$Nd_2Fe_{14}C$ processed by the hydrogenation, disproportionation, desorption and recombination (HDDR) process

Nd$_2$Fe$_{14}$C processed by the hydrogenation, disproportionation, desorption and recombination (HDDR) process

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Abstract. The hydrogenation, disproportionation, desorption and recombination (HDDR) process has been employed to produce Nd$_2$Fe$_{14}$C-based permanent magnets. The master alloys for HDDR are Nd$_2$Fe$_{14}$C-based alloys which are obtained by annealing mechanically alloyed (MA) Nd$_{16}$Fe$_{75}$C$_9$ powder at 850 °C. The disproportionation reaction at 850 °C results in the formation of an intimate mixture of Nd-hydride, α-Fe and Nd$_2$Fe$_2$C$_3$. On desorbing the hydrogen at the same temperature, different constituents recombine to form the thermodynamically stable Nd$_2$Fe$_{14}$C and the Nd-rich phase, depending sensitively on recombination time and slightly on hydrogenation time. The phases obtained by HDDR at 950 °C consist of Nd$_2$Fe$_{17}$C$_x$, α-Fe, the Nd-rich phase and Nd$_2$C$_3$, whereas those obtained at 700 °C are of Nd$_2$Fe$_{17}$C$_x$, the Nd-rich phase and a small amount of α-Fe. For comparison, the Nd$_2$Fe$_{17}$C$_x$-based alloys have also been processed by HDDR, in which more α-Fe and Nd-rich phases are found to coexist with Nd$_2$Fe$_{14}$C after recombination at the same temperature. The Nd$_2$Fe$_{14}$C-based alloy made by MA in conjunction with HDDR has better magnetic properties than that made by MA only.

1. Introduction

The hydrogenation, disproportionation, desorption and recombination (HDDR) process has been employed to produce highly coercive Nd$_2$Fe$_{14}$B-based powder. The disproportionation reaction of the coarse-grained Nd$_2$Fe$_{14}$B phase results in α-Fe, Nd-hydride and Fe$_2$B. The recombination of the above constituents causes the formation of the thermodynamically stable Nd$_2$Fe$_{14}$B with submicron grain size [1–7]. Grain refinement is the main reason for the change in magnetic properties. The kinetics of the disproportionation and the recombination reaction depend on alloy composition, initial microstructure, temperature and hydrogen pressure. The presence of a Nd-rich phase can accelerate the disproportionation and recombination reaction [7]. HDDR has been used successfully to prepare Sm$_2$Fe$_{17}$N$_x$ and NdFe$_{10}$Mo$_2$N$_x$ magnets with improved maximum energy product and intrinsic coercivity [8, 9].

The intrinsic magnetic properties of Nd$_2$Fe$_{14}$C are comparable with those of Nd$_2$Fe$_{14}$B, but it is difficult to obtain Nd$_2$Fe$_{14}$C by annealing the melt-spun precursors or the

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castings [10–12]. Recently, we have synthesized $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$ successfully by mechanical alloying (MA) and subsequent annealing [13]. In this paper, both $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$-based alloys obtained by MA and subsequent annealing are used as the initial alloys for HDDR. Effects of time and temperature of hydrogenation and dehydrogenation on structure, phase transformation and magnetic properties are studied systematically.

2. Experimental procedure

At first, mechanically alloyed nominal $Nd_{16}Fe_{75}C_9$ powders were prepared from 99.5% pure Nd and Fe powders, 99.7% carbon powder, with average particle sizes of 300, 5 and 0.3 μm respectively. The MA was performed in a high energy ball mill under a pure argon atmosphere for 5 h. The $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$-based alloys, obtained by annealing the MA powder at 850 and 1050 °C respectively, were used as the master-alloy for HDDR. Secondly, the $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$ based alloys were hydrided at temperatures between 700 and 950 °C for periods between 10 min and 2 h. To facilitate the experiments, the hydrogen pressure is kept at 1.3 atm during the hydrogenation process. Then the hydrided alloy was degassed at the same temperature for 8 min–2 h. X-ray diffraction (XRD) analysis was performed using Cu K_α radiation with a Rigaku D/max-ra diffractometer equipped with a graphite crystal monochromator. Bonded samples of cylindrical shape were prepared by embedding the Nd-Fe-C powders in epoxy resin, hysteresis loops were measured in a pulsed field magnetometer in fields up to 8 T. The magnetization was related to the amount of magnetic powders, neglecting the dilution effect of resin and the density of the Nd-Fe-C alloys was assumed to be 7.6 g cm^{-3}. Initial AC susceptibility measurement was performed to determine Curie temperatures of the phases in the Nd-Fe-C alloys; it was also employed to verify whether $Nd_2Fe_{17}C_x$ or $Nd_2Fe_{14}C$ phases exist in the alloys.

3. Results and discussion

3.1. Reaction mechanism of HDDR in $Nd_2Fe_{14}C$ compound

3.1.1. Hydrogenation and disproportionation. Figure 1 shows the XRD patterns of (a) the MA $Nd_{16}Fe_{75}C_9$ powder annealed at 850 °C, (b) followed by hydrogenation at 850 °C for 90 min, degassing at the same temperature for (c) 8 min and (d) 60 min. It is shown that $Nd_2Fe_{14}C$ can be formed perfectly with a small amount of the Nd-rich phase and Nd_2C_3 by annealing the MA $Nd_{16}Fe_{75}C_9$ powder at 850 °C for 35 min.

When the $Nd_2Fe_{14}C$-based alloy is exposed to hydrogen at 850 °C for 90 min, it decomposes into a mixture that consists of fine Nd hydride, α-Fe and $Nd_2Fe_2C_3$. Actually, a 10 min duration of hydrogenation at 850 °C is long enough to complete the disproportionation process. Such a short time requisite for the disproportionation of Nd-Fe-C alloys may be caused by the fine grain size and the presence of the Nd-rich phase. The particle sizes of $Nd_2Fe_{14}C$-based master-alloy range from 0.5 to 4 μm, the average grain size is 90 nm determined by Scherrer's method. After HDDR treatment at 850 °C (hydrogenation for 90 min and degassing for 60 min) the particle sizes range from 0.5 to 5 μm and the average grain size is 90 nm. The fine grain of the master-alloy leads to a substantial interface, which acts as a hydrogen diffusion path and nucleation site for the disproportionation reaction, thus a higher disproportionation reaction rate is expected. For coarse-grained $N_2Fe_{14}B$-based alloys, it is reported that the disproportionation reaction begins at the Nd-rich/$Nd_2Fe_{14}B$ boundaries and proceeds towards the centre of the original grains [14], so the presence of the Nd-rich phase contributes to the disproportionation reaction too.
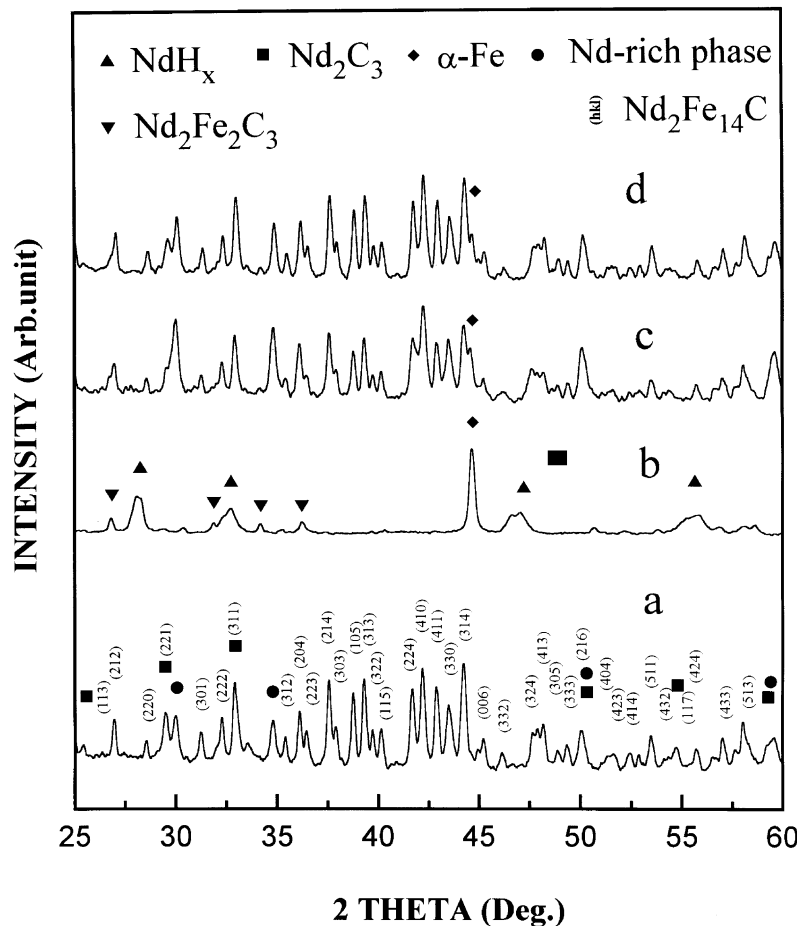
Figure 1. XRD patterns of (a) the MA $Nd_{16}Fe_{75}C_9$ powder annealed at 850 °C, (b) followed by hydrogenation at 850 °C for 90 min, degassing at the same temperature for (c) 8 min and (d) 60 min.

Our experiments show that MA and annealed binary Fe_3C compounds, do not exist in hydrogen at a temperature of 850 °C. Hydrogen reacts with carbon to form CH_4 and only α-Fe is left. Therefore, Nd in $Nd_2Fe_2C_3$ is a crucial element to reserve the carbon in the alloy. The lattice parameters of the hexagonal $Nd_2Fe_2C_3$ phase are $a = 8.59$ Å and $c = 10.48$ Å which differ a little from those formed in MA or melt-spun samples with $Nd_2Fe_{14}C$ as the main phase [12, 13]. This suggests that compositional deviation takes place in this hexagonal phase.

Within the experimental temperature range (700–950 °C) both $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$-based alloys decompose into the same phases, namely, Nd hydride, α-Fe and $Nd_2Fe_2C_3$. It is also found that a $Nd_2Fe_{14}C$-based alloy takes about the same time as that for a $Nd_2Fe_{17}C_x$-based alloy to reach a complete disproportionation and both alloys are fully disproportionated after being exposed to hydrogen at 650 °C for 30 min. A higher temperature can accelerate the disproportionation within the experimental temperature range. All the above mentioned results indicate that the disproportionation does not depend on the initial phase and the microstructure of Nd-Fe-C alloys made by MA.

3.1.2. Desorption and recombination process. It can be seen from figure 1 that a great amount of $Nd_2Fe_{14}C$ is formed on desorbing the hydrogen at 850 °C for 8 min, which means that the recombination reaction rate is very high at the initial stage of desorption. Actually, the desorption and the recombination processes take place simultaneously and it is hard to distinguish one from the other, the high reaction rate is caused by the extremely high chemical activity of the newly born Nd atom resulting from the dissociation of the hydride NdH_x. Meanwhile, the Nd-rich phase is formed during the recombination reaction, which indicates that the formation of both the $Nd_2Fe_{14}C$ and Nd-rich phases are energetically feasible. $Nd_2Fe_{17}C_x$ and α-Fe are present along with the hard magnetic phase. The $Nd_2Fe_{17}C_x$ phase is most probably formed during the cooling process because the formation of $Nd_2Fe_{14}C$ is energetically preferred to that of $Nd_2Fe_{17}C_x$ at 850 °C [11]. When the recombination time (t_r) increases to 60 min, the amount of the Nd-rich phase and α-Fe decrease whereas that of $Nd_2Fe_{14}C$ increases and the $Nd_2Fe_{17}C_x$ phase disappears. When t_r increases up to 90 min, α-Fe still exist in the alloy. One can conclude that the recombination reaction is nearly finished when $t_r = 60$ min since the excessive prolongation of time contributes little to the formation of $Nd_2Fe_{14}C$.

3.2. Phase transformation

3.2.1. Phase transformation by HDDR at different temperatures. When the hydrogenation and desorption times are fixed at 90 and 60 min, respectively, it is found that the temperature range of 800–900 °C is suitable for synthesizing $Nd_2Fe_{14}C$ by HDDR, which is much smaller than that of the Nd–Fe–B alloy under the same treatment [2]. Beyond this temperature range, $Nd_2Fe_{17}C_x$ is present in the samples. For example, the $Nd_2Fe_{14}C$-based alloy processed by HDDR at 750 °C contain $Nd_2Fe_{17}C_x$ when $t_r = 60$ min, hardly any phase transformation from $Nd_2Fe_{17}C_x$ to $Nd_2Fe_{14}C$ or $Nd_2Fe_{14}C$ to $Nd_2Fe_{17}C_x$ could be observed by XRD or thermomagnetic analysis with further extension of recombination time, even for $t_r = 120$ min. One possible reason is that, at the initial stage of desorption, the formation of $Nd_2Fe_{14}C$ can be easily achieved by atom diffusion within a short distance at the expense of Nd hydride, α-Fe and $Nd_2Fe_2C_3$. At the same time, a Nd-rich phase is formed which may separate $Nd_2Fe_{14}C$ from other phases, consequently, the diffusion distance is increased greatly and the formation-rate of $Nd_2Fe_{14}C$ is reduced drastically. So the phase transformations are too slow to be detected at 750 °C when $t_r > 60$ min.

Figures 2 and 3 respectively demonstrate XRD patterns and χ_{AC} versus temperature curves of $Nd_2Fe_{14}C$-based alloy hydrided at different temperatures for 90 min, and then degassed at the above mentioned temperatures for 60 min, respectively. The alloy synthesized by HDDR at 950 °C consists of $Nd_2Fe_{17}C_x$, large amounts of α-Fe, the Nd-rich phase and Nd_2C_3, whereas that obtained at 700 °C consists of $Nd_2Fe_{17}C_x$, a Nd-rich phase and small amount of α-Fe. This indicates that the formation of $Nd_2Fe_{17}C_x$ at higher (or lower) temperature is energetically preferred to that of $Nd_2Fe_{14}C$. The Curie temperature of $Nd_2Fe_{17}C_x$ obtained at 750 °C is 85 °C and that obtained at 950 °C amounts to 180 °C, suggesting that more carbon is dissolved in the interstitial sites of Nd_2Fe_{17} at 950 °C than at 700 °C [15]. Because the diffusion rates of Nd, Fe, C and H atoms increase with increasing temperature [8], the disproportionated mixture of $Nd_2Fe_{14}C$-based alloy obtained at 950 °C consists of grains of a larger size than that obtained at 750 °C, excessive coarsening of grains at higher temperature greatly reduces the interfaces between Nd hydrides, α-Fe and $Nd_2Fe_2C_3$. As the interfaces among the three phases are the only sites where the recombination reaction can take place, great amounts of α-Fe are left in the alloy processed at 950 °C.
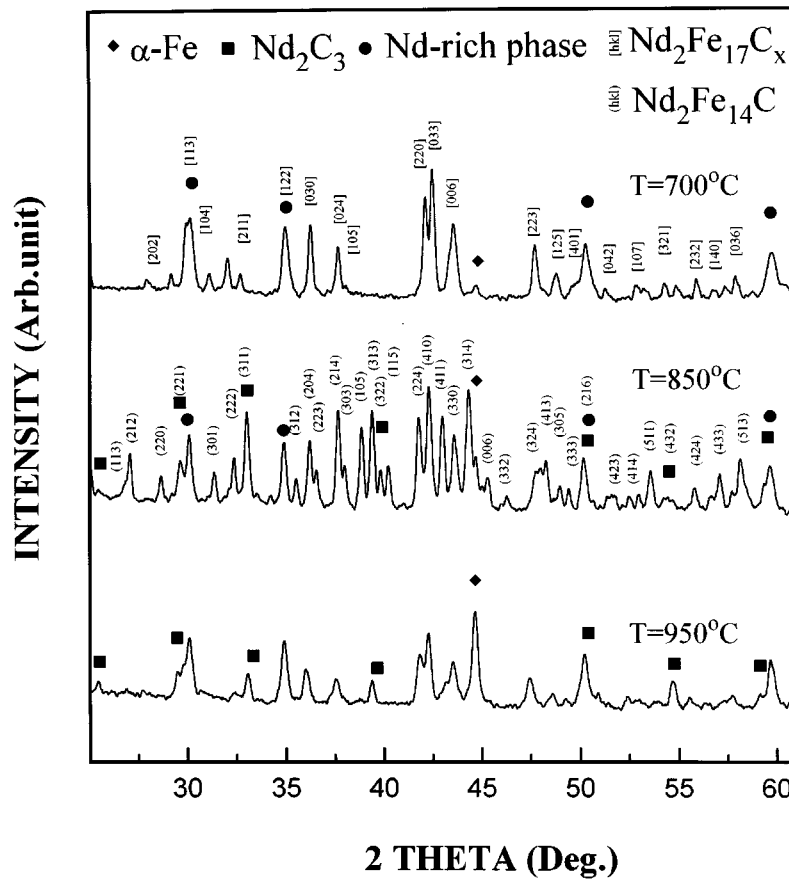
Figure 2. XRD patterns of $Nd_2Fe_{14}C$-based alloy hydrided at 700, 850 and 950 °C for 90 min, then the hydrided compounds were degassed at the above mentioned temperatures for 60 min.

3.2.2. Phase transformation at 850 °C after hydrogenation for different times and degassing for 10 min.

As the hydrogenation time increases to 90 or 120 min, the Nd-hydride, α-Fe and $Nd_2Fe_2C_3$ grow coarse because the average diffusion length of Nd, Fe, and C atoms increases with time. On desorbing the hydrogen for 10 min and cooling down to room temperature, all the alloys hydrided at 850 °C for 10, 90 and 120 min respectively consist of α-Fe, $Nd_2Fe_{17}C_x$, $Nd_2Fe_{14}C$ and the Nd-rich phase. Because the main XRD peaks of $Nd_2Fe_{17}C_x$ and $Nd_2Fe_{14}C$ overlap each other, it is hard to calculate the relative amount of these phases by x-ray analysis. This means that the same kind of final phases are obtained in the alloy after HDDR treatment regardless of hydrogenation time, although the relative amount of these phases may differ from each other.

3.3. Magnetic properties of the $Nd_2Fe_{14}C$-based alloy prepared by MA in conjunction with HDDR

$Nd_2Fe_{14}C$-based master-alloy can be obtained by vacuum annealing to MA $Nd_{16}Fe_{75}C_9$ at 850 °C for 35 min. When the master-alloy is hydrided at 850 °C for 90 min and degassed at the same temperature for 60 min, one gets a $Nd_2Fe_{14}C$-based alloy again. Hardly any

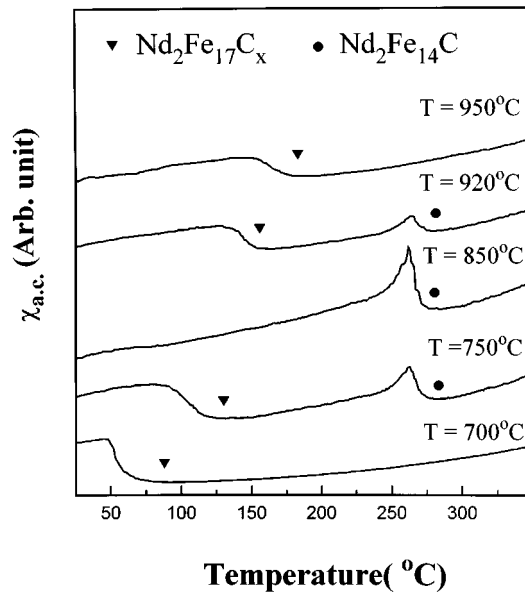**Figure 3.** χ_{AC} versus temperature curves of $Nd_2Fe_{14}C$-based alloy hydrided at different temperatures for 90 min, then the hydrided compounds were degassed at the above mentioned temperatures for 60 min.

α-Fe can be observed in the master-alloy whereas the HDDR processed alloy has a small amount of α-Fe due to the difficulty of further recombination. The HDDR processed alloy has more Nd-rich phase than the master-alloy. The intrinsic coercivity value of the HDDR processed alloy is 8.0 kOe which is higher than that of the master-alloy ($_iH_c$ = 5.6 kOe). The maximum energy product of the HDDR processed alloy increases a little although the remanence is slightly lower than that of the master-alloy. It was reported that the homogeneously distributed nonmagnetic Nd-rich phase in the Nd-Fe-B alloy is advantageous to its coercivity [16–18]. One may expect that more Nd-rich phases in the latter alloy means more complete separation of the $Nd_2Fe_{14}C$ grains which increases the expansion field of the reversed domain and decreases the magnetostatic coupling field between the hard magnetic grains [16, 17]. Thus the microstructure improvement introduced by the HDDR process is responsible for the increment of magnetic properties.

Figure 4 gives the hysteresis loops of $Nd_2Fe_{14}C$-based samples synthesized by (a) MA in conjunction with HDDR (t_r = 8 min), (b) MA and annealing at 850 °C, (c) MA in conjunction with HDDR (t_r = 60 min). The hydrogenation temperature is 850 °C, t_r denotes the recombination time. It is shown that the dehydrogenation time is crucial to the phase formation and the magnetic properties. When the dehydrogenation time is long enough, $Nd_2Fe_{14}C$-based alloys prepared by MA in conjunction with HDDR have better magnetic properties than that made by MA only.

For comparison, a $Nd_2Fe_{17}C_x$-based alloy is processed simultaneously by HDDR under the same procedure adopted by $Nd_2Fe_{14}C$-based alloys. It is found that a $Nd_2Fe_{17}C_x$-based alloy processed by HDDR has more α-Fe and Nd-rich phases than that obtained from the $Nd_2Fe_{14}C$-based alloy, thus lower magnetic properties are achieved. Although the same products of disproportionation are obtained from $Nd_2Fe_{14}C$ and $Nd_2Fe_{17}C_x$-based alloys
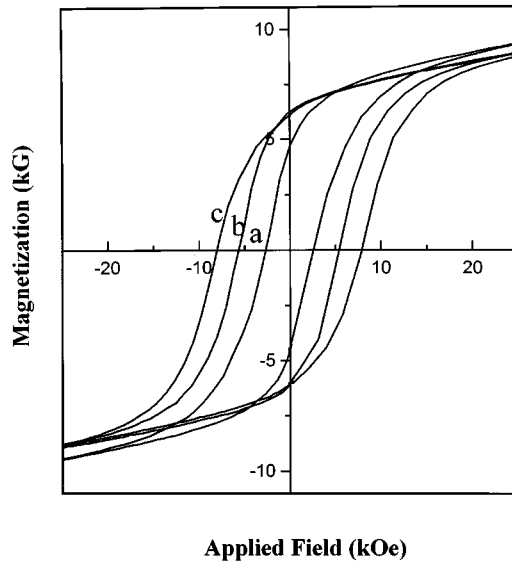
Applied Field (kOe)

Figure 4. Hysteresis loops of Nd$_2$Fe$_{14}$C-based sample synthesized by (a) MA in conjunction with HDDR ($t_r = 8$ min), (b) MA and annealing at 850 °C, (c) MA in conjunction with HDDR ($t_r = 60$ min). The hydrogenation temperature and time are 850 °C and 90 min respectively. t_r represents the recombination time.

under the same hydrogenation treatment, one cannot expect identical distributions and grain sizes of Nd-hydride, α-Fe and Nd$_2$Fe$_2$C$_3$ between these two hydrided alloys which invariably affect the final phase formation by the recombination reaction.

4. Conclusions

It is confirmed that HDDR is based on diffusional phase transformation and that time and temperature are vital to the phase formation and magnetic properties. It has been successfully applied to synthesize Nd$_2$Fe$_{14}$C-based permanent magnets. The disproportionation reaction occurred at 850 °C results in the formation of an intimate mixture of Nd-hydride, α-Fe and Nd$_2$Fe$_2$C$_3$. On desorbing the hydrogen at the same temperature, the different constituents recombine into the thermodynamically stable Nd$_2$Fe$_{14}$C and Nd-rich phase. The alloys obtained by HDDR at 950 °C contain Nd$_2$Fe$_{17}$C$_x$ with higher Curie temperatures and greater amount of α-Fe, whereas those obtained at 700 °C contain Nd$_2$Fe$_{17}$C$_x$ with lower Curie temperatures and smaller amounts of α-Fe. It is found that Nd$_2$Fe$_{14}$C based alloys can also be obtained from Nd$_2$Fe$_{17}$C$_x$-based alloys after the HDDR treatment.

Acknowledgments

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