# Magnetic properties of sintered sendust alloys using powders granulated by spray drying method

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The iron-silicon-aluminum alloys (particularly Sendust) have been widely used in applications requiring high saturation flux density, low coercive force and high electrical resistivity. For this reason they have been promising for magnetic thin film heads, however, they are too hard and brittle to be made into thin films by rolling, or into three-dimensional products of complex shape by mechanical working or a conventional powder metallurgy process. The reduction in the size and weight of devices that can be accomplished through the use of Sendust has had an important effect on technical development. In this report, magnetic characteristics of Sendust ring samples produced by the powder metallurgy process with spray drying were investigated. After gas-atomized Sendust powders were mixed with paraffin compounds, these powders were granulated by the spray drying method using organic binder consisting of polyvinyl alcohol (PVA) and plasticizer in the range from 0.1 to 0.5 wt% of PVA, in order to improve the powder flowability and mechanical strength of compacted bodies. Results show that the present method is an excellent process for producing near-net-shaped parts with high performance and high dimensional precision after sintering. 

## 1. Introduction

Today, various soft magnetic materials are used not only in home electric appliances but also in computer peripheral equipment. In particular, with iron cores and yoke materials of transformers and core materials of magnetic heads, the demand for the realization of complicated shapes, miniaturization, lightweight and high performance has increased significantly.

As representative soft magnetic materials, we can list Mn-Zn and Ni-Zn ferrites, permalloy whose major components are Fe-Ni, Sendust consisting of Fe-Al-Si alloys and permendur consisting of Fe-Co alloys. Among them, Sendust has a permeability comparable to that of permalloy and a high electrical resistivity [1] as compared with permalloy and its raw material cost is very cheap compared with other soft magnetic materials because it does not contain expensive materials such as Ni and Co. From this reason, although much attention has been paid to Sendust as a material for magnetic heads, the extreme brittleness when producing plastic deformation has been a large obstacle to its fabricator [2, 3].

As fabrication processes of Sendust, there are various methods such as a rapid cooling of liquid-metal, a precision casting [4] and plastic processing in which the brittleness was improved remarkably by adding Ni to Sendust alloys [5]. There are also some powder metallurgy methods; a powder rolling [6, 7], a plasma spark sintering [8], a conventional sintering and a peculiar sintering in which pure iron powder instead of organic binder is added as binder to Sendust powder to control the residual oxygen and carbon contents [9]. None of these technologies, however, has made it possible to fabricate complex three-dimensional products with high dimensional precision. For this reason, the application of metal injection molding (MIM) to Sendust has been examined, but there was a troublesome problem that fine Sendust powders react with the oxygen in the organic binder during kneading, resulting in a degradation in the magnetic characteristics. Because the magnetic characteristic of soft magnetic materials are very sensitive to the presence of various impurities and crystal defects such as voids.

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In order to obtain a sintered bodies with relatively high density without using any binder, therefore, fine Sendust powder with poor flowability has ever been subjected to the conventional powder metallurgy methods. Such powders, however, scatters the quantity of powder fed into a die cavity from a powder feeder, resulting in the dispersion in the dimensions after sintering. In addition, as the green body compacted without using binders is very brittle, it was almost impossible to handle without fracturing it even when it was compacted at a high pressure. In order to improve the flowability of powders and the mechanical strength of green body, the application of the spray drying process [10] to Sendust was examined because this process can generally provide not only sintered products with high dimensional precision after sintering, but also firm green bodies. Fine powders of Sendust alloy are chemically aggressive and are apt to react with oxygen and carbon in organic binder, as mentioned above. This has made it more difficult to apply the spray drying process. In our previous papers [11–15], however, we have already succeeded to apply this technique to the fabrication of Nd-Fe-B magnets [16] and permendur, and have suggested that it is possible to fabricate complex-shaped parts with excellent magnetic properties and high dimensional precision using spray drying method [11, 14].

In the present paper, the relationship between the residual oxygen and carbon contents in sintered Sendust and the additional amount of binders, as well as their influence on magnetic properties, were studied and compared with the magnetic properties of a cast material, and the additional amount of binders was also investigated to obtain green bodies with relatively high density, resulting in an improvement in the mechanical strength.

## 2. Experiments

Sendust powder used in the experiment was prepared by gas-atomized method. The chemical analysis and average particle size of the Sendust powder used in the experiment are given in Table I. Fig. 1 shows the experimental procedures used when the spray drying process was employed. After $n$-tetradecane and $n$-hexadecane belonging to a paraffin group compound were mixed at a weight ratio of 1/1 and kneaded, a small amount (i.e., 0.1 and 0.2 wt%) of the mixture was added to the alloy powder and mixed using a planetary mixer. After a mixture of polyvinyl alcohol (PVA saponification level: 86.5–89.0%; polymerization level: $>1500$) as an aqueous polymer and glycerin as a plasticizer was added to three types of alloy powders to which 0, 0.1 and 0.2 wt% paraffin compounds were added, distilled water was added to a mixture to form a slurry with a solid content of 70 wt% and stirred in a stirring tank. Then the additional amount of PVA was 0.1, 0.3 and 0.5 wt% to the alloy powder and the additional amount of glycerin was 30% of each additional amount of PVA. The slurry was granulated using a rotary disc type spray dryer apparatus with nitrogen as the inert gas, with the inlet and outlet temperatures of the heated gas flow set to 358 and 328 K, respectively. The oxygen concentration in the chamber was then maintained below 1%. The diameter of the rotary disc was 60 mm and rotational speed was 15000 rpm.

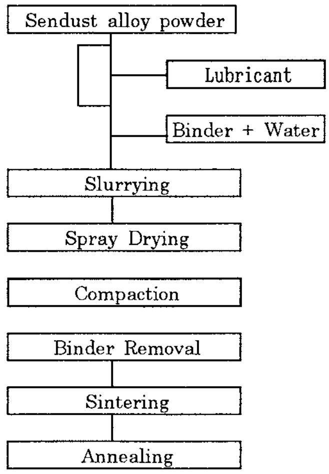


*Figure 1* Experimental procedure of spray drying.

The powder characteristics after spray drying were measured using a powder tester. The average destruction strength of granulated powders was measured using a compression testing machine (Hosokawa Micron Manufacturing Corp., Agrobot) and was obtained from the analysis of stress-compression behavior of the powder. Here the destruction strength was defined as the intersection of two stress-compression lines obtained from the initial compression process and the latter compression densification process [13]. The mechanical strength of green body which was prepared by filling 10 g of powder into a die cavity of $15 \times 20$ mm$^2$ and compacting it at a pressure of 98 MPa, was measured using a rattler test of a diameter of 80 mm in which the rate of weight-reduction of green body was measured after 100 rotations at a rotational speed of 68 rpm. To remove the binder from the green body, it was heated from room temperature to 673 K at a rate of 100 K/h and held at this temperature for 0.5 h in a hydrogen atmosphere. Subsequently, the compacted body was heated from 673 to 1523 K at a rate of 200 K/h and its sintering was carried out at this temperature for 3 h in a hydrogen atmosphere. The magnetic characteristics of the sintered bodies was measured by a BH tracer using a ring-shaped sintered body of $\phi 22.5 \times \phi 17 \times 10$ mm$^3$.

TABLE I Results of chemical analysis and average particle size of Sendust powder

| | Composition (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample no. | Fe | Al | Si | C | S | O | N | Average particle size ($\mu$m) |
| 1 | Bal | 5.7 | 9.9 | 0.03 | 0.001 | 0.05 | 0.002 | 6.7 |

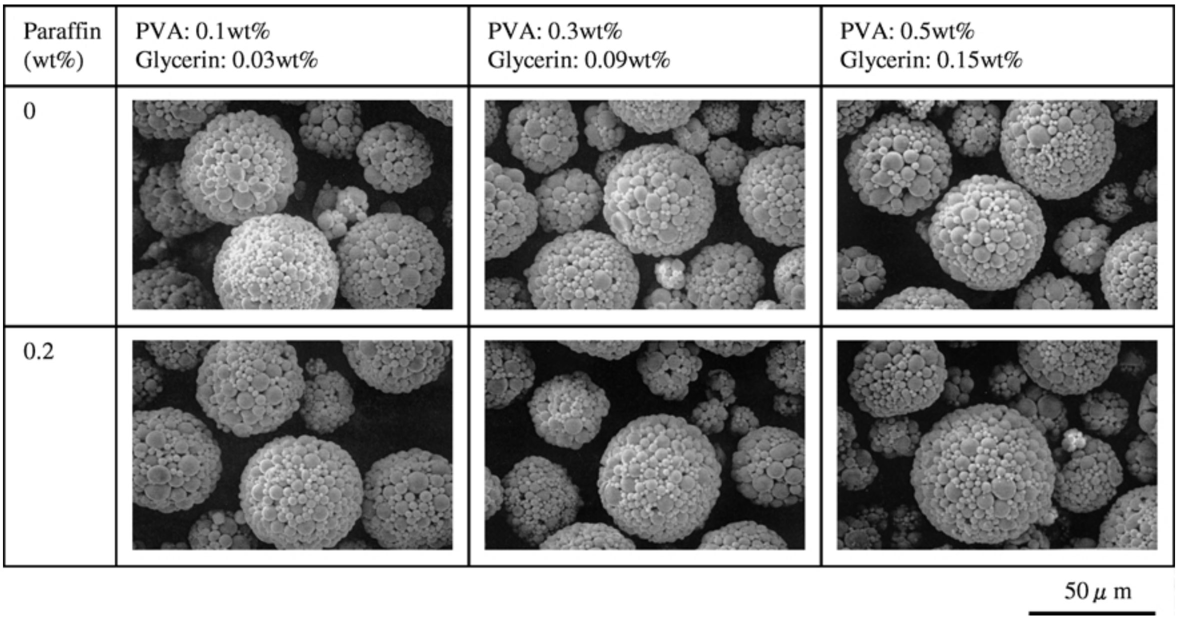


*Figure 2* Scanning electron micrographs of spray-dried powders.

## 3. Results and discussion

### 3.1. Powder characterization of spray-dried products

Fig. 2 shows scanning electron micrographs of spray-dried powders. Three types of powder were used in this study, two of which are powders to which 0.1 and 0.2 wt% paraffin compounds were added before spray drying and the other is a raw powder to which nothing was added. Fig. 2 shows micrographs of spray-dried powders with PVA binder amounts of 0.1, 0.3 and 0.5 wt% and a paraffin amount of 0.2 wt%. As shown in the figure, even when the additional amount of PVA is as small as 0.1 wt%, ungranulated powders are seldom seen and the granulated powder was made almost spherical shape. The granulated Sendust powder exhibited the good granulation characteristics, compared with Nd-Fe-B rare earth magnetic alloy powder [11, 12] and permendur powders [14] consisting of Fe and Co powders spray dried with the same additional amount of PVA. It may be interpreted as follows. The geometrical shape of the primary particles of Nd-Fe-B alloy powders or Fe and Co powders was indefinite, while the shape of the present powders prepared by gas-atomized method was almost spherical, leading to the decrease in the relative surface area of the powders. This is because Sendust powders were granulated effectively with the small additional amount of PVA.

The powder characteristics and residual carbon, oxygen and water contents of Sendust powders after spray drying are given in Table II. The average particle diameter of the granulated powders was 30–40 $\mu$m and remained almost constant regardless of the additional amount of PVA binder and the presence or absence of paraffin. The powder characteristics, however, deteriorated slightly with increasing the additional amounts of both PVA and paraffin. It may be related to the relatively small surface area resulting from the spherical shape of the primary particles or the affinity between the binder and the surface of Sendust alloy particles, although the reason is not clear. The carbon and oxygen contents contained in the granulated powders increase with increasing the additional amount of binder and agreed roughly with the calculated values from carbon and oxygen contents contained in both the raw powder and various organic materials added. In addition, the water content contained in the present granulated powders is

TABLE II Powder characteristics and residual carbon and oxygen contents of Sendust powders after spray drying

| Paraffin content (wt%) | Polymer content (wt%) | Mean size ($\mu$m) | Apparent density ($10^3$ kg/m$^3$) | Tap density ($10^3$ kg/m$^3$) | Loose angle (deg) | Fall angle (deg) | Spatula angle (deg) | Flow-ability[a] (sec) | Residual content (ppm) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | C | O | $H_2O$ |
| 0 | 0.1 | 41 | 2.154 | 2.991 | 42.4 | 31.2 | 61.4 | 2.9 | 1020 | 1330 | <10 |
| | 0.3 | 43 | 2.082 | 2.955 | 47.0 | 35.2 | 59.3 | 4.8 | 1720 | 1810 | 120 |
| | 0.5 | 43 | 2.090 | 2.964 | 49.0 | 35.0 | 61.5 | 5.8 | 2710 | 2530 | 210 |
| 0.1 | 0.1 | 43 | 2.106 | 3.115 | 47.0 | 32.9 | 60.9 | 4.8 | 1000 | 1310 | <10 |
| | 0.3 | 43 | 2.077 | 2.985 | 46.6 | 32.9 | 58.9 | 5.7 | 1990 | 1970 | 90 |
| | 0.5 | 42 | 2.005 | 3.005 | 50.0 | 35.9 | 59.5 | 6.4 | 3050 | 2880 | 300 |
| 0.2 | 0.1 | 43 | 2.082 | 2.955 | 48.2 | 35.6 | 58.0 | 5.2 | 1030 | 1310 | 60 |
| | 0.3 | 46 | 1.997 | 2.934 | 49.7 | 35.3 | 62.3 | 6.0 | 2010 | 2020 | 90 |
| | 0.5 | 46 | 1.952 | 2.919 | 49.0 | 37.1 | 57.7 | 7.3 | 3170 | 2850 | 240 |
| Before spraying | | 6.7 | 2.170 | 3.033 | 47.8 | 42.0 | 79.1 | no flow | 300 | 500 | – |

[a]Time required for 30 g of powder to fall naturally through a funnel tube with an orifice of 8 mm.

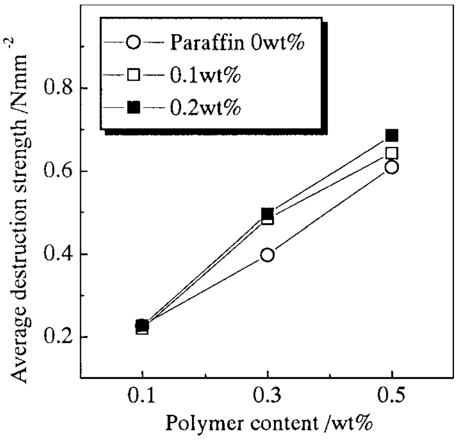


*Figure 3* Relationship between additional PVA amount in granulated powders and average destruction strength of powders.

very small compared with the case of powders spray dried by using the conventional aqueous binders and is not more than 20% of those contained in granulated Nd-Fe-B alloy powders [15]. Probably it may be also attributed to the relatively small surface area of the primary particles, which forms a rough frame dehydrated readily during spray drying.

Next, the average destruction strength of granulated powders was measured using a compression testing machine [13]. The relationship between the additional amount of PVA and the average destruction strength is shown in Fig. 3. In a word, the average destruction strength indicates the strength at which roughly one-half of the granulated powders are destroyed by the compression. The average destruction strength increases almost linearly with the increase of the additional amount of PVA, but it hardly depends on whether or not the paraffin compound was added to the alloy powders before spray drying, unlike the mechanical strength of green body as will be mentioned below. It means that the binding force between the primary particles depends on PVA binder alone.

## 3.2. Characteristics of green bodies consisting of granulated powders

The granulated powders so obtained were compacted at a pressure of 98 MPa. Fig. 4 shows the relationship between the additional amount of PVA binder and the density of the green bodies. When spray dried without paraffin, the density of the green bodies hardly depends on the additional amount of PVA and remained almost unchanged. The density of the green bodies consisting of Fe and Co powders with irregularly shaped particles, however, showed a tendency to decrease with the increase of the additional amount of binder [14]. The spherical shape of the present primary particles may be effective to obtain a high green density in the densification process after breaking out the secondary particles by the initial compression, particularly in a small additional amount of PVA. When mixed with paraffin before spray drying, on the other hand, the density of the green bodies increases with increasing the additional amount of paraffin for any additional amount of PVA binder. Such an increase in the density of the green bodies is attributed to the presence of paraffin acting as an internal lubricant during pressing. Combining with the good powder characteristics of granulated powders, thus, the application of spray drying method to Sendust powders is found to be effective not only for stabilizing the quantity of powder fed into a die cavity from a powder feeder but also for enhancing the density of the green body, particularly when PVA and paraffin were used as a binder and a lubricant. It suggests that the present method may be applicable to the formation of complex-shaped or near-net-shaped products.

The mechanical strength of green bodies was measured by a rattler test as a rate of weight-reduction of green body after 100 rotations, where the green body was compacted to a rectangular parallelepiped shape ($10 \times 15 \times 20$ mm$^3$) at a pressure of 98 MPa. Fig. 5 shows the relationship between the additional amount of PVA binder and the rate of weight-reduction of the green body for granulated powders. As a result, it turned out that the mechanical strength of green body increases significantly with increasing a PVA content and extremely high strength was obtained at a PVA content of 0.5 wt%. The green bodies prepared by adding paraffin to the alloy powder before spray drying have a higher mechanical strength than those prepared without paraffin, so that they were found to have a solidity enough to

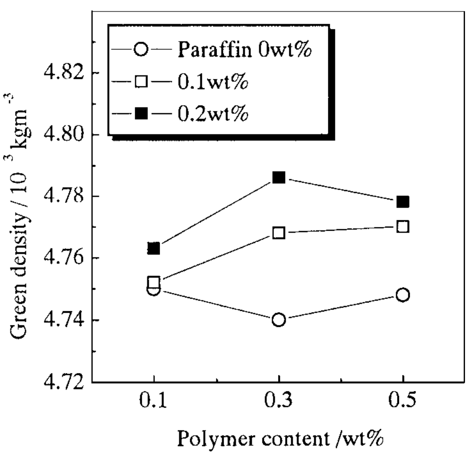


*Figure 4* Relationship between additional PVA amount in granulated powders and density of bodies compacted at a pressure of 98 MPa.

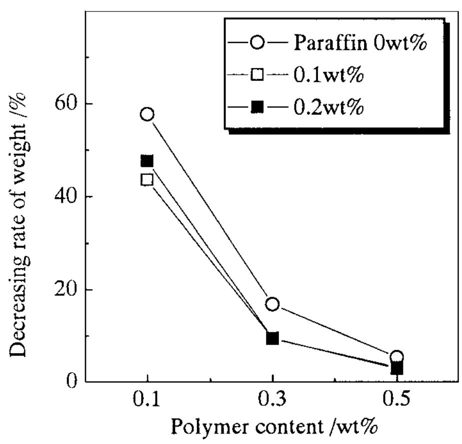


*Figure 5* Relationship between additional PVA amount in granulated powders and mechanical strength of compacted bodies, which was measured by a rattler test as a rate of weight-reduction of compacted body after 100 rotations.

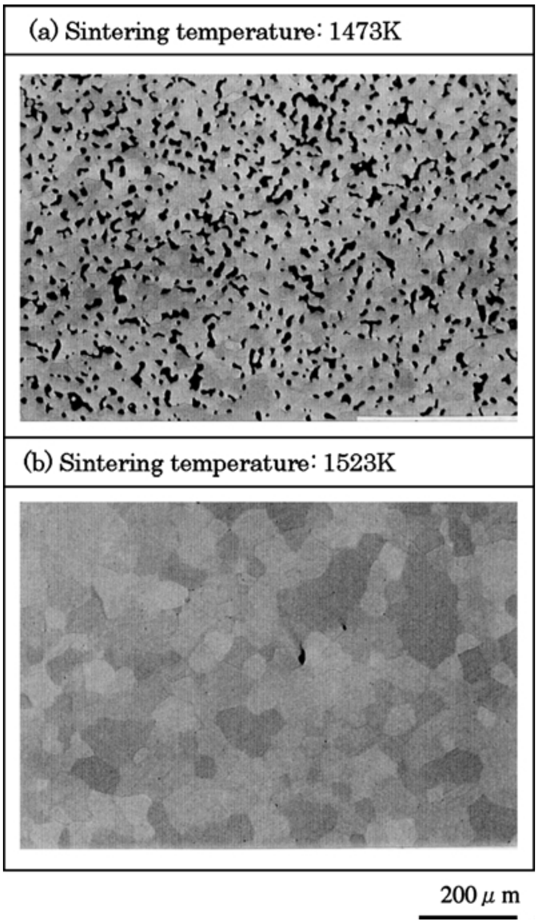


*Figure 6* Optical micrographs of Sendust sintered at 1473 and 1523 K in a hydrogen atmosphere, where the green body was compacted after spray drying by adding 0.3 wt% PVA and 0.09 wt% glycerin to Sendust powders mixed with 0.1 wt% paraffin.

handle. It may be indebted to the presence of paraffin acting as a lubricant to reduce the friction between the primary particles during compacting.

### 3.3. Density of sintered bodies and magnetic characteristics

The sintering conditions for green bodies were investigated to obtain a sintered body with relatively higher density. Fig. 6 shows optical micrographs of Sendust sintered at 1473 and 1523 K in a hydrogen atmosphere, which was spray dried by adding 0.3 wt% PVA and 0.09 wt% glycerin to Sendust powders mixed with 0.1 wt% paraffin. As shown in the figure, there are a large number of voids at a sintering temperature of 1473 K because of the imperfection of the crystal growth, while their voids almost disappeared at a sintering temperature of 1523 K. As a result, the Sendust sintered at 1523 K is found to have an extremely high relative density and a grain size of approximately 100 $\mu$m. Chemically analyzing this sintered Sendust, the residual carbon and oxygen contents were 100 and 1700 ppm, respectively. Comparing it with the carbon and oxygen contents before sintering, it is found that the carbon and oxygen contents contained in the granulated powders have been removed by 95% and 10%, respectively, throughout the present sintering process. The magnetic characteristics and the relative density of Sendust sintered at 1523 K are given in Table III. The relative densities depend neither on the additional amount of PVA binder nor on the amount of paraffin added before spray drying and reached a relative value of approximately 99% for all cases. It may be attributed to a drastic decrease in the carbon content throughout the sintering process. From this reason their magnetic characteristics may be also independent of the additional amount of organic binder. Owing to such an extremely high relative density and such an extremely reduced carbon content, the lowest coercive force ($H_c$) in the present samples became almost the same value as that reported for a cast material of Sendust [17], but the present permeabilities ($\mu$) were lower than that of a cast material. The reason why the present sintered bodies have lower permeabilities may be attributed to either the small grain size of a sintered body or a large content of the oxygen contained in it. From the fact that the magnetic characteristics were indeed independent of the additional amount of organic binder, however, it is clear that such low permeabilities are regardless of the oxygen content contained in the sintered bodies. In fact a cast material generally has a much larger average grain size than the present sintered body. To make the permeabilities higher, therefore, it is necessary to grow the grain size large. As the grain size can be grown large by sintering at higher temperatures, however, the permeability would be improved readily.

TABLE III Magnetic properties of Sendust alloys prepared by spray drying in comparison with cast material

| Paraffin content (wt%) | Polymer content (wt%) | Relative density (%) | Permeability | | Coercivity $H_c$ (A/m) | Remanence Br (T) | Induction[a] $B_{80}$ (T) |
|---|---|---|---|---|---|---|---|
| | | | $\mu$i | $\mu$m | | | |
| 0 | 0.1 | 98.9 | 14000 | 47000 | 7.00 | 0.58 | 1.04 |
| | 0.3 | 99.0 | 18000 | 46800 | 5.65 | 0.47 | 1.02 |
| | 0.5 | 99.1 | 14800 | 47600 | 5.97 | 0.50 | 0.99 |
| 0.1 | 0.1 | 99.1 | 21200 | 46800 | 4.30 | 0.36 | 1.02 |
| | 0.3 | 99.0 | 17200 | 53600 | 5.89 | 0.56 | 1.06 |
| | 0.5 | 99.4 | 16000 | 52800 | 5.49 | 0.50 | 1.05 |
| 0.2 | 0.1 | 99.0 | 16000 | 49600 | 5.89 | 0.54 | 1.06 |
| | 0.3 | 98.3 | 20000 | 37000 | 3.98 | 0.57 | 1.03 |
| | 0.5 | 99.1 | 16000 | 45400 | 5.81 | 0.44 | 1.00 |
| Cast material[16] | | 100 | 30000 | 120000 | 4.00 | – | 1.00 |

[a]Induction at H = 80 A/m.

As well known, Fe-Al-Si alloys exhibit excellent magnetic characteristics within a very narrow composition range [1, 5]. The reason why Sendust alloy produces high magnetic characteristics is explained in the same way as forpermalloy. Sendust exhibits extremely high magnetic characteristics when both the magnetic distortion and magnetic anisotropy coefficient are essentially zero [18–20]. As a matter of course, the strict control of the composition is required to obtain Sendust sintered products with so high magnetic characteristics using granulated powders by spray drying method. If sintered Sendust alloy with an optimal composition was prepared by spray drying method and has an average grain size much larger than 100 $\mu$m, therefore, it would be expected to exhibit the almost same magnetic characteristics as the cast material.

## 4. Summary

The present experimental results can be summarized as follows.

(1) When the additional amount of PVA binder was in the range of 0.3–0.5 wt%, the powders granulated by spray drying method were almost spherical. The density and mechanical strength of green bodies compacted using these granulated powders increased significantly as compared with those of green bodies compacted using the granulated powders with a smaller amount of PVA binder. The addition of paraffin to alloy powders was found to be very effective to enhance both the density and mechanical strength of the compacted body, owing to the internal lubricant effect.

(2) The sintered Sendust with a relative density of approximately 99% was obtained by sintering the compacted body at 1523 K for 3 h in a hydrogen atmosphere. Such a high densification is indispensable to realize high performance of soft magnetic materials. Of course the present value is much higher than the relative densities (90–96%) of ordinary sintered bodies obtained by the conventional powder metallurgy methods.

(3) The lowest coercive force of sintered Sendust so obtained was almost the same as that reported for a cast material of Sendust, but the present permeabilities ($\mu$) are a little small compared with that of a cast material. As such low permeabilities may be attributed to the small grain size, it would be improved readily by growing the grain size large, i.e., by sintering at higher temperatures.


## Acknowledgements

The authors wish to thank T. Saigo and M. Noumi for valuable technical support.


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*Received 8 July*
*and accepted 31 October 2002*