

Mixing effects on sintering properties of recycle and commercial WC nano powders

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To improve the sintering properties of recycle WC powder, the mixture of the recycle WC and commercial WC powders were conducted with the variables of inhibitors and binder. The mixture WC sample (recycle WC powder and commercial WC powder) had a smaller grain and higher densification than the recycle WC sample. The density and hardness of the mixture WC sample were higher than those of the recycle WC sample. The particle size of WC powders and the surface of WC samples were analyzed by field emission scanning electron microscope. And the density and hardness of WC samples were measured by analytical balances and vickers hardness tester. The mixing effects of recycle WC powder and commercial WC powder were studied.

Key words: Recycle WC, commercial WC, mixing effect, Particle size, Agglomeration.

Introduction

Tungsten carbide (WC) hardmetals has been known to excellent materials as cutting tools, mining tools, and machining tools because of their high hardness, toughness and stability in the wide temperature range. Recently, the quality improvement such as hardness, strength and wear resistance has been greatly required for WC hardmetals market. To improve the quality of WC hardmetals, the growth and size control of WC grain has been received attention. Nano-sized WC particles were used to control of WC grain size, and grain growth inhibitors such as vanadium carbide [1, 2], chromium carbide [3], niobium carbide, and tantalum carbide [4] were used to control of WC grain growth. After above mentioned various attempts, the quality improvement of WC hardmetal could be achieved.

Nevertheless, the wastes production of WC hardmetals could be not suppressed due to inefficient and low quality as decrepitude of tools. Furthermore, Tungsten and cobalt are rare metals, and it is a problem that the tungsten and cobalt resources are produced from few country [5]. The wastes of WC were also contained the valuable metals such as vanadium, chromium, niobium and tantalum, which improved the properties of hardmetal. Therefore, WC recycling is necessary for material circulation and environmental protection. The various methods such as chemical modification, melt bath technique, and hydrothermal treatment have been

studied for recycling of WC hardmetals [5-10]. However, the quality limitation of WC hardmetals produced by the recycling WC materials could be existed due to the impurities which occurred from the recycling process and recycling WC materials.

In this study, the sintering properties of the recycling WC nano powder were studied with the variables of inhibitors and binder. To confirm the possibility of the potential quality improvement of the recycling WC materials, the sintering properties of mixture WC nano powder (recycle and commercial WC nano powder) were also observed.

Experimental

Starting WC nano powders were used by the recycle (0.4 μ m, widin, Korea) and commercial (0.4 μ m, Xiamen golden egret special alloy, China) powders. Chromium carbide (Cr₃C₂) and vanadium carbide (VC) were used by inhibitors, and cobalt (Co) was used by binder material. Cr₃C₂, VC and Co powders were added into the WC powder as initial designed amounts (table 1). The WC ball and hexane were added with prepared powder as same amounts. The small amount of paraffin wax was also added into mixture of WC ball, hexane and powder (Co : paraffin wax = 1 : 0.03 wt%) before ball milling for 60 hrs. After ball milling, hexane was removed on the hot plate at 200 °C and the powder was dried. The obtained powder was compacted in a cylindrical steel mold with 20 mm diameter by using oil pressure machine at 200 Mpa pressure. Then compacted powder was calcinated at 400 °C for 1 hr in tube furnace with Ar atmosphere to remove paraffin wax, and cooled to room temperature. The calcinated sample was sintered on carbon crucible with born

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Table 1. Composition ratio of WC with inhibitors and binder used in the study.

Sample No.	Recycle: Commercial	Co adding	[unit: wt%]	
			VC adding	Cr ₃ C ₂ adding
1			0.1	0.2
2		1.0	0.2	0.4
3			0.3	0.6
4	100 : 0		0.2	0.4
5		3.0	0.3	0.6
6			0.2	0.4
7		5.0	0.3	0.6
8			0.1	0.2
9		1.0	0.2	0.4
10			0.3	0.6
11	50 : 50		0.2	0.4
12		3.0	0.3	0.6
13			0.2	0.4
14		5.0	0.3	0.6

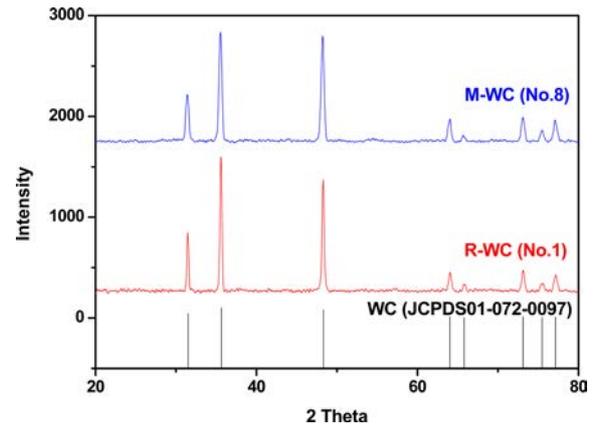
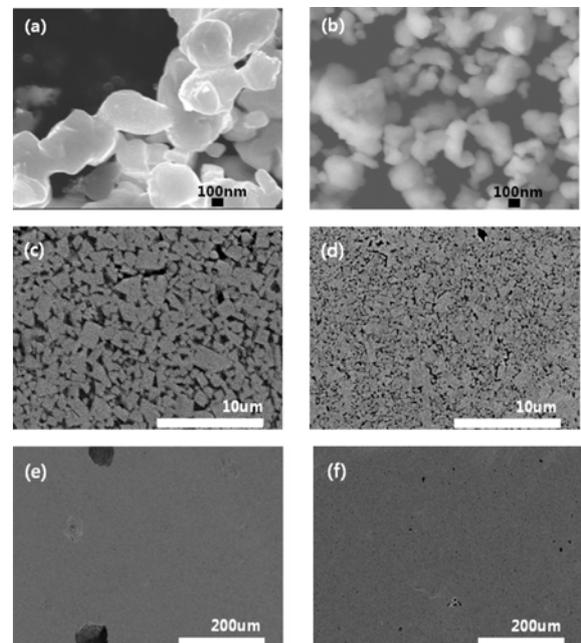
nitride coating in vacuum furnace by using two-step. The sample was heated up 1100 °C with a heating rate of 7 °C/min and then maintained for 10 min to remove the impurities. After that, the sample was heated up to 1400 °C with a heating rate of 2 °C/min and sintered at 1400 °C for 1hr, and then cooled to room temperature. The sintered sample was polished by using diamond plate and diamond paste.

The sintered sample was analyzed by using X-ray diffraction (XRD, CuK α , 12 kW, Rigaku, Japan) with the scanning range from 20 ° to 80 ° and speed of 6 °/min. The morphology of WC powders and the surface of the sintered sample were observed by using field emission scanning electron microscope (FE-SEM, Jeol-JSM7401F and Hitachi S3000H) and the amount of Co element was measured by using energy dispersive X-ray spectroscopy (EDX). The density of the sintered sample was measured by using analytical balances. The hardness of the sintered sample was measured by using vickers hardness tester.

Results and Discussion

Fig. 1 shows the XRD patterns of the recycle WC (R-WC) sample (a) and mixture of recycle and commercial WC (M-WC) sample (b) after sintering. As shown in figure, the diffraction peaks of the samples agreed with the patterns of WC (JCPDS : 01-072-0097) and the difference between the samples could be not found.

Fig. 2 shows the morphology of WC powders before sintering, and the surface of the polished R-WC and M-WC samples after sintering. Figs. 2(a) and 2(b) show the morphology of R-WC powder and commercial WC (C-WC) powder. The particle size of R-WC powder


Fig. 1. XRD patterns of the polished R-WC (No. 1) and M-WC (No. 8) samples after sintering.

Fig. 2. FE-SEM image of (a) recycle WC powder (X 50,000), (b) commercial WC powder (X 50,000), (c) surface of the polished R-WC (X 5,000), (d) surface of the polished M-WC (X 5,000), (e) surface of the polished R-WC (X 200) (f) surface of the polished M-WC (X 200).

was under 400 nm and uniform. C-WC powder was also the particle size of under 400 nm and had a deviation of the particle sizes. However, the particles of R-WC powder agglomerated more than those of C-WC powder. Figs. 2(c) and 2(d) show the surface of the polished R-WC and M-WC samples at high magnification (X 5000) after sintering. As shown in figures, the average grain size of R-WC sample was larger than that of M-WC sample, and the space between WC grains of R-WC sample was less dense than that of M-WC sample. The difference of the average grain size and densification between two samples was caused by particle size and agglomeration. As mentioned above, the particle size and agglomeration of R-WC powder were relatively larger and stronger than those of C-WC powder. Especially, the grain

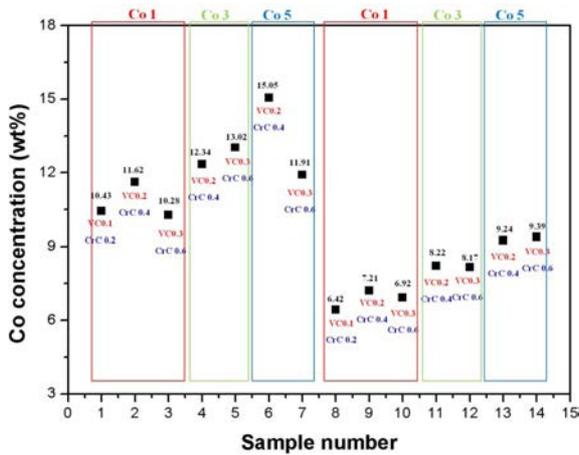


Fig. 3. Co cocentration of the polished R-WC and M-WC samples after sintering.

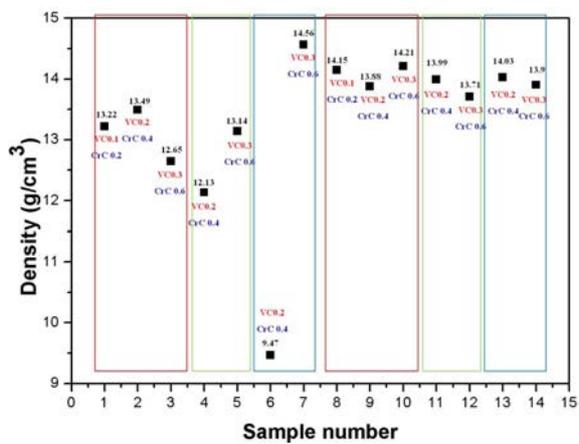


Fig. 4. Density of the polished R-WC and M-WC samples after sintering.

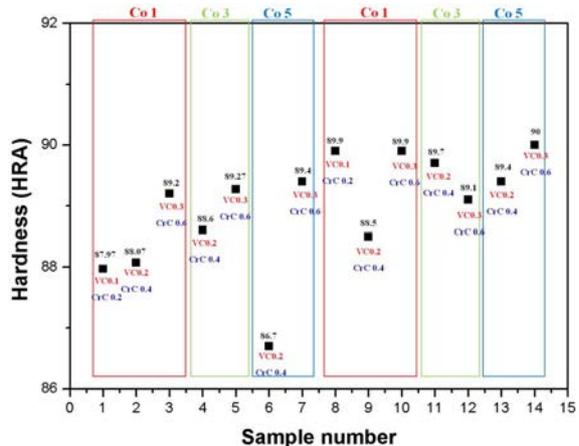


Fig. 5. Hardness of the polished R-WC and M-WC samples after sintering.

growth of WC particles could be easily influenced by the strong agglomeration due to the easy inter-diffusion between the connected WC particles. However, M-WC powder had a small sized and less agglomerative WC particles than R-WC powder due to mixing of C-WC powder. Figs. 2(e) and 2(f) show the surface of the

polished R-WC sample and M-WC sample at low magnification (X 200) after sintering. As shown in figures, R-WC sample had some macropores, and M-WC sample had some micropores. It was expected that this phenomena was also caused by the effect of agglomeration. The removal of macropores formed from pressing process [11] was suppressed by the strong agglomeration of R-WC particles. However, macropores of M-WC sample could be removed by C-WC particles, because a small sized C-WC particles filled the space between R-WC particles with the stong agglomeration during sintering.

Fig. 3 shows the Co cocentration of the polished R-WC and M-WC samples after sintering. The Co concentration of the sintered samples by using R-WC powder had a range from 10.28 wt% to 15.05 wt%, and generally increased with increase of Co concentration from 1 wt% to 5 wt%. That by using M-WC powder had a range from 6.42 wt% to 9.39 wt% and had generally increased with increase of Co concentration from 1 wt% to 5 wt%. The difference of Co concentraion between R-WC sample and M-WC sample was resulted from initial WC powder. Initial R-WC powder contained 9.29 wt% Co, because Co element was not removed by recycle process.

Fig. 4 shows the density of the polished R-WC and M-WC samples after sintering. The density of R-WC samples was lower than that of M-WC samples, because the pore size of R-WC samples (macropores) was larger than that of M-WC samples (micropores). The density of WC was influenced by amount of Co and inhibitors due to their low density than WC. However, it could be confirmed that the pores had more strong influence than binder and inhibitors in density.

Fig. 5 shows the hardness of the polished R-WC and M-WC samples after sintering. The hardness of R-WC samples was generally lower than that of M-WC samples, because the average grain size of R-WC samples was larger than that of M-WC samples, and R-WC samples showed lower densification than M-WC samples. Also, a high amount of Co in R-WC samples comapred with M-WC samples was one of factors in decline of hardness.

Summary

Mixing effects of recycle and commercial WC nano powders were observed on sintering properties. R-WC sample had a larger grain and lower densification than M-WC sample due to particle size and agglomeration of inital WC powders. Also, R-WC sample had some macropores due to agglomeration, and M-WC sample had some micropores because of mixing effects with C-WC powder. The density and hardness of M-WC sample were higher than those of R-WC sample due to difference of pore size and densification of WC grains.

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