ni-20Mo)	1392	5.47	1010
TN20A	TiC-20(Ni-33Mo)	1515	5.50	990
TN20B	TiC-20(Ni-50Mo)	1656	5.54	730
TN30	TiC-30(Ni-20Mo)	1300	5.74	1210
TN30A	TiC-30(Ni-33Mo)	1415	5.80	1180
TN40	TiC-40(Ni-20Mo)	1169	6.04	1460
TN40A	TiC-40(Ni-33Mo)	1239	6.02	1350
TN40B	TiC-40(Ni-50Mo)	1337	6.03	890
TN50	TiC-50(Ni-20Mo)	990	6.40	2180
TN50A	TiC-50(Ni-33Mo)	1150	6.42	1600
TN50B	TiC-50(Ni-20Mo)	1340	6.34	1120
TN60	TiC-60(Ni-20Mo)	750	6.58	2500
TN60A	TiC-40(Ni-33Mo)	853	6.66	2270
TN60B	TiC-40(Ni-50Mo)	1216	6.78	1300

In order to find the relationships between gas pressure applied during sintering and initial grain size grade composition TN20A and high-energy milling was chosen. Reactive sinter/HIP experiments with initial Ti-C-W-Ni powders (composition same as for TN20A with molybdenum substituted for tungsten) and Ti-C-Fe-Ni-Si powders (composition same as T70/14) were performed.

2.2 Technological parameters

2.2.1 Traditional cermet materials

Common powder technology was used for TiC-FeNi steel and TiC- NiMo cermets accompanied with Sinter/HIP sintering (Figure 5) for mapping the performance properties (strength, hardness, wear resistance) for overpressure sintered materials.

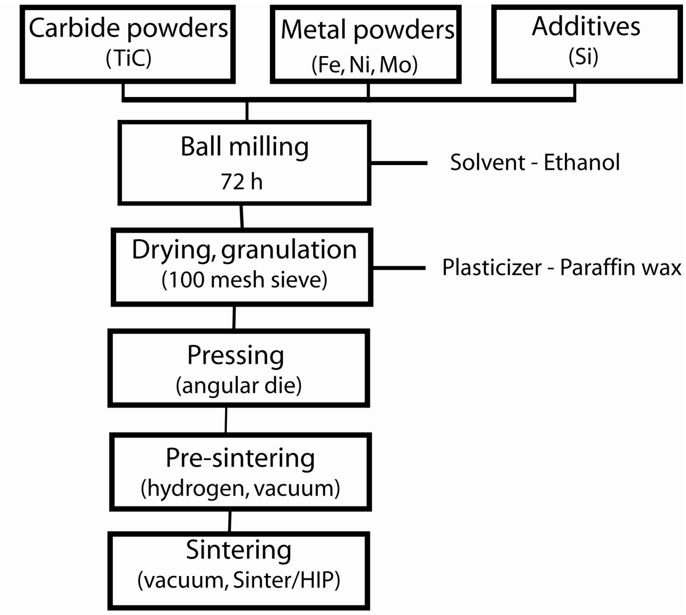


Figure 5. Diagram for sintering technology forregular cermet materials

The milling was done in 1 dm^3 ball mill with WC-Co balls and vial linings. The milling period was set to 72 hours for TiC- Ni alloy materials and 93 hours for steel-bonded cermets. The powders were dried in atmospheric environment and granulated by sieving through 100 mesh sieve. Angular two-directional die pressing at 800 kg/cm^2 was used. Specimens for transverse rupture strength and adhesive wear testing were compacted with 6.2x40 mm^2 die and for abrasive- and abrasive-erosion wear property testing in 25x15 mm^2 die.

Sinter/HIP sintering procedures were done in semi-industrial FPW-300/400-2-1600-100KS/SP Sinter/HIP furnace. Vacuum sintering experiments were conducted utilizing Super VII Vacuum System.

An example schematic for pre-sintering and Sinter/HIP sintering technologies for traditional materials is shown on Figure 6.

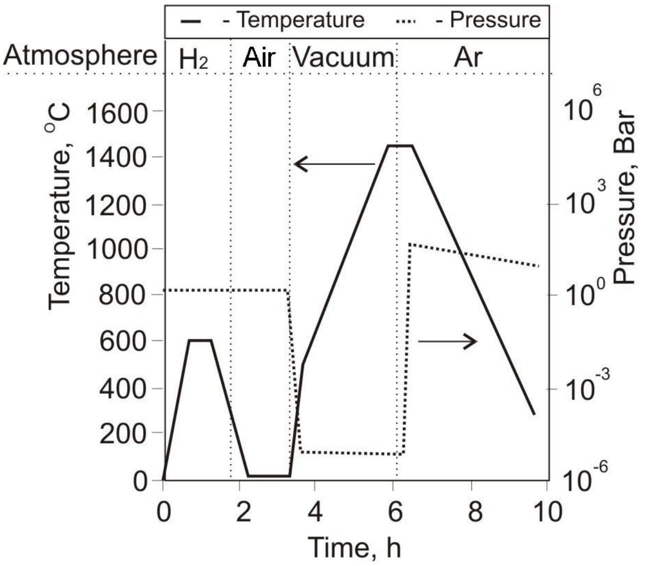


Figure 6 Schematic of two step Sinter/HIP sintering cycle with presintering in hydrogen

For steel binder materials different pre-sintering technologies were investigated. For these types of materials it is known the oxygen pick-up of iron during technological steps (powder handling, milling, sintering) being crucial for final cermet properties. In the present work hydrogen- (low and high dew point), vacuum pre-sintering and one-step pre-sintering – sintering with sintering were investigated for different grades of steel-bonded materials. Additionally sintering technologies with higher and lower vacuum ($5x10^{-2}$ and $2x10^{-1}$ mBar respectively) and pressure assisted technologies for mitigation of oxidation defects were investigated.

The overview of sintering techniques for steel-bonded cermets (perspective for metal forming) can be seen in Table 3.

Table 3. Technological parameters of studied presintering and sintering technologies

Pos	Sintering mode	Presintering		Designation	Finish sintering	
		Atmosphere	Characteristic		Vac, mbar	Ar, Bar
1	One step	–	–	1-1	$2.5\cdot10^{-1}$	-
2	One step	–	–	1-2	$5\cdot10^{-2}$	-
3	Two step	hydrogen	DP* -35°C	2-1	$2.5\cdot10^{-1}$	-
4	Two step	hydrogen	DP -35°C	2-2	$5\cdot10^{-2}$	-
5	Two step	hydrogen	DP -50°C	3-1	$2.5\cdot10^{-1}$	-
6	Two step	hydrogen	DP -50°C	3-2	$5\cdot10^{-2}$	-
7	Two step	vacuum	intermediate	4-1	$2.5\cdot10^{-1}$	-
8	Two step	vacuum	storing in air, 6h	4-2	$5\cdot10^{-2}$	-
10	One-step	-	-	1-1C**	$2\cdot10^{-1}$	60
11	One-step	-	-	1-2C	$7\cdot10^{-2}$	30, 60, 90
12	Two-step	hydrogen	DP – 35°C	2-1C	$2\cdot10^{-1}$	60

*DP – dew point of hydrogen used

**C – compression sintering (Sinter/HIP)

Pre-sintering of TiC-NiMo cermet materials was done in hydrogen environment (DP > 50°C) at 600°C, holding period 30 minutes.

Sinter/HIP for cermets with FeNi-steel and NiMo binder materials was investigated in order to find the sinter/HIP effect on the strength and wear behaviour of these alloys. The parameters of finish-sintering varied in the range of temperatures 1360…1500 °C and in argon-gas compression 20…90 Bar respectively.

As a post-sintering operation grinding (with water-cooled diamond wheel grinder) was performed.

2.2.2 Technologies of grain size manipulation for better performance

Two options for studying initial grain size effect on sintering and obtaining fine-grained cermets were chosen – high-energy milling-sintering (Figure 7a) and high-energy milling of initial powder mixtures-reactive sintering (Figure 7b).

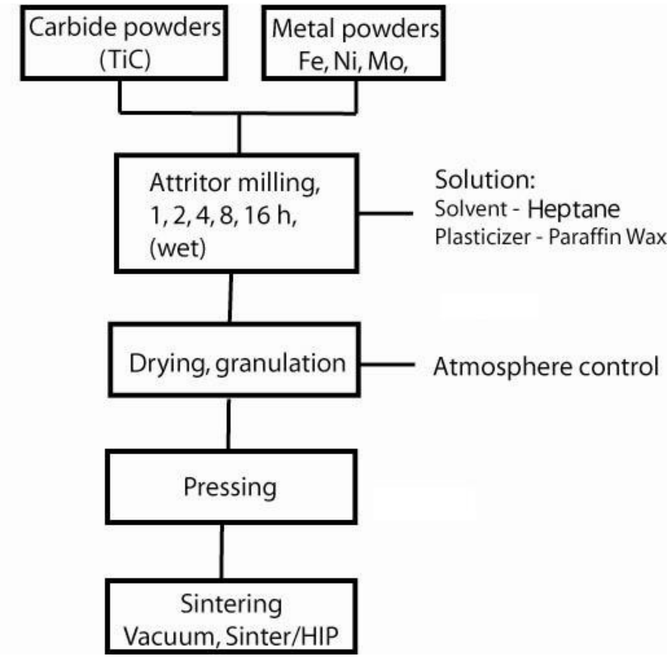


Figure 7A. Diagram of cermet production using high-energy milled powders

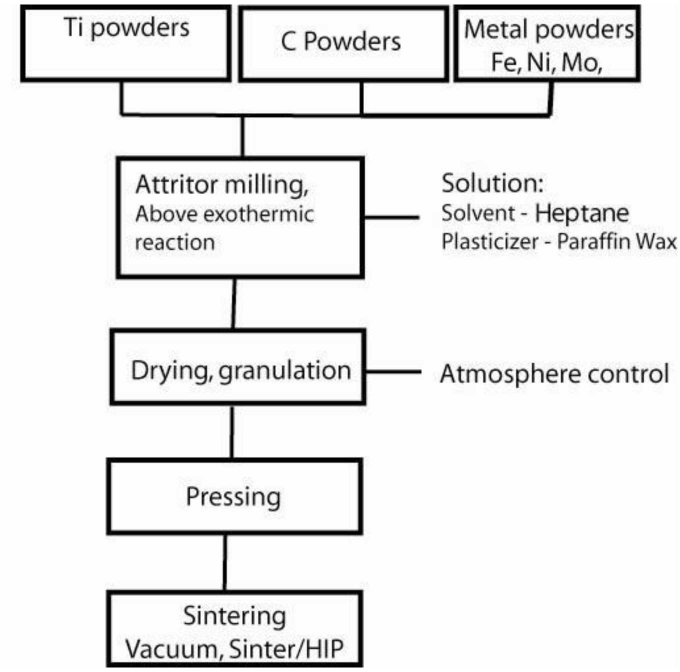


Figure 7B. Diagram of cermet production using high-energy milling and reactive sintering

For both options high-energy milling was performed in laboratory scale attritor with hard metal vial and rotating arms, with rotating speed of 156 rpm. In order to minimize contamination for TiC-NiMo the milling balls had similar material composition as the milled powders (TN40A balls). From technological reasons steel-bonded cermets were milled with 100Cr6 balls. Diameter of 5-6 mm of the balls was used.

Grade TN20A was selected for high-energy milling study and grade compositions comparable with TN20A and T70/14 for reactive sinter/HIP study.

In order to minimize oxidation during milling the vial of the attritor was water cooled and certain amount of plasticizer (paraffin wax) was added to the heptane solution – 1% of powder mass in initial solution plus 0,15wt% after every hour of milling.

For high-energy milled powders (Figure 7a) different milling periods - from 1 to 16h were chosen. Milling of initial powder mixtures (Figure 7b) was adjusted to the time period of no reaction of constituents, but up to pre-reactive state of nanograined powder with some of the carbon transformed amorphous.

After milling the powders were carefully dried up to extent of dough-like mass, sieved and additional plasticizer (couchouc) added, in order to subject a protective thin coating on the surface of granules. Further granulation and die pressing were accomplished as is mentioned previously for traditional materials. Pre-sintering was done in vacuum at temperature of 1300…1360^{o}C or in some cases the one-cycle sintering was used. Sintering (vacuum and Sinter/HIP) was done at temperatures ranging from 1360^{o}C to 1480^{o}C, with vacuum above 10^{-1} mBar and argon gas pressure ranging from 30 to 90 Bar.

2.3 Wear and property testing methods

The measured performance properties of materials were hardness (Vickers hardness, in accordance with the standard EN-ISO-6507) and transverse rupture strength (ISO 3327, specimen B). As an additional characteristic, for selected steel-bonded cermets the compressive strength was determined in an uni-axial compressive test using specimen with height 18 and diameter 10 mm [73].

For attritor milled materials shrinkage behaviour was expressed first by dilatometric behavior by measuring the linear shrinkage of sintered materials in the range of 1000 to 1500^{o}C. Additionally the specimens with closed porosity were measured for Archimedes density (ISO 3369:1975). For both, the traditional and fine-grained materials on selected specimens' microstructure analysis was complemented using scanning electron microscope JEOL ISM840A. As quantitative output the SEM and optical microscopy images were analysed by Büehler Omnimet Image analysis software. On selected specimens following parameters were measured: grain size (spherical mode), porosity (percentage), microstructure contiguity and binder fraction (volume percentage). Additionally microcomposition of binders and grains of different alloys was performed with high-resolution LEO Supra 35 SEM, equipped with the Röntec EDX XFlash 3001 detector.

High energy milled cermet powders and resultant sintered materials were analyzed by means of X-ray diffraction (XRD) methods with CuKa radiation (Bruker AXS D5005).

The wear behaviour of alloys was studied in adhesive, abrasive and erosion wear conditions. Abrasive wear tests were performed using the rubber-rimmed rotary wheel machine (modified ASTM G-65-94 method) [74] as follows: abrasive – quartz sand (amount 3 kg, particle size 0.1 – 0.2 mm), velocity of wheel 0.24 m/s, wear distance 145 m, load 3N. The wear was estimated as the volume loss in mm^3.

Erosion tests were conducted by means of the centrifugal accelerator [14] as follows: abrasive – quartz sand (particle size 0.1 – 0.2 mm), jet velocity of 80 $m \cdot s^{-1}$, attack angle 30°. The wear was estimated as the specific volumetric wear in mm^3/kg as $K = \Delta G/Ga \cdot \rho$ (ΔG – mass wear of specimen, G_a – mass of abrasive per specimen, ρ - density of alloy).

The wear behaviour of traditional TiC-FeNi steel alloys (perspective for metal forming) and selected TiC-NiMo alloys for comparison was studied in adhesive wear conditions. The adhesive wear is featured as a surface failure of very high structure sensitivity [75]. It dominates in the surface failure of cemented carbides used as tools for blanking (metal forming) operations [25]. The adhesive wear conditions were realized by turning mild steel (HV_{30}<170) at low speed (v < 18 m/min). The wear resistance was determined as the length of cutting path (distance) L_1, when the wear track (height h) at the tool (specimen) nose achieves the critical value of h=1 mm (see Figure 8). Fair correlation between the adhesive wear resistance characteristic L_1 of cemented carbides and their wear in blanking (blanking performance Δ D/N) was demonstrated in [25].

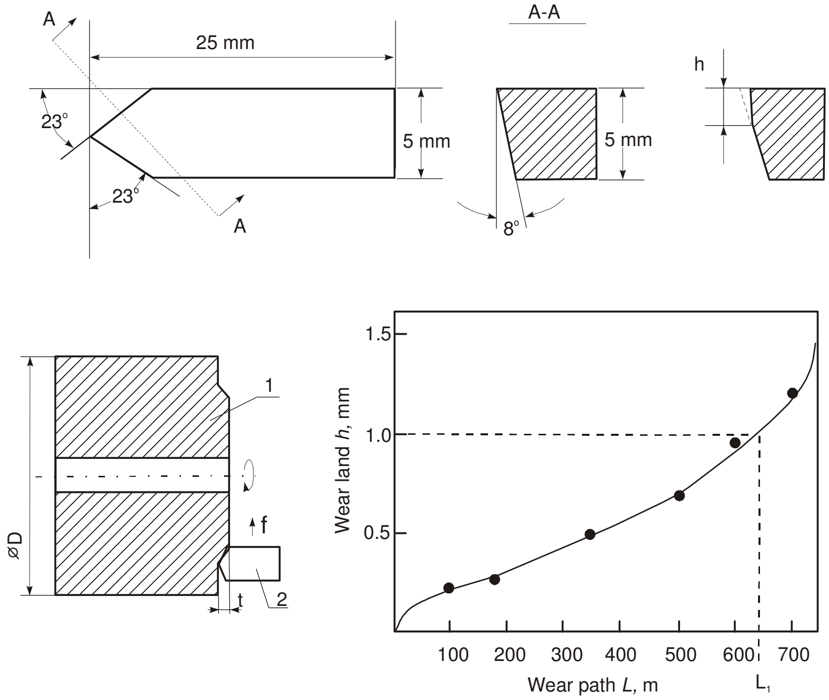


Figure 8 Schematic of adhesive wear test. 1-medium carbide steel; 2 – specimen. Cutting distance after notch wear of 1 mm is measured

A minimum of three tests for adhesive and erosion and four for abrasive wear per composite were performed to ensure confidence interval of 10% with the probability factor of 95%.

3 Development of technologies for TiC-based cermets

For steel binder alloys oxidation prevention during pre-sintering and sintering was investigated. Sinter/HIP technology was investigated for both types of cermets (Fe and Ni-alloy bonded) in order to clarify the pressure effects on pre-sintering parameters (alleviation of oxidation damage), binder content, and in the case of TiC-NiMo cermets on the amount of molybdenum in the composition.

Possibilities of obtaining fine-grained cermets, studying nano-sized powder sintering and property relationship related to microstructure development by high-energy milling and sintering were studied for TiC-NiMo cermets of grade TN20A

Another attempt for grain refinement for grades T70/14 and TW20A was made by concept of high-energy milling of initial powder mixtures and reactive sintering.

3.1 Effect of pre-sintering techniques on TiC-based cermets.

The results in paragraph are covered in paper I (List of publications).

3.1.1 Wear behaviour and mechanical properties.

The results of experiments – adhesive wear kinetics (wear curves) of three TiC-cermets of approximately equal carbide volume fraction and hardness, differing in their binder composition and structure and sintered by two different techniques are shown in Figure 9.

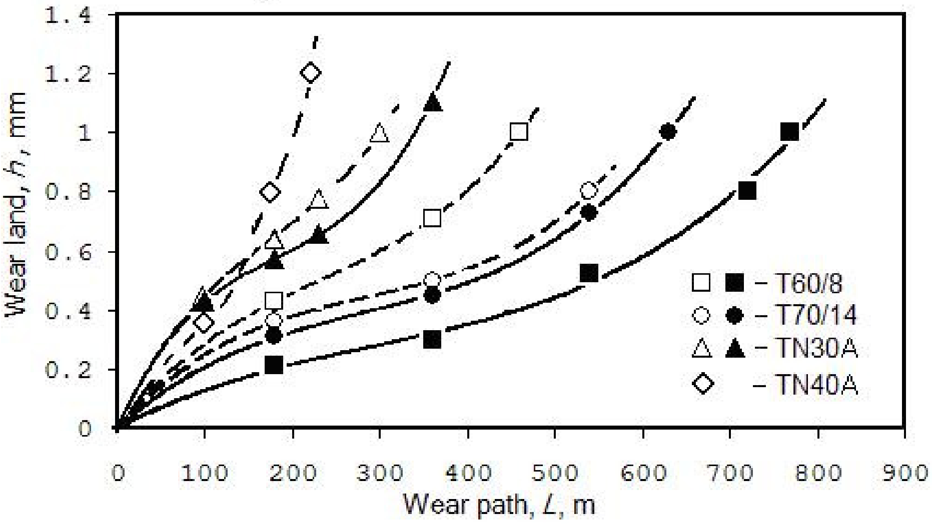


Figure 9. Wear kinetics of TiC cermets, sintered by one step mode in vacuum p<5.10^{-2} *mBar (solid marks) and by two step techniques with pre-sintering in* H_2 *at dew point -50*^{o}*C (open marks)*

It can be seen that in terms of wear performance, TiC-cermets with Ni-steel binder T60/8 and 70/14 are clearly superior over the ordinary cermet with Ni-alloy binder TN30A.

The global presentation plotted in Figure 10 refers to an obvious influence of sintering techniques onto wear performance of TiC-cermets. The influence appears to depend on the TiC content, binder composition and of cermet structure. It is strong for cermets with low TiC content and martensitic-bainitic binder structure (grade T60/8) and uncertain for those with higher TiC content and austenitic steel binder (T70/14) or Ni-alloy ones (TN30).

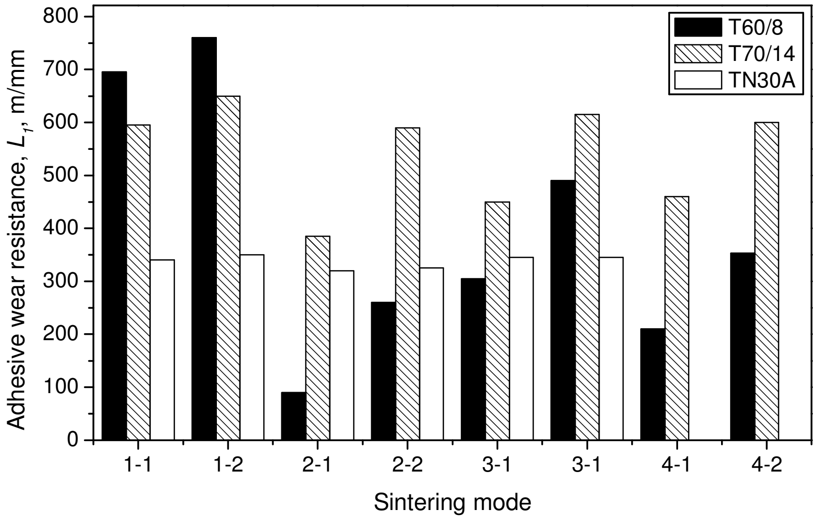


Figure 10. Adhesive wear resistances of TiC based cermets as a function of sintering technique. Designations x-y, where x is for describing pre-sintering technique: 1-one step vacuum; 2- two step H_2, DP=-35°C; 3- two step H_2, DP=-50°C; 4-, two-step vacuum, intermediate storing in atmospheric conditions and y is for describing vacuum level (mBar) of finish sintering: 1-2x10^{-1}; 2- 5x10^{-2}(See Table 4)

In respect to adhesive wear performance, cermets sintered by one-step techniques in vacuum (Figure 10, mode 1) demonstrated an obvious superiority over alloys sintered by two-step techniques with pre-sintering in hydrogen or vacuum (Figure 10, modes 2-1, 2-2, 2-3). Hydrogen of high purity (low dew point <-50°C) used during pre-sintering and high vacuum (pressure $p \leq 5 \cdot 10^{-2}$ mBar) during finish sintering, improves the wear performance of TiC-steel cermets substantially. Decrease in the vacuum level during 1-step sintering up to $3 \cdot 10^{-1}$ mBar does not induce a remarkable reduction of the adhesive wear resistance of TiC-based cermets The wear performance of TiC-cermet with martesitic-bainitic binder structure T60/8 sintered by optimum techniques demonstrated a clear superiority over cermets with austenitic binder (grade T70/14).

The influence of sintering techniques on the strength of TiC-based cermets is demonstrated in Figure 11. In general, the relationship "strength – sintering mode (techniques)" is similar to that of "adhesive wear resistance – sintering techniques" (Figure 10). The influence is remarkable for cermets with martensitic-bainitic steel binder (T60/8) and uncertain for those with austenitic (T70/14) or Ni-alloy (TN30A) ones.

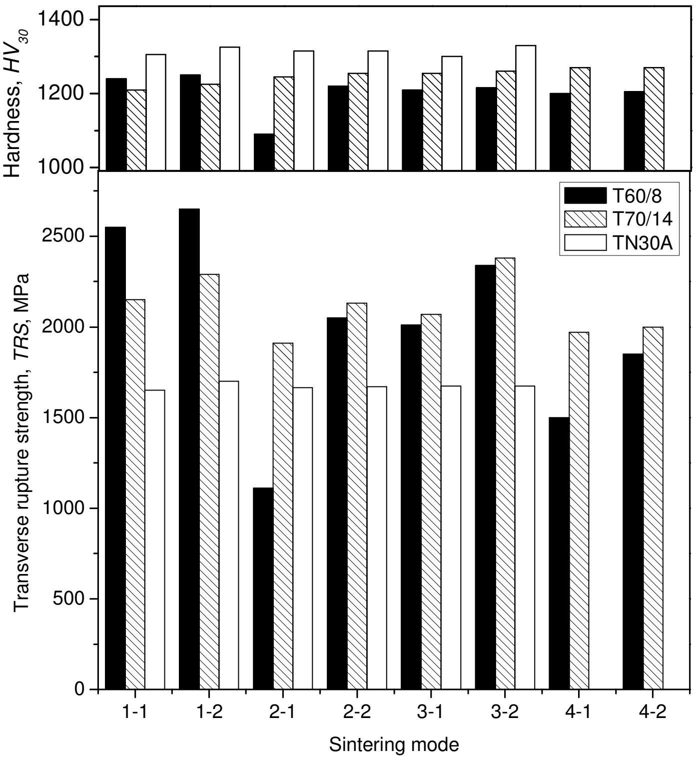


Figure 11. Mechanical properties of TiC cermets as a function of sintering mode (for designations, see Figure 10 captions)

As a result of one-step sintering use instead of two-step one, hydrogen of high purity (low dew point) during pre-sintering and high vacuum during finish sintering improve TiC-cermets with steel binder strength properties.

It should be noted that the influence of sintering techniques on the strength of TiC-cermets is not as sharp as that on its adhesive wear resistance: the wear resistance alters, depending on the sintering technique up to 10 times, while transverse rupture strength TRS does up to 2,5 times.

This fact is attributed to the higher structure sensitivity of cermets adhesive wear in relation to their strength [75].

In contrast to transverse rupture strength, the hardness HV_{30} of TiC-cermets demonstrates a comparatively low sensitivity to changes in sintering technology.

3.1.2 Discussion

The results received of pre-sintering effect refer to an obvious influence of sintering techniques on the microstructure of TiC-based cermets with martensitic Ni-steel binder.

Cermets sintered by one-step-techniques in vacuum that have a considerably higher performance characteristics (strength, wear resistance) in relation to those sintered by the two-step technology are featured by a microstructure of high homogeneity. The high homogeneity is expressed by low porosity, higher uniformity in binder distribution, low contiguity of carbide selection (Fig 12, C).

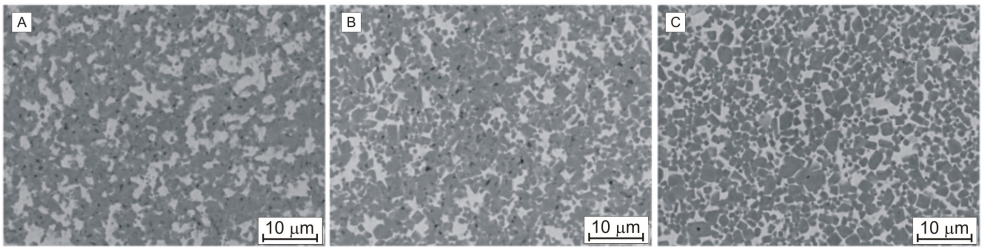


Figure 12. Microstructure of cermet T60/8 sintered by different techniques (A: two step sintering with pre-sintering in H2, dew point -35°C; B: two step vacuum sintering at $2{,}5*10^{-1}$ mBar; C: one step sintering in vacuum at $p=5x10^{-2}$ mBar)

The degradation of the microstructure of a cermet during sintering (Figure 12, A and B) may be related to the oxidation-decarburization processes taking place during pre-sintering and storing in air-atmosphere after pre-sintering [76 - 78].

Oxides in cemented carbide structure act as contaminants, inducing firstly enhanced residual porosity and secondly, deterioration in wettability (between metallic binder and carbide phase) [78 - 80]. The latter results in an increase of the contiguity of carbide skeleton and fail in the uniformity of binder distribution – origin of “lakes” in the structure [6, 79, 80].

The increase in porosity and contiguity induces the degradation of the resistance of carbide composites to brittle fracture – to a failure initiated by tension stresses (decrease in transverse rupture strength R_{TZ} and fracture toughness K_{1C} [81 - 83]).

While transverse rupture strength of a cermet is affected by porosity and contiguity, the adhesive wear resistance is, to a great extent, influenced by the binder distribution in the structure too.

As stated, roots of the adhesive failure of the surface of cemented carbides are in the binder phase, and takes place by extraction (by prevalence of tension stresses). It is preceded by the processes of interaction – local plastic strain of asperities, origin of juvenile surfaces and adhesive bonds between wearing-contacting surfaces [38, 53]. Therefore the adhesive wear resistance of cemented carbides depends on the properties of the binder, its amount and distribution in the structure. Uneven distribution of the binder – origin of binder “lakes” in the structure results in a fail of cermets resistance to local failure (to wear).

Thus, the adhesive wear resistance of cemented carbides is influenced by sintering techniques more strongly than transverse rupture strength.

The results presented in Figure 13 refer to the existence of a fair correlation between the adhesive wear resistance of the alloys investigated and their transverse rupture strength. It confirms the relevant role of tension stresses and similarity in both failure processes – in bending fracture and in adhesive surface failure [53].

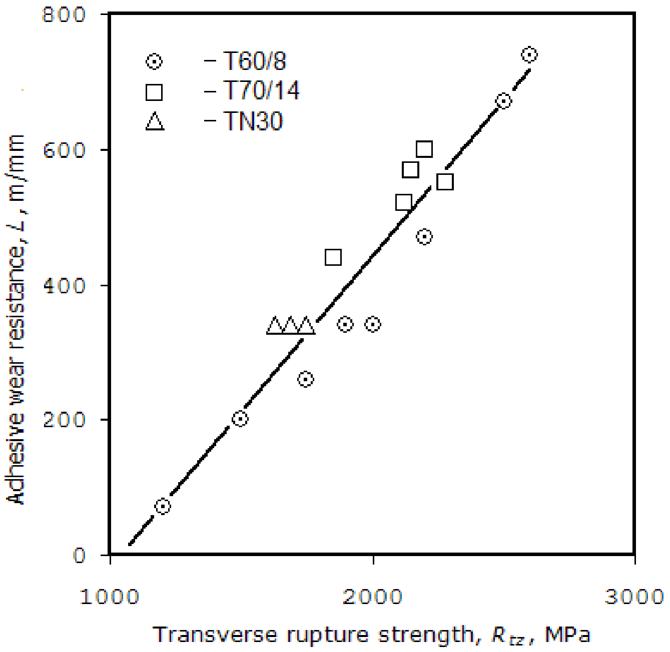


Figure 13. Relationship between transverse rupture strength and adhesive wear resistance of TiC cermets sintered by different techniques

The increase in the purity of hydrogen (decrease in its dew point) results in hindrance of oxidation of cermets during pre-sintering, while application of higher vacuum during finish sintering induces dissociation of oxides and their removal [6, 77, 80]. Both procedures result in the improvement of the microstructure and performance characteristics of the TiC-cermet.

TiC-based cermets with austenitic steel and especially with Ni-alloy binder (grades T70/14 and TN30 respectively) are less inclined to oxidation during sintering [23]. Therefore these alloys demonstrate low dependence of their structure and properties on sintering techniques (Figures 10, 11, 14). It may be related not only to binder composition and structure but also to higher carbide content in cermet grades T70/14 and TN30.

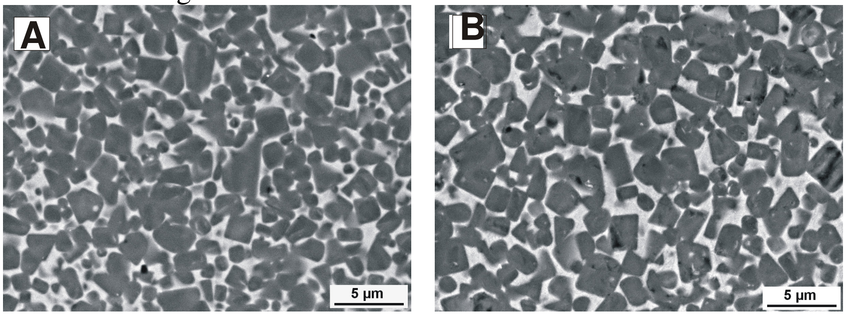


Figure 14 Microstructure of cermet TN30A (A: one step sintering, B: two step sintering)

Although the TiC-cermets with austenitic steel binder (and Ni-alloy one) are featured by a higher adaptability to manufacture (low sensitivity to sintering conditions), their performance characteristics − strength and wear resistance − achievable, are significantly lower in relation to those of cermets with martensitic-bainitic steel binder sintered by an optimum technology (at equal hardness level and carbide fraction).

3.1.3 Conclusions

1. The performance characteristics (in adhesive wear and cyclic loading conditions) of TiC-based cermets with Ni-steel binder exceed those of ordinary TiC-cermets with Ni-alloy binder (at equal hardness level and carbide fraction) substantially.
2. The influence of sintering techniques (sintering atmosphere, sintering mode) on the performance of TiC-cermets depends on their composition and binder structure. It is considerable for cermet with martensitic-bainitic steel binder and negligible for those with Ni-alloy (Ni-Mo) ones.
3. In respect to performance characteristics TiC-cermets with martensitic-bainitic steel binder sintered by optimum technique (one-step vacuum sintering at p $\leq 3\cdot 10^{-1}$ mBar) have a substantial advantage over those with austenitic ones.
4. The improved performance of TiC-cermets with steel binder (sintered by optimum techniques) is related to the high homogeneity of their microstructure.
5. The fair correlation between adhesive wear resistance of cermets and their transverse rupture strength revealed refers to the existence of similarity between both failure processes (bending fracture and adhesive surface failure)

3.2 Sinter/HIP of conventional TiC cermets in conformity with pre-sintering technologies.

TiC-based cermets prospective for metal forming, complying with the general requirements were chosen. Additionally grades T75/14 and T80/14 were added in order to comply with requirements by strength increase through using Sinter/HIP technology. The structural and mechanical characteristics of TiC-cermets investigated are presented in Table 1.

The alloys were sintered by two techniques: one step vacuum sintering (conventional alloys, designated as 1-1 and 1-2 in Table 3) and vacuum sintering combined with argon-gas isostatic compression at sintering temperature (designated as 1-1C in Table 3).

Correlation of temperature and applied argon pressure for property enhancement for selected cermet grades was studied.

The results in paragraph are covered in papers II, III and IV (List of publications).

3.2.1 Strength properties.

Figure 4. demonstrates the influence of the compression sintering on strength of TiC-based cermets sintered at low vacuum levels combined with hydrogen pre-sintering (designation 2-1 and 1-1, in the case of grade T60/8 from Table 3). The results were compared with the ones obtained for high-vacuum sintered materials (designation 1-2 and 2-2)

In general, the influence of sintering atmosphere on strength is remarkable for cermets with lower TiC content martensitic-bainitic steel binder (grade T60/8) and uncertain for those with higher TiC content and austenitic binder (T80/14) and bonded with Ni-alloy (TN40) ones.

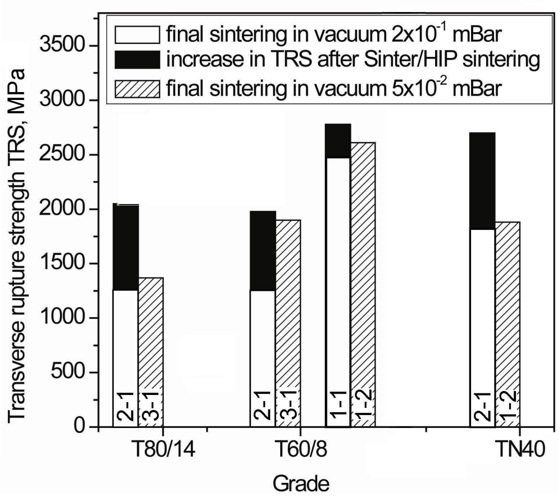


Figure 15. Transverse rupture strength of TiC-cermets vs. sintering mode. 1-2: one step sintering in vacuum; 2-1: two step sintering with pre-sintering in H_2 at dew point -35^oC; 3-1: two step sintering with pre-sintering at dew point -50^oC; 2-3: two step vacuum sintering. (See Table 4)

As a result of one-step sintering instead of two-step one, hydrogen of high purity (low dew point) during pre-sintering and high vacuum during finish sintering TiC-cermets with steel binder strength properties are improved.

Compression during finish sintering (sinter/HIP) results in an additional increase in TRS of TiC-based cermets (Figure 15).

Transverse rupture strength versus carbide fraction for one-step vacuum sintered alloys sintered at high vacuum of 5x10^{-2} mBar (designation 1-2) were investigated. Sinter/HIP sintering was done at vacuum level below 10^{-1} mBar by intermediate holding at 500, 700, 900 and 1150°C for 30 minutes. The results presented in Figure 16 refer to a substantial positive effect of gas compression during sintering on strength of TiC-based cermets with Ni-steel binder. The improvement of transverse rupture strength ranges up to 40% for grades with higher carbide fraction.

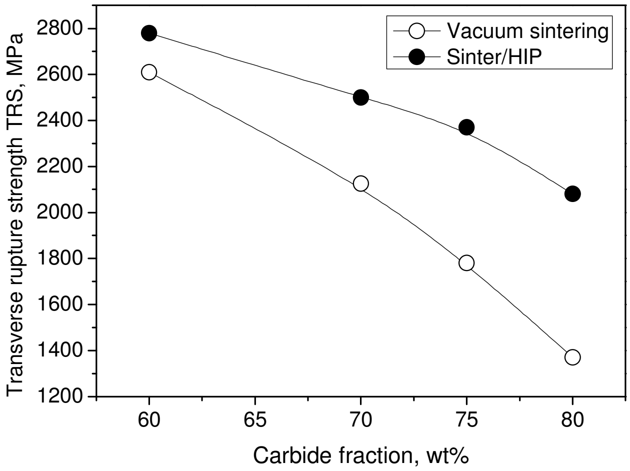


Figure 16 Transverse rupture strength as a function of carbide fraction in TiC based FeNiSi bonded cermets sintered by vacuum (1) and Sinter/HIP(2) sintering

The positive effect of sinter/HIP onto TiC-cermet performance in compressive loading conditions is considerably lower as that in bending (Figure 17). Improvement in strength does not exceed 8% (against 40% in bending).

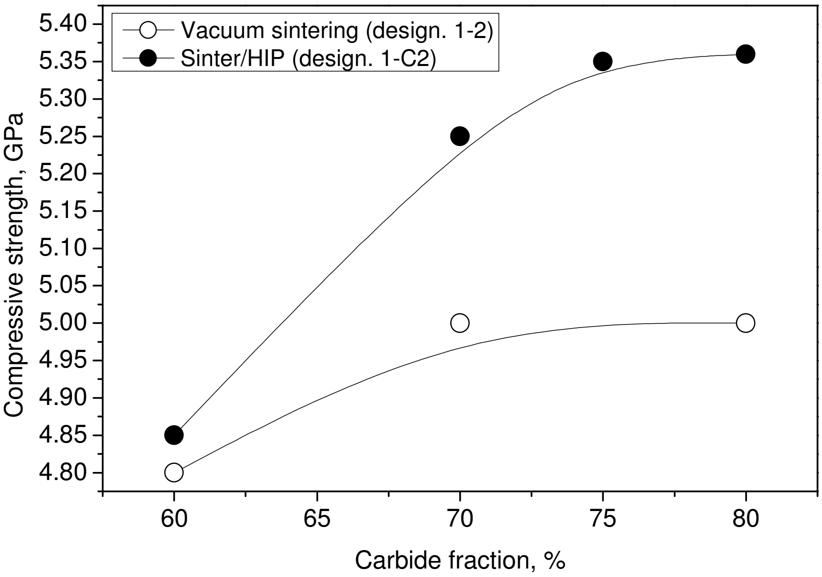


Figure17 Compressive strength as a function of carbide fraction in TiC-based Ni-steel bonded cermets

Temperature and pressure dependence on strength properties presented in Figures. 18 and 19 suggest also to an obvious influence of sintering techniques on the properties of TiC-cermets. The transverse rupture strength alters up to 25% depending on sintering temperature, gas compression and pre-sintering techniques

The relationships “strength-sintering temperature” refers to the existence of a slight maximum (at 1430 °C).

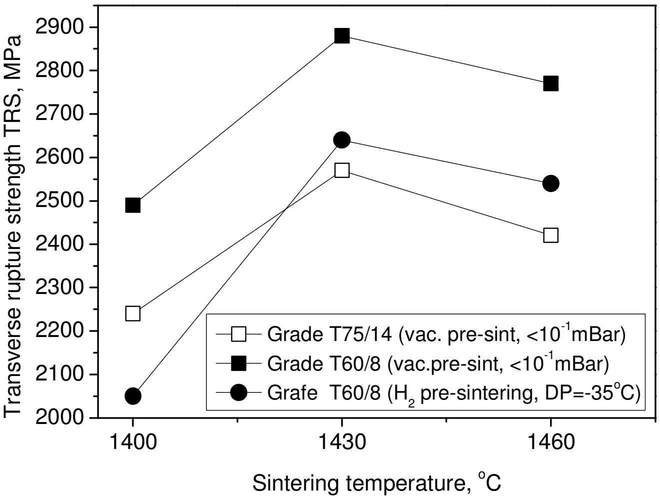


Figure 18. Effect of sintering temperature on transverse rupture strength of composites (compression sintered by p= 60 Bar)

The presence of a maximum is less obvious for the relationship "strength-isostatic gas pressure" in Figure 19, although remarkable increase in strength with increasing pressure up to 60 Bar takes place.

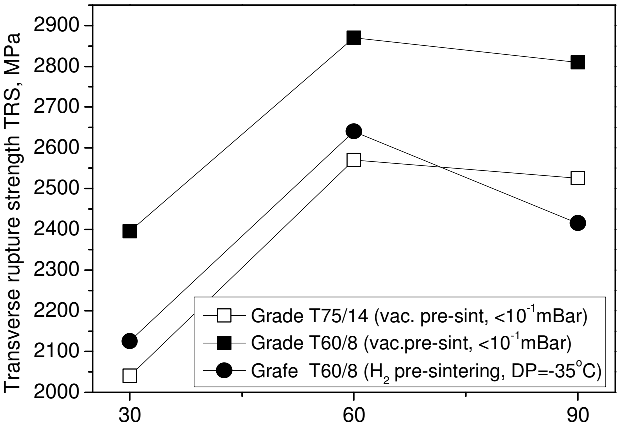


Figure 19. Effect of gas compression on transverse rupture strength of TiC-FeNi steel composites (sintering temperature T = 1430 °C)

Results have confirmed that presintering techniques are relevant to composites with lower TiC content and martensitic steel binder grade T60/8, more inclined to oxidation during production. This alloy sintered by one-step techniques (pre-sintering in vacuum during compression finish sintering) demonstrated a considerable superiority over alloy sintered by the two-step techniques (pre-sintering in hydrogen) – at all ordinary sintering parameters.

It is important to emphasize that the increase in transverse rupture strength (featuring resistance of a material to brittle failure) is accompanied by a remarkable decrease in the scatter of strength (Figure 20). It is obvious that an increase in strength and its stability (decrease in scatter) result in the improvement of alloy performance and reliability in different loading and wear conditions.

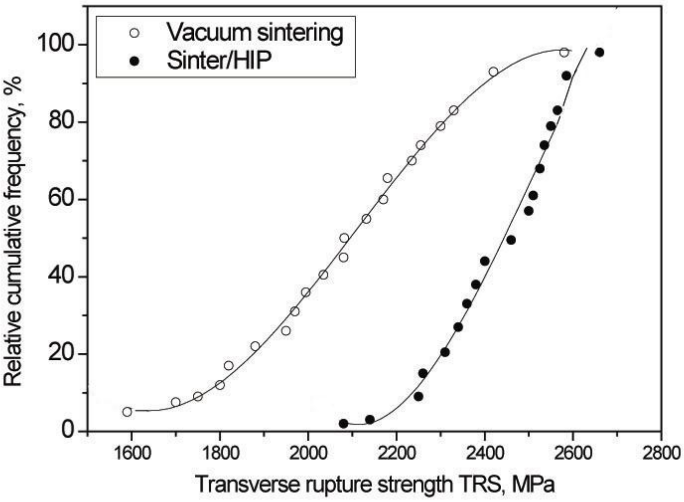


Figure 20 Distribution curves of transverse rupture strength of cermet grade T70/14(open mark – vacuum sintering, $p<5x10^{-2}$mBar; closed mark – Sinter/HIP, argon pressure P = 60 Bar)

Analysis of the results indicates that the relative increase in strength (transverse rupture strength and compressive strength) depends on cermet composition and increases with the increase in carbide fraction in alloy. Transverse rupture strength of grade T80/14 (80 wt% of TiC) is improved by over 40% while that of grade T60/8 (60 wt% TiC) by 15% only (Figure 17).

The increase in compressive strength of these alloys was 8% as maximum.

3.2.2 Hardness

Similarly to that of pre-sintering technologies (see 3.1) the results obtained indicate that sinter/HIP virtually does not affect hardness (the ordinary characteristic of material wear resistance) disregarding of the pre-sintering technology used (Figure 21).

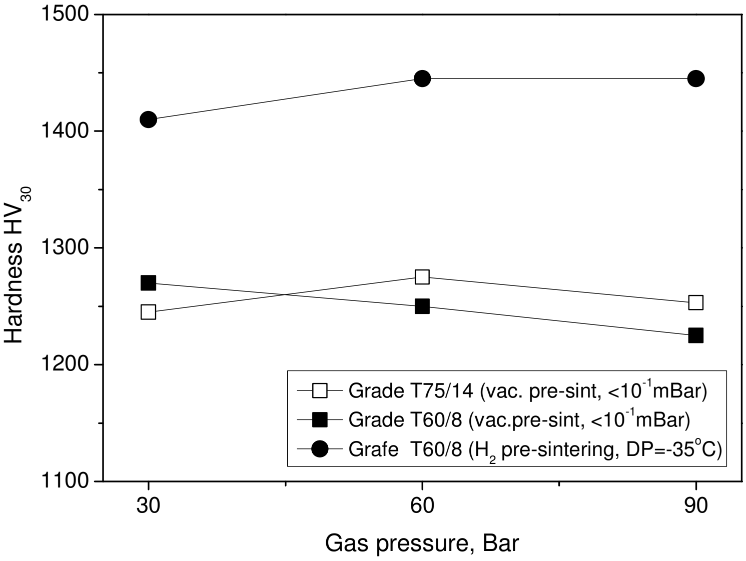


Figure 21.. Influence of sintering parameters on Vickers hardness of TiC-FeNi steel composites

3.2.3 Wear behaviour

The results of adhesive wear tests presented in Figure 22 refer to a remarkable positive effect of sinter/HIP onto wear performance of TiC-steel cermets.

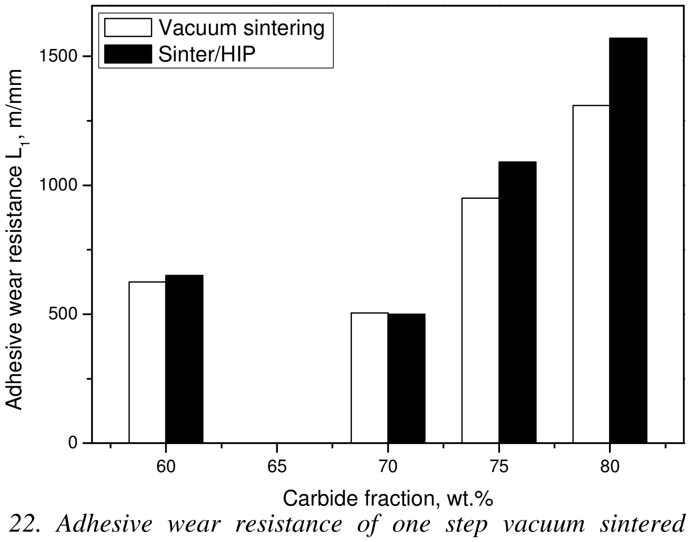


Figure 22. Adhesive wear resistance of one step vacuum sintered and sinter/HIP sintered TiC-FeNi steel alloys

The effect appears to be sharper for low-binder alloys ranging up to 25%.

The results of adhesive wear tests of sinter/HIP sintered alloys as a function of sintering temperature and applied pressure in Figures 23 and 24 show similar relationships to those of transverse rupture strength as a function of compression and temperature for both composites investigated.

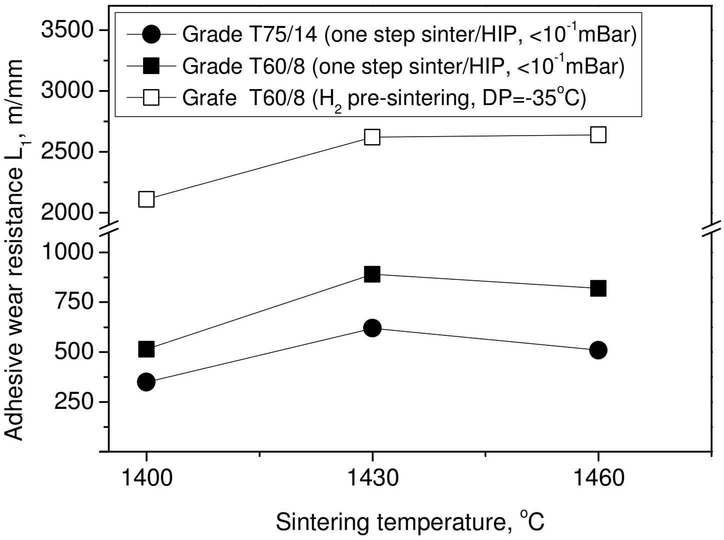


Figure 23. .Effect of sintering temperature on adhesive wear resistance of TiC-FeNi composites

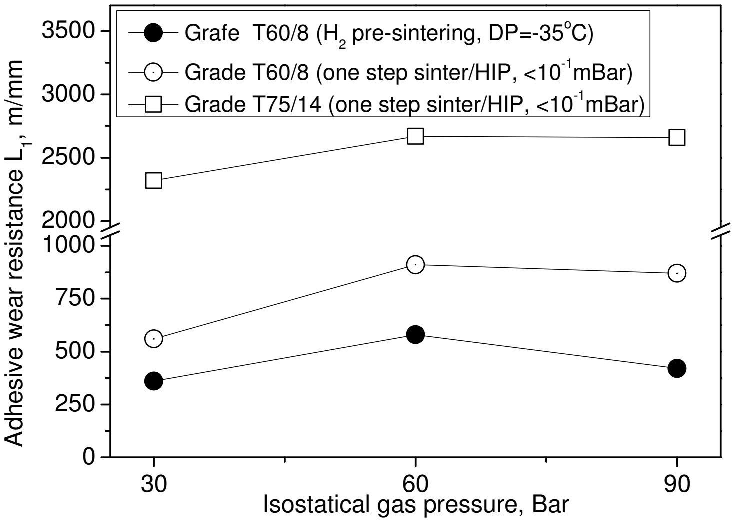


Figure 24. Effect of gas compression on adhesive wear resistance of TiC-FeNi composites

The similarity in behaviour of TiC-FeNi cermets in bending and adhesive wear tests – the dependence of these composite properties (in contrast to hardness) on sintering techniques, may be related to the similarity in failure mechanism (stress state) taking place in material during these tests [3, 29, 69].

Results of abrasive and erosion wear tests presented in Figure 25 A and B, respectively refer to a virtually non-existing positive effect of sinter/HIP sintering.

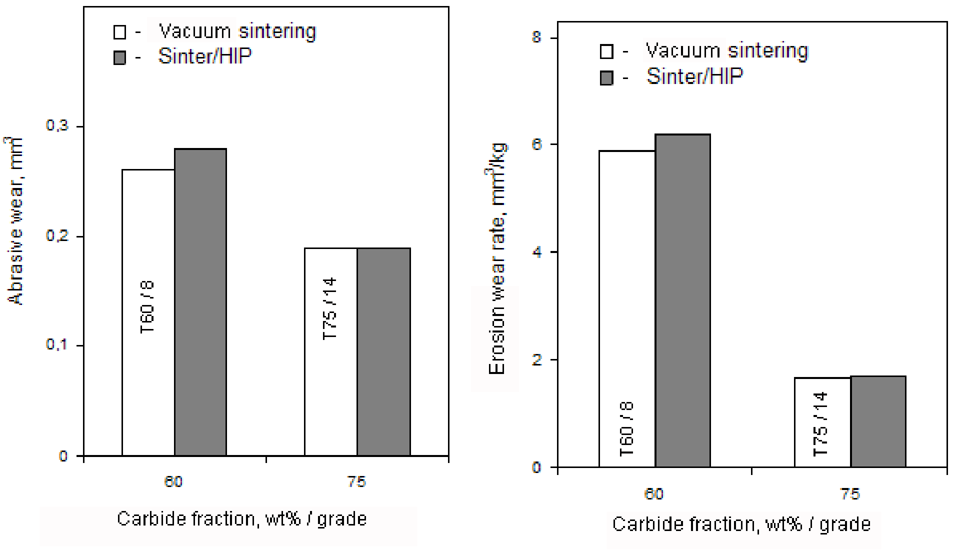


Figure 25. Abrasive (A) and erosive (B) wear of vacuum sintered and sinterhipped TiC-FeNi cermets

3.2.4 Microstructure studies

The results of SEM-studies presented in Figure 26 show improvement of sinter/HIP sintered TiC-cermet microstructure: a substantial reduction of porosity and some increase of homogeneity.

The results indicate that the compression during sintering virtually does not affect the grain size of carbide phase and binder fraction in cermet and results in a slight decrease of contiguity of an alloy (see Table 4).

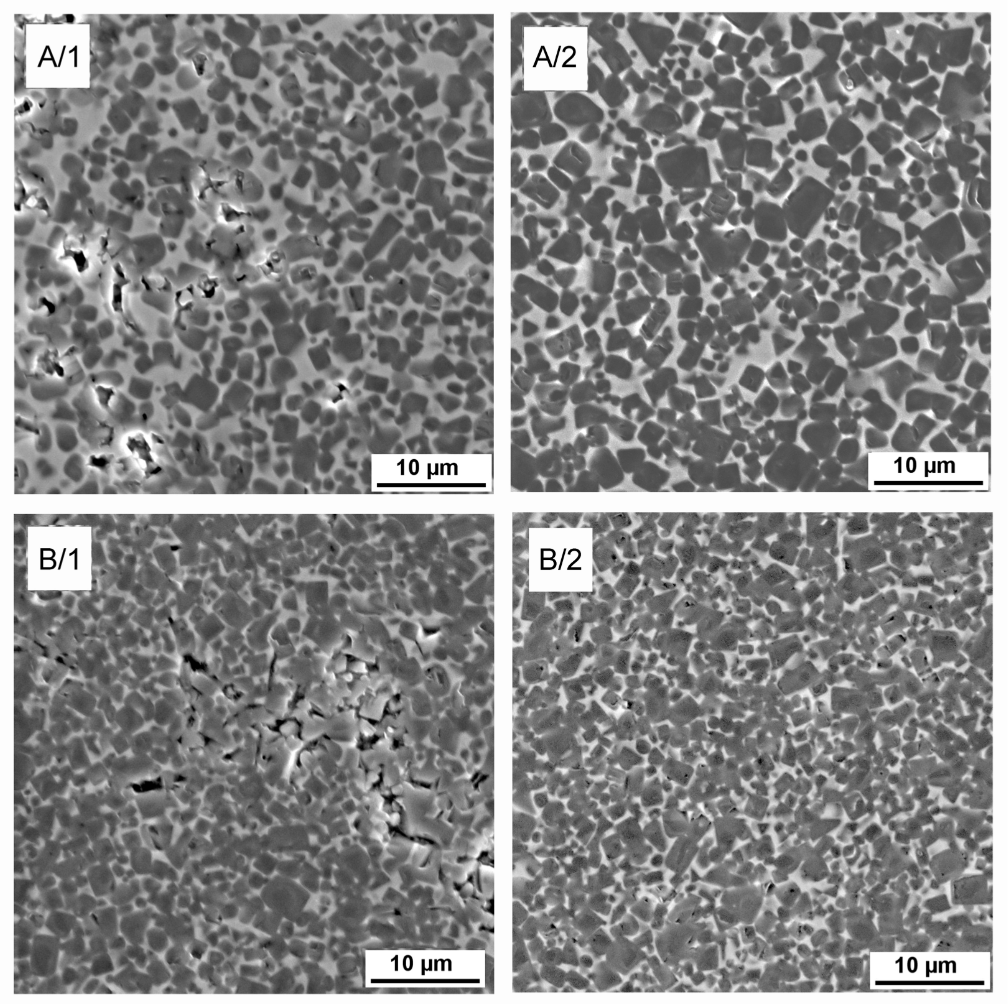


Figure 26. Microstructures of T60/8 (A) and T75/14 (B) cermets (1 – vacuum sintering, 2 – Sinter/HIP sintering)

The results of microanalysis show some changes (slight increase in alloying degree) in the binder composition of Sinter/HIP alloys (Table 4).

The results for temperature- and pressure dependency of Sinter/HIP-ed alloys presented in Table 5 refer to a slight influence of sintering techniques on the microstructure of TiC-based cermets.

Table 4. Microstructural parameters of cermet grade T60/8.

Sintering process	Average grain size *d*, µm	Conti-guity *C*	Binder fraction *V*, %	Binder microcomposition, %		
				Fe	Ni	Ti
Vacuum sintering	2.11	0.23	35.1	86.1	7.2	5.0
Sinter/HIP	2.24	0.18	37.2	84.8	8.01	5.9

Table 5. Microstructural characteristics and properties of cermet T60/8, sinte-hipped by different techniques.

Sample	Sintering		Performance		Microstructure		
	T,°C	*P*, Bar	*TRS*, GPa	L_I, m/mm	d_{TiC}, µm	*C*	*V*, vol %
31	1430	60	2.7	900	2.4	0.32	27.0
40	1400	30	2.3	450	2.3	0.39	26.0

The microstructure of alloys sintered by technological parameters ensuring enhanced performance characteristics (transverse rupture strength and adhesive wear resistance) are featured by an increase in homogeneity (more uniform distribution of phases in structure). Using proper Sinter/HIP technologies additional to porosity driven properties the microstructure driven performance properties can be greatly enhanced.

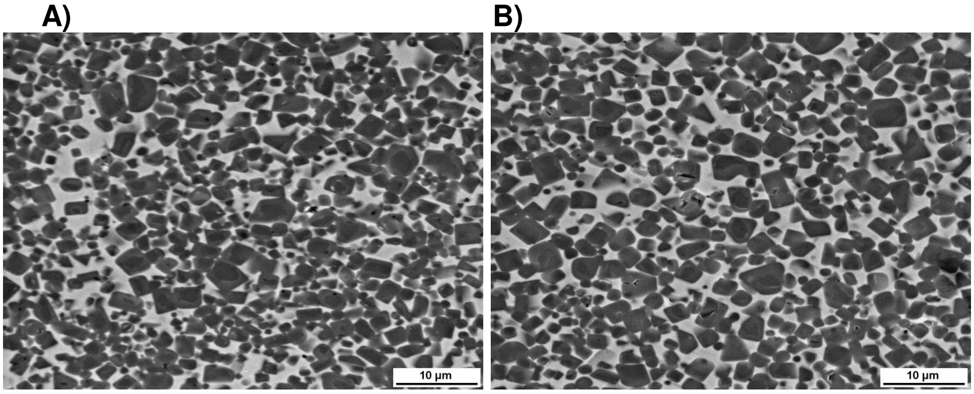


Figure 27. SEM-images of TiC-composite T60/8 sinter/HIP sintered by different techniques and differing in performance characteristics:
A – low performance characteristics (TRS = 2.15 GPa; L_I = 350 m/mm)
B – enhanced performance characteristics (TRS = 2.7 GPa, L_I = 800 m/mm)

3.2.5 Discussion

The substantial improvement of transverse rupture strength (strength with tension stresses prevailing in stress state) and moderate one of compressive strength (strength with shear stresses prevailing) means that sinter/HIP favoring reduction of porosity in carbide composites, improves first the resistance to a brittle failure – to a failure initiated by tension stresses [84].

This conclusion complies with the classical Griffith's strength theory of brittle materials postulating that the failure of a brittle material is initiated as the result of tensile stresses induced at the tips of flaws (pores, microcracks) in material [85]. According to Griffith the strength of a material under conditions of prevailing tension stresses depends on the presence of flaws (pores, microcracks) acting as failure sources (stress concentrators), their distribution in microstructure and resistance of the alloy to crack propagation.

In carbide composites the pores (originated mainly on the basis of impurities) are located preferably at interfaces “carbide-carbide”, “carbide-binder” [78, 86, 87]. In low binder grades (due to the enhanced contiguity), the probability of the location of pores increases at interfaces “carbide-carbide” [86] .

Owing to high rigidity of these interfaces, their inability to release (absorb) elastic strain energy (failure energy) storing at tips of flaws during wear-loading by local plastic strain [83, 87], the strength decreasing effect of pores is much sharper. Removal – reduction of those pores by sinter/HIP results therefore in a relatively sharper increase in strength.

The remarkable increase in adhesive wear performance of sinter/HIP sintered cermets (the strengthening response) and moderate or non-existent improvement of abrasive and erosion wear resistances may be related to the differences in the wear mechanism, in particular, in stress states during wear. As stated, the surface failure of a carbide composite (the material removal) during adhesive wear starts in the binder, takes place by extraction and is preceded by adhesive interaction between contacting surfaces [88]. During abrasive (and erosion) wear, the carbide composite material removal occurs predominantly by extrusion and microcutting [89].

Therefore, in the stress state during adhesive wear tension stresses prevail while in abrasive and erosion wear the relevance of shear stresses is more obvious.

3.2.6 Conclusions

1. Sinter/HIP results in a substantial increase in TiC-based cermets resistance to a brittle failure, i.e. to a failure initiated by tensile stresses (as evaluated by transverse rupture strength) and a remarkable improvement of adhesive wear resistance.
2. The favourable effect of sinter/HIP on the performance (strength and wear resistance) of TiC-FeNiSi cermets increases with the increase in carbide fraction in an alloy.
3. The positive effect of sinter/HIP on TiC-based cermet resistance to a ductile failure, i.e. to a failure initiated by shear stresses (compressive strength, hardness, abrasive and erosion wear) is negligible or non-existent.
4. The favourable effect of sinter/HIP onto the transverse rupture strength and adhesive wear resistance and a negligible or non-existent effect on the compressive strength and abrasive or erosion wear performance may be explained by the classical Griffith’s strength theory of brittle materials, emphasizing the relevance of tensile stresses in a failure and dependence of strength and wear on flaws (pores, microcracks, cracks and their distribution in an alloy.
5. The relevant performance characteristics – transverse rupture strength and adhesive wear resistance increase with an increase in sintering temperature and gas pressure up to a maximum at 1430°C and 60 Bar.

6. Cermets with martensitic steel binder show a remarkable sensitivity to the pre-sintering atmosphere, the application of vacuum pre-sintering (one-step sinter/HIP) instead of hydrogen one (two step sinter/HIP) ensures a substantial improvement of properties.

7. Microstructure of the alloys, sintered by the techniques ensuring enhanced properties is featured by a higher homogeneity (more uniform distribution of phases in structure).

3.3 Functional testing of sinter/HIP sintered TiC-FeNi steel cermets

3.3.1 Experimental

The performance of the sinter/HIP sintered TiC-cermets was evaluated during functional durability tests, carried out in service conditions: during blanking grooves into steel (hardness HV=150, thickness t = 0.5 mm) in a multi-position die. The die was reinforced with the sinter/HIP sintered cermet grade T75/14 and with the ordinary sintered in vacuum, grade T70/14. The ordinary cermet T70/14 has proved its superiority (its higher blanking performance) over the WC-based hard metal WC-15Co, widely used in metal forming [3].

The die was mounted on automatic press (Figure 28), and the blanking performance was estimated by means of measuring the side wear ΔD (increase in diameter of groove) after service time $5x10^5$ strokes. The service time $5x10^5$ corresponds to the time between two consecutive prophylactic sharpenings in exploitation of blanking dies.

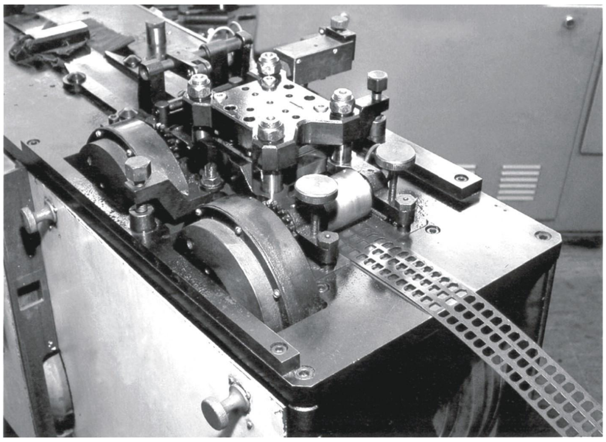


Figure 28. Durability testing of cermets in multiposition die

The side wear measurements were conducted by means of the measuring machine Mitutoyo strato 9166 in constant environmental conditions as an average of 6 measurements.

3.3.2 Results

The results of functional tests are presented in Fig.29 as wear contours *"Δ - H"* (side wear $\Delta = D_1 - D_o$, depending on depth *H* – distance from cutting edge). It has to be noted that during testing ($N=5\cdot10^5$ strokes) neither fracture nor brittle macrochipping of cutting edges could be detected. Cutting edges became blunt as a result of wear.

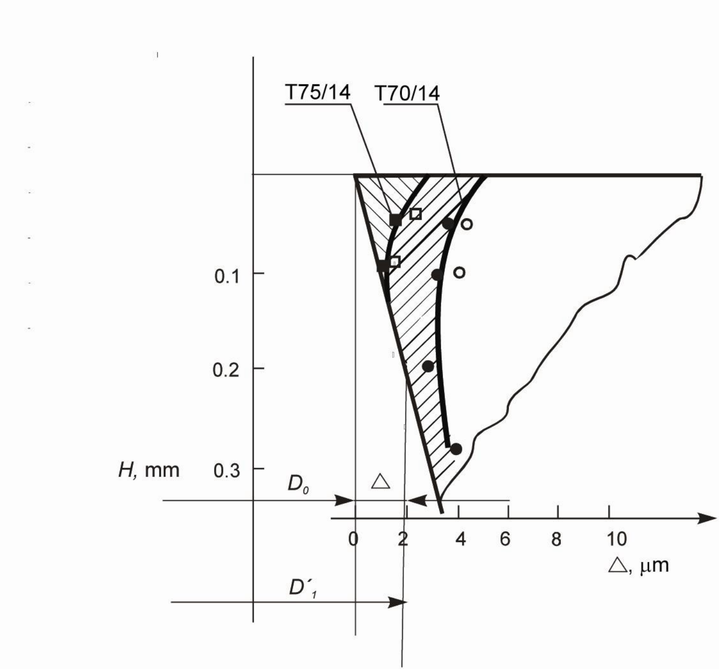


Figure 29. Wear contours Δ-H of TiC-FeNi steel blanking tools (Δ – side wear, measured from the edge of the die; H – distance from the top surface of the die

The wear contours and side wear data demonstrate an obvious superiority of the sinter/HIP sintered TiC-based cermet T75/14 over the ordinary vacuum sintered T70/14 one.

The higher blanking performance of the grade T75/14 may result from:

- the higher adhesive wear resistance L_1
- the enhanced resistance to microchipping (cutting edge stability), resulted from the positive effect (decrease in microfaults) of sinterhipping.

3.4 Sinter/HIP sintering of conventional TiC-NiMo cermets.

As stated previously pre-sintering technologies do not affect the cermets with nickel alloy binder as significantly as they are in the case of FeNi (especially those of low nickel content) binder alloys. Yet there is lack of information about Sinter/HIP of TiC-Ni alloy cermets regarding carbide fraction, effect of temperature, molybdenum addition and applied argon pressure.

Sinter/HIP sintering effect on composition of different grades of TiC-NiMo cermets was investigated. Titanium carbide was ranged from 40 to 80 wt.% and the ratio of nickel to molybdenum in the initial powder composition was 1:1, 2:1 and 4:1 respectively (See Table 2). On selected materials sinter/HIP at different gas pressures was studied.

These materials are perspective in abrasive-erosive environments accompanied with high corrosion and/or temperature. Transverse rupture strength (TRS) and erosion wear resistance as the main performance characteristics were measured.

The majority of the results in paragraph are covered in paper V (List of publications).

3.4.1 Strength properties – normal sintering temperatures.

For the WC-Co materials, it is known that the effect of Sinter/HIP is higher for the grades with less binder fraction. In this work, the binder fraction was scaled from 10 wt. % of Nickel up to 48 wt. % of nickel as a main constituent in ductile phase in the sintered alloys. Sintering temperatures commonly used for vacuum sintering were performed as follows (preliminary tests showed no improvements on strength properties by sintering below the common temperatures):

Table 6. Sintering temperatures of TiC-NiMo cermets under investigation

Grade	Sintering temperature, °C
TN60, TN60A, TN60B, TN50, TN50A, TN50B	1410
TN40, TN40A, TN40B, TN30, TN30A, TN30B	1440
TN20, TN20A, TN20B	1500

For the high binder (above 30wt% of TiC) fraction materials no significant positive effect from pressure sintering on the strength properties was found during sintering at temperatures mentioned in Table 6 (Figure 30.). It seems that higher sintering temperatures are needed for strength improvement.

For the low binder alloys (up to 25 wt. % of nickel) the influence of pressure can be remarkable, amounting to 50% increase in strength.

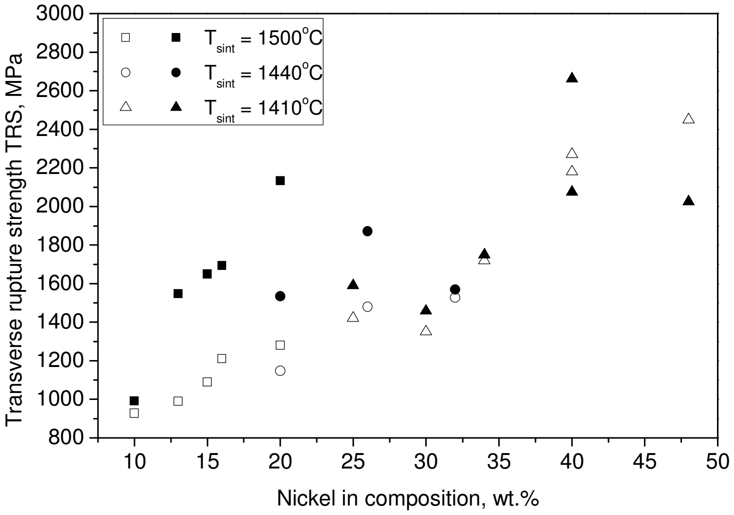


Figure 30. Transverse rupture strengths of vacuum- and sinter/HIP sintered alloys versus nickel in alloy composition (open mark – vacuum sintering, closed mark – sinter/HIP)

The results of strength improvement for low-binder alloys (titanium carbide 70 or 80 wt. % - grades TN20, TN20A, TN20B, TN30, TN30A) in Figure 31 show steady improvement of strength in order of 50% regardless of nickel inclusion. Exception is in the case of grade TN20B with 10wt. % of nickel.

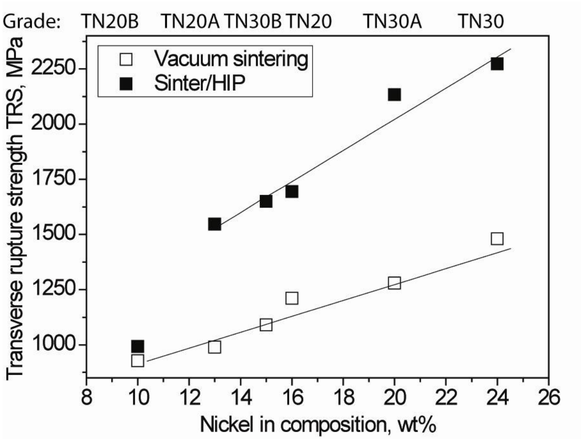


Figure 31. Transverse rupture strengths of vacuum- and sinter/HIP sintered alloys versus alloy grade (sintering temperature 1500°C, argon gas pressure 90Bar)

It can be assumed there is a certain threshold limit of nickel content below which common TiC-NiMo cermet materials cannot be further densified by sinter/HIP (for grade TN20B the volumetric nickel content is as low as 6-7 % [90]).

Decreasing argon pressure do not decrease the strength properties (Figure 32). This indicates to high malleability of the binder phase at high temperatures at which no extensive pressures are needed to remove the closed porosity.

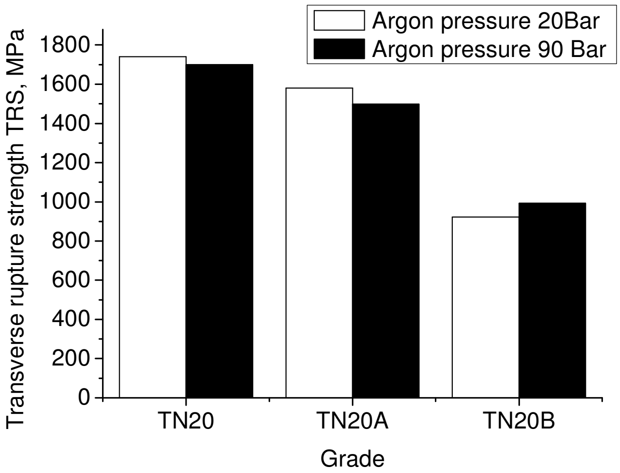


Figure 32. Transverse rupture strength versus low-binder fraction alloy grade

Strength of grade TN20A versus sintering temperature was investigated (Figure 33).

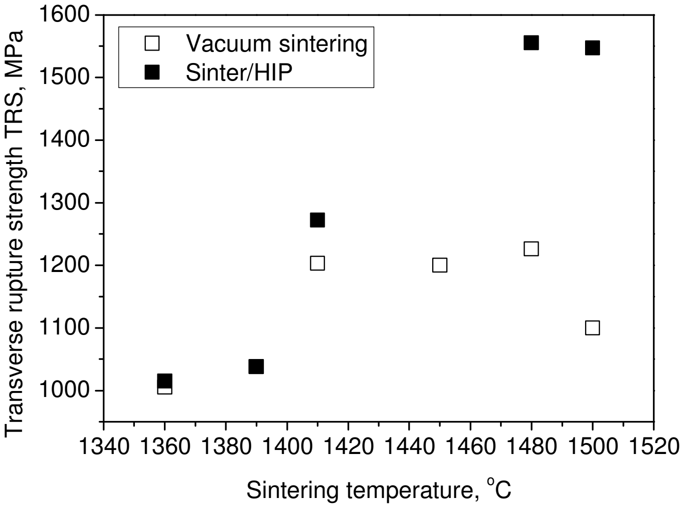


Figure 33. Transverse rupture strength of alloy TN20A versus sintering temperature

Clearly above 1480 °C the transverse rupture strength increases steeply confirming the need for high temperatures for property enhancement of low-binder alloys.

3.4.2 Strength properties - medium binder alloys.

No significant improvement in strength of grades with TiC content of 60 wt.% or less was observed during sintering at common temperatures (Figure 30).

Vacuum sintering of ceramic-metal composites with higher binder compositions at higher temperatures is not recommended due to possible flow out and evaporation of the binder material. Using pressurized gas could hinder those effects due to higher density of the pressurized argon environment (estimated density around 2.7x10^{-2} g/cm^3 at sintering temperature 1400°C and 90Bar) and higher gas constant of binder material in argon atmosphere.

Grades with 60wt.% of TiC, Sinter/HIP sintered at temperature of 1440 °C show only a slight increase in the TRS values (Figure 34). Increase in sintering temperature to 1500°C substantial growth (up to 60%) in bending strength was observed.

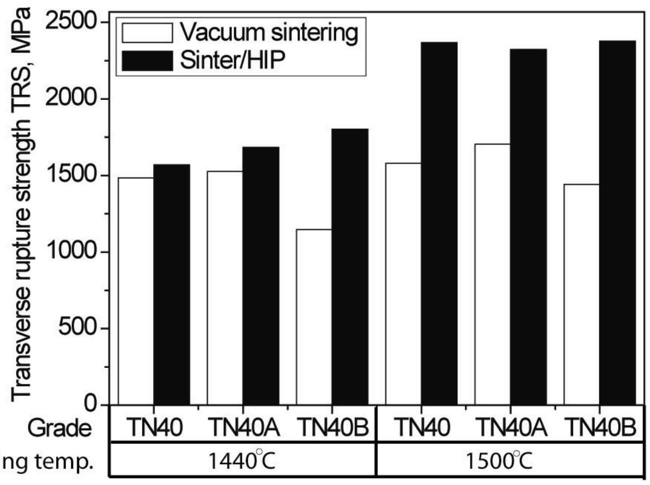


Figure 34. Transverse rupture strength of TiC-NiMo cermets depending on binder content and sintering parameters

Binder outflow observed in some vacuum sintered samples was not detected in sinter/HIP sintered samples (with specimen dimensions of 6x6x40 mm^3 and 6x10x20 mm^3). As seen from Figure 35 decreased gas pressures applied during sintering could even enhance the strength properties of alloys with higher binder content (TN40).

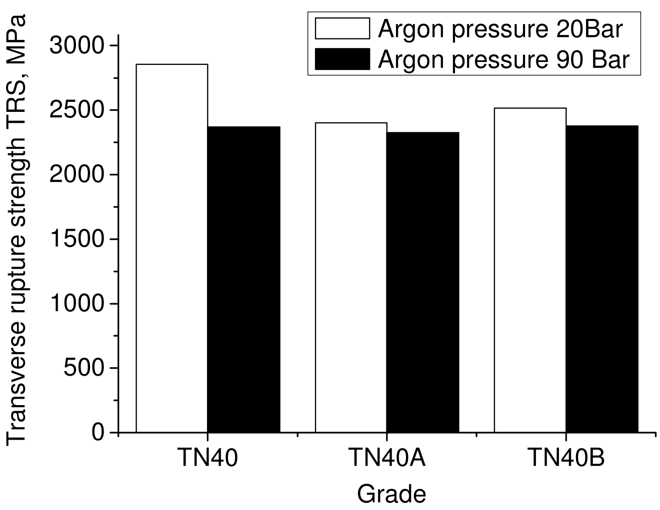


Figure 35. Transverse rupture strength of Sinter/HIP sintered alloys at different argon pressures

The results for medium carbide fraction alloys with binder composition Ni:Mo the highest molybdenum additions as the alloying element do not decrease the strength properties. This suggests on importance of proper molybdenum content on strength property increase and indicates that materials with highly malleable binder do not need high pressures in order to densify the materials and low-pressure sintering could even be preferential for medium carbide grades.

3.4.3 Hardness and wear resistance in erosive environment

As also stated earlier (Paragraph 3.2) the positive effect of sinter/HIP on TiC-based cermet resistance to a ductile failure, i.e. to a failure initiated by shear stresses (compressive strength, hardness, abrasive and erosion wear) is negligible or non-existent (Figure 36).

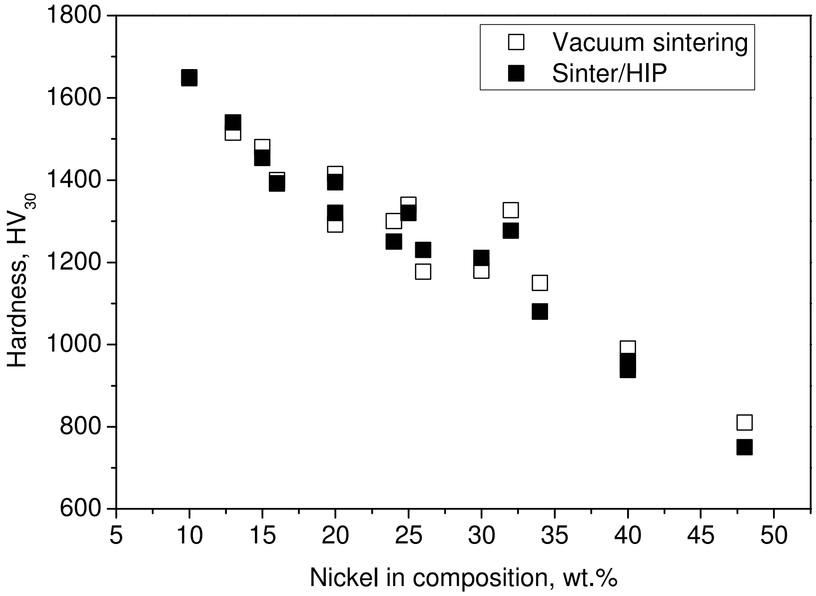


Figure 36. Hardness of TiC-NiMo cermets versus nickel content in alloy composition

Also wear resistance in abrasive-erosive media did not show any improvements compared to vacuum sintered alloys (Figure 37).

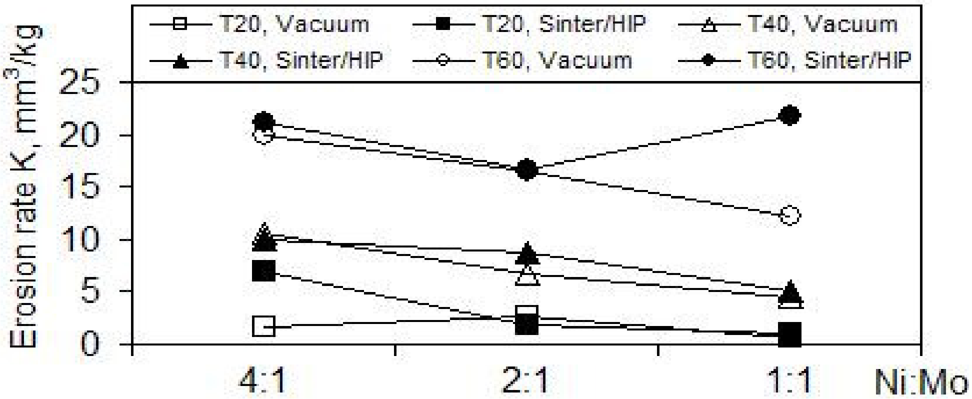


Figure 37. Erosion rates of the cermets with different binder contents and Ni:Mo ratios

3.4.4 Strength improvement, general.

Comparing strength-hardness areas of sinter/HIP sintered TiC-NiMo cermets with other hardmetals (Figure 38) it can be concluded the possibility of application of these cermets in more dynamic stress involved applications.

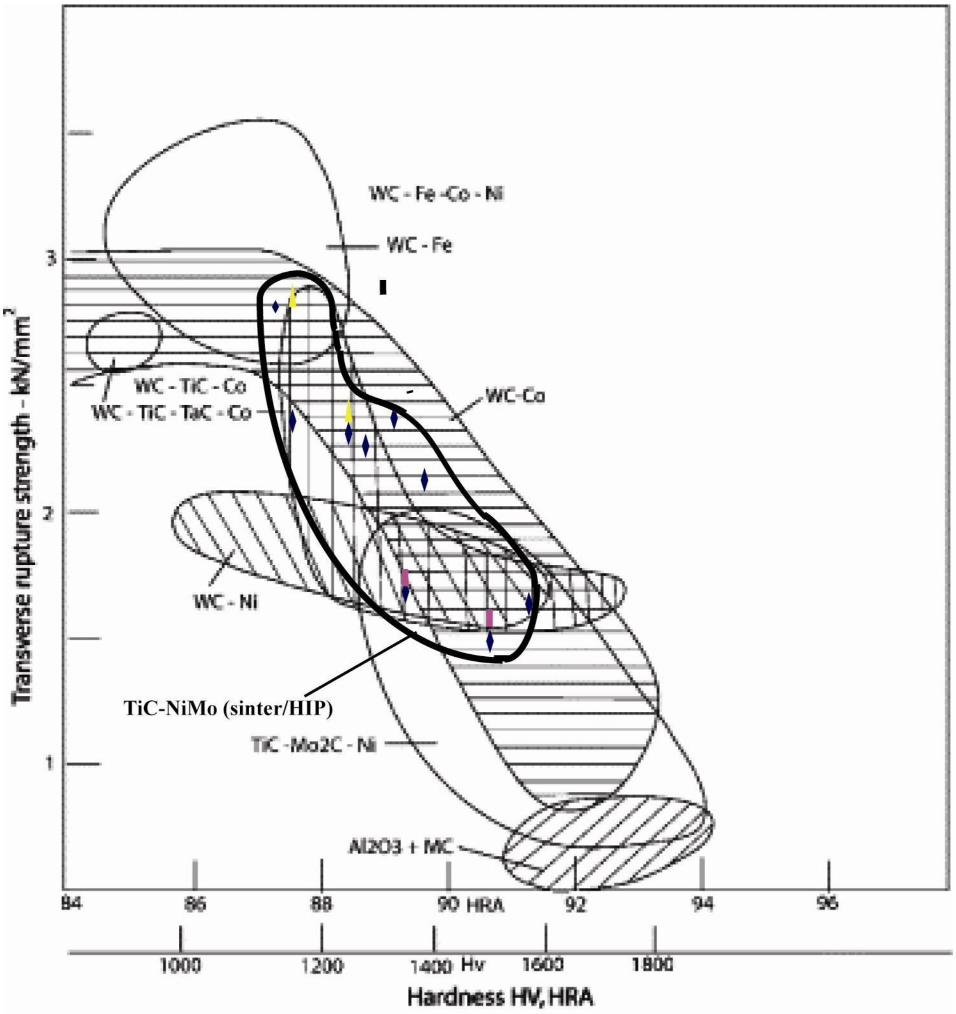


Figure 38. Hardness-transverse rupture strength areas of sinter/HIP sintered cermets compared with common hard metals

3.4.5 Microstructural analysis.

Microstructure analysis was made for the grades with the binder initial Ni:Mo powder mixtures of 2:1. The porosity and the volume fractions of core and rim area were measured in order to find the pressure effects on solubility of constituents and possible binder evaporation occurring during high-temperature sintering reported earlier [91].

It was found that the applied pressure could not completely eliminate the microporosity from the structure (Table 7). Especially, inter-granular porosity occurred in between the core and rim area of carbide grains (Figure 40). The larger pores present in high-carbide alloys were removed by Sinter/HIP.

Table 7. Microstructure parameters for different TiC-NiMo grades (from 20 to 60 wt.% of binder) with Ni:Mo ratio of 2:1

Grade	Porosity		Binder, vol. %		Grain size, core, µm		Grain size, rim, µm	
	Vacuum	Sinter /HIP	Vacuum	Sinter /HIP	Vacuum	Sinter /HIP	Vacuum	Sinter /HIP
T20A	0.95	0.55	8.1	8.0	-	-	-	-
T40A$_1$ (Tsint=1440°C)	0.12	0.26	22.5	18.6	0.76	0.69	0.96	1.08
T40A$_2$ (Tsint=1500°C)	0.08	0.13	28.8	23.1	0.89	0.76	1.40	1.11
T60A	0.03	0.07	24.2	31.2	-	-	-	-

For grades T40A sintered at temperature of 1440°C and at elevated temperatures of 1500°C were studied. As seen from Table 7, the increase in the sintering temperature resulted in higher grain sizes for vacuum sintered alloys. For Sinter/HIP treated materials grain coarsening was less remarkable.

The Figure 39 A and B shows the grain size distribution curves for the cores and rims of these alloys respectively.

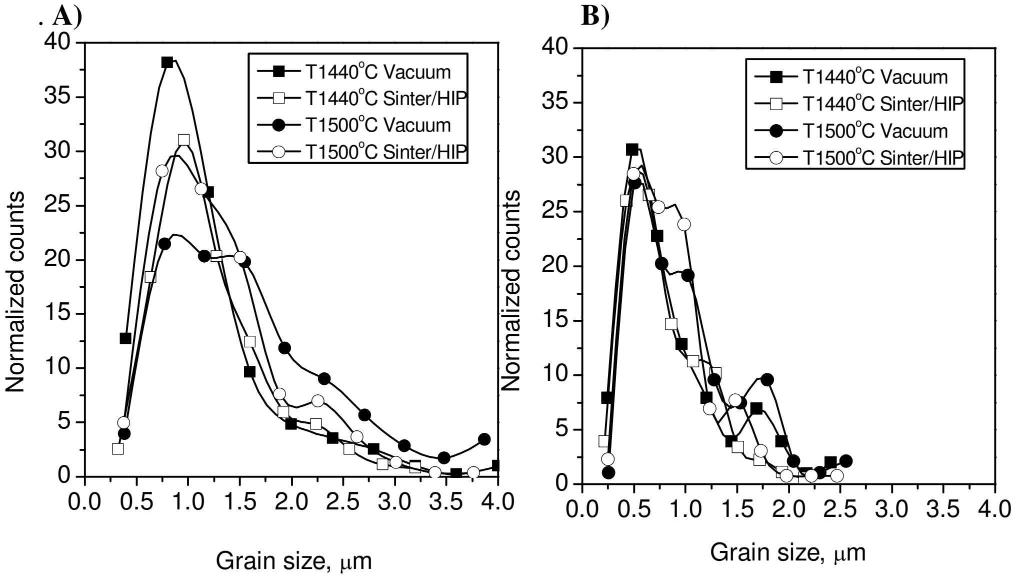


Figure 39. Normalized size distribution of vacuum sintered and Sinter/HIP-ed T40A alloys at normal and elevated sintering temperatures (A – cores, B – Rims)

When small grains of vacuum sintered alloys have disappeared and some large grains in order of 3.5…4.0 µm have appeared after sintering at 1500°C the distribution curves of Sinter/HIP-ed alloys show only slight shift with no significant large grains (Figure 40 A). The cores show no significant change in size distribution.

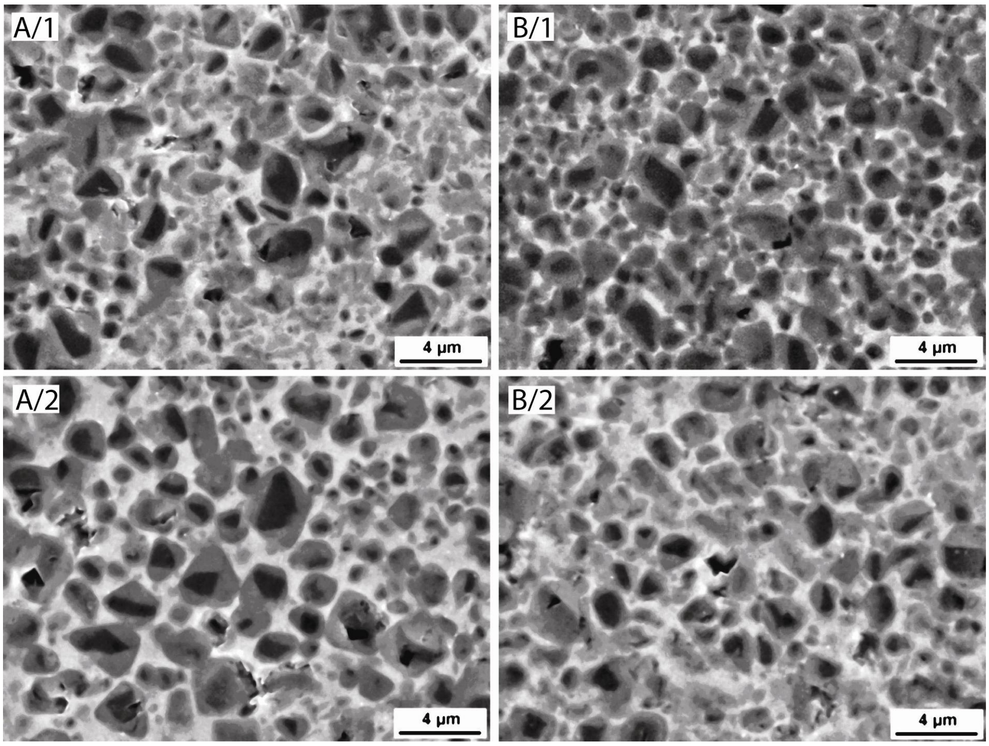


Figure 40. Microstructures of cermets with 60wt.% of TiC, grade T40A. (A – Vacuum sintering; B – Sinter/HIP; 1 – Sintering temperature 1440°C; 2 – sintering temperature 1500°C)

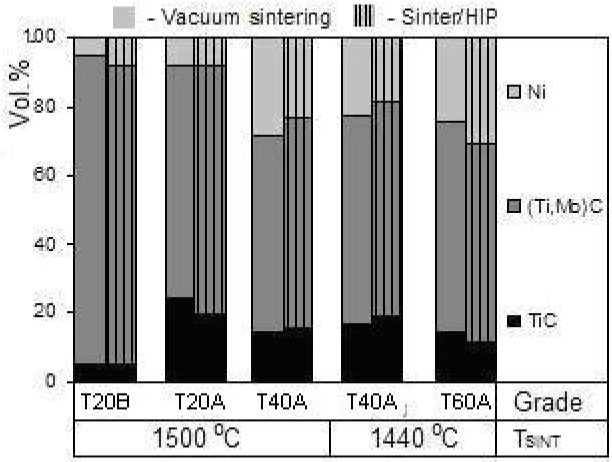


Figure 41. Volumetric fractions of core, rim and the binder area versus alloy compositions and sintering parameters of TiC-NiMo grade composites

The Sinter/HIP microstructures were highly homogeneous. Hindering effect of argon atmosphere on binder evaporation was not observed on alloys (Figure 41). Although some differences in volume fractions of the binder and core area of vacuum and Sinter/HIP alloys was found, the repetitive tests showed that the values stayed in the range of tolerances.

3.4.6 Conclusions

1. Similarly to Sinter/HIP-ed WC-Co alloys, the TRS values for low-binder grades can be improved. Steady strength increase of about 50% was observed for high temperature sintered alloys with nickel content up to 25 wt.% with decrease of the improvement above this level.. At higher temperatures further property increase can be reached by optimizing the sintering gas pressure.
2. Enhancing the property of the TiC-NiMo cermets allows such materials to be used for applications where higher strength is needed in addition to wear resistance.
3. Medium-carbide alloys can be sintered with Sinter/HIP sintering at elevated temperatures, leading to homogeneous microstructures and superior strength properties of the cermets.
4. Due to the prevailing shear stresses the use of Sinter/HIP did not have a positive effect on erosion resistance in abrasive media.

3.5 Development of technological parameters using different powder grain size materials

The mechanical and wear properties of the cermets are known to depend on the microstructure features like grain size, core size, contiguity etc. Also property enhancement through Sinter/HIP sintering is predicted to occur especially for those of fine-grain materials. In this paragraph the microstructural features for cermet grade TN20A for property relationships and sintering and Sinter/HIP mechanisms and grain refinement possibilities were studied using high-energy milling, conventional ball milling and reactive sinter/HIP routes.

From technological viewpoint the milling time is easiest to adjust in order to vary the milling intensity. Milling powders in common ball mill there is a certain value of grain size below which the energy of milling balls is not sufficient for further refinement of the powders. For TiC-30NiMo mixture the critical surface area has found to be $4m^2/g$ [92]. In the case of high-energy attritor milling the obtained grain sizes can be in orders of nanometres. With similar milling parameters the TiC-50NiMo powders were disintegrated up to specific surface area of 27 m2/g (Figure 42 [92]) estimated to average grain size of 40 nm.

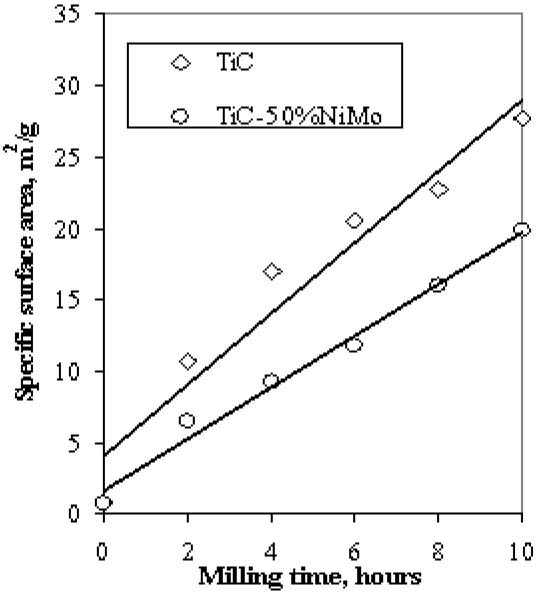


Figure 42. The specific surface area of TiC and TiC-NiMo powders versus milling time [92]

In this work the high-energy milling periods of 1, 2, 4, 8 and 16 hours were chosen (Table 3). Common, ball milled materials were milled for 72 hours.

The vacuum and sinter/HIP sintering were performed at the temperatures of 1360, 1390, 1420, 1450 and 1480°C.

Part of the contents of paragraph (concerning reactive sinter/HIP of cermets) is covered in paper VI (Appendix A). The recent research concerning high-energy milling has not been published yet.

3.5.1 Sintering kinetics

The densification of the specimens was studied by linear shrinkage, measured after sintering or pre-sintering cycle. The specimens were pressed with the same pressure and same amount of plasticizer was used.

As seen from Figure 43 in all the cases the enhanced shrinkage will start at about 1320°C which is around the eutectic temperature of the TiC-NiMo alloy.

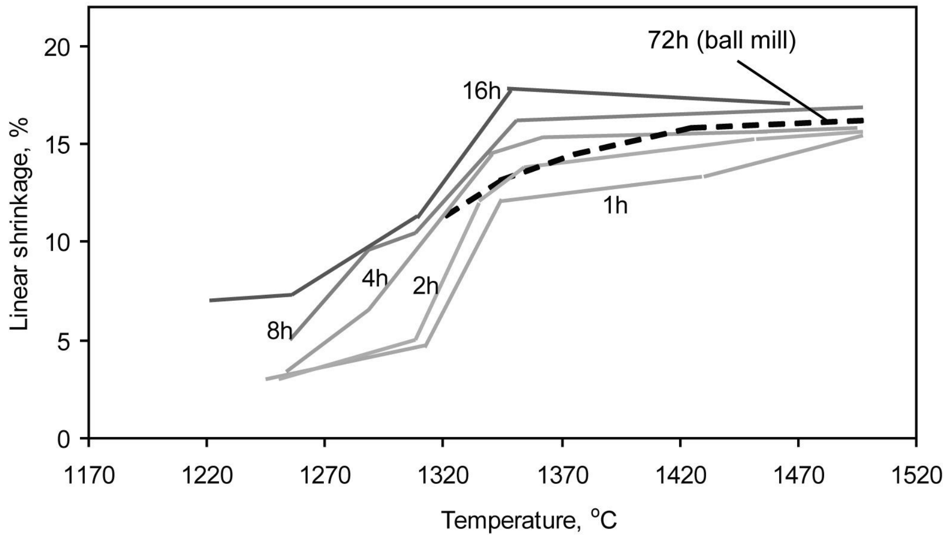


Figure 43. Densification of materials with different milling parameters versus sintering temperature

The solid state sintering occurring between 1200 and 1320 °C is most significant in the case of 16 hours of attritor milling. All the lines are shifted to lower temperatures with higher degree of milling. Densification curve of ball milled specimens lies between 2 and 4 hours of attritor milling, which is compliant with the specific surface area data, being at around 5 m^2/g in both cases.

Table 8. Archimedes densities of vacuum sintered alloys

	Time of milling, h / method	Sintering temperature, °C				
		1360	*1390*	*1420*	*1450*	*1480*
Vacuum sintering	*1 / attritor*	0.94	0.94	0.94	0.94	0.96
	2 / attritor	0.94	0.96	0.96	0.96	0.99
	4 / attritor	0.95	1.00	1.00	1.00	1.00
	8 /attritor	0.97	1.00	1.00	1.00	0.99
	16 / attritor	0.99	1.01	1.00	1.00	1.00
	72 / ball mill	0.99	1.00	1.00	1.01	1.00

Full theoretical densities were obtained for the alloys with at least four hours of high-energy milling. After sintering at 1360°C nearly full density materials were obtained in the case of 16 hours high-energy milled and ball milled materials. Powders milled for two hours reached almost full density after sintering at 1480°C. Further increasing the sintering temperature of less milled samples (1 and 2 hours of milling) could not be performed due to occurred binder boiling.

3.5.2 Microstructure development of vacuum sintered alloys

The grain coarsening for both the rim and core versus sintering and milling range was quantified by the relationship

$$d^2 - d_0^2 = kF(t_{milling}, T_{\sin t});$$

assuming normal grain growth (boundary motion is driven only by the reduction of the total amount of grain boundary surface energy), where d_o is the initial and d is final grain size as the studied range. k is the grain growth constant of function of time of milling or sintering temperature.

The results showed steady state growth for core and the rim as a function of milling period (Figure 44 A and B).

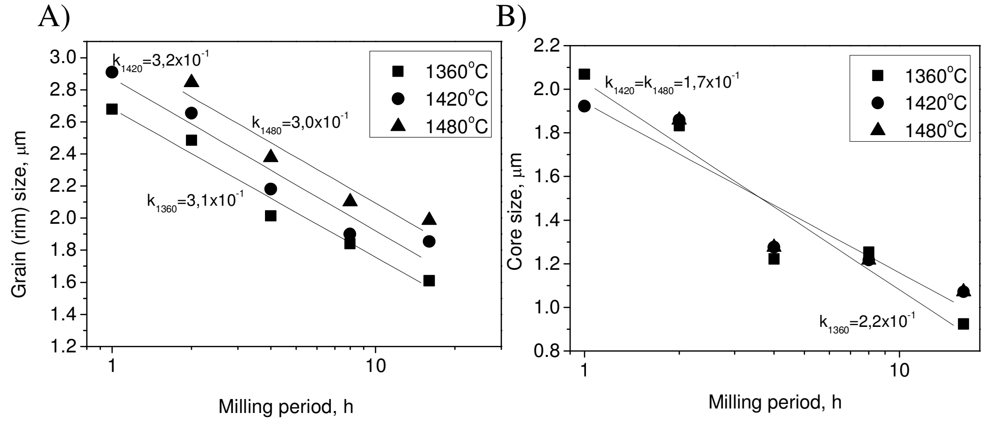


Figure 44. Average grain size of specimens of high-energy milled powders versus milling period (A – rim size; B – core size)

The grain growth constant is considerably higher for the rims than of the cores, irrespectively of the sintering temperature. It is found to be in the range of $3.0…3.2x10^{-1}$ μm/h for the grains and $1.7…2.2x10^{-1}$ μm/h for the cores.

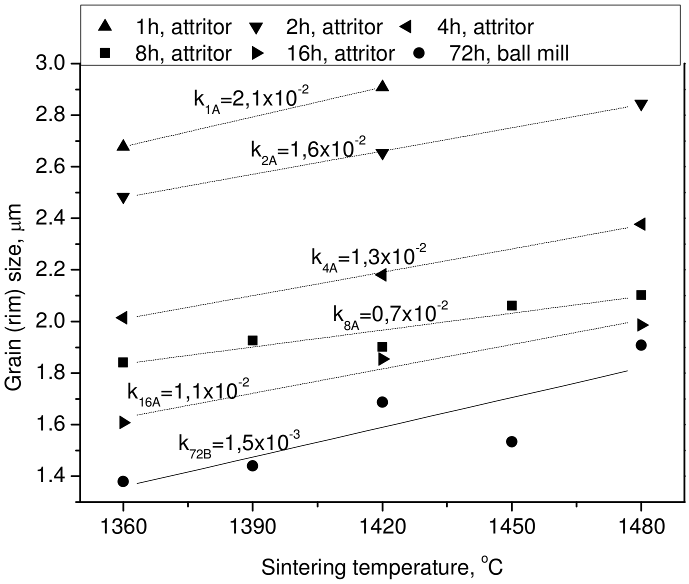


Figure 45. Grain (rim) size development versus sintering temperature

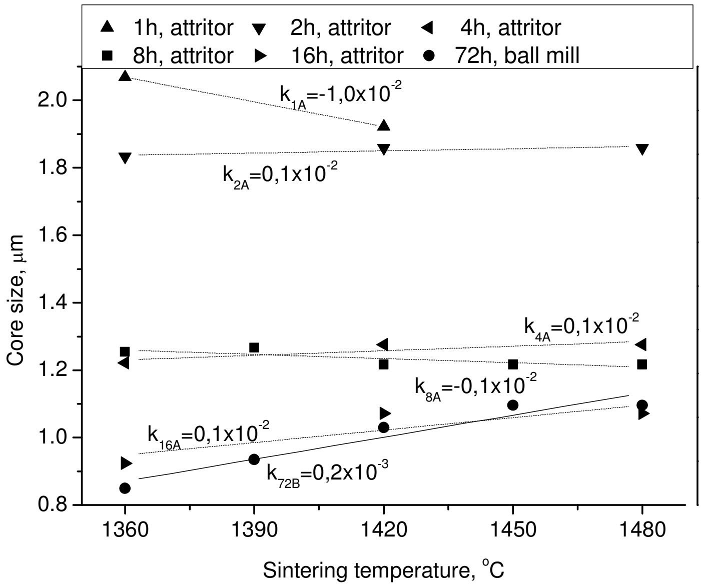


Figure 46. Core size development versus sintering temperature

Comparing grain growth coefficients as a function of sintering temperature (Figure 45 and 46) considerable differences for different milling periods and for conventional and high-energy milling can be observed. Grain coarsening is hindered with increased milling period from k=2.1x10^{-2} mm/°C for one hour of milling to 1.1x10^{-2} mm/°C for 16 hours milled materials.

Although the grain size of conventional ball milled materials is finest the grain growth coefficient is between 2 and 4 hours of attritor milled materials, similarly to that of densification behaviour in Figure 43. The core size is growing in certain amount of ball milled materials. For attritor milled samples it can be seen the core area staying at constant level.

The scanning electron microscopy images (Figure 47) of sintered materials show common core-rim structures for all investigated samples. When ball milled materials sintered at low temperatures (Figure 47, F/1) have fine-grained, homogenous structure, the high-energy milled materials contain large grains even after sintering at 1360^{o}C (D/1 and E/1). At higher sintering temperatures and longer milling periods elongated, plate-like cores in high-energy milled samples were observed (Figure 47, C/3, D/2, D/3, E/1, E/2, E/3), which was not encountered in ball milled materials. This indicates to different mechanisms occurring especially during first stages of sintering.

It is assumed that during sintering of nanometric powders (8 and 16 hours of milling) at first stage of liquid phase sintering remarkable coalescence of carbide particles takes place, referring to high amount of coarse particles in low-temperature sintered materials. At further stages the solid reprecipitation, likewise of other materials will dominate, indicated by growth of only the rim areas.

The plate-like structure formation mechanisms of TiC cores are not known. This could be connected with early-stage TiC particle coalescence processes.

The mechanisms of coherency strain [93]in single particles were observed in some extent for 1 hour milled (and less for 2 hours milled) samples, resulting in core degradation in the course of sintering at higher temperatures..

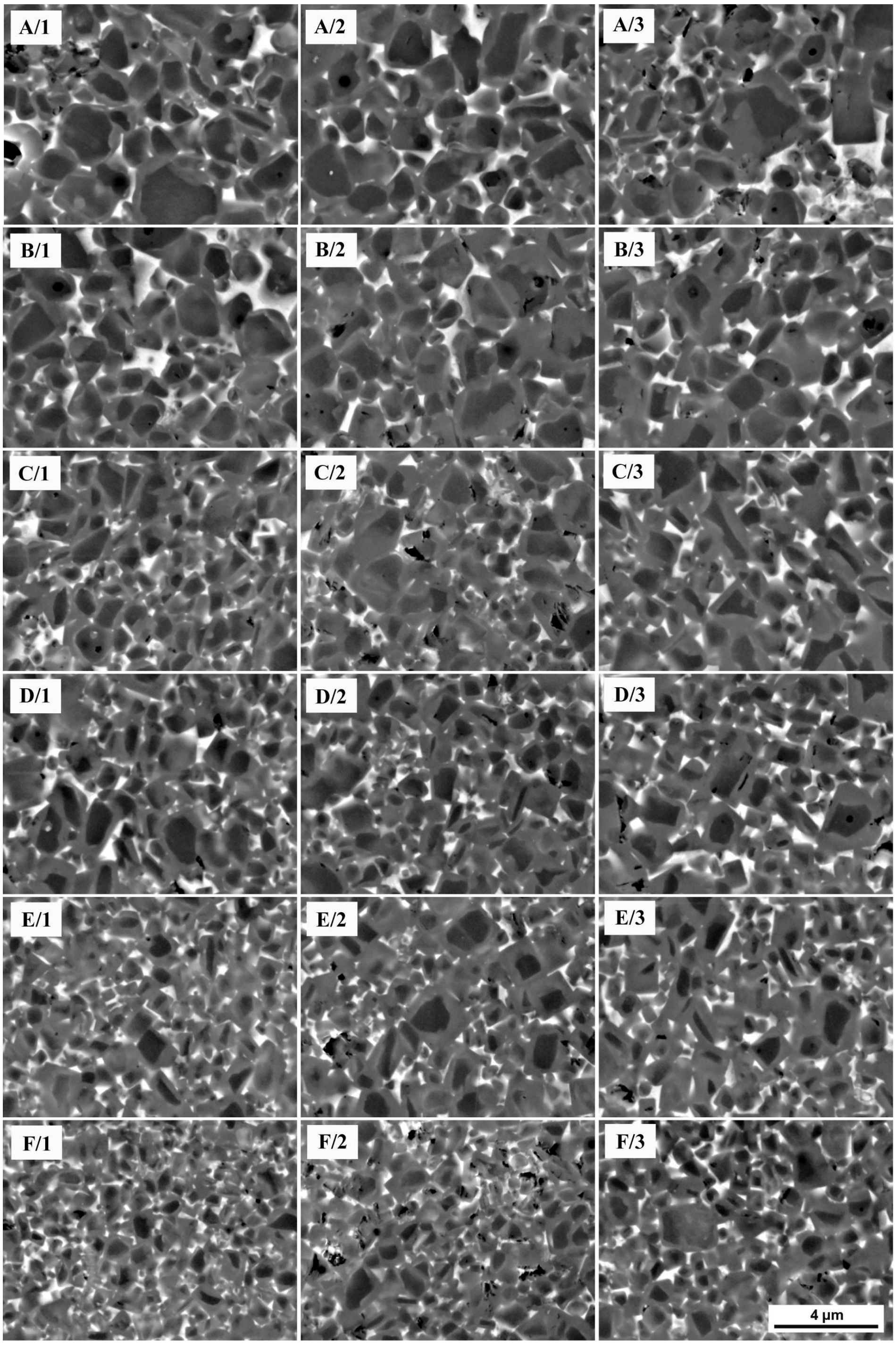


Figure 47. Microstructures of TN20A with varying milling times and sintering temperatures (A, B, C, D, E – 1, 2, 4, 8, 16 hours of attritor milling respectively; F – 72 hours of ball milling; 1, 2, 3 –final sintering at 1360, 1420 and 1480 ^{o}C respectively)

3.5.3 Mechanical properties and wear behaviour

The strength properties of vacuum sintered materials were superior in the case of ball milling (Table 9).

Table 9. Transverse rupture strength(MPa) of vacuum- and Sinter/HIP sintered alloys and the property increase after Sinter/HIP

	Time of milling, h / method	Sintering temperature, °C				
		1360	*1390*	*1420*	*1450*	*1480*
Vacuum sintering	*1 / attritor*	718	753	877	774	897
	2 / attritor	796	818	906	723	914
	4 / attritor	875	886	1162	963	1061
	8 /attritor	780	755	1061	949	925
	16 / attritor	669	766	795	754	999
	72 / ball mill	1005	1038	1203	976	1226
Sinter/HIP sintering	*1 / attritor*	747	807	815	761	1085
	2 / attritor	782	952	1037	795	1066
	4 / attritor	997	1254	1089	1104	1463
	8 /attritor	676	1177	1131	900	1475
	16 / attritor	721	1133	967	1077	1475
	72 / ball mill	1015	1038	1272	-	1555
Difference in TRS, %	*1 / attritor*	4	7	-7	-2	21
	2 / attritor	-2	16	14	10	17
	4 / attritor	14	42	-6	15	38
	8 /attritor	-13	56	7	-5	60
	16 / attritor	8	48	22	43	48
	72 / ball mill	1	0	6	-	27

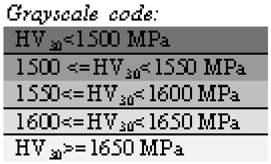
The values of high-energy milled and vacuum sintered samples achieve the strength of ball milled materials only in the case of four hours of attritor milling.

After sinter/HIP sintering there are visible increase in TRS at high sintering temperatures, regardless of the milling time. For at least 4 hours of high-energy milled materials also at 1390°C considerable increase can be seen.

Hardness of the materials with at least 1.00 theoretical density (Table 10) stays unchanged by sinter/HIP regardless of sintering temperature or time of milling. This is consistent with previous results. Generally the hardness values of ball milled vacuum sintered materials were also found to be superior to the ones of attritor milled ones. It must be noted that the exception was with attritor milled and high-temperature sinter/HIP sintered samples resulting in high hardness properties, resulting in extraordinary hardness-strength relationship. The hardness values for vacuum sintered materials were inferior in the range of 30 to 90 of Vickers number for the same times of attritor milling at 1480°C.

Table 10. Hardness HV_{30} of vacuum- and Sinter/HIP sintered alloys

	Time of milling, h / method	Sintering temperature, °C				
		1360	*1390*	*1420*	*1450*	*1480*
Vacuum sintering	*1 / attritor*	770	1126	1307	1099	1356
	2 / attritor	1235	1336	1586	1428	1577
	4 / attritor	1495	1578	1571	1601	1583
	8 /attritor	1517	1624	1570	1567	1577
	16 / attritor	1496	1614	1539	1568	1545
	7 / ball mill	1686	1681	1628	1679	1570
Sinter/HIP sintering	*1 / attritor*	860	1100	-	1140	1601
	2 / attritor	1220	1588	-	1502	1637
	4 / attritor	1453	1570	-	1544	1617
	8 /attritor	1557	1618	-	1618	1632
	16 / attritor	1459	1588	-	1599	1610
	7 / ball mill	1650	1686	1569	-	1573

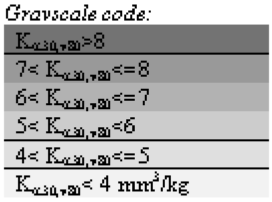

Grayscale code:

HV_{30}<1500 MPa
1500 <=HV_{30}< 1550 MPa
1550<=HV_{30}< 1600 MPa
1600<=HV_{30}< 1650 MPa
HV_{30}>=1650 MPa

Erosion rates for 1.00 theoretical density vacuum sintered alloys (Table 11) are ranging from 3,8 to 7,6 mm^3/kg.

Table 11. Erosion rate K, mm^3/kg of vacuum- and Sinter/HIP sintered alloys (V=80m/s, a=30^o)

	Time of milling, h / method	Sintering temperature, °C				
		1360	*1390*	*1420*	*1450*	*1480*
Vacuum sintering	*1 / attritor*	32.5	20.7	14.3	13.8	11.9
	2 / attritor	17.3	9.5	8.8	9.2	6.8
	4 / attritor	8.0	5.4	7.6	5.7	4.6
	8 /attritor	6.8	5.6	6.0	5.7	6.3
	16 / attritor	6.8	5.3	7.4	5.4	6.0
	72 / ball mill	5.2	3.8	5.1	4.1	6.2
Sinter/HIP sintering	*1 / attritor*	41.1	22.2	-	12.7	7.4
	2 / attritor	20.2	7.7	-	8.1	7.0
	4 / attritor	7.2	5.8	-	6.8	6.4
	8 /attritor	5.7	5.4	-	5.8	6.7
	16 / attritor	6.1	5.2	-	6.3	5.6
	72 / ball mill	4.9	-	8,5	-	8.9


Grayscale code:

$K_{\alpha 30, v80}$>8
7< $K_{\alpha 30, v80}$<=8
6< $K_{\alpha 30, v80}$<=7
5< $K_{\alpha 30, v80}$<6
4< $K_{\alpha 30, v80}$<=5
$K_{\alpha 30, v80}$< 4 mm^3/kg

For material selection in erosive wear applications (using Tables 10 and 11) ball milled materials with low-temperature vacuum sintering can be proposed, as resulted in superior wear resistance and hardness accompanied with fair strength properties. For applications with higher stresses and erosive wear high-energy milling of cermets, milled up to nano-powders (in the present case at least 4 hours of milling, being at about 10m^2/g of BET special surface area) and Sinter/HIP treatment is recommended.

Although there is a fair correlation of erosion rates with hardness values the approximate predictions cannot be made as the wear resistance at the same hardness values can differ in some cases up to 80% (see Figure 48).

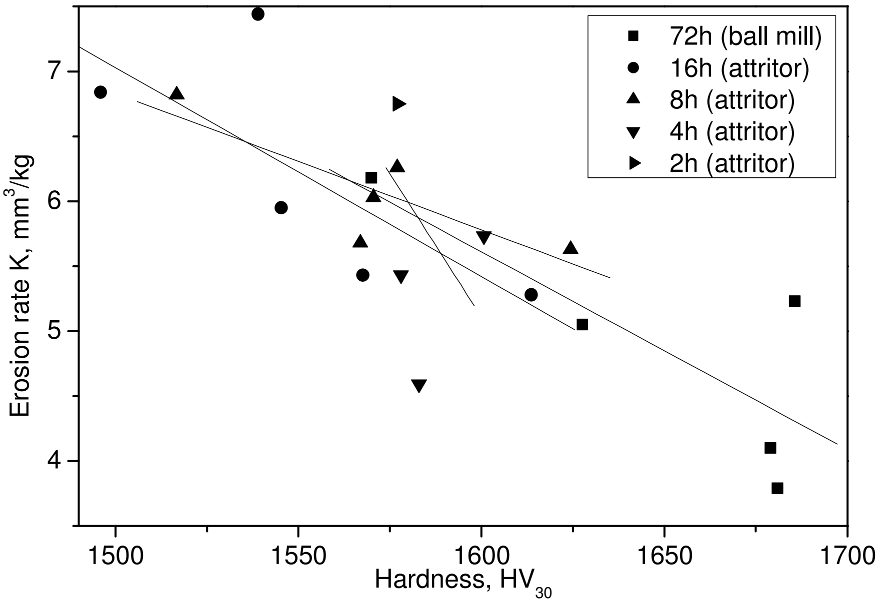


Figure 48. Erosion rate K versus Vickers hardness number vacuum sintered TN20A cermets

3.5.4 Property – structure relations

Microstructure parameters – core and grain size – of vacuum sintered alloys were compared in accordance with strength, hardness and erosive wear properties.

Transverse rupture strength values (Figure 49) of ball milled materials is well in accordance with previous results (Figure 2) postulating that for fine-grain alloys the strength increases with increased thickness of surrounding rim.

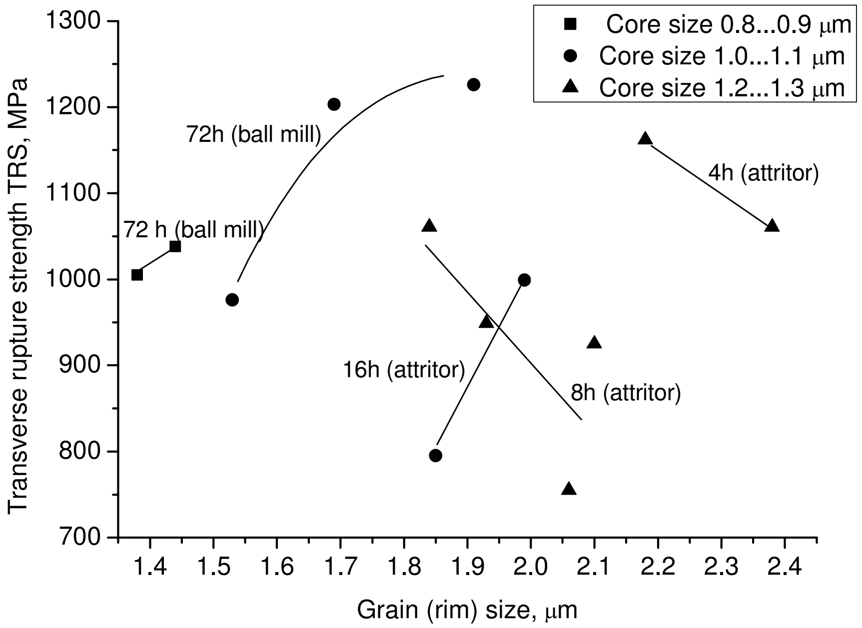


Figure 49. Transverse rupture strength of vacuum sintered alloys versus grain size

For attritor milled materials no conclusions could be drawn about the strength – grain, core size relations. Probably there are other factors prevailing, like different amount of alloying elements in binder, microstructural inhomogeneity, grain morphology factors etc.

Similar situation can be seen in hardness- grain size relationship diagram (Figure 50). The values of ball milled materials are vastly decreasing with the increasing grain size, regardless of core size. For attritor milled samples this trend seems to be opposite. Some differentiation between samples of different milling periods can be made. Cermets from 8 and 16 hours milled powders show steady increase of hardness with higher grain sizes. Samples from 4 hours of milling show similar increase at lower levels and from 2 hours steady decrease can be observed.

The results for erosion wear tests (Figure 51) show again the relevance of degree of milling on performance. When wear rate shows sustained growth with larger particles in the case of ball milled materials, for high-energy milled materials the growth is sustained and turning negative in the case of lower time of milling materials.

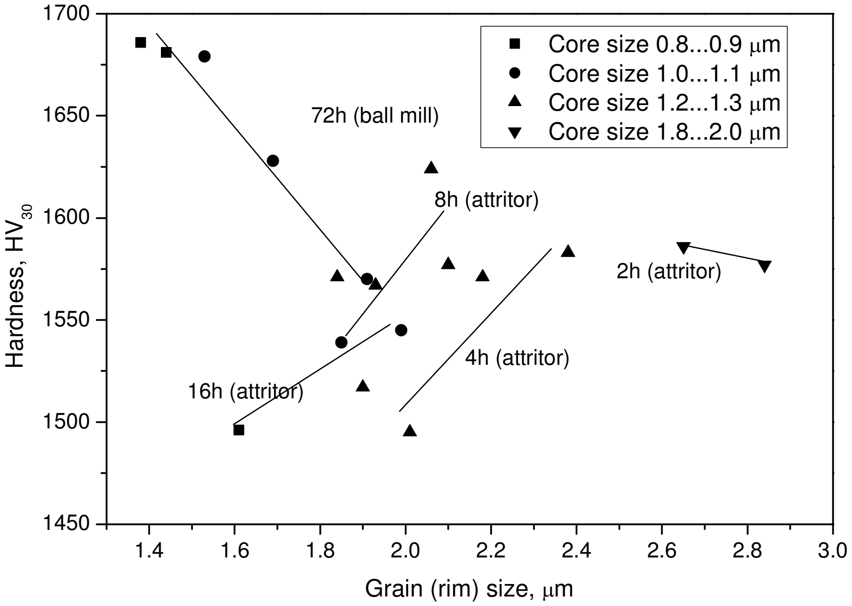


Figure 50. Hardness of vacuum sintered alloys versus grain size

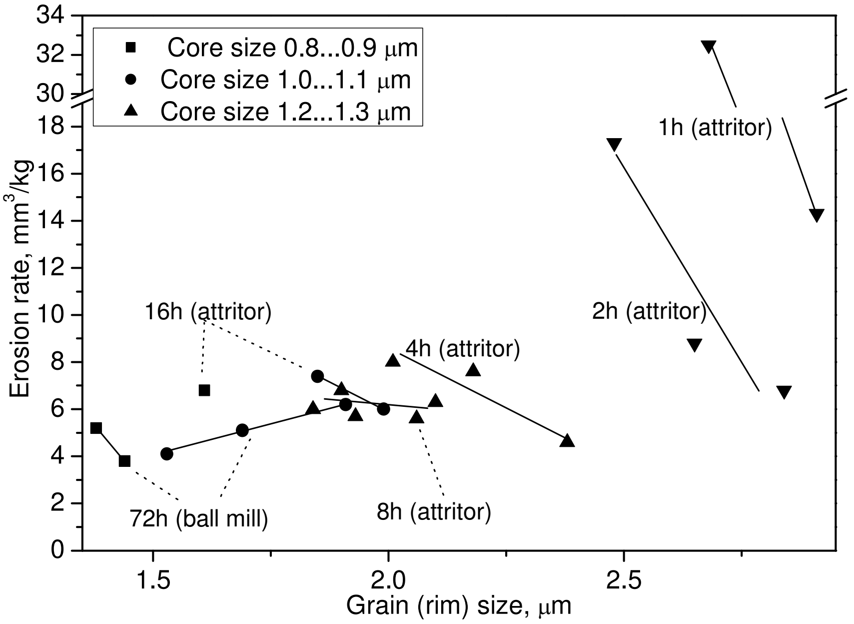


Figure 51. Erosion rate of vacuum sintered alloys versus grain size

3.5.5 Technology of reactive sinter/HIP sintering for grain refinement

It is known that reactive processing enables producing cermets with very fine microstructures (Paragraph 2.1.2). Normal coaxial carbide structures are known not to develop during reactive processing, instead binary (Ti,Me)C; Me=Mo,W in binder alloy matrix have evolved.

This concept is very attractive for its low-cost initial materials, new type of materials properties, new possible materials combinations etc.

The possibility to elaborate fine-grain cermets and structure development during reactive Sinter/HIP sintering was investigated.

Structure development

After eight hours of milling in attritor mill, the XRD phase analysis (Figure 52) confirms the remaining metallic phases. Some grain broadening has occurred, showing grain refinement and strain hardening of the particles. No carbide formation was detected, although a part of carbon phase is expected to have been transformed amorphous.

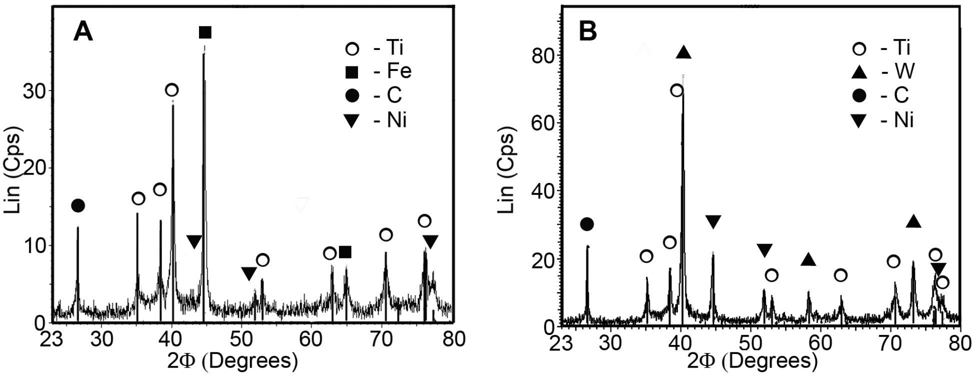


Figure 52. XRD patterns of the milled powders: A) Ti-Fe-C-Ni-Si and B) Ti-W-C-Ni powders

The densification behaviour of the materials is shown in Figure 53. Sustained densification of the materials was observed between 1360 and 1450^{o}C. The samples sintered to maximum temperature were densified up to a porosity level in order of two percents (see Table 3).

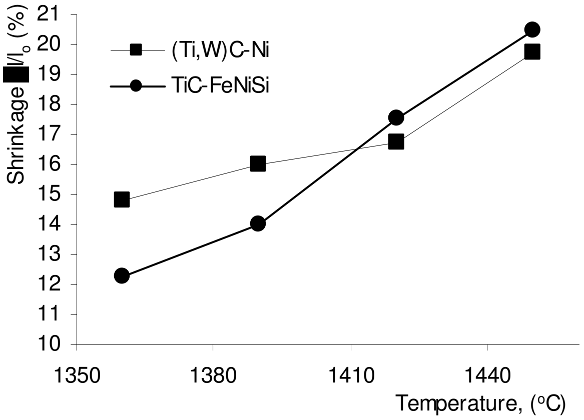


Figure 53. Linear shrinkage of the materials as a function of sintering temperature

Microstructures of cermets sintered at 1360°C and 1450°C are shown in Figure 54. At lower sintering temperatures fine-grained structure of cermets were observed.
At higher temperatures, accompanied with densification both cermets show extensive grain coarsening, being remarkably more intensive compared to regular materials.

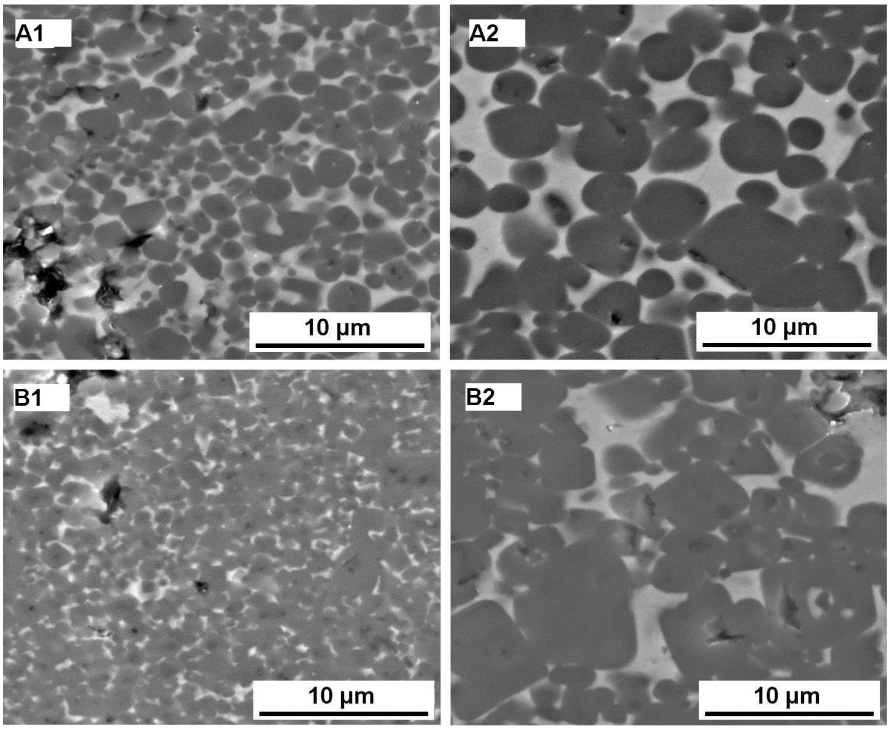


Figure 54. Microstructures of sintered cermets: A – TiC-FeNiSi cermets; B – (Ti,W)C-Ni cermets, sintered at: 1) 1360°C and 2) 1450°C

In the microstructure of (Ti,W)C cermet small cores surrounded by white inner rim can be observed (Figure 3, B2). Energy Dispersive Spectroscopy (EDS) line scan analysis on a large grain was chosen (Figure 55). Core of (Ti,W)C and rim contain tungsten and an enrichment around the core was detected. This enrichment may be traced back to a solution-reprecipitation process which is encountered also in common cermets containing tungsten carbide. Crystallization centres in the present are consisting of (Ti,W)C carbides, around which the inner and outer rim have reprecipitated during the cooling period.

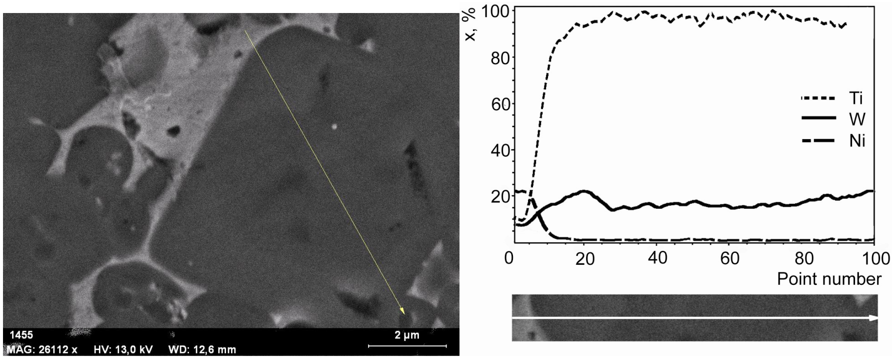


Figure 55. EDS line scan of (Ti,W)C core of cermet sintered at 1450^{o}C

Mechanical properties

Due to the fact that pore-free fine grain materials were not achieved the further investigation on performance properties was not investigated.

Some properties of coarse grained materials were determined (Table 12). The hardness of (Ti,W)C-Ni cermet is considerably lower compared to regular materials due to inferior hardness of carbide grains (also previously stated for coreless cermets [68]). TiC-FeNiSi cermet shows hardness values comparable to common steel bonded cermets with equal carbide fraction [23]. Due to not fully eliminated porosity strength values do not achieve the values of common materials.

Table 12. Hardness, porosity and transverse structure strength of studied materials

Grade	TRS, MPa	Hardness HV_{10}	Porosity, %
(Ti,W)C-13Ni	497	1160	2.33
70TiC-Fe14Ni1,5Si	919	1200	1.89

3.5.6 Conclusions

1. Difference in microstructure development mechanisms for ball milled and attritor milled materials was found. Short high-energy milling periods resulted in prevailing coherency strain and reprecipitation. For materials from higher time period initial coalescence of nanoparticles was presumed, leading to homogenous

grain size distribution. For ball milled samples the reprecipitation processes were found to prevail.

2. Strength enhancement after Sinter/HIP is is more likely for high-energy milled materials. The best results were obtained for high temperature sintered materials.

3. For erosive wear applications conventional ball milled materials with low-temperature vacuum sintering can be proposed. These materials have superior wear resistance and hardness with accompanied fair strength properties.

4. For applications with probability of fracture high-energy milled materials, milled up to BET surface area at least 10 m^2/g and high-temperature Sinter/HIP is recommended.

5. Ball milled materials are following the grain size-mechanical property relationships similar to previous results from literature. The relationships for high-energy milled materials are involving other prevailing mechanisms of structure development still need to be specified.

6. Titanium carbide cermets were produced by reactive sintering of high-energy milled powders. Fine microstructures could be achieved at low sintering temperatures but were accompanied by high porosity of the materials. At higher temperatures extensive grain coarsening was observed. Microstructure development of the cermets has found to proceed through coalescence and solution-reprecipitation processes. After sintering the microstructure of (Ti,W)C-based cermet is consisting of binary carbide cores surrounded with tungsten-rich inner rim and binary carbide outer rim.

7. Technology of high-energy milling and reactive sintering is one possible low-cost production method of wear resistant ceramic-metal composites.

4 Conclusions and suggestions

4.1 Concluding remarks

The main conclusions of the present thesis are as follows.

1. Optimal sintering technologies were developed for TiC-based cermets with FeNi and NiMo binders. Alloys with higher binder content and these bounded with iron alloys are characterized by higher oxygen sensitivity. Oxidation damage was found to result in poor microstructure accompanied with inadequate strength properties and performance in adhesive wear conditions. Two-step hydrogen presintering – vacuum sintering technology is applicable for alloys with higher content of TiC (70wt%).One-step vacuum presintering – vacuum sintering technology is recommendable for alloys with lower TiC content (60wt%) bonded with iron alloy.
2. It was proven that the sinter/HIP technology enables improvement in strength properties of TiC-based cermets. The increase is more pronounced for high carbide fraction alloys.
3. Abrasive-erosion properties cannot be increased by sinter/HIP due to predominant shear stresses in such degradation conditions. Unlike abrasive-erosion considerable adhesive wear performance improvement of sinter/HIP sintered alloys was revealed due to predominant tension stresses prevailing in such surface degradation conditions. Increase in adhesive wear resistance and transverse rupture strength of sinter/HIP sintered TiC-FeNi cermets enables increase of carbide content of cermets for sheet metal blanking tools with superior functional properties compared to these of traditional WC-Co alloys.
4. Optimum Sinter/HIP and vacuum sintering technologies were developed for Ni-alloy cermets from traditional (ball milled) and from nanostructured (high-energy milled) powders. Strength properties could be considerably increased after high-temperature sintering. Such phenomenon was attributed to higher malleability of the binder phase for pore elimination.
5. Different types of structure development mechanisms were revealed in alloys from high-energy milled powders – coherency strain for minimum time of milled samples, resulting in decrease of core size at higher sintering temperatures. Initial coagulation was expected for nanopowder sintering and following normal grain growth by solution reprecipitation, resulting in inhomogeneous grain size distribution. Large grains with plate-like cores were observed in the microstructure.
6. The optimum erosive wear performance of high-energy milled and ball milled TN20A materials was evaluated. For the best erosion wear resistance with fair strength properties low-temperature vacuum sintered alloys are most adequate. If additional high strength is needed high-energy milling up to nanostructured powders, accompanied with high-temperature sinter/HIP is recommended.

4.2 Suggestions for research

The sinter/HIP technologies show great potential for improvement of cermet performance properties. For further understanding of gas pressure effects during sintering the effect of post-sintering operations like thermal treatments, grinding processes and chemical vapour deposited coatings should be studied.

As in the case of TiC-NiMo cermets the mechanical property improvements occurred after sintering high temperatures (for the remained fine microstructures), the mechanisms of such hindered grain growth must be revealed. Accordingly other sintering processes, like pulsed sinter/HIP would be perspective for further property enhancement.

The effects of microstructure on mechanical properties cermets from high-energy milled powders are still not fully understood. The grain morphology, intrinsic stress states in the materials and probably binder microcomposition should be studied in order to explain the grain size-mechanical and wear property relationships. Additionally sinter/HIP sintered cermets grain size-mechanical property relations should be revealed.

Microstructure refinement in this study was not accomplished by using high-energy milled powders due to coalescence of nanoparticles at early stages of liquid phase sintering. As the state of solid state sintering of long-period high-energy milled powders was considerably higher compared to common ball milled materials the solid state sintering and hot isostatic pressing at orders of magnitudes higher gas pressures than sinter/HIP could provide ultrafine or nanostructured materials.

Due to high risk of oxidation it is extremely difficult to produce defect-free TiC-FeNi steel cermets from high-energy milled powders. Nevertheless this route is mostly interesting due to the property of decreased eutectic temperature of nanostructured steel binder, allowing sintering at reduced temperatures.

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List of publications

The majority of the contents of dissertation have been published in following author's original papers:

I H. Klaasen, L. Kollo, J. Kübarsepp, Performance of TiC-base cermets sintered by different techniques. Materials science & technology 21[9] (2005) 1049 – 1053.

II. H. Klaasen, L. Kollo, J. Kübarsepp, Mechanical properties and wear performance of compression sintered TiC-base cermets. Powder Metallurgy, 50 (2007) 132 - 136.

III. H. Klaasen, J. Kübarsepp, L. Kollo, Performance of sinterhipped TiC-base cermets. In: Proceedings of EURO PM 2006 Congress & Exhibition, Ghent, Belgium, 23-26 Oct. 2006, Vol. 1, Hard Materials, 213 - 216.

IV. H. Klaasen, L. Kollo, J. Kübarsepp, M. Viljus, Pressurized sintering of TiC-base cermets. In: Proceedings of EURO PM 2007 Congress & Exhibition, Toulouse, France, 14-17 Oct. 2007, Vol. 1, 213 – 216.

V. L. Kollo, J. Pirso, K. Juhani, Effect of Sinter/HIP technology on Properties of TiC-NiMo Cermets, Materials Science Forum, 534-536 (2007) 1169 – 1172.

VI. L. Kollo, O. Volobujeva, Reactive sintering of (Ti,W)C-Ni and TiC-FeNiSi cermets from high-energy milled powders, Pressurized sintering of TiC-base cermets. In: Proceedings of EURO PM 2007 Congress & Exhibition, Toulouse, France, 14-17 Oct. 2007, Vol. 1, 227 – 231.

Abstract

„Sinter/HIP Technology of TiC-based Cermets"

The losses resulting from wear in life cycle costs of equipment and components may be tremendous. Therefore development of advanced wear resistant materials and related technologies is still important in different industrial sectors.

The present study focuses on TiC-based cermets for metalworking industry (alloys TiC-FeNi) and for application conditions with prevalence of erosion wear (especially mining, oil refinery and paper industry) – alloys TiC-NiMo.

One important property impeding the breakthrough of such materials is strength and erosion wear resistance demanded in many application conditions.

Sintering technologies for wear performance and mechanical reliability improvement were studied in this work. It was proved the ability of proper vacuum sintering and sinter/HIP sintering technology to greatly enhance the strength and wear (in adhesive wear conditions) properties of TiC-based cermets. Functional testing (blanking of sheet steel) proved superiority of sinterhipped cermet with increased TiC content over conditional vacuum sintered one.

Advanced technologies for studying initial powder grain size effect and microstructure refinement (high-energy milling, reactive sinter/HIP) of TiC-based cermets were investigated. The effect of technological parameters on structure development and material characteristics is under discussion.

Key words: Sinter/HIP, cermets, blanking tools, erosion wear, powder metallurgy.

Kokkuvõte

„Titaankarbiidkermiste survepaagutustehnoloogia”

Üks peamisi seadmete ja masinadetailide lühikese elutsükli ja sellega seotud suurte kulutuste põhjuseid on kulumine. Selle tõttu paljudes tööstusharudes on jätkuvalt oluline kulumiskindlate materjalide ja tootmistehnoloogiate väljatöötamine.

Käesolev töö käsitleb titaankarbiidseid kermiseid kasutamiseks tööriistamaterjalina lehtmetalli väljalõikestantsimisel (sulamid TiC-FeNi) ja rakendustes kus prevaleerib erosioonkulumine (eriti mäe-, nafta- ja paberitööstuses) – sulamid TiC-NiMo.

Nimetatud materjalide laialdast kasutamist tööstuses on seni pärssinud mõõdukad tugevusomadused ja kulumiskindlus erosioonkulumisel.

Käesolevas töös uuriti paagutustehnoloogiat eesmärgiga parandada TiC-baasil kermiste kulumiskindlust ja mehaanilist töökindlust. Saavutati märkimisväärne tugevuse ja kulumiskindluse (adhesioonkulumise tingimustes) kasv rakendades sobivat vaakum- ja survepaagutustehnoloogiat. Funktsionaalsetel katsetel (väljalõikestantsimine) leidis kinnitust survepaagutatud kõrgendatud TiC sisaldusega kermise paremus vaakumpaagutatud sulami ees.

Uuriti TiC-kermiste algse pulbri terasuuruse mõju ning mikrostruktuuri peenendamise (karbiiditera suuruse vähendamise) võimalusi rakendades selliseid tehnoloogiaid nagu kõrgenergeetiline jahvatamine ja reaktiiv-survepaagutamine. Töös käsitletakse tehnoloogiliste parameetrite mõju kermiste struktuuri moodustamise protsessidele ja omadustele.

Märksõnad: survepaagutamine, kermised, stantsitööriistad, erosioonkulumine, pulbermetallurgia.

ELULOOKIRJELDUS

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Keel	Tase
eesti keel	emakeel
inglise keel	kõrgtase
soome keel	kõrgtase
vene keel	kesktase
hispaania keel	kesktase
saksa keel	kesktase

5. Täiendusõpe

Õppimise aeg	Täiendusõppe läbiviija nimetus
7-13.05.2005	Euroopa Pulbermetallurgia

	assotsiatsioon (EPMA)

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Töötamise aeg	Tööandja nimetus	Ametikoht
2002-2003	EMPA Thun, Šveits	praktikant
2003-2004	Tallinna Tehnikaülikool	insener
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7. Teadustegevus

   Komplitseeritud töötingimustes töötavate karbiidkermiste tehnoloogia

8. Kaitstud lõputööd

   A. Tuuling, BSc,

9. Teadustöö põhisuunad

   Loodusteadused ja tehnika, Protsessitehnoloogia ja materjaliteadus (Kõvasulamid, kulumiskindlad materjalid, paagutustehnoloogiad)

10. Teised uurimisprojektid

    WC-Co jäätmeist ülipeene- ja nanostruktuuriga kõvasulamite valmistamine;

    Õhukeste TiC/a-C:H pinnete nano- ja mikrotriboloogia.

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4. Language competence/skills (fluent; average, basic skills)

Language	Level
Estonian	mother tongue
English	fluent
Finnish	fluent
Russian	average
Spanish	average
German	average

5. Special Courses

Period	Educational or other organisation
7-13.04.2005	European Powder Metallurgy Association (EPMA)

6. Professional Employment

Period	Organisation	Position
2002-2003	EMPA Thun, Switzerland	trainee
2003-2004	Tallinn University of Technology	engineer
2004-…	Tallinn University of Technology	reseacher

7. Scientific work

   Technology of cemented carbides for complicated wear conditions
8. Defended theses
9. Main areas of scientific work/Current research topics

   Natural Sciences and Engineering, Process Technology and Materials Science (Hardmetals, cermets and related production technologies)
10. Other research projects

    Production of ultrafine and nanostructured WC-Co hardmetals from recycled scrap;

    Nano- and microtribology of TiC/a-C:H thin coatings.