

Processing and microstructural characterization of WC-based cermets doped by ZrO₂

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Received 30 June 2009, in revised form 9 October 2009

Abstract. In the present work we report the processing of the WC-based and ZrO₂-doped cermets with the addition of oxides of 6 wt% through sinter/HIP routine. Microstructural characterization of the final products has been conducted with the help of XRD-analysis and scanning electron microscopy combined with energy dispersive spectroscopy. Influence of the binder metal on the developed microstructure and possibility to sinter a fully dense bulk cermet with zirconia is discussed in detail.

Key words: tungsten carbide, hardmetal, zirconia, powder metallurgy, HIP.

1. INTRODUCTION

Many thousands of components have benefited from advanced ceramic–metal composite solutions for wear resistance, providing considerable lifetime increases over conventional metal components. WC-Co hardmetals are extremely important materials in engineering applications from cutting tools through dies and press moulds to teeth on gravel extractors. In many applications of these composites the tribological performance of the materials is crucial. Wear is one of the most common problems in engineering and mining applications that costs industry an enormous amount of money each year. For a desirable service life, material selection is obviously crucial to minimize wear of a component in these applications. With improved manufacturing technologies and design criteria, the range of wear applications for ceramics has broadened considerably.

It has been shown [^{1,2}] that the main mechanisms of hardmetals failure under wear conditions are attributed to binder metal removal and accumulation of plastic

deformation in tungsten carbide WC grains followed by fracture and fragmentation. Insufficient fracture toughness of WC-based and Co-bonded materials represents some obstacles in their general use. Optimization of wear resistance is therefore a major consideration in the development of WC-based hardmetals.

One of the toughest ceramics known is based on zirconium dioxide ZrO_2 . The promising properties of this ceramics are attributed to the stress-induced phase transformation from tetragonal to monoclinic structures. Moreover, yttria stabilized tetragonal zirconia polycrystalline ceramics exhibit an excellent combination of strength, wear resistance and chemical stability [3]. Adding of both stabilized and undoped ZrO_2 is expected to increase fracture toughness without loss in hardness. The attempts to incorporate ZrO_2 into WC matrix seem to be a promising way in the development of new engineering materials.

Some noteworthy results have been obtained through sintering of WC- ZrO_2 ceramics. For example, Basu et al. [4] applied pressureless sintering process to the fabrication of WC- ZrO_2 composites with high hardness of 22 GPa and quite low fracture toughness of $5 \text{ MPa m}^{1/2}$. Vleugels et al. [5] added WC particles to nanosized zirconia and sintered fully dense ceramic with the help of hot-pressing technique. WC- ZrO_2 -VC ceramic composites, produced by hot press sintering, possess fracture toughness of about $11.5 \text{ MPa m}^{1/2}$ that is quite high and encouraging result for such kind of materials [6]. The preliminary study on processing and properties of WC-Co hardmetals, doped by ZrO_2 , has revealed a remarkable improvement in bending strength and impact toughness of the sintered material [7].

In metallurgical processes an important and sometimes a predominant role is played by the phenomena, occurring at the interfaces of the liquid and the solid state. Thus, understanding of the physical-chemical processes, occurring between a liquid and a solid, is a significant physical and metallurgical problem that has not been completely solved yet. Also, cermets and fine ceramics are known to be very sensitive to the presence of coarse grains and pores in their structures. Applying of a high isostatic pressing (HIP) technique is one of the most reliable ways to eliminate such kind of defects in composites [8].

The presented study considers the first stage of design of zirconia-doped and WC-based composites for tribological applications and focuses on the development of a new route for the synthesis of novel structures and their microstructural characterization.

2. PROCESSING

2.1. Starting powders

The commercially available high-purity WC (crystallite size $0.92 \mu\text{m}$, Wolfram GmbH, Austria), Co ($71 \mu\text{m}$, purity 99.2%), Ni ($20 \mu\text{m}$, purity 99.7%) and ZrO_2 powders ($10 \mu\text{m}$) were used as starting powders. Undoped ZrO_2 was used to reinforce the WC-based alloys.

As a first step towards cermet production, the initial powders were multi-directionally milled in an attritor, using benzene as the process control agent and WC-Co balls as grinding media during 8 h with ball-to-powder ratio 10:1. Drying and sieving of the processed powders were performed to avoid agglomeration. In all cases the powder mixtures contain 86 wt% of WC, 8 wt% of Co or Ni and 6 wt% of ZrO₂. For fabrication of binderless ceramic, WC powder with 14 wt% ZrO₂ was also prepared.

2.2. Sintering

Milled and dried powder mixtures were subjected to cold pressing at 6 MPa to obtain green compacts with a green density of about 55% of the theoretical density. Green bodies have been held at 600°C in vacuum during 30 min to burn off plasticizers.

Sintering of the powder compacts was performed via sinter/HIP route with the help of AIP6-30H (American Isostatic Press, Inc.) through the following scheme: heating up to the temperature of 1500°C under 0.26 mbar vacuum with heating rate of 16°C/min, then HIPing with a pressure of 206 MPa at 1700°C in Ar for one hour, and cooling down to 150°C with cooling rate of 5°C/min. The holding time influences the materials properties significantly. Based on the previous experience, the time of one hour was chosen as a promising duration of sintering although the effect of the holding time and sintering temperatures should be considered in the nearest future.

2.3. Characterization

Before investigations, all samples of 25 × 14 × 3 mm in size were smoothly polished with diamond paste to obtain optically reflective surfaces. Porosity of the materials sintered was estimated by analysing of SEM-micrographs with the help of image processing software JMicroVision.

The microstructural examination of the composites was conducted by means of a scanning electron microscope Leo Supra-35, equipped with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was performed with a Siemens Bruker D5005 analyser with CuK α -radiation (scanning range 2θ from 20° to 80° with a step of 0.04°). Contiguity of phases was evaluated by the linear intercept method.

The bulk Vickers hardness was measured using Indentec 5030 SKV according to ISO 6507.

3. RESULTS AND DISCUSSION

Materials of three different compositions were produced from three powder mixtures:

- C – mixture with cobalt (86 wt% WC, 8 wt% Co and 6 wt% ZrO₂)
- N – mixture with nickel (86 wt% WC, 8 wt% Ni and 6 wt% ZrO₂)
- Z – mixture without metal (86 wt% WC and 14 wt% ZrO₂)

The representative SEM images of the materials produced are shown in Fig. 1. The bright zones are WC grains while light grey ones are Co or Ni binder and dark grey spots are ZrO₂ particles. The residual porosity is shown by black zones.

Microstructural analysis of the hot pressed specimens revealed quite good densification although the residual porosity of 1.8% and 2.9% in C and Z specimens, respectively, pointed to some intrinsic problems in the WC-ZrO₂-Co system related to poor wettability between zirconia and metal. Porosity of N grade is insignificant and the contiguity of hard phase is 0.68.

Porosity due to poor wettability between components in the composite is one of the toughest problems in manufacturing the cermets with oxide additives. Wetting in a liquid–solid system depends on many parameters such as temperature, surface energy and interfacial energy of phases in contact. The Co-ZrO₂ as well as Ni-ZrO₂ systems are non-wetting ones in nature. The initial transient equilibrium (or quasi-equilibrium) contact angles do not significantly vary with temperature. However, satisfactory work of adhesion between zirconium dioxide and cobalt and nickel (about 0.7 Jm⁻² and 0.8 Jm⁻² [9], respectively, at the temperature of sintering applied in this study) gives a chance to produce a dense body. Applying high temperatures and pressures enables partially to overcome this problem.

The method of fabrication of the metal–zirconia interface influences its properties [9–11], since local chemistry and bonding characteristics can be highly dependent on the processing conditions. Therefore, the fabrication procedure has to be studied in detail and the optimal conditions should be precisely followed during materials fabrication.

Analysis of the micrographs of the C and N specimens (Figs. 1a and b) reveals the formation of the so-called η-phases, which occur in the form of complex carbides of W_xCo_yC_z in the Co-W-C and Ni-W-C systems [12]. It is well proven that carbon content has a critical value on WC-based composite production and material quality. For the monotungsten carbides WC, the stoichiometric content of C is 6.13 wt%. The two-phase WC-Co(Ni) cermet

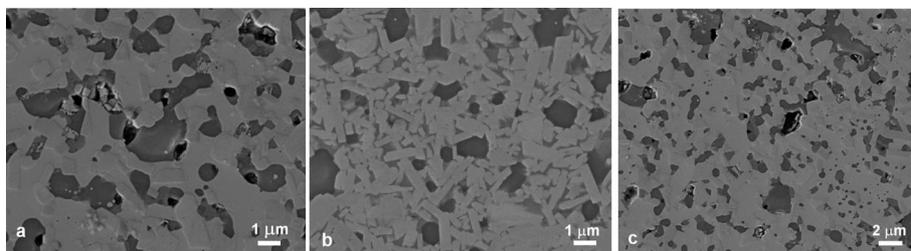


Fig. 1. SEM micrographs of the materials produced: (a) – C; (b) – N; and (c) – Z.

exists only in a narrow range of carbon concentration. Insignificant deviations from the stoichiometric carbon content will result in the presence of either free graphite, if the carbon content is above the stoichiometric value, or the η -phase, if the carbon content falls below the stoichiometric value. Formation of ZrO and $ZrO_{1.87}$ is a direct indication of the reduction process, associated with carbon dioxide and its release.

In Fig. 1a (grade C) at least three phases are well recognized. The XRD analysis for grade C (Fig. 2) indicates ZrO_2 , small amount of monocarbides WC, and two undesirable Co-deficient η -phases W_4Co_2C and $W_{10}Co_3C_{3.4}$ instead of cobalt.

At a sintering temperature of 1700°C, the binder is completely melted and dissolution of W and C in the mold metal is a quite rapid process and the most of the WC grains are dissolved. The total volume of double carbides is about 56%. Therefore, the technology of WC-Co-ZrO₂ materials should be further considered.

The elements distribution throughout the cermet C can be extracted from Fig. 3, where presence of two types of η -phase bi-carbides is well recognizable.

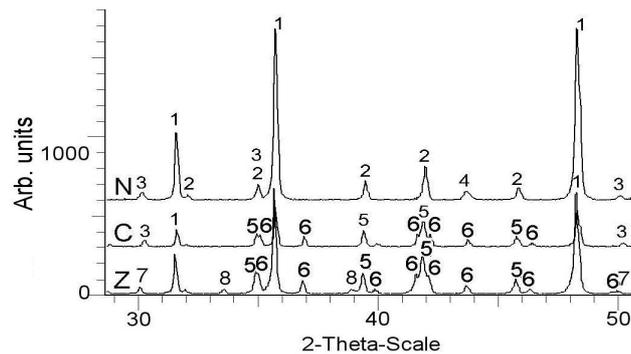


Fig. 2. XRD pattern of grades N, C and Z: 1 – tungsten carbide WC; 2 – tungsten nickel carbide W_3Ni_3C ; 3 – zirconium dioxide ZrO_2 (cubic); 4 – tungsten nickel $W_{0.15}Ni_{0.85}$; 5 – tungsten cobalt carbide W_4Co_2C ; 6 – tungsten cobalt carbide $W_{10}Co_3C_{3.4}$; 7 – zirconium oxide $ZrO_{1.87}$ (cubic); 8 – zirconium oxide ZrO (cubic).

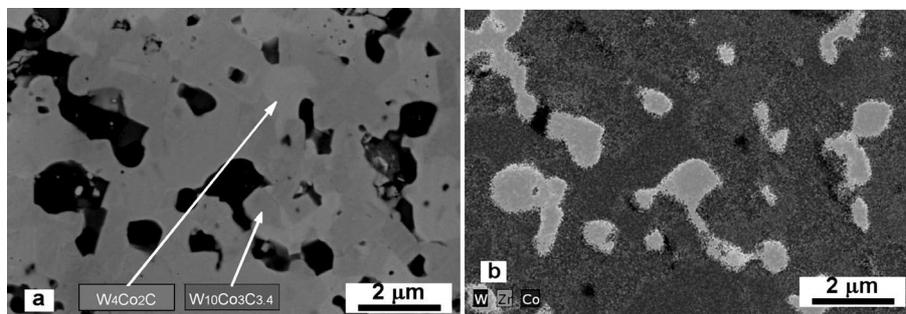


Fig. 3. SEM-micrograph (a) and EDS-map (b) for grade C.

Figure 1b displays a SEM-micrograph of the grade WC-Ni-ZrO₂. No significant porosity, associated with metal-ZrO₂ or ZrO₂-WC interfaces, was observed. That fact points to full densification of the material. Theoretical investigations on adhesion at Ni-ZrO₂ interfaces, carried out in [10], have reported that the compaction during sintering may be caused by fast formation of layered structures, surrounding carbide grains.

According to XRD (Fig. 2), the solidified microstructure of grade N is composed of tungsten carbide particles WC, zirconium dioxide ZrO₂, nickel tungsten carbide Ni₃W₃C, and tungsten nickel W_{0.15}Ni_{0.85} alloy is a binder phase. The image in Fig. 4a indicates uniform distribution of the oxide particles (black zones) throughout the material, development of stable WC phase (bright grains) surrounded by the binder metal (grey areas) and the presence of η-zones Ni₃W₃C (bright pools in Figs. 4a and b). The formation of such zones may be controlled by the amount of carbon involving into the sintering process and holding time at the sintering temperature.

Most of the ZrO₂ grains are presented in a relatively spherical form and at the areas of carbide grains boundaries/interfaces. However, there is also some amount of nanosized particles incorporated into WC grains. W₃Ni₃C phase allows the ZrO₂ particles precipitation inside the η zones as it is indicated in Fig. 4b. Zirconia grains' size is ranged between some nanometers up to 2 μm. The presence of ZrO₂ particles on the grain boundaries suggests inhibition of the carbides grain growth. Usually, using the initial powder of WC particles of sizes that are similar to used in this study and without any additives, the final product contains triangular carbides of 3–5 μm. As it can be seen from the images in Figs. 1b and 4, WC grains are mostly faceted and elongated, and of rectangular shape with the aspect ratio of about 3:1 and nanometer-sized short side of the rectangle. The faceted shape of WC crystals is characteristic for C-rich alloys [13] and this is not inconsistent with the simultaneous formation of the η-phase that has generally occurred in the case of carbon deficit. This fact can be explained by the non-equilibrium solidification.

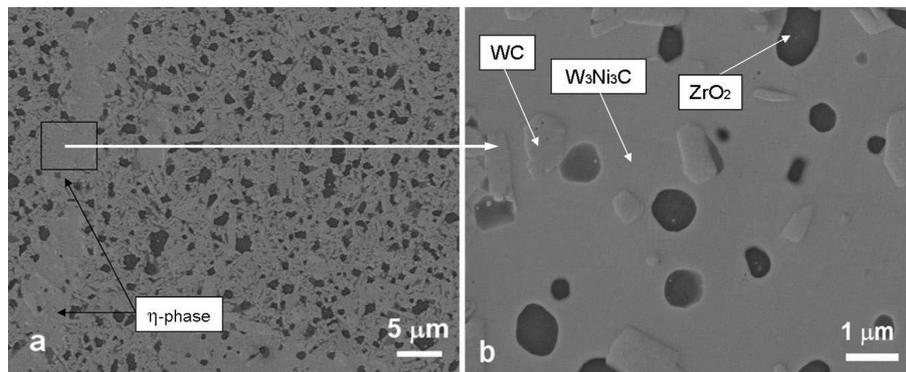


Fig. 4. SEM micrograph of the surface of grade N (a) and ZrO₂ distribution throughout the η-phase (b).

XRD analysis has confirmed that zirconium dioxide appears in a tetragonal modification, which indicates that desirable phase structure of zirconia in cermet is achieved.

Particular attention should be drawn to the porosity level, which is negligible, so the composite appears to be fully dense. The material of chosen composition demonstrates good sinterability and reveals appropriate bulk mechanical properties. For example, the values of the Young modulus and hardness are 540 GPa and 1600 HV₁₀, respectively.

Microstructural analysis of grade Z (Fig. 1c) suggests that WC-ZrO₂ structure without binder metal cannot be fully densified under sintering conditions, applied in this research. Metal binder phase promotes liquid phase sintering while the addition of only zirconia implies solid state sintering. XRD analysis (Fig. 2) of the sintered ceramic (grade Z) indicates the presence of some amount of cobalt in the structure and formation of W₄Co₂C phase together with WC and ZrO₂ phases. Cobalt may originate from the WC-Co mixing media and eta-phase content was estimated to be around 4%. For high-quality ceramic manufacturing the technology should be controlled and maintained as clean as possible. While there is a broad variety of scientific hypothesis concerning application of a zirconia doped ceramic, WC-ZrO₂ remains under investigation.

4. CONCLUDING REMARKS

The analysis of theoretical and experimental studies on Ni-ZrO₂ interfaces has demonstrated that, in principle, the strong interfacial adhesion in this system is possible [10]. Therefore, the production of the fully dense bulk materials of outstanding mechanical properties is possible by well developed technological conditions. This study has shown that the composition of WC-Ni-ZrO₂ (grade N) is the most promising developed structure for further development and detailed investigations. Reasonable correlation between manufacturing parameters and the obtained cermet morphology and properties have been found.

The results presented in this study are promising, but further work is needed to optimize the sintering process to produce the material of superior characteristics. The efforts to improve the wettability of metals by incorporation of additional elements are in progress.

ACKNOWLEDGEMENTS

Authors are grateful to DSc Juri Pirso, TUT, who has contributed substantially to our knowledge of cermets technology, and for fruitful discussions of experimental results. Also, the authors would like to thank PhD O. Volobujeva, TUT, for the helpful assistance in SEM imaging of the materials. This work has been supported by the Estonian Science Foundation (grant No. 6660) and

Estonian Ministry of Education and Research (target financing SF0140062s08 - T062).

REFERENCES

1. Gee, M. G., Grant, A. and Roebuck, B. Wear mechanisms in abrasion and erosion of WC/Co and related hardmetals. *Wear*, 2007, **263**, 137–148.
2. Hussainova, I. Microstructural design of ceramic-metal composites for tribological applications. *Adv. Comp. Mater. Struct.*, 2007, **334–335**, 125–128.
3. Bakshi, S. D., Basu, B. and Mishra, S. K. Microstructure and mechanical properties of sinter-HIPed ZrO₂-ZrB₂ composites. *Composites A*, 2006, **37**, 2128–2135.
4. Basu, B., Venkateswaran, T. and Sarkar, D. Pressureless sintering and tribological properties of WC-ZrO₂ composites. *J. Eur. Ceram. Soc.*, 2005, **25**, 1603–1610.
5. Jiang, D., der Biest, O. and Vleugels, J. ZrO₂-WC nanocomposites with superior properties. *J. Eur. Ceram. Soc.*, 2007, **27**, 1247–1251.
6. Yang, F., Zhao, J. and Ai, X. Effect of initial particulate and sintering temperature on mechanical properties and microstructure of WC-ZrO₂-VC ceramic composites. *J. Mater. Proc. Tech.*, 2009, **209**, 4531–4536.
7. An, L., Han, J. and Chen, J. Microstructure and mechanical properties of WC-20%Co/ZrO₂(3Y) cermet composites. *J. University of Science and Technology Beijing*, 2006, **13**, 174–177.
8. Bocanegra-Bernal, M. H. Hot isostatic pressing technology and its applications to metals and ceramics. *J. Mater. Sci.*, 2004, **39**, 6399–6420.
9. Nikolopoulos, P. and Sotiropoulou, D. Wettability between zirconia ceramics and the liquid metals copper, nickel and cobalt. *J. Mater. Sci. Lett.*, 1987, **6**, 1429–1430.
10. Munos, M. C., Gallego, S., Beltran, J. and Cerda, J. Adhesion at metal-ZrO₂ interfaces. *Surface Sci. Rep.*, 2006, **61**, 303–344.
11. Zhu, J., Kamiya, A., Yamada, T., Shi, W., Naganuma, K. and Mukai, K. Surface tension, wettability and reactivity of molten titanium in Ti/yttria-stabilized zirconia system. *Mater. Sci. Eng. A*, **327**, 117–127.
12. Li, Q., Lei, T. C. and Chen, W. Z. Microstructural characterization of WCp reinforced Ni-Cr-B-Si-C composite coatings. *Surface Coatings Technol.*, 1999, **114**, 285–291.
13. Wang, Y., Delanoë, A., Lay, S., Pauty, E. and Allibert, C. H. Morphology and growth of WC grains in WC-Co cermets. *Materiaux*, 2002, AF-01-082.

ZrO₂-ga dopeeritud WC-kermiste süntees ja mikrostruktuurne analüüs

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On käsitletud dopeeritud tsirkooniumdioksiidi ZrO₂ lisandiga volframkarbiidi WC baasil kõvasulamite valmistamise tehnoloogiat (kuum isostaatiline pressimine – sinter/HIP). Sünteesitud materjalide mikrostruktuuri iseloomustamiseks kasutati röntgenkiirte difraktsiooni, skaneerivat elektronmikroskoopiat ja energia dispersiooni spektroskoopiat. Artiklis on analüüsitud sideaine (Ni, Co) mõju komposiitmaterjali mikrostruktuurile ja dopeeritud ZrO₂-ga kermiste valmistamise võimalikkust WC baasil. Esitatud tulemused on esialgsed ja tarvilik on läbi viia täiendavaid eksperimente.