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Microstructural development and sintering of NdFeB alloys

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The reactions and phase changes occurring during sintering of NdFeB permanent magnet alloys were studied by differential thermal analysis and scanning electron microscopy. The powders were produced by hydrogen decrepitation and on heating, hydrogen evolution occurred in two stages: firstly from the matrix phase (~170 °C) and then from the neodymium-rich phase (350–750 °C). The neodymium-rich phase melted at ~630 °C and no significant microstructural changes occurred below this temperature. Above 630 °C the neodymium phase is mobile, wetting the matrix grains and leading to their magnetic isolation. Densification occurs by a solution/precipitation mechanism.

1. Introduction

The ideal permanent magnet material would have a high Curie temperature, large spontaneous magnetization, large uniaxial magnetocrystalline anisotropy, and low-temperature coefficients of coercivity and remanence.

To approach the above ideal material it has been necessary to investigate the effects of:

(a) crystal structure and chemical composition of the magnetic phase, which determine the intrinsic magnetic properties such as atomic magnetic moments, spontaneous magnetization, Curie temperature and magnetocrystalline anisotropy, and

(b) the microstructure, which affects the extrinsic magnetic properties such as remanence and coercivity [1] and, therefore energy product.

In the case of NdFeB materials, their magnetic properties, especially coercivity, are sensitive to microstructure and, therefore, to heat-treatment. The ideal microstructure can be achieved by slow cooling from the sintering temperature, or by rapidly cooling, followed by an anneal. The sintering temperature is related to the milling process and varies from 1020–1080 °C.

2. Experimental procedure

Commercial ingots of the as-cast material of $Nd_{16}Fe_{76}B_8$ alloy were powdered by a combination of hydrogen decrepitation (HD) and ball milling to a mean size of approximately 2 μm. The powder was then aligned and compacted in an isostatic press at 200 MPa.

Another route used to produce green compacts involved reducing the ingots to a particle size less than approximately 1 mm by squeezing them repeatedly between hard steel platens under cyclohexane. The particles were then milled, aligned and compacted in the same way as for the HD method. This offered the opportunity of comparing the sintering behaviour of the powders obtained with and without use of the HD process.

Transition temperatures of sintered materials, produced either by HD or the conventional route, were identified by differential thermal analysis (DTA) using samples of approximately 25 mg. The specimens were heated at 5 °C min^{-1} in an inert atmosphere. Because the DTA apparatus could not be used above 900 °C, the study was not pursued beyond this temperature.

Microstructural development during sintering was studied by SEM observation of the fracture surfaces of specimens heated to particular temperatures, held for 1 h and rapidly cooled to room temperature.

3. Results and discussion

3.1. Study of sintering using DTA

The curves in Fig. 1a and b, begin from room temperature with an endothermic peak around 70 °C which

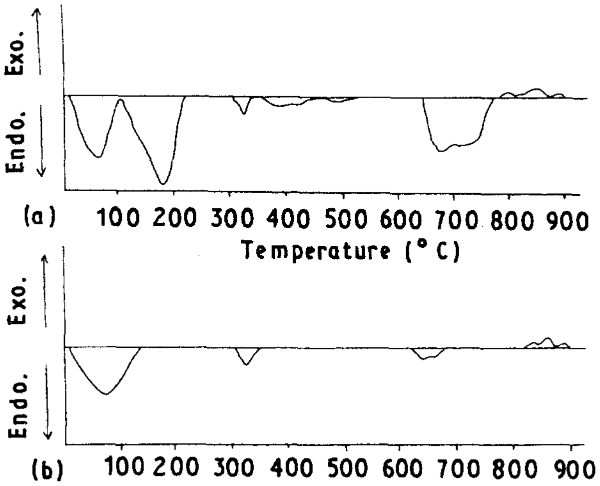

Figure 1 DTA curves of the $Nd_{16}Fe_{75.5}Al_{0.5}B_8$ compound produced by (a) the hydrogen decrepitation route, and (b) the conventional milling route.

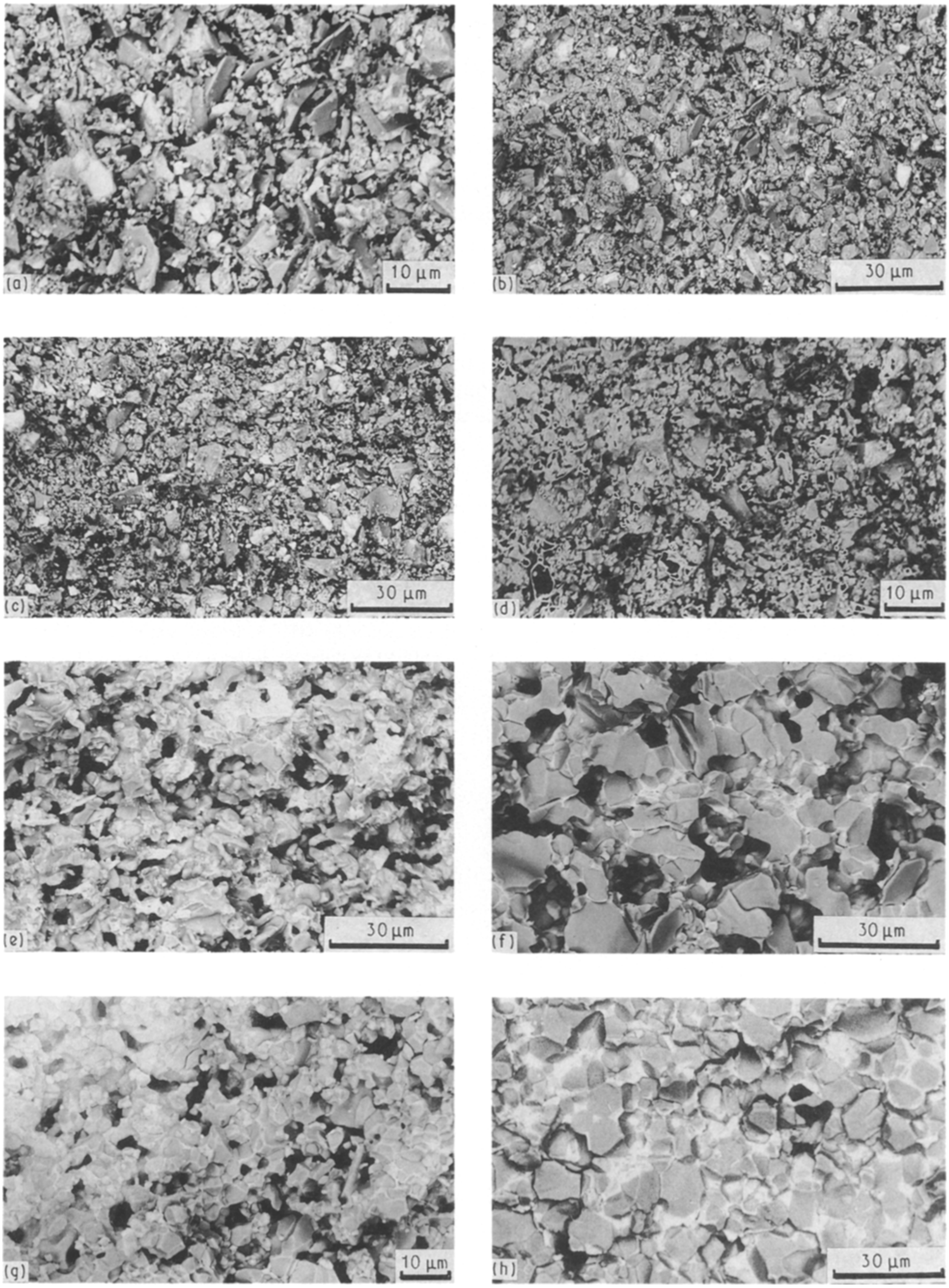

Figure 2 Microstructure of specimens heated to particular temperatures and held for 1 h. (a) As-green-compacted material, (b) 300 °C, (c) 600 °C, (d) 650 °C, (e) 800 °C, (f) 950 °C, (g) 1010 °C, (h) 1050 °C.

corresponds to the expected removal of cyclohexane which was used as a milling medium. As seen in Fig. 1a for specimens produced by the HD route, this peak is followed by a second endotherm at about 170 °C which can be associated with the desorption of hydrogen. Hydrogen desorption from the matrix phase has also been confirmed by X-ray diffraction [2]. As is evident from Fig. 1b, this endothermic peak is absent for the specimen produced by the conventional method.

In both cases an endothermic peak appears at about 315 °C, which corresponds to the Curie temperature where the specimens lose their magnetism. It corresponds with observations from thermo-mechanical analysis experiments [3]. For the specimen produced by the HD route this peak is followed by multiple minor peaks which are absent in the specimen produced by the conventional method, as shown in Fig. 1a and b. These peaks are possibly generated by the multi-stage nature of the hydriding process. Harris *et al.* [4] have also reported this multi-stage nature during hydrogen absorption in the HD process.

Fig. 1a and b show an endothermic peak which starts at approximately 630 °C. Around this temperature the neodymium-rich phase starts to melt. This temperature corresponds with the eutectic temperature of the neodymium-rich phase as reported by Mishra *et al.* [5] and Savitsky *et al.* [6]. In the present study it is also confirmed by the microstructural changes taking place during the sintering process, as described in the following section. As recorded in Fig. 1a, this endothermic peak is a broad peak for the specimen produced by HD route, which tends to suggest that the hydrogen is simultaneously removed from the neodymium-rich phase.

Finally, as demonstrated in Fig. 1a and b, there are some minor exothermic peaks which start at approximately 770 and 810 °C from specimens produced by HD and conventional routes, respectively. These are difficult to explain. One possible explanation is that the effects are related to different rates of densification of the two differently prepared powders. The powder produced by the HD route has relatively clean surfaces and there are no neodymium-rich phase particles within the matrix phase. The initial clean-surface particles and neodymium-rich grain-boundary phase encourage sintering at a lower temperature. A similar explanation but concerning the higher sintering temperature has been reported by Moosa *et al.* [7] and McGuiness *et al.* [8].

3.2. Microstructural development study using SEM

Fig. 2a–h show the progressive microstructural development in $Nd_{16}Fe_{76}B_8$ for specimens heated to particular temperatures, held for 1 h in argon, and rapidly cooled under the same atmosphere to room temperature. From these micrographs changes in pore size and shape, phase transitions, the elimination of pores and shrinkage, and increases in grain size are evident. The observations are helpful in elucidating the densification mechanism.

Fig. 2a shows the compacted particles, pressed at 200 MPa at room temperature; the density of the green compact was 4.0 $g\,cm^{-3}$. As is evident from Fig. 2b and c, there are no significant changes in the microstructure of the compact when it is heated to below the eutectic temperature of the neodymium-rich phase, while the density measurements show the density of the compact has increased to 4.2 $g\ cm^{-3}$ on being heated to 600 °C. One possible explanation is that when the sample is heated under vacuum, cyclohexane and hydrogen are removed from the sample and this causes the increase in density. The removal of cyclohexane and hydrogen may be accompanied by rearrangement of the particles to a denser configuration. Fig. 2d shows clearly the onset of melting of the neodymium-rich phase at a little above 600 °C. Fig. 2e shows a micrograph of a compacted specimen heated to 800 °C. As seen in the figure, the liquid neodymium-rich phase wets the matrix phase and, on formation of the liquid phase, primary rearrangement of particles occurs because of capillary forces. Pores change their shape and the particle contact areas are increased. The smaller particles are dissolved and the larger ones then grow by Ostwald ripening.

From Fig. 2f, which corresponds to a specimen heated to 950 °C, it is evident that the neodymium-rich phase wets the solid particles, so that it isolates the hard magnetic phase grains. This is a crucial factor in determining the magnetic properties of neodymium-Fe–B magnets, especially with regard to increasing coercivity. As seen in this figure, the smaller particles have been almost completely absorbed into the larger particles which are rounded. Also more changes occur in pore shape; they become smaller and rounded and subsequently they fill with solid material, leading to shrinkage. At higher temperature further shrinkage occurs by further recrystallization and elimination of pores, as seen in Fig. 2g which is for a sample heated to 1010 °C. Finally, as shown in Fig. 2h for the compact sintered at 1050 °C, the small grains have disappeared and the rounded pores decreased in size to complete the densification.

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