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WC기 초경합금중 WC/WC界面의 구조와 입계편석

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Structure and Intergranular Segregation of WC/WC Grain Boundaries in WC-Based Cemented Carbides

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초 록 WC-Co와 WC-VC-Co 초경합금중 WC/WC입계의 구조와 입계 편석상태를 알아볼 목적으로 HRTEM과 EDS를 이용하여 연구하였다. 일부의 입계들은 액상에 의하여 분리된 상태로 관찰되었으나, 상당수는 원자적 상태의 연속계면이었다. 또 연속계면 중 WC-Co 합금에서는 Co상이 편석되어 있었으며 WC-VC-Co 합금에서는 Co와 V이 동시에 편석되어 있음을 알 수 있었다. 그 편석의 폭은 약 6nm였다. 연속 계면 중 V의 편석은 소결 또는 열처리 시에 일어나는 입계 이동을 억제하는 데 효과적인 역할을 할 것으로 여겨졌다. 동시에 이것은 WC-Co 초경합금에서 VC첨가에 의한 입성상 억제기구를 설명할 수 있는 것으로 사료되었다.

Abstract The WC/WC grain boundary structure and intergranular segregation in WC-Co and WC-VC-Co cemented carbides were investigated by high-resolution transmission electron microscopy and energy dispersive X-ray spectroscopy in order to elucidate whether contiguous boundaries were present or not at the atomic level. Some grain boundaries were separated by liquid phase, while others were contiguous at the atomic level. Cobalt was found to be segregated to WC/WC grain boundaries in WC-Co. Cobalt and vanadium were co-segregated to grain boundaries in WC-VC-Co. The segregation width in both materials was about 6 nm. These results suggest that the vanadium present in contiguous boundaries acts as an effective barrier to the migration of boundaries during sintering and annealing. This could explain the grain growth inhibiting mechanism of VC added to WC-Co.

Key words : Boundary structure, Intergranular segregation, Contiguous boundary, Cemented carbide, HRTEM.

1. Introduction

Cemented carbides consisting of tungsten carbide and cobalt (WC-Co) are widely used in cutting tools and wear resistant components. These cemented carbides are fabricated by a liquid phase sintering process at high temperature around 1700K. WC grains tend to be coarsened during the liquid phase sintering and the grain size strongly affects the mechanical properties and hence cutting performance of the cemented carbides. Therefore, control of the grain growth behavior is important for producing high quality carbide tools. Previous studies have reported that the grain growth of WC in WC-Co occurs predominately due to solution-reprecipitation of WC grains in the Co-W-C liquid phase. However, Exner[1], Warren[2] and Suzuki et al.[3] mentioned that the grain growth of WC in WC-Co cannot be explained merely by an Ostwald ripening process, because, WC grains are not completely surrounded by Co-W-C liquid phase but are connected with other WC grains to form contiguous boundaries. The relative fraction of WC/WC grain boundaries can be expressed by contiguity, defined as the relation $G=2N_{ss}/(2N_{ss}+N_{sl})$, where N_{ss} and N_{sl} are the numbers of interceptions of WC/WC and WC/Co boundaries, respectively, per unit length of the test line. It has been suggested that the contiguity plays an important role in the grain growth of cemented carbides.[4]

In order to understand the sintering and grain growth mechanism in WC-Co cemented carbides, detailed microstructural examination of grain boundaries is needed on the atomic scale. However, in spite of many previous investigations, the structure of grain boundaries in WC-Co has not been clarified, particularly in regard to the presence of a liquid phase. Grain boundaries in WC-Co composites have been studied by Auger electron spectroscopy (AES), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) and field ion microscopy (FIM). An AES study showed that a cobalt monolayer is present at WC/WC grain boundaries.[5] TEM and HRTEM studies[6~9] confirmed the existence of contiguous grain boundaries without cobalt phase. Jayaram,[7] using lattice imaging, reported that some grain boundaries were contiguous at the atomic level and that the others were separated by integranular cobalt films. In contrast, the TEM study by Egami et al.[10] reported that all WC grains were surrounded by cobalt phase and there were no contiguous grain boundaries. The STEM-EDS study by Sharma et al.[11] found that cobalt was present as a thin 2nm layer between WC grains. Friederich[12] also detected cobalt at WC/WC grain boundaries using STEM-EDS. FIM studies by Henjered et al.[13,14] showed that cobalt does not exist as a phase, but segregates with half a monolayer coverage. As shown above, there has been a lot of argument about whether contiguous boundaries are present or not at WC/WC grain boundaries.

It is also well known from experiment that the grain growth of WC is inhibited by the addition of VC, Cr_3C_2 and TaC[3,15~17] However, some of the basic questions about the location of the inhibiting phase and grain growth inhibition mechanism are still not completely understood. The purpose of this study is to investigate the structure and intergranular segregation of WC/WC grain boundaries in WC-Co and WC-VC-Co by using field emission type HRTEM and EDS in order to understand the mechanism of grain growth in the presence of liquid phase. Moreover, we pay special attention to the location of VC additives in the WC-VC-Co microstructure.

2. Experimental Procedure

WC and VC powder with average particle sizes of 1.5 ㎛ and Co powder with a particle size of 1.2㎛ were used. VC was chosen as an additive because vanadium is one of the most effective elements to inhibit WC grain growth. WC-30vol%Co powders with VC (2.4 mol%) and without VC were mixed by ball-milling in ethanol for 48hrs, and then uniaxially pressed. The green compacts were sintered without applying pressure at 1673K under vacuum for 1hr. These samples were mechanically ground and polished down to a thickness of 0.05mm and then subsequently ion beam thinned to electron transparency with argon ions under a 5kV accelerating voltage.

HRTEM was carried out using a HITACHI HF-2000 microscope (field emission gun type 200kV). In order to investigate grain boundary structure accurately by HRTEM, grain boundary planes were set parallel to the incident electron beam. Nano-probe EDS quantitative analysis was performed in spot mode. The electron probe was set to be 1nm and was aligned parallel to the WC/WC grain boundary.

3. Results

3-1. WC-Co

Figure 1 shows a typical bright field image of WC-Co. WC grains show well-defined crystallographic facets formed by liquid phase sintering, and the dislocation density in WC grains is relatively low. The WC grains seem to connected to each other to make contiguous boundaries. However, such a low magnification bright field image does not reveal clearly the details of WC/WC grain boundaries.

Figure 2 is a high-resolution micrograph of a WC/

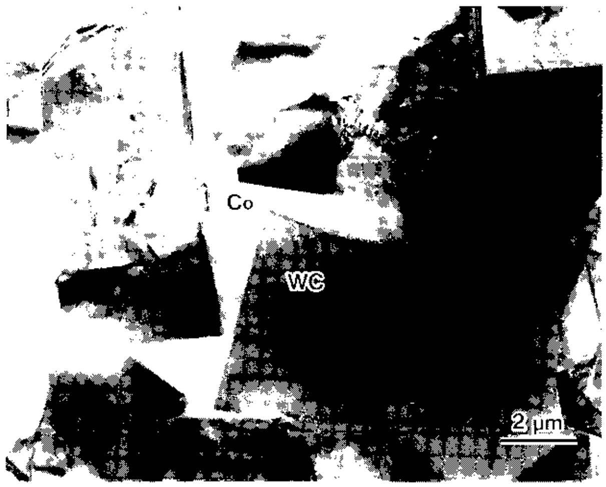

Fig. 1. TEM image of WC-30vol%Co, sintered at 1673K for 1hr.

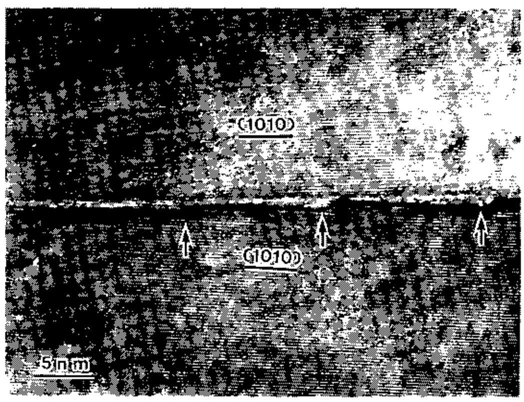

Fig. 2. A high-resolution electron micrograph of a WC/WC grain boundary in WC-30vol%Co. Arrows indicate pockets of Co.

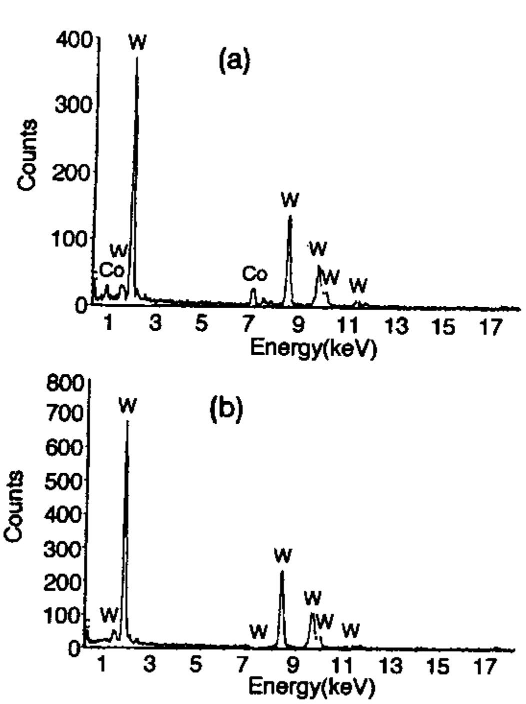

Fig. 3. EDS spectra of the grain boundary in Fig. 2. (a) point on the grain boundary, (b) a point 2nm from the grain boundary.

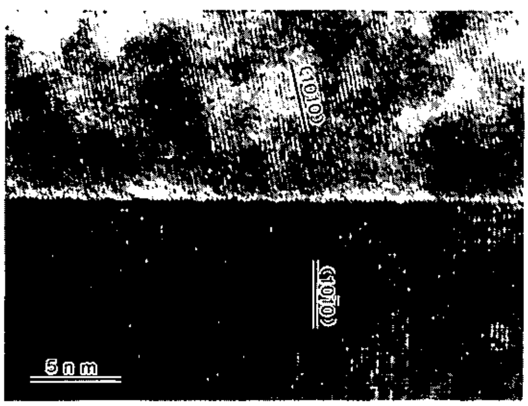

Fig. 4. A high-resolution electron micrograph of a grain boundary in WC-30vol%Co.

WC grain boundary in WC-Co, which contains an intergranular phase of cobalt. Intergranular cobalt pockets (indicated by arrows in Fig. 2) are observed along the boundary. Figure 3 shows the EDS spectra obtained from the intergranular phase and from a point 2nm away from the grain boundary. Figures 2 and 3 show that each WC grain is separated by a cobalt phase in this grain boundary. In the micrograph image, microfaceting of the grain boundary is also visible.

Figure 4 shows a high-resolution micrograph of a different type of grain boundary in WC-Co. No continuous grain boundary phase is observed. From CSL (Coincidence Site Lattice) theory[18], this grain boundary does not have a low Σ value and is defined as a general grain boundary. In this lattice image, an intergranular

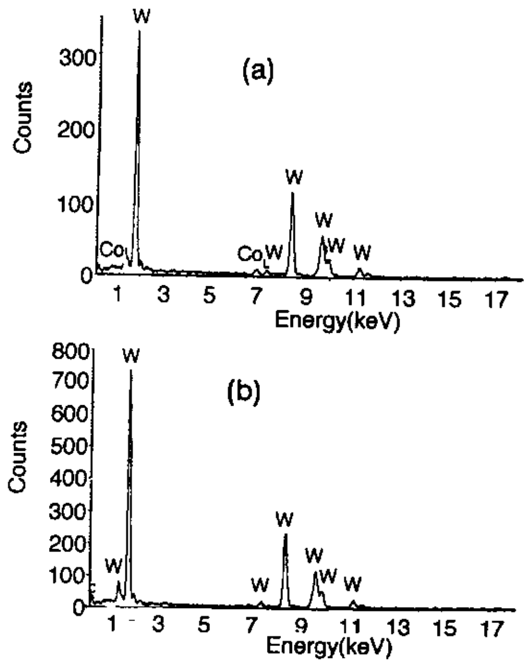

Fig. 5. EDS spectra of the grain boundary in Fig. 4. (a) a point on the grain boundary, (b) a point 2nm from the grain boundary.

cobalt phase cannot be observed at the grain boundary and the WC grains come into direct contact. However, cobalt is detected at the grain boundary by EDS analysis when the 1 nm diameter probe, which is the incident electron beam of the TEM, is fixed in position over the grain boundary (Fig. 5). At a point 2nm from the grain boundary, no cobalt is detected. Figures 4 and 5 thus confirm that Co atoms are segregated to the grain boundary. These observations indicate that some WC grains are contiguous at the atomic level while others are separated by intergranular phase. The present results are in accordance with several previous studies.[6~8]

3-2. WC-VC-Co

Figure 6 shows a typical bright field image of WC-VC-Co. In WC-VC-Co, the crystal habit plane of the WC crystals and the WC grain shape are not clear, and the crystals have a high density of dislocations. These dislocations may originate from strain during the milling process or pre-existing dislocations in the raw W powders before carbonization.[19]

Figure 7 shows the lattice fringe image of a WC/WC grain boundary that is defined as a general boundary by CSL theory. In this image, an intergranular cobalt phase was not observed at the grain boundary and the lattice of WC grains was continuous. Figure 8 shows the EDS profile across this WC grain boundary in which strong segregation of Co and V was detected.

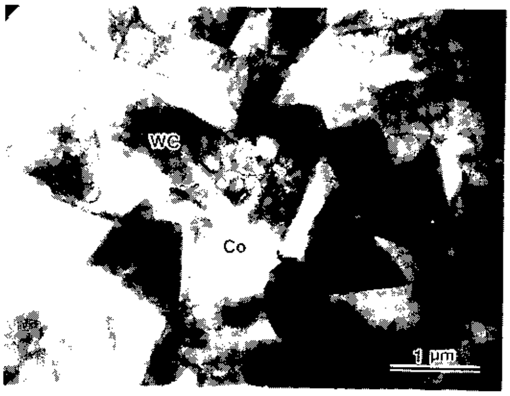

Fig. 6. TEM image of WC-VC-30vol%Co, sintered at 1673K for 1hr.

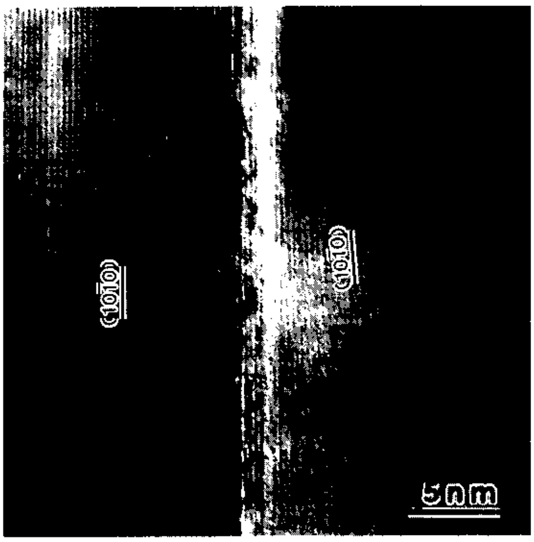

Fig. 7. A high-resolution electron micrograph of a grain boundary in WC-VC-Co.

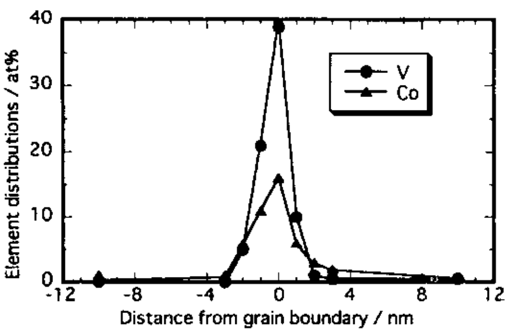

Fig. 8. EDS profiles of Co and V distributions around the WC/WC grain boundary in Fig. 7.

The segregation width was about 6nm.

Figure 9 shows the lattice fringe image of a different WC/WC grain boundary in WC-VC-Co that is identified as a $\Sigma 2$ coincidence boundary by CSL theory. In this image, no cobalt phase was observed at the grain boundary. But as shown in Fig. 10, EDS analysis of this grain boundary reveals the presence of cobalt and vanadium at the grain boundary. These results indicate that both Co and V atoms co-segregate to the grain boundary and the WC grains are contiguous at the atomic level.

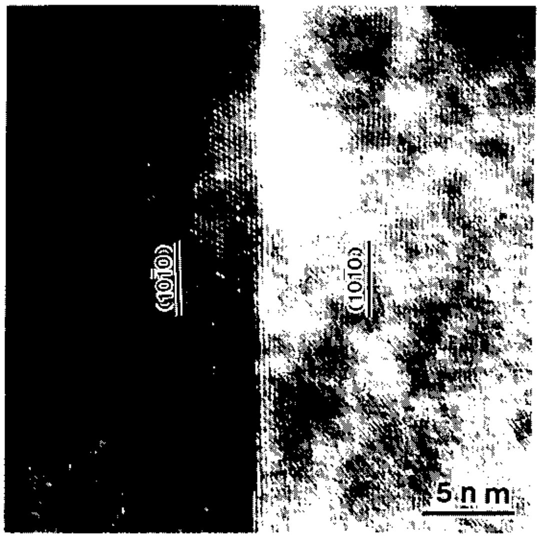

Fig. 9. A high-resolution electron micrograph of a $\Sigma 2$ grain boundary in WC-VC-Co.

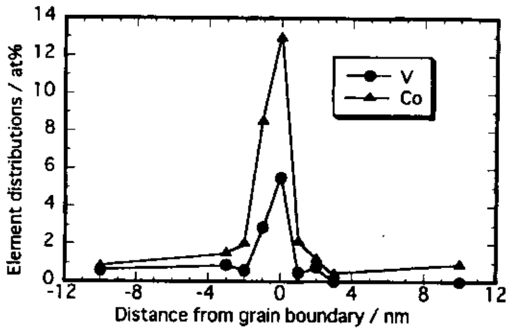

Fig. 10. EDS profiles of Co and V distributions around the WC/WC $\Sigma 2$ grain boundary shown in Fig. 9.

4. Discussion

4-1. WC/WC boundary characterization

WC/WC grain boundaries can be classified into three possible types as shown schematically in Fig. 11. The first type of grain boundary has a small amount of segregation, as typified by the grain boundaries shown in Figs. 4, 7 and 9. The second type of grain boundary is free from the segregation of cobalt and vanadium. The third possible type is the grain boundary with an intergranular Co phase or film, which corresponds to the grain boundary shown in Fig. 2.

Some of the WC/WC grain boundaries in the present work were found to be contiguous (Type Ⅰ) and others separated by intergranular cobalt phase (Type Ⅲ). The second type of grain boundary was not observed in the present study.

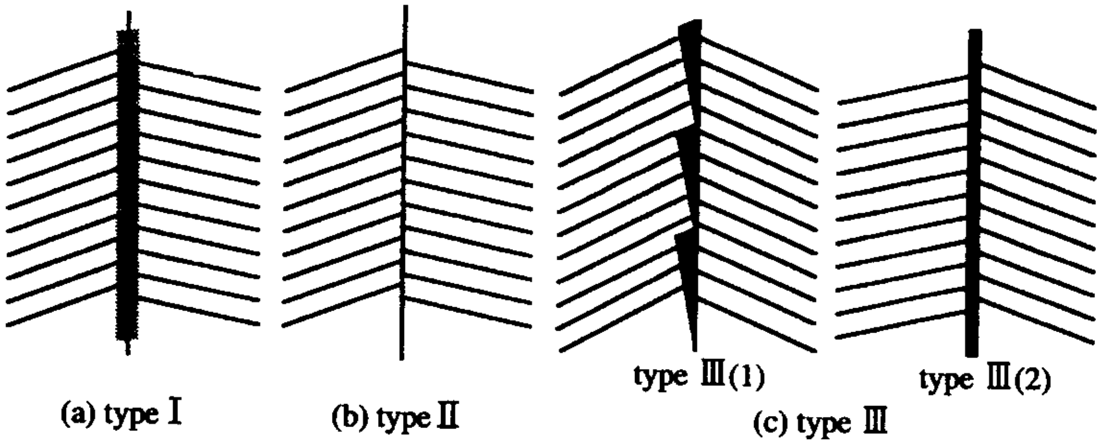

Fig. 11. Schematic of grain boundary structures in WC-based cemented carbides.

Tungsten carbide and vanadium carbide are known to be soluble in Co at normal sintering temperatures. Co-W-C and Co-W-V-C solid solutions may be squeezed out of the intergranular region or retained as a continuous film or second phase between the WC grains. In the former case, only a small amount of Co and V can remain in the WC/WC grain boundaries (Type Ⅰ). In the latter case, non-contiguous WC/WC boundaries are formed with Co and V atoms predominantly in the intergranular Co-W-V phase (Type Ⅲ).

From the present results, the width of segregated region of Type Ⅰ boundaries is estimated to be less than 6 nm. The grain boundary segregation of Co in WC-Co was previously observed to be about several tens of nanometers wide along the boundaries.[6] However, the probe size in the previous work was too large to investigate the element distribution in the vicinity of grain boundaries on the nanometer scale. In this study, Co and V intergranular segregation at WC/WC boundaries was confirmed on the nanometer scale. In another previous study, Co and V were detected at WC/WC grain boundaries in WC-VC-Co[20], but the authors didn't examine the grain boundary structure in detail. Henjered et al. reported that Cr segregates to WC/WC grain boundaries in WC-Cr_3C_2-Co cemented carbide.[14] The present results therefore are in good agreement previous results.[4,20]

4-2. Intergranular segregation

The degree of segregation to grain boundaries generally depends upon the boundary structure, and therefore will vary from boundary to boundary.[21] Low-angle and CSL boundaries usually exhibit smaller amounts of segregation than general high-angle boundaries. This behavior has been confirmed by experiments and calculations reported in the literature.[22~24] The present results show good correspondence to these previous experimental and calculated results.

As shown in Fig. 8 and Fig. 10, the amount of segregation at the general high-angle boundary is greater than that at the $\Sigma 2$ grain boundary. The low segregation level at the $\Sigma 2$ grain boundary can be attributed to the fact that the lattice planes of the two grains have a high atomic density. Vicense et al. deduced from their observations that the amount of cobalt intergranular segregation depends on the geometry of the grain boundary and the configuration of intergranular dislocations in WC-Co.[2] But, in the present study, the relation between the amount of segregation and the configuration of grain boundary dislocations is not clear.

According to the equilibrium segregation theory of McLean[25]:

$$E = 24\pi K S r_1 r_2 (r_2 - r_1)^2 / (3K r_2 + 4S r_1) \qquad (1)$$

where E is the strain energy due to solute misfit, K the bulk modulus of the solute, S the shear modulus of the solvent, r_1 the solvent radius, and r_2 the solute radius. From equation (1), the strain energy is estimated to be about 4.9 kJ/mol when Co dissolves into the WC lattice. When V is dissolved into the WC lattice, the energy is about 3.7 kJ/mol. These values suggest that even though V is more easily dissolved in the WC lattice, the strain energy for both atoms is sufficiently high that both Co and V can only penetrate into the low density grain boundary regions, where the strain energy can be accommodated.

4-3. The effect of V segregation on grain growth

Exner et al. remarked that WC grain growth during sintering occurs by both grain boundary migration and deposition of tungsten and carbon on to WC grains.[1,26]

In the present study, the existence of contiguous boundaries was confirmed at the atomic level. Moreover, the grain growth inhibitor VC was observed to be segregated even at the contiguous grain boundaries. In our recent paper, we have proposed that the existence of contiguous boundaries affects the migration of the solid/liquid interface during coarsening through the liquid phase.[4,27,28] The lower mass transport rate at the contiguous boundaries compared to that at the solid/liquid interfaces should act as the rate controlling step for grain growth, so that the carbide grains will grow at a much slower rate than that expected from solute diffusion in the liquid phase alone. It is likely that the V atoms decrease the grain boundary mobility and grain boundary energy. The grain boundary segregation of V atoms, therefore plays a particularly important role in inhibiting the grain growth. It is likely that it decreases the grain boundary mobility and grain boundary energy. It was confirmed that V atoms segregated at the grain boundaries, however, it was not proved in this paper that segregation of V atoms to grain boundaries can act as an effective barrier to the migration of WC/WC grain boundaries during sintering. This explains why VC has a strong grain growth inhibiting effect when added to WC-Co.

5. Conclusions

WC/WC grain boundaries in WC-Co and WC-VC-Co were investigated by HRTEM and EDS to determine whether contiguous boundaries are present or not at the atomic level. The following results were obtained:

1) Some WC/WC grain boundaries were not contiguous but were separated by cobalt solution phase. Other boundaries were contiguous at the atomic level. Cobalt was found to be segregated at WC/WC grain boundaries in WC-Co. Cobalt and vanadium co-segregated to the contiguous boundaries in WC-VC-Co.

2) In WC-VC-Co, the vanadium present at contiguous boundaries acts as an effective barrier to the migration of the boundaries during sintering and annealing. This can explain the grain growth inhibiting effect of VC added to WC-Co.

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