

Effects of Phosphorus Addition on the Magnetic Properties of Sintered Fe-50 wt.% Ni Alloys

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Phosphorus was added to Fe-50 wt.% Ni in the form of a coated composite powder via an electroless plating process. Addition of phosphorus to Fe-50 wt.% Ni facilitated increases in density and grain size, both of which were beneficial to magnetic performance. Because of the homogeneous distribution of phosphorus in the powder, the optimal phosphorus addition was much lower than for those using Fe_3P as the phosphorus precursor. The optimal phosphorus addition was close to its maximum solubility in Fe-50 wt.% Ni (about 0.5 wt.%), above which precipitation of excessive phosphorus in the form of iron nickel phosphide, $(\text{Fe,Ni})_3\text{P}$, effectively degraded the magnetic properties of Fe-50 wt.% Ni. Without the addition of phosphorus, good magnetic properties could be achieved only when the sintering temperature was high enough ($>1200^\circ\text{C}$) to result in a high sintered density and large grains in the sintered structure.

Keywords electroless nickel plating, Fe-Ni alloy, magnetic properties, phosphorus addition

1. Introduction

Powder metallurgy is an effective route for economical mass production of soft magnetic components. Different materials, such as Fe-Ni and Fe-Si alloys, are produced using this process.^[1,2] However, products fabricated via powder metallurgy usually have a porosity in excess of 10 vol.%, which results in relatively poor and erratic magnetic characteristics in the final product. For example, mixtures of elemental Fe and Ni powders of fine particle size can hardly achieve a theoretical sintered density higher than 95% theoretical value, even at a sintering temperature higher than 1300°C .^[3] For sintered products having low sintered densities, postsintering secondary repressing followed by thermal annealing is usually needed to enhance their magnetic performance. An approach to improve the sintered density of ferrous alloys is to enhance the material transfer rate during sintering via alloying, such that a higher sintered density can be achieved by activated solid-state sintering or liquid-phase sintering. In these approaches, P and B are the most frequently added elements to promote the formation of a liquid phase at low temperatures.^[4,5]

Enhanced magnetic performances have been documented for iron with phosphorus addition.^[6] The improved magnetic properties with the addition of P to Fe have been attributed to the enhanced sintered density, large grain size, and spheroidization of residual pores.^[7] For Fe-P alloys, P is generally added to the Fe powder in the form of Fe_3P . The principal limitation of such an approach is that the addition of Fe_3P in the form of a powder with a particle size larger than $10\ \mu\text{m}$ always results in nonuniform distribution of phosphorus and, consequently,

existence of large pores in the sintered structure. The distribution of phosphorus in the sintered structure can be improved by adding a higher concentration of phosphorus, but the best magnetic properties are achieved only when the phosphorus concentration varies in the range between 0.4 and 0.8 wt.%.^[6,8,9] However, even higher concentrations of phosphorus (up to 1.2 wt.%) have been documented to yield optimal magnetic performance.^[10] Increase in the phosphorus addition can improve the uniformity of phosphorus distribution in the sintered structure, but the major drawback of this approach is the distortion associated with a relatively large sintered shrinkage ratio, which precludes the feasibility of fabricating components by the press-and-sinter process. For example, Fe-0.8 wt.% P alloy is often regarded as an improved material beyond the commonly used Fe-0.45 wt.% P alloy, but it exhibits greater sintered shrinkage and distortion when the alloy is processed by press-and-sinter practice.^[8] For the press-and-sintered Fe-0.8 wt.% P, a coining operation is often needed to control the dimensions of the part, and a subsequent low-temperature thermal anneal is required to remove the surface deformation without altering the dimensions.

A large portion of the phosphorus atoms added in the form of Fe_3P does not enhance the sintering events because of the large grain size of Fe_3P . If the relative degree of distribution homogeneity of phosphorus can be improved microscopically in the powder mixture, a higher portion of the phosphorus atoms added to the system can participate in enhancing sintering events and the optimal concentration of phosphorus addition can accordingly be reduced. For example, ternary iron-nickel-phosphorus alloy powders, the phosphorus concentrations of which are usually low ($<0.5\ \text{wt.}\%$) have been prepared by electroless plating.^[11,12]

In this study, the effects of phosphorus addition on the sintering behavior and magnetic properties of Fe-50 wt.% Ni were investigated. Iron and nickel powders that are commonly used in powder injection molding were studied. The degree of distribution homogeneity of phosphorus in the powder was improved by introducing the phosphorus atoms to the Fe-Ni powder surface via electroless nickel plating, which was ex-

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pected to enhance the sintering behavior of the alloy and, therefore, the magnetic properties.

2. Experimental Procedures

A nickel salt in solution was autocatalytically reduced to coat suspended carbonyl iron powder. The base powders were a carbonyl iron powder (OM grade, BASF, Germany) and a carbonyl nickel powder (Inco 123 grade, Novamet, Wyckoff, NJ). The mean particle sizes of the iron powder and nickel powder were 4.5 and 9.8 μm , respectively. The major impurities of the iron powder were carbon (0.74 wt.%), nitrogen (0.66 wt.%), and oxygen (0.15 wt.%), whereas those of the nickel powder were oxygen (0.15 wt.%) and carbon (0.10 wt.%). These fine powders are suitable for metal injection molding processes. To improve the results of electroless plating, the as-received iron powder was treated with an acidic water solution prior to plating. Initially, the powder was immersed in a 1 vol.% diluted HCl aqueous solution, maintained at 50 °C for 10 min. The weight ratio of the powder to the aqueous solution was 7:20. The powder was then washed with distilled water and then with acetone. Finally, the powder was dried in a vacuum oven at 60 °C for 2 h.

Electroless plating was carried out using an acidic solution maintained at 85 °C. The bath solution was prepared by dissolving 20 g of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 27 g of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), and 16 g of sodium succinate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot 6\text{H}_2\text{O}$) in 1000 cm^3 diluted H_2SO_4 aqueous solution. The initial pH value of the solution was 6. Under the assumption of complete reaction, there will be 7.9 g of P and 5 g of Ni precipitating from the solution, whereas there will be 4.7 g of Fe dissolving into the solution. With this as the basis of calculation, various quantities of iron powder were poured into different batches of plating solution to yield plated powders having different amounts of phosphorus deposited onto the surface of iron powder. The bath solution and the powder were stirred for 2 h. After plating, the powder was washed and dried according to the same procedures executed prior to plating. The plated powders were then mixed and milled with the appropriate quantities of nickel powder in heptane with 1.5 wt.% paraffin wax for 8 h. Subsequently, the slurry was dried and sieved, and the granules were pressed in disks under a pressure of 450 MPa. The specimens were then sintered in a tube furnace in hydrogen atmosphere. The sintering profile comprised several ramps and soaks at low temperatures to burn out the wax and to reduce oxides from the powder surface. It was followed by a ramp of 3 K/min from 900 °C to the sintering temperature, which ranged from 900-1250 °C, and the isothermal holding time at the sintering temperature was 60 min.

The compositions of the alloys were determined by a glow discharge spectrometer (GDS-750QDP, Leco, St. Joseph, MI), using sintered bulk specimens. Table 1 shows the designations, compositions, and theoretical densities of the alloys investigated in this study. The theoretical density for each composition was calculated on the basis of the law of mass action. It was initially intended to prepare the powders having concentrations of P ranging from 0-1 wt.% by a step of 0.2 wt.%. Nevertheless, the results yielded dramatic deviations for P6 and P8, which deviated from the intended compositions by 0.13 and

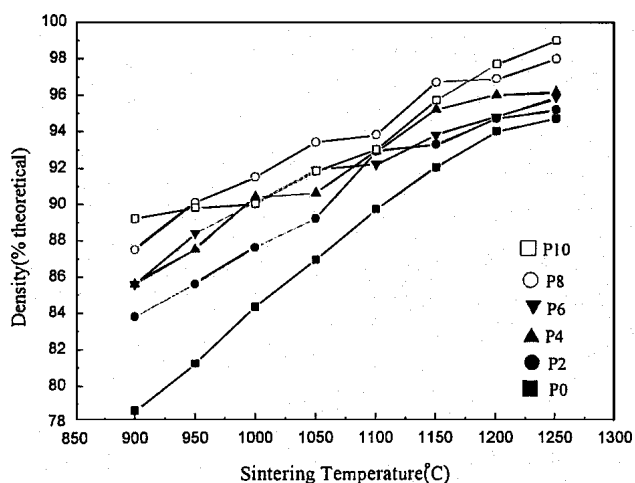


Fig. 1 Variation of sintered density with sintering temperature (hydrogen temperature)

Table 1 Designations, Compositions, and Theoretical Density of the Alloys Investigated

Designation	Fe, wt. %	Ni, wt. %	P, wt. %	C, ppm	S, ppm	Theoretical Density, g/cm^3
P0	51.23	48.76	0.015	58	16	8.29
P2	49.50	50.29	0.21	71	9	8.25
P4	48.64	51.00	0.36	38	19	8.21
P6	46.78	52.75	0.47	56	16	8.19
P8	47.33	52.12	0.55	44	18	8.17
P10	47.55	51.55	0.90	26	19	8.06

0.25 wt.% P, respectively. The sintered density was measured by the water immersion method. The specimens were polished and etched to reveal their microstructures. Because of the difficulty encountered in etching the alloys of different compositions, different etching processes were used. For P0, the specimens were etched using dilute acidic solution (15 vol.% lactic acid + 3 vol.% HNO_3 + 0.3 vol.% HF) for 10 s. For P2, P4, and P6, the specimens were etched in a series of steps until the grain boundaries fully developed. The specimens were first etched using 5 wt.% Nital solution for 60 s, and then a Marshall reagent (5 cm^3 H_2SO_4 + 8 g oxalic acid + 1 cm^3 H_2O_2 + 100 cm^3 H_2O) for 3 s. The grain boundaries could be better revealed by further etching the specimens using 5 vol.% Nital for 30 s and then glyceresia (HCl/ HNO_3 /glycerin, 3:1:2) for 30 s. For P8 and P10, the specimens were etched using 5 vol.% Nital for 60 s. Phase analysis of the bulk-sintered specimens was performed using x-ray diffraction (XRD) with Cu-K α radiation at an accelerating voltage of 40 kV. Morphological analysis of the sintered microstructure was carried out using both optical microscope and scanning electron microscopy (SEM) at an accelerating voltage of 20 kV.

3. Results and Discussion

Figure 1 shows the variation of sintered density with sintering temperature for the six alloys investigated in this study.

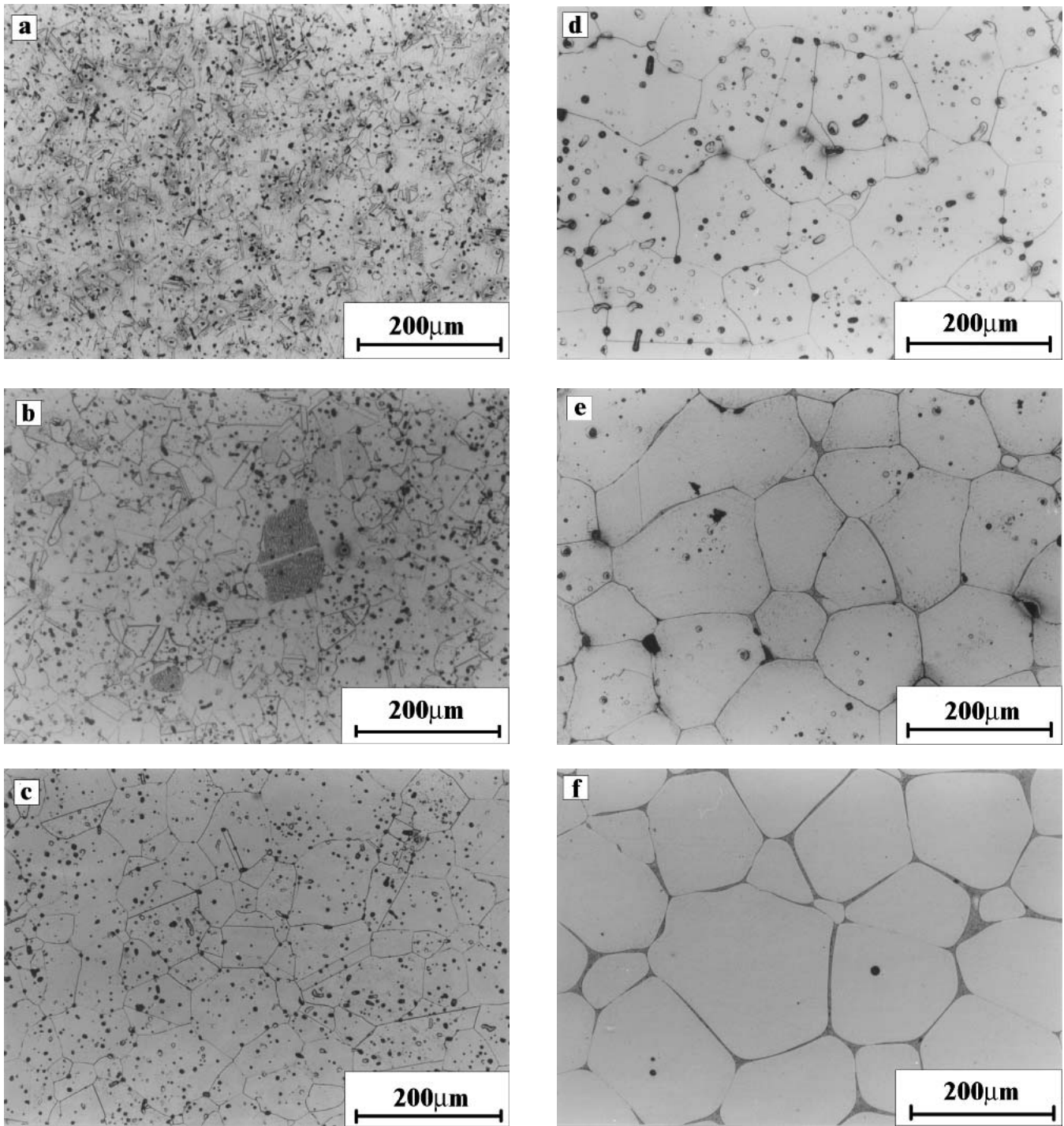


Fig. 2 Representative microstructures for P0 (a), P2 (b), P4 (c), P6 (d), P8 (e), and P10 (f) sintered at 1250 °C

In the temperature range investigated, the alloys with phosphorus addition always exhibited improved sintered density with respect to that without phosphorus addition. A density higher than 98% theoretical value was achieved at a sintering temperature of 1250 °C, with at least about 0.5 wt.% phosphorus addition (P8 and P10). Representative microstructures for the six alloys sintered at 1250 °C are shown in Fig. 2. The morphology of phases in the structures is dependent on the alloying

concentration of phosphorus. Generally, the grain size increases and the grain shape becomes more spheroidal with an increase in phosphorus addition. The population of pores decreases while the relative dimensions of pores increase with increases in phosphorus addition. Distribution of phosphorus in the form of an intergranular phase is appreciable only for P8 and P10, which is characteristic of persistent liquid phase sintering. The microstructures shown here are dramatically differ-

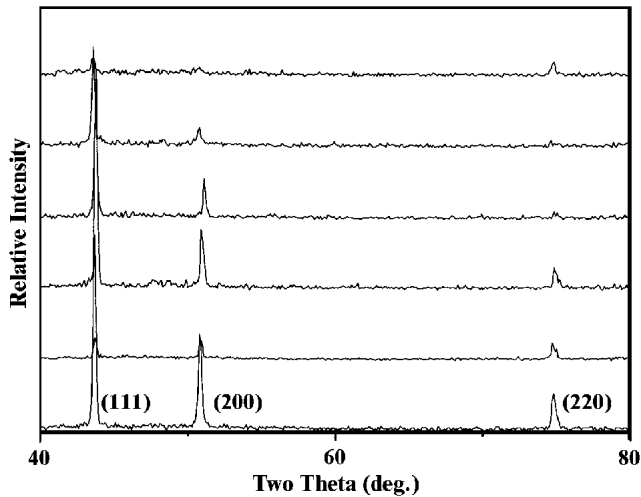


Fig. 3 XRD patterns of the six alloys sintered at 1250 °C. Only the diffraction peaks of γ -(Fe,Ni) could be easily identified in these patterns.

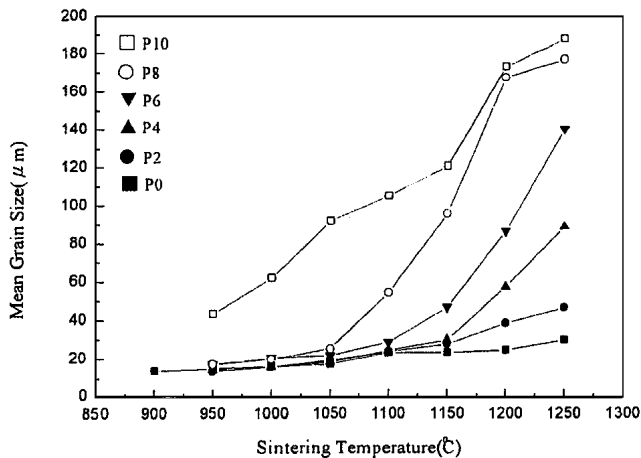
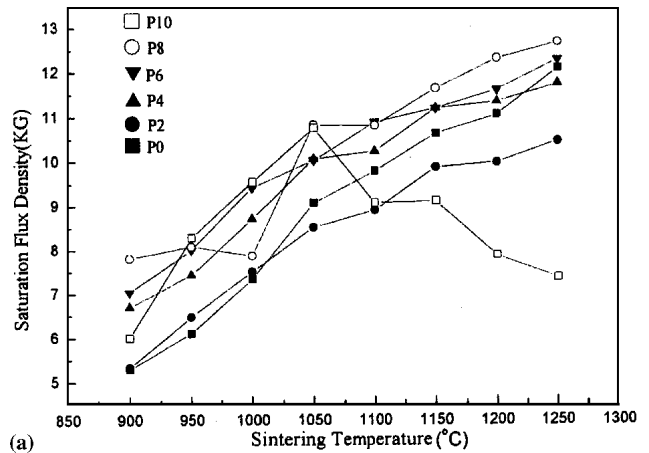
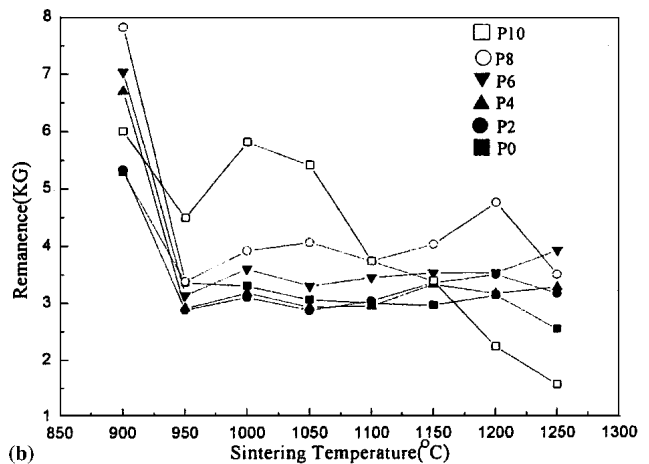


Fig. 4 Variation of grain size with increase in sintering temperature

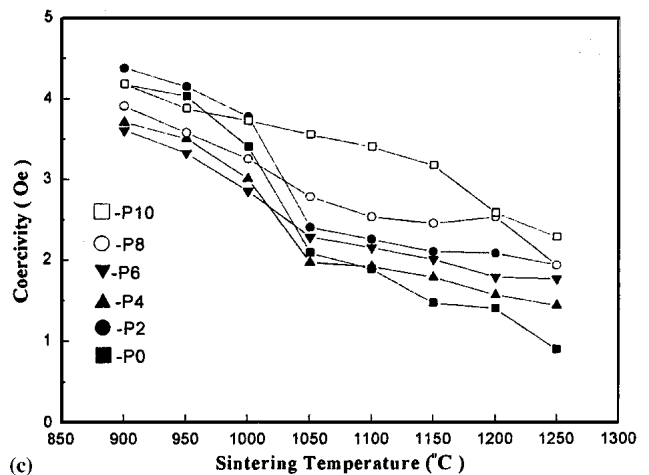
ent from those for which phosphorus was added in the form of Fe_3P ,^[7-10] in which grains were more angular and large Fe_3P grains either existed in the grain boundaries or within iron grains. On the basis of this observation, it can be inferred that the maximum solubility of phosphorus in Fe-50 wt.% Ni alloy at 1250 °C lies between 0.47 wt.% (P6) and 0.55 wt.% (P8). Previous study had found that the intergranular phase was the phosphide phase of iron and nickel, $(\text{Fe,Ni})_3\text{P}$.^[13] However, except for the patterns of γ -(Fe,Ni), no distinct diffracted signal arising from the second phase could be observed in XRD patterns, as shown in Fig. 3. In addition, no significant change of lattice was observed, although phosphorus has an atomic radius much smaller than that of iron and the dissolution of phosphorus in iron is substitutional.^[10] Figure 4 shows the variation of grain size with increase in sintering temperature. Note that the eutectic temperature of (Fe-50 wt.% Ni)-P is about 900 °C.^[14] Thus, the liquid phase formed during sintering (either transiently or persistently) for the alloys with phosphorus addition, and the sintering behavior of the six alloys could be categorized



(a)



(b)



(c)

Fig. 5 Variations of saturation flux density (a), remanence (b), and coercivity (c) with sintering temperature, tested in a direct magnetic field intensity with a maximum magnetic field of 25 Oe

into three different groups.^[15] For the alloy without phosphorus addition (P0), sintering in the solid state was the only mechanism that led to densification and grain growth. For the alloys with low phosphorus additions (P2, P4, P6), a transient liquid phase composed of Fe, Ni, and P formed, which subsequently

dissolved into the lattice of Fe-Ni during sintering. On the other hand, a persistent liquid phase dominated the sintering events of P8 and P10 at 1250 °C. Because of the increased material transfer rate during sintering, not only were the sintered densities obviously enhanced, but the mean grain sizes for the persistent liquid phase sintered group were about six times those of samples sintered purely in solid state.

Densification can be retarded by the existence of differential stresses near the interfaces between two foreign grains when mixed elemental powders are sintered. Such a phenomenon is most pronounced when the composition of the alloy is near equal parts. For example, sintering Fe-Ni^[3] and Co-Ni^[16] alloys of different alloy concentrations shows that the lowest sintered densities occur at compositions near Fe-60 wt.% Ni and Co-50 wt.% Ni, respectively, although the interdiffusion coefficients are the greatest near these ranges of composition. Because the Fe and Ni powders used in this study differ greatly in their sintered densification profiles (plots of sintered shrinkage versus sintering temperature),^[3] the differential stress between grains of two different materials will substantially inhibit densification. With the existence of an intergranular liquid phase during sintering, not only can the diffusion of Fe and Ni be enhanced, but the differential stress between neighboring grains can also be reduced. Both of these effects are beneficial to densification.

The variations of saturation flux density, remanence, and coercivity with sintering temperature are shown in Fig. 5, tested in a direct magnetic field with a maximum magnetic field of 25 Oe. For the alloys with low concentrations of added phosphorus (P2 and P4), increase in saturation flux density with phosphorus addition was achieved only at lower sintering temperatures because of the higher sintered density than that without phosphorus addition. However, when the sintering temperature was high enough to yield a high sintered density, the alloy without phosphorus addition exhibited a greater saturation flux density. For the alloys with phosphorus concentrations lying close to the maximum solubility in Fe-50 wt.% Ni (P6 and P8), the saturation flux densities were always better than those for the alloy without phosphorus addition, with the advantage only becoming less obvious at higher sintering temperatures. For the alloy with excessive intergranular precipitation of (Fe,Ni)₃P (P10), the saturation flux density was not much better than that without phosphorus addition, and was even worse at higher sintering temperatures. The trend of remanence closely resembled that of saturation flux density, only with one additional factor affecting its value, i.e., a lower saturation flux density always led to a lower remanence. The alloy without phosphorus addition exhibited a lower coercivity than the other alloys at a sintering temperature higher than 1100 °C when its sintered density is higher than 90% theoretical. For the alloys with phosphorus addition, low values of coercivity could be achieved with phosphorus addition lying between 0.36 wt.% (P4) and 0.47 wt.% (P6). Such an observation confirms the general belief that incorporation of foreign atoms into the lattice of soft magnetic materials can lead to the slow response of the magnetic materials to a magnetic field. In addition, it could also be concluded that excessive precipitation of intergranular (Fe, Ni)₃P led to deterioration of magnetic response in a direct magnetic field. Previously, it was pointed out that the optimal magnetic properties could be achieved at a phosphorus addition

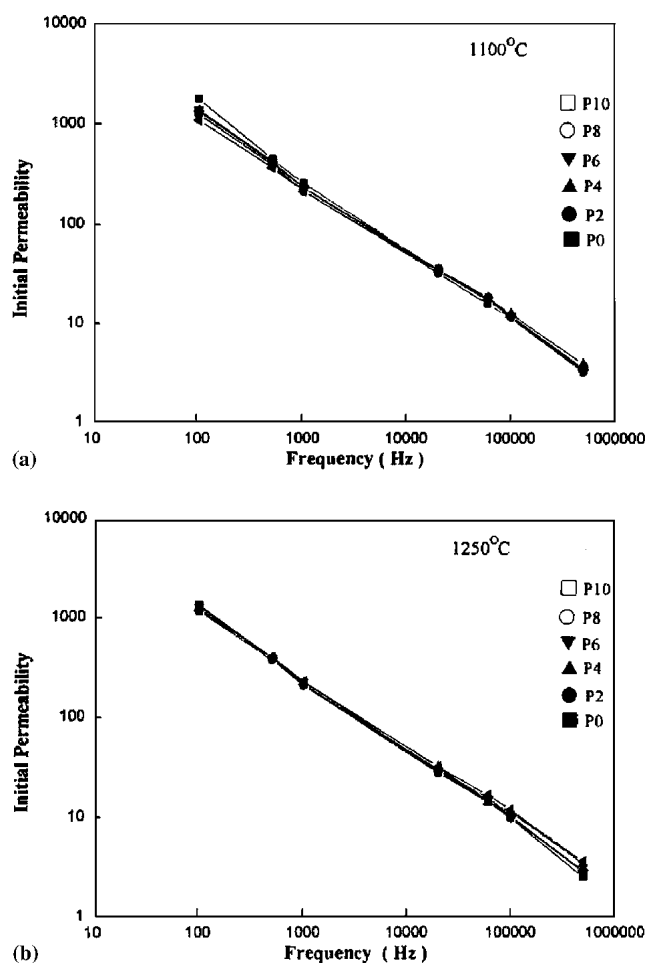


Fig. 6 Variation of initial permeability with frequency in alternating magnetic fields for all the alloys sintered at (a) 1100 °C and (b) 1250 °C

lying between 0.4 and 0.8 wt.%,^[6,8,9] or even between 0.8 and 1.2 wt.%.^[10] However, the optimal concentration of phosphorus addition found in this study was close to 0.47 wt.% (P6). Such a discrepancy arose from the fact that phosphorus was added in the form of Fe₃P in previous studies such that a large portion of the phosphide remained in the form of large grains that did not participate in the formation of a liquid phase.

All of the alloys were also tested in alternating magnetic fields. Figure 6 shows the variation of initial permeability with frequency for all the alloys sintered at 1100 and 1250 °C, respectively. Initial permeability indicates how easily the magnetic domains can rotate in an alternating magnetic field. It was surprising to find that the alloy without phosphorus addition exhibits a better response to an alternating magnetic field of low frequencies (100-1000 Hz), even when its sintered density at a sintering temperature of 1100 °C was low (90% theoretical value) and its mean grain size was relatively small. Accordingly, substitution of lattice sites of Fe-Ni by P atoms caused substantial pinning of domain during the rotation of magnetic domains in an alternating magnetic field of low frequencies. At higher frequencies, the response of magnetic domains to the alternating field became inert for all of the alloys and there was not much difference in the initial permeability for these six

alloys. It was also noted that sintering temperature, and thus sintered density, had only a slight effect on initial permeability.

The addition of phosphorus to Fe-Ni alloys prepared using mixed elemental powders had several effects on the magnetic performance of the sintered alloys. Increases in sintered density, mean grain size, and spheroidization of grains with the addition of phosphorus could yield beneficial effects for the magnetic performance.^[6] The other consequence of adding phosphorus to Fe-Ni alloys is the increase in resistivity, primarily caused by the precipitation of semiconducting $(\text{Fe,Ni})_3\text{P}$ in grain boundaries.^[6,13] A high resistivity is beneficial to the magnetic response in high-frequency alternating circuit applications because the core loss can be reduced.^[6] On the other hand, the negative effect of adding phosphorus arises from the impediment of magnetic domain movement as phosphorus either dissolves in Fe-Ni lattice in a substitutional manner^[10] or is precipitated out as $(\text{Fe,Ni})_3\text{P}$ in the grain boundaries. In addition, homogenization of Fe and Ni elements in the sintered microstructure was found to be difficult in that sintering the powder mixtures of Fe-Ni at a sintering temperature as high as 1300 °C for 1 h still left behind a duplex structure after cooling, which was composed of α -Fe- and γ -Ni-based phases.^[3] The magnetic performance of the sintered alloy depended on the relative abundance of each phase, with stabilization of α -Fe leading to better magnetic properties.^[6] Although phosphorus addition facilitates stabilization of the ferromagnetic α -Fe-based phase, homogenization of Fe and Ni can also be achieved at lower temperatures. Homogenization of Fe and Ni resulted in difficulty in transforming the γ -Ni-based phase to α -Fe-based phase during cooling.^[17] The magnetic properties of the sintered alloys are degraded because of the decrease in the relative abundance of the ferromagnetic α -Fe-based phase, even at a low sintering temperature. Because of these complicating effects, phosphorus addition was effective in improving the magnetic performance of Fe-50 wt.% Ni only when the alloys were sintered at low temperatures (<1100 °C). At high sintering temperatures, high sintered densities, and therefore, enhanced magnetic properties of Fe-50 wt.% Ni could be achieved without phosphorus addition. The loss of magnetic response caused by the incorporation of phosphorus into the lattice sites of Fe-Ni, the precipitation of $(\text{Fe,Ni})_3\text{P}$, and the inability to transform into α -Fe-based phase could not completely be compensated for by the slight increase in sintered density and larger grains.

4. Conclusions

This study examined the effect of phosphorus addition on the magnetic properties of sintered Fe-50 wt.% Ni. The powder was used in powder injection molding, by which intricate parts possessing good soft magnetic properties can be fabricated. Ternary iron-nickel-phosphorus powders with various concentrations of phosphorus were prepared by simultaneous electroless plating of nickel and phosphorus onto the surface of iron powder. The plated powders were then milled with appropriate amounts of nickel powder and their final compositions were adjusted to near Fe-50 wt.% Ni, but with phosphorus concentrations varying from zero to slightly above the maximum solubility in Fe-50 wt.% Ni (0.9 wt.%). Sintering at low temperatures produced parts with a high sintered density and large

spheroidal grains when the concentration of phosphorus was high enough to induce a persistent liquid phase during sintering. Magnetic properties tested in direct magnetic fields showed that the optimal performance was achieved at 0.5 wt.% phosphorus. For magnetic properties tested in alternating magnetic fields, the benefits of enhanced density and increased grain size from phosphorus addition could not effectively compensate for the drawback of deterioration of the magnetic response arising from the interruption of the Fe-Ni lattice by phosphorus, the precipitation of $(\text{Fe,Ni})_3\text{P}$, and the inability to transform the high-temperature γ -Ni-based phase into the ferromagnetic α -Fe-based phase.

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