MAGNETIZATION VERSUS HEAT TREATMENT IN RAPIDLY SOLIDIFIED NdFeB ALLOYS

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Abstract - NdFeB melt spun amorphous or partially amorphous alloys of four compositions were prepared. The crystallization kinetics induced by thermal treatment was studied by differential scanning calorimetry and scanning and transmission electron microscopy. Scanning electron microscopy demonstrated that heterogeneous nucleation occurred preferentially at the ribbon surface which was in contact with the wheel. The explicit form of the kinetic equation that best describes the first stage of crystallization under high undercooling conditions was obtained for each alloy. From the crystallization results, the lower part of the experimental time-temperature-transformation curves was deduced for each alloy and extrapolated up to the high temperature limit of their validity. Microstructural observations showed a typical size of the microcrystals obtained by heat treatment of -100 nm. From the magnetic properties measured with a vibrating sample magnetometer, the same magnetic behavior of partially crystallized alloys is observed regardless of the temperature of annealing provided the same crystallization fraction, x, is maintained, at least for small values of x (typically -10%).

INTRODUCTION

The development of the rapid solidification route to produce permanent magnets began in the late 1970s when, for the first time, commercial ribbons in excess of 15 mm were obtained in melt-spun Fe-Pr(BSi) alloys which were subsequently crystallized [1]. This discovery opened a new horizon for magnetic materials research and revolutionized the world of permanent magnets [121]. The development of the rapid solidification route to the production of NdFeB magnets the control of the final grain size is crucial in the development of the hard magnetic properties.

The aim of this study was to investigate morphologically and calorimetrically the crystallization kinetics of some amorphous melt-spun NdFeB alloys and to correlate it with the magnetic properties. Some preliminary results are presented here.

EXPERIMENTAL

Master alloys of NdFeB were provided by Dr. S. Sattelberger from Gesellschaft für Elektrometallurgie, Nürnberg. The compositions of the as-cast materials used are indicated in Table 1. Melt-spun alloys were obtained by quenching the molten materials on the surface of a rapidly spinning (1-30 m/s) cooper wheel under a helium atmosphere. Melt spun alloys #1 to #3 were obtained as a mixture of short ribbons and pellets. The X-ray diffraction patterns of the pellets showed a small degree of crystallinity on them (less than 5 vol%). Melt-spun alloy #4 was obtained in normal ribbon form. X-ray diffraction confirmed the amorphous state of all the ribbons (within the experimental limit of detection of crystals).

Differential scanning calorimetric (DSC) measurements were performed in a computerized Perkin Elmer DSC-2 equipment in both isothermal and continuous heating regimes (for more details see ref. [3]) on the melt-spun ribbons. Isothermal anneals were performed in the range 800-850 K by heating the sample (-10 mg) from room temperature to the annealing temperature at a rate of 360 W/min. The interval of crystallization temperatures scanned in continuous heating experiments extended from 830 to 980 K with heating rates in the range 10-320 K/min. To analyze the crystallization kinetics, both the crystallized fraction, x, and the transformation rate, dx/dt, at a given time or temperature, were determined following the current procedure [3]. The uncertainty in temperature was ±3 K, those on x and dx/dt (in the range 0.1<x<0.9) were less than 5%.

Microstructural observations were carried out on thin foils prepared by ion beam milling with a Philips EM 300 transmission electron microscope (TEM) at the Birmingham University (Prof. I.R. Harris) and on fresh fracture surfaces with a Hitachi S-570 SEM at the Autonomous University of Barcelona. The magnetic properties were measured with a vibrating sample magnetometer (Birmingham University) in fields up to 14 kOe.

RESULTS AND DISCUSSION

The DSC curves for the four amorphous ribbons obtained at a heating rate of 40 K/min are compared in fig. 1. One to four crystallization peaks, often overlapping, appear on heating. The general form of the exothermic peaks agrees with that published for melt-spun alloys of similar compositions [4.5].
As regards to fig. 1, the most stable material versus crystallization is alloy #3. It shows no Curie transition in the as-quenched state in the temperature interval 400-640 K (neither do amorphous alloys #1, #2). Once crystallized it shows a Curie transition at 648 K which can be ascribed to the metastable NdzFe7B3 compound [6]. Next material stable versus crystallization (at that heating rate) is alloy #2. In the crystallized state it shows a Curie transition at 579 K. This Curie temperature corresponds to the off-stoichiometric NdzFe8B7 compound [7,8]. In decreasing stability versus crystallization, next material is alloy #1. The observed Curie transition at 575 K for the crystallized material was ascribed to off-stoichiometric NdzFe8B7. Finally, alloy #4 is the least stable versus crystallization at these temperatures. A clear Curie transition of the amorphous alloy appears at 577 K while the Curie temperature of the crystallized material is 765 K. The value expected for metastable NdzFe8B7 compound [9].

The observed crystallization processes were observed in the limited temperature interval experimentally accessible by DSC measurements, each crystallization exotherm has a kinetics that follows a general equation of the form

$$\frac{dx}{dt} = K(T) f(x)$$

We further assume that the rate constant follows an Arrhenius behaviour

$$K(T) = K_0 \exp\left(-\frac{E}{kT}\right)$$

with $K_0$ the pre-exponential factor and $E$ the apparent activation energy.

Since the crystallization peaks were somewhat overlapping at various heating rates, the apparent activation energy was deduced by the Kissinger method from the continuous heating data. The values obtained for $E$ are quoted in Table 1. They are very similar to those published for other NdFeB alloys [10].

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition(at.%)</th>
<th>Peak</th>
<th>$E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Nd 82.2, Fe 4.8</td>
<td>first</td>
<td>2.99</td>
</tr>
<tr>
<td>#2</td>
<td>Nd 79, Fe 8</td>
<td>first</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>second</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>third</td>
<td>4.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fourth</td>
<td>5.18</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>Nd 80.5, Fe 11</td>
<td>first</td>
<td>4.54</td>
</tr>
<tr>
<td>#4</td>
<td>Nd 77, Fe 20</td>
<td>first</td>
<td>5.91</td>
</tr>
<tr>
<td></td>
<td>third</td>
<td>3.95</td>
<td></td>
</tr>
</tbody>
</table>

As a consequence, isothermal measurements on each alloy provide the value of $g(x)/K_0$ with $x$ in the range 0.1-0.9 for the first crystallization peak. Note that $x=1$ applied to the first crystallization peak gives the completion of this peak, but other crystallization processes can still occur (mostly on increasing the temperature).

The DSC technique is very powerful for determining the classical time-temperature-transformation (T-T-T) curves. Effectively, equation (4), when represented as a function of $x$ or $g(x)/K_0$ allows construction of the T-T-T curve. The resulting T-T-T curves for a crystallized fraction of $x=0.1$ are shown in fig. 3. The analysis of this figure shows that above 830 K the time needed to crystallize an alloy decreases in the sequence #3, #2, #1 and #4, or in other words, this is the sequence of decreasing stability against crystallization (these are the results observed in the continuous heating DSC curves of fig. 1). But below 830 K the ordering of the sequence changes and alloy #4 becomes more stable than #1 and #2 on decreasing the temperature.

To elucidate the microstructure versus heat treatment, the four amorphous alloys were subjected to annealings of 10 min and 1 hour at the temperatures needed to get $x=0.1$ (see fig. 3). Fig. 4 shows the fine microstructure of crystallized portions of heat treated (HT) alloy #2. Similar results were obtained for the other alloys. At low annealing temperature

![Fig. 2. - Experimental values of ln(dx/dt) vs. ln(1-x) obtained under isothermal conditions for the four alloys. When a theoretical model gives good agreement with the experimental data it is shown as a solid line (see ref. [1]).](image1)

![Fig. 3. - Predicted low temperature part of the T-T-T curves for the four NdFeB alloys studied.](image2)
Amorphous melt-spun NdFeB ribbons were prepared under controlled conditions and their crystallization kinetics was studied both morphologically and calorimetrically. DSC analysis reveals that crystallization proceeds generally in various stages. Microscopic analysis shows that the size of the crystalline zone is about 50 nm. The crystallization of the melt-spun material is achieved by heat treatment rather than with the temperature or time of annealing independently. This result agrees with the fact that the crystalline size is rather insensitive to the temperature of annealing.

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REFERENCES


