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Effect of Co-Substitution on the Crystallization and Magnetic Properties of a Mechanically Milled $Nd_{15}(Fe_{1-X}Co_X)_{77}B_8$ (x = 0-0.6) Alloy

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Mechanical milling technique is considered to be a useful way of processing the fine Nd-Fe-B-type powder with high coercivity. In the present study, phase evolution of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.6) alloys during the high energy mechanical milling and annealing was investigated. The effect of Co-substitution on the crystallization of the mechanically milled $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ amorphous material was examined. The Nd-Fe-B-type alloys can be amorphized completely by a high-energy mechanical milling. On annealing of the amorphous material, fine α-Fe crystallites form first from the amorphous. These fine α-Fe crystallites reacts with the remaining amorphous afterwards, leading to crystallization to $Nd_2Fe_{14}B$ phase. The Co-substitution for Fe in $Nd_{15}(Fe_{1-x}Cox)_{77}B_8$ μx= 0~0.6) alloys lower significantly the crystallization temperature of the amorphous phase to the $Nd_2Fe_{14}B$ phase. The mechanically milled and annealed $Nd_{15}Fe_{77}B_8$ alloy without Co-substitution exhibits consistently better magnetic properties with respect to the alloys with Co-substitution.

Key words : $Nd_{15}(Fe_{1-X}Co_X)_{77}B_8$, mechanical milling, crystallization

1. Introduction

Magnetically coercive Nd-Fe-B powders are produced mainly by two commercial routes; the melt-spinning [1] and HDDR processes [2]. In addition to these routes, a mechanical milling technique [3-6] has been considered to be a useful way of producing the high coercivity Nd-Fe-B powder. In this technique a pre-alloyed Nd-Fe-B lump is milled with high-energy to become an almost amorphous state and then annealed to crystallize the $Nd_2Fe_{14}B$ phase with extremely fine grain structure. Meanwhile, Co is usually added to the Nd-Fe-B-type alloy as a substituting element for Fe for improving the thermal stability of magnetic properties of the Nd-Fe-B materials [7-9]. In this article, phase evolution of the Nd-Fe-B-type alloy during the high-energy mechanical milling and annealing was investigated. A particular emphasis was placed on the effect of Co-substitution on the crystallization and magnetic properties of the mechanically milled Nd-Fe-Co-B amorphous material.

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2. Experimental

Alloys with composition of $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x= 0~0.6) were prepared by an induction melting. The alloy ingots were annealed at 1050 °C for 3 days under Ar gas, and pulverized into a powder with grain size less than 100 μm. The pulverized alloy powder was charged into a hardened steel vial together with hardened steel balls. The mass ratio between the charged material powder and milling balls was 1:10. The charged vial was evacuated and then filled with a high purity argon gas. The material was then milled in a shaker mill. The milled powder was annealed in vacuum. Phase change during the milling and subsequent annealing was examined mainly by an XRD (x-ray diffraction) using CuKα radiation. TMA (thermo-magnetic analysis) and DTA (differential thermal analysis) were also used to investigate the phase change during the milling and annealing. The TMA with an applied field of 800 Oe was performed with very high heating rate (swift TMA) in an attempt to suppress unnecessary phase change during heating as much as possible. For the swift TMA, heating oven was previously heated to the required temperature, and then the hot oven was moved on to the sample. The sample was heated rapidly up to 850 °C within 5 minutes. Magnetic properties of the annealed powder were measured by VSM (vibrating sample magnetometer) with a maximum applied field of 1.5 Tesla. Prior to the VSM measurement, the sample was magnetized by applying pulsing field of 6 Tesla.

3. Results and Discussion

Fig. 1 shows the XRD spectra for the $Nd_{15}Fe_{77}B_8$ alloy milled for 1 and 48 hrs. It can be seen that the materials milled for 48 hrs has become an almost amorphous state. The phase evolution of this amorphous material on heating was performed by the swift TMA, and the results are shown in Fig. 2. Two obvious magnetization decreases are observed at around 120 °C and 530 °C. The magnetization decrease at around 120 °C is thought to be due to the magnetic transition of the amorphous phase. The magnetization decrease at around 530 °C may be due to the crystallization of amorphous phase into the $Nd_2Fe_{14}B$.

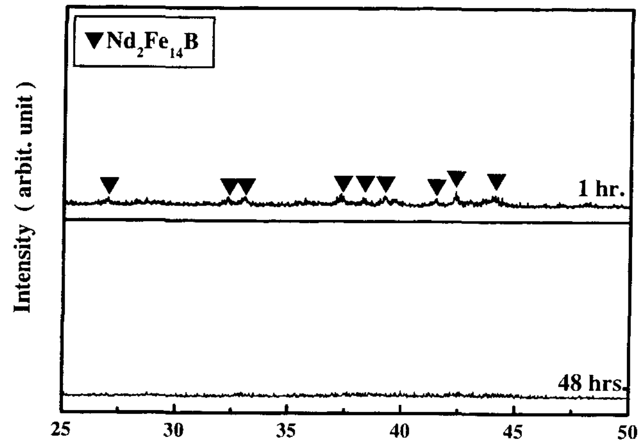

Fig. 1. XRD spectra for the $Nd_{15}Fe_{77}B_8$ alloy milled for 1 and 48 hrs.

It is noted that magnetization unusually remains constant in spite of increasing temperature in the range from around 400 °C to 500 °C. This is thought to be due to the crystallization of α-Fe from the amorphous phase. This interpretation is evidenced by XRD result. The $Nd_{15}Fe_{77}B_8$ alloy milled for 48 hrs was heated up to 450 °C in vacuum and then quenched immediately. The quenched alloy was subjected to XRD, and the result is shown in Fig. 3. As can be seen, a broadened diffraction peak corresponding to α-Fe is observed, indicating that extremely fine α-Fe grains first crystallize from the amorphous phase. This crystallization of α-Fe may result in the unusual constant magnetization in the temperature range from around 400 °C to 500 °C in the swift TMA. At an elevated temperature around 530 °C, the finely crystallized α-Fe crystallites are thought to react with the remaining amorphous phase. This reaction may result in formation of the $Nd_2Fe_{14}B$ phase with extremely fine grain structure. This formed $Nd_2Fe_{14}B$ phase is, however, already in the paramagnetic range at this temperature, thus only magnetization decrease may occur due to the consumption of α-Fe. The crystallization to the $Nd_2Fe_{14}B$ is also confirmed by the cooling TMA tracing from 850 °C to room temperature also shown in Fig. 2. Large magnetization increase at around 310 °C in cooling TMA tracing indicates that most of the material has been crystallized into the $Nd_2Fe_{14}B$ phase.

Effect of Co-substitution for Fe on the crystallization of the milled $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0 0.6) alloys (milled for 48 hrs) was investigated by DTA, and the results are shown in Fig. 4. The milled alloys with x=0 and 0.45 in $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ show exothermic heat flows at 534 °C and 435 °C, respectively. This may be attributed to the formation of $Nd_2Fe_{14}B$ phase resulting from the reaction

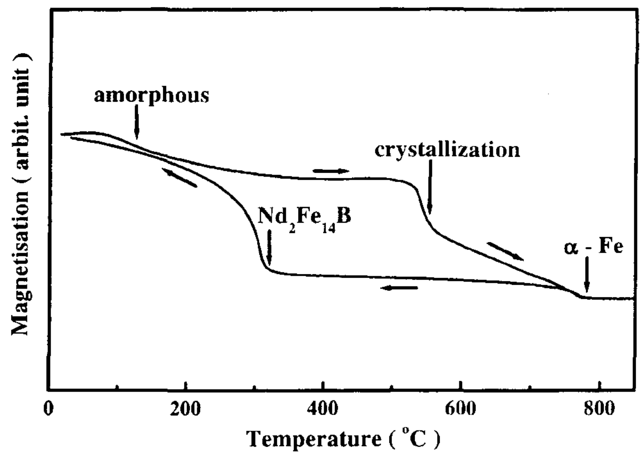

Fig. 2. Swift TMA tracings (heating and cooling) of the $Nd_{15}Fe_{77}B_8$ material milled for 48 hrs.

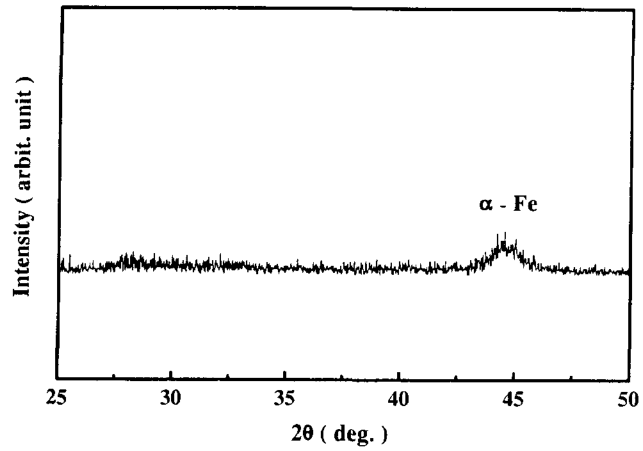

Fig. 3. XRD spectrum of the $Nd_{15}Fe_{77}B_8$ alloy (milled for 48 hrs) heated up to 450 °C and quenched.

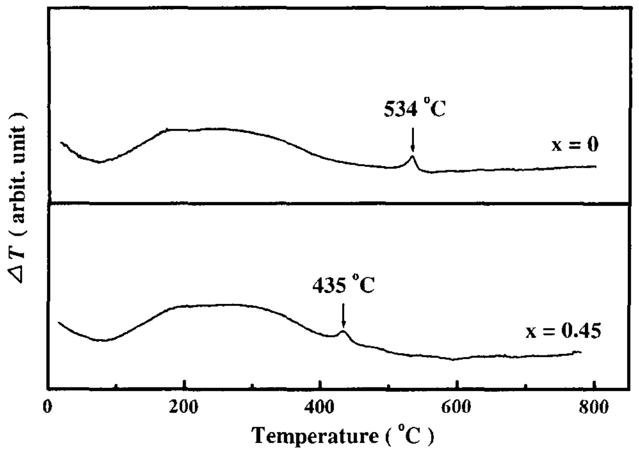

Fig. 4. DTA results of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys milled for 48 hrs.

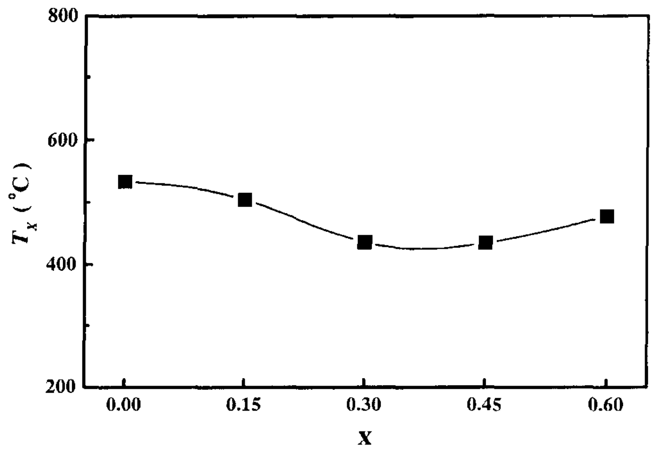

Fig. 5. Dependence of the crystallization temperature on the Co-content in $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0 0.6) alloy.

between the previously formed α-Fe and remaining amorphous phase. Dependence of the crystallization temperature (T_x) on the Co-content in $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0 0.6) alloy is shown in Fig. 5. As can be seen, the Co-substitution reduces significantly the crystallization temperature.

The magnetic properties of milled $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys after annealing for 20 min at various temperatures are shown in Fig. 6 and Fig. 7. For all the alloys used in the present study, the intrinsic coercivity increases, shows maximum and then decreases with increasing annealing temperature. The reduction of coercivity at higher temperature may be attributed to an excessive grain growth of the $Nd_2Fe_{14}B$ phase. The peak coercivity of the alloy without Co-substitution exhibits consistently higher value with respect to the alloys with Co-substitution. Remanence of the materials also increases, shows maximum and then slightly decreases with increasing annealing temperature. The reduction of remanence at higher temperature may be

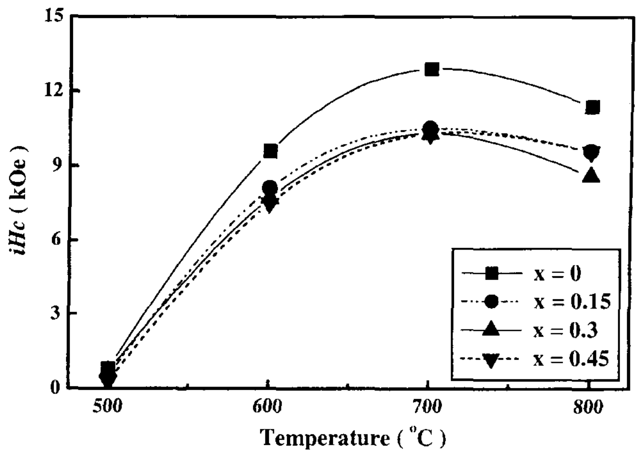

Fig. 6. Effect of annealing temperature on the intrinsic coercivity of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.45) alloys milled for 48 hrs.

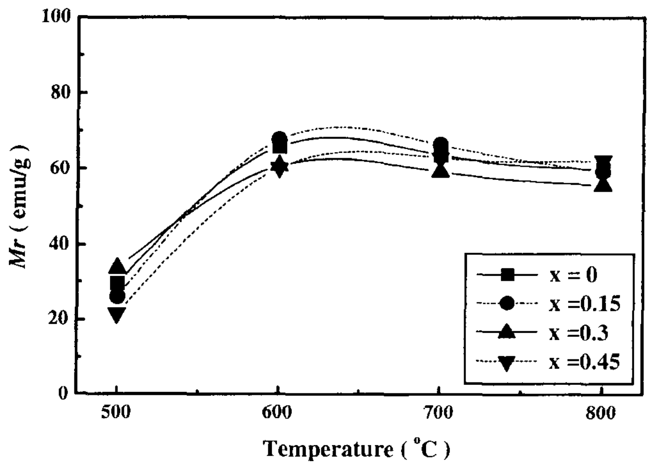

Fig. 7. Effect of annealing temperature on the remanence of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.45) alloys milled for 48 hrs.

attributed to the deterioration of demagnetization character caused by the excessive grain growth.

Effect of annealing time at a particular temperature (700 °C) on the coercivity and remanence of the alloys with and without Co-substitution (milled for 48 hrs) is shown in Fig. 8 and Fig. 9. Coercivity of the alloy without Co-substitution appears to increase and then decrease after showing maximum with increasing the annealing time. Meanwhile, coercivity of the alloy with Co-substitution decreases gradually. As revealed in Fig. 5, the Co-substitution reduced significantly the crystallization temperature of the $Nd_2Fe_{14}B$ phase, indicating an enhanced kinetics of crystallization. Thus, the alloy with Co-substitution may show an excessive grain growth from the beginning at 700 °C, and the coercivity continuously decreases. The remanence of alloy without Co-substitution appears to increase with increasing annealing time. The

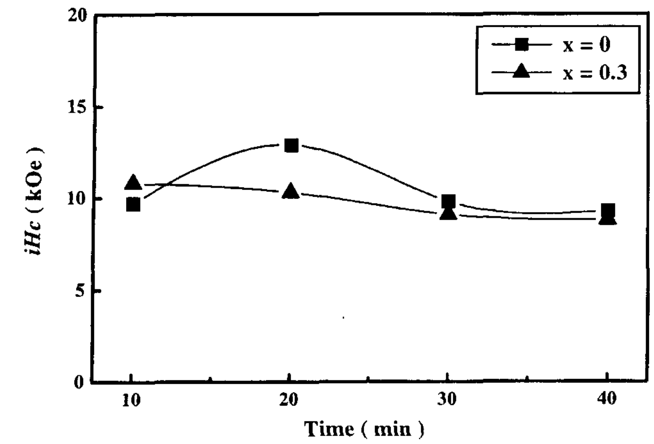

Fig. 8. Effect of annealing time on the intrinsic coercivity of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0, 0.3) alloys milled for 48 hrs.

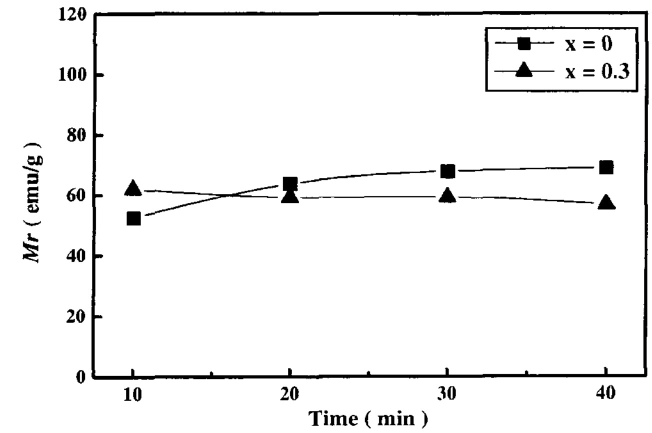

Fig. 9. Effect of annealing time on the remanence of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0, 0.3) alloys milled for 48 hrs.

alloy with Co-substitution, however, shows coercivity decreasing slightly with time. These remanence variations with annealing time seem to be related to the change of demagnetization character. Demagnetization curves of the milled $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.45) alloys after annealing at 700 °C for 20 min are shown in Fig. 10. The demagnetization character of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys is deteriorated with increasing the Co-substitutions.

4. Conclusion

The Nd-Fe-B-type alloys can be amorphized completely by a high-energy mechanical milling. On annealing of the amorphous material, fine α-Fe crystallites form first from the amorphous. These fine α-Fe crystallites react with remaining amorphous phase afterwards, leading to a crystallization of $Nd_2Fe_{14}B$ phase. The Co-substitution for Fe in $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.6) alloys decreases significantly the crystallization temperature of the amorphous

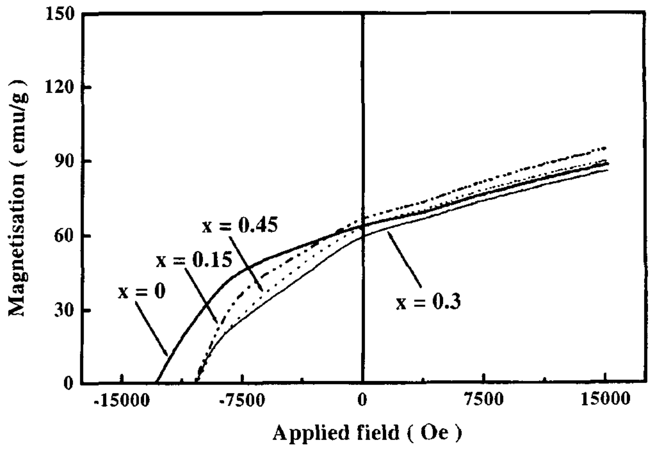

Fig. 10. Demagnetization curves of the milled $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x=0~0.45) alloys after annealing at 700 °C for 20 min.

phase into the $Nd_2Fe_{14}B$ phase. The mechanically milled and annealed $Nd_{15}Fe_{77}B_8$ alloy without Co-substitution exhibits consistently better magnetic properties with respect to the alloys with Co-substitution.

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