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## Sintering Analysis of NdFeB Materials

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**Abstract:** *Nd-Fe-B magnets present high magnetocrystalline anisotropy that leads to outstanding magnetic properties. This anisotropy is also present during the sintering and plays a role into the mechanisms driving the densification. Sintering was studied along and perpendicular to the easy magnetization axis for an optimized thermal cycle leading to high magnetic properties and full densification. The perpendicular strain rate is significantly lower than the parallel strain rate, especially at low temperature. The sintering kinetics at high temperature would be mainly controlled by solid state diffusion with a high apparent activation energy (450-474 kJ/mol).*

**Keywords:** *Nd-Fe-B; sintered magnets; sintering anisotropy; liquid-phase sintering; activation energy*

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### 1. Introduction

Nd-Fe-B permanent magnets are known as high energy product  $(BH)_{\max}$  materials. Coercivity decrease with temperature is the weakness of this material. Indeed, theoretical anisotropy field value of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  (73 kOe [1]) is far from coercivity values currently obtained. Moreover studies concerning coercivity improvements by means of heavy rare earth addition usually leads to a drastic remanence loss and price increase. Another way to improve the coercivity without significant remanence decrease is to control the microstructure.

High-coercivity Nd-Fe-B magnets are currently obtained through a powder metallurgy route. Nd-Fe-B magnetic materials have a complex microstructure mainly constituted of two phases:  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and a Nd-rich phase which plays a key role on coercivity increase. Liquid phase sintering process allows to optimize the magnetic properties of the material by controlling the phase repartition and microstructure during the thermal cycle.

Previous investigations have been carried out by Popov et al. [2] and Davies et al. [3] on the sintering of Nd-Fe-B material. The first one deals with the optimization of powder manufacturing as well as processing parameters in order to have the best final magnetic properties. The second one gives a complete analysis of the sintering shrinkage along the easy magnetization axis.

In this study, sintering of Nd-Fe-B powder has been evaluated based on dilatometric experiments along the easy magnetization axis as well as along the perpendicular direction (called parallel direction and

perpendicular direction, respectively). DSC measurements have been performed to identify phase transformations during sintering. Samples have been quenched to observe the microstructure at different temperatures. This allows us to establish a better understanding of the sintering path.

### 2. Experimental

Strip-cast ribbons of nominal composition of  $\text{Dy}_{0.2}(\text{Nd},\text{Pr})_{13.6}\text{Fe}_{78.6}\text{B}_6(\text{Co},\text{Cu},\text{Al})_{1.6}$  were used. Ribbons were hydrogenated and desorbed (HD), then turned into powder with a jet mill under nitrogen gaz. Powder is characterized by  $D50 = 5.0 \mu\text{m}$ ,  $D10 = 1.3 \mu\text{m}$  and  $D90 = 10.1 \mu\text{m}$  and  $\text{SBET} = 0.6 \text{ m}^2/\text{g}$ . Powder was then filled in a cylindrical mold and oriented parallel to the axial direction of the cylinder using a pulsed magnetic field of 6 T. Finally samples were shaped at a pressure of 150 MPa into a cold isostatic press to obtain a green density close to  $4 \text{ g/cm}^3$ .

A thermal treatment consisting in a  $2 \text{ }^\circ\text{C}/\text{min}$  temperature ramp until a 4 h plateau at  $750 \text{ }^\circ\text{C}$  (to remove hydrogen induced by powder's synthesis) followed by  $2 \text{ }^\circ\text{C}/\text{min}$  ramp until  $1050 \text{ }^\circ\text{C}$  for a 4 h plateau was used.

Dilatometric experiments were done in a Setaram vertical differential high temperature dilatometer with a vacuum below  $6 \cdot 10^{-5} \text{ mbar}$ .

To identify phase transformations happening during sintering, DSC measurements were performed on HD ribbons with a Netzsch Pegasus. This material has the same composition as the powder used during dilatometric studies but has a lower specific surface and is less sensitive to oxidation. Samples of 50 mg

underwent a thermal cycle similar to dilatometric experiments until 950 °C (maximum temperature of the device) using an alumina crucible with He as heat transfer gaz.

Interrupted heat treatments were performed in a dedicated high vacuum. Thermal ramp up were followed by a quenching at a speed of 60 °C/min at several temperatures. Microstructures were observed in SEM and magnetic properties were determined with a hysteresigraph.

**3. Results & Discussion**

Densification of 99.5% and high magnetic properties were obtained at 1050 °C for 4 h ( $B_r = 1.38$  T,  $H_{cj} = 11.3$  kOe,  $(BH)_{max} = 46.7$  MGOe).

*3.1. Sintering anisotropy*

Fig. 1 represents the sintering parallel and perpendicular to easy magnetization axis. At the end of the sintering, at room temperature, the ratio between the two strains is about 2. Popov et al. [2] have found the value of 1.5. The difference can be explained by a different powder processing.

On Fig. 2, at low temperature (before dehydration plateau at 750 °C) sintering starts at 570 °C for the parallel direction and 20 °C later for the perpendicular direction. The two strain rate curves have the same shape as they reach a plateau but parallel strain rate increases again at 650 °C whereas perpendicular strain rate remains constant for a temperature increase of almost 100 °C. The large endothermic DSC signal which can be attributed to the dehydration of NdH<sub>2</sub> phase [4,5] occurs in the same temperature range. This temperature range also covers possible liquid formation through NdCu/Nd or Nd<sub>2</sub>Fe<sub>14</sub>B/Nd eutectics. Thus the onset of shrinkage can be

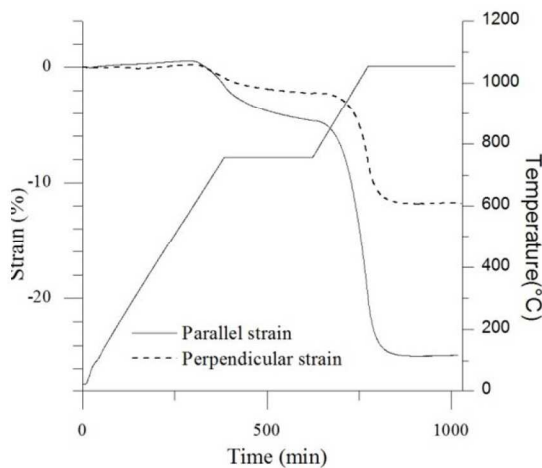


Fig. 1. Parallel versus perpendicular strains.

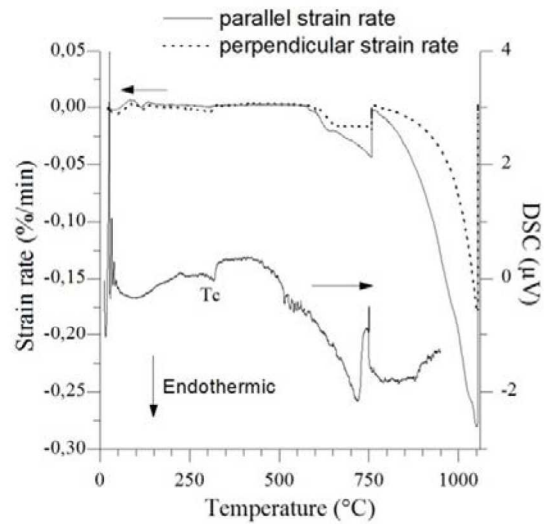


Fig. 2. Perpendicular, parallel strain rates and DSC analysis of the hydrated ribbons versus temperature.

attributed to liquid formation, to dehydration of NdH<sub>2</sub> or both.

The strain rate curves differences in the two directions reveal two different behaviors that could be attributed to an anisotropy of interface energy or to a heterogeneous distribution of Nd-rich phase in the green compact. Figs. 4(a) and 4(b) compare the powder and the compact quenched at 670 °C during sintering. Before sintering, Nd-rich phase (white on the picture) is spread on grain surfaces. After quenching at 670 °C, Nd-rich phase is drop-shaped on grain surfaces and forms localized necks (black arrows) between grains indicating a fusion before quenching temperature.

After the dehydration plateau, during the temperature increase until the final plateau at 1050 °C, the two strain rate curves have the same kind of shape. The

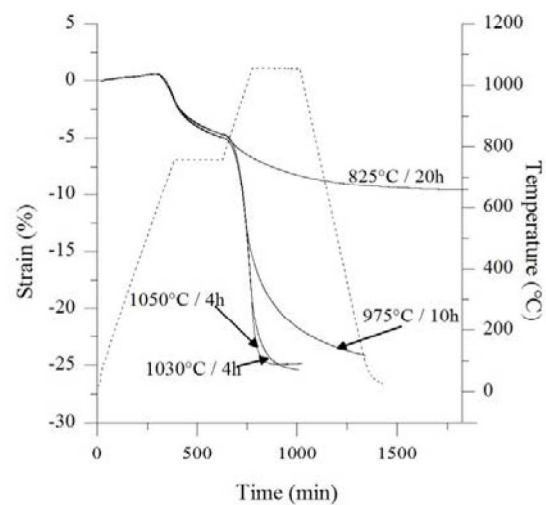


Fig. 3. Isothermal treatments strain parallel to easy magnetization axis (the dotted line represents the thermal cycle at 1050 °C).

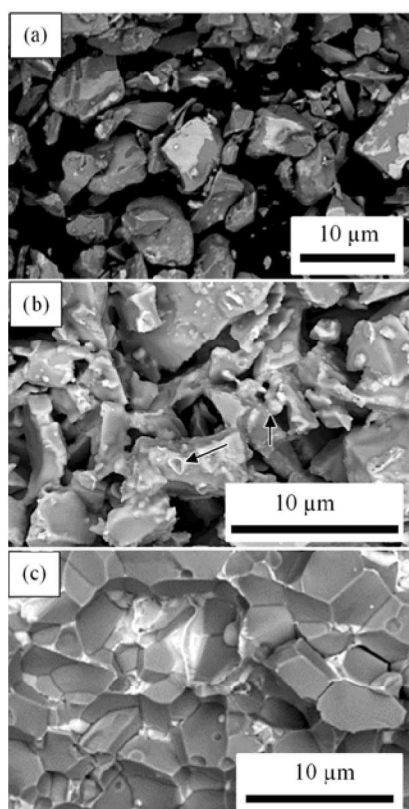


Fig. 4. Backscattered SEM image of: (a) the powder, (b) the sample quenched at 670°C, (c) the sample quenched at 1054°C after a 1 h plateau.

strain rate is smaller in the perpendicular direction but it tends to increase relative to the parallel direction as temperature increases. The strain rate curve shapes could not be compared to those obtained by Popov et al. [2] and Davies et al. [3] as a dehydration plateau was used in our study.

### 3.2. Sintering kinetics at higher temperatures

Isothermal dilatometric experiments have been made in order to find the activation energy of sintering after the dehydration plateau. This study was done in the parallel direction (Fig. 3).

In order to calculate the activation energy, the following equation was used:

$$\dot{\epsilon} = A(\epsilon) \times \exp\left(-\frac{Q}{RT}\right)$$

where  $\dot{\epsilon}$  is the strain rate,  $\epsilon$  is the strain,  $Q$  is the apparent activation energy,  $R$  is the gas constant and  $T$  is the temperature.  $A(\epsilon)$  is a strain-dependent constant.

Fig. 5 shows the Arrhenius plots at fixed strains between -20.4% and -23.4%. The activation energy calculated for these strains is comprised between 450 kJ/mol and 474 kJ/mol which would indicate a control either by solid state diffusion or interfacial reaction rather than diffusion through the liquid. In Fig.4(c) the

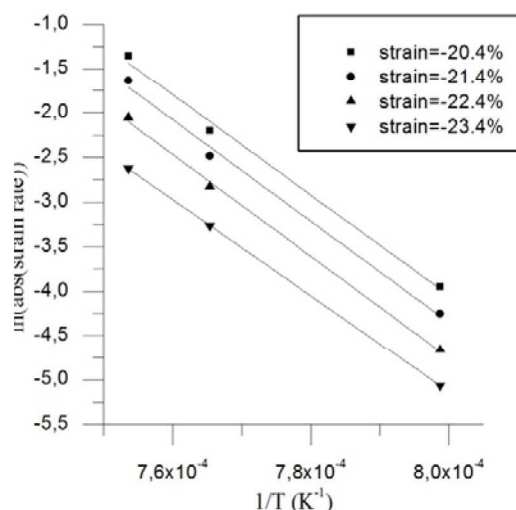


Fig. 5. Arrhenius plot of the strain rate for different fixed strains.

quenched sample exhibits flat contact surfaces between  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains which seem to be free from liquid, whereas former liquid phase is localized at triple grain boundaries and in former pores that have been filled. If quenched microstructures are representative of the microstructure at the sintering temperature, this observation is in agreement with a kinetic control by lattice or grain boundary diffusion in the solid state.

## 4. Conclusion

High magnetic property dense Nd-Fe-B magnets have been made using liquid phase sintering process. The onset of sintering is related with the dehydration of the powder and probably to the early formation of a eutectic liquid. Anisotropic shrinkage behavior parallel and perpendicular to the easy magnetization axis is observed at the beginning of the sintering and tends to be reduced as sintering proceeds. Sintering kinetics at high temperatures would be controlled by diffusion in the solid state from activation energy measurements and microstructural observations. Still, more work is needed to precise the exact sintering mechanism and to explain the anisotropic shrinkage behavior.

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