Synthesization of WC/Co Composite Powders Doped V and Cr by Mechanochemical Method

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Abstract

Nano-sized WC particles in WC/Co composite powders were synthesized by mechanochemical method. The raw powders(WO_3, Co_3O_4, VC, Cr_3C_2 and graphite) were mixed by planetary milling for 30 hours. The compositions were WC-10 and -20 wt% Co added VC and Cr_3C_2. The direct reduction and carburization of the mixed powders were carried at 900℃ for 1 to 3 hours under flowing Ar gas. The mean size of WC particles in WC/Co composite powders was about 16 nm. The resultant powders were compacted and sintered at 1300~1360℃ for 0.5 hour. After sintering the mean size of WC particles was about 50 nm.

Keywords : mechanochemical method, nano-sized WC, WC/Co composite powder, direct reduction and carburization, sintering

1. Introduction

The WC-Co cemented carbides have been used for cutting, mining tools and wear-resistant parts.[1,2] Recently, the synthesis of nano-sized WC powder have drawn much attention in connection with the improvement of both hardness and toughness of cemented carbide.[3] Several processes for the manufacture of nano-sized WC or WC/Co composite powder have been developed, such as spray conversion processing, mechanical alloying(MA), mechanochemical method. [4,5,6]

Nano-sized WC powder or WC/Co composite powder has been used manufacturing tools and bulk pieces.[7] High energy ball milling has been used to make amorphous alloys and nanocrystalline materials. This method is one of the powerful techniques for synthesizing nanocrystalline materials due to its simplicity and low cost.[8] However, it has low efficiency in fabricating nano-sized WC powders. Moreover, the ranges of compositions and/or size of powder are required to be very narrow. Nano-sized WC grain grows very rapidly during sintering due to the large surface area. Few large WC grains deteriorate the mechanical properties of nano-sized WC-Co materials.[9,10,11] One of the ways to control the grain growth in any nano-sized WC-Co materials is by properly selecting the grain growth inhibitors. VC and/or Cr_3C_2 are known to be the most effective inhibitors for nano-sized WC grain due to their high solubility and mobility in cobalt phase at relatively low temperatures.[11,12]

In this study, the effects of inhibitors on nano-sized WC grain in WC/Co composite powders synthesized by mechano-chemical method and the optimal process of nano-sized WC/Co composite powders in terms of the time of reduced and carburized reaction and the sintering temperature.

2. Experimental and Results

The raw powders of WO_3 (Taegu Tec Ltd., 1.5 ㎛), Co_3O_4 (Kojundo Chemical Laboratory Co. Ltd., 1㎛), VC (H.C. Stark, 1.4 ㎛), Cr_3C_2 (H.C. Stark, 2.9 ㎛), Carbon black (Cancard Co., 0.6 ㎛) were used. These powders were mixed to be the compositions of WC-10, -20 wt% Co. VC and Cr_3C_2 powders were added to be 1.0 wt% in Co content. These powders were milled by planetary mill (FRITSCH, P-5) with ethyl alcohol for 30 hours. The mixed powders were directly reduced and carburized at 900℃ for 1～3 hours under flowing Ar gas (99.999 %, 300 mL/min) in furnace.

The shape and size of the reduced and carburized powders were observed by SEM (JEOL Co., JSM-6330F). The powders were analyzed by XRD (Rigaku Co., DMAX-2500) with Cu Kα. The mean size of WC particles was calculated by Scherrer's formula from WC(101) peaks of XRD.

The resulting powders were compacted and sintered at the temperatures of 1300, 1330 and 1360℃ for 0.5 hour in vacuum. After sintering, the shape and size of WC particle were observed by SEM. The mean size of WC particle was calculated by the same method as above.

During the direct reduction and carburization of mixed powders at 900℃, the volume ratio of CO/CO_2 gas was about 16:1. The CO gas showed two peaks of the reduction of Co_3O_4 at about 600℃ and WO_3 at about 900℃. Those gases almost stopped after 1 hour at 900℃ and after which, the carburizing reaction started.

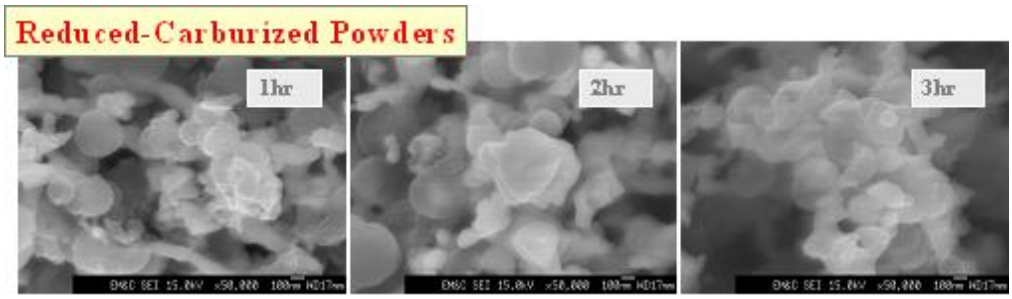

Fig. 1. SEM photographs of the reduced and carburied powders of WC-10 wt% Co at 900℃.

Fig. 1 shows the SEM photographs of the reduced-carburized WC/Co composite powders of in the compositions of WC-10 wt% Co. After the reduction and carburization at 900℃ for 3 hours, the mean size of WC/Co composite powder is about 220 nm. In WC-20 wt% Co, the mean size of them is about 140 nm. The longer the holding time, the smaller the particle sizes were. Furthermore, the more the cobalt, the smaller the mean sizes of WC/Co composite powder were.

From the XRD diffraction patterns, the peaks of WO_3 and Co_3O_4 phases in mixed powders are found, while the peaks of WC, Co and a little intermediate phase (Co_3W_3C) are found in the reduced-carburized powder. Looking at the XRD peak of WC (101) plane, the mean size of WC grains in WC/Co composite powder is about 17 nm for 3 hours in WC-10 wt% Co. On the other hand, the mean size of WC grains is about 20 nm for 3 hours in WC-20 wt% Co.

The reduced and carburized WC/Co composite powders were compacted with 100 MPa and sintered at 1300~1360℃ for 0.5 hour. The linear shrinkages were about 18% in WC-10 wt% Co and about 24% in WC- 20 wt% Co. The higher the Co content and the sintering temperature, the higher the shrinkage due to increased liquid phase.

From the SEM fractographs of the sintered compacts with different sintering temperatures, the mean sizes of WC/Co composite grains are about 280 nm in WC-10 wt% Co and about 260 nm in WC- 20 wt% Co, respectively. The peaks of XRD diffraction patterns of WC-10 and -20 wt% Co sintered at the different temperatures were only WC and Co phases. It was thought that the unfinished carburization of W completed during sintering process.

The mean size of WC grains in WC/Co composite powder was calculated by Scherrer's formula from the XRD diffraction data of WC(101). The mean sizes of WC grains were about 50 nm in WC-10 wt% Co and about 30 nm in WC-20 wt% Co. These results suggest that the WC grain growth depends on more of the content of solute as inhibitor, i.e. V and Cr in liquid phase than temperature

3. Summary

The mixed powders of WO_3, Co_3O4 and carbon black were reduced and carburized at 600~900℃ for 3 hours. The phases of WC, Co, and Co_3W_3C were observed after reduction and carburization at 900℃ for 1 hour. The mean size of WC/Co composite powder was about 220 nm. The mean size of WC grains was about 20 nm. These WC/Co composite powders were sintered at 1300~1360℃ for 0.5 hour. After sintering, the phases of WC and γ(Co) were only observed. The compacts linearly shrank by about 16% in WC-10 wt% Co and about 24% in WC-20 wt% Co. The mean sizes of WC/Co composite powders were about 280 and 260 nm in each alloy. And the mean sizes of WC particles were about 50 and 30 nm, respectively.

4. References

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