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# Characterization of TiC-FeCrMn Cermets Produced by Powder Metallurgy Method

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TiC-NiMo cermets combine relatively low density with high hardness. Because nickel is known as a toxin and allergen and allergy to nickel is a phenomenon which has assumed growing importance in recent years there has been a flurry of activity to find alternatives to the nickel binder in cermets. It is also the global research and technical development trend in the powder metallurgy cermets industry. In present research TiC-based cermets with FeCrMn binder system were fabricated. Three different sintering conditions were used (vacuum sintering, sinter/HIP and sintering under low Ar pressure). Because of high vapor pressure of manganese different sintering conditions and technologies were investigated to depress the Mn-loss during sintering. Chemical composition of TiC-FeCrMn cermets after different sintering conditions were analyzed by energy-dispersive X-ray spectroscopy (EDS) and mechanical properties – hardness and fracture toughness were evaluated on the samples. Results of research showed that Ni-free TiC-based CrMn-steels bonded cermets compare unfavorably with cermets bonded with CrNi austenitic steels in terms of fracture toughness and corrosion resistance. Noticeable Mn-loss during vacuum sintering can be avoided when sintering under low Ar gas pressure.

*Keywords:* Ni-free cermets, austenitic stainless steel, titanium carbide-based cermets, pressurized sintering, manganese loss.

## 1. INTRODUCTION

Stainless steels containing more than 12 % Cr have been proved to be the most used corrosion resistant materials due to their good mechanical properties and fabricability. The most frequently used corrosion resistant materials are conventional stainless austenitic steels. Such steels contain in addition to chromium (16 … 23 wt.%) a large amount (10 … 28 wt.%) of nickel because nickel is the primary austenite stabilizing element. However, the greatest drawback with conventional stainless steel is susceptibility to localized corrosion in chloride-containing aqueous solutions. The alloying elements that increase the resistance of corrosion resistant steels to pitting and crevice corrosion are chromium, molybdenum and nitrogen [1]. Content of molybdenum in austenitic steels used in chloride containing aqueous solutions is usually 2 ... 8 wt.%.

REACH (The Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals) is classifying Ni and Co as very toxic for human health [2].The reports of metallic allergy and toxicity caused by these metals is increasing. Therefore removal of Ni from stainless steel for a number of applications is largely demanded.

Ni-free austenitic stainless steels having a large amount (wt.%) of manganese and nitrogen such as Fe- (15 – 23) Cr- (10 – 24) Mn- (0.5 – 6) Mo- (0.85 – 1.1) N have been developed. In such steels manganese and nitrogen are employed instead of nickel to obtain austenitic phase [3, 4].

Hardmetals (WC-based ceramic metal composites) are extensively used in applications demanding wear resistance, e.g. metal cutting or forming tools. The excellent wear resistance exhibited by the hardmetals is due to their combination of high hardness, wear resistance and moderate fracture toughness [5]. The most common are hardmetals WC-Co. Cobalt is widely used as the binder metal because of its good wetting behavior and good mechanical properties. However, cobalt has been in short supply and there are toxicity concerns. Additionally, in accordance to United States National Toxicology Program (NTP) the tungsten carbide-cobalt hardmetal dust has been shown to be more toxic in combination than either pure cobalt or tungsten carbide alone [6]. Therefore, there have been activities to find alternatives to the cobalt binder in hardmetals. The alternative to cobalt as a binder is either iron based or nickel based. From the health and safety aspect, nickel as a binder metal in hardmetals does not offer any advantage. On the other hand, the complete substitution of nickel for cobalt has proven to be the most effective means of extending the life of hardmetal in highly corrosive environments. Literature on the advantages and disadvantages of using iron as an alternative base component of binder shows that replacing cobalt (as well as nickel) by application tailored iron base grades is possible, but more research work is necessary [7, 8].

Previous research carried out in Tallinn University of Technology has proved possibility to produce and employ cobalt and tungsten free cermets on basis of titanium carbide produced using powder metallurgy press-and-sinter process. Vacuum sintering has been and is usually used for titanium carbide based cermets [9 – 11].

Mechanical properties (hardness, transverse rupture strength, plasticity, strain energy and fracture toughness) of

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iron-alloy (steel) bonded TiC-based cermets have been investigated to characterize their serviceability as material for tools and wear resistant parts of equipment. Both hardenable martensitic and austenitic steels, in particular corrosion resistant grades were used as metallic binder of carbide-metal composites [9]. Corrosion and corrosion-abrasive resistance of such corrosion resistant TiC-based cermets under neutral, acid and alkaline conditions have also been investigated [10]. Both high mechanical characteristics and corrosion resistance are characteristic of TiC-based cermets bonded with austenitic Fe-Cr-Ni stainless steels. Transverse rupture strength and fracture toughness of such composites are comparable to these of WC-Co hardmetals.

At the same time TiC-based cermets bonded with Cr-Ni austenitic steels compare favorably with corrosion resistance of hardmetals. From the health aspect it is better to replace Ni in austenitic steels by alternative austenite stabilizing elements.

Performance and reliability of ceramic-metal composites depends to a great extent on their production technology in particular sintering technology (mode). Investigation of the influence of a sintering mode (vacuum sintering, sinter/HIP and sinter + HIP in different cycles) on the performance and reliability of TiC- and $Cr_3C_2$-based cermets revealed that sinter/HIP-ed TiC-based cermets are featured by a microstructure of high homogeneity and are characterized by decreased porosity when compared to vacuum sintered cermets. In general the positive effect of sinter/HIP on performance increases with an increase in the carbide fraction in the composite. HIP conducted in two different cycles (sinter + HIP) is at a disadvantage as compared to the one-cycle sinter/HIP technology [11].

In present work the aim was to develop and produce TiC-based cermets bonded with Ni-free austenitic steels. The cermets should demonstrate the following minimum characteristics: Vickers hardness (HV) upper than of silica sand (HV 1100...1200), fracture toughness ($K_{IC}$) upper than ceramics ($K_{IC} \geq 6.0$ MPa $m^{1/2}$) and corrosion resistance in chloride containing solutions.

## 2. EXPERIMENTAL DETAILS

Characteristics of starting powders used in production of composite are listed in Table 1.

Cermets were produced using conventional PM route: mechanical milling (grinding and mixing in ball mill) in liquid media (ethanol) using ball mill (WC-Co lining and balls) with rotating speed of 60 rpm, ball-to-powder ratio of 1:10. Milling time was set at 72 hours.

The uniaxial pressed specimens were sintered under vacuum (vacuum level was approximately 5 x $10^{-2}$ mbar), by sinter/HIP (30 bar) and by sintering under low Ar gas pressure (see Fig. 1).

**Table 1.** Chemical composition (wt%), average particle size (μm) of powders used for production of TiC-FeCrMn cermets

| Powder | Basic components, % | Impurities | Average particle size, μm |
|---|---|---|---|
| TiC | Ti, $C_{comb}^{19,12}$,<br>$C_{free}^{0,15}$ | O – 0.30;<br>N – 0.02 | 2.6 |
| Fe | 99.72 | Si – 0.01<br>P – 0.07<br>Mn – 0.02 | < 100 |
| Mn | Mn – 99.84 | O – rest | 7.95 |
| Cr | Cr – 99.5 | O = < 0.38<br>Fe – 0.01 | 6.65 |
| Mo | > 99.80 | Fe – 0.0025<br>O – 0.110 | 2.48 |
| Fe-Si | Si – 48.2,<br>Fe – 50.1 | Al – 1.1<br>Cr – 0.2<br>Mn – 0.4 | < 100 |

Fracture toughness and hardness were determined using ground test pieces of 5 x 5 x 17 mm. Hardness measurements (Vickers hardness) were carried out in accordance with the standard EN-ISO-6507.

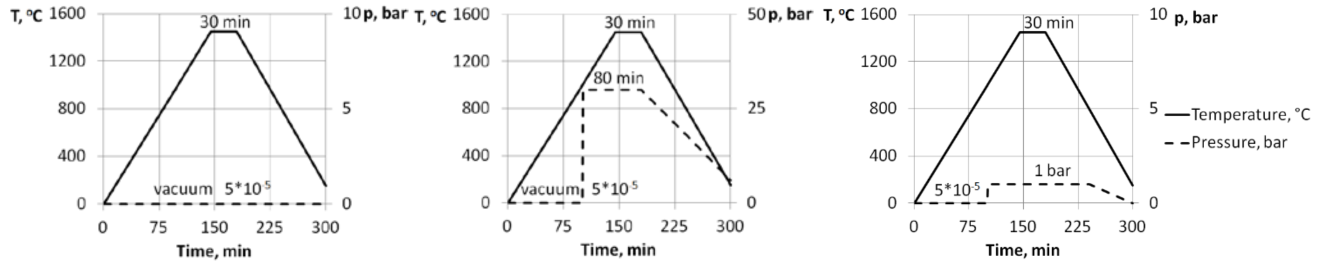
Indentation fracture toughness ($K_{IC}$) was measured using one of the most used empirical equations proposed by Evans [12].

$$K_{IC} = 0.16 \cdot \left(\frac{c}{a}\right)^{-1.5} \cdot \left(H \cdot a^{\frac{1}{2}}\right), \tag{1}$$

where $c$ is the average length of the cracks obtained in the tips of the Vickers indentations, (μm); $a$ is the half average length of the diagonal of Vickers indentations, (μm); $H$ is Vickers hardness, (MPa).

Corrosion resistance was assessed using immersion test in NaCl containing (3 %) water solutions during 72 hours. The corrosion resistance was evaluated using observation method (quality).

Microstructural analysis was carried out using scanning electron microscope (SEM) JOEL JSM 840A. Chemical composition of cermets after sintering was analyzed using X-ray spectroscopy (EDS). The porosity of cermets was determined using optical microscope Axiovert25 microscope and software Buehler Omnimet.



Mode 1 Mode 2 Mode 3

**Fig. 1.** Sintering modes of cermets TiC-FeCr26Mn20 (Mode 1 – vacuum sintering, $5 \cdot 10^{-2}$ mbar; Mode 2 – sinter/HIP, 30 bar; Mode 3 – sintering in Ar, 1 bar)

**Table 2.** Calculated chemical composition and mechanical characteristics of TiC-based (70 wt.% TiC) vacuum sintered (sintering mode 1) and sinterhipped (sintering mode 2) cermets

| Grade | Sint. Mode | Chemical composition (calculated), wt.% | | | | | Porosity, % | Hardness, $HV_{30}$ | $K_{IC}$, $MPa \cdot m^{1/2}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | TiC | Cr | Mn | Mo | Ni | | | |
| T70/FeCr21Mn14 | 1 | 70 | 6.3 | 4.2 | - | - | 0.60 | 1400 | 7.0 |
| T70/FeCr26Mn20 | 1 | 70 | 7.8 | 6.0 | - | - | 0.56 | 1520 | 6.9 |
| T70/FeCr26Mn20 | 2 | 70 | 7.8 | 6.0 | - | - | 2.34 | 1350 | 9.8 |
| T70/FeCr26Mn20Mo5 | 1 | 70 | 7.8 | 6.0 | 1.5 | - | 0.24 | 1310 | 5.7 |
| T70/FeCr22Ni16 | 1 | 70 | 6.6 | - | - | 4.8 | 0.30 | 1230 | 13.8 |

## 3. RESULTS AND DISCUSSION

The study covers the TiC-based cermets cemented with Ni-free corrosion resistant CrMn and CrMnMo steels. Manganese was used as austenitizing element replacing nickel while molybdenum was used as alloying element which in combination with chromium is effective in terms of stabilizing the passive film in presence of chlorides. Cermet bonded with regular austenitic nickel containing corrosion resistant steel was used as reference material. Calculated chemical composition and mechanical characteristics of TiC-based cermets are presented in Table 2.

Results of screening experiments demonstrate that Ni-containing austenitic steel-bonded cermet (reference material) is characterized by higher performance characteristics – fracture toughness (Table 2) and corrosion resistance in presence of chlorides in water in comparison with TiC-FeCrMn-type cermets. Marked decrease in austenitizing Mn content during vacuum sintering should probably account for such a result first of all because binder of TiC-FeCrMn cermets, unlike TiC-FeCrNi ones is not austenitic (nonmagnetic).

Depression of manganese loss during sintering can be achieved using gas compression during sintering. Manganese loss in different sintering modes (regular vacuum liquid-phase sintering, sinter/HIP under isostatic gas (Ar) pressure of 30 bar and sintering in argon gas pressure of 1 bar) was determined. Chemical composition of cermet gradesafter sintering using different sintering modes is presented in Table 3.

Results in Table 3 prove drastic reduction of manganese content during vacuum sintering. Both sintering under gas pressure 1 bar and 30 bar enable to retain the majority of Mn in alloy (calculated Mn content in cermet 6 wt.%). There are no remarkable differences in chemical compositions using two pressurized sintering modes (Ar gas pressure of 30 bar or 1 bar, respectively sintering mode 2 and 3).

Sinterability evaluated by residual porosity of alloys is in general the better the lower gas compression during sintering. Therefore mechanical characteristics of cermets of different chromium content in binder (20 and 26 wt.%) were determined after sintering using sintering mode 3 – sintering at 1450 °C under gas pressure of 1 bar, sintering time 0.5 h (see Table 4).

Most cermets have acceptable mechanical characteristics. However, cermets alloyed by silicon (used in high chromium cermets for better sinterability [9, 10]) demonstrate more homogenous microstructure (compare microstructures Fig. 2 and Fig. 3) and reduced porosity.

**Table 3.** Sintering technology vs chemical composition of TiC-based cermet grade T70/FeCr26Mn20 (EDS analysis)

| Sintering mode | Sintering Technology | Chemical composition, wt.% | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | C | Ti | Cr | Mn | Fe | W | Total |
| 1 | T=1450°C, vacuum $p=5 \cdot 10^{-5}$ bar | 14.49 | 60.26 | 5.25 | 0.45 | 12.38 | 7.19 | 100.00 |
| 2 | T=1450°C, p=30bar (Ar) | 15.43 | 59.15 | 3.47 | 3.69 | 11.16 | 7.09 | 100.00 |
| 3 | T=1450°C, p=1bar (Ar) | 14.21 | 54.13 | 7.20 | 4.05 | 13.62 | 6.01 | 100.00 |

**Table 4.** Calculated chemical composition and mechanical characteristics of 70TiC-FeCrMn cermets (sintering mode 3 in Fig. 1.)

| Grade | Binder composition (calculated), wt.% | | | | Porosity, % | Hardness, $HV_{30}$ | $K_{IC}$, $MPa \cdot m^{1/2}$ |
|---|---|---|---|---|---|---|---|
| | TiC | Cr | Mn | Si | | | |
| T70/FeCr20Mn20 | 70 | 6.0 | 6.0 | - | 0.83 | 1450 | 5.6 |
| T70/FeCr20Mn30Si2 | 70 | 6.0 | 9.0 | 0.06 | 0.23 | 1305 | 7.6 |
| T70/FeCr26Mn20 | 70 | 7.8 | 6.0 | - | 2.33 | 1220 | 6.6 |
| T70/FeCr26Mn20Si2 | 70 | 7.8 | 6.0 | 0.06 | 0.67 | 1590 | 8.7 |
| T70/FeCr30Mn20 | 70 | 9.0 | 6.0 | - | 1.54 | 1300 | 8.9 |
| T70/FeCr30Mn20Si2 | 70 | 9.0 | 6.0 | 0.06 | 0.81 | 1380 | 6.4 |

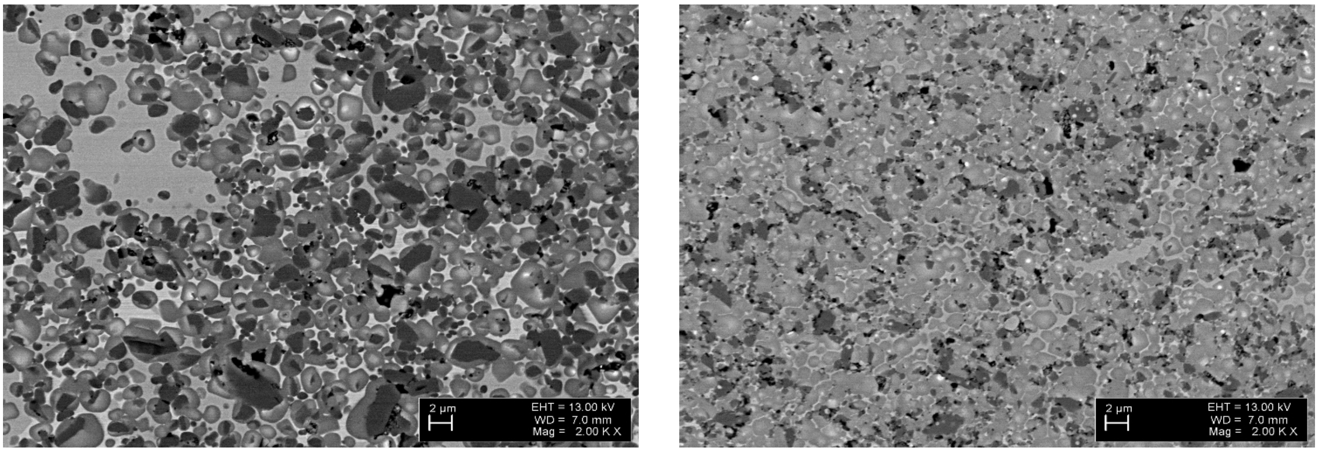


**Fig. 2.** Microstructure of cermets 70TiC-FeCr26Mn20 (left) and 70TiC-FeCr26Mn20Si2 (right) after sintering in argon (sintering mode 3 in Fig. 1)

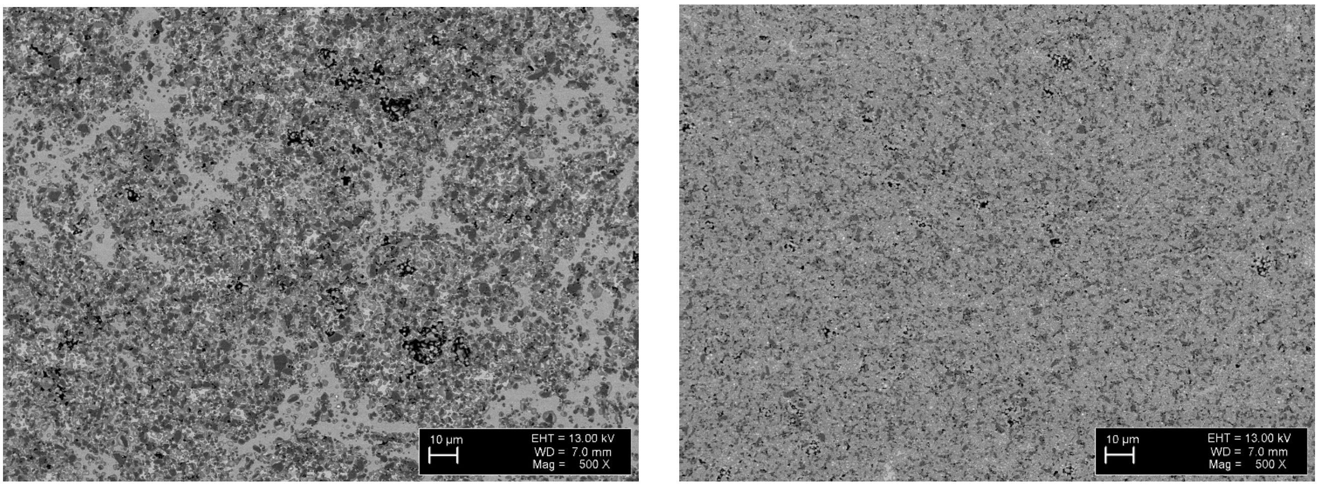


**Fig. 3.** Microstructure of cermets 70TiC-FeCr26Mn20 (left) and 70TiC-FeCr26Mn20Si2 (right) after sintering in argon (sintering mode 3 in Fig. 1)

Higher homogeneity in microstructure and acceptable mechanical characteristics do not ensure sufficient corrosion resistance of such cermets in chloride containing water solutions. TiC-FeCrNi cermets with austenitic steel binder compare favorably with Ni-free TiC-FeCrMn cermets in terms of corrosion resistance (Fig. 4) and fracture toughness (Fig. 5). Further research must be done to optimize both composition and technological peculiarities of Ni-free cermets.

**Fig. 4.** Corrosion resistance immersion tests in chloride containing solution: TiC-FeCr20Mn30Si2 (left) and 70TiC-FeCr22Ni16 (right)

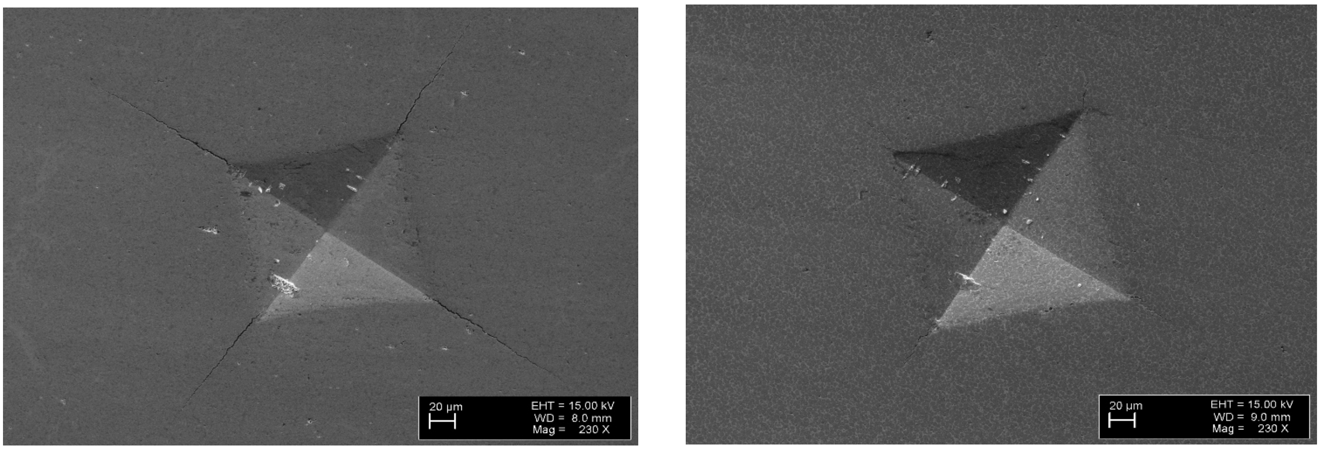


**Fig. 5.** SEM images of Vickers indentation ($HV_{30}$) of cermet 70TiC-FeCr22Ni16 (left) and TiC-FeCr20Mn30Si2 (right)

## 4. CONCLUSIONS

- Goals of research were achieved in terms of mechanical characteristics – hardness and fracture toughness Corrosion resistance in chloride containing solutions of TiC-FeCrMn composites is not acceptable.
- Ni-free TiC-based CrMn-steels bonded cermets compare unfavorably with cermets bonded with CrNi austenitic steels in terms of fracture toughness and corrosion resistance.
- Marked decrease in austenitizing manganese content during vacuum sintering takes place.
- Depression of Mn loss can be achieved using gas compression during sintering leading, however to decrease in sinterability (increase in porosity).
- Further research must be done to optimize both composition and technological peculiarities of Ni-free cermets.

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