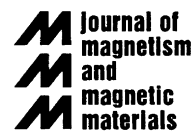




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A comparative study of the sintering behaviour of NdFeB and PrFeB for permanent magnet applications

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Abstract

Liquid phase sintering plays an important role in the production of rare-earth magnets. Dilatometry has shown that $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$, sintered in low vacuum (10^{-2} bar) has a greater densification rate compared with that of $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$. This has been confirmed using SEM analysis and density measurements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sintered magnets; Rare earth; Ferromagnetic; Crossover

1. Introduction

The ideal RE-Fe-B-type magnet (RE=Nd or Pr) would be fully dense with a mean grain size of around $5\mu\text{m}$ [1]. It would have a maximum proportion of magnetic phase, $\text{RE}_2\text{Fe}_{14}\text{B}$, aligned in the *c*-axis direction and each grain would be isolated by a thin layer of a non-ferromagnetic RE-rich phase giving a high remanence, high coercivity and large energy product. Previous work in this laboratory [2,3] has focused on the sintering behaviour of NdFeB whereas, the current study also investigates the sintering behaviour of PrFeB using contact dilatometry to identify any differences in the principal densification mechanisms. A full understanding of these mechanisms is vital if processing conditions are to be optimised to achieve maximum magnetic properties.

The primary driving force for sintering is the reduction in the surface energy of particles. As grains coalesce this driving force decreases until final density is attained. In the sintering of NdFeB and PrFeB-type magnets, liquid phases are formed at 655°C and 690°C , respectively [4,5], which aid sintering and increase the rate of densification. Liquid phase sintering (LPS) can be described as a set of sequential steps during heating. A densification burst occurs almost immediately after the liquid is formed due to the capillary forces exerted by

the liquid on the solid particles. This is the first stage of LPS and is known as “Rearrangement”. With the further increase in the temperature, rearrangement slows and solubility and diffusion dominate. This is the beginning of stage two which is known as “Solution Re-precipitation”. The dissolution of smaller particles in the liquid occurs and the material is precipitated onto larger grains, predominantly around neck regions between particles. The third and final stage of LPS is known as “Microstructural Coarsening” or “Solid Phase Sintering”. It corresponds to the period where grain growth continues and slow densification is controlled by solid-state diffusion due to the formation of a solid rigid skeleton.

In LPS, good wetting of particles by the liquid phase is necessary for a high rate of densification [6]. Rare-earth (RE) compounds oxidise readily and the resulting surface oxide layer can drastically reduce the wettability, thus inhibiting densification. Achieving maximum density is vital for good magnetic properties [7], hence it is clear that careful control of oxygen levels during powder processing and sintering is a key factor in producing high-energy products.

2. Experimental procedure

The powder production method employed in the present work has been described elsewhere [2,3].

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Samples of $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ and $\text{Pr}_{16}\text{Fe}_{76}\text{B}_8$ (HD) powder were aligned by pulsing in a magnetic field of 4.5 T, pressed isostatically at a pressure of 1200 kg m^{-3} and then sintered in a temperature range (800–1100°C for 2 h). Prior to sintering the system was evacuated to 10^{-2} bar using a rotary pump. The densities of all the magnets were measured using Archimedes' principle prior to microstructural examination. Samples were fractured along the *c*-axis of the magnet and examined using a Joel 6300 SEM.

3. Results and discussion

A comparison of the dilatometer traces (Fig. 1) reveals similar curves for the two compositions with slight but significant differences. The first noticeable difference is in the small peaks that correspond to the

hydrogen desorption process. This difference has been attributed to the different hydrogen desorption kinetics of Pr and Nd [8–10].

At 100 min (640°C), densification begins as the liquid phases begin to form. The curve of the Pr-based material has a steeper initial gradient compared to that of the Nd-based curve and the curves cross at 118 min (830°C), the temperature corresponding to the first major peak. In these early stages, densification is mainly due to primary rearrangement, with the Nd densification rate initially lower than that of Pr but subsequently increasing. The main difference between the two curves is that there is a clearly defined dip in the Nd but not in the Pr curve. Studying the Pr curve suggests that, during LPS, solution re-precipitation merges with the rearrangement stage, whereas, in the case of Nd, densification occurs as a defined two-stage process. It is known that in many cases, the LPS mechanisms do overlap [6], however, in

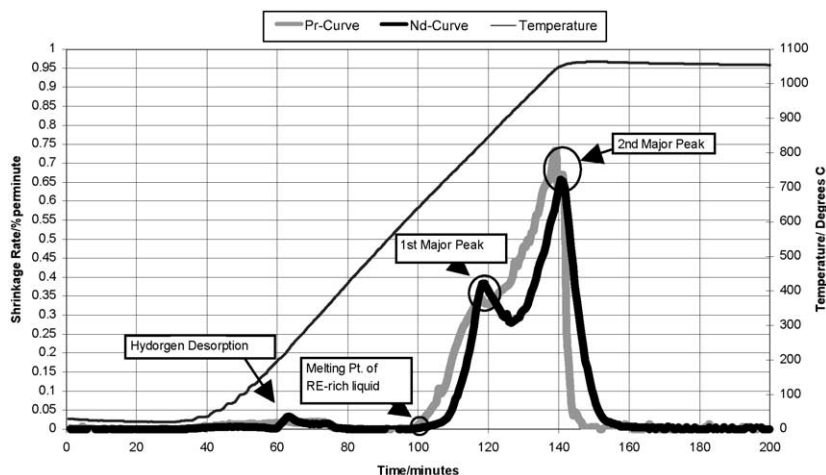


Fig. 1. Shrinkage rate curves of Pr1060°C and Nd1060°C against heating rate.

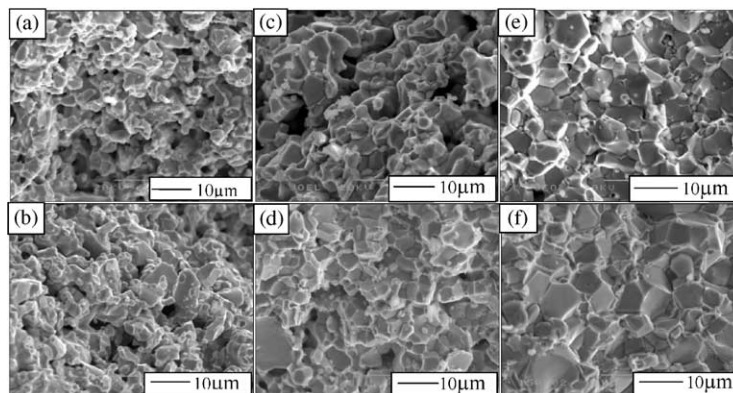


Fig. 2. Comparisons of Nd and Pr fractographs including density values: (a) Sample Nd800°C, $\rho = 5.92 \text{ g cm}^{-3}$; (b) Sample Pr800°C, $\rho = 6.09 \text{ g cm}^{-3}$; (c) Sample Nd950°C, $\rho = 6.52 \text{ g cm}^{-3}$; (d) Sample Pr950°C, $\rho = 6.72 \text{ g cm}^{-3}$; (e) Sample Nd1060°C, $\rho = 7.37 \text{ g cm}^{-3}$; (f) Sample Pr1060°C, $\rho = 7.52 \text{ g cm}^{-3}$.

the present case there is a noticeable difference in the behaviour of the two alloys.

It has been reported that NdFeB exhibits solution re-precipitation behaviour at $\sim 900^\circ\text{C}$ [2], whereas this study appears to show PrFeB samples densifying by solution re-precipitation at a lower temperature. This could be due to $\text{Pr}_2\text{Fe}_{14}\text{B}$ being more soluble in the Pr-rich liquid phase, and this could enhance solution re-precipitation at lower temperatures in Pr-based samples. As the densification rates increase both curves reach a maximum at similar temperatures, with densification reaching a higher final rate in the Pr magnet. The final section of each curve shows a decrease in the rate as solid-state events dominate densification. It is known that the Nd-based magnets exhibit more grain growth than the corresponding Pr-based magnets [11] and this is supported by the more gradual decrease in the rate of solid-state sintering in the Nd curve. Fig. 2 shows the microstructural development of the two compositions and the micrographs reveal a gradual increase in density up to 950°C and at 1060°C a completely dense microstructure is observed with classical “trapped” porosity visible at grain the boundaries.

4. Conclusions

- Pr-based compacts exhibit faster densification in the lower temperature ranges. This is attributed to a crossover of the rearrangement and solution re-precipitation mechanisms.
- This higher rate of densification in PrFeB could indicate that the liquid phase has better wetting characteristics or that there are differences in the solubilities of $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ in the respective liquid phases.

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