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TMA Study on Phase Evolution During Hydrogen-assisted Disproportionation of Nd-Fe-B Alloy

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Phase evolution during the hydrogen-assisted disproportionation of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy was investigated mainly by using a magnetic balance-type thermomagnetic analyser (TMA). In order to avoid any undesirable phase change in the course of heating for TMA, a swift TMA technique with very high heating rate (around 2 min to reach 800 °C from room temperature) was adopted. The hydrided $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy started to be disproportionated in hydrogen from around 600 °C, and the alloy after the early disproportionation (from 600 to 660 °C) has been partially disproportionated. The partially disproportionated alloy consisted of a mixture of NdH_x, Fe_3B, α-Fe, and the remaining undisproportionated $Nd_2Fe_{14}BH_x$-phase. During the subsequent heating to 800 °C in hydrogen, two additional phases of $Fe_{23}B_6$ and Fe_2B were formed, and the material consisted of a mixture of NdH_x, $Fe_{23}B_6$, Fe_3B, Fe_2B, and α-Fe phases. During the subsequent isothermal holding at 800 °C for 1 hour, the phase constitution was further changed, and one additional unknown magnetic phase was formed. Eventually, the fully disproportionated $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy consisted of NdH_x, $Fe_{23}B_6$, Fe_3B, Fe_2B, α-Fe, and one additional unknown magnetic phase.

Keywords : Nd-Fe-B alloy, HDDR, disproportionation, TMA

Introduction

The HDDR (hydrogenation, disproportionation, desorption, and recombination) process is a well-established technique for producing a highly coercive Nd-Fe-B powder with fine grain structure directly from a magnetically non-coercive ingot alloy with coarse grain structure. The disproportionation reaction of the HDDR technique is the most critical step for controlling the magnetic properties of the Nd-Fe-B HDDR powder [1-7]. It has been widely known that the Nd-Fe-B alloy fully disproportionated in hydrogen consists of a multi-phase mixture of NdH_x, Fe_2B, and α-Fe, and the final magnetic properties (in particular, the grain texture) of the HDDR material are affected heavily by the phase constitution in the disproportionated state [4, 5]. Therefore, it is important to understand precisely the phase constitution of the fully disproportionated material. The most common tool for the analysis of the phase constitution of the disproportionated alloy is x-ray diffraction (XRD). However, a trace amount of a phase can hardly be identified by XRD. Recently, we have found that the phase constitution of fully disproportionated Nd-Fe-B alloy was rather complicated and a thermomagnetic analysis (TMA) technique was useful for the phase analysis. In the present study, the phase constitution and evolution during the hydrogen-assisted disproportionation of the Nd-Fe-B alloy were investigated mainly by magnetic balance-type TMA. The present findings may be used as important knowledge for the preparation of highly textured Nd-Fe-B-type HDDR powder.

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2. Experimental Work

The $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy was first fully hydrogenated by heating it at 400 °C for 1 hr in hydrogen gas (P = 0.1 MPa). The fully hydrogenated alloy was subjected to a disproportionation by heating from 400 °C towards 800 °C in a thermopiezic analyser (TPA) filled with hydrogen gas (P = 0.1 MPa). During the course of heating, the hydrogen pressure in the reaction chamber of the TPA was monitored (Fig. 1). As can be seen in the TPA curve shown in Fig. 1, the hydrogen pressure started to drop from around 600 °C, and this indicated the initiation of

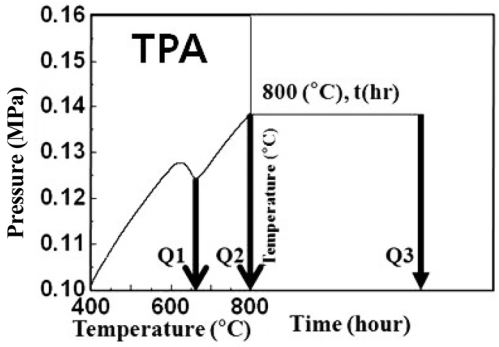

Fig. 1. TPA result and quenching profile of the hydrogenated $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy during the disproportionation in hydrogen.

disproportionation of the hydride material. The material was further heated up to 800 °C and held at there for 1 hr. The alloy was quenched at various points during disproportionation as shown in Fig. 1. Q1 indicates a quenching right after the hydrogen pressure drop corresponding to the hydrogen absorption due to the disproportionation of the hydrided alloy. Q2 indicates a quenching as soon as the sample reaches 800 °C. Q3 indicates a quenching after holding for 1 hour at 800 °C. The quenching was fast enough that any undesirable phase change during quenching could be suppressed and the high temperature phase constitution could be kept unchanged at room temperature. The sample was cooled down from 800 °C within 90 sec to around 400 °C, below which virtually no phase change would occur. The phase constitution in the quenched samples was analysed mainly by a magnetic balance-type thermo-magnetic analyser (TMA). In order to avoid any undesirable phase change in the course of TMA heating, the sample was heated swiftly up to 800 °C in Ar gas flow. The swift TMA was carried out by quickly placing the sample into the oven pre-heated to 820 °C. In this swift heating mode the sample could be heated up to 800 °C from room temperature within 134 seconds, therefore any unwanted phase change could be practically suppressed during the TMA heating. The magnetic field applied to the sample in the TMA was approximately 500 Oe. The Curie temperature of a magnetic phase was determined by observing the derivative (dM/dT) of the magnetisation – temperature curve [some of the derivative – temperature curves were shown as insets in the TMA curve (see Fig. 4)]. X-ray diffraction (XRD) was also used to support the TMA.

Results and Discussion

Fig. 2 shows TMA results of the alloy quenched in the

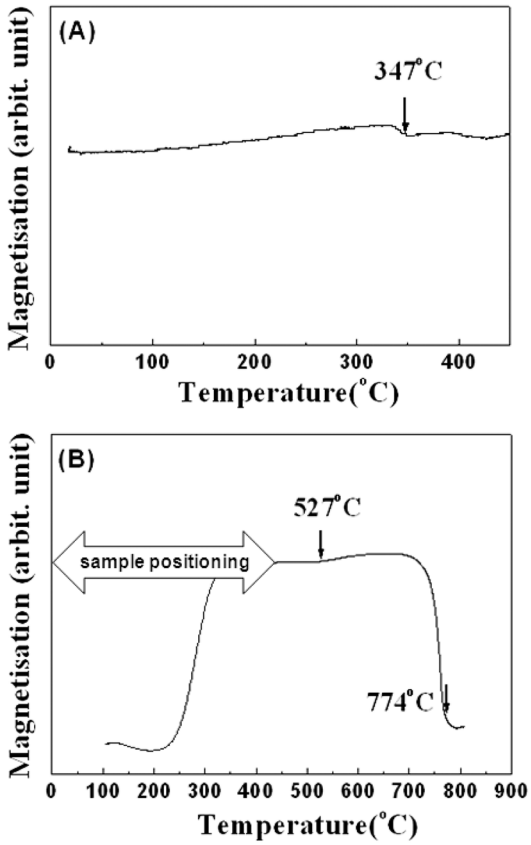

Fig. 2. TMA phase analysis ((A) slow, (B) swift) of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy quenched in the Q1 mode during the disproportionation.

Q1 mode. The TMA results shown in (A) and (B) are obtained by a slow and a swift technique, respectively. The major technical drawback of the swift TMA is that when the sample is approaching the required position in the magnetic field it is heated unintentionally, thus the magnetisation vs. temperature curve in the lower temperature range corresponding to the sample positioning (see (B) in Fig. 2) could not provide any meaningful information about the phase constitution. This practical drawback was overcome by using a combination of the swift and slow TMA. The magnetisation variation for a lower temperature range (up to around 450 °C), which corresponds to the sample positioning in the swift TMA, was measured by a slow TMA (7 °C/min). It is believed that in this lower temperature range no phase change is caused. The combination of the slow TMA up to 450 °C and the swift TMA from 450 °C can, therefore, provide a full analysis of the magnetic phase constitution without unwanted phase change during heating. As can be seen in Fig. 2, the sample quenched in the Q1 mode contains three magnetic phases with Curie temperatures (T_c) of 347 °C, 527 °C, and 774 °C. The magnetic transition at

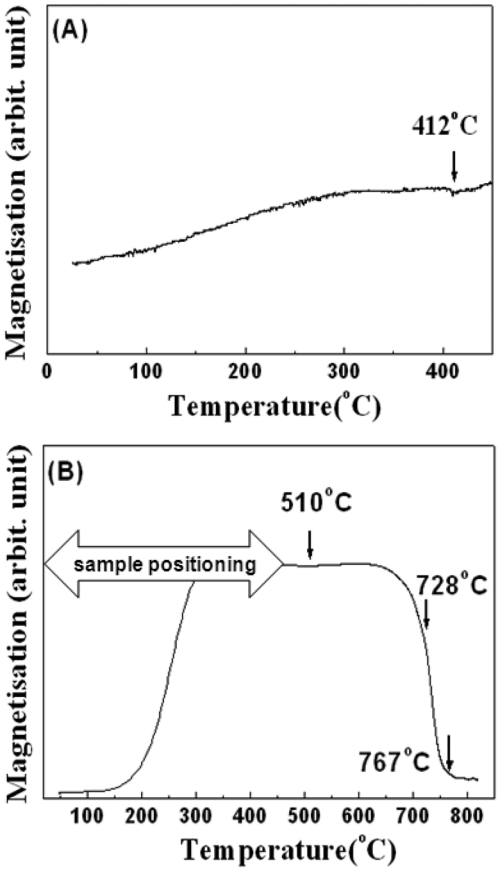

Fig. 3. TMA phase analysis ((A) slow, (B) swift) of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy quenched in the Q2 mode during the disproportionation.

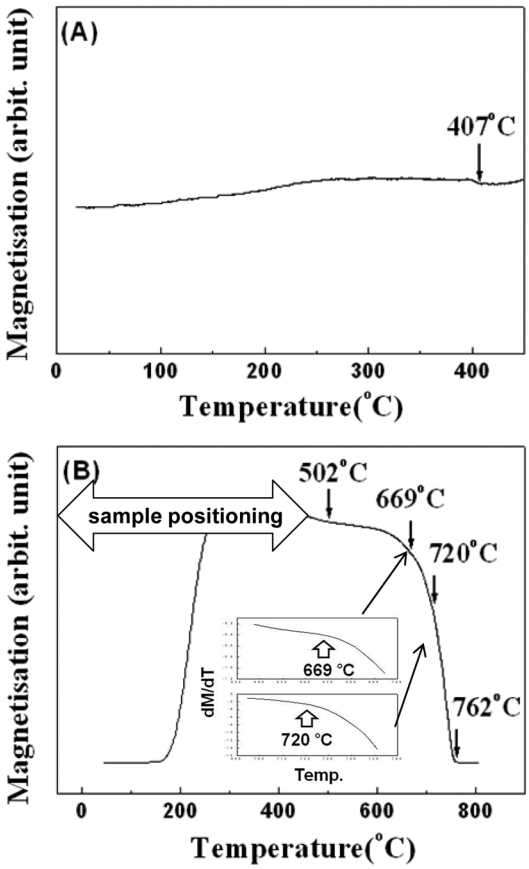

Fig. 4. TMA phase analysis ((A) slow, (B) swift) of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy quenched in the Q3 mode during the disproportionation.

347 °C corresponds to the T_c of the $Nd_2Fe_{14}BH_x$-phase. The hydrogen pick-up in the $Nd_2Fe_{14}B$-phase significantly increased its T_c from 312 °C to 347 °C [5]. The presence of the $Nd_2Fe_{14}BH_x$-phase in the alloy quenched in the Q1 mode suggests that the alloy has not been fully disproportionated but partially disproportionated. The magnetic transitions at 527 °C and 774 °C may correspond to the T_c of Fe_3B (tetragonal) [9] and α-Fe (cubic) [9] phases, respectively. This result clearly indicates that the sample after the initial disproportionation reaction from around 600 °C to 660 °C contains three magnetic phases: $Nd_2Fe_{14}BH_x$, Fe_3B, and α-Fe phases. Fig. 3 shows the TMA results of the alloy quenched in the Q2 mode. It appears that the sample heated up to 800 °C contains four magnetic phases with T_c of 412 °C, 510 °C, 728 °C, and 767 °C, respectively. The disappearance of the magnetic transition at around 347 °C suggests that the sample contains no $Nd_2Fe_{14}BH_x$-phase and has been fully disproportionated. The magnetic transition at 412 °C probably corresponds to the T_c of the cubic $Fe_{23}B_6$-phase [9]. The magnetic transitions at 510 °C, 728 °C, and 767 °C may correspond to the T_c of Fe_3B, Fe_2B (tetragonal) [9], and α-Fe phases, respectively. This result clearly indicates that the sample heated up to 800 °C has been fully disproportionated and includes four magnetic phases: $Fe_{23}B_6$, Fe_3B, Fe_2B, and α-Fe phases. Fig. 4 shows the TMA results of the alloy quenched in the Q3 mode. It appears that this sample contains five magnetic phases with T_c of 407 °C ($Fe_{23}B_6$), 502 °C (Fe_3B), 669 °C, 720 °C (Fe_2B), and 762 °C (α-Fe), respectively. In this sample, in addition to the four magnetic phases discussed above, another magnetic phase with a T_c of 669 °C exists. Identification of this extra phase has not been fully understood yet. It is clear that the phase constitution has been changed further by the isothermal heating at 800 °C. Needless to say, the TMA analysis can only identify the presence of magnetic phases, thus the TMA phase analysis need to be supported by other means such as XRD. Fig. 5 shows the XRD phase analysis of the alloy quenched in the Q3 mode, and it appears that this material would seem to consist of NdH_x, Fe_2B and α-Fe, and some trace of oxides. Interestingly, this XRD result showed somewhat different phase

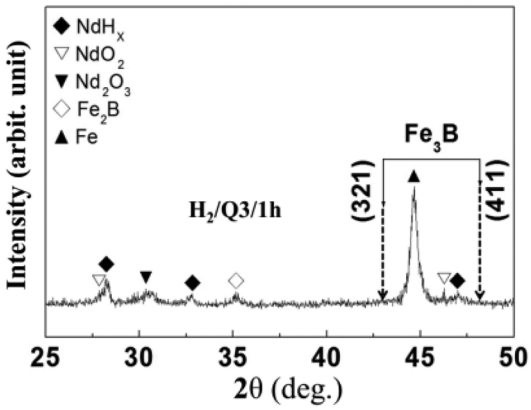

Fig. 5. XRD phase analysis of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy quenched in the Q3 mode during the disproportionation.

constitution compared to the TMA results (Fig. 4) especially in terms of magnetic phase constitution. For instance, although the TMA result clearly shows the presence of the Fe_3B phase (T_c = 502 °C), the XRD analysis shows no sign of the Fe_3B phase presence. The major (321), (411) interferences of the Fe_3B phase are not observed in the XRD result. However, the XRD result clearly indicates the presence of the non-magnetic NdH_x phase. The NdH_x phase contained in the sample quenched in the Q3 mode was also contained in the samples quenched in the Q1 and Q2 modes. The TMA supported by XRD can provide full details about the phase evolution during the hydrogen-assisted disproportionation of the Nd-Fe-B-type alloy. The phase evolution during the disproportionation discussed above is summarised in Fig. 6. A slight difference in the T_c of the identical phase is thought to be due to a slight composition variation within the corresponding stoichiometry. Here, it is worth noting that there are two tetragonal phases in the fully disproportionated material.

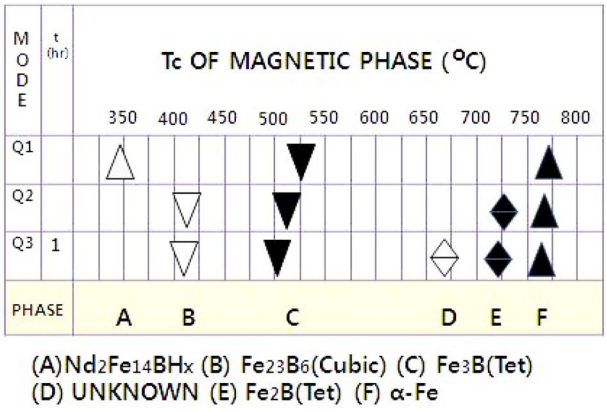

Fig. 6. (Color online) Magnetic phase constitution of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy quenched in different modes during the disproportionation.

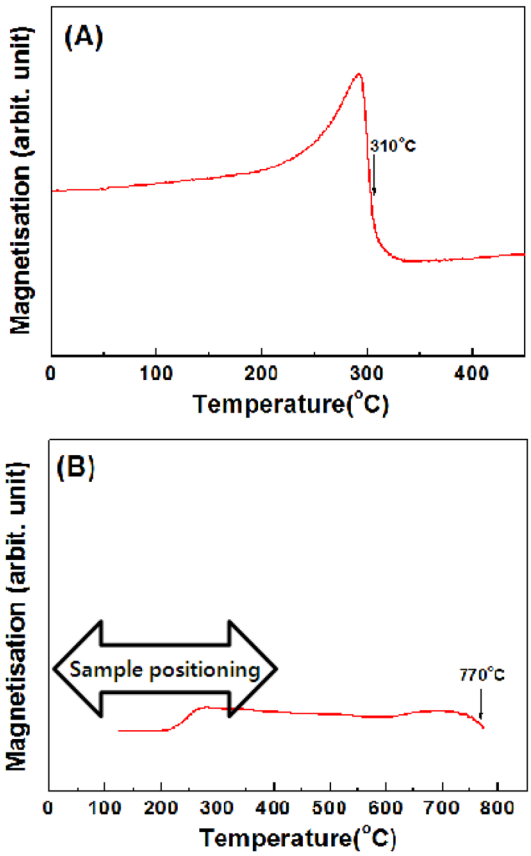

Fig. 7. (Color online) TMA phase analysis ((A) slow, (B) swift) of the fully recombined $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy.

It has been known that the texture in HDDR materials is closely related to the presence of the Fe_2B phase in the disproportionate state, which has the same tetragonal structure as that of the $Nd_2Fe_{14}B$ mother phase [4, 5]. The Fe_2B phase crystals can keep their crystallographic orientation the same as that of the mother phase and act as a nucleation site for the $Nd_2Fe_{14}B$ phase during the recombination, thus leading to a texture. As found in the present study, in addition to the Fe_2B an additional tetragonal Fe_3B phase also presents in the fully disproportionated material. The presence of this Fe_3B phase crystal in the disproportionated state is also thought to play an important role in inducing the texture.

The fully disproportionated multi-phase mixture is expected to be converted to the initial $Nd_2Fe_{14}B$-type mother phase if the mixture is subjected to a desorption and recombination. The fully disproportionated alloy just before the Q3 mode quenching was further held at 800 °C for 1 hour in vacuum and then cooled down to room temperature. Slow and swift TMA were carried out on this material. As can be seen in Fig. 7, the recombination-treated material only has a single phase, the $Nd_2Fe_{14}B$-

type phase with a T_c of 310 °C. It can be proposed, therefore, that the fully disproportionated phases have been recombined into the initial $Nd_2Fe_{14}B$ via the reaction as follows: $NdH_x + Fe_{23}B_6 + Fe_3B + Fe_2B + \alpha$-Fe + unknown magnetic phase (T_c = 669 °C) $\rightarrow$ $Nd_2Fe_{14}B$. The slight increase in the magnetisation at around 610 °C in the swift TMA may be due to some oxidation. The oxidation will lead to the formation of Fe, and this is verified by the magnetic transition at around 770 °C in the swift TMA.

Conclusion

Phase evolution during the hydrogen-assisted disproportionation of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy was investigated mainly by a TMA technique. The early disproportionation from 600 °C to 660 °C led to a partial disproportionation, and the material consisted of a mixture of NdH_x, Fe_3B, α-Fe, and the remaining undisproportionated $Nd_2Fe_{14}BH_x$-phase. During the subsequent heating to 800 °C, two additional magnetic phases of $Fe_{23}B_6$ and Fe_2B were formed, and the material consisted of a mixture of NdH_x, $Fe_{23}B_6$, Fe_3B, Fe_2B, and α-Fe phases. The isothermal holding at 800 °C led to further phase change, and one additional unknown magnetic phase was formed. The fully disproportionated alloy eventually consisted of a mixture of NdH_x, $Fe_{23}B_6$, Fe_3B, Fe_2B, α-Fe, and one additional unknown magnetic phase.

Acknowledgement

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