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Phase Relationships and Magnetic Properties of HDDR-treated $Sm_3(Fe,Co,V)_{29}$ Alloy

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Phase relationships of the HDDR (hydrogenation, disproportionation, desorption and recombination)-treated $Sm_3(Fe,M)_{29}$-type alloy with chemical composition of $Sm_9Fe_{65}Co_{20}V_6$ were studied by X-ray diffraction (XRD) and by thermomagnetic analysis (TMA). The alloy was disproportionated into a mixture of SmH_x and α-Fe at high temperature under hydrogen gas. The disproportionated material was recombined into a mixture of Sm-(Fe,M) (M = Co and/or V) and α-Fe phases. The structure of the Sm-(Fe,M) phase was dependent upon the recombination conditions, and a detailed phase diagram showing the phase relationships in the HDDR-treated alloy has been established. The Sm-(Fe,M) phase in material recombined above 900 °C had the Sm_2Fe_{17}-type structure, and it exhibited the $SmFe_7$-type structure when recombined at temperatures ranging from 700 °C to 850 °C. Recombination below 650 °C led to the $SmFe_3$-type structure of the Sm-(Fe,M) phase. Curie temperatures of the Sm-(Fe,M) phases in the recombined material were significantly higher than those of the corresponding stoichiometric phases. It was suggested that the chemical composition of the Sm-(Fe,M) phases may be significantly different from that of the corresponding stoichiometric phases. All the HDDR-treated $Sm_9Fe_{65}Co_{20}V_6$ materials showed the soft magnetic features regardless of the phase constitution.

Key words : $Sm_3(Fe,Co,V)_{29}$ alloy, HDDR

1. Introduction

The $Sm_3(Fe,M)_{29}$ compound (M = V, Ti, Cr, Mn) [1, 2] is considered to be a an attractive material as a promising candidate for a permanent magnet application because its nitride, $Sm_3(Fe,M)_{29}N_x$ [3-5], has attractive hard magnetic properties with a high Curie temperature and strong uniaxial anisotropy. In order for the $Sm_3(Fe,Co,V)_{29}N_x$ to be exploited as a useful permanent magnet, it has to have a high coercivity. The high coercivity in a rare-earth – transition metal hard magnetic alloy can be realised usually by obtaining a fine grain structure. One of the effective ways of obtaining fine grain structure in the rare earth-transition magnetic alloys is a HDDR process. The $Sm_3(Fe,M)_{29}$ compound has been known to exhibit an unique HDDR features. Unlike the other rare-earth-transition metal magnetic alloys, such as Nd-Fe-B-type and Sm_2Fe_{17} alloys, the $Sm_3(Fe,M)_{29}$-type alloy does not recombine into the initial 3:29 phase after the HDDR treatment, but rather, recombines into a two-phase mixture of Sm-(Fe,M) and α-Fe(M) phases [6, 7]. The Sm-(Fe,M) phase has a different structure from that of its parent 3:29-type. In the present study, the phase relationships and magnetic properties of the HDDR-treated $Sm_3(Fe,Co,V)_{29}$ alloy were studied.

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2. Experimental Work

The $Sm_9Fe_{65}Co_{20}V_6$ alloy used in the present study was prepared by induction melting the high purity constituent metals. The prepared alloy ingot was homogenised at 1150 °C for 40 hrs under argon gas and then rapidly cooled to room temperature. X-ray diffraction (XRD, with Cu-K_α radiation) on this homogenised ingot showed that the material was composed of near single 3:29 phase. The material was then pulverised into a powder with a particle size of 40-60 μm. Hydrogenation and disproportionation reaction of the alloy powder in hydrogen gas was examined using TPA (thermopeizic analysis) and DTA (differential thermal analysis) in hydrogen gas (p = 1.2 kgf/cm^2). The powder material was subjected to a HDDR treatment. Hydrogen pressure for the hydrogenation and disproportionation was maintained at 1.2 kgf/cm^2. Fully disproportionated material was recombined in vacuum at various conditions, and phases in the recombined material were analysed by XRD. Phase analysis of the recombined material was also performed by thermomagnetic analysis (TMA) using Sucksmith-type magnetic balance with applied magnetic field of 600 Oe. Magnetic characterisation of the HDDR-treated material was undertaken by means of VSM (vibrating sample magnetometer with a maximum magnetising field of 1.5 T). For the VSM measurement, the powder sample was consolidated with a wax and then magnetised with a pulsing field of 4.5 T prior to the measurement.

3. Results and Discussion

Fig. 1 represents the TPA and DTA results of the $Sm_9Fe_{65}Co_{20}V_6$ alloy undertaken in hydrogen gas, showing the hydrogenation and disproportionation reactions of the alloy. The alloy is hydrogenated and disproportionated at around 250 °C and 600 °C, respectively. Phases in the material heated above 600 °C in the DTA were analysed by XRD, and the result is shown in Fig. 2. XRD spectrum for the annealed alloy before exposing to the hydrogen is also included in the Fig. 2 for comparison. It can be seen that the alloy is disproportionated into a mixture of SmH_x and α-Fe at high temperature under hydrogen gas. The TPA result also shows an evidence for the hydrogenation and disproportionation of the alloy. Two hydrogen pressure drops are clearly observed at around 250 °C and 600 °C, and those are due to the hydrogen absorption on the hydrogenation and disproportionation. It can be seen that the 3:29-type alloy exhibits a similar hydrogenation and disproportionation behaviour with other rare-earth – transition metal magnetic alloys, such as Nd-Fe-B and Sm_2Fe_{17}.

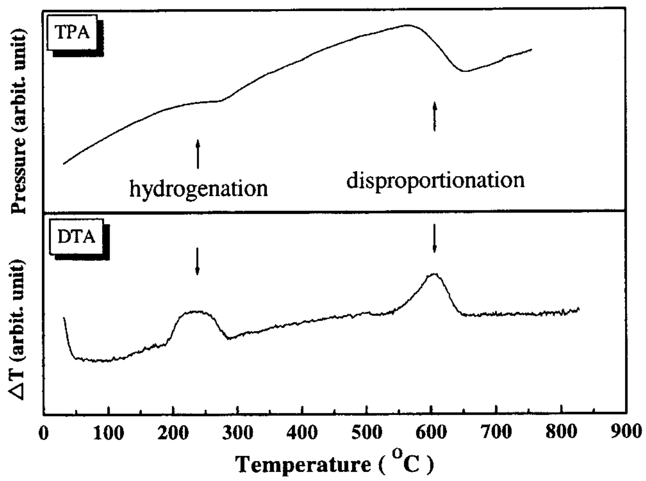

Fig. 1. TPA and DTA tracings of the $Sm_9Fe_{65}Co_{20}V_6$ alloy undertaken in hydrogen gas.

Recombination of the material was studied under various conditions using fully disproportionated material. Full disproportionation of the alloy was achieved by heating it at 750 °C for 1 hr in hydrogen gas (p = 1.2 kgf/cm^2). Subsequently, the material was held at various temperatures for 1 hr in vacuum to induce a recombination and then cooled rapidly to room temperature. XRD phase analysis on the material recombined at 900 °C for 1 hr was performed, and the result is shown in Fig. 3. The disproportionated material is not recombined into the initial 3:29 phase after HDDR, but rather, recombined into a two-phase mixture of Sm_2Fe_{17}-type and α-Fe phases. This result is in good agreement with previous reports [6, 7]. The fully disproportionated material was also recombined at temperatures of 800 °C and 650 °C for 1 hr, and XRD phase analysis results on theses materials are also shown in Fig. 3. The materials recombined at 800 °C and 650 °C consist of a two-phase mixture of $SmFe_7$-type phase and α-Fe and of $SmFe_3$-type phase and α-Fe, respectively. The structure of the Sm-(Fe,M) phase depends on the recombination temperature, and it changes from 1:3-type to 1:7-type and then to 2:17-type as the recombination temperature rises. It can be noted from the XRD results of the recombined materials that the amount of α-Fe in the material recombined at 650 °C is much greater than that in the materials recombined at higher temperatures. This can be readily understood by considering the stoichiometry of Sm-(Fe,M) phase formed at different recombination temperatures. The stoichiometry achieved at the lower temperature (650 °C) is 1:3, thus more α-Fe should be precipitated in the recombined material.

It is believed that the structure of the Sm-(Fe,M) phase in

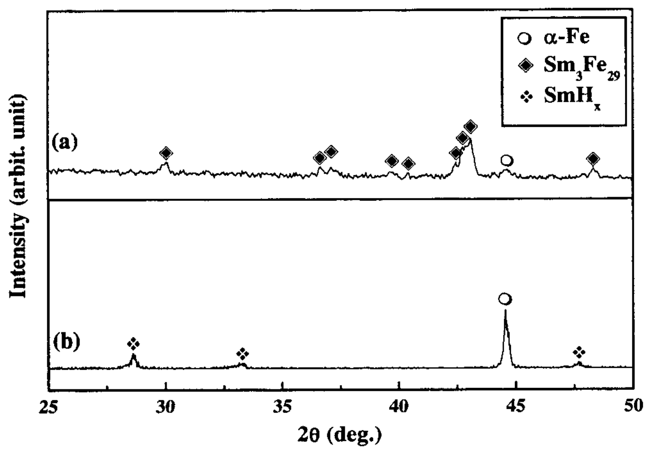

Fig. 2. XRD spectra of the $Sm_9Fe_{65}Co_{20}V_6$ alloy (a) before and (b) after heating up to 850 °C in hydrogen DTA.

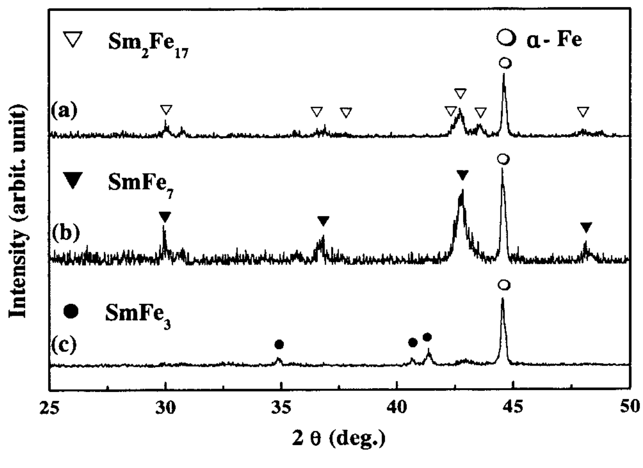

Fig. 3. XRD spectra of the $Sm_9Fe_{65}Co_{20}V_6$ alloy recombined for 1 hr at various temperatures. (a) 900 °C, (b) 800 °C, (c) 650 °C.

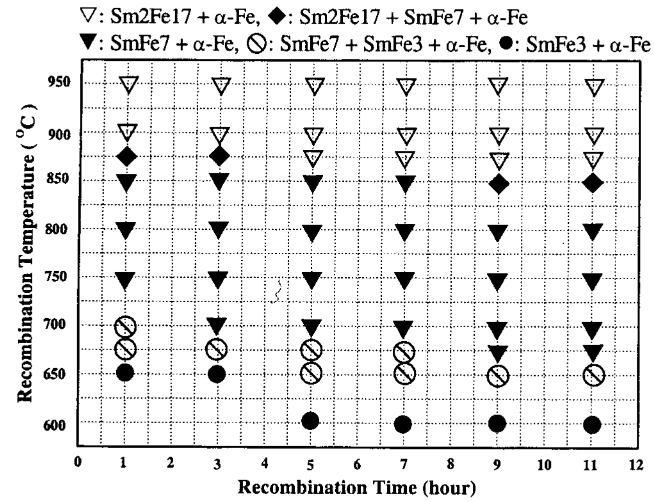

Fig. 4. Phase diagram showing the phase relationships in the HDDR-treated $Sm_9Fe_{65}Co_{20}V_6$ alloy.

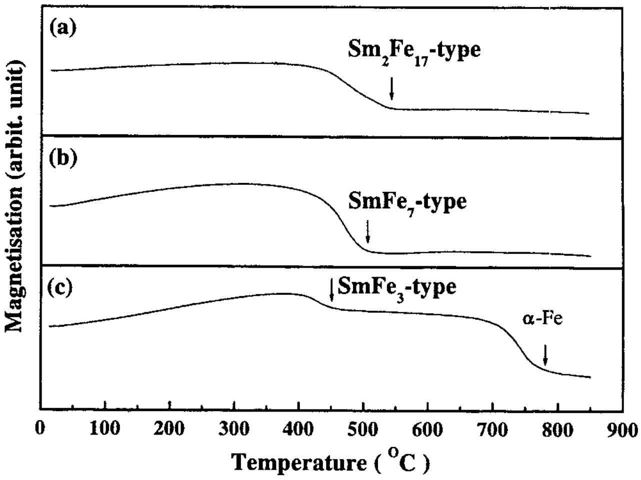

Fig. 6. TMA results of the $Sm_9Fe_{65}Co_{20}V_6$ alloy recombined for 1 hour at various temperatures. (a) 900 °C (b) 800 °C (c) 650 °C

the recombined state may depend, not only on the recombination temperature but also on the recombination time. Through a wide range of recombination experiments in various conditions, we could establish a detailed phase diagram showing the phase relationships in the HDDR-treated $Sm_9Fe_{65}Co_{20}V_6$ alloy, and a full phase diagram is shown in Fig. 4. It can be seen that the structure of the Sm-(Fe,M) phase in the material recombined above 900 °C exhibits 2:17-type phase in the time range examined in the present study. The structure of the Sm-(Fe,M) phase formed in the temperature range from 750 °C to 850 °C is characteristic of the 1:7 form, and that formed at lower temperatures tended characteristic of the 1:3-type. It is noted that the Sm-(Fe,M) phase in the material recombined at 650 °C exhibits the 1:3-type structure in the beginning and then the 1:7-type structure begins to appear after 5 hrs, so that the two structures coexist thereafter. This sort of structure change with recombination time can be seen clearly at 675 °C. In the beginning, the Sm-(Fe,M) phase exists in the 1:3-type, and then two structures of 1:3-type and 1:7-type coexist (Fig. 5(a)), and finally it exhibits the 1:7-type structure on prolonged recombination. Structural change from 1:7-type to 2:17-type through the mixed phase of 1:7-type and 2:17-type was also observed at 875 °C (Fig. 5(b)). A complete recombination of the disproportionated material was not achieved at 600 °C for a time period of less than 3 hrs.

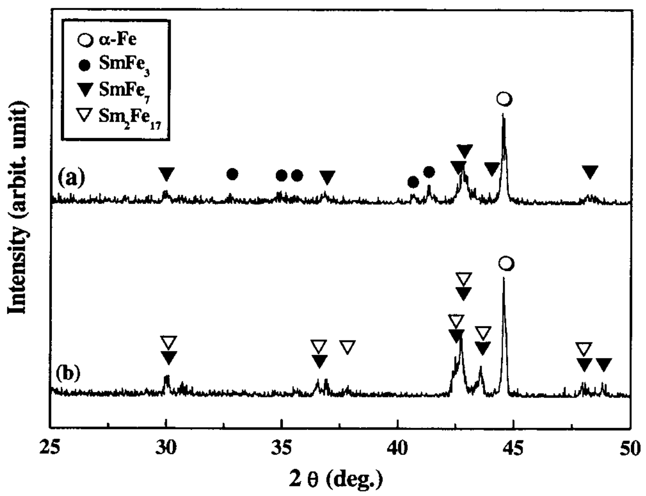

Fig. 5. XRD spectra showing the coexistence of the $SmFe_3$- and $SmFe_7$-type phases, and of the $SmFe_7$- and Sm_2Fe_{17}-type phases in the $Sm_9Fe_{65}Co_{20}V_6$ alloy recombined for 3 hrs at different temperatures. (a) 675 °C (b) 875 °C.

Thermomagnetic properties of the material recombined under various conditions were examined using TMA, and the results are shown in Fig. 6. The material recombined at 900 °C for 1 hrs shows a magnetic phase with Curie temperature (T_c) of around 540 °C and a trace of magnetisation inflection is seen at around 780 °C. Relating this to the phase analysis results by XRD (Fig. 3), the phase with T_c of 540 °C is thought to be the 2:17-type and the slope change at around 780 °C to be due to α-Fe. The material recombined at 800 °C for 1 hr shows a magnetic phase with T_c of around 500 °C and a slight inflection at around 780 °C. The phase with T_c of 500 °C is probably the 1:7-type structure phase. The material recombined at 650 °C for 1 hr shows a magnetic phase with T_c of around 450 °C and a large magnetisation inflection is also seen at around 780 °C. The phase with T_c of around 450 °C is probably 1:3-type structure phase. It is interesting to compare the Curie temperatures of the phases examined in this TMA study with those of the corresponding stoichiometric phases. The comparison is given in Table 1. The Curie temperatures of the phases existing in the recombined materials are significantly higher than those of the corresponding stoichiometric phases. This may be attributed to the chemical composition of the phases, which may be significantly different from that corresponding to stoichiometry. It can be noted that the Curie temperatures of the 2:17 and 1:7 phases in the recombined material are significantly higher than those of the sto-

Table 1. Comparison of Curie temperatures of the phases (°C)

phase	stoichiometric	reference	in recombined state	ΔT
2:17	116	[8]	540	424
1:7	210	[9]	500	290
1:3	371	[10]	450	79

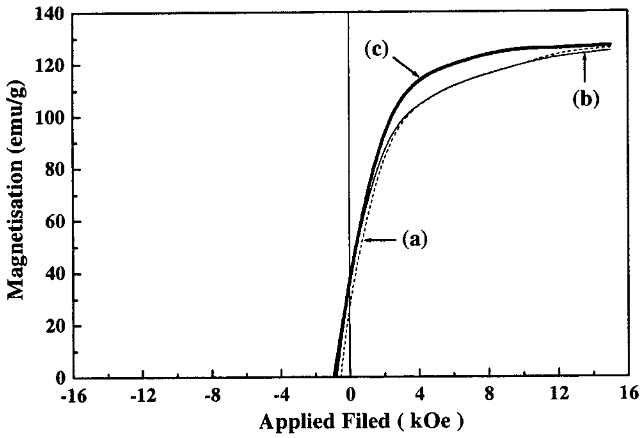

Fig. 7. Demagnetisation curves of the $Sm_9Fe_{65}Co_{20}V_6$ alloy recombined for 1 hr at various temperatures. (a) 900 °C (b) 800 °C (c) 650 °C.

ichiometric phase. Much greater amounts of α-Fe in the material recombined at 650 °C is clearly seen in the TMA result.

Fig. 7 represents the magnetic characterisation results measured by VSM for the materials HDDR-treated under various conditions. The material recombined at 900 °C for 1 hr consists of the Sm_2Fe_{17}-type phase and α-Fe, and the material recombined at 800 °C for 1 hr consists of the $SmFe_7$-type phase and a-Fe. The material recombined at 650 °C for 1 hr consists of the $SmFe_3$-type phase and α-Fe. All the three types of materials show a poor coercivity. It is not surprising to see the poor coercivity in the materials consisting of the Sm_2Fe_{17}-type phase and α-Fe and consisting of $SmFe_7$-type phase and α-Fe because both the Sm_2Fe_{17}- and $SmFe_7$-type phases are magnetically soft. It is rather surprising, however, that the material consisting of the $SmFe_3$-type phase and α-Fe after the recombination at 650 °C for 1 hr also shows a poor coercivity. The stoichiometric $SmFe_3$ compound is known to be magnetically hard phase with very high anisotropy field (H_A = 70.9 kOe at room temperature) [10]. The material consisting of the $SmFe_3$-type phase and α-Fe shows no evidence for the presence of a hard phase. This may be explained by the α-Fe which may act as a nucleation site of the reverse domain under the application of reverse field. Alternatively, the poor coercivity may also be explained by the far off-stoichiometric $SmFe_3$-type phase in the recombined material, of which chemical composition may be significantly different from that of the corresponding stoichiometric $SmFe_3$ compound as suggested by the TMA result, and thus the phase may be no longer a hard phase.

4. Conclusion

A detailed phase diagram showing the phase relationships in the HDDR-treated $Sm_9Fe_{65}Co_{20}V_6$ alloy has been established. After recombination the alloy consisted of a two-phase mixture of Sm-(Fe,M)-type and α-Fe phases. The Sm-(Fe,M)-type phase in material recombined above 900 °C had the Sm_2Fe_{17}-type structure, and the phase exhibited the $SmFe_7$-type structure when recombined at temperatures ranging between 700 °C and 850 °C. Recombination below 650 °C led to a two-phase mixture of $SmFe_3$-type and α-Fe phases. The Curie temperatures of the Sm-(Fe,M) phases in the recombined material were significantly higher than those of the corresponding stoichiometric phases. It was suggested that the chemical composition of the Sm-(Fe,M) phases may be significantly different from that of the corresponding stoichiometric phases. All the HDDR-treated $Sm_9Fe_{65}Co_{20}V_6$ materials showed the soft magnetic features regardless of the phase constitution.

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References

[1] J. M. Cadogan, H. S. Li, A. Margarian, J. B. Dunlop, D. H. Ryan, S. J. Collocott and R. L. Davis, J. Appl. Phys. **76**, 6138 (1994).

[2] Z. Hu and W. B. Yelon, Solid State Commun. **91**, 223 (1994).

[3] H. S. Li, J. M. Cadogan, R. L. Davis, A. Margarian and J. B. Dunlop, Solid State Commun. **90**, 487 (1994).

[4] C. D. Fuerst, F. E. Pinkerton and J. F. Herbst, J. Magn. Magn. Mater. **129**, L115 (1994).

[5] M. Kataoka, T. Satoh and E. Otsuki, J. Appl. Phys. **85,** 4675 (1999).

[6] D. Book, H. Nakamura, S. Sugimoto, M. Okada and M. Homma, Proc. 14th Intl. Workshop on RE Magnets and Their Applications (Sao Paulo, 1996) p.138.

[7] D. Book, K. Kato, H. Nakamura, S. Sugimoto, T. Kagotani, M Okada and M. Homma, Proc. 15th Intl. Workshop on RE Magnets and Their Applications (Dresden, 1998) p.543.

[8] K. H. J. Buschow, Handbook of Magnetic Materials, **vol. 9**, ELSEVIER SCIENCE B.V., Amsterdam, The Netherlands, (1995), 317.

[9] M. Katter, J. Wecker and L. Schultz, Journal of Applied Physics **70**, 3188 (1992).

[10] H. Samata, N. Fujiwara, Y. Shimizu, Y. Nagata, T. Uchida and M. D. Lan, Japanese Journal of Applied Physics **36**, 3492 (1997).