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Dynamic mechanical analysis of copper-containing magnetic Pr–Fe–B alloys

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Abstract

The mechanical properties of magnetic alloys with compositions $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ and $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ were studied with the aid of a dynamic mechanical analyzer. The elastic modulus of the annealed $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy varied substantially (~24%) and irreversibly when it was heated to 450 °C and cooled to room temperature. Conversely, the elastic modulus of the annealed $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy varied only slightly upon heating to 450 °C and cooling to room temperature. This behavior has been attributed to the precipitation of excess rare earth from the lattice of the matrix phase and to the $Pr_6Fe_{13}Cu$ and $Pr_{1+\varepsilon}Fe_4B_4$ phases.

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Keywords: Magnetic alloys; Hot pressing; PrFeBCu magnets; DMA

1. Introduction

Hot deformation is an essential step in the production of many magnetically anisotropic PrFeB-Cu magnets [1]. Cast PrFeBCu alloys that are dense and isotropic, are hot-deformed by reducing the height of the ingot. Alloys thus deformed can exhibit anisotropic magnetic properties providing the right conditions have been used during the deformation stage. These conditions vary considerably and depend on alloy composition and microstructure. Knowledge of the elastic modulus behavior, which is also dependent on alloy composition and microstructure, would be useful for determining the optimum processing condition.

Copper has always been associated with good magnetic properties in cast and hot-pressed magnets (see, for example, Refs. [1,2]). Among the several elements added to cast and hot-pressed magnetic alloys, copper in combination with praseodymium has shown the lowest eutectic

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temperature (461 °C) [3]. A slightly higher eutectic temperature, 472 °C, has also been reported [4]. The copper-containing nonmagnetic grain boundary phase has been reported to decrease the coupling exchange field between neighboring grains [4]. A lower eutectic temperature is considered desirable as it would not only avoid grain growth and oxidation but also save energy during the heat treatment stage. Grain refinement in cast alloys and improvement of hot-workability have been attributed to this element [5].

Praseodymium-containing rare earth–iron–boron permanent magnets, have shown better magnetic properties than those containing neodymium. This was attributed to the large anisotropy field in $Pr_2Fe_{14}B$ compared to that in $Nd_2Fe_{14}B$ [6], and to the smaller grain size in cast Pr–Fe–B compared to that in cast Nd–Fe–B alloys [7]. The eutectic temperature of Pr–Cu (472 °C) compared to that of Nd–Cu (520 °C) [4] is also a factor in favor of Pr-based magnets. The improvement in intrinsic coercivity of PrFeBCu permanent magnets annealed at a low temperature has been attributed to the smoothing and magnetic isolation of $Pr_2Fe_{14}B$ grains by the eutectic Pr–Cu phase [8–11]. Formation of a $Pr_6Fe_{13}Cu$ phase ($Pr_{32.5}Fe_{62}Cu$) at the grain boundary has also been claimed to improve intrinsic coercivity [12]. This antiferromagnetic phase is formed peritetically only in alloys with boron less than 5.5 at% and upon annealing at temperatures around 500 °C [12].

The two-step annealing procedure is necessary to yield hot-pressed $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ magnets with good magnetic properties [5]. Hence, the effects of heat treating praseodymium-containing alloys with compositions $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ and $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ at 1000 °C for 24 h, followed by (or not) annealing at 500 °C for 2 h, on its mechanical properties have been studied. Dynamic mechanical analysis has been used to determine the mechanical properties.

2. Experimental

Two commercial alloys in the as-cast state, and after high- and low-temperature vacuum annealing have been studied. The as-cast ingot alloys were prepared by vacuum induction melting in rectangular ($10 \times 10 \times 0.7\,cm^3$) water-cooled copper mold with a high cooling rate (chill cast). The high-temperature annealing was carried out under vacuum at 1000 °C for 24 h to homogenize and eliminate any free iron (α-Fe) in the alloys [10]. The low-temperature annealing was carried out under vacuum at 500 °C for 2 h to improve the surface features of the magnetic grain boundary phases [10]. Even though the alloy $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ is not appropriate for preparing hot-pressed magnets with good magnetic properties, it was included in this study for comparison. The elastic modulus measurements were carried out in a Netzsch dynamic mechanical analyzer (DMA) in the single cantilever method at an oscillation frequency of 1 Hz (accuracy: 1%). To prepare single cantilever bending-type specimens, thin slices, approximately $25 \times 5 \times 2\,mm^3$, were cut from the alloys (perpendicular to the grain growth direction). This mode requires short specimens but is inappropriate to measure the absolute elastic modulus value. Thus, it was used to measure variations on the elastic modulus. For measurement of absolute values of the elastic modulus three-point bending mode was used. A few samples were tested using this mode due to specimen length ($50 \times 5 \times 2\,mm^3$) requirement. The oscillation amplitude was limited to 15 µm and a heating rate of 3 °C/min was used. The temperature interval used was from room temperature to a maximum of 450 °C and the heating was carried out in air. Microstructural observations were carried out using an optical and a scanning electron microscope.

3. Results and discussion

Figs. 1 and 2 show the variation in elastic modulus with temperature for the as-cast $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ and $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloys. The elastic modulus of the two alloys decreased gradually with increase in temperature up to 265 °C and then increased slightly as the temperature approached 300 °C. It then decreased considerably as the melting temperature of the eutectic Pr–Cu (472 °C) was reached. During cooling, the

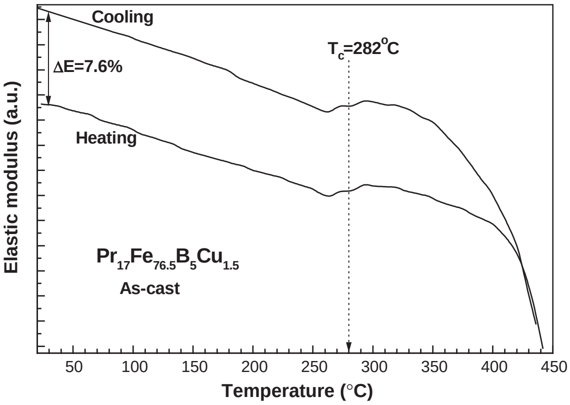

Fig. 1. Variation of elastic modulus with temperature, for the as-cast low-boron PrFeBCu alloy.

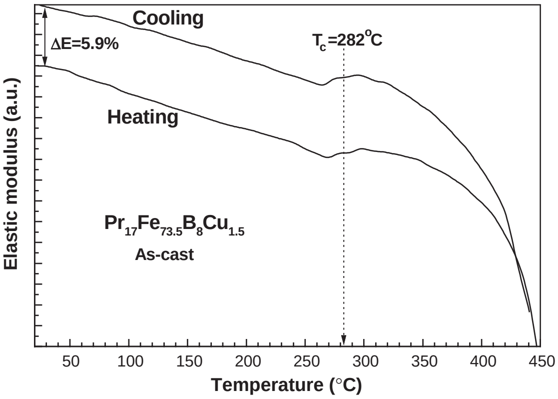

Fig. 2. Variation of elastic modulus with temperature, for as-cast high-boron PrFeBCu alloy.

elastic modulus showed a minimum once again at 265 °C. At room temperature, the elastic modulus is higher by 7.6% for the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy and by 5.9% for the $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy. Absolute values of the elastic modulus for the former and latter at room temperature were (126 ± 13) and (127 ± 13) GPa.

The decreasing monotonic behavior of E, commonly found upon heating a metal, is due to expansion of the crystal lattice. Other factors that could affect the behavior of E in these alloys include: relief of residual stresses in rare-earth alloys; precipitation of excess rare earth from the lattice of the matrix phase or dissolution of rare earth in the ϕ-phase lattice; internal friction anomalies in ferromagnetic material near the Curie point; and oxidation of the rare-earth alloy [13]. Magnetostriction could also play a role in the mechanical behavior of these alloys. The abnormal change in the elastic modulus over T_c is most probably due to precipitation of excess rare earth from the lattice of the matrix phase or dissolution of rare earth in the ϕ–phase lattice [14]. This also could cause the variation of the elastic modulus on cooling to room temperature.

Figs. 3 and 4 show the variation in elastic modulus with temperature, for both alloys, after heat treatment at 1000 °C for 24 h. Behavior similar to that shown in Figs. 1 and 2 was observed after heat treatment at high temperature.

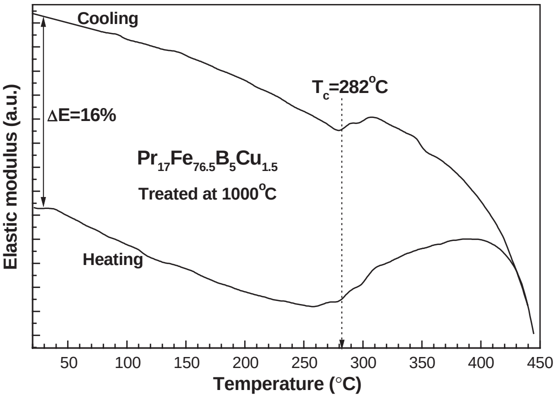

Fig. 3. Variation of elastic modulus with temperature for the low-B alloys annealed at 1000 °C for 24 h.

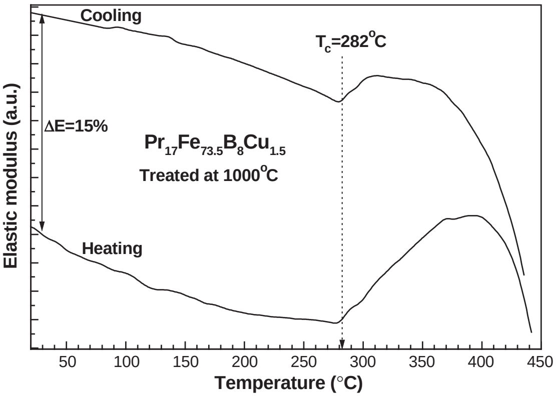

Fig. 4. Variation of elastic modulus with temperature for the high-B alloy annealed at 1000 °C for 24 h.

However, the variation in elastic modulus after cooling to room temperature was about twice that of the as-cast alloy (about 15%). Figs. 5 and 6 show the variation in elastic modulus with temperature for both alloys treated using the two-step heat treatment. In this case a distinct behavior is observed. The $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy showed a significantly higher variation (24%) in the elastic modulus at room temperature after heating and cooling. In contrast, the $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy showed the lowest variation (~4%) in elastic modulus at room temperature. This change in behavior is possibly attributable to the formation of a $Pr_6Fe_{13}Cu$ phase in the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy during the second step of heat treatment or during the testing on the DMA.

The as-cast state of the Pr–Fe–B–Cu alloys is shown in Figs. 7(a) and (b) and is very heterogeneous. Phase analysis indicates that the alloys are composed of the matrix phase $Pr_2Fe_{14}B$ (plate-like grains), copper and praseodymium-rich phases in the grain boundary regions and free iron inside the matrix phase. This is consistent with the peritectic nature of these alloys. The $Pr_{1+\varepsilon}Fe_4B_4$ boride phase (B-rich or η) has been observed only in the as-cast $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy. A comparison between these microstructures reveals that the as-cast $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy shows larger grains of the matrix phase (Φ). Details of the microstructure of these alloys are shown in Figs. 8(a) and (b). The compositions of the various phases found in both as-cast alloys are presented in

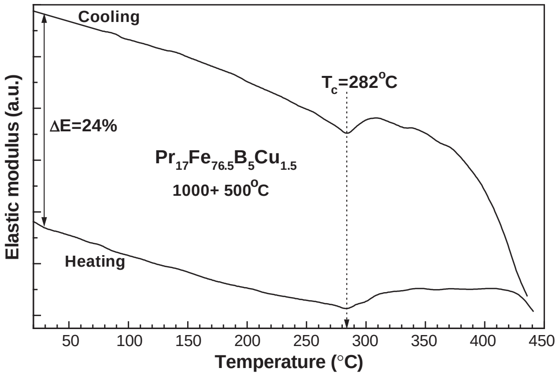

Fig. 5. Variation of elastic modulus with temperature for the low-B alloy annealed at 1000 °C for 24 h and subsequently heated to 500 °C for 2 h.

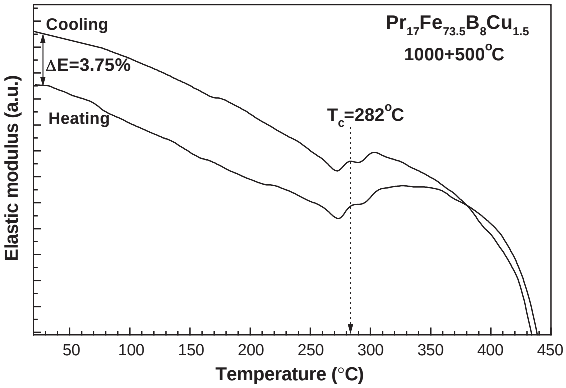

Fig. 6. Variation of elastic modulus with temperature for the B-rich alloy annealed 1000 °C for 24 h and subsequently heated to 500 °C for 2 h.

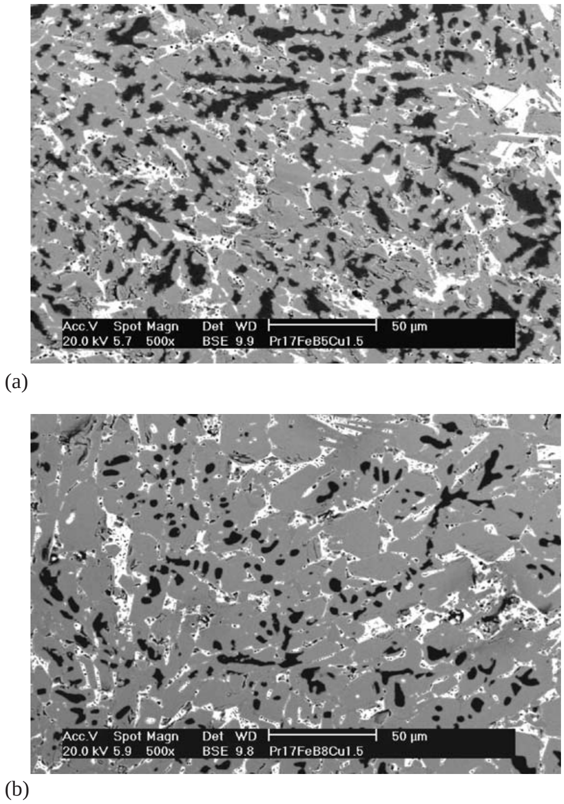

Fig. 7. Backscattered electron image showing a general view of the as-cast microstructure of the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ (a) and $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloys (b).

Table 1. On annealing at 1000 °C for 20 h the α-Fe phase is completely eliminated from the matrix phase in both alloys. After the two-step annealing the boron-rich phase (η) was also found in the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy. Annealing also changed the grain boundary regions of both alloys by producing a finely defined eutectic mixture, as shown in Fig. 9, for the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy. This is in agreement with results of a previous study [10]. The chemical analysis of this eutectic phase is also given in [10]. The $Pr_6Fe_{13}Cu$ phase, if present in the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy after the two-step heat treatment, could not be analyzed by EDX.

The $Pr_{1+\varepsilon}Fe_4B_4$ phase was present in both alloys after annealing at low temperature (greater amount in the $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy). Hence this phase could not be responsible for the substantial variation (opposite) in elastic modulus of both alloys. Formation of the $Pr_{1+\varepsilon}Fe_4B_4$ phase in the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy has been reported previously, in the as-cast condition and after annealing at 1000 °C for 20 h [10]. This study also reported the presence of the B-rich phase after the two-step annealing, 1000 °C for 25 h followed by annealing at 500 °C for 7 h [10]. Since α-Fe is not present in the alloys after annealing it also cannot be responsible for the opposite variation in the elastic modulus.

The increase in intrinsic coercivity of the Pr-based hot pressed magnets was attributed to change in the grain boundary on annealing at low temperature [10]. Change in the grain boundary alone could not be responsible for this marked opposite change in elastic modulus, since it also occurs in both alloys. The formation of a

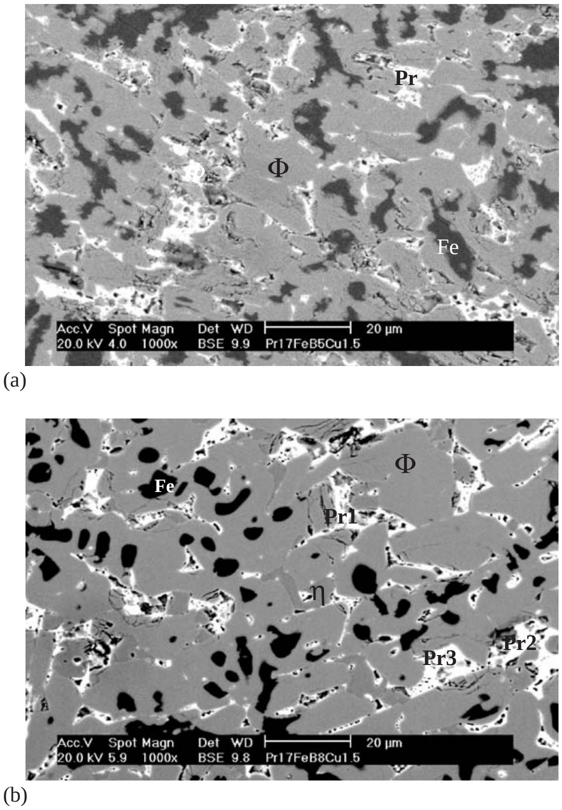

Fig. 8. Backscattered electron image of details of the as-cast microstructure of the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ (a) and $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloys (b).

Table 1
Compositions determined by EDX in the various phases found in the Pr-based as-cast alloys (error bars = ±2 standard deviation)

Alloy	Phase	Pr (at%)	Fe (at%)	Cu (at%)
$Pr_{17}Fe_{76.5}B_5Cu_{1.5}$	Φ ($Pr_2Fe_{14}B$)	13.2±1.1	86.8±0.5	—
	Pr-rich	64.9±0.7	10.5±0.9	24.6±1.0
	α-Fe	1.6±1.0	98.4±0.5	—
$Pr_{17}Fe_{73.5}B_8Cu_{1.5}$	Φ ($Pr_2Fe_{14}B$)	14.9±1.0	85.1±0.7	—
	Pr-rich (area 1)	69.7±0.8	10.8±0.8	19.5±1.1
	Pr–rich (area 2)	46.1±1.0	11.3±0.9	42.6±1.0
	Pr-rich (area 3)	89.6±0.5	9.4±1.3	<1.0
	α-Fe	1.7±1.5	98.3±0.5	—
	η ($Pr_{1+\varepsilon}Fe_4B_4$)	24.4±1.1	73.7±0.6	1.9±1.5

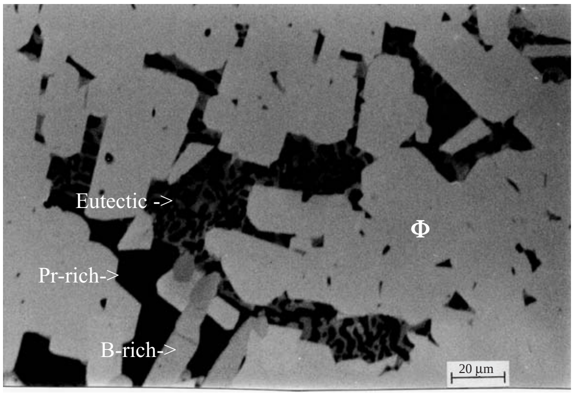

Fig. 9. Optical micrograph showing details of the eutectic mixture of the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy after treatment at 1000 °C followed by annealing at 500 °C.

$Pr_6Fe_{13}Cu$ phase in the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy on annealing at low temperature or during the test in the DMA could alter the diffusion of rare earth on the ϕ-phase lattice and lead to a larger variation in the elastic modulus. Annealing at low temperature the $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy, without formation of a $Pr_6Fe_{13}Cu$ phase and with a greater amount of the B-rich phase, led to a small variation in the elastic modulus. Oxidation during measurements in air on the DMA should be pretty much the same for both alloys (since the amount of praseodymium and copper is identical in both alloys).

4. Conclusions

The standard two-step annealing procedure, essential to obtain the hot-pressed magnets with good magnetic properties, also affects the elastic modulus of the $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy. Annealing at 1000 °C for 24 h affects the elastic modulus of copper-containing Pr-based alloys with 5 and 8 at% B to a lesser extent. The $Pr_{17}Fe_{76.5}B_5Cu_{1.5}$ alloy, which has the appropriate composition for good hot-pressed magnets, showed the highest variation in elastic modulus (24%) after the two-step annealing treatment. The $Pr_{17}Fe_{73.5}B_8Cu_{1.5}$ alloy, which is unsuitable for good hot-pressed magnets, showed the smallest variation in elastic modulus (~4%) after the two-step annealing treatment. Apparently, the distinct behavior of these two alloys is related to the precipitation or dissolution of rare earth in or from the lattice of the matrix phase and to the $Pr_6Fe_{13}Cu$ and $Pr_{1+\varepsilon}Fe_4B_4$ phases changing this process.

Acknowledgments

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