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The Influence of Cr_3C_2 and VC as Alloying Additives on the Microstructure and Properties of Reactive Sintered WC-Co Cermets

Kristjan JUHANI [1] *, Jüri PIRSO [1], Mart VILJUS [2], Sergei LETUNOVITŠ [3], Marek TARRASTE [1]

[1] *Department of Materials Engineering, Tallinn Univesity of Technology,Ehitajate tee 5, 19086 Tallinn, Estonia*
[2] *Centre for Materials Research, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn Estonia*
[3] *Centre of Engineering Graphichs, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn Estonia*

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Investigated WC-Co cermets were produced via reactive sintering. In case of reactive sintering the elemental powders of tungsten, carbon black as graphite source and cobalt at first activated throw high energy milling and then the carbide synthesis is taking place in the same cycle with liquid phase sintering of the cermets. Because there is a lack of information about the influence of alloying additives on the reactive sintered WC-Co cermets, small amount of chromium carbide or vanadium carbide was added to the powders. To investigate the influence of carbon content in initial powder mixture on the microstructure and properties of reactive sintered WC-Co cermets alloyed with Cr_3C_2 and VC cermets with different carbon content were produced. The hardness, transverse rupture strength and erosion resistance of alloyed WC-Co cermets depending on carbon content in initial powder mixture is exhibited.
Keywords: WC-15 % Co, reactive sintering, alloying additives, mechanical and tribological properties.

1. INTRODUCTION

WC-Co cermets are widely known material for their high wear resistance [1 – 4]. They are mainly used in metal cutting and rock drilling tools and wear parts for various applications. It is well known that the mechanical properties of cemented carbides can be improved by the reduction of a carbide grain size up to nanosize scale [5 – 7]. Nanograin and sub-micron WC-Co composites have superior properties and more homogeneous microstructure than those of the conventional WC-Co composites. WC is conventionally synthesized through a solid/solid reaction by heating a mixture of tungsten powder and carbon black at temperatures in the range of 1400 °C – 1800 °C under a hydrogen atmosphere [1]. For fabricating sub-micron or nanocrystalline WC-Co composites, nanosize WC powder is used as a starting powder [8]. There are many ways to produce nanocrystalline WC and WC-Co powders, such as spray conversion process [9, 10], electric discharge machining [11], chemical vapor condensation [12, 13], thermal plasma process [14], high energy milling [15], integrated mechanical and thermal activation [16]. Integrated thermal and mechanical activation combines mechanical and thermal activation to enhance the formation of carbides *in situ* (the carbide phase is formed during sintering) [16]. The reactive sintering of WC-Co hardmetals is investigated in [17].

One way to decrease the grain coarsening is to use special alloying elements – so called grain growth inhibitors. Grain growth inhibitors have been used to mitigate grain growth during sintering. During the sintering process, small WC grains are dissolved into Co binder as W and C atoms and precipitated to large WC grains. The use of grain growth inhibitors is widely practiced in the industry for sintering ultrafine WC-Co materials. Vanadium carbide (VC) and chromium carbide (Cr_3C_2) are by far the most effective grain growth inhibitors due to their high solubility and mobility in cobalt phase at lower temperatures [18 – 21].

Additionally, the combinations of VC and Cr_3C_2 have better inhibition effects than that doped alone [22]. Moreover, VC has been recognized as the most effective grain growth inhibitor to retard the WC grain growth [18]. To control the grain growth in nanostructured WC-Co composites, one of the keys is the proper selection of the second-phase additives as grain growth inhibitors.

The solubility of VC in the Co binder is 8.19 wt %. The content of VC in WC-Co is usually kept at 0.7 wt %, which is regarded as the practical upper limit, in order to avoid embrittlement due to (V,W)C precipitation at the interface of WC-Co [21]. Some investigations indicate that in order to achieve better overall properties, the weight ratio of VC/Co should be less than 5 wt %.

Specifically, the grain growth of WC during sintering can be divided in two parts: during heat-up and during isothermal hold at liquid phase sintering temperatures. Until now, the most successful way of controlling WC grain growth during sintering is the addition of small amounts (about 1 wt. % – 2 wt. %) of several metallic carbides (as VC, Cr_3C_2, Mo_2C, TaC etc) to the powder mixture. However, the physical mechanisms of the grain growth control are still unclear.

The aim of present work was to investigate the influence of Cr_3C_2 and VC as alloying additives and different graphite contents in the initial W-C-Co powder mixture, on the microstructure and properties of reactive sintered WC-Co compositions.

*Corresponding author. Tel.: +372-620-3356; fax.: +372-620-3196.
E-mail address: *kristjan.juhani@ttu.ee* (K. Juhani)

2. MATERIALS AND EXPERIMENTAL

Investigated WC-Co cermets were produced via a novel technology – reactive sintering [17] developed in Tallinn University of Technology. Different cermets producing routines is exhibited in Figure 1. Seven types of W-Co-C powder mixtures with different graphite contents but the same binder content (15 % Co) were investigated. To investigate the influence of alloying elements, in case of different carbon contents, 0.4 wt % of VC and 0.4 wt % of Cr_3C_2 were added to powder mixtures.

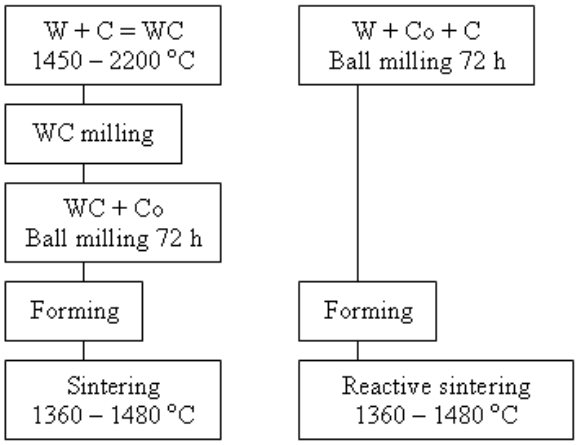


Fig. 1. WC-Co cermets producing technologies: a – conventional technology; b – reactive sintering

The milling of Co, W, C and alloying elements powders with different W : C mole ratio was carried out in conventional ball mill for 72 hours. The initial free carbon concentration in the W powder mixture was from 6.2 wt % up to 7.12 wt %. To avoid the contamination of powders WC-Co balls were used during milling. Ball to powder weight ratio was 15 : 1 in case of all millings. The mechanically activated powder mixtures were compacted to the green bodies by uniaxial pressing. The green compacts were directly sintered in vacuum furnace (T = 1400 °C, t = 30 minutes) and in sinter/HIP furnace (T = 1400 °C, t = 15+10+15 minutes, p = 30 bar).

Reference materials were produced using the conventional powder technology route, i. e. pressing of commercially available powders following by sintering, using the same sintering regimes as in case of reactive sintered materials.

The microstructure was investigated by SEM (JEOL JSM 840A). Phase identification was carried out using X-ray diffraction (XRD) methods with CuK_α radiation (Bruker AXS D5005).

Vickers hardness was measured in accordance to the ASTM Standard E384. Transverse rupture strength (TRS) was determined by three point bending tests in accordance to ASTM B528. Each test point indicates the average value of six measured results.

Abrasive erosion tests were obtained in centrifugal accelerator CAK-3m in accordance to the standard test method [23], at room temperature, using quartz sand stream with 80 m/s velocity at 30° impact angle. The volumetric erosion rates for each specimen were obtained by dividing weight loss rate by the density of composites.

3. RESULTS AND DISCUSSION

3.1. Microstructure

Microstructure of WC-Co cermets consists of WC grains and a cobalt binder phase. The composition where WC-Co microstructure is in the two phase region is very narrow. Two high or low carbon content in the initial powder mixture results in the formation of graphite or η-phase (W_xCo_yC) in the microstructure respectively.

In Figures 2 – 4 the microstructure of reactive sintered WC-15 % Co cermets with alloying additives depending on carbon content in initial W-Co-C powder mixture and sintering route is exhibited. The microstructure of materials with lower carbon content has η-phase in the microstructure (Fig. 2). η-phase is hard and brittle; it increases the hardness and wear resistance of materials, but in the same time decreases the strength properties. Although in case of lower carbon content the microstructure is not homogeneous and carbide grains are elongated.

The microstructure of materials with 6.7 % C is more homogeneous and fine grained (Fig. 3). It is although free of η-phase and free carbon.

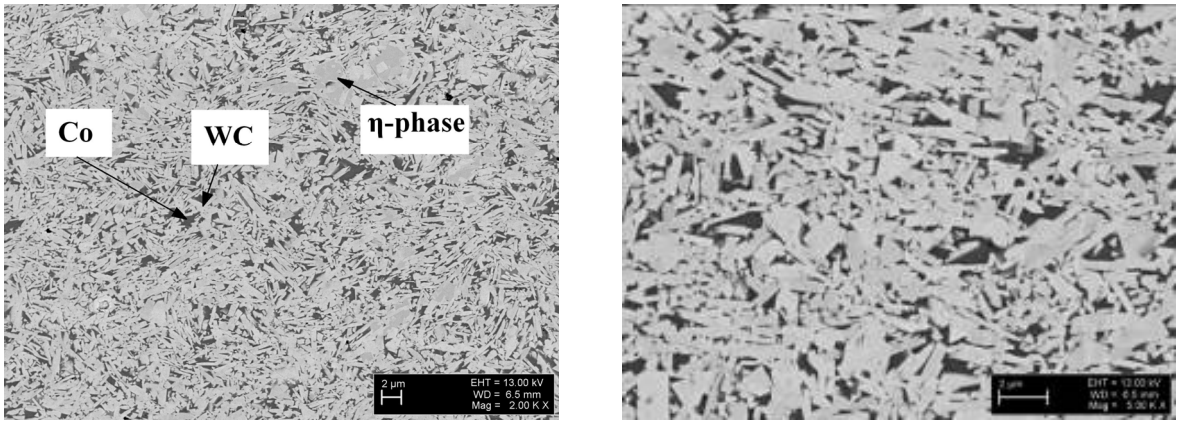


Fig. 2. Reactive sintered WC-15 % Co cermet alloyed with Cr_3C_2 and VC with 6.3 % C in initial powder mixture

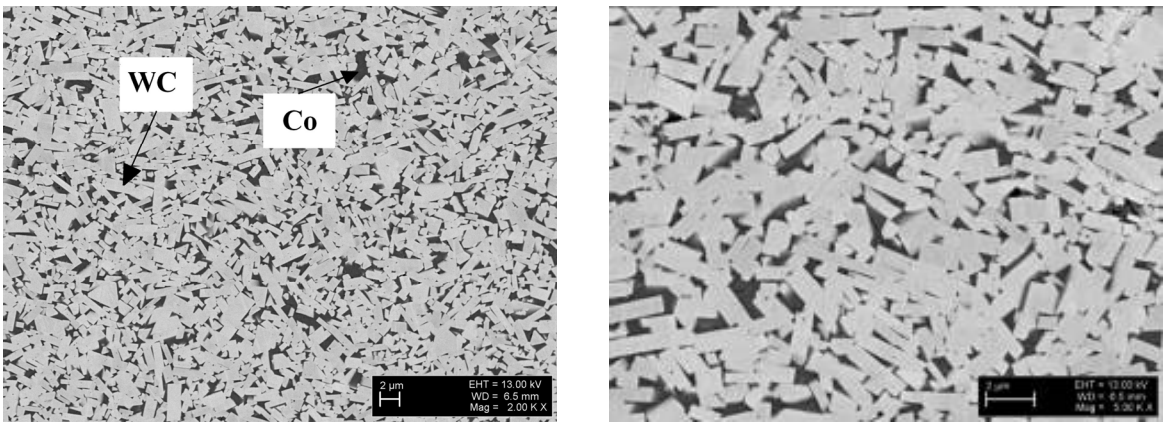


Fig. 3. Reactive sintered WC-15 % Co cermet alloyed with Cr_3C_2 and VC with 6.7 % C in initial powder mixture

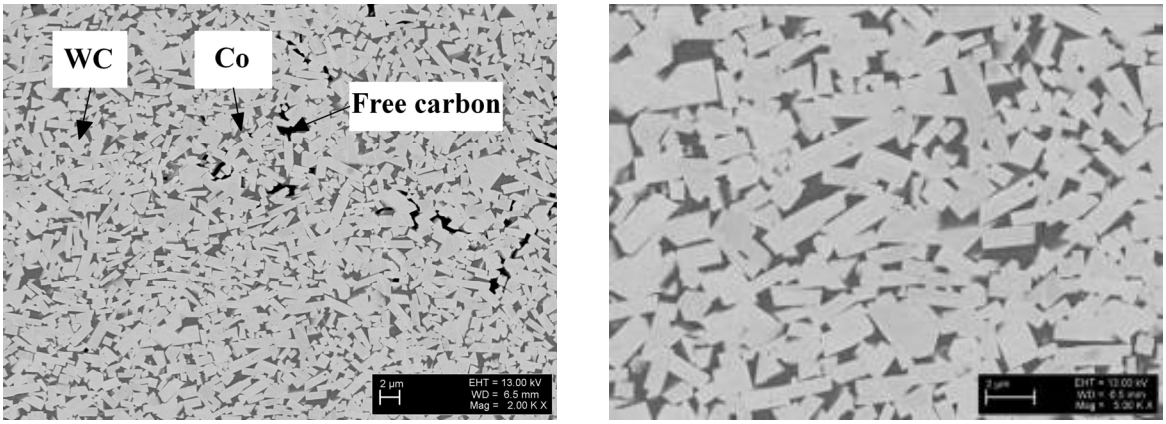
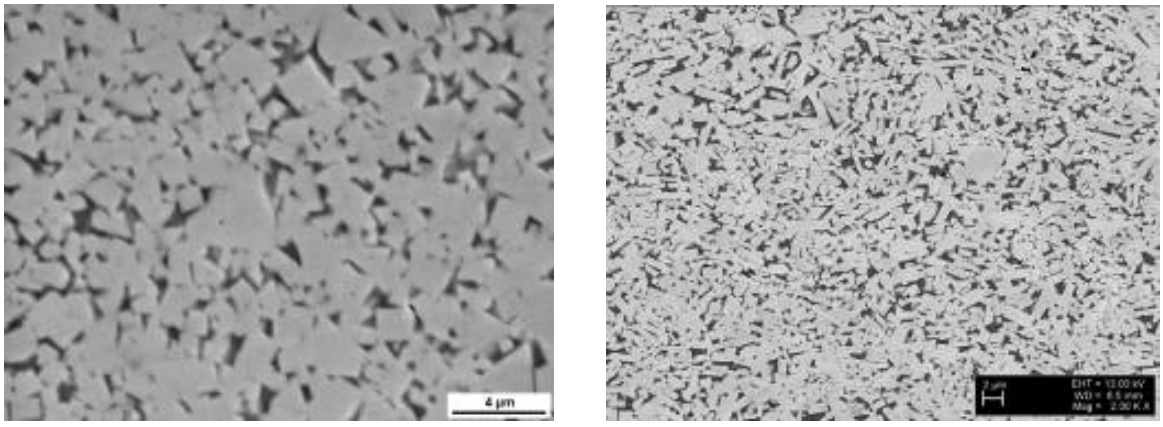


Fig. 4. Reactive sintered WC-15 % Co cermet alloyed with Cr_3C_2 and VC with 7.12 % C in initial powder mixture



a b

Fig. 5. Microstructure of WC-15 % Co cermets produced by different technologies: a – conventional technology, b – reactive sintering

In Figure 4 is exhibited the microstructure of materials with 7.12 % C in initial powder mixture. Too high carbon content results in formation of free carbon in the microstructure; it has not been reacted to synthesize WC or burned out during sintering. Free carbon decreases materials mechanical and tribological properties. Despite of the free carbon in the microstructure cermets with 6.7 % C in is fine-grained and homogeneous. Finer microstructure exhibited materials produced via sinter/HIP.

In Figure 5 are compared microstructures of WC-15 % Co cermets produced by different technologies. The microstructure of reactive sintered WC-15 % Co with alloying additives and optimal carbon content in initial powder mixture is more fine-grained and homogeneous than microstructure of material produced via conventional technology.

3.2. Mechanical properties

In Figure 6 is exhibited the hardness of reactive sintered WC-15 % Co cermets with alloying additives depending on carbon content in initial powder mixture and sintering route. Higher hardness value shows material with 6.3 wt % C in initial powder mixture; those cermets have high and brittle η-phase in microstructure, which increases the materials hardness. When carbon content increases the hardness decreases due to the smaller content of η-phase in microstructure, materials with 6.7 wt % C in initial powder mixture is free of η-phase and free carbon (Fig. 3) and due

to that the hardness is lower compared to materials with lower carbon contents. The decrease of the hardness in case of cermets with 7.12 % C in initial powder mixture is due to the free carbon in microstructure. Alloyed cermets with optimal C % exhibited higher hardness compared to conventional material (15e) and reactive sintered materials without alloying elements (6.5e).

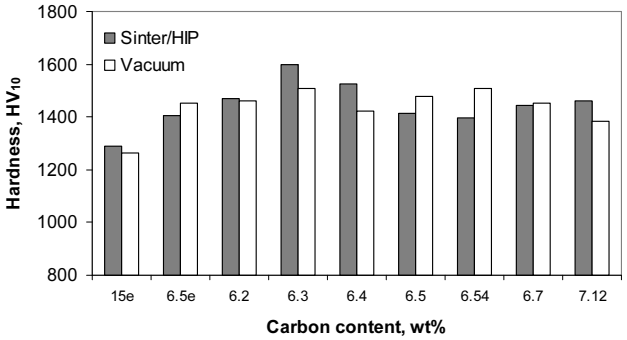


Fig. 6. Hardness of reactive sintered WC-15%Co alloyed with Cr_3C_2 and VC depending on carbon content in initial powder mixture and sintering technique, compared to conventional material (15e) and reactive sintered material without alloying (6.5e)

Figure 7 shows the transverse rupture strength values of alloyed reactive sintered WC-15 % Co cermets depending on carbon content in initial powder mixture and sintering technique. TRS increases in increase of carbon content in initial powder mixture. Materials with lower carbon contents have η-phase in microstructure, which is hard and brittle and so decreases the transverse rupture strength. Microstructure of cermets with 6.7 % of carbon, exhibiting the highest TRS value, is free of η-phase or free carbon (Fig. 3). There is free carbon in the microstructure of cermets with carbon content 7.12 % (Fig. 4), free carbon in microstructure acts as porosity and decrease the transverse rupture strength. Higher transverse rupture strength exhibited materials produced via sinter/HIP. The transverse rupture strength of reactive sintered and alloyed materials with carbon content 6.7 % in initial powder mixture and produced via sinter/HIP exhibits higher value compared to conventional material (15e) and reactive sintered material without alloying (6.5e).

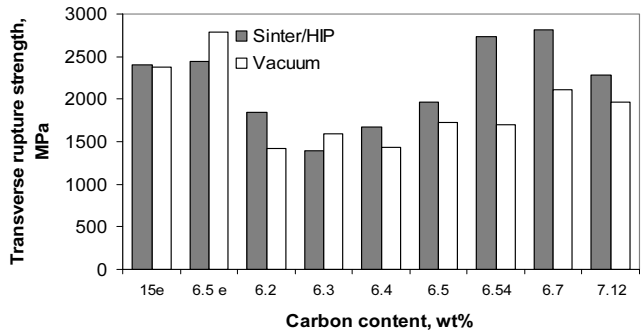


Fig. 7. Transverse rupture strength of reactive sintered WC-15 % Co alloyed with Cr_3C_2 and VC depending on carbon content in initial powder mixture and sintering technique, compared to conventional material (15e) and reactive sintered material without alloying (6.5e)

3.3. Abrasive erosion resistance

The abrasive erosion resistance of reactive sintered WC-15 % Co cermets with alloying elements is exhibited in Figure 8. Erosion resistance decreases in the increase of carbon content in initial powder mixture. Cermets with lower carbon content have η-phase in the microstructure; η-phase increases cermets hardness and therefore the erosion resistance. Cermets produced via vacuum sintering exhibited better erosion resistance compared to materials produced via sinter/HIP. The wear resistance of reactive sintered cermets with alloyed additives is higher than in case of materials produced via conventional technology (15e).

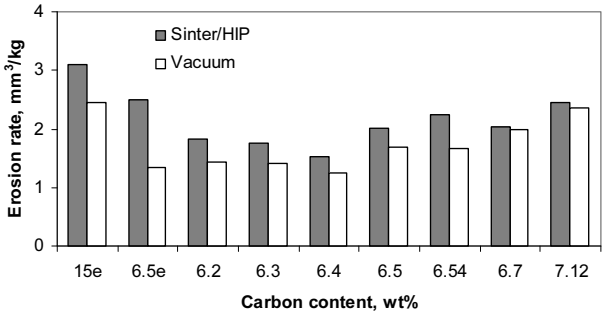


Fig. 8. Erosion rate of reactive sintered WC-15 % Co alloyed with Cr_3C_2 and VC depending on carbon content in initial powder mixture and sintering technique, compared to conventional material (15e) and reactive sintered material without alloying (6.5e)

4. CONCLUSIONS

1. Several compositions of reactive sintered Cr_3C_2 and VC alloyed WC-Co cermets were produced;
2. The microstructure and properties of reactive sintered alloyed WC-15 % Co cermets depends on the carbon content in initial W-Co-C powder mixture. The microstructure of materials with 6.7 % C in initial powder mixture is free of both η-phase and free carbon, in case of lower carbon contents there is η-phase in the microstructure and in case of higher carbon content the free carbon is exhibited;
3. Higher hardness exhibited materials with lower carbon content, having η-phase in the microstructure, due to what their transverse rupture strength values are low; the most promising hardness and transverse rupture strength combination is in case of 6.7 % C in initial powder mixture, produced via sinter/HIP;
4. Abrasive erosion resistance of the reactive sintered Cr_3C_2 and VC alloyed WC-Co cermets depends on the hardness of materials, materials with higher hardness exhibited better erosion resistance.

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