2006 POWDER METALLURGY
World Congress
PM2006

PC07-T-18

A Study of Reduced and Carburized Reactions in Dry-milled WO_3+Co_3O_4+C Mixed Powders with Different Carbon Content

Hoo-Soon Im[1,a], Wan-Jae Lee[2,b]

[1,2]Department of Metallurgy and Materials Engineering, Hanyang University,
Ansan, 425-791, Korea
[a] hooson@hanet, [b]wan-lee@hanyang.ac.kr

Abstract

The dry-milling technique was used for mixing and crushing oxides and graphite powders. The ratio of ball-to-powder was 30:1 and argon gas was filled in jar. The excess carbon was 10~ 20wt% of the stoichiometric amount. The dry-milling was carried for 20 hours. The mixed powders were reduced and carburized at 900~980℃ for 3 hours flowing Ar gas in tube furnace. The dry-milled powders showed the wide diffraction patterns of X-ray. The reactions of reduction and carburization were completed in 3 hours at 980℃. After the reactions, the mean size of WC particles was about 200 nm. The content of free carbon in WC/Co mixed powders was less as the reaction temperature increased.

Keywords : cemented carbide, reduction and carburization, nano-sized WC, WC/Co composite powder

1. Introduction

WC-Co cemented carbides are very important for cutting, mining, forming tools and wear resistant parts.[1,2] Recently, many researchers were interested in the synthesis of nano-sized WC or WC/Co powder by the direct reduction and carburization of tungsten oxide and cobalt oxide with graphite. The mechanical properties of cemented carbides depend on the size of carbides, such as WC, TiC, TaC, and the binder content, Co or/and Ni. Also the carbon content is very important in WC-Co cemented carbide. There are various phases in WC-Co cemented carbide and their phases are sensitively affected by the carbon content.[3,4] The free carbon and η phase(Co_6W_6C and Co_3W_3C) in the microstructure worse the mechanical properties of cemented carbide.[5,6] Thus, the carbon control in synthesizing WC/Co mixed powders is very important through the processes.

In this study, we tried to find the optimal processes, the conditions of the reduced and carburized reactions of the oxides/graphite mixture, the required carbon content during the synthesis of uniform and nano-sized WC/Co composite powders.

2. Experimental and Results

The raw powders were WO_3(Taegu Tec Ltd., 1.5 ㎛), Co_3O_4(Kojundo Chemical Laboratory Co. Ltd., 1 ㎛), Carbon black(Cancard Co., 0.6 ㎛), VC(H.C. Stark, 1.4 ㎛) and Cr_3C_2(H.C. Stark, 2.9 ㎛). These powders were mixed to make the compositions of WC-10wt%Co. The amount of graphite was changed from 0.9 to 1.2 times of stoichiometric content that required the reduction of oxides and the carburization of tungsten (6.13wt%C in WC). The dry-milling was carried in planetary mill (Fritsch, P-5) under the conditions of ball-to-powder ratio 30:1 and Ar gas(99.999%) atmosphere for 20 hours. Dry-milled powders were reduced and carburized at the temperatures of 900, 930, 950, 980℃ for 3 hours flowing Ar gas(300 mL/min) in an alumina tube furnace.

For the powders, the size and dispersion state of the particles were observed by FE-SEM(JEOL Co., JSM-6330F) and TEM(JEOL Co., JEM-2010). And the mean size of WC grains was measured by Image Analyzer. Each content of elements was observed by EDX(Oxford). The phases of WC, Co and other were examined by XRD(Rigaku Co., DMAX-2500). The carbon content of WC/Co composite powders was analyzed by Carbon Analyzer(Leco Co., CS-300).

Results and Discussion

From the SEM micrograph and distribution of the mixed WO_3/Co_3O_4/graphite powders after dry-milled for 20 hours, the mean size of the mixed powders was about 150 nm. And the particles of each component, such as W, Co, V, Cr and C were uniformly dispersed from the results of EDS analysis. The dry-milled powders showed the broaden peaks of XRD pattern. It was thought that the mixed powders were broken and strained during the high energy milling. At last, the mixed powders would be amorphous.

The XRD patterns of the composite powders after reduction and carburization at 900~980℃ showed the peaks of WO_3, WO_2, Co_3W_3C and Co_6W_6C phases at 900, 930℃. And at 950℃ the peaks of WO_3, WO_2 and Co_3W_3C were low while the peaks of WC, Co were observed. Finally, only the peaks of WC and Co phases were observed at

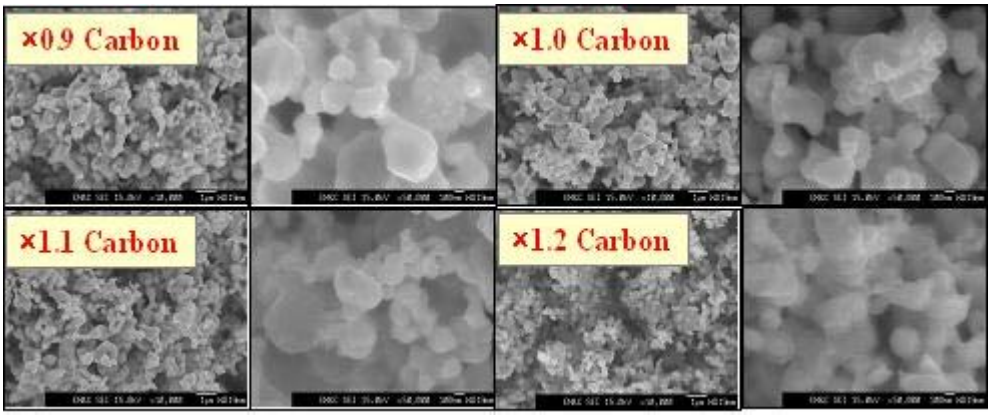

Fig. 1. SEM photographs of the WC/Co composite powders reduced and carburized at 980 for 3 hours with different carbon content.

980℃. Therefore, we supposed that the direct reduction and carburization of the mixed powders became in sequence,

$$WO_3 \rightarrow WO_2 \rightarrow Co_6W_6C \rightarrow Co_3W_3C \rightarrow WC/Co.$$

Fig. 1 showed the SEM photographs of the WC/Co composite powders reduced and carburized at 980℃ for 3 hours for different carbon content, the mean size of WC/Co was about 200 nm. And the Co phase between WC particles was observed by TEM image shown in Fig. 2. From the results of SEM and TEM microphotographs, we imagined that each particle of WC combined with Co as a binder.

The carbon content of the powders was analyzed before and after milling, after reduction-carburization, respectively. The carbon content of each sample was reduced about 2~3wt% after dry ball-milling. It seems that the carbon consumed to reduce the oxide powders during dry milling. Then the carbon content decreased rapidly to about 7wt% after the reduced and carburized reactions. From the relationship with the reduced and carburized temperature, the carbon content of WC/Co composite powder was decreased from about 18.5wt% at 900℃ to about 9wt% at 980℃ as the temperature increased. The high temperature was more useful for the reactions. The content of 9wt%C in WC/Co powder was far over the sudo-binary region(WC+γ), 6.04 ~ 6.22wt%C in WC-10wt%Co cemented carbide.

3. Summary

The dry-milled powders of WO_3, Co_3O_4, C, VC and Cr_3C_2 were examined in relation with the carbon content, the temperature of the reduced and carburized reactions.

The dry-milled powders for 20 hours became amorphous. The reduced and carburized reactions were completed in 3 hours at 980℃. The mean size of the reduced and carburized WC was about 200 nm. The carbon content of WC/Co composite powder was decreased about 9wt% at 980℃ for 3 hours as the reaction temperature increased.

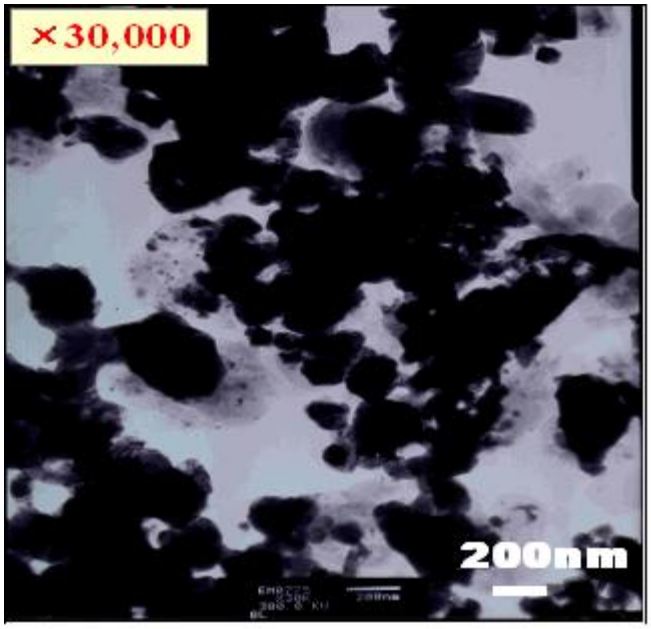

Fig. 2. TEM photograph of WC/Co composite powders, dark ones are WC particles and gray ones are Co particles.

4. References

1. S.I. Cha, S.H. Hong, G.H. Ha, B.K. Kim: Scripta Materialia, **44**, p. 1039(2001).
2. G. Gille, J. Bredthauer, B. Gries, B. Mende, W. Heinrich: Int. J. of Refractory Met. & Hard Mat., **18**, p. 87 (2000).
3. J. Gurland: Trans. AIME., Feb. p. 285(1954),
4. H. E. Exner, J. Gurland: Powder Metal., **25**, p. 13(1970).
5. V. Adelskold, A. Sundelin, A. Westgren, Ztsch. Allogen. Chem., p. 212(1933).
6. Nishiyama, Ishida: J. of Sumitomodenki, **7**, p. 26 (1958).