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Complexions at carbide/binder grain boundaries of Re-containing submicron cemented carbide

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Samples of submicron WC-Co-Re cemented carbide were produced and examined by different techniques. The microstructure of the samples is fine and extremely uniform indicating the strong inhibiting effect of Re with respect to the WC grain growth during liquid-phase sintering. Results of examination of hot hardness at a temperature of 500°C provide evidence for the significantly higher hardness value of the WC-Co-Re cemented carbide in comparison with that of a conventional submicron WC-Co grade. Studies of creep rates of WC-Co-Re and WC-Co cemented carbides at 800°C indicated dramatically improved high-temperature creep-resistance of the Re-containing cemented carbide. Carbide/binder grain boundaries in a FIB lamella prepared from the WC-Co-Re cemented carbide were examined by high-angle annular dark field scanning transmission electron microscopy and energy dispersive X-ray spectroscopy at a high resolution. Rhenium was found to segregate at the grain boundaries forming complexions of 2 to 3 atomic monolayers, which presumably consist of mixed W-Re carbide. Such complexions are believed to suppress the phenomena of grain boundary sliding at elevated temperatures and WC grain growth at sintering temperatures thus dramatically improving the high-temperature creep-resistance of the WC-Co-Re material in comparison with conventional WC-Co cemented carbide.

Keywords: creep rates, hot hardness, cemented carbide, grain boundaries, Co-Re binders, complexions.

1. Introduction

Ni-based superalloys are presently the most important class of materials for the fabrication of gas turbines. This is so, because they uniquely combine three key properties at a favorable performance to cost ratio: toughness, strength at elevated temperatures and oxidation resistance. However, there is also an important limitation related to relatively low melting point of such alloys. Results of the fabrication and examination of Co-Re alloys indicate that they are characterized by outstanding high temperature properties due to special features of Co-Re solid solutions and their high melting point. Such alloys are presently being developed for ultra-high-temperature applications to supplement Ni-based superalloys in future gas turbines. The main objective of the alloy development is to increase the maximum service temperature of the alloy beyond 1473 K [1, 2]. The unique properties of Co-Re alloys can be applicated to other composite materials, in particular, to cemented carbides in which Co-Re alloy can be used as a binder phase.

Cemented carbides employed for high-pressure high-temperature (HPHT) components used for diamond and cubic boron nitride (c-BN) synthesis and production of polycrystalline diamond (PCD), including anvils and dies, are subjected to extremely high pressures and elevated temperatures. Such unfavorable conditions lead to their deformation and, if the deformation exceeds a certain level,

the HPHT components fail. Therefore, it is very important to have cemented carbides with a high level of hot hardness and high temperature creep resistance to reduce the deformation at high pressures and temperatures. This should improve the deformation resistance and lifetime of the HPHT components, especially those operating at ultra-high pressures (above roughly 10 GPa) [3].

Cemented carbides with the binder phase consisting of Co-Re alloys represent a new class of composite materials having significantly improved high-temperature properties due to exceptional properties of the Co-Re alloys mentioned above [3–7]. They can be employed for applications characterized by the presence of extremely high temperatures, for example, for machining Ni-based superalloys. Nevertheless, the reason for such high properties of the WC-Co-Re cemented carbides is presently not fully understood, as it is unlikely that the high temperature properties of the WC-Co-Re cemented carbides are related only to the solid-solution strengthening effect of the Co-based binder as a result of forming Co-Re alloys. One of the possible explanations of the outstanding high-temperature properties of the WC-Co-Re materials can be the suppression of grain boundary sliding at high temperatures, which might be related to special features of the carbide/binder grain boundaries. It can be expected that Re segregates at the carbide/binder grain boundaries thus suppressing the process of their sliding at elevated temperatures. However, there is no information in

the literature on the atomic structure and composition of the carbide/binder grain boundaries in the WC-Co-Re cemented carbides.

Microstructure, performance and some mechanical properties of the WC-based cemented carbides with Co-Re binders were examined in refs. [3–7]. It was established that such cemented carbides are characterized by significantly improved performance in comparison with conventional WC-Co materials when machining Ni-based superalloys at high cutting temperatures. The Co-Re binders of the cemented carbides were also studied by transmission electron microscopy and scanning electron microscopy in [8,9]. It was found that rhenium added to the Co-based binder phase forms a solid solution with cobalt decreasing the stacking fault energy of the binder phase, which leads to the stabilization of the hcp Co modification.

In [3,10] it was established that rhenium acts as a strong WC grain growth inhibitor suppressing the WC grain growth during liquid-phase sintering of the WC-Co-Re cemented carbides. A generally accepted mechanism explaining the influence of conventional grain growth inhibitors (e. g., VC) on the WC mean grain size in WC-Co cemented carbides is based on the segregation of the grain growth inhibitors forming complexions consisting of mixed carbides at WC/Co grain boundaries [11–14]. Such complexions suppress the dissolution of fine WC grains in a Co-based liquid binder during liquid-phase sintering of cemented carbides resulting in the WC grain growth inhibition [15].

The major objective of this work was to examine high temperature properties of the submicron WC-Co-Re cemented carbide, and atomic structure and composition of grain boundaries between the tungsten carbide phase and Co-Re binder in the WC-Co-Re cemented carbide.

2. Experimental details

A powder mixture of WC-Co-Re cemented carbide containing 5.5 wt.% Re and 3.7 wt.% Co was milled in a ball-mill in hexane. WC powders with mean grain sizes of 0.8 μm, a Co powder with a grain size of about 1 μm, and a Re powder with a grain size of 1–3 μm were employed. The Co-Re binder content was calculated in such a way that the binder volume share would be equal to the volume share of the Co binder in the submicron WC-6 wt.% Co carbide grade, which was employed as a control for examinations

of high-temperature creep-resistance and hot hardness. After milling and drying a slurry obtained in such a way cemented carbide samples were pressed and sintered at 1520°C in vacuum followed by hot-isostatic pressing (HIP) under argon pressure. High-temperature creep resistance was examined at a temperature of 800°C by the use of the technique described in [3]. The hot hardness of the WC-Co-Re cemented carbide and conventional WC-Co grade with the same volume percentage of the Co binder was measured at a load of 300 N at a temperature of 500°C in an Ar atmosphere.

Cross-sections of the cemented carbide samples were examined by the use of a high-resolution scanning electron microscope Philips XL-30S and a transmission electron microscope (TEM). For TEM studies cross-sectional lamellae were prepared by the focused ion beam (FIB) technique on a FEI Quanta 2003D FIB instrument. High angle annular dark field scanning TEM (HAADF-STEM) imaging and energy-dispersive X-ray microanalysis (EDX) were carried out on a probe- and image aberration-corrected FEI Titan 80-200 ChemiSTEM TEM operating at 200 kV.

3. Results and discussion

Figure 1 shows the microstructure of the submicron WC-Co-Re cemented carbide. As one can see in the figure, the microstructure of the WC-Co-Re cemented carbide is fine and uniform and does not contain large or abnormally large WC grains. Note that no conventional grain growth inhibitors (e. g. VC, Cr_3C_2, Mo_2C, TaC, or their combination) were added to the powder mixture comprising the submicron WC powder. Therefore, rhenium acts as a strong grain growth inhibitor during liquid-phase sintering of the WC-Co-Re materials than that of the conventional WC-Co cemented carbide. Note also that this cemented carbide was sintered at a temperature of 1520°C, which is noticeably higher than the temperatures usually employed for sintering submicron WC-6 wt.%Co grades ($T_{sint.} = 1420 – 1440$°C). Therefore, rhenium acts as a very strong WC grain growth inhibitor suppressing the WC coarsening process.

Figure 2 shows the results on hot hardness of submicron WC-Co-Re and WC-Co cemented carbides with the same volume percentage of the binder. The results shown in Fig. 2 indicate that the hot hardness value established at 500°C of the WC-Co-Re material is significantly higher than that
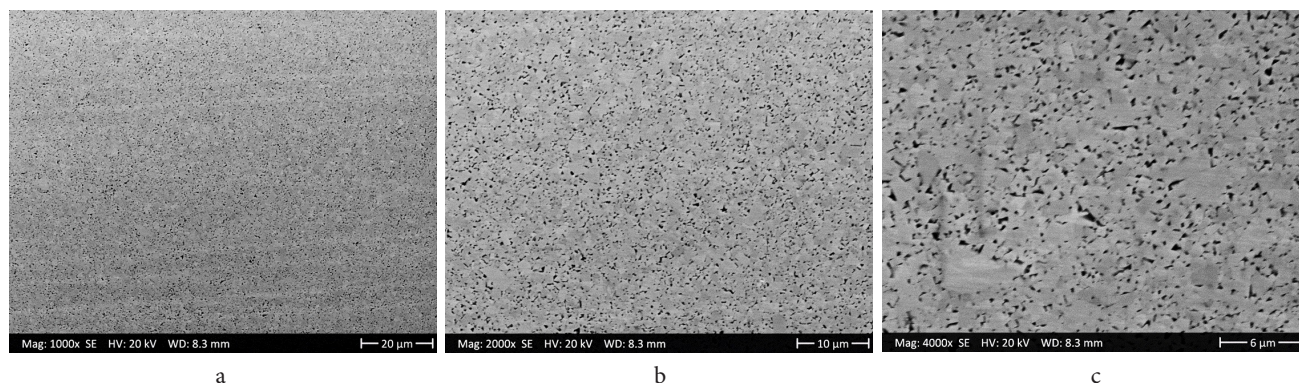

Mag: 1000x SE HV: 20 kV WD: 8.3 mm | 20 μm

Mag: 2000x SE HV: 20 kV WD: 8.3 mm | 10 μm

Mag: 4000x SE HV: 20 kV WD: 8.3 mm | 6 μm

a   b   c

Fig. 1. HRSEM images of the microstructure of the WC-Co-Re cemented carbide at different magnifications: ×1000 (a), ×2000 (b) and ×4000 (c).
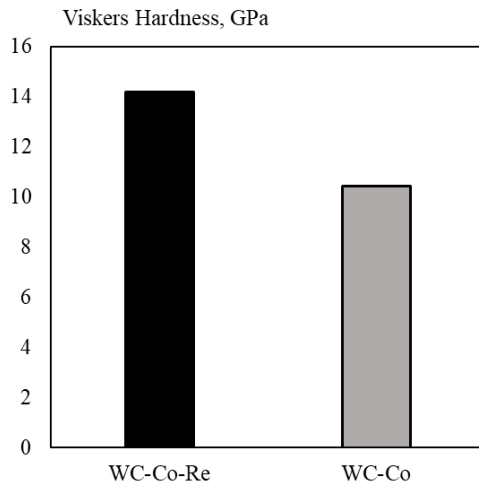
Fig. 2. Hot hardness of the WC-Co and WC-Co-Re cemented carbides with the same volume percentage of the binder phase at 500°C.

of the conventional WC-Co grade. Such temperatures are typical for the operation of HPHT components employed for synthesis of diamond and cubic boron nitride, so that the WC-Co-Re cemented carbides can be presumably very effective for the fabrication of such components.

Curves indicating the dependence of the strain rate on the stress, which were obtained when examining the creep process of the WC-Co-Re and WC-Co cemented carbides at 800°C after extrapolation of the curve for the WC-Co cemented carbide are shown in Fig. 3.

The following regression Eq. (1) obtained by use of the Levenberg-Marquardt algorithm in the Mathcad software package was employed for the curve corresponding to the WC-Co cemented carbide:

$$\dot{\varepsilon}_{WC-Co} = 3.395 \cdot 10^{-5} \sigma^{8.1539} \qquad (1)$$

where σ is the stress in gigapascals.

As it can be seen in Fig. 3, the creep rate of the WC-Co-Re cemented carbide is dramatically reduced in comparison with the WC-Co material (by a factor of more than 50 at a stress of 1885 MPa). Such a significant improvement in creep resistance of the WC-Co-Re cemented carbide is believed to be related to both the significantly increased high-temperature properties of the Co-Re binder [1,2] and special state of carbide/binder grain boundaries leading to a reduced rate of their sliding at elevated temperatures. Another possible explanation for the improvement in creep resistance is associated with the phenomenon of complete or incomplete wetting of boundaries between WC grains by the Co-Re melt, as well as with the morphology of intergranular phase layers.

There is no information in literature on the state and composition of WC/binder grain boundaries in WC-Co-Re cemented carbides. Nevertheless, when taking into account the significant inhibiting effect of rhenium additions with respect to the WC grain growth during liquid-phase sintering established in [10], it can be expected that Re-containing complexions should form at the WC/binder grain boundaries of the Re-containing cemented carbides. Modern ideas with respect to the mechanism of the influence of grain growth inhibitors on the microstructure of cemented carbides are related to the experimentally established fact of the segregation of grain growth inhibitors on the surface of WC grains. They form complexions consisting of thin carbide layers (of the order of several atomic monolayers) consisting of (W, Me)C, where Me is a metal forming the carbide phase of the grain growth inhibitor [11–14]. For example, when VC is employed as a grain growth inhibitor for WC-Co cemented carbides, the WC/Co grain boundary is characterized by the presence of complexions of cubic carbide (V, W)C of the order of 2–4 atomic monolayers in thickness [13]. The presence of such complexions was established at the grain boundaries of cemented carbides containing additions of practically all the grain growth inhibitors (except for molybdenum carbide) according to [11,14]. In [14] it was also found that almost all the grain growth inhibitors except for TaC segregate at WC/WC grain
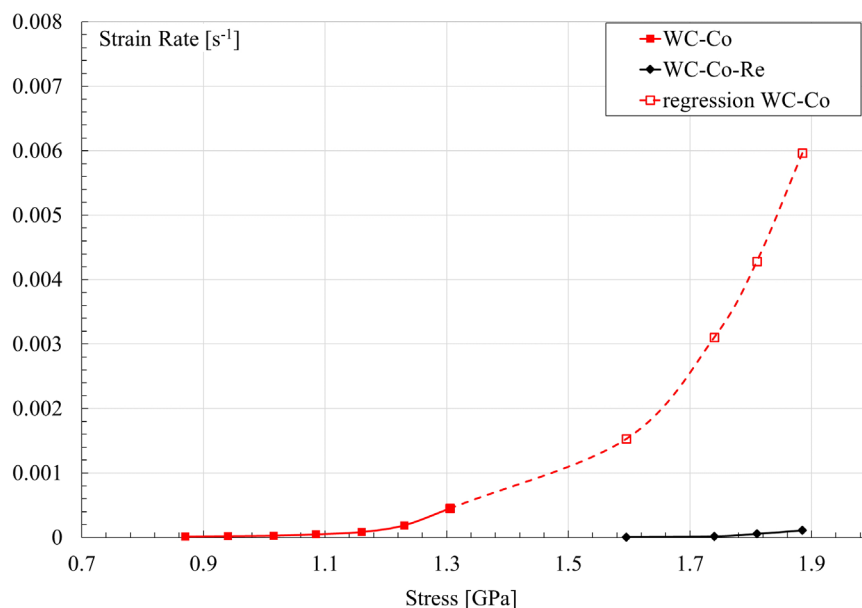

Fig. 3. (Color onilne) Curves indicating the dependence of the strain rate on stress obtained when examining the creep process of WC-Co-Re and WC-Co cemented carbides at 800°C after extrapolation of the curve for the WC-Co material.

boundaries forming the complexions of several atomic monolayers in thickness. It is believed that such complexions consisting of mixed carbides on the base on metallic component of the grain growth inhibitor are present on the surface of fine grains of tungsten carbide during liquid-phase sintering thus suppressing their dissolution in the liquid phase during sintering and stabilizing the fine-grain microstructure of submicron ($d_{WC} = 0.5 - 0.8$ µm), ultrafine ($d_{WC} = 0.2 - 0.5$ µm) and nanograin ($d_{WC} < 0.2$ µm) cemented carbides [15].

The state and composition of the carbide/binder grain boundaries were studied by transmission electron microscopy. Figure 4a shows an ADF STEM image of the microstructure of WC-Co-Re cemented carbide and Fig. 4b shows a HAADF STEM image of the carbide/binder grain boundary in the region indicated in Fig. 4a. It can be seen that the periodical diffraction contrast areas are present at the carbide/binder grain boundary. They can be related to the periodical misfit dislocations forming at the grain boundary. The crystal lattice of the CoRe binder

is found to be epitaxial with respect to that of some WC grains and the mutual orientation of the crystal lattices is {001}<1–10>CoRe//{100}<001>WC. It appears in Fig. 4b that the last atomic plane of the CoRe binder adjacent to the WC grain is characterized by a higher contrast than that of the CoRe binder matrix, which can be related to a higher Re concentration at the grain boundary.

Figure 5 shows elemental maps of W and Co at the carbide/binder grain boundary and the corresponding HAADF STEM image as well as an image showing spots corresponding to tungsten (red) and rhenium (green) atoms. It can be clearly seen in Fig. 5d that there is a Re segregation at the carbide/binder grain boundary forming a complexion of 2 to 3 atomic monolayers, in which W and Re atoms are mixed. The presence of such a complexion at the WC/binder grain boundary of about 0.5 nm in thickness enriched with rhenium can be seen in Fig. 5 showing distributions of different chemical elements in the interface region. The Re-enriched layer presumably consists of mixed (W, Re) carbide, the existence of which was reported in
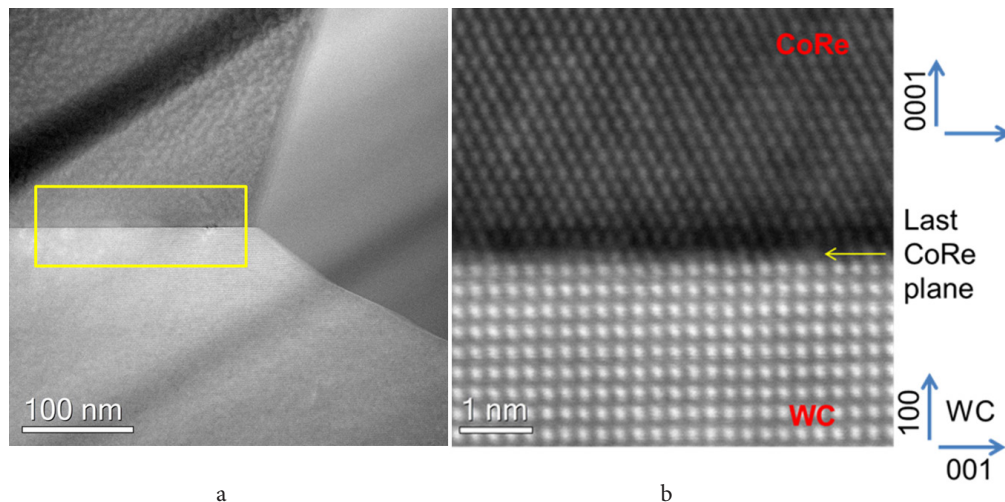

Fig. 4. (Color online) ADF STEM image of the interfacial region of the WC-Co-Re cemented carbide (a) and HAADF STEM image of the carbide/binder interface (b).
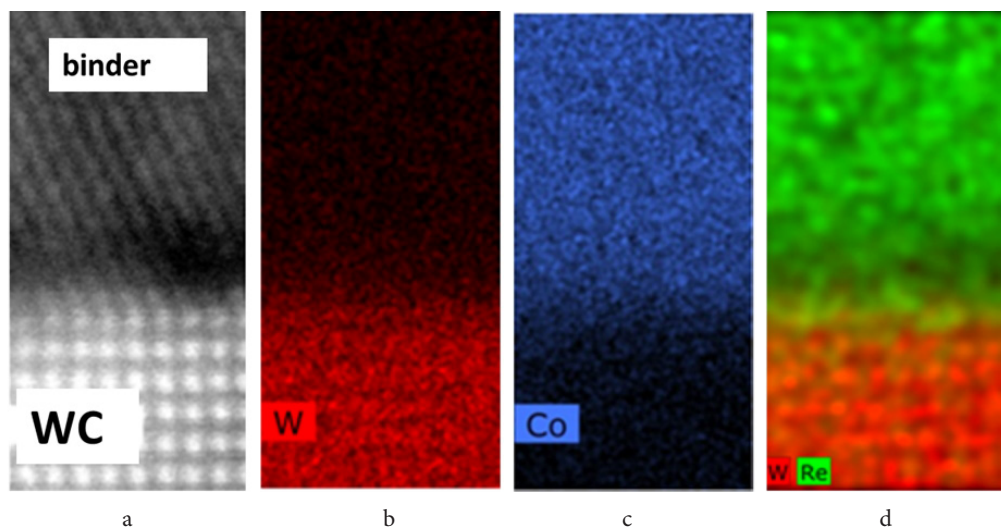

Fig. 5. (Color online) Carbide/binder grain boundary of the WC-Co-Re cemented carbide: HAADF STEM image (a); corresponding element maps of W (b) and Co (c); the interface region with red and green spots corresponding to tungsten (red) and rhenium (green) atoms (d). Note that there is a layer of about 2 to 3 atomic monolayers, in which W and Re atoms are mixed at the WC/binder interface.

[16]. The presence of such a layer is thought to be a reason for the significantly increased value of hot hardness and dramatically improved high-temperature creep resistance of the WC-Co-Re cemented carbides, as it can significantly reduce the rate of the WC/binder grain boundary sliding at high loads and elevated temperatures. The presence of the complexions at the WC/binder grain boundaries presumably also leads to the suppression of the WC grain growth during liquid-phase sintering of the WC-Co-Re cemented carbides resulting in their fine and uniform microstructure.

Despite the high prices of Re powders and consequently higher production costs of the WC-Co-Re cemented carbides they can find applications in the fields, where their unique high temperature properties, namely significantly improved high-temperature creep resistance and hot hardness, are expected to play a critical role. These can be HPHT components for diamond and c-BN synthesis. It is well known that cutting tools for machining superalloys are subjected to extremely high cutting temperatures [11]. The WC-Co-Re carbide grades can be effectively employed in cutting Ni- and Co-based superalloys, which was established in [6,17], due to their high hardness retained at elevated temperatures.

4. Conclusions

The microstructure of the WC-Co-Re submicron cemented carbide is fine and extremely uniform indicating the strong inhibiting effect of Re with respect to the WC grain growth during liquid-phase sintering. Hot hardness of the WC-Co-Re cemented carbide at a temperature of 500°C is significantly higher than that of conventional submicron WC-Co cemented carbides. The high-temperature creep-resistance of the WC-Co-Re material at 800°C is dramatically improved in comparison with the conventional WC-Co cemented carbide. Rhenium was found to segregate at the grain boundaries forming complexions of 2 to 3 atomic monolayers, which presumably consist of mixed W-Re carbide. Such complexions are believed to suppress the phenomena of grain boundary sliding at elevated temperatures and WC grain growth at sintering temperatures thus dramatically improving the high-temperature creep-resistance of the WC-Co-Re material in comparison with conventional WC-Co cemented carbides.

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