High resolution transmission electron microscopy study in VC-doped WC–Co compound

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Abstract

Microstructure evolution in VC-doped WC–Co was investigated using high-resolution transmission electron microscopy (HRTEM) associated with X-ray energy dispersive spectroscopy (EDS) with a special interest in WC/Co and WC/WC boundaries. It was found that the morphology of carbide grains changed largely by the addition of VC. The WC/Co interfaces tend to form facetting with fine multi-steps of (0001) and {1010} habits by VC-doping. In addition, the faceting morphology of WC/Co interfaces was confirmed to be already formed in solid state from an examination with a quenched compound from 1200°C, which is below the eutectic temperature of 1320°C between WC and Co system. EDS analysis with the sub-nano scale probe revealed that the doped V was strongly concentrated to the two habits. However, the amount of concentrated V was different among them, i.e. more at (0001) habit than at {1010} habits. V is considered to be concentrate at the boundary during grain growth to accompany the migration of the two habits because most of the doped V solves into the Co-phase and not into WC grains. Thus it can be supposed that the retardation of the grain growth of WC grains is due to the concentration of V at the migration front of the two habits.

Meanwhile, WC/WC boundaries were found to be directly in contact each other and free from the second phase such as the amorphous phase whereas the segregation of Co and also V could be detected by EDS analysis. This fact suggests that the grain boundary migration between the adjacent WC grains may be mainly controlled by the solid–solid diffusion.

Keywords: WC-Co; Microstructure; Grain growth; HRTEM; EDS; Boundaries

1. Introduction

High hardness and high strength are crucial factors for mechanical machining tools such as high speed steel, ceramics, cermets and so on. Fe–C–W–Cr based alloy is widely used as the typical high-speed steel, and Al2O3–TiC or Al2O3–ZrO2 based composites are known to be one of the ceramics suitable for practical use. However, the hardness of the high-speed steel is not so high and the fracture toughness of ceramics is relatively low. Although these disadvantages are the intrinsic properties of metal and ceramics, respectively; however, they have other advantageous properties, i.e. metal possesses high fracture toughness, and the ceramics generally have high hardness. To simultaneously provide these advantageous properties in the materials, many kinds of metal–ceramic composites have been intensively fabricated mainly by the powder metallurgical method. Among the large amount of composites investigated, TiC–Mo2C–Ni [1,2,3] and WC–Co based compounds [4] are well known to have excellent properties as machining tools for practical purposes, and called as “cermets” in this field. These cermets have been already used as commercial-based materials, and many researchers are competing to improve the mechanical properties of the materials further. In particular, WC–Co based compounds are paid much attention because their hardness, strength and wear-resistance are well balanced at the high level with a possibility to expand their markets. The mechanical properties of WC–Co compounds are reported to be dependent on the grain size of carbides, i.e. the materials with smaller grain size show high mechanical properties [5]. In order to improve the mechanical properties of WC–Co compounds, we need to obtain the microstructure with a smaller grain size [6,7]. WC–Co compounds normally consists of WC grains with the Co-rich phase in between [8,9]. So far, the addition of a small amount of transition metal carbides such as TiC, VC, Cr2C3 and NbC have been recognized to be an effective method to control the WC grain size [10,11,12,13].
The additives are considered to play an important role in inhibiting the grain growth during sintering at high temperatures. Among the various transition metal carbides, VC would be the most effective dopant to retard the grain growth of WC, and VC-doped WC–Co compounds have been investigated from various kinds of approaches. It was also known that a few wt% of VC addition is enough to effectively retard the grain growth in the WC–Co compounds, but the retardation mechanism has not been clarified in detail yet. Microstructure characterization is one of the useful experiments to find the nature of the retardation mechanism. Egami et al. firstly observed the microstructure of VC-doped WC–Co compound with a special interest in the WC/Co interfaces [14]. They found that the precipitates are formed periodically along the boundaries and identified the precipitates to be (W,V)C compound by using TEM–EDS (X-ray energy dispersive spectroscopy) analysis. They insisted that the grain growth retardation in VC-doped WC–Co compounds was related to the precipitation of (W,V)C compound at the WC/Co interface. That is, (W,V)C compounds first precipitates during cooling after liquid-phase sintering and hence the grain growth is considered to be retarded in the WC grains. According to their interpretation, the grain growth is inhibited only during cooling. Meanwhile, the microstructure studies for the WC–Co based compounds have thus been focused to the liquid-phase sintered compounds because WC–Co compounds are generally fabricated by liquid-phase sintering [15,16]. Fig. 1 shows a pseudo-binary phase diagram in the WC–Co system [17]. The sintering temperature for liquid-phase sintering is usually set above the eutectic point [18]. The sintering temperature in WC–Co system is generally investigated by HREM and EDS to mainly reveal the atomic structures and the localized chemical composition at the WC/Co interface and WC/WC grain boundary. The obtained results were then compared with each other to clarify the grain growth retardation mechanism in the VC-doped WC–Co compounds.

2. Experimental procedure

Powders of WC (Japan New Metal, nominal grain size of 0.8 μm), Co (United Metal, 1.2 μm) and VC (Starck, 1.6 μm) were used as raw materials. Each powder was mixed in a planetary-mill for 2 h. After milling, the mixture was dried, sieved and pressed under a pressure of 150 MPa to a size of 0.5 × 0.5 × 5 mm³. Two kinds of sintering processes were then compared with each other to clarify the grain growth retardation mechanism in the VC-doped WC–Co compounds.
Japan). EDS (Voyager System, Noran) was conducted with a field-emission type HRTEM (EM-002BF, TOPCON, Japan). Chemical analysis was made with an extremely small electron probe size of 0.5 nm.

3. Results

3.1. Liquid-phase sintered compound

Fig. 2 shows typical microstructures in (a) non-doped and (b) doped compounds in as-sintered state. The grains with black contrast represent for WC grains, and the phase with white contrast the Co-phase as indicated in (a), respectively. The average grain size of carbide grains is estimated to be 0.67 μm in the non-doped compound and 0.13 μm in the doped one. It is thus clear that a small amount of VC addition is effective to suppress the grain growth of the carbide grains as previously reported [18]. As seen in the figure, the non-doped compound exhibits the well-known microstructure that consists of WC grains scattered in a metallic binder phase that comprise mainly Co. Most of WC grains are faceted and therefore the WC/Co interfaces are plateau. On the contrary, the morphology of the WC/Co interface largely changes by the addition of VC as seen in Fig. 2(b). Fine multi-steps are generated along the WC/Co interfaces in the doped compound as indicated by the arrows in Fig. 2(b). This distinct feature of multi-stepped boundaries is particularly observed only in the VC-doped WC–Co.

Fig. 3 is a HRTEM image of the doped compound in as-sintered state. The WC/Co boundary consists of (0001) and (10\(\bar{1}0\)) habits. The contrast like other compounds can be seen on the B–B boundary and near the corner of the two habits as shown by the arrows A. The circles represent for the areas where EDS analysis was carried out at every 1 nm interval.

Fig. 2. Bright field images in: (a) non-doped; and (b) doped compounds in as-sintered state. Note that the magnification is different between the two micrographs and that the WC/Co interfaces are faceted with fine multi-steps as shown by the arrows in (b).

Fig. 3. A HRTEM image in the doped compound in as-sintered state. The WC/Co boundary consists of (0001) and (10\(\bar{1}0\)) habits. The contrast like other compounds can be seen on the B–B boundary and near the corner of the two habits as shown by the arrows A. The circles represent for the areas where EDS analysis was carried out at every 1 nm interval.

tendency that the width of the (0001) habit is longer than that of the (10\(\bar{1}0\)) one as seen in the figure. On the other hand, other compounds can be observed along the habit B–B and at the corner of a cross of the two habits as indicated by the arrows A. The details about the compound will be discussed later.

Fig. 4 is the EDS spectra taken from the (0001) habit of B–B boundary and 2 nm apart from the habit inside a WC grain as indicated in Fig. 3. The peak of V K\(\alpha\)-line clearly appears at the habit, i.e. WC/Co interface, as in (a) whereas it disappears in the WC grain interior as in (b). The EDS analysis clearly reveals that the content of doped V increases strongly at the WC/Co interface in the doped compound.

Fig. 5 is a plot of the content of V as a function of distance from the boundary as shown by dots in Fig. 3. EDS analysis was carried out systematically at every 1 nm across the boundaries for the two habits, i.e. (0001) and (10\(\bar{1}0\)). The V content increases at both habits; however, the amount of its content is very different in the two habits. The concentration of V is higher at the (0001) habit than at the (10\(\bar{1}0\)) one. The behavior of V-concentration as in the plot was similar in the other WC/Co interfaces examined in this study.

Fig. 6 shows a HRTEM image in the vicinity of a triple junction of WC grains of the doped compound in as-sintered state. The electron probe direction is parallel to the [12\(\bar{1}0\)] of the WC grain, and the WC/Co interface is set at the edge-on condition. The areas for EDS analyses are also shown with the circles in the figure. It is noted that the fine multi-steps are composed of two kinds of habits, i.e. (0001) and (10\(\bar{1}0\)) type habits, respectively. From the examination of other many WC/Co interfaces, there is found to be a
boundary A−A. The grain boundary of A−A is estimated to be a small-angle boundary with a rotation axis of near [0001]. There are no second films or precipitates at the grain boundaries and WC grains directly contact each other.

Fig. 7 is a plot of the content of Co and V across the WC/WC grain boundary estimated from EDS analysis. EDS analysis are systematically conducted at every 1 nm interval across the grain boundary A−A as shown in Fig. 6. The content of both Co and V increases at the grain boundary and they distribute in the region less than 2 nm in the vicinity of the grain boundary. This tendency can be also observed in the other WC/WC grain boundaries examined. This means that both V and Co can solve into the WC lattice and segregate at the boundary.

3.2. Solid-state sintered compound

Fig. 8 shows bright field images in (a) non-doped and (b) doped compounds in as-quenched state from 1200°C, at which the sintering process is in the solid state. The morphology of WC grains in the non-doped compound is not so largely different from that in the liquid-phase sintered compounds as seen in Fig. 2. This indicates that the typical microstructure of cemented carbide is already formed even in the solid state at 1200°C in the non-doped compound. On the other hand, the edge of WC grains are somewhat round in the doped compound as indicated by the arrows in (b). In addition, the WC/Co interfaces are facetted with fine steps, which is similar to that of the liquid-phase sintered compound as seen in Fig. 2(b). These characteristics are commonly observed in the doped compounds examined in this study. Meanwhile, the averaged grain size of WC grains...
is 0.36 μm in the doped compound while that in the doped compound it is 0.12 μm. The grain size of the non-doped quenched compound is almost the same as that of the fully sintered compound. A small amount of VC addition to the WC–Co compound is thus confirmed to be very effective to suppress the grain growth of WC grains even at 1200°C, i.e. in the solid state as seen in Fig. 8.

A HRTEM image of the doped quenched compound is shown in Fig. 9. The areas for EDS analysis are alphabetically indicated in the figure. The WC/Co interface is set at the edge-on condition and an electron beam is parallel to [1210] of the WC grain. The HRTEM image clearly shows the formation of stepped boundaries at an atomic scale, which is similar to that in the fully sintered compound as seen in Fig. 3. Namely, the multi-stepped boundary is already formed with the two kinds of habits in the solid-state reaction, i.e. (0001) and {1010}, respectively. Although the contrast like other compounds can be seen along the (0001) habit in the liquid-phase sintered compound as seen in Fig. 3; no other compounds can be detected at boundaries between WC grains and Co-phases in the solid-state sintered compound. Meanwhile, comparing with the multi-stepped boundaries as in Fig. 3, the width of the two habits is not so different in the quenched compound. Both (0001) and (1010) habits in the quenched compound have similar width; whereas the (0001) habit tends to be wider than the (1010) one in the fully sintered compound.

Fig. 10 shows the EDS spectra taken from the points of A and B as indicated in Fig. 9. The peak of V Kα-line appears clearly in the EDS profile just at the WC/Co interface while it disappears at 2 nm off from the boundary inside the WC grain. This result clearly shows that the concentration of doped VC at the WC/Co interface takes place even in the solid state.

Fig. 11 is a HRTEM image of WC/WC grain boundary in the doped compound quenched in the solid state. Adjacent WC grains contact without any second film. On the other hand, both Co and V segregate at this WC/WC boundary as seen in Fig. 12, which shows EDS profiles taken from the areas as indicated by the circles in Fig. 11. The segregation of Co and V is also confirmed even in the solid state, which is similar to the WC/WC grain boundaries in the liquid-phase sintered compound as in Fig. 7.

4. Discussion

4.1. The morphology change of WC grains in VC-doped WC–Co

The addition of VC makes the WC/Co interfaces facetted and the morphology of WC grains changes from plateau to fine multi-stepped feature consisting of the two habits (0001) and {1010}. Fig. 13 shows an example of a schematic of WC grain in the doped compound. In the
figure, the plane as indicated by a shade is normal to the observed direction of the HRTEM image, i.e. [1210], and the dotted areas represent the concentration behavior of V. Comparing with the EDS analysis, doped V concentrates at the two habits and the concentration differs among them. The amount of V is more at the (0001) habit than at the (1010) one as seen in Fig. 5. In addition, V concentrates strongly near the corner of the two habits as shown by the arrow in Fig. 3. These phenomena are considered to be closely related to the migration of the two habits. The morphology change of WC/Co interface is also observed in the solid-phase sintered compound. However the length of the two habits is different among the two compounds.

Comparing with the length of these two habits in these compounds as shown in Figs. 3 and 9, the length of the (0001) habit becomes longer after liquid-phase sintering, which means that the migration rate normal to the {1010} habit increases with an increase in the sintering temperature. In other words, the migration normal to (0001) is effectively retarded. As seen in Fig. 4, doped V does not solve into WC grains but to the Co-phase. Namely, V concentrates at the migration front of the two habits during grain growth, and consequently, the amount of V increases at the two habits. As mentioned above, there exists the V-concentration area near the cross points of the two habits. This is also consistent with the migration direction model associated with V concentration.

Fig. 14 shows a HRTEM image in the vicinity of multi-stepped WC/Co interface of the doped compound in as-liquid-phase sintered state. In the figure, some other structure can be seen at the front of the (0001) habit of the WC grain as indicated by the arrows, irrespective of concentration. These precipitates were not observed in solid-phase sintered compounds as seen in Fig. 9. From the EDS profile taken from the compound, the atomic fraction of W is estimated to be about 80%, if the content of Co is ignored. According to the phase diagram of the W–V–C system, there exist two kinds of WC and VC solid solution, i.e. (W, V)C and (W, V)2C, respectively [23]. As several amounts of Co solutes into the precipitates, a detail structure...
of the precipitates cannot be precisely determined. However it is reasonable to consider that the structure has a type of \((W, V)_2C\) because the solubility of W into \((W, V)C\) is limited at 25 at.% to form a fixed structure; whereas \((W, V)_2C\) is a completely solubility type. The formation of \((W, V)_2C\) may be closely related to the over-concentration of V. The solubility of V into the Co-phase is about 4.7 at.% at an equilibrium state [24]. If the concentration of V caused by the migration of WC grains is over at the concentration of the solubility limit, it is reasonable to form the compound such as \((W, V)_2C\). In addition, the lattice mismatching between WC and \((W, V)_2C\) is very small as recognized in the HRTEM image, as shown in Fig. 14. This would be one of the reasons for the formation of \((W, V)_2C\) precipitates at the WC/Co interface.

4.2. The grain growth inhibition in VC-doped WC–Co

It is well known that a small amount of VC-doping to WC–Co compound is very effective to suppress the grain growth of WC grains during sintering. Egami et al. first observed the microstructure of VC-doped WC/Co compound and reported that small \((W, V)C\) particles are formed periodically along the WC/WC or WC/Co interfaces [14]. They concluded that the inhibition of the grain growth of WC grains was due to the pre-precipitation of \((W, V)C\) compounds during cooling after the sintering process. They insisted that pre-precipitation of \((W, V)C\) compounds prevents the solution-reprecipitation of WC through the Co-phase during cooling after liquid-phase sintering. In this study, the interesting result that the microstructure formation is already completed in the solid state is obtained. In addition, the grain size in the doped compound is not so largely different in the solid-phase and liquid-phase sintering, i.e. 0.12 and 0.13 μm, respectively, as previously reported [18]. Thus the retardation of the grain growth does not take place during the cooling process after sintering. Egami’s interpretation is not considered to be suitable for the recognition of the inhibition mechanism of VC-doping.

Taniuchi et al. reported that the amount of solved W in the Co phase is decreased by the addition of VC, i.e. 25.2 wt% in the non-doped compound and 9.8 wt% in the doped one [18]. Taking into account their results and considering the present results, the inhibition of the grain growth caused by the VC-doping can be interpreted as follows. Firstly the doped VC solves into the Co-phase while heating during sintering. The segregation of doped V to the WC/Co interfaces takes place, and then the WC grains are surrounded by the concentrated V layers at around 1200°C and facetted with fine multi-steps. A part of the segregated V forms \((W, V)_2C\) precipitates at an elevating temperature. After the formation of the segregation layer, the solution-reprecipitation process of carbide grains may be limited. It is noted that the retardation of the grain growth has already taken place in the solid state. At the quenched state from 1200°C, impingement between the carbide grains is not so heavy because of the density of about 80% respective to the theoretical density. Thus it is not necessary to consider the solid–solid diffusion process for WC ripening. The details are not clear yet, but the interpretation as described above is considered to be reasonable.

4.3. The WC/WC boundary

The grain growth behavior of WC grains is often discussed by two kinds of limitation mechanism. One is the solution-reprecipitation process caused by Ostwald ripening among the carbide grains through Co metallic phase, and the other the solid–solid diffusion among carbide grains at contact areas among adjacent WC grains [25,26,27]. On the basis of these mechanisms, it has been often discussed whether a thin Co layer exists along WC/WC boundaries or not [28,29,30]. The grain growth of WC grains progresses through the solution-reprecipitation process if the liquid phase exists at WC/WC boundaries. As for the existence of Co at WC/WC grain boundaries, Vicens et al. reported that the content of Co depends on the orientation relationship of WC grains [8]. According to their result, the mount of Co decreases with an increase in the coherency of the WC/WC boundaries. But it is unclear that an amorphous phase mainly consisting of Co exists or not at the WC/WC boundary, judging from their result because the results about the grain boundary structure were not shown in their report. On the contrary, in this study the segregation of Co was revealed even at a small-angle WC/WC boundary as seen in Fig. 6. In addition, WC/WC grains contact each other without any second film even if Co segregation takes place. This fact means that the mass flow during the grain growth across adjacent WC grains can be considered to be mainly controlled by solid–solid diffusion.

5. Conclusion

The effect of V-doping on the morphology of WC grains was examined by HRTEM and EDS. The following conclusions are obtained.

1. The WC/Co interfaces become facetting with fine multi-steps consisting of the two habits, i.e. (0001) and \{10\bar{1}0\}. The increment of the V content at the two habits can be revealed from EDS analysis with sub-nano-scale probe. The concentration of V is different among the two habits and it increases at \{0001\} habit.
2. The morphology change in WC grains caused by VC addition has occurred already in the solid state reaction. In addition, the grain size of WC grains is not so largely different between the liquid-phase and the solid-phase sintered compounds. This fact means that the suppression of the grain growth takes place even in the solid state at relatively low temperatures.
3. The length of the habits is found to be different when the sintering temperature is raised. The (0001) habit becomes longer with an increase in the sintering temperature.

4. The retardation of the WC grain growth is due to the reduction of the amount of W into the Co phase, which is caused by VC doping. This is because the solution-reprecipitation process of W through the Co-phase may be limited by the increment of V concentration at the two habits.

5. HRTEM study revealed that the grain boundary of WC/WC is free from the second phase such as the amorphous phase. But the segregation of Co and V take place at the boundaries. The mass flow between the adjacent WC grains is controlled by the solid–solid diffusion.

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