CURIE TEMPERATURE OF A NON-IDENTIFIED METASTABLE PHASE IN THE AS-CAST AND ANNEALED FE-(ND+MM)-B ALLOYS (MM=MISCHMETAL)

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ABSTRACT

The partial replacement of neodymium by cerium-rich Brazilian Mischmetal (MM) in as-cast and annealed Fe-(Nd+MM)-B alloys was studied using XRD (XRD), thermomagnetic analysis (TMA), electron microprobe analysis and metallography. The compositions of the alloys studied were: $Fe_{75}Nd_{7,5}MM_{7,5}B_8$, $Fe_{74}Nd_{10}MM_{10}B_6$, $Fe_{74}Nd_9MM_9B_8$, $Fe_{75}Nd_9MM_9B_7$ and $Fe_{75}Nd_{15}B_8$. These alloys were prepared by arc melting, starting from 99.9 weight % pure primary materials, and annealed at 1100 ºC for 7 days. The metallography and XRD revealed that the microstructures of these alloys consist of a 14:2:1 matrix (i.e., $Fe_{14}(Nd,MM)_2B$), a MM-rich phase and another phase whose composition is Fe_2MM for the $Fe_{74}Nd_{10}MM_{10}B_6$ alloy and Fe_4MMB_4 for the others. The TMA for all MM containing alloys showed that the Curie temperature for the matrix was around 285^{o}C. The TMA also revealed the existence of a metastable ferromagnetic phase in all alloys, including the $Fe_{77}Nd_{15}B_8$, with a T_C around 445 ^{o}C, and an intensity that was as high as that of the 14:2:1 matrix. The signal of this metastable phase disappeared when the alloy was heated over 500 ºC *in spite of the 1100C annealing temperature?* After some heating/cooling measurement cycles from room temperature to 450 ºC, it was verified that the signal from the metastable decreased while that from the 14:2:1 phase increased.

Keywords: Magnetism, Fe-Nd-B, Mischmetal, Curie temperature

1 INTRODUCTION

It is known that the magnets of $Fe_{14}Nd_2B$ announced by Sagawa [1] and Croat [2] in 1984 have a great importance commercially and that the main technological challenges for its production are dominant. One very important aspect corresponds to the fact that these magnets use pure Neodymium usually in combination with other pure rare earths, which are added for improvements of specific characteristics [3-7]. A research perspective in these materials corresponds to the substitution of the pure rare earths by Mischmetal, which is cheaper and available in reasonable quantities in Brazil. The partial substitution of Nd by Mischmetal in the 14:2:1 compound has been studied with reports of encouraging results [8-16]. Alves [16] studied the substitution of Nd by Brazilian MM in as-cast alloys and reported that the substitution is plausible up to 50%. In this work, samples of nominal composition Fe-($Nd_{0.5}MM_{0.5}$)-B were prepared with different concentrations of Fe and B. The purpose of the present investigation was to determine the possible effects of these variations, as well as of the annealing treatment, on the microstructure and T_C of the 14:2:1 compound. Results are compared with the properties of the $Fe_{77}Nd_{15}B_8$ commercial alloy.

2 EXPERIMENTAL

The samples were prepared by arc melting from 99,9% purity starting elements on a water-cooled copper boat, under a purified argon atmosphere. The composition of the Mischmetal was Ce 56%, La 18%, Nd 13%, Pr 5%, Y 2%, Fe 2% and 4% of other rare earth elements (Wt. %). To guarantee a good homogeneity in the samples, each sample was melted three times. For the annealing treatment, these ingots were wrapped in Ta foil and sealed under argon atmosphere in quartz capsules. These were then placed in a furnace and held at 1100ºC for one week after which, they were removed from the furnace and quenched into room temperature water. The microstructural observations were carried out using optical microscopes with samples polished in a abrasive liquid of 0.25μm. The microprobe analysis was done in a JEOL device, model JXA using 20 kV. For XRD (XRD) and thermomagnetic analysis (TMA) the samples were hand ground followed by ball-milling to around 30μm in a protective liquid of cyclohexane and then dried in a vacuum chamber [17]. The Curie temperatures were determined using a device that was built in our laboratory [18], which can do measurements up to 1000ºC at a rate of 50 K/min.

3 RESULTS AND DISCUSSION

As shown in Figure 1, the as-cast and the heat treated alloys contain a major phase $Fe_{14}MM_2B$ (A), a rare earth rich phase (B), and a third phase (C) for which the microprobe analysis revealed a composition close to the Fe_2Ce phase for the $Fe_{74}Nd_{10}MM_{10}B_6$ alloy and for the others a composition similar to the Fe_4NdB_4 paramagnetic compound.

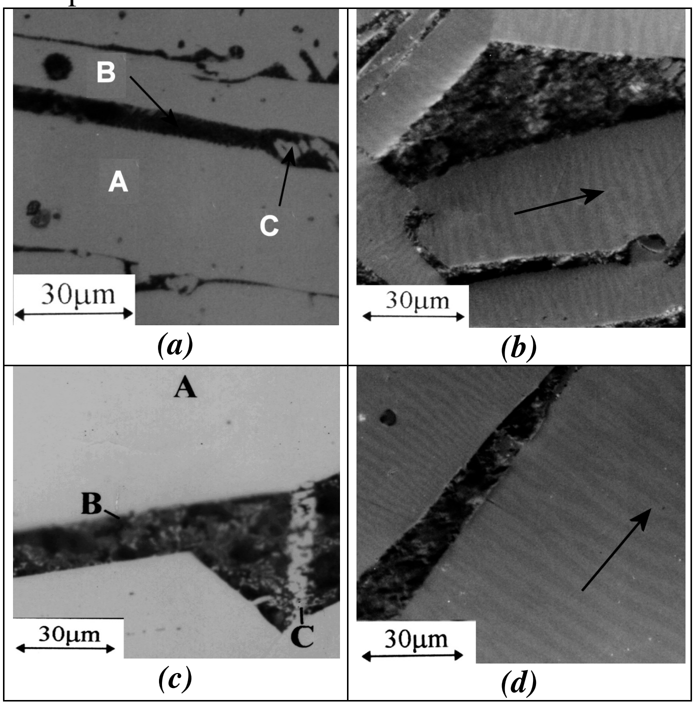

Figure 1: Micrographs of as-cast (a,b) and annealed (c,d) $Fe_{74}Nd_{10}MM_{10}B_6$ alloy, where A is the 14-2-1 phase; B the eutectic phase and C the Fe_2MM phase. The figures 1(b) and 1(d) are Kerr effect micrographs that show the magnetic domains in the matrix phase.

These results are not in agreement with those by Alves [16] who reported the existence of the 2:1 phase only for alloys with more than 50% Nd substituted by MM. Besides, for all annealed samples, except for the $Fe_{77}Nd_{7.5}MM_{7.5}B_8$ alloy (whose results are similar to those obtained for the $Fe_{77}Nd_{15}B_8$ alloy), the grains of the rare earth phase (C) were bigger than those in the as-cast alloys. In the same way, all the alloys presented intense magnetic domains (figures 1(b) and 1(d)) confirming the conservation of the magnetic anisotropy. All these results were confirmed by XRD. Figure 2 exhibits the XRD pattern for the as-cast $Fe_{74}Nd_{10}MM_{10}B_6$ alloy. It reveals the existence of a large number of peaks corresponding to the 14:2:1 compound in addition to a fewer number of peaks with angles close to those from the Fe_2Ce phase (extra peaks), as reported by Alves [16], which are related to Fe_2MM.

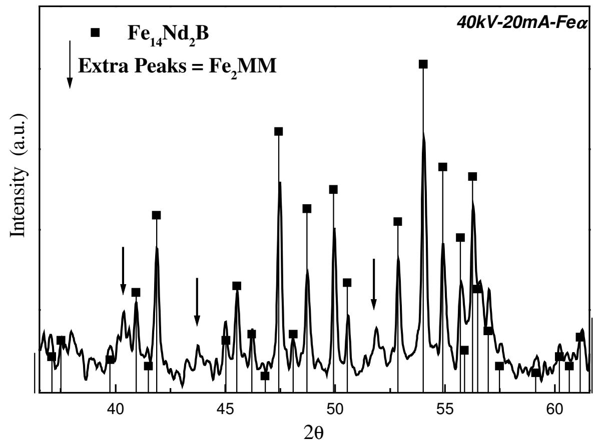

Figure 2: XRD pattern for the as-cast $Fe_{74}Nd_{10}MM_{10}B_6$ alloy.

XRD patterns for the other as-cast alloys exhibited similar results to the $Fe_{74}Nd_{10}MM_{10}B_6$ alloy, but with less intense extra peaks for the values of $2\theta \approx 28^o$, 34.5^o and 41^o, whose intensity varies with alloy composition (Figure 3).

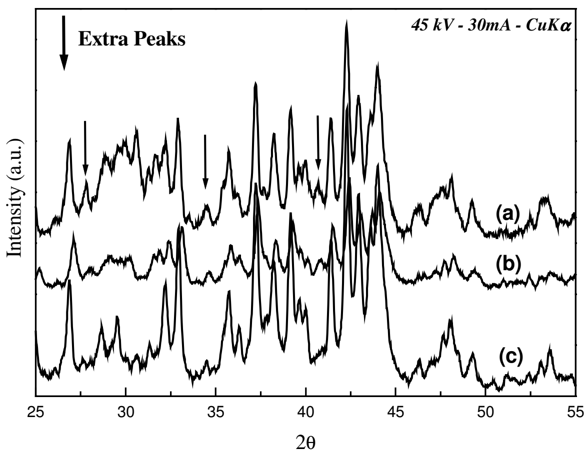

Figure 3: X-ray diffraction patterns for the (a) $Fe_{74}Nd_9MM_9B_8$, (b) $Fe_{75}Nd_9MM_9B_7$ and (c) $Fe_{77}Nd_{7.5}MM_{7.5}B_8$ as-cast alloys.

As in the analysis by optical microscopy, the XRD patterns obtained for the annealed samples were similar to those from the as-cast samples (Figure 4) indicating that the annealing did not effect the phase constitution of the alloys. The displacements observed between the diffraction peaks of the samples and the indexed diffraction angles from JCPDS can be explained by recalling that the elements present in Mischmetal, especially Ce and La, are soluble in the phases in the alloys.

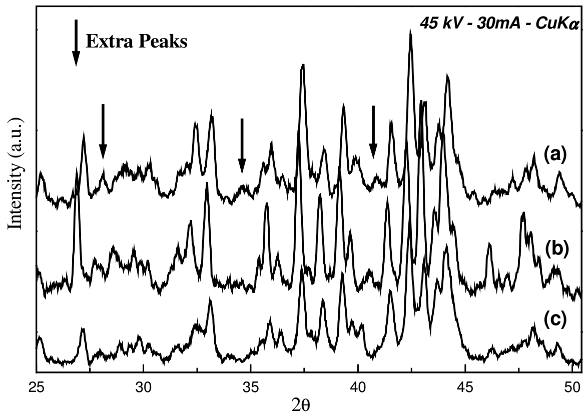

Figure 4: X-ray diffraction patterns for the (a) $Fe_{75}Nd_9MM_9B_7$, (b) $Fe_{74}Nd_{10}MM_{10}B_6$ and (c) $Fe_{77}Nd_{7.5}MM_{7.5}B_8$ annealed alloys.

The TMA revealed that the T_C of the 14:2:1 compound is around 285ºC for both the as-cast and annealed alloys with MM (Table 1).

Table 1: Curie temperatures for the $Fe_{14}MM_2B$ phase in the various alloys.

Alloy	As-cast	Annealed
$Fe_{74}Nd_9MM_9B_8$	288ºC	286ºC
$Fe_{75}Nd_9MM_9B_7$	288ºC	282ºC
$Fe_{74}Nd_{10}MM_{10}B_6$	280ºC	285ºC
$Fe_{77}Nd_{7,5}MM_{7,5}B_8$	286ºC	286ºC

A magnetic transition with equivalent intensity to that of the 14:2:1 compound was observed at 445ºC. This signal is associated with a compound we designate from now on as ϕ_1 phase, which disappeared when the alloy was heated to 500ºC (Figure 5).

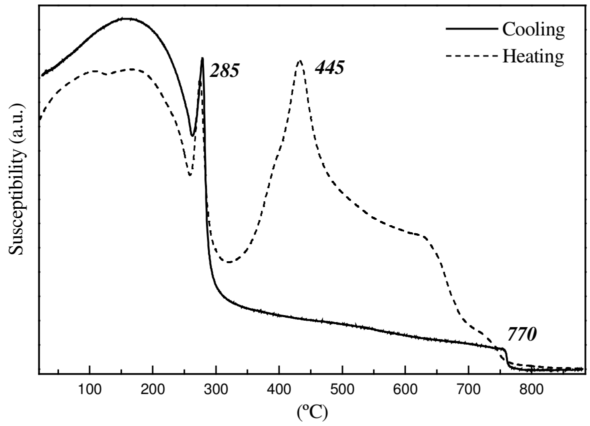

Figure 5: TMA curves for the $Fe_{74}Nd_{10}MM_{10}B_6$ annealed alloy (first heating/cooling measurement cycle).

After these initial experiments, a series of heating/cooling cycle measurements up to 450ºC were carried out. For each measurement cycle, the intensity of the TMA signal for the ϕ_1 phase was observed to decrease while that of the 14:2:1 phase increased (Table 2). These results indicate that ϕ_1 is a metastable phase in the microstructures of these Fe-Nd-B based alloys.

Table 2: Curie temperatures of the ϕ_1 metastable phase for the heating/cooling measurement cycles up to 450ºC.

Cycle	Heating Curve	Cooling Curve
First	440 ºC	412 ºC
Second	412 ºC	400 ºC
Third	400 ºC	380 ºC
Fourth	380 ºC	345 ºC
Seventh	-	-

4 CONCLUSIONS

The microstructures of the as-cast and heat-treated Fe-Nd-MM-B alloys are similar to the microstructure of the Fe-Nd-B based alloys. However, we verified the presence of Fe_2MM, instead of Fe_4MMB_4, for the $Fe_{74}Nd_{10}MM_{10}B_6$ alloy. This result contradicts that reported by Alves [16], who only observed the presence of Fe_2MM in alloys with more than 50% Nd substituted by MM.

The 14:2:1 compound had a T_C around 285 ºC for all the samples with Mischmetal. This is a reasonable value considering the amount of MM in these alloys that preserve the phase anisotropy, as confirmed by the presence of the magnetic domains. The compound with T_C = 445ºC appears to be a metastable phase (ϕ_1) although the composition and structure have not yet been confirmed. We believe that this phase is a result of the quenching stresses in the matrix during the arc melting cooling stage or the rapid cooling of the sample after the long time anneals at 1000ºC. The metastable nature of this phase is indicated by the fact that it appears to decompose when the samples are reheated slightly above its Tc; the decomposition reaction produces the $Fe_{14}Nd_2B$ phase. *Were these last two points ever discussed in the body of the paper?*

ACKNOWLEDGEMENTS

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