Alloying of TiC-FeCr cermet in manganese vapor

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Abstract. Conventional vacuum sintering is not suitable for producing manganese containing cermets because of the physical-chemical properties of manganese, high vapor pressure, combined with high sintering temperature of cermets (1400-1600 °C). Sintering in Mn-rich microatmosphere does not only prevent Mn loss, but also enables additional in-situ alloying of the binder phase during sintering. We studied alloying of TiC-based cermet bonded with high chromium steel during sintering in Mn-rich atmosphere. Sintering in manganese vapor was found to increase sinterability of the TiC-FeCr cermet, resulting in the formation of ~1 mm thick Mn-rich surface layer with homogeneous microstructure while the core region of the material remained unaffected. This core region exhibited highly increased Mn content and competitive mechanical properties – hardness of ~1200 HV30 and indentation fracture toughness of ~13 MPa*m¹/². In addition, an unusual ε-type martensitic phase was observed in the surface layer.

1. Introduction
Nickel and cobalt are toxic for humans. Therefore, efforts have been made to find nontoxic alternatives for a binder in ceramic-metallic composites (cermets). Iron-based binder systems, in particular FeCr-alloys, are promising [1, 2] since iron is known as a nontoxic, accessible and cost-effective metal.

Manganese is a chemical element present in all commercial steel grades; moreover, it is a low-priced alloying element. Characterized as an active deoxidizer that improves the machinability, it enhances mechanical properties. Besides interstitial elements (carbon and nitrogen), manganese is also an effective γ-Fe (austenite) stabilizer. Our suggestion is that alloying iron-bonded TiC cermet with manganese can improve the mechanical properties of cermet. Manganese belongs to the group of crystalline materials, which, based on their physical–chemical properties, sublimate at the barometric pressure at temperatures below their melting point. The manifestation of the high vapor pressure during sintering is sublimation of elements from the powder or bulk material and its rate is dependent on the sintering temperature. These temperatures embrace practically the main range of sintering temperatures [3].

Alloying of powder compacts by the manganese gas phase was addressed by Salak et al. [4]. The study shows uniformly alloyed surface layers on iron particles in the compacts formed as a result of condensation of manganese vapor combined with high rate surface diffusion. Manganese vapor treatment for alloying is also used for platinum group metals [5].

In this study we investigated the alloying effect of the manganese vapor during the sintering of the TiC-FeCr cermet. The main focus was on the changes in the chemical composition and its effect on the microstructure.
2. Experimental Details

Nickel- and cobalt-free TiC-FeCr cermet powder mixture with 30 wt% of binder (initial, calculated value) was prepared using a common powder metallurgy process for ceramic-metallic composite powders: ball milling for 72 h in ethanol by WC-Co balls with ball-to-powder weight ratio of 10:1. Chemical composition, characteristics and producer of starting powders are presented in Table 1.

Table 1. Description of starting powders

| Powder | Chemical composition, wt% | Particle size, μm | Producer |
|--------|--------------------------|------------------|----------|
|        | Basic components | Impurities |        |            |
| TiC    | C<sub>comb</sub> - 19.12; Ti - bal. | O - 0.30; N - 0.02 | 2-4 | PPM Ltd. |
| AISI430L (X2Cr17) | Cr - 16.8; Mn - 0.69; Si - 0.64; Fe - bal. | C - 0.02; P - 0.01; S - 0.01 | 10-45 | Sandvik Osprey Ltd. |
| Mn     | Mn - 99.84 | O - rest | 7.95 | PPM Ltd. |

Paraffin wax was added to the powder mixture as compacting aid and green samples were prepared employing uniaxial pressing. In-situ alloying sintering was carried out in a vacuum furnace (Red Devil) using a specially designed chamber for the generation of manganese vapor microatmosphere [6]. Heating rate, maximum sintering temperature and holding time were 10 °C min⁻¹, 1400 °C and 30 min, respectively. The cross-sections of sintered specimens were prepared (ground and polished) for characterization.

Scanning electron microscope (SEM) Zeiss EVO MA15 equipped with the X-ray spectroscopy (EDS) system INCA was used for microstructural and elemental composition analysis. Phase composition was analyzed with Rigaku Smartlab using Cu Kα radiation and the step size of 0.02°. Vickers hardness and microhardness were measured with Indetec 5030 KV (load 294.2 N) and Micromet 2001 (load 1 N), respectively. The indentation fracture toughness (K<sub>IC</sub>) was measured using the Palmqvist method and the equation described in [7] (Eq. 8):

\[ K_{IC} = 0.16 \times \left( \frac{c}{a} \right)^{-1.5} \times \left( H \times a^2 \right), \]

where \( c \) is the average length of the cracks emanating from the tips of the Vickers indentations (μm); \( a \) is the half length of the diagonal of Vickers indentations (μm); \( H \) is Vickers hardness (MPa).

3. Results and Discussion

Table 2 demonstrates the calculated chemical composition before milling and after vacuum and alloying sintering (EDS elemental analysis). EDS analysis was performed near the surface and from the core region of the sintered samples. Chromium and manganese content in the surface and in the core of vacuum sintered TiC-FeCr cermet decreased considerably. The vacuum level during the vacuum sintering was approximately 10⁻⁵ mbar, which causes reduction of chromium and intense decrease of manganese content due to the sublimation and evaporation of these elements. On the other hand, during alloying sintering in Mn-rich atmosphere, the manganese content increases drastically in the surface layer of the TiC-FeCr cermet. It correlates with the change in weight – the mass decrease of vacuum sintered cermet was 3.1 wt% while the mass increase of alloying sintered cermet was 8.3 wt%. Nevertheless, the manganese content of the cermet core remained at the same level as the calculated chemical composition. This demonstrates that Mn losses can be prevented by creating a manganese vapor microatmosphere and manganese vapor in the sintering device has an alloying effect, however only in the surface layer of the cermet. The sublimation of manganese and formation of manganese vapor starts already at temperatures around 900-1000 °C [3]. The major densification of TiC-FeCr cermet does not occur earlier than the formation of the liquid phase at sintering temperatures around 1300 °C. Despite the fact that open porosity and manganese vapor coexist, alloying of specimen core does not occur during solid-state sintering (see Table 2.). The small fraction of tungsten in sintered specimens is caused by the wear of WC-Co milling balls.
Table 2. Chemical composition and weight change of TiC-FeCr cermet

|                  | Chemical composition, wt% | Weight change** |
|------------------|---------------------------|-----------------|
|                  | Ti*          | C*          | Fe | Cr | Mn | Si | W* |               |
| Calculated       | 56.63       | 13.37       | 24.56 | 5.04 | 0.21 | 0.19 | - |               |
|                  | Total Binder| 81.87       | 16.80 | 0.69 | 0.64 | - | - |               |
| Vacuum sintering | Surface layer | 63.06       | 15.02 | 14.22 | 3.09 | 0.12 | - | 4.49          |
|                  | Total Binder | -            | 91.96 | 6.34 | 0.50 | 1.20 | - | -              |
|                  | Core         | 59.26       | 14.44 | 17.91 | 4.20 | 0.11 | - | 4.08          |
|                  | Total Binder | -            | 92.97 | 5.41 | 0.65 | 0.98 | - | -              |
| Alloying sintering| Surface layer | 40.56       | 12.87 | 26.67 | 5.58 | 10.97 | - | 3.35          |
|                  | Total Binder | -            | 67.58 | 6.22 | 25.47 | 0.73 | - | -              |
|                  | Core         | 58.84       | 13.96 | 18.42 | 4.35 | 0.19 | - | 4.24          |
|                  | Total Binder | -            | 91.95 | 6.18 | 0.91 | 0.96 | - | -              |

*Although small Ti, C and W signals were detected in the binder as well, an assumption was made that the majority of them come from nearby TiC grains and not from the binder. Thus, the binder composition was recalculated excluding Ti, C and W.

**Weight change that occurs due to the debinding (removal of paraffin wax during sintering) is excluded.

Different sintering conditions have dissimilar influence on the microstructure of TiC-FeCr cermets sintered at 1400 °C. The SEM images of visually two-phase microstructures of TiC-FeCr cermets (darker TiC grains embedded in a brighter binder) after vacuum sintering and alloying sintering in Mn-rich atmosphere are presented in Figure 1. Microstructures of the surface layer and the core region are presented. As can be seen, the whole cross-section of the vacuum sintered cermet and the core of the alloying sintered cermet is characterized by an uneven distribution of the metallic binder phase (binder pools) and residual porosity. The inferior sinterability is caused by the insufficient reduction of oxides and limited wettability. In case of vacuum sintering, the TiC-FeCr cermet requires temperatures above 1475 °C for developing a uniform microstructure with low porosity [8]. However, the distribution of the binder on the surface of the sintered cermet is significantly improved during alloying sintering in manganese microatmosphere – the microstructure is homogeneous and the porosity has been decreased.

Figure 1. The SEM images of microstructures of TiC-FeCr cermet after vacuum sintering (top) and alloying sintering in Mn microatmosphere (bottom). Microstructures of the surface layer (left) and the core region (right) are presented.
It is the result of high deoxidation ability of manganese influencing the sinterability – it improves wetting conditions between the solid carbide grains and the liquid metallic binder phase. Figure 2 presents the optical microscope (OM) images of the surface layer and the core of the TiC-FeCr cermet after alloying sintering and EDS line scan as an indication of the Mn content. The thickness of the Mn-rich surface layer that exhibits uniform microstructure and low porosity is roughly 1 mm. The hardness of the surface layer is around 1200 HV30 and as the Mn content decreases, the hardness of the cermet increases. Such result was expected since the fraction of a more ductile and plastic metallic binder is considerably higher in the surface layer. However, the hardness near the core of the sample has very high uncertainty due to the highly heterogeneous microstructure. Due to the uniformity of the microstructure, the indentation fracture toughness was measured only from the surface layer and the result, 12.7±0.4 MPa*m\(^{1/2}\), is comparable with the research reported in [1].

Figure 2. The OM images of TiC-FeCr cermet after alloying sintering in Mn microatmosphere (top) and EDS Mn line scan of the cross-section (bottom). Macrophotography and fracture toughness of the surface layer and microhardness of the cross-section and the core are shown.

Figure 3. X-ray diffractograms of the core region (top) and the surface layer (bottom) of TiC-FeCr sintered in Mn microatmosphere.
XRD phase analysis showed that after the alloying sintering, the bulk of the TiC-FeCr cermet is composed of three phases: TiC, ferrite (α) and chromium-based double carbide (Cr, Fe)\(_7\)C\(_3\). While the ferrite is expected in the binder phase, double carbide has formed during sintering due to the high affinity of chromium for carbon [9]. Interestingly, an additional phase, ε-type hexagonal martensite, is present in the surface layer. While equilibrium state of the Mn-rich binder is austenite (γ), XRD results indicate that during cooling γ \(\rightarrow\) ε transformation took place, resulting in the ferritic-martensitic binder. To the authors’ knowledge, ε-type martensite has not been reported in TiC cermets with the Fe-based binder before.

4. Summary
Titanium carbide cermet bonded with ferritic high-chromium steel was alloyed with manganese employing sintering in Mn-rich microatmosphere. The following conclusions can be drawn:

- Mn vapor microatmosphere in the sintering device prevents Mn losses. However, regardless of open porosity before the formation of the liquid phase, the alloying effect of the bulk of TiC-FeCr cermet body was not achieved. As a result, composition and non-uniform microstructure of the samples sintered using conventional vacuum sintering and alloying sintering remained similar.
- Sintering in Mn microatmosphere allows considerable increase in Mn content only in the surface layer of the TiC-FeCr specimens with a thickness of about 1 mm. The metallic binder of the Mn rich surface layer is composed of ε-type martensite and α-type ferrite. This surface layer is characterized by structural homogeneity and high mechanical properties – hardness of \(\sim 1200\) HV\(_30\) and indentation fracture toughness of \(\sim 13\) MPa*m\(^{1/2}\).

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