Fabrication of Nano-sized WC/Co Composite Powder by Direct Reduction and Carburization with Carbon

Dong Ryoul Lee[1,a], Wan Jae Lee[2,b]

[1,2]Dept. of Metallurgy and Materials Engineering, Hanyang University
Ansan, 425-791 Korea
[a]forever2010@lgmicron.com, [b]wan-lee@hanyang.ac.kr

Abstract

Direct reduction and carburization process was thought one of the best methods to make nano-sized WC powder. The oxide powders were mixed with graphite powder by ball milling in the compositions of WC-5,-10wt%Co. The mixture was heated at the temperatures of 600~800 ℃ for 5 hours in Ar. The reaction time of the reduction and carburization was decreased as heating temperatures and cobalt content increased. The mean size of WC/Co composite powders was about 260 nm after the reactions. And the mean size of WC grains in WC/Co composite powders was about 38 nm after the reaction at 800 ℃ for 5 hours.

Keywords : WC/Co composite powder, direct reduction and carburization, nano-sized WC, mixed powder of WO_3/Co_3O_4/graphite

1. Introduction

Synthesis of nano-sized WC/Co mixed powder has been studied widely for the wear resistance materials due to its high hardness. WC powders are made by the direct reduction and carburization of tungsten oxide powder with carbon or methane gas.[1] There are several reaction steps from WO_3 to WC by CO gas. The reductions of tungsten oxides with CO gas and solid carbon were studied and compared the results.[2] Thus, the reduction of tungsten oxides could be expected to proceed as follows:

$WO_3 + C_{(s)} \rightarrow CO$ and CO_2 , $WO_{\chi(s)} + CO_{(g)} \rightarrow WO_{y(s)} + CO_{2(g)}$ ($\chi > y$) and $WO + CO \rightarrow W + CO_2$

Nowadays, the production of nano-sized WC powder became important for tool materials. The solution technique was developed to make nano-sized WC/Co particle from 60 to 300 nm in size.[3] The reduction and carburization process of the mixed powders, tungsten oxide, cobalt oxide and graphite, in H_2 gas became the successful mass production of nano-sized WC/Co composite powder.[4] The process parameters were temperature, time, and gas species and flow rate in producing nano-sized WC/Co powders.[5]

In this study, nano-sized WC/Co composite powders were made by the direct reduction and carburization of the mixed powders of oxides and carbon black. We tried to find the optimal conditions to get nano-sized WC-5,-10wt%Co composite powders in relationship with the mixing conditions, the reaction temperature and time, and the flow rate of Ar gas.

2. Experimental and Results

The raw powder were WO_3(TaeguTec Ltd., 1.5 ㎛), Co_3O_4(Kojundo Chemical Laboratory Co. Ltd., 1.0 ㎛) and carbon black(Cancard Co. Ltd., 0.6 ㎛). These powders were balanced to be the final composition of WC-5,-10wt%Co. These powders were mixed and crushed in high energy planetary mill with ethyl alcohol for 30 hours. The weight ratio of ball to powder was 10 to 1. After drying, the mixed powders were heated under Ar gas(99.999%, 300mL/min). To find the optimal reduction temperature, the mixed powders were examined from 20℃ to 1000℃ under flowing Ar gas by T.G. Analyzer. From the results of T.G. test, the mixed powders were heated at 600, 700 and 800℃ for 5 hours in Ar gas. The reduction and carburization procedures were carried out by two-steps in furnace. After the reactions, the powders were examined by XRD(Philips Co., PW 1730), SEM(JEOL Co., JSM-6330F) and Carbon/Sulfur Analyzer(Leco CS-300). The mean size of the powders was estimated by Image Analyzer and Scherrer's formula from the peaks of XRD.[6,7] The size and morphology of WC/Co composite powders were observed by SEM.

From the weight-loss results of T.G. Analyzer, the reduction of WO_3/C mixture started at 970℃ and rapidly progressed. The mixture of Co_3O_4/C showed two steps, one was very little decrease at 80℃ and another was large decrease at 950℃. The little decrease was supposed to be the vaporization of moisture in the mixture. Finally the mixture of WO_3/Co_3O_4/C showed different two steps from the above. One started at 550℃ and was gradually decreased about 10% until 650℃. Another was rapidly decreased about 25% around 880℃ and became stable. Therefore we decided to examine the reactions of direct reduction and carburization at 600, 700 and 800℃ for 5 hours. The gases of CO and CO_2 decreased nearly zero after

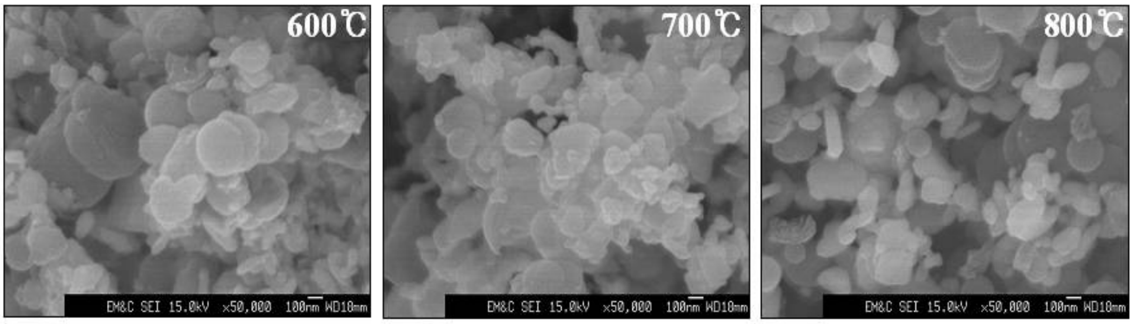

Fig. 1. SEM photographs of WC/Co composite powders after reduction and carburization for 5 hours at each temperature in WC-10%Co.

about 4 hours by CO/CO_2 gas analyzer during the reduction and carburization.

From the XRD patterns of the mixed powders before and after the direct reduction and carburization at each temperature, the peaks of the mixed powders were changed as the reaction temperature increased. The peaks of WC, W_2C, WC_x and Co appeared as the peaks of WO_3, Co_3O_4 and graphite disappeared at 800℃. These results were supposed that the reactions of reduction and carburization could occur at the relatively low temperature in the mixed powders due to the fine powders of oxides by milling. And the cobalt oxide was reduced to metallic cobalt at first, the cobalt helped reduce and carburize the tungsten oxide. Therefore the peaks of cobalt appeared higher as the content of cobalt increased.

Fig. 1 shows the SEM photographs of the raw powders and the WC/Co composite powders reduced and carburized at 600, 700 and 800℃ for 5 hours in WC-5,-10%Co. The mean sizes of raw WO_3, Co_3O_4 and graphite particles were about 1.5, 1.0 and 0.5 ㎛ respectively. The shapes of WC/Co composite powders showed round and their sizes increased with the reaction temperature.

After ball-milling, the mean size of the mixed particles decreased to be about 250 nm by Image Analyzer in Fig. 3(a). And the mean sizes of WC/Co composite powder by Image Analyzer were about 257~266 nm in WC-5wt%Co and about 264~270 nm in WC-10wt%Co at the reaction temperatures in Fig. 3(a). And the WC size was calculated by Scherrer's formula from the (112) peak of WC particles. So the mean sizes of WC in WC/Co composite powder by calculating from were about 34~37 nm in WC-5wt%Co and about 38~39 nm in WC-10wt%Co in Fig. 3(b). From the above results, WC/Co composite particle was supposed that many microcrystalline WC grains combined with cobalt together. The mean size of microcrystalline WC increased as the cobalt content and the reaction temperature increased.

The carbon content in WC/Co composite powder was over 0.64% than the stoichiometric amount. The excess free carbon was considered that the reduced tungsten was not fully carburized due to the low reaction temperature.

3. Summary

The raw WO_3, Co_3O_4 and graphite powders were mixed with the compositions of WC-5,10wt%Co. The mixed powders were reduced and carburized at 600~800℃ for 5 hours to get nano-sized WC/Co composite powders.

The mean size of mixed WO_3, Co_3O_4 and graphite powders was about 250 nm after ball-milling for 30 hours. The reduction of $WO_3/Co_3O_4/C$ mixture was step-by-step at two temperatures, 550℃ and 880℃. The mean size of WC/Co composite powders was about 260 nm by Image Analyzer. The direct reduction of WO_3 with graphite in Ar gas was completed in 4 hours at 600~800℃.

The mean size of WC in WC/Co composite powder reduced and carburized at 800℃ was about 38 nm. The excess free carbon was remained in WC/Co composite powders due to the low reaction temperature.

4. References

1. T. Millner and J. Neugebauer: Nature (London), **163**, p. 601(1949).
2. D.S. Venables and M.E. Brown: Thermochim. Acta, **251**, p. 282(1996).
3. B. K. Kim, G. H. Ha, G. G. Lee, D. W. Lee and D. W. Lee: Nanostructured Materials, **9**, p. 233(1997).
4. P. Arato, L. Martha, R. Porat, S. Berper and A. Rason: Nanostructured Materials, **10**, p. 245 (1998).
5. S. Decker. A. Lofberg, J. M. Bastin and A. Frennet: Catalysts Lett., **44**, p. 229 (1997).
6. R. L. Fullman : J. Metals, **5**, p. 447 (1953).
7. L.L. Shaw, Z.G. Yang and R.M. Ren: Mater. Sci. Eng. A, **244**, p.113 (1998).