EFFECT OF POST-SINTERING ANNEALING TREATMENT ON MAGNETIC PROPERTIES OF SOME Nd-Fe-B BASED MAGNETS

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Abstract Effects of post-sintering annealing treatment between 300 and 1000ºC for up to 8 hrs time periods followed by either furnace cooling (FC) or air-cooling (AC) on the hard magnetic properties of some Nd-Fe-B based sintered magnets was investigated. It was shown that the intrinsic coercivity (H_{ci}), second quadrant demagnetization loop shape and thus the energy density $(BH)_{max}$ varied considerably as a result of the annealing treatment. However, no significant changes occurred in the remanence (J) values of the magnets. Annealing at 500ºC for 1 hr followed by FC resulted in a considerable deterioration in the demagnetization loop shapes and thus in $(BH)_{max}$ values in all the magnets. These changes were almost recoverable. By annealing at 500ºC, followed by AC, no deterioration in the demagnetization loop shape occurred for any of the magnets and thus there were some increases in $(BH)_{max}$ values of the magnets due to increase in their H_{ci} values. The highest H_{ci} in magnets A and C was obtained by a standard annealing treatment for 1 hr at 600ºC, while in magnet B, the highest H_{ci} occurred after an annealing treatment for 2 hrs at 500ºC, both followed by AC. No deterioration in the demagnetization loop shape was identified for any of the magnets either in FC or AC from 600ºC. However, the coercivity enhancement in magnet A and in particular, in magnet B, was found to be much higher after AC than FC. In all the annealing treatments, the improvement in H_{ci} and/or $(BH)_{max}$ values occurred in the first 1 or 2 hrs of annealing. Any further annealing beyond these times resulted in significant falls in the magnetic properties. Thus, long term annealing for up to 300 hrs at 400ºC resulted in dramatic reductions in the hard magnetic properties, which could only be partially recovered. This behavior has been related to the oxidation of the magnets during long term annealing in a roughing pump vacuum. In this paper, the changes in H_{ci} and $(BH)_{max}$ values during these annealing treatments are related to possible microstructural changes reported elsewhere.

Key Words Nd-Fe-B Based Permanent Magnets, Post-Sintering Annealing Treatment, Intrinsic Coercivity, Remanence, Energy Density, Demagnetization Loop Shape

چکیده بررسی تاثیر عملیات حرارتی بازپخت بعد از تفجوشی بین دماهای سیصد و هزار درجه سانتیگراد در زمانهای مختلف تا هشت ساعت و سردکردن بعدی در کوره (FC) یا هوا (AC) بر خواص مغناطیسی تعدادی از آهنرباهای تفجوشی‌شده با پایه Nd-Fe-B نشان داد که عملیات بازپخت، نیروی وامغناطیسی و شکل منحنی مغناطیس زدائی ربع دوم و درنتیجه چگالی انرژی مغناطیسی آهنربا را بطور قابل ملاحظه ای تغییر می‌دهد؛ اما با این عملیات هیچ تغییر قابل توجهی درمقادیر پسماند مغناطیسی بوقوع نمی‌پیوندد. بازپخت آهنربا در دمای پانصد درجه سانتیگراد بمدت یک ساعت و سردکردن بعدی در کوره، باعث تخریب قابل ملاحظه شکل منحنی مغناطیس زدائی و انرژی مغناطیسی شد. این تغییر غالبا قابل اصلاح بود. با بازپخت آهنرباها در دمای پانصد درجه سانتیگراد و سرد کردن بعدی در هوا، منحنی مغناطیس زدایی هیچ افتی نشان نداد. در ضمن بالاترین مقادیر $(BH)_{max}$ آهنرباها، در اثر افزایش H_{ci}، اندکی اضافه شد. بالاترین H_{ci} در آهنرباهای A و C با اعمال عمل بازپخت استاندارد در دمای ششصد درجه سانتیگراد بمدت یک ساعت حاصل شد؛ درحالیکه در آهنربای B، بالاترین H_{ci} در نتیجه اعمال بازپخت در دمای پانصد درجه سانتیگراد بمدت دو ساعت حاصل شد. در هر دو مورد، سردکردن آهنرباها در هوا انجام گرفت. هیچ تخریبی در شکل منحنیهای مغناطیس زدایی در هیچیک از آهنرباها در اثر بازپخت در ششصد درجه سانتیگراد و سرد کردن بعدی در کوره یا هوا ملاحظه نشد. اما با سرد کردن آهنرباها بعد از بازپخت در هوا، افزایش H_{ci} در آهنربای A و بالاخص آهنربای B، بمراتب بیشتر از سردکردن بعدی در کوره بود. همچنین در تمامی عملیات بازپخت ملاحظه گردید که بهسازی در مقادیر H_{ci} و یا $(BH)_{max}$ در آهنربای A و مخصوصا در آهنربای B در اثر سرد کردن بعدی آهنرباها در هوا بمراتب بیشتر از سرد کردن آنها در کوره است. در تمامی عملیات بازپخت مشاهده شد که اصلاح در مقادیر H_{ci} و $(BH)_{max}$ در یک یا دو ساعت اول عملیات انجام می‌شود. افزایش مدت بازپخت به بیش از یک یا دو ساعت، باعث افت قابل توجه در خواص مغناطیسی آهنرباها شد. بنابراین بازپخت طولانی بمدت تا سیصد ساعت در دمای چهارصد درجه سانتیگراد باعث افت شدید در خواص مغناطیسی سخت آهنرباها گردید. این افت فقط بطور نسبی قابل اصلاح بود. این رفتار به اکسید شدن آهنربا در طول عملیات بازپخت طولانی تحت خلا با درجه نسبی پایین ارتباط داده شد. در این مقاله، تغییر در مقادیر H_{ci} و $(BH)_{max}$ حین عملیات بازپخت به تغییر ریز ساختار گزارش شده در مقالات قبلی مرتبط گردیده است.

INTRODUCTION

The intrinsic coercivity (H_{ci}) of Nd-Fe-B based sintered magnets has proved to be strongly dependent on their thermal history [1-7]. It has been shown that post sintering annealing treatments have in general a beneficial effect on the coercivity and that the coercivity could even be doubled, in comparison to that of the as-sintered values, by a suitable heat treatment process [1]. It has also been reported that there is a decrease in H_{ci} when the magnet is slowly cooled in the temperature range of 450-650°C, after the post sintering annealing treatments [7]. Since in general, the coercivity is very dependent upon the microstructure, thus there must be important microstructural changes occurring during these thermal treatments, which in turn influence the coercivity [8]. It is now well known that the coercivity in these magnets is controlled predominantly by nucleation of reverse domains [9], which occur preferentially at grain boundaries. A number of investigations have been undertaken to explain the changes in H_{ci} enhancements during the heat treatment processes [8-16]. Thus, the increase in H_{ci} due to the post sintering annealing treatments has been related to the changes in the structures and compositions of the minor phases, which exist at grain boundaries, such as the Nd-rich phase(s) [10-16]. An f.c.c. crystal structure was reported for the Nd-rich grain boundary phase by Ramesh et al. [9-11] and in addition to f.c.c. Nd-rich phase, Knoch et al. [14] and Tang et al. [15] reported h.c.p and d.h.c.p. (double hexagonal closed packed) grain boundary phases respectively. Yang et al. [16] have recently investigated a $Nd_{15}Fe_{77}B_8$ type sintered magnet and found that the occurrence of a d.h.c.p. Nd-rich phase at grain boundaries, during a post sintering cyclic heat treatment, is essential in developing a high H_{ci} value in this magnet. In a recent investigation in a Cu-containing $Nd_{17}Fe_{76}B_5Cu_{1.5}$ type sintered magnet [17-23], a two-step heat treatment process was developed in order to increase the H_{ci} values in these magnets. Microstructural studies [19-21] revealed that the appearance of a non-magnetic $Nd_6Fe_{13}B_1$ type phase at the grain boundaries was responsible for the coercivity enhancements in these magnets, during the heat treatment processes.

The present experiment has been undertaken in order to study the effect of post sintering annealing treatments at temperatures between 300 and 1000°C, followed by either furnace cooling (FC) or air cooling (AC) (both in vacuum) on the permanent magnetic properties of these types of commercial type sintered magnets. The main aim of this work were: 1) to establish an optimal annealing treatment for each magnet under conditions similar to those usually employed in industry, in order to develop the full H_{ci} and energy density $[(BH)_{max}]$ values in these magnets and 2) to establish possible recovery procedures for degraded magnetic properties and 3) to relate the changes in magnetic properties to reported changes in the microstructure.

EXPERIMENTAL PROCEDURE

The composition of the commercial type grade sintered magnets (identified as magnets A, B, and C), employed in this work are summarized in Table 1 together whit the mean values of density, surface are, and thickness. The magnets had been sintered at 1070°C for 1 hr followed by FC to room temperature (RT).

In each experiment, three separate magnets of one of each composition (i.e. A, B, or C) were annealed at temperatures between 300 and 1000°C inclusively, for 1, 2, 4, and 8 hrs under a roughing pump vacuum and were then either furnace cooled (F-cooled) or air cooled (A-cooled) to RT. The

TABLE 1. Nominal Compositions and Mean Values of Density, Surface Area and Thickness in the Sintered Magnets.

Magnet	Nominal Composition	Density (gr/cm^3)	Surface Area (cm^2)	Thickness (cm)
A	$Nd_{12.6}Dy_{2.6}Nb_{0.5}Fe_{75.9}A1_{1.2}B_{7.2}$	7.59	0.55	0.565
B	$Nd_{14.0}Dy_{1.4}Nb_{0.5}Fe_{76.5}Al_{0.6}B_{7.0}$	7.55	3.14	0.314
C	$Nd_{14.1}Dy_{0.6}Nb_{0.3}Fe_{77.9}Cu_{0.1}A1_{0.7}B_{6.4}$	7.57	0.37	0.227

Note: Results are the average of 3 samples.

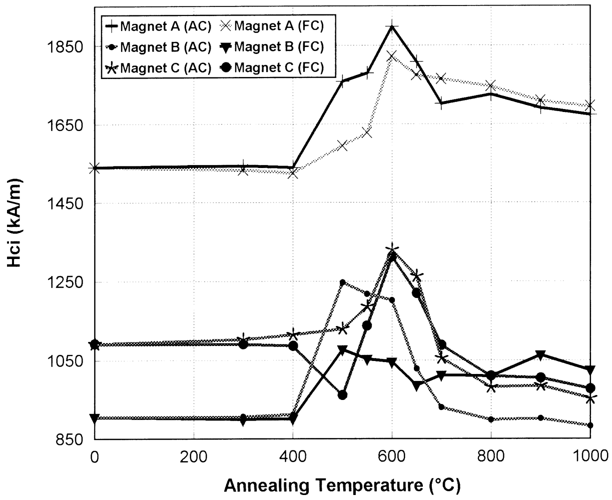

Figure 1. Variations of H_{ci} values with annealing temperature (t = 1hr) in magnets A, B and C. H_{ci} values at 0°C correspond to as-sintered values.

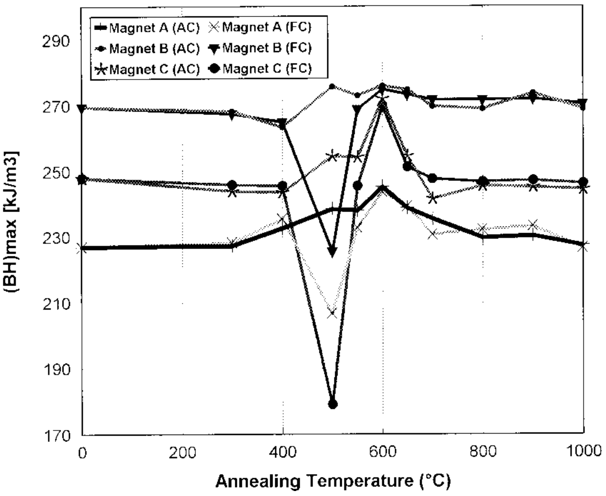

Figure 2. Variations of $(BH)_{max}$ values with annealing temperature (t = 1 hr) in magnets A, B and C. $(BH)_{max}$ values at 0°C correspond to as-sintered values.

roughing pump vacuum (~10^{-2} bar) was employed in order to provide a condition similar to that normally used in industry. Some of the magnets were also annealed at 300 or 400°C for up to 300 hrs in order to investigate the effect of long term annealing on the magnetic properties of the magnets.

After each annealing treatment, both the surfaces of the magnets were polished and the density of the magnets was determined using Archimedes principles. The magnets were then pulse magnetized using a LDJ pulse magnetizer and their permanent magnetic properties measured using a permeameter.

RESULTS AND DISCUSSION

Plots of the variations in H_{ci} and $(BH)_{max}$ values in magnets A, B, and C with annealing temperatures (1 hr at each annealing temperature) are shown in Figures 1 and 2, respectively. While annealing the magnets at the lower temperatures of 300 or 400°C for 1 hr, did not bring about any significant changes in any of the permanent magnetic properties, some pronounced changes occurred in H_{ci} and $(BH)_{max}$ values, on annealing for 1 hr at each of the temperatures between 500-1000°C and in particular between 500-650°C (Figures 1-2). Similar results have been reported for the effects of post sintering annealing treatments [12] on the intrinsic coercivity of water quenched Nd-Fe-B based magnet.

The remanence values (J) remained almost constant at around 1085, 1170, and 1140 mT for the magnets A, B, and C, respectively, after annealing for 1 hr, in all the annealing treatments. Thus, it can be concluded that the remanence in the Nd-Fe-B based sintered magnets is almost independent of any post sintering annealing treatments. This is consistent with the dependence of the remanence in these sintered magnets, on the initial composition, average grain size and its distribution, the degree of alignment of the grains, and the density of the magnets [24], and these should not be affected significantly by transformations in minor phase(s) during subsequent annealing treatments.

Annealing for 1 hr at 500°C, followed by either AC or FC, resulted in a large increase in H_{ci} for magnets A and B, while almost no change (upon AC) and a significant reduction (upon FC) was obtained in H_{ci} for magnet C (Figure 1). The different behavior in magnet C upon annealing at 500°C could be related to presence of a small amount of Cu in this magnet. It has already been shown that the Cu-containing Nd-Fe-B based alloys behaved differently during annealing at

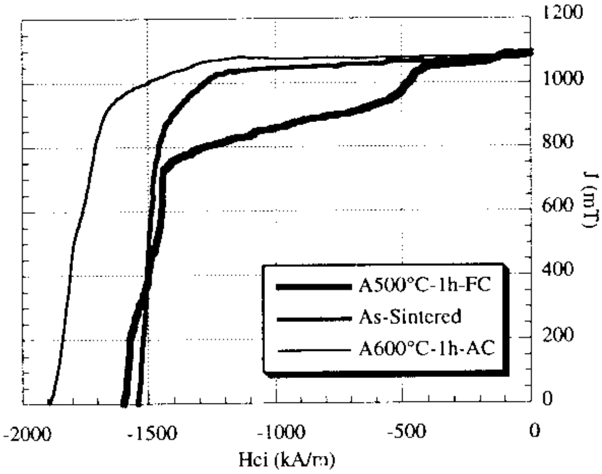

Figure 3. Demagnetization curves of magnet A in as-sintered state, annealed at 500°C for 1 hr and then F-cooled, and annealed at 600°C for 1 hr and then A-cooled.

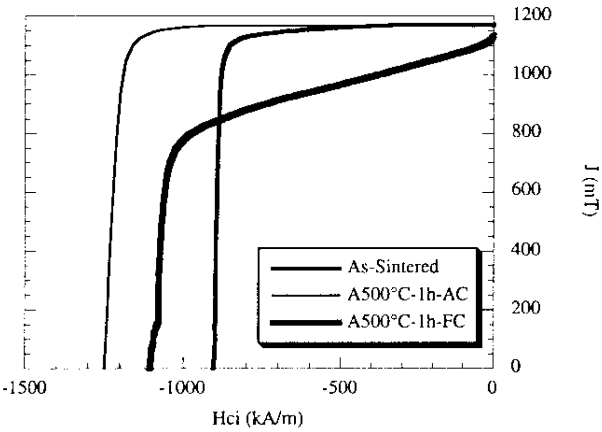

Figure 4. Demagnetization curves of magnet B in as-sintered state, annealed at 500°C for 1 hr and then F-cooled, and annealed at 600^{0}C for 1 hr and then A-cooled.

500°C [18,22,23].

Interesting features of the annealing at this temperature can be summarized as follows:

1) The increase of H_{ci} in magnets A and B, after annealing for 1 hr at 500°C, was considerably higher, when followed by AC rather than FC (Figure 1).

2) Considerable reduction in $(BH)_{max}$ values observed for all the magnets, upon FC from this annealing temperature (Figure 2), while, in comparison to $(BH)_{max}$ values in as-sintered state,

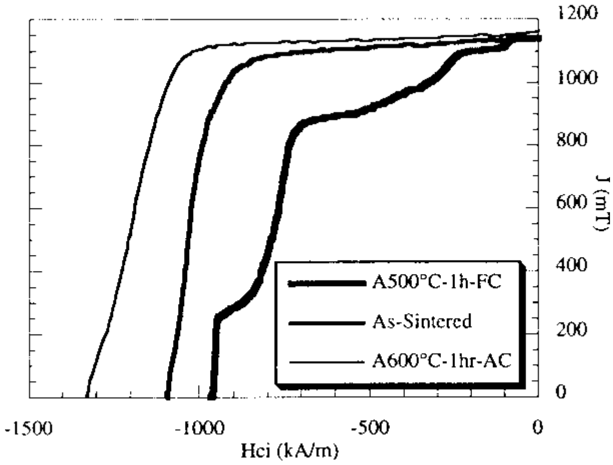

Figure 5. Demagnetization curves of magnet C in as-sintered state, annealed at 500°C for 1 hr and then F-cooled, and annealed at 600^{0}C for 1 hr and then A-cooled.

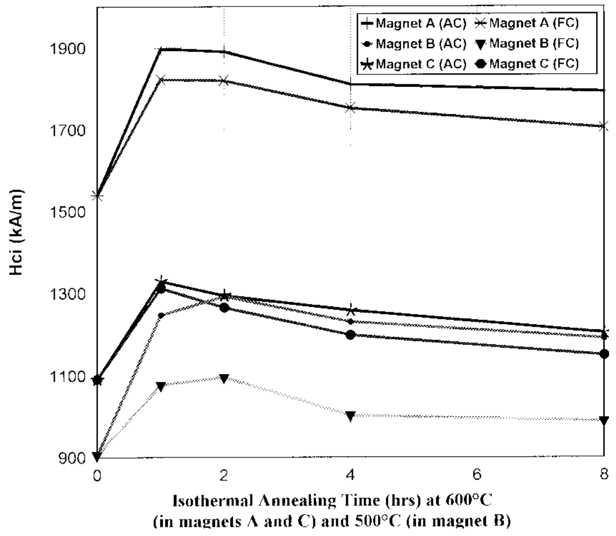

Figure 6. Variations in H_{ci} values with isothermal annealing time at 600°C in magnets A and C, and at 500°C in magnet B. H_{ci} values at time 0 correspond to as-sintered values.

some increases in $(BH)_{max}$ values occurred in all the magnets upon AC, following the annealing treatment for 1 hr at 500°C (Figure.2); however, in the case of magnet B, this treatment resulted in the highest H_{ci} and $(BH)_{max}$ values within this magnet (Figures.1,2). Annealing the magnets at 550-650°C for 1 hr, resulted in almost similar effects on H_{ci} , as annealing at 500°C for magnets A and B, however, the highest H_{ci} in magnets A and C

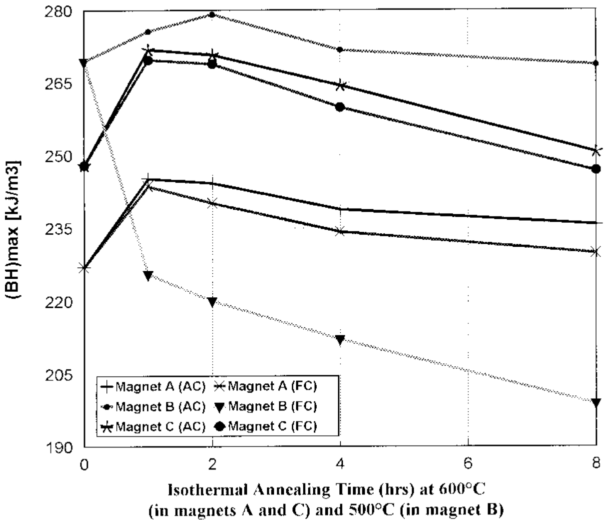

Figure 7. Variations in $(BH)_{max}$ values with isothermal annealing time at 600ºC in magnets A and C, and at 500ºC in magnet B. $(BH)_{max}$ values at time 0 correspond to as-sintered values.

obtained upon annealing for 1 hr at 600°C, while as it has been already mentioned the highest H_{ci} in magnet B was achieved in annealing at 500°C, following AC. The rate of cooling from the annealing temperatures of 500-650°C was found to influence the H_{ci} values of magnets A and B, i.e., AC after annealing treatments at these temperatures, resulted in the higher H_{ci} values, compared with FC (Figure 1), while no significant changes occurred in the H_{ci} values of magnet C upon either FC or AC from these temperatures (Figure 1). However, unlike annealing at 500°C, the demagnetization loop shapes in the magnets remained almost unchanged compared with those of as-sintered magnets, as a result of either FC or AC after annealing at 550-650°C.

Annealing the magnets for 1 hr at each of the temperatures: 700, 800, 900 and 1000°C, brought about some pronounced increases in H_{ci} values of magnet A, some slight increase in H_{ci} values of magnet B and some slight reduction in H_{ci} values of magnet C (Figure 1). The different behavior of magnet C due to annealing at these temperatures, can be again attributed to presence of a minor amount of Cu in this alloy.

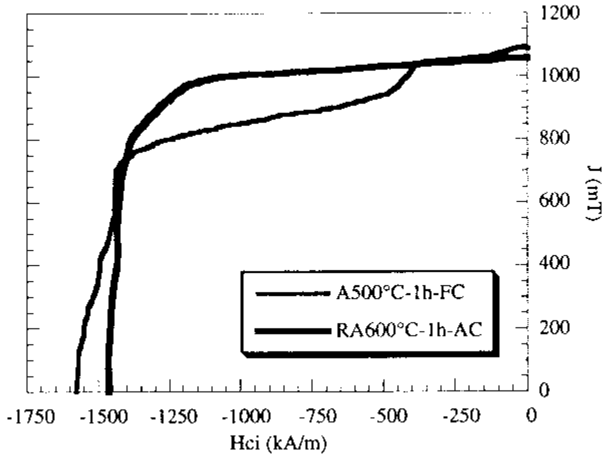

Figure 8. Demagnetization curves of magnet A in annealed condition at 500ºC for 1 hr, followed by FC, and after re-annealing at 600ºC for 1 hr, followed by AC.

The interesting features of annealing at these temperatures is that, unlike annealing at 500-650°C, particularly 500°C, FC after the annealing treatments at these temperatures, brought about slightly higher H_{ci} values than after AC. The temperature range of 500-650°C was therefore found to be crucial from the point of developing the hard magnetic properties within the magnets. Thus, among the annealing temperatures investigated in this work, the optimum temperatures were 500°C for magnet B and 600°C for magnets A and C, both followed by AC to RT, from annealing temperatures.

The second quadrant demagnetization curves of magnets A, B, and C, in the as-sintered states, annealed for 1 hr at 600°C (in the case of magnets A and C) and at 500°C (in the case of magnet B), followed by AC to RT (as an optimal annealing treatment) and annealed for 1 hr at 500°C, followed by FC to RT (as an undesirable annealing treatment) are compared in Figures 3, 4, and 5, respectively.

Variations in the H_{ci} and $(BH)_{max}$ values of magnets A and C with isothermal annealing time at 600°C and those of magnet B with isothermal annealing time at 500°C are shown in Figures 6 and 7, respectively. In the case of magnets A and C, an isothermal annealing

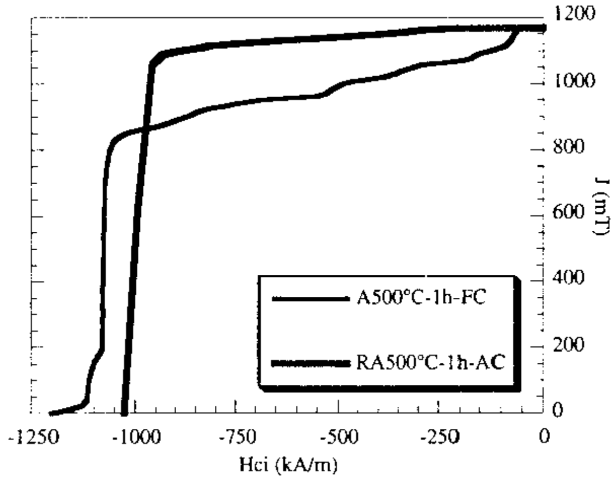

Figure 9. Demagnetization curves of magnet B in annealed condition at 500°C for 1 hr, followed by FC, and after re-annealing at 500°C for 1 hr, followed by AC.

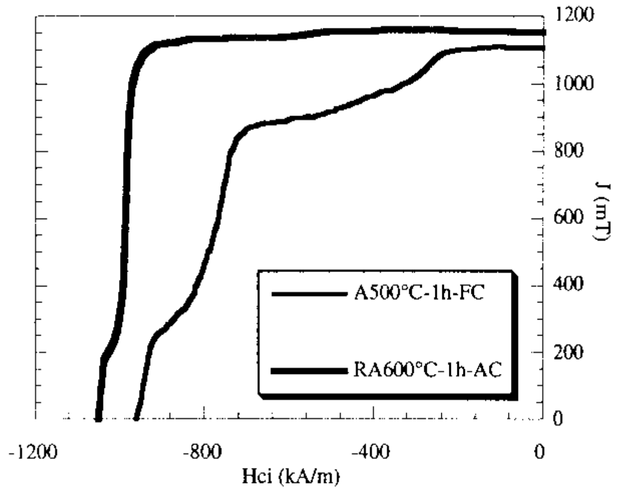

Figure 10. Demagnetization curves of magnet C in annealed condition at 500°C for 1 hr, followed by FC, and after re-annealing at 600°C for 1 hr, followed by AC.

time of 1 hr at 600°C and in the case of magnet B, an isothermal annealing time of 2 hrs at 500°C, brought about the highest H_{ci} and $(BH)_{max}$ values. Further annealing of the magnets A and C beyond 1 hr at 600°C, or magnet B beyond 2 hrs at 500°C, resulted in slight and continuous decrease in the H_{ci} and $(BH)_{max}$ values. The reductions in H_{ci} and $(BH)_{max}$ values upon increasing the annealing times, could be related to gradual oxidation of the grain boundary phase(s) which is expected to occur in a rotary pump vacuum, during extension of the annealing periods. Oxidation of the Nd-rich grain boundary phase(s) has been shown to reduce the local magnetocrystalline anisotropy and to provide easy nucleation sites for reverse domains [12], thus reducing the H_{ci} and $(BH)_{max}$ values.

By re-annealing the magnets A, B and C, which had already been annealed at 500°C for 1 hr and subsequently F-cooled to RT, at 500°C (in magnet B) or at 600°C (in magnets A and C) for 1 hr, followed by AC to RT, the deterioration in the second quadrant demagnetization loop shapes were recovered and permanent magnetic properties similar to those of as-sintered states were obtained (Figures 8, 9, and 10). This behavior could be interpreted in terms of the reversal of the structural changes which has been reported to occur in the minor Nd-rich grain boundary phase(s) during annealing treatments and the subsequent cooling processes with different cooling rates [16]. Thus, improvements in H_{ci} values during annealing at 500°C (in magnet B) or 600°C (in magnets A and C), following AC, or deterioration in $(BH)_{max}$ values of the magnets during annealing at 500°C, following FC, could be related to the presence of Nd-rich grain boundary phase(s) with either a d.h.c.p. or f.c.c. structure, respectively [16]. Therefore with regard to the present work, it might be argued that, during the annealing treatment at 500°C, only a partial transformation of the Nd-rich phase occurred which was completed during the following cooling processes. So, it could be proposed that during FC after annealing at 500°C, most of the Nd-rich phase appears with an f.c.c. structure, while upon AC from this temperature, the majority of Nd-rich phase transforms to a d.h.c.p. structure. However, on annealing at 500-650°C, it might be argued that most of the transformation to d.h.c.p. form, occurred during annealing treatments and perhaps only a small remaining fraction of this phase forms during the

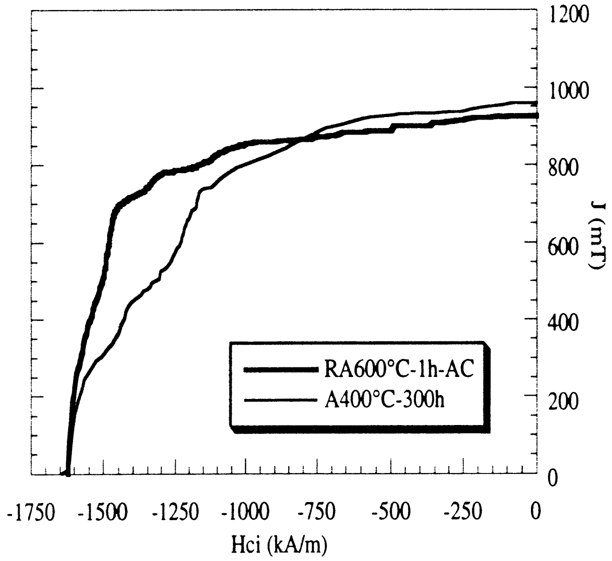

Figure 11. Demagnetization curves of magnet A in long term annealed condition at 400°C for 300 hr and after re-annealing at 600°C for 1 hr, followed by AC.

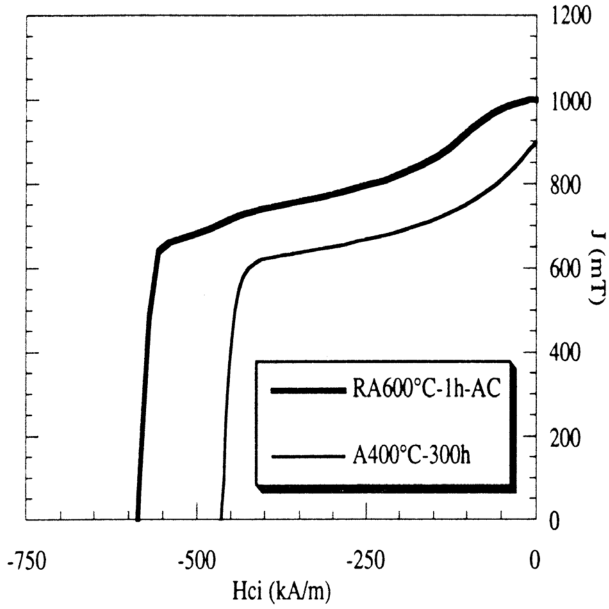

Figure 12. Demagnetization curves of magnet B in long term annealed condition at 400°C for 300 hr and after re-annealing at 600°C for 1 hr, followed by AC.

subsequent cooling process. Therefore, during FC, the precipitates are likely to form with an f.c.c. structure, while after AC the Nd-rich phase exists in the d.h.c.p. form.

Annealing the magnets at 300 or 400°C for up to 300 hrs, brought about only very small reductions in the magnetic properties at 300°C, and dramatic reductions in the magnetic properties at 400°C. Pronounced changes in the magnetic properties upon long term annealing at 400°C, occurred in first 100 hrs of annealing; further annealing up to 300 hrs only resulted in slight further reductions in the magnetic properties.

The second quadrant demagnetization curves of magnets A, B, and C, in annealed conditions at 400°C for 300 hrs and after re-annealing at 500°C (magnet B) or 600°C (magnets A and C) for 1 hr, followed by AC, are shown in Figures 11-13, respectively.

The most important features of the long term annealing at 400°C were as follows:

1) Among other magnetic properties, the J values were also reduced significantly during these treatments (Figures 11-13). This could mean that the main cause of deterioration in the magnetic properties during long term annealing at 400°C, was essentially oxidation of both the Nd-rich grain boundary phase(s) as well as the hard magnetic $Nd_2Fe_{14}B_1$ type matrix phase.

2) By re-annealing the previously annealed magnets (at 400°C for 300 hrs), at 500°C (magnet B) or 600°C (magnets A and C) for 1 hr, followed by AC, only a very small recovery in the magnetic properties was obtained (Figures 11-13). This might be considered as a further indication that oxidation is the main cause of the reductions in the magnetic properties.

CONCLUSIONS

1) The temperature range of 500-650°C is the optimal annealing temperature range following by AC to RT. This is reconfirmation of results obtained on other magnet compositions by previous investigators [1-13].

2) The lack of any changes in the magnetic

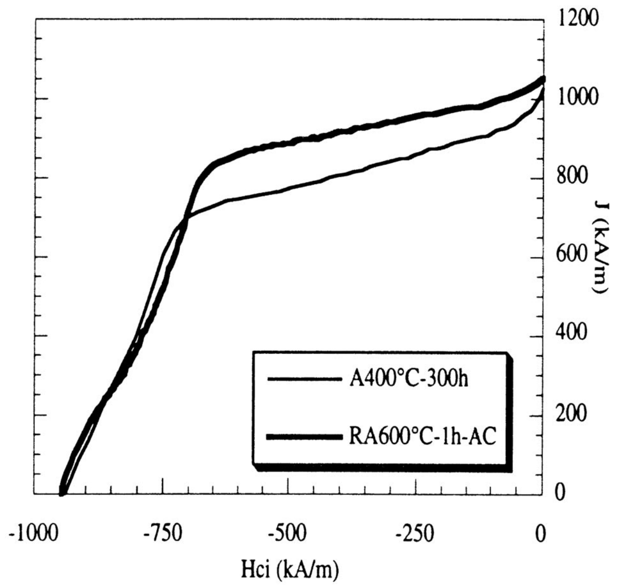

Figure 13. Demagnetization curves of magnet C in long term annealed condition at 400°C for 300 hr and after re-annealing at 600°C for 1 hr, followed by AC.

properties of the magnets, on annealing at 300-400°C for one hour, means that no magnetically deleterious phase transformations occur at and during cooling from these temperatures.

3) The crucial effect of the cooling rate, on the magnetic properties of the magnets, after annealing at 500°C, could mean that most of the transformations occur during the subsequent cooling process. Thus, it might be proposed that during annealing at 500°C, only a small proportion of the Nd-rich phases, possibly with a favorite d.h.c.p. structure precipitates and the majority of precipitates will form during the subsequent cooling process with either a favorite d.h.c.p. structure upon AC, or an unfavorable f.c.c. structure upon FC, to RT. In annealing at 550-650°C, it is believed that the dominant precipitation process performs during annealing itself rather than during the subsequent cooling process. Therefore, a Nd-rich phase is proposed to form with either a dominant d.h.c.p. structure on AC or a dominant f.c.c. structure on FC.

4) Annealing at 700-1000°C is thought to bring about precipitates mainly during the annealing treatment with both d.h.c.p. and f.c.c. structures. Thus, either some improvements or reductions occur in the magnetic properties of the magnets upon annealing in this temperature range.

5) Effects of annealing treatment at 500° C on the H_{ci} value of magnet C, which was different compared with those of magnets A and B, can be attributed to the minor presence of Cu in this magnet. It has been reported that a very small amount of Cu influences considerably the H_{ci} of the Nd-Fe-B based magnets, on the subsequent annealing treatment [25,26].

6) Recovery of the magnetic properties of the magnets which were previously annealed at 500°C for 1 hr and then F-cooled, during a re-annealing treatment at 500 or 600°C for 1 hr, following AC, proves that the nature of precipitates plays a crucial role in developing the hard magnetic properties. This means that during re-annealing treatments, following AC, the precipitates form predominantly with a d.h.c.p. structure and so recovers the magnetic properties [16].

7) The falls in the permanent magnetic properties of the magnets upon long term annealing at 400° C for 300 hrs, which were only partially recoverable, showed that the main cause of falls in these treatments was due to oxidation of the Nd-rich grain boundary phase(s) as well as the $Nd_2Fe_{14}B_1$ type matrix phase. Oxidation of the 2:14:1 type phase has already been shown to reduce the magnetocrystalline anisotropy of this phase locally [12] and thus reduce the properties.

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