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Microstructural studies on Pr–Fe–B–Cu magnets produced by upset forging of cast ingot

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Abstract

Recent work has shown that Pr–Fe–B–Cu-type permanent magnets have been produced from cast ingot materials using upset forging and that intrinsic coercivity can be enhanced substantially by a post forging heat treatment at 1000°C for 5 h plus 500°C for 3 h. In the present work, the microstructures of both as-upset forged and heat treated magnets have been investigated by optical and by scanning electron microscopy (SEM) in an attempt to explain the origin of this increase in the intrinsic coercivity. Backscattered electron images on the SEM, energy dispersive X-ray analysis (EDX) and thermomagnetic analysis confirm the presence of Pr_2Fe_{17} ($Fe/Pr \approx 8.2$) after the upset forging process and heat treatment at 1000°C. The quantity of this phase is substantially reduced after the second heat treatment at 500°C. In addition a $Pr_{34}Fe_{62}Cu_4$ ($Pr_6Fe_{13}Cu$) phase has also been observed by SEM and EDX analysis after the anneal at 500°C. The increase in the coercivity on annealing has been attributed to the grain boundary improvement isolation and to the reduction in the amount of the Pr_2Fe_{17} phase after heat treatment at 500°C.

Keywords: Microstructural studies; Upset forging; Permanent magnets

1. Introduction

There has been much interest in the development of permanent magnets via hot deformation directly from the as-cast state, without having to resort to powder and other processing routes. Previous work has shown that Pr-based materials can exhibit significant coercivities both in the as-cast state, after annealing and after the deformation process [1–9]. These and other researchers [10] have shown that the magnetic properties of these materials are influenced by degree of deformation, composition, temperature and post forging treatments. Anisotropic $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets with good magnetic properties have been produced from cast ingot materials using an upset forging process [11]. These hot deformed magnets exhibited high coercivities after a post forging heat treatment [12] consisting of a two stage anneal at 1000°C for 5 h and at 500°C for 3 h, this resulted in a substantial increase in the intrinsic coercivity from 1197 kA m^{-1} (15.0 kOe) to around 1595 kA m^{-1} (20.0 kOe). This increase in coercivity has been attributed to the better magnetic hard grains isolation as a result of annealing at 500°C [13]. In the present work, the microstructure of upset forged permanent magnets of the above composition have been investigated using optical microscopy and scanning electron microscopy (SEM) in an attempt to detect the precise phase changes that take place in the material which appears to have a positive effect on the coercivity. Thermomagnetic analysis (TMA) and differential thermal analysis (DTA) have also been employed in these investigations to determine Curie temperatures and to assist in phase determination.

2. Experimental

Alloy ingots were prepared by induction melting the pure constituents under a purified argon atmosphere.

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The alloy was poured into rectangular water cooled copper moulds and several rectangular blocks of cross section 1×1 cm^2 and heights of 2.5–5 cm were cut from the cast ingot. The longest length of specimen was chosen so as to be perpendicular to the copper mould cooling direction, i.e. the columnar grains growth direction was perpendicular to the upset forging direction. The PrFeBCu blocks were inserted into close fitting copper sheaths of wall thickness of approximately 0.3 mm. These sheaths provided some lateral constraint when cracks formed in the sample as well as significantly reducing the rate of evaporation of the praseodymium during the vacuum upset forging procedure.

The upset forging was carried out on a 50 kN ESH mechanical testing machine fitted with a large vacuum chamber and employing four halogen lamps. The machine could be operated in a vacuum of better than 5×10^{-4} mbar over a temperature range of 25–810°C.

Suitable samples ($8 \times 8 \times 5$ mm^3) were cut from the centre of the deformed ingot for magnetic measurements on a Permeameter. The magnetic applied field was parallel to the upset forging direction. The microstructural observations and microanalysis were carried out using an optical microscope, a JEOL 840A scanning electron microscope (+EDX) and a Hitachi S4000 high resolution SEM. In all cases a parallel view to the upset forging direction was analyzed. Thermomagnetic analysis was carried out in a Sucksmith balance, DTA was undertaken using a Linseis LDT2.

3. Results and discussion

Fig. 1 shows the second quadrant demagnetization curves of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet before and after the post upset forging heat treatment. During forging at 750°C, a height reduction of 90% at a strain rate of 8.0×10^{-2} s^{-1} was employed. In the as-upset forged condition (curve 1) quite reasonable magnetic properties are obtained and after annealing at 1000°C for 5 h with a quench to room temperature (curve 2), very little improvement was achieved. However, by further annealing at 500°C for 3 h (curve 3) a 25% increase in the intrinsic coercivity (${}_{i}H_{C}$) was obtained. Small variations in the remanence have also been observed but the origin of these changes has not been the subject of this investigation.

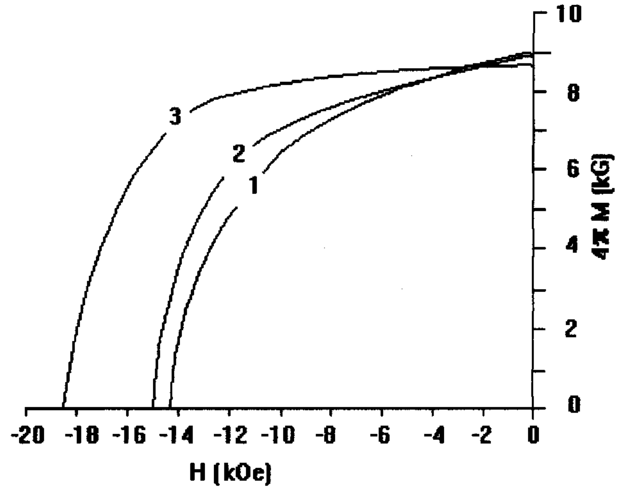

Fig. 1. Second quadrant demagnetization curves of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet: (1) as upset forged; (2) after the heat treatment at 1000°C/5 h; and (3) after the heat treatment at 1000°C/5 h + 500°C/3 h.

These coercivity changes are consistent with earlier work [13] which has shown that most of the free iron, which exists in the alloy in its cast form and is detrimental to the magnetic properties, is removed during the upset forging process at 1000°C. Indeed, no significant increase in the ${}_{i}H_{C}$ after high temperature annealing at 1000°C was observed in these magnets upset forged at 1000°C.

In the present work a lower forging temperature (750°C) was used with the expectation that dendritic free iron might have been present after the upset forging process. This was not the case however, as almost no iron was observed in the upset forged material and only a small increase in ${}_{i}H_{C}$ was achieved after the 1000°C high temperature heat treatment. It seems therefore that the act of deformation during the upset forging procedure accelerates the dissolution of iron into the microstructure presumably by the transgranular cracking of grains and the exposure of the iron to the Pr rich liquid intergranular eutectic as proposed by Kwon et al. [4]. In other words a combination of ~1000°C heat treatment + upset forging at 750°C produces a similar effect as at 1000°C in terms of the elimination of dendritic free iron.

It has also been shown [13] that lower temperature annealing at 500°C of magnets upset forged at 900°C was beneficial to the magnetic properties and this fact also was the case for upset forged magnets processed at 750°C. This improvement with annealing at 500 ^{0}C was attributed previously [13] to the modification of the grain boundary caused by heating to just above the melting point of the grain boundary eutectic phases.

Fig. 2 shows the microstructure of the as-upset forged, heat treated at 1000°C, $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet in the etched condition. The sample was etched because the contrast between the different phases and grain boundaries was improved in this condition. In this state, the upset forged magnets contained a grey phase identified by EDX as Pr_2Fe_{17} which appears within the matrix phase (Fig. 2).

The microstructure of the as-upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet in the as-polished condition is shown in Fig. 3(a), and the microstructures of this magnet after annealing at 1000°C for 5 h + 500°C for 3 h

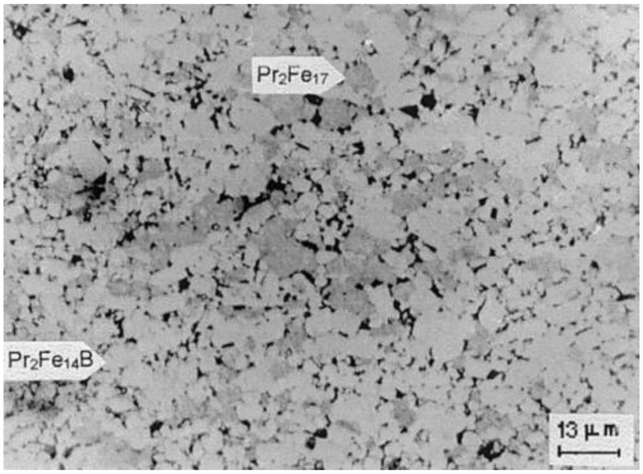

Fig. 2. Optical microstruture of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet heat treated at 1000°C/5 h. Etched with Nital 5%/10 s.

Fig. 3(b) and (c), only shows the matrix phase ($Pr_2Fe_{14}B$) and Pr-rich regions. As discussed above, the free iron which existed inside of the matrix phase in the as-cast alloy is almost not detected in this magnet. After a heat treatment at 1000°C, Fig. 3(b), the magnet exhibited the same microstructure and a comparison between the demagnetization curves is shown in Fig. 1 indicating that very little change has taken place. There is, however, a significant change in the microstructure after annealing at 500°C (Fig. 3(c)) which is consistent with the observed increase in the intrinsic coercivity. Fig. 4 is a polarized light micrograph of this last condition and, in this microstructure the presence of a $Pr_{34}Fe_{62}Cu_4$ phase is observed. This phase was also confirmed by SEM and EDX analysis, in addition to the grain boundary eutectic phase. This could indicate that the presence of the non ferromagnetic Pr-rich material together with the newly formed $Pr_{34}Fe_{62}Cu_4$ phase, reported as $Pr_6Fe_{13}Cu$ antiferromagnetic phase [14], has enhanced the coercivity by creating an microstructure which offers resistance to the detrimental effects of reverse magnetic fields.

Fig. 5 shows a back scattered electron image of the as-polished upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet after annealing at 1000 + 500°C. In this figure, the presence of a dark phase (the grey phase when viewed optically, Fig. 2) is detected; EDX analysis indicated that the matrix phase exhibited an Fe:Pr ratio of about 7:1 and this dark phase an Fe:Pr ratio ≈ 8.2, indicating a 2:17 type phase. Its occurrence is much less pronounced than in the heat treated at 1000°C condition and it appears to be in the form of isolated grains surrounded by white (Pr-rich) and grey ($Pr_{34}Fe_{62}Cu_4$) phase. This could indicate another reason for the increase of the intrinsic coercivity after this second heat treatment because the magnetically soft 2:17 phase appears to have been reduced in quantity and is largely magnetically isolated. This is consistent with previous studies [15], which have shown that in sintered magnets of the $Pr_{17}Fe_{83-x}B_x$-type, the magnetically soft Pr_2Fe_{17} phase always occurs when x is less than 5. The equivalent Nd_2Fe_{17} magnetically soft phase has also been found in Nd based sintered magnets with similar compositions [15–17]. It has been shown [16] that the amount of this phase was reduced with a high tempera-

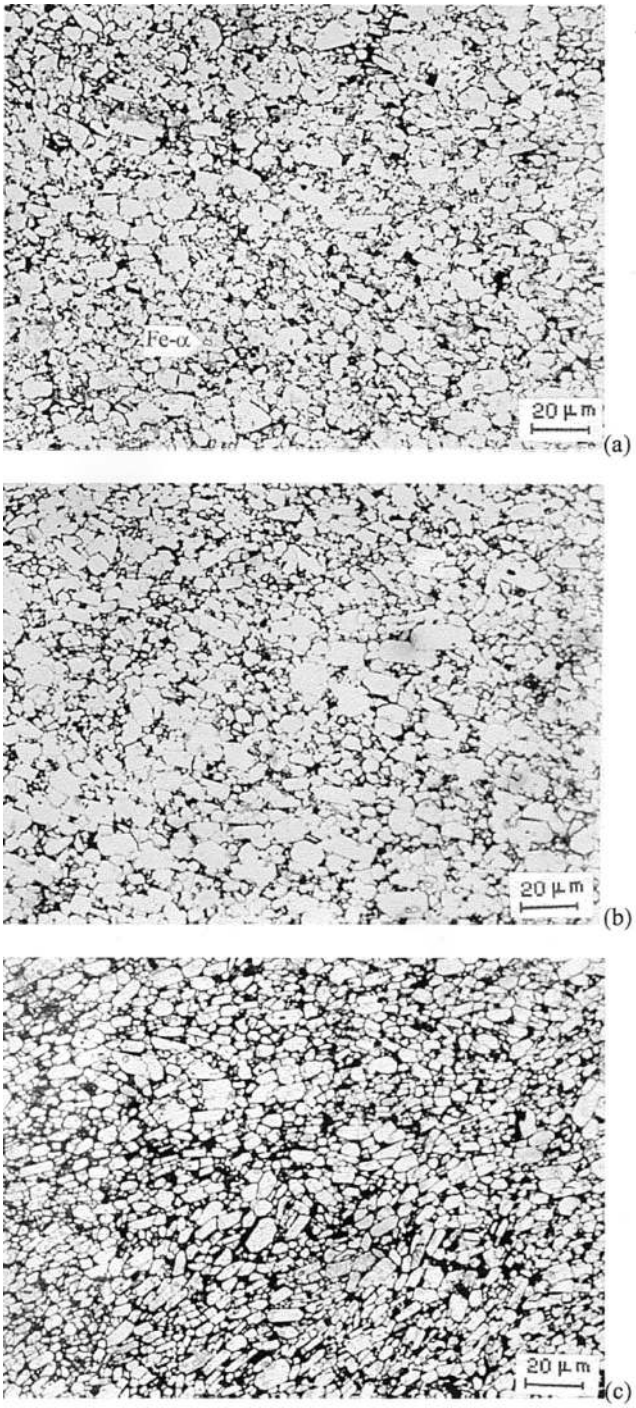

Fig. 3. Optical microstrutures of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet: (a) as upset forged; (b) after the heat treatment at 1000°C/5 h; and (c) after the heat treatment at 1000°C/5 h + 500°C/3 h.

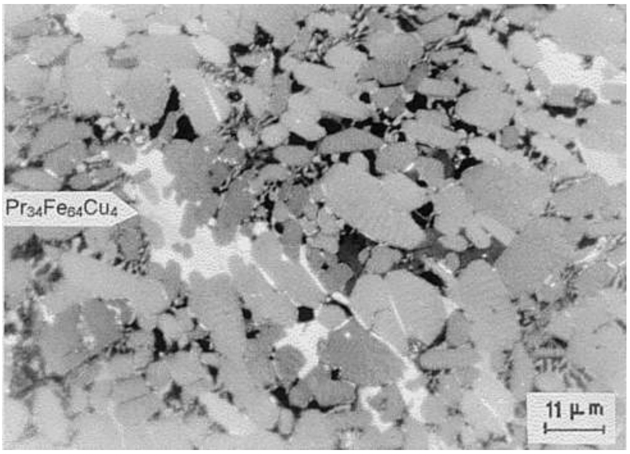

Fig. 4. Optical microstruture of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet after the heat treatment at 1000°C/5 h + 500°C/3 h (polarized light).

ture heat treatment leading to significant improvements in the intrinsic coercivity. In the present study the amount of 2:17 phase was observed to diminish during the low temperature heat treatment at 500°C, as indicated by the thermomagnetic results in Fig. 6(a)–(d).

A thermomagnetic analysis curve of the cast $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ ingot is shown in Fig. 6(a), and this indicates a Curie point of the matrix phase 293 ± 5°C, consistent with earlier reports [18–20]. There was a significant change in the TMA traces after the forging process and after the heat treatment of the upset forged magnet at 1000°C (Fig. 6(b) and (c)). The TMA curves show, that, in addition to the matrix phase, there was evidence of a phase with a lower Curie point of around 37°C. The Pr_2Fe_{17} phase has a reported Curie point in this range of temperatures (10–37°C) [15,21,22]. This in combination with the optical metallography, SEM and EDX studies confirms the presence of the Pr_2Fe_{17}

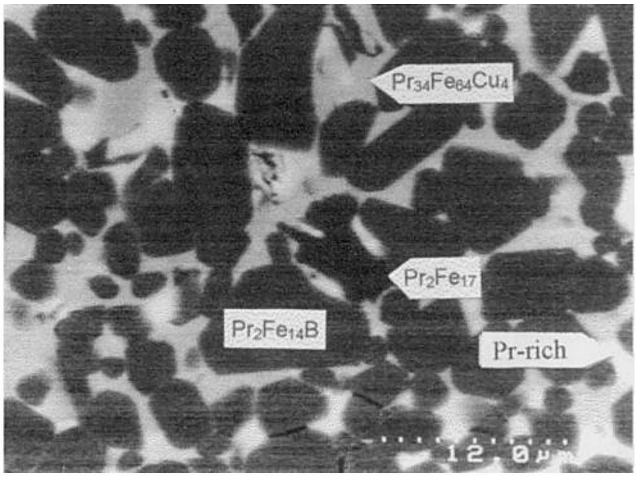

Fig. 5. Scanning electron microscopy (SEM) microstruture of an upset forged $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet after the heat treatment at 1000°C/5 h + 500°C/3 h.

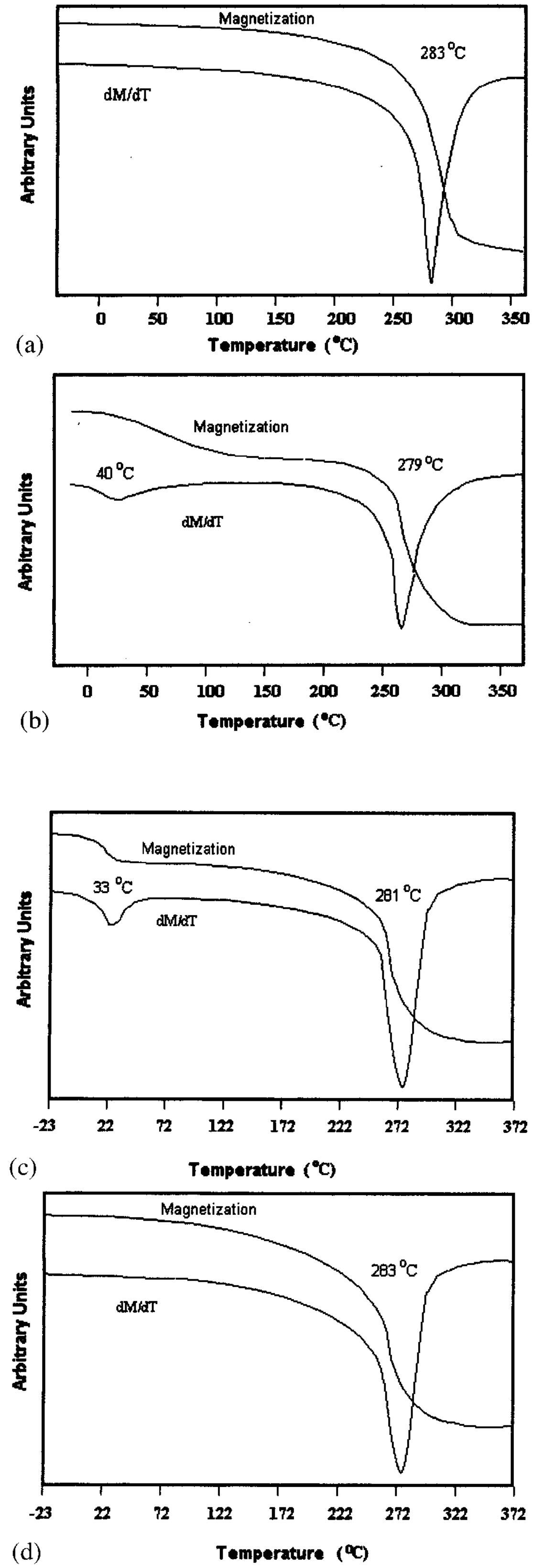

Fig. 6. Thermomagnetic curves of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnets: (a) as cast condition; (b) as upset forged; (c) after the heat treatment at 1000°C/5 h; and (d) after the heat treatment at 500°C/3 h.

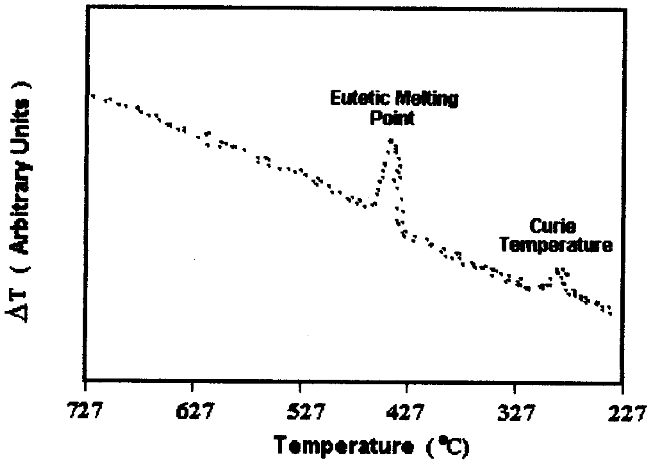

Fig. 7. Differential thermal analysis (DTA) (the cooling curve) results of the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ magnet after forging and heat treatment at 1000°C/5 h + 500°C/3 h.

phase. Fig. 6(d) shows that for the 1000 + 500°C condition, this phase did not appear in significant quantities, in good agreement with the SEM observations.

The Curie temperature of the matrix phase for the upset forged magnet after heat treatment at 1000 + 500°C determined by DTA (the cooling curve) was found to be 287°C (see Fig. 7), and it is in good agreement with that determined by TMA (Fig. 6(d)). At around 447 ± 7°C (Fig. 7), a small peak was observed at a similar temperature to that reported to be the melting temperature of the Pr–Cu eutectic grain boundary phase [20,23].

4. Conclusions

In its as cast state the $Pr_{20.5}Fe_{73.8}B_{3.7}Cu_2$ alloy contains basically three phases: the $Pr_2Fe_{14}B$ matrix phase, dendritic free iron and a eutetic mixture at the matrix grain boundaries which we refer to as the Pr-rich intergranular phase. After the material is subjected to the upset forging procedure at 750°C, the material undergoes a structural, microstructural and magnetic transformation. The material is partly crushed and partly deformed resulting in the formation of a refined grain structure, the dissolving away of the dendritic iron, and the formation of small quantities of the Pr_2Fe_{17} phase. At this stage the material is now in the form of a hard, anisotropic permanent magnet. Subsequent annealing at 1000°C for 5 h has little effect on the magnetic properties or the distribution of phases but promotes densification via the healing of cracks formed during the upset forging procedure. Heat treatment at 500°C for 3 h results in a substantial improvement in intrinsic coercivity as a result of the formation of $Pr_{34}Fe_{62}Cu_4$ ($Pr_6Fe_{13}Cu$) phase at the expense of the Pr-rich phase in the intergranular region. This, together with what appears to be improved isolation of the matrix ($Pr_2Fe_{14}B$) and Pr_2Fe_{17} grains explains the much improved coercivity after the 500°C heat treatment.

Acknowledgements

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