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THERMAL BEHAVIOUR OF Nd-Fe-B ALLOYS STUDIED BY T.E.M.

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Abstract. – Thinned samples of as-cast and sintered Nd-Fe-B magnets have been observed by transmission electron microscopy during *in-situ* heat treatments. Strip-like contrast was observed in the Nd₂Fe₁₄B phase. A transition from cubic to hexagonal Nd₂O₃ occurs at about 200 °C.

1. Introduction

The discovery of boron stabilized Nd-Fe-B compounds has opened the possibility to achieve the goal of low cost high performance permanent magnets. The improvement in magnetic properties of the Nd-Fe-B magnets over the existing high energy Sm Co based magnets ($BH_{\max}$ is multiplied by a factor 1.5) broaden the range of applications. In addition, the basic raw materials required for the new material have a price advantage and fewer supply restrictions than either Sm or Co.

However, the development of Nd-Fe-B magnets still shows very unfavorable behaviour at elevated temperatures: for a continue service, the maximum temperature is only 120 °C while it reaches 300 °C for 2 : 17 systems. Corrosion and oxidization problems are mainly associated with the free Nd present in the grain boundary eutectic phase.

The aim of this work is to study the thermal behaviour of as-cast and sintered Nd-Fe-B magnets by *in-situ* transmission electron microscopy observations.

2. Experimental procedure and results

Two compositions: Nd_{14.3}Fe_{77.7}B₈ and Nd_{16.6}Fe_{75.4}B₈ (atomic percentage) were studied. The ingots elaborated from raw materials containing traces of Al, Ca, Mg, and Si were prepared in UGIMAG S.A. laboratories. After a vacuum induction melting, the melt was cast into a walled copper mould, then crushed under inert atmosphere and milled to produce a narrow size distribution of particules. The powder was magnetically aligned, pressed, sintered for one hour at 1100 °C and heat treated. For the TEM observation, specimens were thinned by ion milling and held into the microscope with a heating specimen holder. Thermal treatments were performed *in-situ*, from room temperature to 600 °C.

The ternary diagram predicts three phases at low temperature for the choosen compositions and we report successively on each one.

a) The main phase Nd₂Fe₁₄B, at room temperature, is always found to be free of crystal lattice defects and

corresponds to the hard magnetic phase (tetragonal structure, $a = 0.880$ nm, $c = 1.220$ nm).

At about 200 °C, it sometimes appears on electron micrographs a strip-like contrast with spacing of about 20 nm (Fig. 1a). On the corresponding diffraction

Fig. 1. – (a) Strip-like contrast in the Nd₂Fe₁₄B phase. The c -axis of the tetragonal structure is perpendicular to the micrograph plane. (b) Micro-diffraction pattern with satellites connected with the previous stripes; [001] zone axis.

pattern, satellites of diffraction spots are observed in $[100]^*$ and $[010]^*$ directions (Fig. 1b). Rings of polycrystalline iron and amorphous Nd oxide appear simultaneously. The precipitation of α -Fe seems to result from the oxidation of Nd in the main phase.

At higher temperature (500 °C), the oxidation of the main phase is very rapid; $\text{Fe}(\text{OH})_3$ rings appear while tiny Fe grains coarsen.

b) The secondary phase is paramagnetic with a tetragonal structure. This boron-rich phase $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ always shows a high crystalline defect density. It remains very stable during the heating treatment.

c) A Nd-rich phase (about 80 % at. Nd and 20 % at. Fe) has a FCC structure with $a = 0.52$ nm. At room temperature, the sesquioxide Nd_2O_3 is already present with large diffraction spots indicating a bad crystallisation. Its structure is cubic ($a = 1.11$ nm) [C-type]. This oxide is formed during the elaboration of the alloy and also during the thinning of the specimen.

From 200 °C, a new diffraction pattern due to a hexagonal structure allotropic form of Nd_2O_3 (A-type) progressively replaces the previous diagram (Figs. 2a and 2b).

3. Conclusion

The modulated or strip-like contrast in the main phase is not explained now, but it is interesting for its possible consequences on magnetization mechanisms. The stripes periodicity (20 nm) is such that they could strongly interact with the moving domain walls and justify the coercivity by wall pinning previously noticed at the same temperature (200 °C) [1].

The rapid oxidation of Nd and the precipitation of magnetically soft α -Fe drastically reduce the magnetic properties and produce steps in the demagnetization curve of sintered magnets [2].

The phase transition from cubic to hexagonal Neodymium oxide in Nd-Fe-B alloys has not been reported before. In samples containing aluminium, this transformation takes place at lower temperature than without aluminium and the study of this phenomenon is in progress.

We have to emphasize that electron microscopic observations present particular conditions as vacuum, magnetic field of the objective lens, reduced thickness of the samples. The size effect on oxidation was already reported [3].

Fig. 2. - (a) Nd_2O_3 (C-type), at room temperatures; $[112]$ zone axis. (b) Nd_2O_3 (A-type), at 450 °C, after the phase transition; $[0001]$ zone axis.

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