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Processing Issues for Cryomilled WC-Co Nanopowders

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Processing issues of cryomilled WC-VC-Co nanopowders were investigated. A powder mixture of WC-9.8Co-0.8VC-xC was milled at −50°C in liquid nitrogen, using WC-Co balls. The particle sizes of the powders, in the form of agglomerates, were reduced to 18 nm and 13 nm for WC and Co, respectively by this process. The roles of some of the processing parameters such as compacting pressure, reduction of powders, and temperatures for the heating schedule were evaluated at a sintering temperature of 1450°C. The use of CIP resulted in a more uniform microstructure and enhanced mechanical properties: hardness (13-14 GPa) and K_{IC} (12-15 MPam$^{1/2}$). The findings herein suggest that carbon control and the use of a proper compaction technique were key factors in the successful production of nano-sized WC-Co alloys with no detectable η phase.

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1. Introduction

Nano-sized powders have attracted considerable attention from many researchers in the recent post. The superior mechanical properties and morphologies of nanoscale materials can be attributed to the nano-sized grain size and high volume fraction of grain boundaries.[1)] Therefore, a variety of methods for producing nanoscale powders, *e.g.* inert gas condensation,[2)] rapid solidification,[3)] electrodeposition,[4)] sputtering,[5)] crystallization of amorphous phases by annealing[6)] and chemical processing,[7)] all of which can be used to produce the nano-sized grain alloys, have been explored. However, these techniques are not able to provide quantities of nano-sized powders for structural applications.

The mechanical processes have been powerful methods for the production of nano-sized powders. Among the available mechanical methods, cryomilling is noted as a new and effective technique. The technique is similar to high-energy ball milling but is performed in liquid nitrogen at <-50°C. Because of cryogenic temperature and the high-speed rotation of the milling balls, the size of original powder mixtures is reduced to nano-size in a relatively short time period. It has recently been reported that the cryomilling in liquid nitrogen can be used to produce nanocrystalline structures with enhanced thermal stability, although the mechanisms responsible are not well understood.[8)]

WC-Co is the most widely used material in the cutting tool industry. There has been a continuing emphasis on the improvement of the cutting efficiency of these materials. Recent researches reported the enhanced properties of ultrafine ($<$500 nm) and nanocrystalline ($<$100 nm) WC-Co based tool materials.[9–11)] Thus, the mechanical processes have been frequently used for the production of nano-sized WC-Co powders, including cryomilling technique. As the size of powder particles falls below 100 nm, not only the particle coarsening during sintering but also various processing techniques become critical issues to overcome. Previous studies have shown that the addition of vanadium carbide improves the growth inhibition of nano-sized WC-Co alloy.[12)]

It is known that the stoichiometric composition of WC-Co system is a critical factor in determining the properties of an alloy. The characteristics of WC-Co alloys in particular, are greatly affected by carbon content. The carbon content changes phases during the formation of a WC-Co alloy and even the shape of the WC crystals.[13)] An increase in carbon content leads to a decrease in the largest grain size and an increase aspect ratio (a/c).[14)] This indicates that the difference in the size among the particles is reduced with an increase in carbon content. It has been reported that the eta phase (η) which results from a deficient carbon supply in the reprecipitation process leads to deterioration in mechanical properties. Not only excess but also a deficiency in carbon contents lowers the mechanical properties.[15)] Carbides that are commonly used as grain growth inhibitors such as VC and Cr_2C_3 promote the formation of η phase. Therefore, the control of carbon content is an important issue in producing a stoichiometrially stable WC-Co-VC alloy.

A fine size of cobalt powder is known to be effective in reducing residual porosity and cobalt pooling.[16,17)] Mort and Riman have shown that by reducing the particle size of the minor phase in multi-component systems, the homogeneity of the localized composition is drastically improved due to the decrease of the length between neighboring particles of minor phases.[18)] Since the nano size of cobalt powders makes it possible to reduce the melting point of the binder phase, the sintering temperature used can be lower than the one normally used.[18)] The reduction and homogeneity of cobalt binder particle size in WC-Co alloy can be achieved via the use of cryomilling.

The cryomilling process has been used for Al/AlN and Zn systems.[19,20)] The oxidation and nitridation of these alloys during the milling process have both advantages and disadvantages. Thus, the control of chemical influence by the cryomilling process has been important factor in the success of sintering process. The excessive amount of oxygen and nitrogen could cause many pores in the alloys after sintering process.

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It has been found the most important and difficult to obtain the nano-sized microstructure after sintering process. In this study we concentrated on the effect of free carbon content and attempted to control the oxygen and nitrogen contents. Efforts were made to understand the role of each processing step in the production of a refined microstructure from a WC-Co nanopowder, which are necessary to achieve improved mechanical properties and grain structure.

2. Experimental

Commercial WC-12 mass% Co powders of −325 mesh (<53 μm, Sulzer-Metco Inc., NY, USA) and VC of 1.5-2.0 μm in average (Aldrich Chemical Co. Inc., WI, USA) were used for the alloy preparation. Alloys were prepared with the compositions of WC-9.8%Co-0.8%VC by varying the content of free carbon (0.2-1.0% in mass). The powders were milled with WC-Co balls in liquid nitrogen at −50°C for 8 h using an attritor (Szegvary system, Union process, USA). The BPR (ball to powder ratio) was 20:1 and the attrition speed was 180 rpm. Slurry mixtures were dried in a vacuum oven for 12 h.

The dried powder was sieved through a 120-mesh (<120 μm) sieve to improve the packing density of green compacts. Disk-type compacts of 1 cm in dia. were prepared using a pressure in the range of 100-500 MPa. Most specimens were compacted at a pressure of 100 MPa, except in the case of experiments designed to investigate the effect of compacting pressure. The green compacts of nano-WC-9.8Co-0.8VC-xC systems were sintered at 1450°C for 1 h in a vacuum. In order to minimize pore formation during the sintering process, a separate reduction step was used for cryomilled powders in hydrogen prior to the sintering process.

A typical sintering schedule was used in this study, which has a few holding steps at intermediate temperatures. The first step was at 500-700°C for 1 h to reduce Co_3O_4 while the second holding step was made at 1150°C for 30 min to provide a uniform temperature distribution in the samples prior to the final sintering at 1450°C. The heating rate was maintained at 10°C/min. A thermal analysis was performed on the cryomilled powders, using DTA (DSC 910S, TA Instrument, USA) in order to determine an acceptable heating schedule.

Sintered specimens were ground with a diamond wheel and then polished from 1 to 6 μm with diamond slurry. The microstructure of the polished specimens was observed by scanning electron microscopy (FE-SEM, JSM-6330F, JEOL, Japan, 30 kV) and transmission electron microscopy (JSM-200CX, Joel, Japan, 200 kV). The average particle size of the milled powders was measured using X-ray diffraction (M18XHF-SRA, MAC Science Co., Japan). The contents of carbon, nitrogen and oxygen in alloy were measured with a CNO analyzer (Leco, USA). Density was measured by Archimedes's principle. Hardness and toughness values were obtained by an indentation technique with a micro-hardness tester.

3. Results

3.1 Variation in compositions

The cryomilled powders are shown in Fig. 1. After an 8 h cryomilling process, WC, Co and VC particles remained agglomerated as shown in Fig. 1(a) and carbides were embedded in the soft Co matrix (Fig. 1(b)). The sizes of WC and Co powders were determined to be about 18 nm and 13 nm, respectively, by XRD. However, the size of the particles would be larger if there is a strain effect in WC. The size of VC was not determined by XRD due to its small quantity. Fig. 1(c) also shows the powder size and morphol-

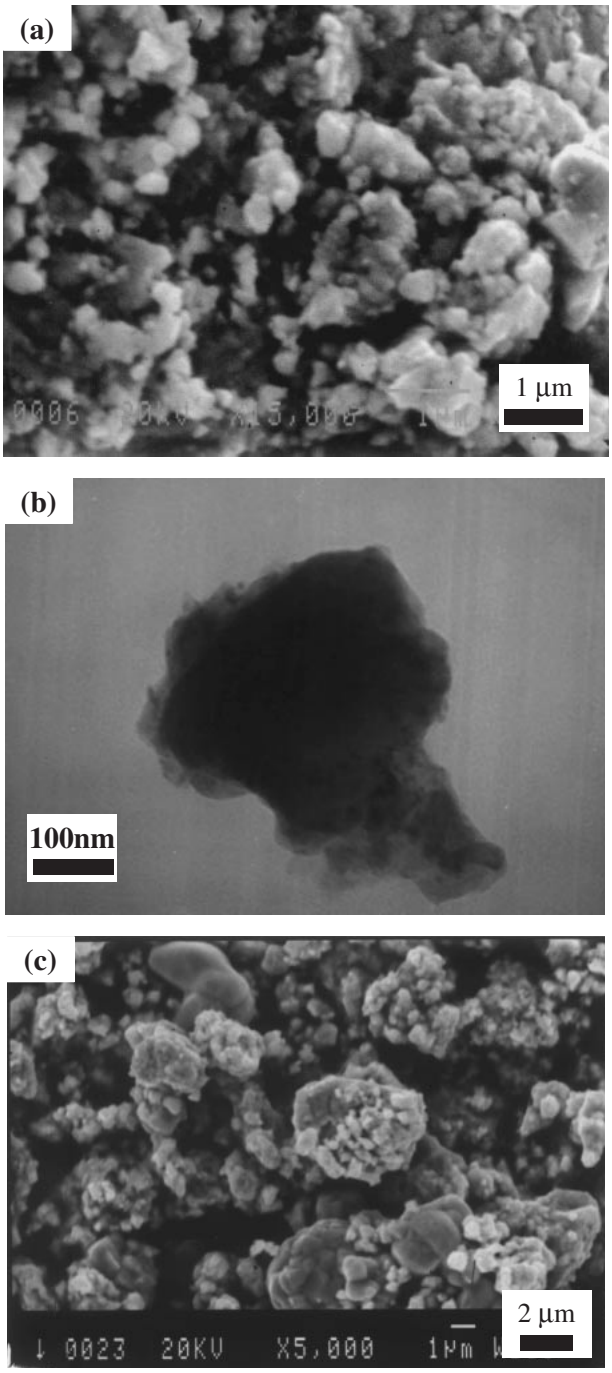

Fig. 1 (a) SEM and (b) TEM images of WC-9.8Co-0.8VC-1.0C powders after cryomilling. In Fig. 1(c), SEM image shows the agglomerated powders reduced in hydrogen at 700°C.

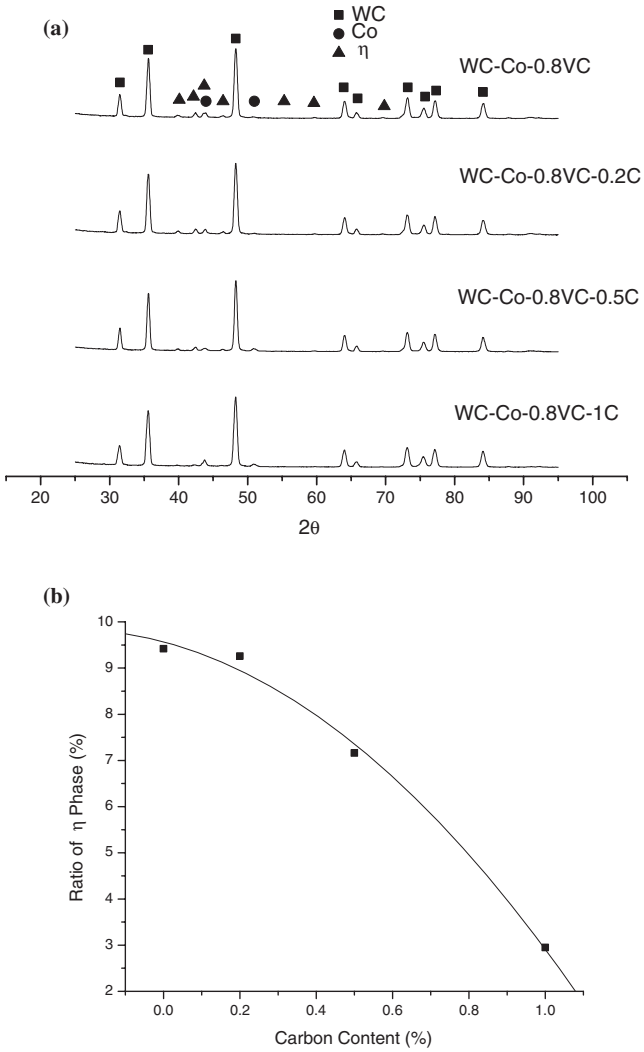

Fig. 2 (a) XRD results and (b) the ratio of 7 to WC in WC-9.8Co-0.8VC-xC sintered at 1450°C.

ogy of powders agglomerated further more after reduction process in hydrogen at 700°C.

The cryomilled WC-Co-VC system was investigated in order to define an acceptable range for carbon addition to suppress the formation of the η phase, W_3Co_3C. The addition of free carbon was in the 0.2-1.0 mass% range. Figure 2 shows XRD profiles of WC-VC-Co with various amounts of carbon. The fraction of η phase, expressed as the ratio of η phase to WC, was determined from the integrated area of the corresponding XRD peaks. The addition of free carbon tended to reduce the fraction of η phase. However, η phase was still present, even with a 1 mass% addition of carbon to the systems.

Figure 3 shows SEM microstructures of WC-9.8Co-0.8VC-xC. A sintering temperature of 1450°C, which is typical for micron-sized WC-Co, was used to prepare the samples. The effect of VC was not apparent on the inhibition of WC growth in this system. However, the addition of carbon reduced the aspect ratio (a/c) of the WC grains. In addition, it inhibited the rapid coarsening of the WC-Co-VC system as shown in Fig. 3(c). The porosity level and homogeneity of microstructure were improved as well.

The system exhibited a high fraction, in numbers, of WC

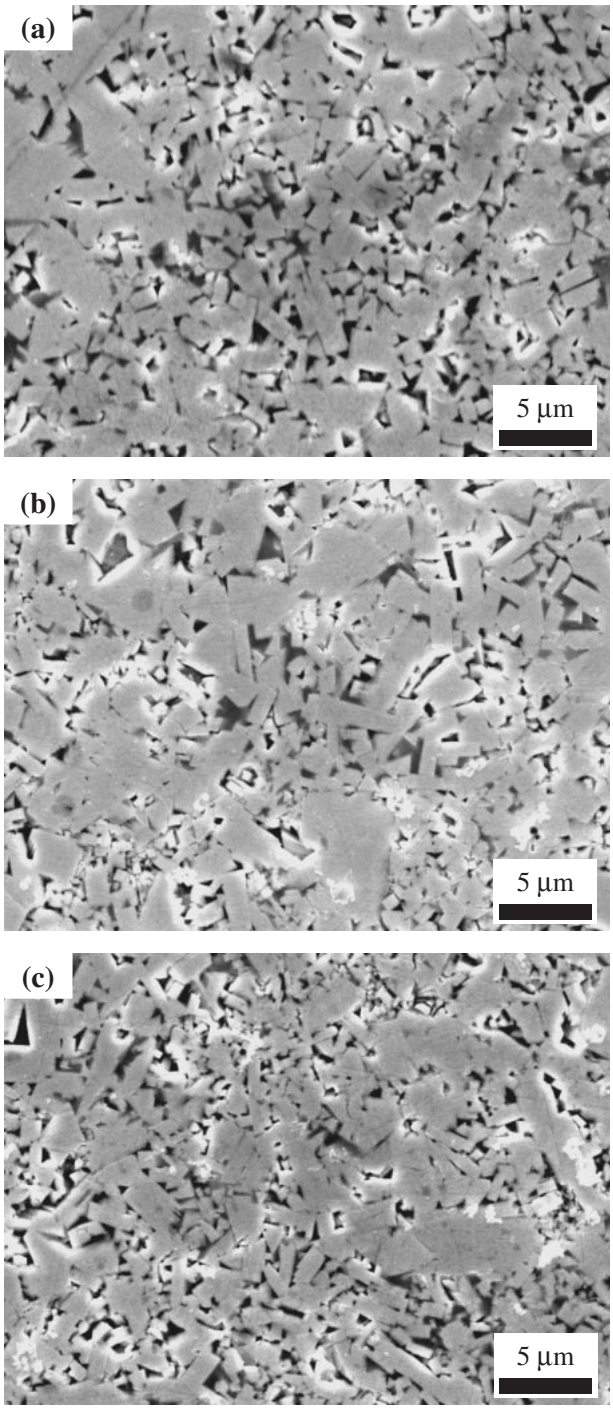

Fig. 3 SEM images of WC-9.8Co-0.8VC-xC sintered at 1450°C: The contents of free carbon were (a) 0%, (b) 0.5%, and (c) 1.0%.

particles that are less than average size when the carbon content was increased. This is graphically shown in Fig. 4. The particle fraction was determined by comparing the total number of particles with the number of WC particles in a specified size range. This value was plotted with respect to normalized particle size; $L/L_{\mathrm{avg.}}$, where L_{avg} is in the range of 0.86∼1.13 μm. In general, the size of WC particles becomes finer with higher carbon content. Moreover, the density of sintered alloy increases with free carbon content as discussed below.

The carbon, nitrogen and oxygen contents in cryomilled powders of WC-9.8Co-0.8VC-1.0C were analyzed. The C/

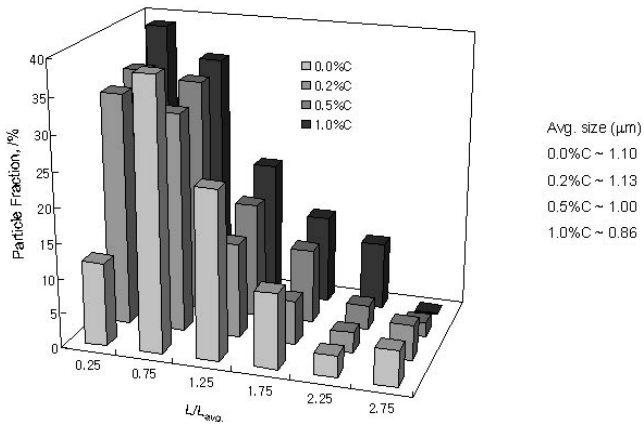

Fig. 4 The particle fraction, in number of particles, vs. normalized particle size for WC-9.8Co-0.8VC-*x*C sintered at 1450°C.

Table 1 Changes in C, N, O contents (mass %) after various processing

System & condition		Total carbon	Nitrogen	Oxygen
WC-9.8Co-0.8VC-1C powder mixture before cryomilling		5.24	0.001	0.11
WC-9.8Co-0.8VC-0.5C	After cryomilling	5.42	0.12	0.30
	Cryomilled and reduced at 500°C	5.16	0.06	0.26
	Sintered at 1450°C w/ reduc. 500°C: 2-step	5.07	0.05	0.10
	Sintered at 1450°C w/o reduction: 1-step	5.24	0.03	0.08
WC-9.8Co-0.8VC-1.0C	After cryomilling	5.51	0.13	0.37
	Cryomilled and reduced at 500°C	5.19	0.06	0.25
	Sintered at 1450°C w/ reduc. 500°C: 2-step	5.09	0.05	0.11
	Sintered at 1450°C w/o reduction: 1-step	5.39	0.03	0.11

N/O analysis in Table 1 reveals that the milled-powders contain significant amounts of nitrogen and oxygen. According to the table, these elements behave similarly when the contents vary after various processing steps. A significant loss of carbon occurs during the sintering process. All these elements are responsible for the loss of carbon and for the formation of η phase. Thus, an adequate process control was devised as follows for the cryomilled system in order to improve densification and to minimize the formation of η phase.

3.2 Effect of processing parameters

Figure 5 demonstrates the effect of compacting pressure on the microstructure of the cryomilled samples. As the compacting pressure increases to 500 MPa, the microstructure becomes fine with a reduced porosity. But more pores were observed from the samples compacted between 200 and 400 MPa, Figs. 5(a) and (b). This is significantly different when compared with Fig. 3, in which a compacting pressure of 100 MPa was used. All the compacts were sintered at 1450°C without holding steps in this case.

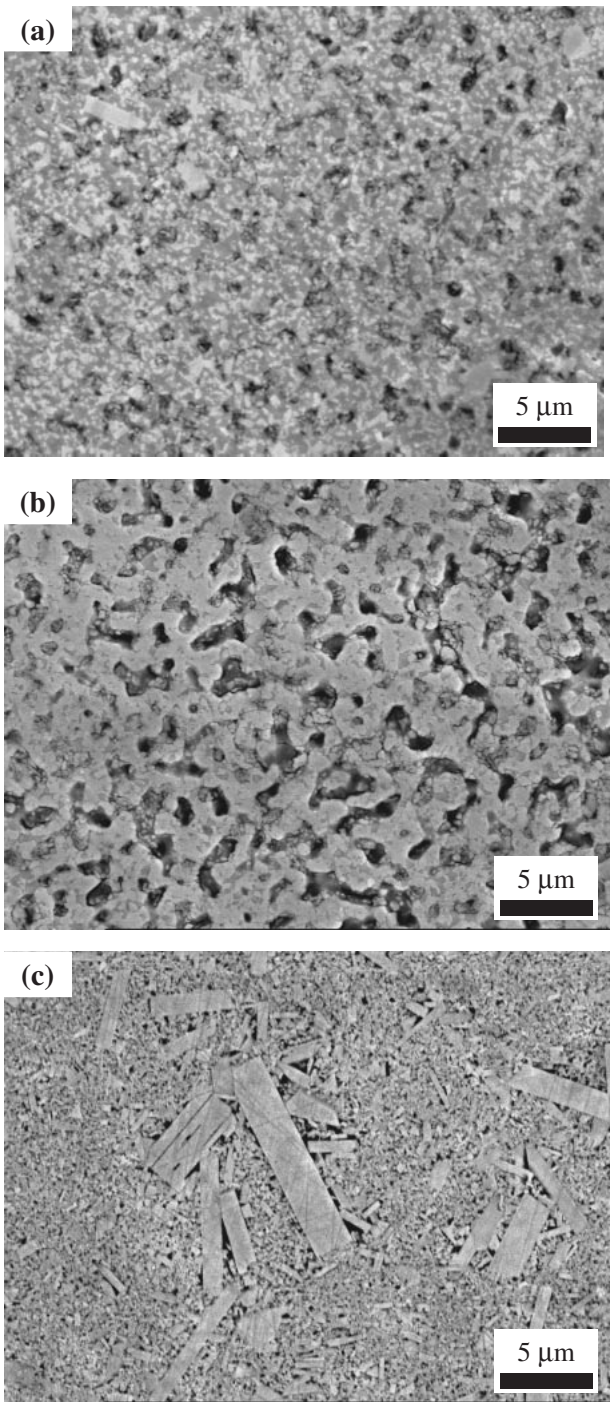

Fig. 5 SEM images of WC-9.8Co-0.8VC-1.0C system compacted in various pressures and sintered at 1450°C without holding steps. The compacting pressures were (a) 200 MPa, (b) 400 MPa and (c) 500 MPa

The change in the green densities, with respect to the compacting pressure, is shown in Table 2. The compacting pressure of 100 MPa resulted in a green density of 56%. Higher compacting pressure caused the green densities of those compacts to reach 59-63% of theoretical value, which is 14.5 g/cm^3 for WC-9.8Co-0.8VC. All these values are higher than that of conventional micron-sized WC-10Co (~53%). Nonetheless, there was little increase in sintered densities with high compacting pressures. This indicates that a high green density, which is obtained through a uniaxial pressing, provides a limited contribution in the densification

Table 2 Effect of carbon content and compacting pressure.

Systems	Variables	Green density, (g/cm^3)	Sintered density, (g/cm^3)	Hardness, HV30 (GPa)	Toughness, (MPa·m$^{1/2}$)
Effect of carbon content (WC-9.8Co-0.8VC-xC sintered at 500-1200-1450°C)	0.0%C	—	13.34	10.73	8.60
	0.2%C	—	13.57	11.22	8.84
	0.5%C	—	13.65	11.82	8.18
	1.0%C (100 MPa)	8.10 (55.9%)	13.74	11.86	8.90
Effect of compacting Pressure (WC-9.8Co-0.8VC-1.0C sintered at 1450°C)	200 MPa	8.53 (58.8%)	13.33	13.22	—*
	300 MPa	8.66 (59.7%)	13.18	13.34	—
	400 MPa	8.89 (61.3%)	13.35	13.66	—
	500 MPa	9.10 (62.7%)	13.35	13.08	—
Conventional WC-10Co	100 MPa	7.72 (53%)	14.55	13.67	12

-*toughness values were not obtained due to the high level of porosity.

of nano-sized WC-Co.

The volume fraction of η phase was found to increase with a decrease in compacting pressure. The compacting pressure changes not only the densities, but also the composition and grain morphology in the system. With a high compacting pressure, abnormal grain growth was noted as shown in Fig. 5(c) and the aspect ratio, a/c, of the WC grains increased.

The unusually high pore density in the cryomilled systems may be due to the presence of high oxygen and nitrogen content. In order to reduce this influence, a separate reduction process was performed, using a hydrogen gas flow prior to the sintering process based on DTA analysis. The DTA result for cryomilled WC-9.8Co-0.8VC-1.0C powders is shown in Fig. 6. This shows that a reaction occurred in the powders around 470~790°C, typical temperature range for the decomposition of Co_3O_4. In addition, an endothermic reaction starts at 1130°C where, presumably, the cobalt binder begins to melt. It has been reported that the melting temperature of nano-sized cobalt powder becomes lower than that of normal-sized cobalt powder.[19)]

Thus, the powder reduction process was performed in the temperature range of 500~700°C for 1 h under flowing hydrogen gas. The powders were then compacted and sintered at 1450°C. However, the reduction process did not remove the nitrogen effectively (Table 1). This two-step process caused more loss of carbon than the simple one-step sintering. Further, the one-step sintering resulted in better outcome even in the removal of nitrogen and oxygen than the two-step process.

The influence of the temperature used in the sintering schedule was examined with powders that had been reduced

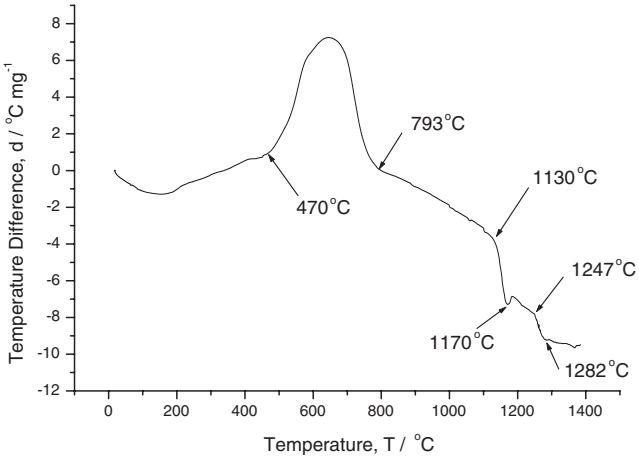

Fig. 6 DTA result of WC-9.8Co-0.8VC-1.0C powders prepared by cryomill for 8 h.

at 700°C for 1 h. The temperature of the first hold during sintering was varied from 500 to 700°C based on the DTA results shown in Fig. 6. The second and third temperatures were fixed at 1150°C and 1450°C, respectively. Cold isostatic pressing (CIP) of 300 MPa was employed to improve the microstructure after an initial uniaxial pressing. The increase in the first holding temperature (700°C) resulted in less pores in the microstructure as shown in Fig. 7. The size of WC particles and microstructure become more uniform than those prepared at 600°C.

3.3 Mechanical properties

The mechanical and physical properties of cryomilled WC-9.8Co-0.8VC-1.0C were examined after the changes in compositions and/or processing parameters. The focus of this study was not on determining optimum properties but on understanding the effects of various parameters on the microstructure. Table 2 also summarizes the effect of carbon content and compacting pressure on those properties. An increase in carbon content resulted in an improvement in densification and mechanical properties such as hardness and toughness. Though many pores were present, which made the measurement of toughness difficult, a high compacting pressure enhanced the hardness of WC-9.8Co-0.8VC-1.0C. In this system, a pressure of 400 MPa resulted in the best hardness with negligible η phase.

Table 3 lists the effect of temperature for the powder reduction on densification and mechanical properties. A notable improvement in densification was observed along with enhanced properties when the cryomilled powders were reduced separately. No significant difference in the properties was observed between two temperatures of reduction, 600 and 700°C. The combined effect of compaction and reduction process was examined by CIP (Cold Isostatic Pressing) and the results are shown in Table 4. A compacting pressure of 300 MPa was used in the CIP process. Although the pressure was lower than the optimum pressure of 400 MPa in uniaxial pressing, the results are greatly improved. Table 4 shows that a significant improvement in hardness (13-14 GPa) and K_{IC} (12-15 MPam$^{1/2}$) was achieved.

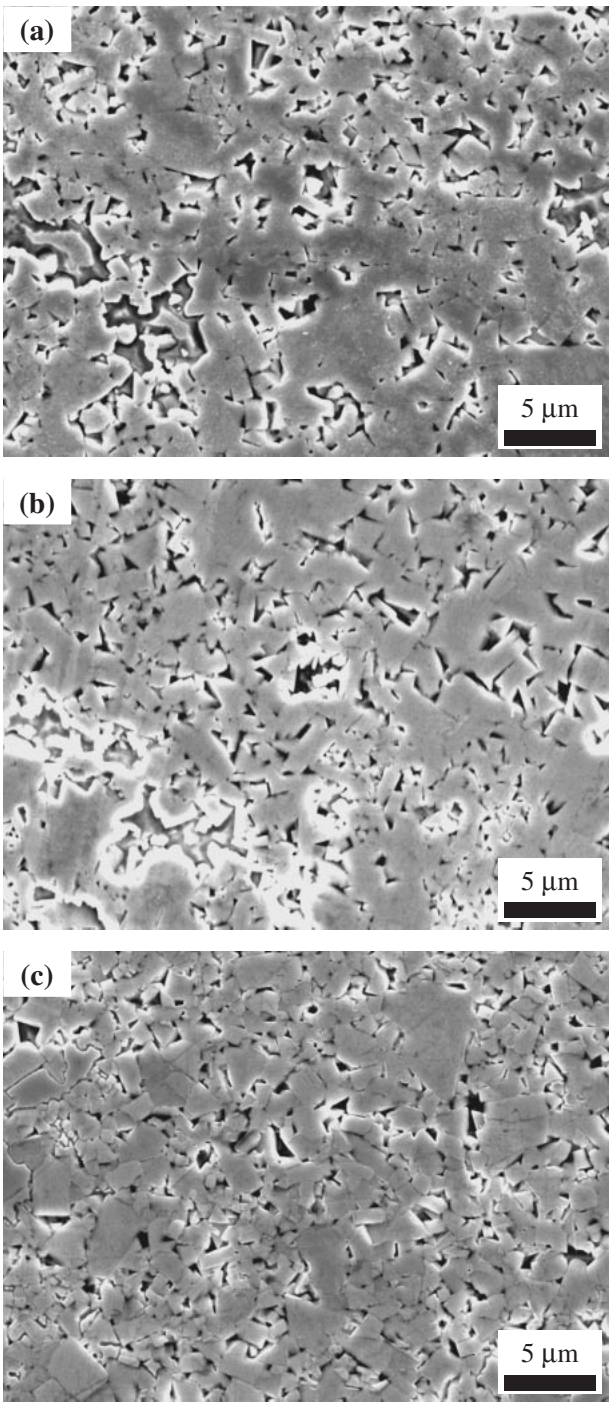

Fig. 7 SEM images of WC-9.8Co-0.8VC-1.0C system compacted with CIP and sintered with powders reduced under hydrogen flow at 700°C. The each sintering schedules were (a) 500-1150-1450°C, (b) 600-1150-1450°C and (c) 700-1150-1450°C.

Table 3 Effect of powder reduction temperature.

Composition	Variables	Sintered density, g/cm^3	Hardness, GPa (HV30)	Toughness, MPa·m$^{1/2}$
WC-9.8Co-0.8VC-0.5C	600°C	14.1	13.2	9.64
sintered at 1450°C	700°C	14.2	14.1	8.22
WC-9.8Co-0.8VC-1.0C	600°C	14.2	13.9	9.53
sintered at 1450°C	700°C	14.3	14.5	8.6

Table 4 Effect of CIP and holding temperature.

Composition	Temp. for first step hold (°C)	Sintered density, g/cm^3	Hardness, GPa (HV30)	Toughness, MPa·m$^{1/2}$
WC-9.8Co-0.8VC-0.5C	500	14.2	14.4	6.5
reduced at 700°C, CIPed	600	14.2	13.2	14.8
WC-9.8Co-0.8VC-1.0C	500	14.3	14.5	5.7
reduced at 700°C, CIPed	600	14.3	14.1	11.9

*Specimens were held at 1150°C and finally sintered at 1450°C for 1 h.

4. Discussion

4.1 Powder production

In general, the cryomilling of WC-Co provided an advantage in producing nano particles in a short time. However, the use of liquid nitrogen as a milling and cooling media increased the nitrogen and oxygen contents in the system (Table 1). Since the presence of these elements and defects in the WC-Co particles makes the system unstable, particle coarsening is facilitated, resulting in moderate hardness values. The oxygen in the cryomilled powder caused a significant loss of carbon via the formation of CO gas during sintering process.

The deficiency of carbon in WC-Co-VC promotes the formation of η phase in the system. The presence of η phase degrades the mechanical properties and, subsequently, the performance of WC-Co based tool alloys although it is claimed to curb the growth of WC particles.[21,22] The tendency of η phase to be formed becomes further intensified as the surface area of the particles increases. Compared to micron-sized WC-Co systems, the loss of carbon was great due to the increase in oxygen content and particle surface. It is noted that the control of carbon and oxygen contents is a more sensitive factor for the successful production of nano WC-Co than micron-sized WC-Co system.

4.2 Processing parameters

Optimal compacting conditions for producing nano-sized powders are reported to be different from those for micron-sized powders. The increase in the total surface area of nano-sized powders imposes more friction for the powder flow not only between powders and die-wall but among powder particles themselves. Mechanically-alloyed powders can also contain many defects and entrapped gases. Thus, a high compacting pressure was generally considered to bring those powders into contact and to facilitate effective sintering.

However, high values of green density obtained from uniaxial pressing never guaranteed full densification in the case of (cryomilled) nano WC-Co. Other factors such as pore size, distribution and pore channeling seemed to play important roles in the densification of nano systems. For example, an additional agglomeration of nano powders by reduction heat treatment was always found to be beneficial for densification and mechanical properties (Tables 2 and 3). The improvement in mechanical properties by employing cold isostatic pressing (CIP) is another good example that demonstrates the significance of pore morphology and compacting conditions in densification. The decrease in η

phase with an increase in compacting pressure is directly associated with a reduction in free surface.

A separate reduction was employed to remove nitrogen and oxygen since a high pore density was commonly observed in the cryomilled systems. The powder reduction process, performed in the temperature range of 500∼700°C for 1 h under flowing hydrogen gas, failed to remove nitrogen and oxygen completely (Table 1). Instead this two-step process caused more oxidation and an additional loss of carbon due to extended heat exposure. The overall results indicate that one-step sintering is preferred over two-step sintering. The results might be improved if a reduction step was included in the one-step process.

4.3 Mechanical properties

The mechanical properties of nano WC-Co systems, produced by cryomilling, were not found to be superior to those of other methods. The main reason of this observation must be the presence of high nitrogen and oxygen contents and their reactions with carbon during sintering process. Thus, an effective control of those elements would be expected to improve the properties. In addition, the advantage of a cryomilling technique in reducing particle size would be further conserved when it is combined with a proper compaction technique and sintering conditions.

5. Summary

WC-VC-Co powders were prepared using a cryomilling technique. Although the mixture of WC-Co powders was in the form of agglomerates, WC and Co powders were determined to be ∼20 nm by XRD. By maintaining the sintering temperature at 1450°C, the roles of processing parameters such as compacting pressure, reduction of powders, and temperatures for heating schedule were evaluated. This investigation revealed that carbon control and compaction of the powders were the key factors in the successful production of nano-sized WC-Co alloys with no η phase. The following are some results of this study.

(1) Cryomilled WC-Co nano-powders, in general, contain high contents of oxygen and nitrogen. The combination of oxygen and nitrogen in the system led to a carbon deficiency during high-temperature processing. Cryomilled WC-Co powders must have a proper carbon adjustment to ensure homogeneous microstructure and a low level of porosity.

(2) The composition and quality of nano-sizes WC-Co alloy was closely related to powder size, morphology and compacting conditions. The employment of CIP provided uniform microstructure and enhanced mechanical properties: hardness (13-14 GPa) and K_{IC} (12-15 $MPam^{1/2}$). An innovative and economical compacting technique is needed ensure a proper densification of nano-sized WC-Co.

(3) The removal of oxygen and nitrogen from cryomilled WC-Co powders was not effective when a separate reduction process was used before sintering. The mechanical properties would be improved if the reduction process were to be included in a one-step process.

Acknowledgements

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