Mechanical and electrochemical properties of ultrafine hard alloys with different grain growth inhibitors

A V Terentev¹, N V Isaeva¹, Yu V Blagoveshchenskiy¹, A V Nokhrin², A A Murashov² and N V Saharov²

¹ Baikov Institute of metallurgy and material science of the Russian Academy of Sciences, 49 Leninsky prospect, 119334, Moscow, Russia
² Lobachevsky State University of Nizhny Novgorod, 603950 Nizhny Novgorod, Russia

E-mail: terentev.alxndr@yandex.ru

Abstract. A 90WC-10Co powder mixture with TaC, VC and Cr₃C₂ grain growth inhibitors with average particle size about 50 nm was produced by deposition of Co. Two different sintering techniques had been used for consolidation. Microhardness and fracture toughness measurements of sintered materials had showed agreement with Hall-Petch equation. The corrosion behavior was investigated in neutral and acid solutions by electrochemical methods. The observed pseudo-passive transition had been associated with the so-called salt passivity — formation of cobalt sulfate salt layer on hard alloy surfaces.

1. Introduction
Traditional hard alloys have grains of micrometer order, due to the needs of improvement performance of hard alloys (crack resistance, wear resistance, etc.) in recent decades, there has been a steady trend towards the development of compact materials with submicron and nanoscale grain size [1]. High reactivity and the rapid grain coarsening of ultrafine and nanosized powders in the sintering process is the primary limitation. Common practice, in order to reduce and suppress grain growth during high temperature sintering, is including carbides of transition metals (IV-VI groups) to the hard metals powder mixtures [2]. The experimental results of the effect of grain size and grain grow inhibitors on corrosion resistance in that range of values are poor and contradictory [3,4].

2. Materials and experimental techniques
Base tungsten carbide nanopowders produced via two-stage process, including DC arc plasma synthesis and subsequent recovery annealing in hydrogen. A powder mixtures showed in Table 1 was produced by deposition Co from Cobalt (II) chloride hexahydrate with adding grain grow inhibitors (GGI) and following reduction in hydrogen [5]. Figure 1 represent typical view of powder mixture. Values of specific surface area listed in Table 1 respond mean particle sizes about 50 nm.
Figure 1. Microphotography of 90 wt.% WC-10 wt.% Co powder.

Two sintering techniques were applied for consolidation – spark plasma sintering (SPS) and vacuum sintering (VS). SPS was performed using a sintering machine “Dr. Sinter model SPS-625” at pressure 75 MPa on temperatures typical for liquid phase sintering (LS) – 1400°C and for solid phase sintering (SS) – 1100°C. Vacuum sintering was performed using a vacuum furnace “BOzh-2,5-20”. Microhardness was measured using Vicker's indenter on “Struers Duramin-5” microhardness tester with a 2 kg load. Fracture toughness $K_{IC}$ was calculated using the Palmqvist method. Measure grain size were calculated from microphotographs obtained by Jeol JSM-6490 scanning electron microscope (SEM).

| Powder mixture                          | Specific surface area, m$^2$/g |
|-----------------------------------------|---------------------------------|
| WC-10 wt.%Co                           | 9.23                            |
| WC-10 wt.%Co+0.7 wt.%TaC+0.7 wt.%Cr$_2$C$_3$ | 8.76                            |
| WC-10 wt.%Co+1 wt.%TaC+0.1 wt.%VC       | 9.54                            |
| WC-10 wt.%Co+1 wt.%Cr$_2$C$_3$           | 9.61                            |

Current-potential curves and the open circuit potential (OCP) was monitored against silver chloride electrode (SCE) in a three electrode arrangement with the sample as working electrode, a large coiled platinum wire as the counter silver chloride electrode and a with a Luggin–Haber capillary as reference. The sample area in the various electrochemical experiments varied between 0.3 and 1cm$^2$. In all cases the testing solution was quiescent naturally aerated aqueous 1M Na$_2$SO$_4$ (pH≈7) and 1M H$_2$SO$_4$ (pH≈14). This solutions was chosen as model environments for showing features of the electrochemical process in acidic and neutral media.

3. Experimental results

3.1. Microstructure and mechanical properties
To estimate the microstructure formed in the process of sintering powder compositions, in addition to the investigation of micrographs, it is necessary to give its quantitative assessment. From the above images of the microstructure, and calculated on the basis of their average grain size. It can be argued that the inhibition really affects the average grain size of the formed structure (figure 2a, b). In the process of liquid-phase SPS formed more coarse-grained structure, in comparison with vacuum sintering. Most likely, this is due to the fact that the real temperature of the sintered material rises above the temperature fixed by the pyrometer on the walls of graphite die. This results agree well with the data on the microstructure character obtained with the sintering temperature in excess of the optimal modes for the 100-150°C (figure 2c, d) [6]. Solid phase SPS allow to obtain the
nanostructured hard alloys with high mechanical properties, the mean grain size of manufactured samples is about 0.3 µm (figure 2e,f).

**Table 2.** Mechanical properties and mean WC grain size of sintered hard alloys

| Composition | Microhardness $HV$, GPa | Fracture toughness $K_{IC}$, MPa m$^{1/2}$ | $D_m$, µm |
|-------------|--------------------------|---------------------------------------------|-----------|
| WC-10 wt.%Co+ 1 wt.%Cr$_2$C$_3$ | 21.5 | 6 | 0.27 |
| WC-10 wt.%Co+1 wt.%TaC+ 0.1 wt.%VC | 19.9 | 5.9 | 0.35 |
| WC-10 wt.%Co+ 1 wt.%TaC+0.1 wt.%VC | 10.3 | 8.6 | 1.89 |
| WC-10 wt.%Co+ 1 wt.%Cr$_2$C$_3$ | 11.9 | 7.1 | 1.6 |
| WC-10 wt.%Co | 14.8 | 4.8 | 1.37 |
| WC-10 wt.%Co + 0.7 wt.%TaC+0.7 wt.%Cr$_2$C$_3$ | 16.3 | 5.8 | 0.98 |

Hardness and crack resistance are generally regarded as the most important mechanical properties of WC-Co composites. Other properties, such as wear resistance and transverse tensile strength, depend significantly on the above-mentioned properties. The mechanical properties listed below in Table 2. This data in agreement with Hall-Petch relation and the hypothesis that grain refinement to be the main mechanism responsible for the increase in hardness.

### 3.2. Electrochemistry

Samples were immersed in the electrolyte in the cell and after the samples reached equilibrium conditions the open-circuit potential (OCP) was recorded until corrosion potential reached.

### 4. Analysis of experimental data

In Table 2 presented results of mechanical tests for the sintered hard alloys and mean WC grain sizes obtained from SEM microphotographs (figure 2). It is seen that the values of microhardness for solid phase SPSed samples exceed the values for vacuum sintering samples and the lowest values for the liquid phase SPSed samples, this is due to the fact that the real temperature above 1400°C. It is taken that the grain refinement due to GGI is the main mechanism responsible for increasing the hardness, in accordance with the Hall-Petch equation.

It can be seen that the highest hardness values are achieved by using vanadium carbide or mixed doping [1]. It is believed that the addition of Cr$_3$C$_2$ leads to the highest ratio of crack resistance to hardness, experimental confirmation of which was obtained. At the same time, the addition of mixed carbides can also be very effective, but as practice has shown, the mixed inhibition of 1 wt.%TaC-0.1 wt.%VC is on the same level with Cr$_3$C$_2$, if we talk about crack resistance, and is a little less in microhardness values.

Figure 3 shows chronopotentiograms for the hard alloys and pure cobalt in sodium sulfate and sulfuric acid solutions. As can be seen, during the exposure, all samples undergo spontaneous cathodic polarization, which indirectly indicates the corrosion process by the mechanism of active dissolution. However, the stationary potentials of all alloys in both media, except WC-10Co in neutral media, have significantly more positive values (on average about 100-150 mV) compared to the stationary potential of cobalt, which indicates a lower electrochemical activity of alloys and, consequently, a higher corrosion resistance. However, the nature of the GGI (1% Cr$_2$O$_3$ or 1% TaC+0.1% VC) has literally no effect on the electrochemical activity of the compositions in the acid solution and significantly affects the behavior in a neutral media.
Figure 2. SEM microphotographs: a — WC-10 wt.%Co (vacuum sintering); b — WC-10 wt.%Co + 0.7 wt.%TaC + 0.7 wt.%Cr2C3 (vacuum sintering); c — WC-10 wt.%Co + 1 wt.%Cr2C3 (liquid phase SPS); d — WC-10 wt.%Co + 1 wt.%TaC + 0.1 wt.%VC (liquid phase SPS); e — WC-10 wt.%Co + 1 wt.%Cr2C3 (solid phase SPS); f — WC-10 wt.%Co + 1 wt.%TaC + 0.1 wt.%VC (solid phase SPS).

Figure 4 shows the polarization diagrams of cobalt and hard alloys obtained by liquid-phase and solid-phase sintering techniques with different grain growth inhibitors. It is known that the indirect characteristic for retardation electrode (cathode or anode) process is the slope of the polarization curve. The figure shows that, both for cobalt and alloys, regardless of the sintering technology and the composition of the GGI, the cathode process (with hydrogen depolarization) proceeds at a very low overvoltage, which indicates its high speed.

However, the process of anodic dissolution of cobalt and alloys are fundamentally different. If for cobalt a small increase in the external polarization potential leads to a significant increase in the anodic dissolution current, the hard alloys are characterized by very low values of anodic dissolution currents (50-70 µA/cm²) in the potential region by 100-150 mV more positive than the transition point potential. Despite the low values of anode currents, usually characteristic of the passive state, the alloys are in the active state, which is confirmed by the nature of potential changes during exposure to sulfuric acid solution.
Figure 3. Open circuit potential diagrams for hard alloys and pure cobalt.

Figure 4. Polarization diagrams of cobalt and hard alloys techniques with different grain growth inhibitors obtained in H₂SO₄ (a, b) and Na₂SO₄ (c, d): a, c — liquid phase sintering; b, d — solid phase sintering.

Further anodic polarization is accompanied by a significant increase in the anode current, the appearance of activation peaks of complex configuration with a high critical current density (13-23 mA/cm²). The subsequent shift of the potential to the region of positive values leads to the appearance of a pseudo-passive state (high current density of 5-10 mA/cm²), which according to the literature [7, 8] can be associated with the so-called salt passivity – the formation of cobalt sulfate, which provides limited access to the corrosive media.

Unlike the behavior of alloys in sulfuric acid, the development of the corrosion process in sodium sulfate solution is characterized by a significant overvoltage, both the cathode process with oxygen depolarization and the anode process in a sufficiently wide potential area, relative to the transition point potential (300-400 mV), and low current densities (cathode and anode), which indicates high corrosion resistance, although the alloys are in the active state.
Further anodic polarization, as well as in the sulfuric acid solution, causes a significant increase in the anode dissolution current, the appearance of the activation peak and the subsequent transition to a pseudopassive state due, according to the literature, to the formation layer of cobalt sulfate salt. As can be seen, liquid-phase sintering provides a more stable state of the alloys from an electrochemical point of view (lower critical current values at critical points).

5. Summary
The structure and properties of compact materials based on tungsten carbide with different GGI synthesized by different sintering techniques were investigated by methods of scanning electron microscopy, metallography, mechanical and electrochemical tests.

It is shown that the microstructure formed during solid-phase SPS is nanoscale. In all three cases, normal and abnormal growth, as well as coalescence were recorded. It was found that the addition of chromium carbide as a GGI is more effective in comparison with mixed alloying with tantalum carbide and vanadium carbide.

The results of mechanical tests of the obtained samples showed the dependence of strength properties on the average grain size of a compact material, with a decrease in grain size, the microhardness increases and the crack resistance decreases.

Obtained chronopotentiograms illustrate the spontaneous cathode polarization, which may be an indication of the corrosion process via active dissolution. It is established that, regardless of the composition and sintering technology, the stationary potentials of all alloys, except for WC-10Co without additives in a neutral medium, have a more positive value, indicating their higher thermodynamic stability.

It was found that the potential shift to positive values leads to a transition into a passive state associated with the formation of cobalt sulfate. It is also shown that GGI have a significant effect on the critical current density of the activation peak in a neutral solution.

Acknowledgements
The research is carried out with the support of the Russian Foundation for Basic Research Grant project 19-03-00925.

References
[1] Farag S, Konyashin I and Ries B 2018 Int. J. Refract. Met. Hard Mater. 77 12
[2] Upadhyaya G S 2001 Mater. Design 22(6) 483
[3] Zhang L, Chen Yi, Wan Q-L, Liu T and Tian W 2016 Int. J. Refract. Met. Hard Mater. 57 70
[4] Kellner F J J, Hildebrand H and Virtanen S 2009 Int. J. Refract. Met. Hard Mater. 27(4) 806
[5] Isaeva N V, Blagoveshchenskii Y V, Blagoveshchenskaya N V, Mel’nik Y I, Samokhin A V, Alekseev N V and Astashov A.G. 2014 Russian J. Non-Ferr. Met. 55(6) 585
[6] Spark Plasma Sintering of Materials: Advances in Processing and Applications 2019 ed P Cavaliere (Springer)
[7] Human A M and Exner H E 1997 Int. J. Refract. Met. Hard Mater. 15(1-3) 65
[8] Mori G, Zitter H, Lackner A and Schretter M 2001 Proc. 15 Int. Plansee Seminar (Plansee Holding AG Reutte) vol 2 ed G Knieringer, P Rodhammer and H Wildner pp 222-236