

## **Manufacturing of the Permalloy Soft Magnet by Powder Injection Molding Process**

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### **Abstract**

**The permalloy soft magnet was produced by powder injection molding process. Rheological characteristics of mixtures, debinding conditions and the magnetic properties of permalloy after sintering were investigated. The permalloy soft magnet with a permeability of 14200 could be obtained by preparing a mixture with a powder loading of 65.4 vol.% and PP/PEG binder system, solvent extraction, thermal debinding and subsequent sintering at 1350 °C in hydrogen. The permalloy soft magnet sintered in hydrogen showed a 95 % of theoretical density and a magnetic induction of 13.2 kG at the applied magnetic field of 50 Oe**

### **1. Introduction**

Powder injection molding (PIM) process is now widely used for the production of relatively complex shape components with ceramic or metal powders. This process has been developed mainly in the field of structural material and its application field is gradually increased to the functional material [1][2]. The powder injection molding of permalloy involves preparing a homogeneous mixture by mixing the polymer binder system with permalloy powder, forming the mixture in the cavity of mold, debinding a used binder system and subsequent sintering. The binders used must be removed without distortion and contamination of the compact before sintering process. Most important features in this process are the selection of binder composition and the debinding technique.

The Fe-Ni alloy (Permalloy) shows various magnetic properties with the Ni content from 35 to 70 wt.% [3]. The Fe-47.5 wt.% Ni permalloy is used as materials for the transformation of electric signal to mechanical signal, the magnetic shielding and the power of switch due to its high saturation magnetization. The permalloy is used in the form of sheet, powder and film produced by melting and rolling process. However, new

process for manufacturing of permalloy components without mechanical working is needed with a trend of downsizing the electronic devices.

In producing magnetic material by PIM process, the magnetic properties could be decreased by residual material and oxidation. Therefore, it was demanded to minimize residual carbon and oxygen by selection of binder system and debinding technique. In addition to this, process control is also important to prevent oxidation.

In this study, development of a new process was carried out to fabricate a permalloy components by PIM. Rheological characteristics of mixtures, debinding conditions and the magnetic properties of permalloy after sintering were investigated.

## 2. Experimental

Table 1 shows the chemical composition, density and particle size of permalloy powder used in this study. The morphology and the particle size distribution of permalloy powder are shown in Fig. 1 (a) and (b).

Table 1. Chemical composition and average particle size of permalloy powder

Component	HEF325	PB47(PF-5)
Composition	46.6wt.%Ni-Fe	47.2 wt.%Ni-Fe
Density(g/cm <sup>3</sup> )	8.25	8.25
Average particle size( $\mu\text{m}$ )	29.4	3.3
Notation	a1	b1

The PEG(Polyethylene glycol) with molecular weight of 1000 –20000 g/mol were used for the binder system. The PP(Polypropylene) used is a commercial grade of PP-141 (supplied by Daelim Co.) with a melt index of 25 g/min. (by ASTM D1238L-1) and a density of 0.91 g/cm<sup>3</sup>. The mixture was prepared by mixing the permalloy powder and binder system in a Brabender mixer at 190 °C for 15 min.. The binder system is composed of 40 vol.% PP and 60 vol.% PEG. The viscosity of mixture was measured by a capillary rheometer. Samples were injection molded by a simple ram type machine at a barrel temperature of 200 °C. The sample was a ring type and its dimension was 23.3 $\phi$  × 13.3 $\phi$  × 12 mm.

PEG was extracted by immersion in ethanol at 40, 50, 60 and 70 °C for 1 hr., respectively. The extracted samples were dried in a vacuum oven to calculate the PEG weight loss by extraction. The residual binder component was removed by a thermal debinding. Thermal debinding was carried out in a vertical tube furnace at 600 °C for 1

hr. with a heating rate of 5 °C/min. up to 150 °C and 1.5 °C/min. up to 600 °C. The gases for the thermal debinding were introduced at a flowrate of 300 mL/min. The debound samples were sintered between 1300 °C and 1400 °C in vacuum and hydrogen atmosphere. Magnetic properties of sintered sample were measured using a recording fluxmeter (TRF 5AH1 DC-fluxmeter, Toei Co.) and 4192A impedance analyzer(Hewlet Packard Co.)

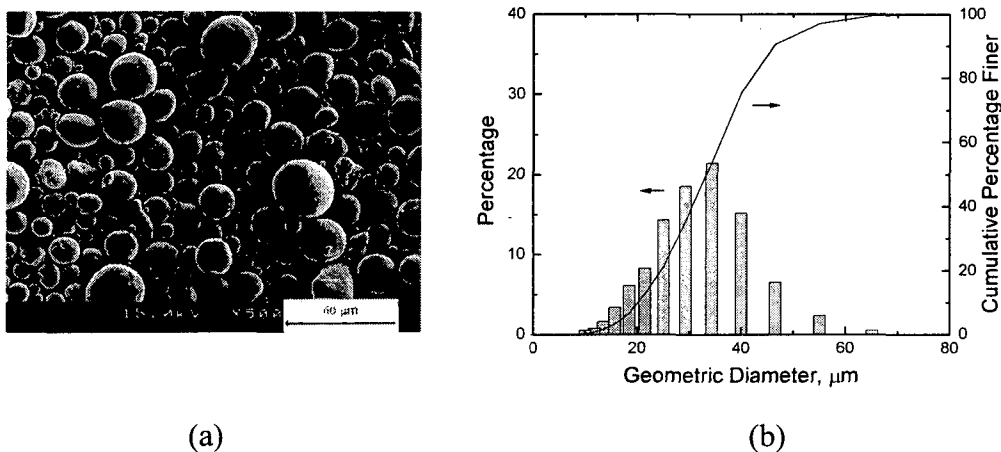


Fig. 1 Morphology (a) and particle size distribution (b) of permalloy powders denoted as a1

### 3. Results and Discussion

#### 3.1 Effect of powder loading and injection molding temperature on the viscosity of mixture

The fluidity of mixture depends on the mixing ratio of sphere type permalloy powder and binder. When the powder loading is lower than the optimum powder loading, binder could be separated during molding and the compact cannot maintain its shape after debinding. In case of higher powder loading than the optimum, injection molding will be difficult due to its high viscosity. Fig. 2 shows the apparent viscosity of mixtures with the variation of permalloy powder loading. The average particle size of permalloy powder was 29.4 μm. As shown in Fig. 2, the fluidity of mixture is rapidly decreased when the permalloy powder loading was increased from 65.4 vol.% to 67.4 vol.%. Therefore, the maximum powder loading for injection molding was 65.4 vol.%, when the sphere type permalloy powder of 29.4 μm was used.

The injection molding of permalloy/binder mixture should be carried out in the temperature range where the mixture has a moderate viscosity and the decomposition of binder is not occurred. In this study, therefore, injection molding must be carried out

below 250 °C, because the decomposition of PEG-10000 and PEG-20000 starts at 250 °C. Fig.3 shows the apparent viscosity of mixture as a function of shear rate and injection molding temperature. The injection molding using industrial machine is carried out at the temperature where the mixture has a viscosity of about 200 Pa·S. In this study, however, the injection molding temperature at which the viscosity of mixture is lower than that of the industrial scale was selected, because the injection molding machine used in this study was a vertical ram type machine manufactured in a laboratory scale. Therefore, the powder loading must be increased or the injection molding temperature should be lowered in case that the industrial machine is used. The optimum injection molding temperature was 200 °C in this study. At 190 °C, injection molding was impossible due to high viscosity of mixture. On the other hand, the separation between PEG and permalloy powder or PP was occurred due to low viscosity of PEG at the temperature higher than 210 °C.

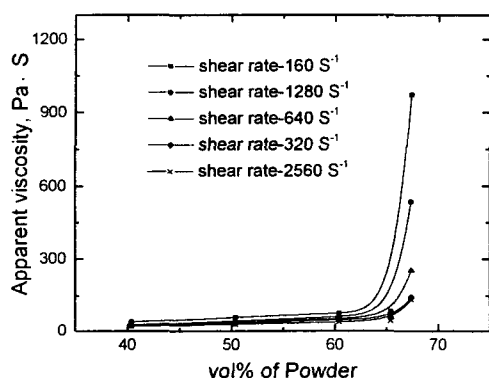


Fig. 2. Variation of apparent viscosity with the powder loading.

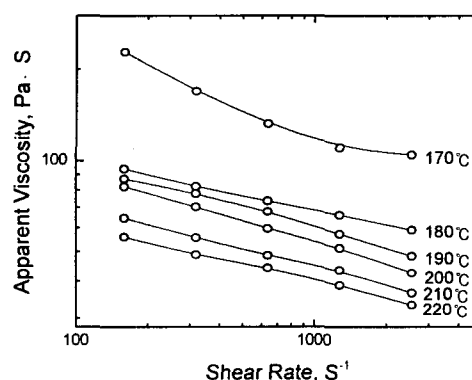


Fig. 3 Variation of apparent viscosity with the shear rate and temperature.

When a mixture for injection molding is prepared, the powder loading should be maximized. The maximum powder loading prevents the binder separation during injection molding and reduces the amount of residual carbon after debinding and sintering, which results in the improvement of magnetic properties of final products. Therefore, two kinds of permalloy powder with different particle size were used to increase the powder loading of mixture in this study. The Mooney's equation, which predicts the viscosity in case that the filler is added to polymer, is as follows [4].

$$\ln \eta_r = \ln(\eta / \eta_m) = \frac{k\phi}{1 - (\phi / \phi_m)} \quad (1)$$

where  $\eta_r$  is a relative viscosity,  $\eta$  is a viscosity of pure polymer,  $\eta_m$  is a viscosity of mixture,  $k$  is a Einstein coefficient,  $\varphi$  is a packing density and  $\varphi_m$  is a maximum packing density. As shown in Eq. 1, the maximum packing density,  $\varphi_m$ , could be increased by entering small powders into voids between large powders, and hence the fluidity of mixture could be increased. The mixing ratio of large and small powders for maximum powder loading was calculated by inserting the particle sizes of a1 and b1 powders, 29.41  $\mu\text{m}$  and 3.33  $\mu\text{m}$ , into the following equation [5][6] ;

$$\varphi_m = \frac{\sum D_i^3 f_i}{\max \left[ \sum (D_i \sim \bar{D})^3 + \frac{1}{n} \sum_{i=0}^m \left\{ (D_i \sim \bar{D}) - (D_i \sim \bar{D})^3 \right\} f_i \right]} \quad (2)$$

where  $D_i$  is a average particle size of  $i$  powder,  $f_i$  is a fraction of  $i$  powder and  $\bar{D} = \sum D_i f_i$ .

$$(D_i \sim \bar{D}) = 0 \quad \text{for } D \leq \bar{D} \quad (3)$$

$$= D_i - \bar{D} \quad \text{for } D > \bar{D} \quad (4)$$

The mixtures were prepared by varying the mixing ratio between a1(29.4  $\mu\text{m}$ ) and b1(3.3  $\mu\text{m}$ ) permalloy powders from 90:10 to 75:25 (in vol.%), respectively. In this case, the mixture was composed of 65.4 vol.% permalloy powder, 13.84 vol.% PP and 20.76 vol.% PEG. The apparent viscosity of mixture shows the lowest value in case that 85 vol.% of a1 and 15 vol.% of b1 permalloy powder were mixed. This value is differ form the calculated one (79 vol.% a1 and 21 vol.% of b1 powder) by Eq. 2, because the particle size distribution was not considered in Eq. 2.

The mixtures containing the powder loading from 65.4 vol.% to 73.4 vol.% were prepared and then the apparent viscosity was measured. The mixing ratio of a1:b1 powder was 85 :15 (in vol.%). Fig. 4 shows the apparent viscosity of mixtures as a function of shear rate. The apparent viscosity decreased with increasing the shear rate. However, the apparent viscosity was 100 Pa·S, which is a possible viscosity value for injection molding, even at the shear rate of 160  $\text{S}^{-1}$  and the powder loading of 73.4 vol.%. Therefore, the injection molding of mixture with higher powder loading could be possible when the industrial injection molding machine is used. A high powder loading in mixture prevents the distortion of sample during debinding and gives a constant shrinkage ratio after sintering.

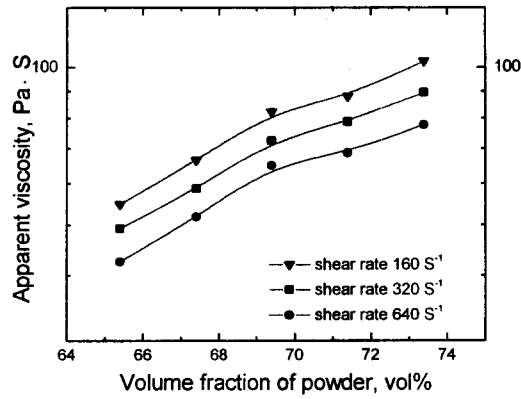


Fig. 4 Variation of apparent viscosity with the powder loading (a1:b1=85:15).

### 3.2 Debinding behavior and magnetic properties after sintering

A solvent extraction and a thermal debinding processes are used to reduce the time for removal of binders in compacts. A solvent extraction should be carried out prior to thermal debinding process, because the formation of open pore channels between powders by solvent extraction prevents the cracking occurred during thermal debinding. The solvent extraction behavior is affected by the solubility of solute, extraction temperature and time, molecular weight of solute and powder size. Fig. 5 shows the solvent extraction behavior of PEG with a extraction time. The PEG weight loss by solvent extraction showed a linear increase with square root time.

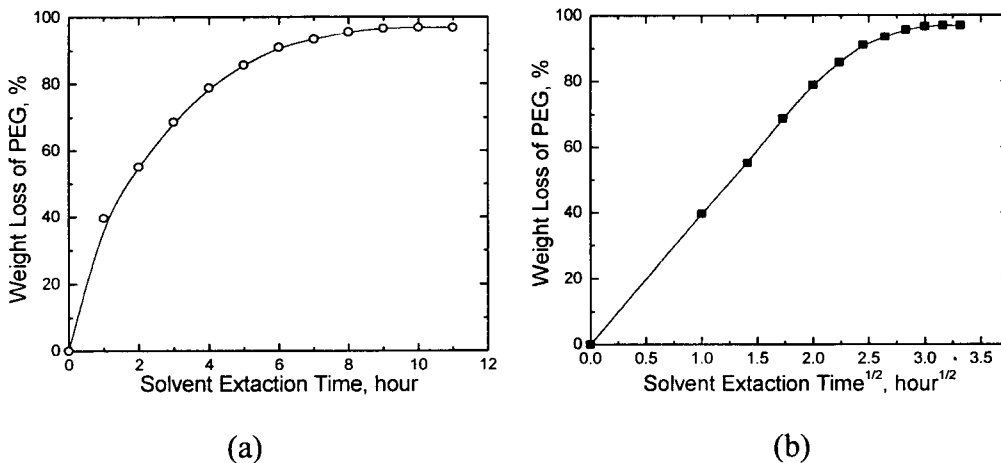


Fig. 5. PEG weight loss as a function of (a) time and (b) square root time.

Lin and German explained a solvent extraction mechanism by nonsteady-state

diffusion model when the thickness is  $2L$  [7-10].

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_{bs} \frac{\partial C}{\partial t} \right) \quad (5)$$

where the initial condition is  $C = C_i$  at  $t=0$ ,  $-L \leq x \leq L$  and the boundary condition is  $C = C_0$  at  $x=L$ ,  $t>0$ .

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x=0, t=0 \quad (6)$$

where  $D_{bs}$  is a interdiffusion coefficient between binder and solvent. Following equation can be derived from this model.

$$\ln(-\ln(1-W)) = \ln\left(\frac{D_0 t \pi^2}{4L^2}\right) - \left(\frac{E}{k}\right) \frac{1}{T} \quad (7)$$

where  $W$  is a fraction of extracted binder and  $D_0 t \pi^2$  represents a  $D_{bs}$ .

Therefore,  $D_{bs}$  can be obtained by fitting the  $\ln(-\ln(1-W))$  to  $1/T$  at a constant time. Fig. 6 shows the result of fitting at  $t=5$  hrs. In this study,  $2L=0.5$  cm, which is a half of the difference between inner and outer diameter of ring type sample. The mutual diffusion coefficient in accordance with this model is shown in Eq. 8.

$$D_{bs} = 1.234 \exp(-4044.33/T) \quad (\text{cm}^3/\text{s}) \quad (8)$$

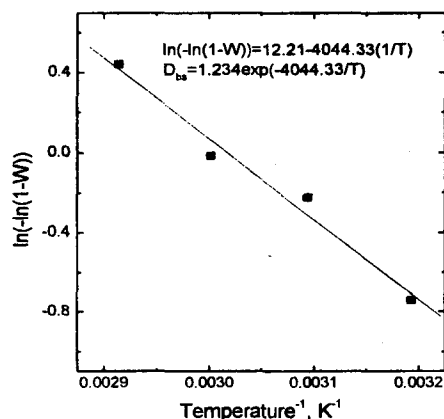
This value was verified by the Eq. 9 with which the mutual diffusion coefficient between solvent and solute in dilute solution can be calculated [11].

$$D_{AB} = \frac{kt}{6\pi\eta_B r_A} \quad (9)$$

where  $\eta_B$ , a viscosity of ethanol at  $50^\circ\text{C}$ , is  $0.68451 \times 10^{-7}$  N·s/cm<sup>2</sup> and  $r_A$ , a molecular size of sphere type solute regarded as a terminal distance of free rotation for PEG at  $50^\circ\text{C}$ , is  $7.651 \times 10^{-7}$  cm<sup>2</sup>/s [12]. When these values are inserted into Eq. 9,  $D_{AB}$  is  $4.517 \times 10^{-7}$  cm<sup>3</sup>/s, which shows a large difference from  $D_{bs}=4.53 \times 10^{-6}$  cm<sup>3</sup>/s in Eq. 8 at  $50^\circ\text{C}$ . Lin and German model, therefore, can not explain the solvent extraction behavior of such mixture as PP and PEG are mixed together. According to scanning electron micrograph of the compact after solvent extraction, PEG was removed by ethanol and remained PP prevented the cracking of compacts during solvent extraction and thus maintained the compact shape.

Fig. 7 shows the TGA results with a variation of powder loading. The weight loss by thermal decomposition was started at about  $160^\circ\text{C}$  and showed a maximum at about  $210^\circ\text{C}$  at the powder loading of 40.4 vol.%. The bending point appeared at  $260^\circ\text{C}$ . The starting and ending temperatures of thermal decomposition for PEG are  $150^\circ\text{C}$  and  $260^\circ\text{C}$ , respectively. The thermal decomposition of PP starts at about  $250^\circ\text{C}$ .

Therefore, the heating rate should be slow at about 210 °C during thermal debinding, because PEG is decomposed rapidly at this temperature. The bending point at about 260 °C is caused by the decomposition of residual PP. As shown in Fig. 7, the starting temperature of thermal decomposition was decreased with increasing the powder loading. The activation of thermal decomposition for polymer is known to be affected by the sort of powder [13] and this phenomenon is also considered to be occurred in this



investigation.

Fig. 6 The fraction of PEG residue as a function of temperature for a given time(5 hrs.), the slope indicate the activation energy of interdiffusion between PEG and ethanol.

Fig. 8 shows the magnetic properties and density of permalloy sintered after solvent extraction and thermal debinding with sintering temperature and atmosphere. The magnetic induction was measured at an applied field of 50 Oe. The sintered density increased with increased sintering temperature, and the density of permalloy sintered in hydrogen atmosphere was higher than that in vacuum. This may be due to the acceleration of desinification through grain growth by reducing the permalloy powder oxidized during mixing and debinding. The magnetic induction at 50 Oe of permalloy

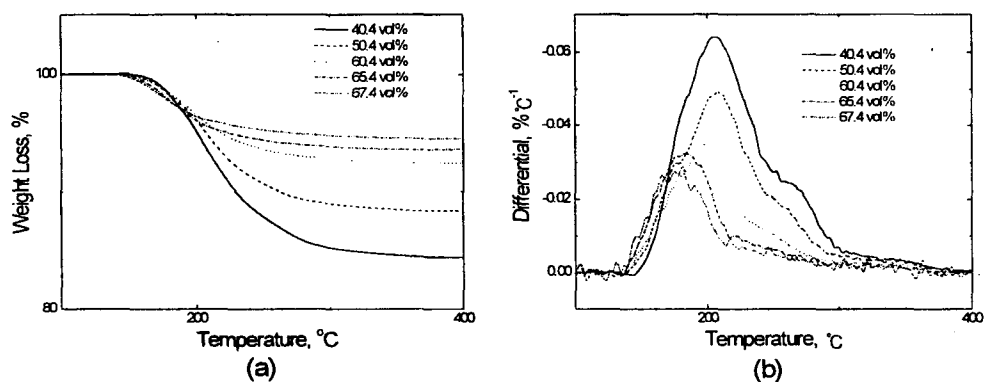


Fig. 7. TGA analyses showing the effect of powder concentration on binder burn-out behavior.



sintered in hydrogen atmosphere increased with increasing the sintering temperature. However, the magnetic induction at 50 Oe of permalloy sintered in vacuum showed a maximum at 1370 °C and decreased again with further increasing the sintering temperature. This phenomenon can be ascribed to the hindrance of rotation of magnetic domain by residual oxygen and carbon remained in sintered body due to a low applied magnetic field of 50 Oe.

The variation of maximum relative permeability with sintering temperature is shown in Fig. 9.

Fig. 9. Variation of the maximum relative permeability with the sintering temperature.

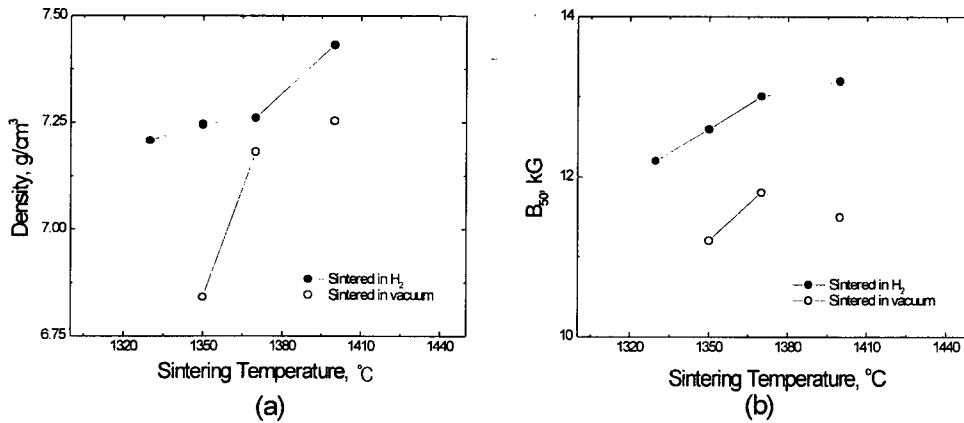
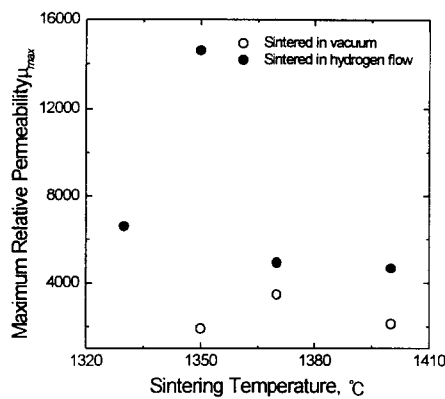


Fig. 8. Variation of (a) sintered density and (b) magnetic induction at 50 Oe ( $B_{50}$ ) with the sintering temperature and atmosphere.



The maximum relative permeability tended to decrease with increased sintering temperature. The grain grows as the sintering temperature increased. When the grain grows, the energy needed for magnetic domain rotation to the direction of applied magnetic field will be increased, and this results in the decrease of maximum relative

permeability.

### Conclusions

The permalloy soft magnet was produced by powder injection molding process. From the investigation of binder system, debinding and sintering conditions, following conclusions can be drawn.

1. The permalloy soft magnet with a permeability of 14200 could be obtained by preparing a mixture with a powder loading of 65.4 vol.%, solvent extraction with ethanol, thermal debinding and subsequent sintering at 1350 °C in hydrogen. The average particle size of used permalloy powder was 29.4 μm, and the binder system was composed of 40 vol.% PP and 60 vol.% PEG-1000.
2. The permalloy soft magnet sintered in hydrogen after debinding showed a 95 % of theoretical density and a magnetic induction of 13.2 kG at an applied magnetic field of 50 Oe

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