2006 POWDER METALLURGY
World Congress
PM2006

A Consideration on Segregation Process of Dopant at WC/Co and WC/WC Interfaces in VC Doped WC-Co Submicro-grained Hardmetal

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Abstract

WC/WC interface in VC mono-doped WC-10mass%Co submicro-grained hardmetals of 0.5 μm was investigated together with WC/Co interface by using HRTEM and XMA. The thickness of V-rich layer and the analytical value of V at WC/WC interface were almost the same as those at WC/Co interfaces. These results, etc., suggested that the V-rich layers at both interfaces were not generated by an equilibrium segregation mechanism in the sintering stage, but generated by a preferential precipitation mechanism during the solidification of Co liquid phase in the cooling stage. Based on this suggestion, we succeeded in developing a nano-grained hardmetal with 100 nm (0.1 μm).

Keywords : **submicro-grained hardmetal, grain growth inhibition, segregation, interface, HRTEM**

1. Introduction

In recent years, WC-Co submicro-grained hardmetals with finer WC grain size (0.1-0.3 μm) than the present available ones (0.5-0.7 μm) are strongly demanded as a promising material of shaping-mold/punch for high precision micro components [1]. In the fabrication of WC-Co submicro-grained hardmetal, a small quantity of WC grain growth inhibitors such as VC and Cr_3C_2 are doped. HRTEM and XMA revealed that 2-3 atomic layer containing these dopants was segregated at WC(0001)/Co interface in the sintered alloy [2-6]. The following two hypotheses as the mechanism of grain growth inhibition are proposed: (a) equilibrium segregation of dopant atoms on total WC(0001)/Co interface [2,3], and (b) intermittent adsorption of dopant atoms at the crystalline kink/step on the surface of WC grain [4-6]. The necessary dopant amounts that are suggested by these hypotheses are different with each other. In this study, we investigated in detail the segregation layer at WC/WC interface following the study on WC/Co interface, and considered the segregation process at WC/WC interface as well as at WC/Co interface. Based on the conclusion about the process, we tried to develop the finer submicro-grained hardmetal than the present one.

2. Experimental and Results

WC-0.5mass%VC-10mass%Co hardmetal with WC mean grain size of 0.5μm was used. An example of HRTEM microstructure of two kinds of WC/WC/Co triple points in rapidly cooled specimen is shown in **Fig. 1**. A segregation layer, which was confirmed with XMA to contain V, was observed clearly at WC(0001)/WC(0001) interface and slightly at WC(10$\bar{1}$0)/WC(10$\bar{1}$0) interface. Both layers directly connected with the segregation layer at WC(0001)/Co and WC(10$\bar{1}$0) /Co interfaces, respectively.

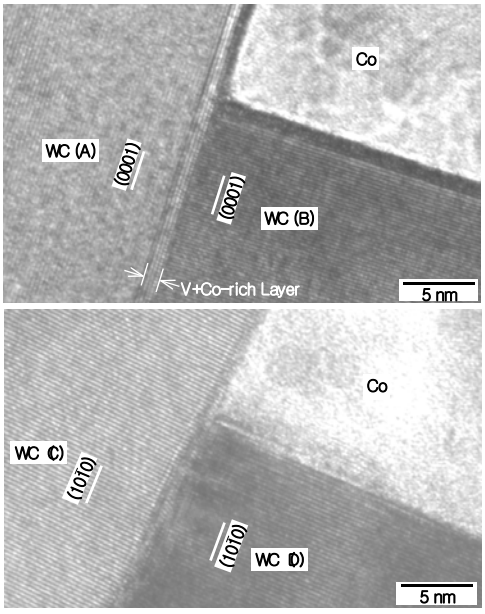

Fig. 1. HRTEM microstructure of two kinds of WC/WC/Co triple points in rapidly cooled (50K/s) WC-0.5 mass%VC-10mass%Co hardmetal with WC mean grain size of 0.5 μm.

Table 1 shows XMA analytical values at the above three kinds of WC/WC interfaces. These values were nearly the same as those at WC/Co interfaces [4] for the same kind of WC plane.

Table 1. XMA analytical values at WC/WC interfaces in hardmetal shown in Fig. 1
B: WC(0001), C: WC(10$\bar{1}$0), G: WC(general planes)

Position / Element	B/B	B/G		C/C		
		1	2	1	2	3
V	9	11	7	5	2	2
Co	10	18	15	28	6	16
W	81	71	78	67	92	82

Based on the above experimental results, the V-rich layer at WC/WC interface as well as at WC/Co interface are suggested to be generated by a preferential precipitation of the solute in Co liquid phase by a constitutional super cooling mechanism during the solidification in the cooling stage of sintering, as schematically shown in **Fig. 2.**

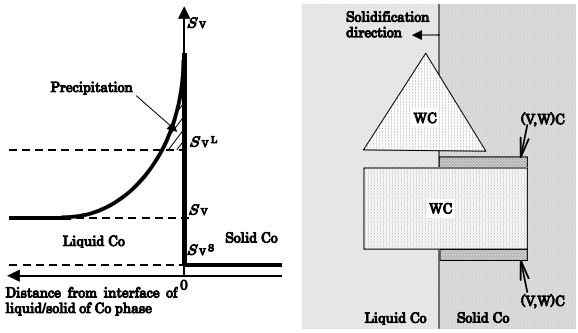

Fig. 2 Schematic drawing for the preferential precipitation process at WC/Co and WC/WC interfaces during solidification of Co liquid phase in the cooling stage.

Furthermore, if the segregation layer was generated by an equilibrium segregation mechanism during the sintering stage, (1) WC grains should preferentially grow to WC[10$\bar{1}$0] direction and hardly to WC[0001] direction, because the segregation amounts at WC(10$\bar{1}$0) interface were less than that at WC(0001), (2) WC layer should be observed at the Co phase-side of the above V-rich segregation layer at WC/Co interface, because WC solves in the Co liquid phase and precipitate during the solidification of the Co liquid phase, as described above. However, the experimental results were as follows: (1) WC grains grew isotropically with increasing sintering time, and (2) WC layer was not observed at the Co phase-side of the V-rich segregation layer, as shown in the above Fig. 1.

These all results suggest that V rich layer at WC/WC as well as at WC/Co interface were not generated by an equilibrium segregation mechanism in the sintering stage, but a preferential precipitation in the cooling stage. Therefore, the necessary amount of the dopant is considered to be not the amount that generates the observed segregation layer of 2-3 atomic layer at all WC(0001)/Co and WC(0001)/WC(0001) interfaces, but the solubility limit in the Co liquid phase that causes the adsorption amount and time at step/kink of WC surface to be both a maximum.

Then, we tried to develop WC-Co hardmetal by doping VC and Cr_3C_2 whose amount are both nearly the solubility limit and by using nano-size (70 nm) WC powder that was developed by A.L.M.T. Corp. As the result, we have succeeded in preparing nano-grained hardmetal of 100 nm (0.1 μm) as shown in **Fig. 3.**

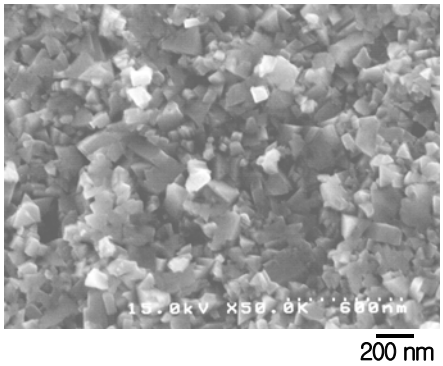

Fig. 3 SEM microstructure of fracture surface of nano-grained WC-10mass%Co hardmetal. The hardness (HV) of the hardmetal was 2300.

3. Summary

Both WC/WC and WC/Co interfaces in VC doped hardmetal with WC mean grain size of 0.5μm were investigated with HRTEM and XMA. Based on the results, it was suggested that V rich layer at WC/Co interface, etc., was generated by a preferential precipitation during the cooling stage. Based on the suggestion, we developed a nano-grained hardmetal of 100 nm by selecting the dopant amount, etc.

4. Acknowledgements

The authors gratefully acknowledge for The New Energy and Industrial Technology Development Organization (NEDO) for financial support of the "Development Project on Fusion Technology of Material and Mold Processing for High-Precision Component", and also Mr. Hiroaki Matumoto, a technical staff of Hitachi Science Systems, Ltd., for the operation of HRTEM and XMA.

5. References

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