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Microstructure and composition of segregation layers at WC/Co interfaces in ultrafine-grained cemented carbides co-doped with Cr and V

Weiteng Guo [a,b,c,d], Kai Li [a,c,*], Yong Du [a,c], Zhongjian Zhang [b], Tao Xu [b], Chao Yin [b], Zhuo Zhang [c], Peng Zhou [a], Xiangzhong Liu [b], Baiyun Huang [a]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China
[b] State Key Laboratory of Cemented Carbide, Zhuzhou, Hunan 412000, China
[c] Institute for Materials Microstructure, Central South University, Changsha, Hunan 410083, China
[d] School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China

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ABSTRACT

VC-Cr_3C_2 is the most widely used grain growth inhibitor for ultrafine-grained cemented carbides. However, the mechanism for the high effectiveness of this inhibitor is still unclear. This work aims to clarify the inhibiting mechanism involving VC-Cr_3C_2 inhibitor through investigations of a commercial ultrafine-grained WC–Co–VC–Cr_3C_2 cemented carbide in an objective-aberration-corrected transmission electron microscope. Our results show that continuous segregation layers enveloping WC grains [$(V,W,Cr)C_x$ on $(0001)_{WC}$ basal facets and (Cr,W,V)C on $\{10\bar{1}0\}_{WC}$ prismatic facets] account for the high effectiveness of VC-Cr_3C_2 inhibitor. Especially, the newly observed continuous and coherent (Cr,W,V)C layers on $\{10\bar{1}0\}_{WC}$ prismatic facets give an explanation for the superiority of VC-Cr_3C_2 inhibitor compared with VC inhibitor.

1. Introduction

WC–Co cemented carbides are widely used as machining tools due to their excellent hardness and wear resistance. Ultrafine-grained WC–Co cemented carbides with average WC grain sizes varying from 0.2 to 0.5 μm, exhibit higher hardness and wear resistance than traditional cemented carbides [1–3]. However, during their fabrication, smaller grain size of raw powders is required, which enhances the surface reactivity and produces a higher possibility of abnormal grain growth according to Ostwald-ripening mechanism [4]. Several methods [5–7] have been developed to retard this abnormal grain growth. The most widely applied one among them is the addition of transition metal carbides, such as VC, Cr_3C_2, TiC, TaC, and NbC, which act as grain growth inhibitors for WC.

When a single type of inhibitor is doped on WC–Co interfaces, the effectiveness of inhibiting grain growth is in the order of VC > Cr_3C_2 > NbC > TaC > TiC [8]. In WC–Co cemented carbides doped with only VC [9–13], smooth and continuous V-rich segregation layers were observed on $(0001)_{WC}$ basal facets of the triangular prism shape of WC grains, while rough and discontinuous V-rich layers were found to adhere to $\{10\bar{1}0\}_{WC}$ prismatic facets. When individual Cr_3C_2 was added, Cr-rich layers were also observed on both types of facets [13,14], and the layers on $(0001)_{WC}$ facets were thinner and rougher than the counterparts observed in VC doped cemented carbides. On the other hand, the Cr-rich layers on $\{10\bar{1}0\}_{WC}$ prismatic facets tend to be more uniform than the ones observed in WC–Co–VC. These segregation layers are believed to act as barriers to prevent W in liquid Co from diffusing into WC grains [15]. However, the usually observed growth of WC grains on their $\{10\bar{1}0\}$ facets into steplike bulges which were termed as nanosteps, revealed that the inhibiting effectiveness of a single type of inhibitor was not satisfactory. This situation might result from the phenomenon that inhibitors only form rough films on prismatic facets rather than form continuous films as in the case of $(0001)_{WC}$ basal facets [12,14]. On the other hand, the uniform distribution of grain sizes observed in WC–Co cemented carbides co-doped with VC and Cr_3C_2 indicates a higher inhibiting effectiveness than single doping [16]. However, the mechanism for the outstanding inhibiting effectiveness of VC-Cr_3C_2 mixed inhibitor is still unknown.

By calculating MC/WC (M represents V or Cr) interface energies based on density functional theory (DFT), Johansson et al. [17–19]

* Corresponding author at: State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China.
E-mail address: leking@csu.edu.cn (K. Li).

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predicted the existence of segregation layers with V and Cr enrichment during sintering and reported the higher propensity for the formation of VC thin film than CrC thin film on WC/Co interfaces. So far, an experimental observation of the microstructure and compositions concerning these interfaces is missing. In particular, whether there are layers of inhibitors on both basal and prismatic facets of WC grains, and the microstructure and compositions of these inhibitor layers, are not clarified yet. This work is aimed at obtaining detailed experimental information about the microstructure of segregation layers along the WC/Co interfaces in cemented carbides co-doped with Cr and V by means of objective-aberration-corrected high-resolution transmission electron microscopy (HRTEM), high-resolution energy dispersive X-ray (HREDX) spectroscopy and high-angle annular dark field (HAADF) imaging. Such an experiment is performed with a desire to clarify the inhibiting mechanism of VC-Cr_3C_2 co-doping.

2. Experimental procedure

A commercial WC–Co cemented carbide co-doped with V and Cr was prepared with the powder metallurgy method. WC powders with an average size of 0.3 μm were mixed with Co, VC and Cr_3C_2 powders, and the pellets were sintered at 1410 °C in Ar for 40 min followed by furnace-cooling. The composition of the sample was WC-6.5Co-0.35VC-0.55Cr_3C_2 (in wt.%). TEM specimens were prepared by focused ion beam (FIB) in an FEI Helios 600i NanoLab instrument using 30 keV Ga^+ ions (5 keV Ga^+ in the final thinning process). HRTEM and HAADF observations of the prepared thin foil specimens were performed in an FEI Titan G2 60-300 transmission electron microscope operated at 300 kV with an objective aberration corrector. The microscope is equipped with a Super-X detector, which is composed of four separate EDX detectors symmetrically placed around the specimen to obtain a high detection efficiency. This detector design is dedicated to HREDX elemental mapping and compositional analysis at the nanoscale.

3. Results

3.1. TEM observations of the segregation layers

Fig. 1a is a HAADF image showing the Z-contrast around the basal WC/Co interface. The contrast of the layer between WC and Co suggests there is a phase with different composition from both of WC and Co. The HRTEM image inserted in the top right corner shows the projection of a face centered cubic (fcc) structure of the layer along its $[1\bar{1}0]$ axis. The concentration (in at.%) profiles of V and Cr across the layer given in Fig. 1b display the higher concentration of V at the basal interface, meanwhile it is more closely adhered to WC. This HREDX line scan was conducted from m_1m_2 to n_1n_2 along their normal, with an extended width of 15 nm (see the yellow box in Fig. 1a) in order to improve the statistics. The belt is referred to as $(V,W,Cr)C_x$, as will be discussed later. It is also found that the belt will grow into semicircular areas when the basal plane meets another WC grain, as shown in Fig. 1c. The HRTEM image in the red box and relevant FFT pattern shows that the orientation relationship between WC and $(V,W,Cr)C_x$ at the basal $(0001)_{WC}$ facet can be obtained as: $(0001)_{WC}//(111)_{(V,W,Cr)Cx}$, $[1\bar{2}10]_{WC}//[1\bar{1}0]_{(V,W,Cr)Cx}$. The lattice parameter of the $(V,W,Cr)C_x$ crystal is measured to be $a_{(V,W,Cr)Cx} = 4.11$. The growth of semicircular areas does not change the structure or orientation of the $(V,W,Cr)C_x$ compound. Meanwhile, the schematic showing atomic occupancy model (obtained by observing the model in Fig. 5 along $[1\bar{2}10]_{WC}$) near the $(0001)_{WC}/(111)_{(V,Cr,W)Cx}$ basal interface is displayed in the bottom right corner in Fig. 1c. Fig. 1d shows that the concentration profile of Cr is close to that of V across the semicircular area. Both elements are enriched in this area.

As shown in Fig. 2a, the WC prismatic facet is covered by planar segregation layers, which also contains semicircular areas located near the dihedral angle assembled by two WC grains. Fig. 2b is the Fourier-filtered HRTEM image showing the same area of Fig. 2a with noises dismissed. Fig. 2a displays the same structure as that in Fig. 1a with

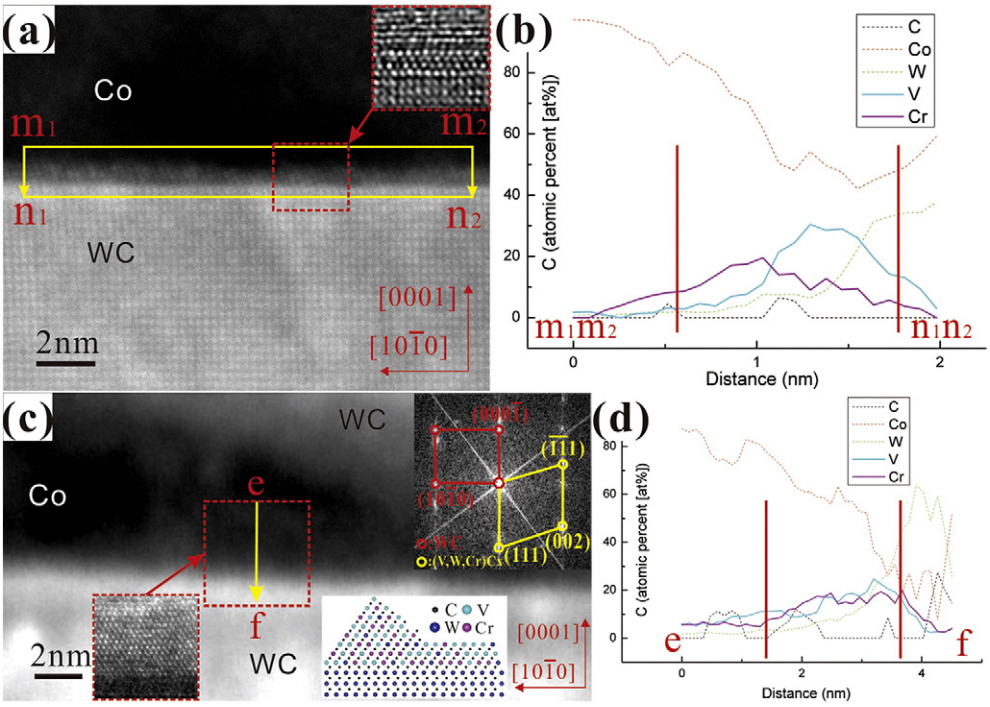

Fig. 1. EM studies of the basal $(0001)_{WC}$ WC/Co interface co-doped with Cr and V, viewing direction is parallel to $[1\bar{2}10]_{WC}$. (a) HAADF image of the basal WC/Co interface. (b) HREDX line scan profile from m_1m_2 to n_1n_2 along their normal, as indicated by the rectangle in (a). (c) HAADF image of the basal WC/Co interface. (d) HREDX line scan profile along *ef* shown by the arrow in (c).