Preparation for WC–Ni₃Al Hard Metal by Vacuum Sintering^{*1}

Kiyotaka Katou^{*2}, Koji Shimojima and Hiroyuki Hosokawa

Magnetic Powder Metallurgy Research Center, National Institute of Advanced Science and Technology, Nagoya 463-8560, Japan

WC–Ni₃Al hard metal of the composition for WC–25 vol% (Ni–24 at%Al–0.5 at%B) was prepared by vacuum sintering. The powder mixtures of WC, Ni, NiAl (Ni–50 at%Al) and B were treated by wet milling with a tumbling ball mill machine for 24 h or 48 h. The average particle size of the powder mixtures after wet-milling for 24 h and 48 h were 1.69 μm and 1.23 μm , respectively. These powder mixtures were press-moulded into the test-pieces and sintered in vacuum of $(7\sim9) \times 10^{-3}$ Pa at various temperature for 1 h. The densities, microstructures and mechanical properties of the obtained sintered compacts were investigated. When 48 h wet-milled powder was used and the green compact was sintered at 1425°C for 1 h, the compact had relative density more than 99%, transverse rupture strength of 2.2 GPa and Vickers hardness of 1330 HV. On the other hand, using 24 h wet-milled powder, the sintered compact had lower mechanical properties than the compact of 48 h wet-milled powder because of low density and inhomogeneous microstructure. [doi:10.2320/matertrans.Y-M2018856]

(Received October 2, 2018; Accepted December 19, 2018; Published February 25, 2019)

Keywords: WC–Ni₃Al, vacuum sintering, wet milling, density, mechanical property

1. Introduction

WC–Co alloy is a useful hard metal with its high strength, hardness, and fracture toughness because of high wettability between the binder phase of Co and hard phase of WC. Therefore, the WC–Co alloy has been widely used for cutting tools, metal dies, and so on.

Recently, because of the increase of demand for hard-machining materials and high-melting-point materials, such as titanium and titanium-based alloys, hard metals have been expected to have excellent mechanical and chemical properties at high temperature. However, WC–Co is not suitable to be tools for hard-machining materials and high-melting-point materials, because the properties of Co at high temperature, especially more than 600°C, drastically deteriorate.

Furthermore, there are two social problems about Co. First, Co has been classified in the rare metals; therefore, there is concern about the supply. Second, Co has been designated a specified chemical substance in Japan from 2013 as a suspected human carcinogen. As a result, special environmental measures are needed to avoid an adverse influence on the human body.

As mentioned above, a substitute material for Co is necessary for WC hard materials. There have been several studies using heat-resistant intermetallic compounds, such as Fe–Al and Ni–Al, as the binder phase to improve the properties at high temperature, utilizing unique properties, such as inverse temperature dependence to strength, which indicates a higher strength at high temperature than that at room temperature. Especially, Ni₃Al is probably a promising substitute for the binder phase because of excellent mechanical properties from room temperature up to 800°C.¹⁾

In previous work, WC–Ni₃Al hard metals were mainly produced by pressure sintering, such as hot press and current pressure sintering.^{2,3)} Sintered compacts with nearly full density can be obtained by pressure sintering. However, near-net-shape forming of complex-shaped parts is difficult

by pressure sintering, so this process is considered to be unsuitable for mass production. Therefore, the development of a process for WC–Ni₃Al by pressureless sintering is desired. However, there have been few previous reports^{4,5)} of a WC–Ni₃Al process using pressureless sintering.

The purpose of this study is the preparation of a high-density WC–Ni₃Al hard metal by vacuum sintering. In this study, Ni powder and NiAl (Ni–50 at%Al) powder were selected as the raw materials of the Ni₃Al binder phase. NiAl is a brittle material, so that NiAl powder can be expected to be crushed finely by ball milling. Previous studies reported that a dense Ni₃Al compact was synthesized from Ni powder and NiAl powder by vacuum sintering.^{6,7)} Furthermore, a small amount of boron powder was added to raw materials to improve the mechanical properties of sintered compacts.⁸⁾ The powders of raw material were treated by wet ball milling. The powders after wet milling were press-moulded into the test pieces and then sintered in vacuum. The densities, microstructures, and mechanical properties of the obtained sintered compacts were investigated.

2. Experimental Procedure

The powder materials used for this study were WC (2.5 μm , Japan New Metals Co., Ltd., Japan), Ni (5 μm , Nippon Atomized Metal Powders Co., Ltd., Japan), NiAl (–45 μm , KCM Corporation Co., Ltd., Japan), and B (–20 μm , Kojundo Chemical Laboratory Co., Ltd., Japan) powders. Figure 1 shows the scanning electron microscopy (SEM) images of these powders. The powders with a chemical composition of WC–25 vol% (Ni–24 at%Al–0.5 at%B) were mixed by wet milling with a tumbling ball mill machine for 24 or 48 h. Hereafter, WC–25 vol% (Ni–24 at%Al–0.5 at%B) is called “WC–Ni₃Al.” The pot used for wet milling was made of stainless steel, and its volume was 420 ml. The crash medium was a ϕ 7 mm WC–Co hard metal ball. The particle size distributions of the obtained wet-milled powders were measured by laser diffractometry (Microtrac 9320-HRA, NIKKISO Co., Ltd., Japan). In the pressureless sintering of hard metal, the liquid phase promotes consolidation during sintering.⁹⁾ Therefore, differential

^{*1}This Paper was Originally Published in Japanese in J. Jpn. Soc. Powder Powder Metallurgy 64 (2017) 615–620.

^{*2}Corresponding author, E-mail: kiyotaka.katou@aist.go.jp

Fig. 1 SEM images of powder materials. (a): WC (2.5 μm), (b): Ni (5 μm), (c): NiAl ($\sim 45 \mu\text{m}$), (d): B ($\sim 20 \mu\text{m}$).

thermal analysis (DTA, TG-DTA2200SA, NETZSCH Japan Co., Ltd., Japan) of the powder mixtures was done in an Ar gas flow atmosphere to find the temperature of liquid-phase formation.

The wet-milled powders were press-moulded into the test piece (length: 20 mm $\times$ width: 5 mm $\times$ thickness: 3.5 mm) at a pressure of 100 MPa and sintered in a vacuum of $(7\sim 9) \times 10^{-3}$ Pa at various temperatures using a graphite furnace (PVSG 20/20, Shimadzu Corporation Ltd., Japan). The heating rate and holding time at maximum temperature were 300°C/h and 1 h, respectively.

The oxygen contents of the wet-milled powders and sintered compacts were measured by a melt extrusion method (EF-400, LECO Corporation). The densities of the sintered compacts were measured by a water Archimedeian method. The sintered compacts were analysed by X-ray diffraction (XRD) using Cu K_{α} radiation (RINT-2500HF, Rigaku Corporation Ltd., Japan) to identify phases. SEM observation and wavelength dispersive spectroscopy (WDS) mapping of the sintered compacts were done by an electron probe micro analyser (EPMA, JXA-8900L, JEOL Ltd., Japan). As the mechanical properties, transverse rupture strength (TRS, Auto graph AGS-G, Shimadzu Corporation Ltd., Japan) and Vickers hardness (HV-114, Akashi Corporation Ltd., Japan) were measured. The TRS was measured by a three-point bending test with a span of 10 mm and 0.5 mm/min of cross-head speed. The size of the test piece was 4 $\times$ 2 mm, and the number of tests was seven or eight. The Vickers hardness was measured at a load of 294 N, and the number of tests was six.

3. Results and Discussion

Figure 2 shows the particle size distribution curves for the wet-milled powders. The curve of the 48 h wet-milled powders shifts to a small size compared with that of the 24 h wet-milled powder. The average particle size (D_{50}) was 1.69 μm for 24 h wet-milled powder and 1.23 μm for 48 h wet-milled powder. The 48 h wet-milled powders had no particles of more than 10 μm ; however, the 24 h wet-milled powders had particles larger than 10 μm . This indicates that

Fig. 2 Curves of particle size distribution for WC-Ni₃Al powder mixtures after wet milling.

Fig. 3 DTA curves of powder mixtures. Atmosphere: Ar gas flow, (a): Ni + NiAl (correspond to Ni-24 at%Al), (b): Ni + NiAl + B (correspond to Ni-24 at%Al-0.5 at%B), (c): WC-Ni₃Al after wet milling for 24 h, (d): WC-Ni₃Al after wet milling for 48 h.

milling for 48 h is sufficient time to become fine and achieve homogeneity, and it is expected that the sintered compacts produced by the 48 h wet-milled powders will have more-excellent properties than those by the 24 h wet-milled powders.

Figure 3 shows DTA curves of powder mixtures of 1) Ni-NiAl corresponding to Ni-24 at%Al, 2) Ni-NiAl-B corresponding to Ni-24 at%Al-0.5 at%B, 3) 24 h wet-milled powder for WC-Ni₃Al, and 4) 48 h wet-milled powder for WC-Ni₃Al. Referring to the Ni-Al binary-phase diagram,¹⁰⁾ the melting point of Ni-24 at%Al is 1385°C. In the DTA curve of Ni-NiAl, there is an endothermic peak at 1385°C. This result indicates that the reaction of Ni + Al $\rightarrow$ Ni₃Al (Ni-24 at%Al) occurs during the heating process, and the reacted Ni₃Al melts at 1385°C. The endothermic peak of Ni-NiAl-B indicates 1375°C less than that for Ni-NiAl. It is considered that boron doping to Ni₃Al decreases the melting

Fig. 4 Relationship between relative density and sintering temperature for WC–Ni₃Al compacts.

point. The wet-milled powders of WC–Ni₃Al had an endothermic peak at approximately 1390°C. The liquid-phase formation is thought to occur at this temperature.

As the preliminary investigation, the sintered compact of Ni–24 at%Al and Ni–24 at%Al–0.5 at%B was prepared by MIM (Metal Injection Molding)-vacuum sintering process with the above-mentioned powders, and then their tensile properties at room temperature were investigated. The 0.2% proof stress, tensile strength, and elongation for the Ni–24 at%Al sintered compact were 0.42 GPa, 0.49 GPa, and 4.0%,⁷⁾ respectively, whereas those for Ni–24 at%Al–0.5 at%B sintered compact were 0.59 GPa, 1.01 GPa, and 14.2%, respectively. The tensile properties of Ni–24 at%Al were enhanced widely by the addition of 0.5 at%B.

Figure 4 shows the relationship between sintering temperature and relative densities for WC–Ni₃Al compacts. The relative densities were calculated based on the full density of WC–Ni₃Al. It was estimated to be 13.57 g/cm³ from the density of WC for 15.60 g/cm³ and Ni–24 at%Al for 7.41 g/cm³. The relative densities for the sintered compact from the 24 h wet-milled powder increased with increasing sintering temperature. The relative density reached 98% at 1450°C sintering. However, the relative densities of the sintered compact by 48 h wet-milled powder indicated an almost constant value of 99% up to 1425°C sintering. The reason why the relative density of the sintered compact from the 48 h wet-milled powder is high is that the particle size of 48 h wet-milled powder is sufficiently small. At 1375°C, the relative density is more than 99%, despite a lower temperature than the melting point of 1390°C measured by DTA. This suggests that the liquid-phase temperature is less than that of DTA, because the sintering process proceeded at vacuum atmosphere. However, DTA measurements were carried out in Ar gas flow under atmospheric pressure. At 1450°C, the relative density of the sintered compact by 48 h wet-milled powder went down to approximately 98%. Decline of density at high sintering temperature was also reported for TiC–Ni and WC–Co alloys by previous researchers.^{11,12)} According to these studies, the decline of the relative density was caused by the evaporation or exudation of binder components during sintering.^{3,11)}

Fig. 5 WDS mapping images of cross-sections WC–Ni₃Al compact. Sintering temperature: 1425°C for 1 h. Milling time: 48 h. (a): SEM, (b): W, (c): C, (d): Ni, (e): Al, (f): O.

Table 1 Oxygen content in powder mixtures after wet milling and sinter compacts for WC–Ni₃Al. Sintering temperature: 1450°C at 24 h wet-milled powder and 1425°C at 48 h wet-milled powder.

	Wet-milling time	
	24h	48h
Powder material after wet-milling	0.61	0.96
Sintered compact	0.19	0.38

(mass%)

Figure 5 shows WDS mapping images of cross sections of WC–Ni₃Al sintered compact at 1425°C using 48 h wet-milled powder. Comparing the mappings of each element and the SEM image, it is clear that in the SEM image, the white parts are WC grain, and the grey parts around the WC grain are the binder phase of Ni₃Al. The black parts could be considered aluminium oxide, because the densities of Al and O are high.

Table 1 shows the oxygen content in the wet-milled powders and sinter compacts of WC–Ni₃Al. The oxygen content in the wet-milled powders comes from raw powder materials and process contamination. The oxygen content of

Fig. 6 X-ray diffraction pattern of cross-sections for WC–Ni₃Al compact sintered at (a) 1375°C, (b) 1425°C and (c) 1450°C. Milling time: 48 h. ■: WC, ●: Ni₃Al, ▼: Ni₂W₄C, ◆: unknown.

48 h wet-milled powder is higher than that of 24 h wet-milled powder. The reason is that the former has a smaller particle size than the latter, in other words, a larger powder surface area. The oxygen of the sintered compacts decreased to one-third or so of that for the wet-milled powders. The oxygen on the powder surface reacted with the free carbon existing in the furnace to form CO gas, and then the gas was expelled from the furnace.¹³⁾ However, as shown in Fig. 5, the oxygen combining with aluminium cannot be deoxidized; therefore, oxygen remains in the sintered compact as aluminium oxide.

Figure 6 shows XRD patterns of the cross section for WC–Ni₃Al sintered compacts using 48 h wet-milled powder. For the compact sintered at 1375°C, WC and Ni₃Al peaks were identified. However, for the compact sintered at 1450°C, Ni₂W₄C peaks were identified, as well as WC and Ni₃Al peaks. As for the compacts sintered at 1425°C, WC and Ni₃Al peaks predominate; however, a small number of Ni₂W₄C peaks exist. Unknown peaks exist in the compact sintered at 1450°C.

Figure 7 shows SEM images of cross sections of WC–Ni₃Al compacts. Several-μm pores existed in the sintered compacts from 24 h wet-milled powder. These pores tend to

become spherical with increasing sintering temperature. Furthermore, the pools of binder phase of approximately 10 μm existed in the sintered compacts at all the sintering temperatures. As mentioned above, inhomogeneous microstructures for the sintered compacts from 24 h wet-milled powder were observed. The coarse grains of NiAl powder still remained in the 24 h wet-milled powder, as shown in Fig. 2, which is considered to be a reason for the inhomogeneous structure. However, the microstructures at 1400°C and 1425°C for the sintered compacts from 48 h wet-milled powder seemed more homogeneous than those from 24 h wet-milled powder. However, different phases of 20~30 μm were observed on the microstructure for the compact sintered at 1450°C. From the quantitative analysis by WDS of EPMA, this phase had a composition of 17.3~18.8 at%Ni, 2.4~2.5 at%Al, 25.9~54.7 at%W, and 24.1~26.5 at%C. It was considered that this phase was Ni–W–Al-type carbide corresponding to the Ni₂W₄C peaks in the XRD patterns in Fig. 6. From the results of the XRD measurements in Fig. 6, it is supposed that the creation of this carbide started at approximately 1400°C. This carbide increased with increasing sintering temperature and became coarse and noticeable at 1450°C sintering. This carbide was also observed on the microstructure for the sintered compact at 1450°C from 24 h wet-milling powder. The size of this carbide was less than 10 μm, smaller than that for the sintered compact of 48 h wet-milling powder.

Figure 8 shows the relationship between TRS and sintering temperature for WC–Ni₃Al compacts. The TRS for the sintered compact of 24 h wet-milled powder increased with increasing sintering temperature. This corresponds to increasing density, as shown in Fig. 4. The TRS was 1.42 GPa at 1450°C sintering. However, the TRS of the sintered compact by 48 h wet-milled powder was higher than that by 24 h wet-milled powder, regardless of the sintering temperature. It increased with increasing sintering temperature up to 1425°C. The TRS was 2.18 GPa at 1425°C sintering. However, it went down to 1.88 GPa at 1450°C. This TRS decrease is thought to result from the formation of large Ni–W–Al-type carbide, as shown in Fig. 7. The

Fig. 7 SEM images of cross-sections WC–Ni₃Al compact. Milling time: (a), (b), (c) 24 h, (d), (e), (f) 48 h. Sintered temperature: (a), (d): 1400°C, (b), (e): 1425°C, (c), (f): 1450°C.

Fig. 8 Relationship between transverse rupture strength and sintering temperature for WC–Ni₃Al compacts. Wet milling time: ■ 24 h, ● 48 h.

Fig. 9 Relationship between vickers hardness and sintering temperature for WC–Ni₃Al compacts. Wet milling time: ■ 24 h, ● 48 h.

decrease of strength by the formation of a large carbide at high sintering temperature was reported previously for WC–Fe hard metal.¹⁴⁾

Figure 9 shows relationship between Vickers hardness and sintering temperature for WC–Ni₃Al. The Vickers hardness for the sintered compact from 24 h wet-milled powder increased with increasing sintering temperature. This tendency was similar to TRS, corresponding to increasing density, as shown in Fig. 4. The Vickers hardness was 1272 HV at 1450°C. However, the Vickers hardness of the sintered compacts by 48 h wet-milled powder was higher than that by 24 h wet-milled powder. The Vickers hardness was 1341 HV at 1375°C and 1331 HV at 1450°C. It decreased slightly with increasing sintering temperature. The reason for this hardness decrease is considered to be grain growth by increasing sintering temperature. As shown in Fig. 4, the density of the sintered compact at 1450°C reached 98%, even using the 24 h wet-milled powder. Nonetheless, the TRS and Vickers hardness were at a low level compared with those for the sintered compact using the 48 h wet-milled powder.

The reason could be that the microstructure is inhomogeneous, as shown in Fig. 7.

4. Conclusions

A WC–Ni₃Al hard metal was prepared in this study. The powder mixtures of WC, Ni, NiAl (Ni–50 at%Al), and B with a composition of WC–25 vol% (Ni–24 at%Al–0.5 at%B) were treated by wet milling for 24 or 48 h. Then, these milled powders were press-moulded into the test piece and sintered in vacuum at various temperatures for 1 h. The densities, microstructures, and mechanical properties of the sintered compacts were investigated. The obtain results are as follows.

- (1) When 48 h wet-milled powder was used, the compact sintered at 1425°C gave a relative density of 99%, TRS of 2.18 GPa, and Vickers hardness of 1330 HV. However, the TRS of the compact sintered at 1450°C decreased because of the creation of coarse Ni–W–Al-type carbide in the microstructure.
- (2) The sintered compacts from the 24 h wet-milled powder had coarse pores and pools of binder phases in the microstructure, and the densities and mechanical properties were not sufficient compared with the sintered compacts from the 48 h wet-milling powder. The reason is considered to be the lack of grinding for raw materials.

Acknowledgment

This work was supported by JSPS KAKENHI Grant number JP16K06763.

REFERENCES

- 1) S.C. Deevi and V.K. Sikka: *Intermetallics* **4** (1996) 357–375.
- 2) T.N. Tiegs, K.B. Alexander, K.P. Plucknett, P.A. Menchhofer, P.F. Becher and S.B. Waters: *Mater. Sci. Eng. A* **209** (1996) 243–247.
- 3) X. Li, J. Chen, D. Zheng, S. Qu and Z. Xiao: *J. Alloys Compd.* **544** (2012) 134–140.
- 4) T.N. Tiegs, P.A. Menchhofer, C.B. Thomas and P.K. Liaw: *Adv Powder Metall Part Mater* **1** (1998) 1.93–1.103.
- 5) G.V. Talanova, A.G. Padalko, V.S. Panov, A.N. Veselov and L.I. Shvorneva: *Inorg. Mater.* **44** (2008) 244–247.
- 6) K. Tokuda and K. Hayashi: *J. Jpn. Inst. Met.* **57** (1993) 821–826.
- 7) K. Kato and T. Masui: *J. Jpn. Soc. Powder Powder Metallurgy* **47** (2000) 1277–1282.
- 8) K. Aoki and O. Izumi: *J. Jpn. Inst. Met.* **43** (1979) 1190–1196.
- 9) K. Shinba and H. Mitani: *Funmatsuyakingaku*, The Fourteenth Edition, (Corona Publishing Co., Ltd., 1985) pp. 162–173.
- 10) T.B. Massalski (ed.): *Binary Alloy Phase Diagrams II Edition*, 1 (ASM International, 1991) pp. 147–149, Kattner U.
- 11) S. Sugiyama and H. Suzuki: *J. Jpn. Soc. Powder Powder Metallurgy* **24** (1960) 689–692.
- 12) T. Ono, K. Kamata, M. Nakamura and T. Saitou: *Journal of Iwate Industrial Research Institute* **10** (2003) 37–40.
- 13) H. Suzuki: *Choukougoukin to Shoukutsu koushitsu zairyuu*, The Fourth Edition, (Maruzen Co., Ltd., 1991) pp. 22–23.
- 14) Y. Miyakoshi, K. Takazawa, K. Tagashira, S. Kamota and H. Takahashi: *J. Jpn. Soc. Powder Powder Metallurgy* **45** (1998) 1111–1115.