JOURNAL OF MATERIALS SCIENCE 27 (1992) 5445–5448

Thermal oxidative deterioration and its prevention in Nd–Fe–B series plastic magnets

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Thermal oxidative behaviour of Nd–Fe–B series magnetic powders and effects of surface treatment of the powders with polyacrylonitrile (PAN) and coupling agents on thermal oxidation were examined by thermal analysis (thermogravimetric and differential thermal). In addition, plastic magnets were prepared with magnetic powders (untreated, pre-oxidized and PAN treated) and nylon 12 and their magnetic properties were compared. Oxidation of the magnetic powders easily occurred and weight gain started at ~ 100 °C and suddenly increased at ~ 280 °C. Thermal oxidation of the magnetic powders greatly deteriorated the magnetic properties of the plastic magnets. The surface treatment of the powders was found to be effective for the prevention of the oxidation, especially when treated with PAN, and provided thermally stable plastic magnets.

1. Introduction

Plastic magnets composed of polymer matrices and magnetic powders have been widely used in various fields, especially in electronic and communication instruments. Among the rare earth–Fe series plastic magnets, which are greatly superior to the ferrite series, special attention has recently been paid to the Nd–Fe–B series because of the shortage of Sm and Co resources [1–6]. However, the Nd series magnetic powders oxidize easily, losing their magnetic properties [7–9].

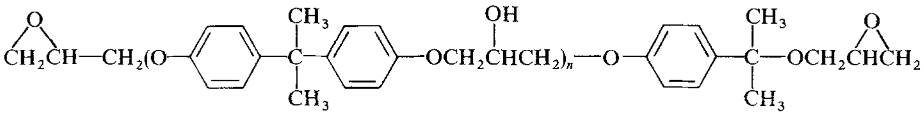
Thermal oxidative behaviour of the Nd–Fe–B series magnetic powders and the effect of surface treatment of the powders on oxidation are examined.

2. Experimental procedure

2.1. Materials

The magnetic powders, the main component of which was $Nd_2Fe_{14}B$, were supplied by the Dai-Chi Kasei Co. Ltd, Japan and had an average particle size of approximately 6.3 μm. They were prepared by immersing masses of the magnets ($Nd_2Fe_{14}B$)(1 kg) into n-hexane (1.2 kg) and then by crushing them in a crushing mill rotating at 200 r.p.m. under Ar gas flow (3.5 ml min^{-1}) for 30 min. The magnetic powders were kept in cyclohexane under Ar gas and used by taking out the necessary amount at any time.

Polyacrylonitrile and coupling agents used for the surface treatment of the magnetic powders were as follows: Polyacrylonitrile (PAN) (Toray Co. Ltd), number average molecular weight: 3.1×10^5; *N*-(β-aminoethyl)-γ-aminopropylmethoxysilane (TSL 8340) (Toshiba Silicone Co. Ltd): $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$; Isopropyl-tri(*N*-aminoethyl-aminoethyl)titanate (KR-44) (Azinomoto Co. Ltd): $\mathrm{CH_3\underset{\displaystyle CH_3}{C}HOTi(OC_2H_4NHC_2H_4NH_2)_3}$; Epikote 1255-HX-30 (Yuka-Shell Epoxy Co. Ltd):



The matrix polymer used was nylon 12 for plastic magnets (Ube Kosan Co. Ltd, UBE-7115U).

2.2. Surface treatment

2.2.1. With PAN

The magnetic powders (25 g) were immersed in a solution of PAN (2.5 g) in 60 g N,N-dimethylformamide (DMF) in a test tube (length, 200 mm; ϕ, 30 mm) and DMF was removed under reduced pressure by vibrating the test tube.

2.2.2. With coupling agents

The magnetic powders (10 g) were immersed in isopropyl alcohol solution of each coupling agent (1 g/99 g isopropyl alcohol) and agitated thoroughly. Then the magnetic powders were filtered out and Epikote 1255-HX-30 was successively added and mixed, followed by drying under reduced pressure for more than 48 h.

2.3. Preparation of plastic magnets

In a mixing vessel previously warmed at 180 °C, nylon 12 (5.2 g) was melted and then magnetic powders (5 g) were added and mixed at 180 °C for 10 min. The pellets obtained were pressed at 160 °C for 5 min and cylindrical samples (ϕ, 10.8 mm; height, 10 mm) were prepared for the measurement of magnetic properties. The magnetic powder content of the plastic magnets was 12 vol % (49 wt %).

2.4. Measurement

Thermal oxidative behaviour of the magnetic powders was recorded on a thermal analyser (Rigaku Denki DTA-TG 8110). Measurement conditions were as follows: sample, 10 mg; rate of temperature increase, 5 °C min^{-1}; air flow, 80 ml min^{-1}; alternatively, isothermal temperatures of approximately 234 ~ 276 °C were used. In addition, the magnetic powders (100 mg) were exposed to ambient atmosphere at 200 °C for 10 h in an oven and weight gain was measured.

Magnetic properties were measured by a direct current magnetic flux meter (Riken Electronic Co. Ltd, BHH-3) recording the demagnetization curve (4πI–H curves) at room temperature from which coercivity, residual magnetization and saturation magnetization were determined. For the measurement the external magnetic field was fixed at 15 kÖe

3. Results and discussion

3.1. Thermal oxidative behaviour of magnetic powders

The distribution curve of the magnetic powders shown in Fig. 1 indicates that in > 90% of the powders the grain size is < 10 μm.

Thermogravimetric (TG) and differential thermal analysis (DTA) curves of the untreated magnetic powders are shown in Fig. 2. The TG curve indicates that weight gain starts at ~ 100 °C and suddenly increases at ~ 280 °C. The DTA curve also shows the occurrence of an exothermic reaction at the corresponding temperatures. The results apparently suggest that thermal oxidation occurs easily in relatively low temperature regions.

Successive weight gain of the magnetic powders was measured at various isothermal temperatures (see Fig. 3). As would be expected, the higher the temperature, the greater the weight gain.

Reciprocal of the time required for 1% weight gain was plotted against the reciprocal absolute temperature (Fig. 4). Here, 1% weight gain corresponds to 0.68 mol oxygen atom bonded to 1 mol magnetic powders. A bending point can be observed at ca. 250 °C; activation energy determined in the region lower than 250 °C was 3.5 kcal mol^{-1} and in the region higher than 250 °C was 6.5 kcal mol^{-1}. The results suggest different oxidation mechanisms of the magnetic powders, namely, that in the lower temperature region oxidation occurs on the surface of the magnetic powders, while in the higher temperature region oxidation proceeds on inner parts of the powders.

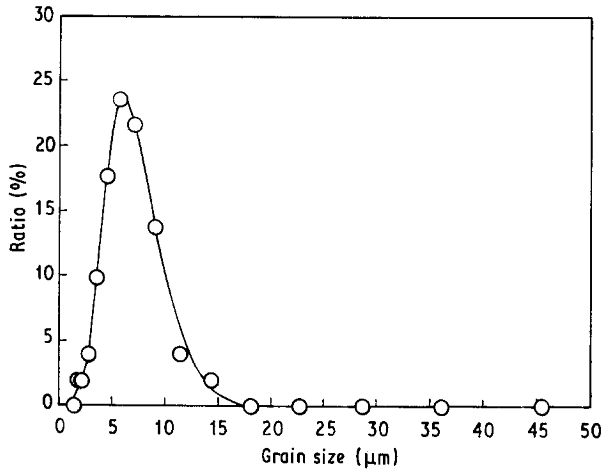


Figure 1 Distribution of grain size in magnetic powders.

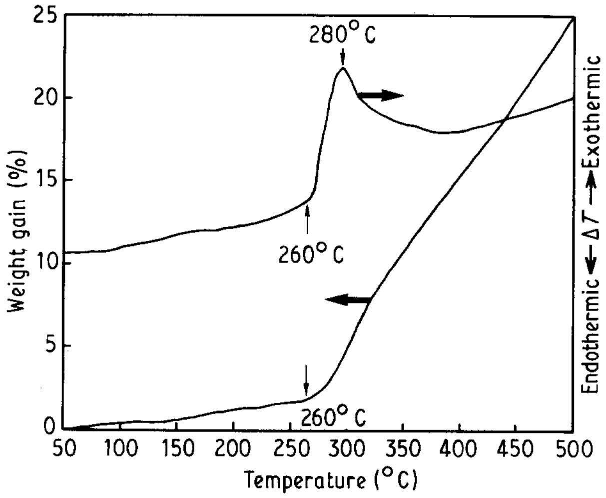


Figure 2 TG (lower) and DTA (upper) curves of untreated magnetic powder.

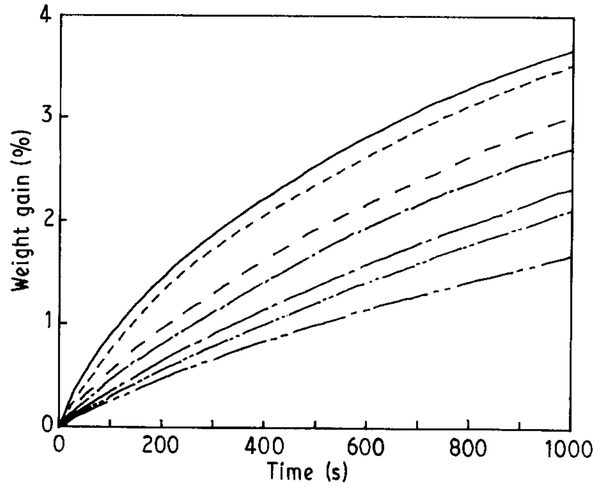


Figure 3 Weight gain of magnetic powders at various isothermal temperatures. Weight gain of 1% = 0.68 mol O/1 mol $Nd_2Fe_{14}B$. Isothermal temperatures: –·–·–, 234 °C; –··–, 245 °C; –·–, 253 °C; –·–, 260 °C; ———, 265 °C; ----, 273 °C; ——, 276 °C.

3.2. Effect of surface treatment of magnetic powders

It can easily be assumed that surface protection of the magnetic powders prevents oxidation. As an experi-

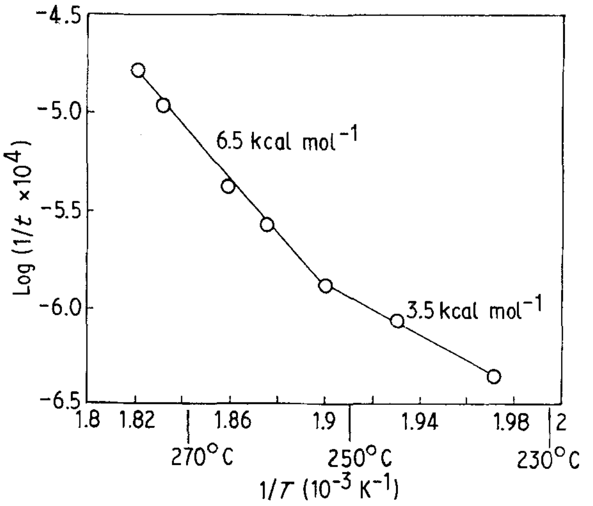


Figure 4 Arrhenius plot for untreated magnetic powders; reciprocal of time required for 1% weight gain versus reciprocal of absolute temperature.

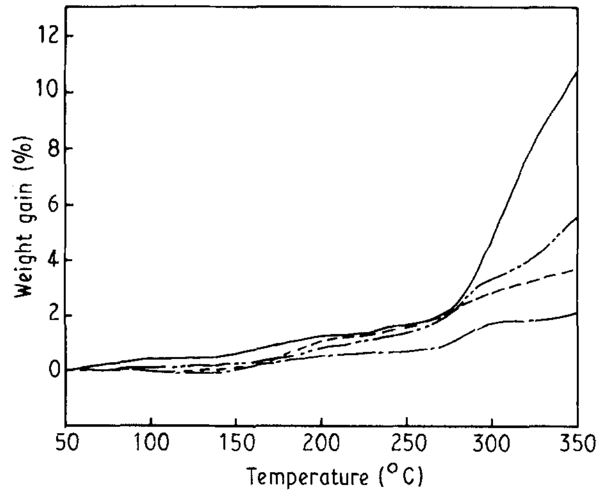


Figure 5 Effect of surface treatment on weight gain. Samples were treated with: ‒ ‒ ‒, PAN; – – –, Si-epoxy; – · – ·, Ti-epoxy; ———, untreated sample.

mental approach, surface coating with polymeric materials having low gas permeability and surface treatment with coupling agents could be considered. PAN was chosen since it has extremely low gas permeability (O_2 permeability coefficient at 25 °C: low density polyethylene, 216; high density polyethylene, 30.2; PAN, 0.015 $cm^3\,cm\,s^{-1}\,cm^2$ PPa) [10]. As coupling agents, conventional silane and titanate series were applied.

TG curves of the magnetic powders treated with PAN and coupling agents are shown in Fig. 5. The results obtained apparently demonstrate that surface treatment is effective for the prevention of oxidation of the magnetic powders, especially treatment with PAN.

3.3. Magnetic properties and thermal stability

Since oxidation of the Nd–Fe–B series magnetic powders causes deterioration of the magnetic properties, surface treatment of the magnetic powders could be expected to provide thermally stable plastic magnets. Therefore, three kinds of plastic magnets were prepared with the magnetic powders (untreated, thermally treated at 200 °C for 1 h and treated with PAN) and nylon 12.

Demagnetization curves of the plastic magnets prepared were measured and coercivity (Öe), residual magnetization (G) and saturation magnetization (G) were determined (see Fig. 6 and Table I). It is apparent that magnetic properties of the plastic magnets prepared with previously oxidized magnetic powders decreased remarkably. Coercivity and residual magnetization of the plastic magnets prepared with untreated powders are 2400 Öe and 230 G, respectively, and these values drop to 180 Öe and 52 G when preoxidized magnetic powders are used. On the other hand, plastic magnets prepared with PAN-treated magnetic powders provides much better magnetic properties which indicates that oxidation of the magnetic powders during blending and moulding at high temperatures (160–180 °C) could be prevented by PAN treatment.

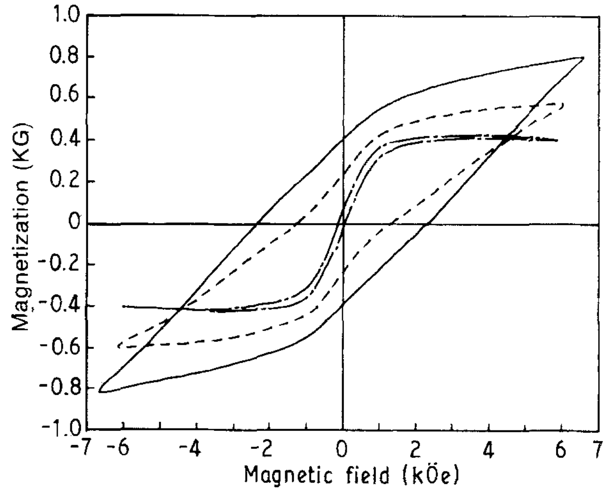


Figure 6 Demagnetization curves of plastic magnets oxidized in air for 10 h at 200 °C. ———, PAN-treated; – – –, untreated; – · –, oxidized.

TABLE I Magnetic properties of plastic magnets

Treatment	Coercivity (kÖe)	Residual Magnetization (G)	Saturation Magnetization (G)
Untreated	2400	230	572
Thermal	180	52	400
PAN	4710	394	800

Now that surface treatment has proved to be an effective method to protect the Nd–Fe–B series magnetic powders from oxidation and to provide thermally stable plastic magnets, further investigations are being made.

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Received 19 June
and accepted 25 November 1991