研 究

Application of Metal Injection Molding to W-Ni-Fe Heavy Alloy

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SYNOPSIS

A study was carried out to investigate the possibility whether MIM process could be applied to the compacting process of W-Ni-Fe heavy alloy in order to obtain an intricate shape. The multi binder system of 45PW+30PE+15BW+10SA was used for injection molding and compacts from the powder-binder mixture of metal powder fraction of 60 vol.% were studied for debinding and sintering behaviors. In debinding process, heating rate in temperature range from 120°C to 290°C had an important effect on the weight loss of the binder. The binder could be fully removed by three stage debinding treatment. The microstructure of the sintered specimen was dependent on the sintering atmosphere. The W-4.9wt.%Ni-2.1wt.%Fe alloy of full sintered density was obtained by sintering at 1470°C for 1 h in a wet hydrogen atmosphere and there was no difference in microstructure compared to that of W heavy alloy by die compaction.

KEY WORDS

Metal injection molding, W heavy alloy, liquid phase sintering, wet hydrogen

1 Introduction

Tungsten heavy alloys are two-phase composites characterized by their high densities and microstructures consisting of W grains embedded in an alloy matrix. In general, tungsten heavy alloys have been used as kinetic energy penetrator, armor, shaped charge liners, and inertial counterweight balances due to their unique combination of high hardness, high strength, high ductility and high density^{1,2)}. Most of these applications require final configuration of complex shape. Thus, the final fabrication involves a great deal of machining of the expensive materials.

Metal injection molding (MIM) is a unique powder processing technique suitable for net shape manufacturing of complex shaped parts from metal, ceramics and composite³⁻⁵⁾. The application of MIM to the W heavy alloys may provide an economic advantage in the mass production of complex shapes⁶⁾.

In the present study, therefore, the possibility whether MIM process could be applied to the compacting process of W-Ni-Fe heavy alloy was investigated in order to obtain an intricate part without the machining process.

2 Experimental procedure

2.1 Materials

Fig.1 and Table 1 shows that SEM morphologies and characteristics of elemental powders used in this study, respectively. W-Ni-Fe powders with composition of W-4.9Ni-2.1Fe (in wt.%) were mixed in a Turbula mixer for 4 h. The binder used for the preparation of MIM feedstock was a multi-component binder system with a composition of 45wt.% paraffin wax (PW)-15wt.% bees wax (BW)-30wt.% polyethylene (PE)-10wt.% stearic acid (SA). This was based on the result of previous study⁷⁾. Table 2 shows composition and characteristics of binder system used in this study.

2.2 Mixing & molding

For MIM, SA was first mixed with the mixed powder for 1 h in a Turbula mixer. Then, the powder was mixed with the binder in a single cam mixer. The powder-binder mixture was injection molded with molding pressure of 40 MPa at the cylinder temperature of 125°C and mold temperature of 75°C. The green density was determined by volume and weight measurement. The feedstock used in the present experiment was formulated at a solid loading of 60 vol.%

2.3 Debinding

The binder of the green part was removed by the melt wicking in 0.05 μ m-alumina powders and the thermal decomposition. Debinding process was determined on the

basis of previous study⁷⁾ and thermogravimetric analysis (TGA). Such a process had three steps of holding temperatures at 120°C, 290°C and 480°C. The debinding was carried out in nitrogen up to 480°C and in hydrogen above 480°C. The holding temperature step at 600°C was introduced as a presintering stage to provide a strength for the sample handling.

Fig.1 SEM morphologies of elemental (a) W, (b) Ni and (c) Fe powders.

Table 1 Characteristics of elemental powders used in this study.

	W	Ni	Fe
Shape	polygonal	spiky	spherical
Size(μm)	1.77	4.0	1.95
Purity(%)	99.9	99.9	99.7
Density(g/cm ³)	19.3	8.91	7.87

The amounts of the removed binder were analyzed by the measurement of the weight loss of green part after the debinding process. Debound parts were also checked for any defects generated during the debinding.

2.4 Sintering

The debound part was held at 800°C for 1.5 h for oxide reduction and sintered at 1460°C, 1470°C, and 1480°C for 1 h. The heating rate to the sintering temperature was 10°C/min and the cooling rate was 2°C/min to 1300°C. The sintering cycle of W heavy alloy is shown in Fig.2.

The sintered density was measured using the densimeter by Archimedes' principle. The microstructure of the sintered part was observed by the optical microscope and scanning electron microscope (SEM).

3 Results and discussion

3.1 Debinding behavior

Fig.3 shows TGA analysis of green part for MIM W-4.9Ni-2.1Fe. From the results of TGA analysis and the previous study⁸⁾, the debinding process for the binder

Table 2 Composition and characteristics of the binder component.

	Melting point (°C)	Density (g/cm ³)	Composition (wt%)
Paraffin wax (PW)	68.3	0.9	45
Bees Wax (BW)	69.4	0.95	15
Polyethylene (PE)	114.6	0.93	30
Stearic Acid (SA)	77.3	0.85	10

Fig.2 The sintering cycle of W-4.9Ni-2.1Fe heavy alloy used in this study.

removal consisted of three-stage of temperature ranges from 0°C to 120°C, 120°C to 290°C, and 290°C to 480°C. By examining parameters of debinding process such as the heating rate and holding time, it was found that heating rate in temperature range from 120°C to 290°C, in which most of waxes were evaporated, had an important effect on the weight loss of binder as well as the crack generation. Table 3 shows the weight loss and shape stability after debinding at various heating rates in temperature range from 120°C to 290°C. As shown in this Table, the binder was removed completely after debinding process at slow heating rate of 0.5°C/min. Debinding process used in this experiment is represented in Fig.4.

Fig.3 TGA analysis of W-4.9Ni-2.1Fe green part.

Table 3 The weight loss and shape stability of green parts with various debinding processes.

Debinding process	Weight loss(%)	Shape stabilazation
120°C~290°C, 0.5°C/min	100.08	O
120°C~290°C, 1°C/min	98.29	O
120°C~290°C, 2°C/min	97.21	O

Fig.4 The debinding cycle used in this study.

Fig.5 shows the Fourier transform infrared spectroscopy (FT-IR) analysis curve for the MIM W-4.9Ni-2.1Fe specimen. The characteristic peak for organic substance as marked with asterisk in Fig.5(b), which was introduced by the binder, was not detected in the FT-IR curve for the debound part. This means that all of the binders were

Fig.5 Result of FT-IR analysis for (a) powder, (b) green part and (c) brown part.

removed in brown part after the debinding process. The complete removal of the binder during debinding was also confirmed by carbon analysis as shown in Table 4.

Table 4 The carbon content of the brown and sintered parts.
wt.%)

Debinding process	Brown part	Sintered part
120°C~290°C, 0.5°C/min	0.0734	0.0025
120°C~290°C, 1°C/min	0.1168	0.0052
120°C~290°C, 2°C/min	0.3556	0.0069

Fig.6 Optical micrographs of MIM W-4.9Ni-2.1Fe heavy alloy sintered at 1480°C for 1 h in dry hydrogen atmosphere showing (a) pore formation and (b) blister formation.

3.2 Sintering behavior

Fig.6 shows the microstructures of MIM W-4.9Ni-2.1Fe heavy alloy sintered at 1470°C for 1 h in a dry hydrogen (dew point -60°C). As shown in this figure, the defects such as pore and blister were observed even though the sintered density was over 99% of theoretical one. It seemed to be responsible for the sintering atmosphere. Bose *et al.*⁹⁾ reported that dry hydrogen often causes swelling during liquid phase sintering due to water trapping. This swelling becomes more severe with higher liquid contents or longer sintering times. It was suggested that swelling could be minimized using a wet hydrogen (dew point 20°C) in the sintering process. Thus, in order to avoid defects during sintering, sintering atmosphere changed to wet hydrogen from dry hydrogen at 1250°C and then was held in wet

Fig.7 SEM morphologies of MIM W-4.9Ni-2.1 Fe heavy alloy sintered at (a) 1460°C, (b) 1470°C and (c) 1480°C for 1 h in wet hydrogen atmosphere.

hydrogen atmosphere up to sintering temperature.

Fig.7 shows the microstructures of MIM W-4.9W-2.1Fe heavy alloy sintered at 1460°C, 1470°C and 1480°C for 1 h in wet hydrogen atmosphere, respectively. After liquid phase sintering using wet hydrogen, nearly full density was obtained irrespective of sintering temperature and as shown in Fig.8, no blister was formed. There was no difference in microstructure compared to that of W heavy alloy made of die compaction.

3.3 Microhardness of the sintered part

Fig.8 shows microhardness change with the sintering temperature for MIM W-4.9Ni-2.1Fe specimens sintered for 1 h in wet hydrogen atmosphere. As shown in this figure, microhardness value decreased with increasing the sintering temperature due to the W grain growth. The microhardness of the top region of the sintered specimen was higher than that of the bottom region.

In W heavy alloy, there was the gravitational effect during liquid phase sintering due to the high density of W¹⁰⁾, so that the solid content increased from the top to the bottom of the sintered specimen. Accordingly, higher microhardness value in the bottom region was attributed to the gravitational effect during liquid phase sintering.

4 Conclusion

This research has revealed that the MIM method could possibly be applied for the fabricating process of the W heavy alloy with the complex shape, showing moderate molding and debinding as well as sintering characteristics.

The W-4.9wt.%Ni-2.1wt.%Fe heavy alloy was suitably injection molded into a complex shaped part by adopting the multi binder system of 45PW+30PE+15BW+10SA, and the binder could be fully removed by three stage debinding treatment. The full sintered density was obtained by sintering at 1470°C for 1 h in a wet hydrogen atmosphere and there was no difference in microstructure compared to that of W heavy alloy by die compaction.

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Fig.8 Microhardness values in MIM W-4.9Ni-2.1Fe parts sintered for 1 h using wet hydrogen.

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