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Re-exchange of Fe and Cu at the interface in sintered Nd–Fe–B magnets: A method to eliminate Fe precipitation at grain boundaries

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ABSTRACT

According to the decoupling hypothesis for magnetic grains, the coercivity in sintered Nd–Fe–B magnets is increased after Cu doping, which is due to the formation of non-magnetic grain boundaries. However, this method partially fails, and ferromagnetic Fe-segregation occurs at the grain boundary. We discovered both experimentally and through calculation that the Fe content at the grain boundaries can be tuned across a wide range by introducing another element of Ag. Segregated Fe at high temperature at the grain boundary re-dissolves into $Nd_2Fe_{14}B$ grains during annealing at low temperature. Both configurable and magnetic entropies contribute a large driving force for the formation of nonmagnetic grain boundaries. Almost zero Fe content could be achieved at the grain boundaries of sintered Nd–Fe–B magnet.

1. Introduction

If hard magnetic $Nd_2Fe_{14}B$ grains, which are uniformly covered with a layer of a grain boundary (GB) phase, are non-ferromagnetically isolated, the coercive force will be increased by about ~20% [1,2]. The GB phases consists of eutectic systems such as (4Nd+3NdCu) [3], infiltrating along GBs by annealing at a low temperature (~600 °C), is essential to the formation of this micro-structure. However, in addition to the infiltration, ferromagnetic Fe atoms precipitated at the grain boundaries, lead to insufficient intergranular magnetic decoupling of $Nd_2Fe_{14}B$ grains [3]. The lack of sufficient understanding of the mechanism for Fe segregation at the GBs, impeded further coercivity improvement. To resolve the problem, it is important to study the Fe segregation and clarify its formation mechanism.

Theoretically, all Fe atoms should be used to form the $Nd_2Fe_{14}B$ phase when the composition is close to its stoichiometric ratio. Therefore, the Fe atoms at GBs should be attributed to the substitution by non-Fe atoms from the $Nd_2Fe_{14}B$ lattice. By a thermodynamic perspective, if non-Fe atoms have negative substitution energies in the $Nd_2Fe_{14}B$, the substitution will happen and Fe atoms will be free at the GB. But, even if the non-Fe atoms have positive substitution energies such as Cu in the $Nd_2Fe_{14}B$ [4], 65 at.% Fe atoms still precipitate at the GB [3].

In this paper, we investigate the diffusion of Fe in sintered Nd–Fe–B magnets.

2. Material and methods

A series of component designs for $Nd_2Fe_{14}B$ added 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 wt.% Cu, and then Nd, in excess to fully form the eutectic (4Nd+3NdCu) (70 at.% Nd) [5], was adapted. The Fe–B alloy, pure Fe, Cu and Nd were melted together via arc melting. This was followed by annealed at 1100 °C for 16 hours to ensure homogeneity, and subsequent annealing at 600 °C for 20 hours to improve the micro-structure.

Scanning electron microscopy (SEM), x-ray diffraction (XRD) with a Co-target x-ray diffractometer and energy-dispersive x-ray spectroscopy (EDS) were performed. The Si(220) peak of polycrystalline Si powder was used to correct the peak position. The first-principle calculations are based on the full-potential, relativistic linearized augmented plane wave (FLAPW) method [6] and the following reaction:

$$Nd_2Fe_{14}B + 0.25Cu = Nd_2Fe_{13.75}Cu_{0.25}B + 0.25Fe. \quad (1)$$

The $Nd_2Fe_{14}B$ structure [7] were fully optimized as $a = b = 8.81$ Å, $c = 12.18$ Å for $Nd_2Fe_{14}B$. The Gibbs energy was calculated using $\Delta G = E_{sub} - T\Delta S$, and the effect of volume was neglected.

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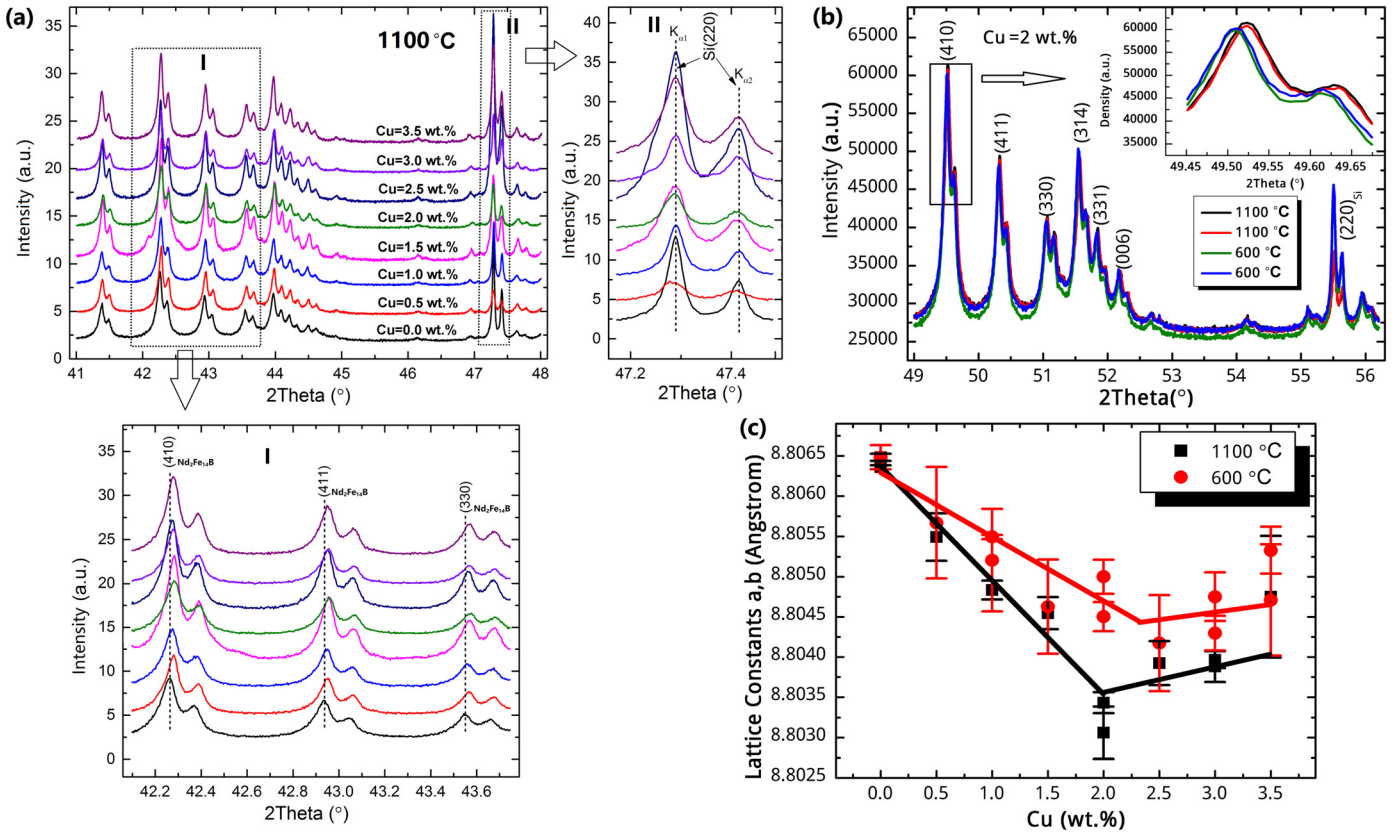

Fig. 1. XRD curves of Cu- added samples (a), (b) and the Cu dependence of the lattice constants (c) of the $Nd_2Fe_{14}B$ phases for annealing at 600 and 1100 °C, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Here, ΔG, E_{sub}, T, ΔS are the free energy change, substitution energy, temperature, and entropy change, respectively. The entropy change is presented as: $\Delta S = \Delta S_c + \Delta S_m + \Delta S_v$, where ΔS_c, ΔS_m, ΔS_v are configurational, magnetic, and vibrational entropy changes, respectively. The formula to calculate the configurational entropy is the same as the formula to calculate magnetic entropy: $\Delta S_c = \Delta S_m = -nk_B[clnc + (1-c)ln(1-c)]$. Where $n = 4$ is the multiplication factor for the Fe atoms (16k1 site) per unit cell, $c = 0.25/4$ for ΔS_c is the content of Cu in $Nd_2Fe_{13.75}Cu_{0.25}B$, and $c = 0.5$ for ΔS_m is the magnetic order parameter (0.5 for paramagnetic) when the temperature exceeds the Curie temperature, and k_B is the Boltzmann constant. The vibrational entropies were calculated from phonon frequencies using the finite displacement method [8,9].

3. Results

With the increase of (4Nd+3NdCu) eutectic, the lattice constant decreased (Cu % < 2.0 wt.%) after both annealing at 1100 and 600 °C – see Fig. 1. The decrease of lattice-constant dependence on the eutectic content suggests that Cu atoms entered the $Nd_2Fe_{14}B$ phase, which causes a certain degree of contraction in the $Nd_2Fe_{14}B$ lattice. After annealing at high temperature (1100 °C), additional annealing at 600 °C restores the $Nd_2Fe_{14}B$'s lattice. Fig. 1(b) shows the XRD spectrum for Cu content of 2 at.%. The left shift of the peaks after 600 °C annealing indicates the most recovered lattice at 2 at.% Cu. This proves that Fe atoms at the GBs are re-dissolved into the $Nd_2Fe_{14}B$ grains. The Fe atoms filling the vacancies produced by Cu, lead to trace Fe and Cu atoms have re-exchanged at the GBs during 600 °C annealing.

Fig. 2(b) shows that a thin GB layer forms during annealing at 600 °C. The slightly brighter area (region B) in the figure is the stoichiometric (4Nd+3NdCu) eutectic, while the darker area

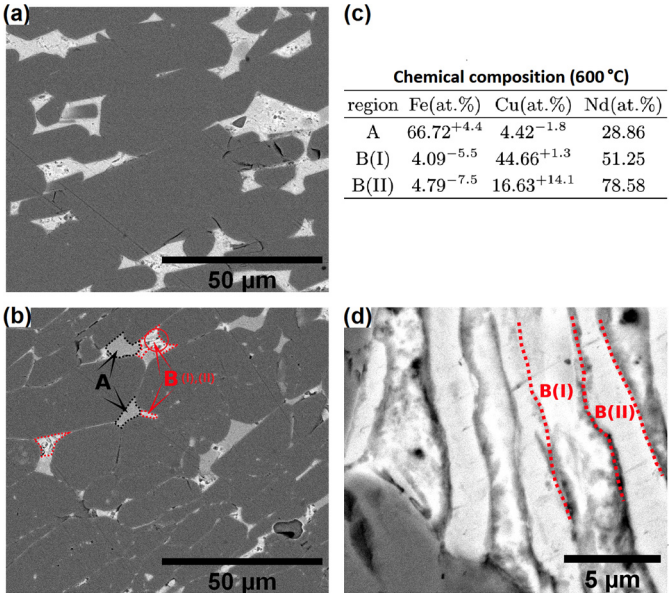

Fig. 2. Back-scattered electron images of the samples after annealing at 1100 °C (a) and 600 °C (b), (d). The chemical compositions after annealing at 600 °C are also shown (c). The plus sign shows that an increased content and negative sign represents a decrease of the content compared to annealing at 1100 °C.

(region A) is the Fe-rich phases at triple junctions of GBs. The observed micro-morphology is not different from previous reports [1,10]. EDS results show that the Cu content in the eutectic at the GB increased by 14.1 at.% (Fig. 2(c), B(II)), while the Fe contents in the same areas decreased from 12.3 at.% to 4.8 at.% after annealing at 600 °C (region B(II)). This increase also occurred in another eu-

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