Phase Relation of Sm-Fe-V Alloys around the Compound $\text{Sm}_3(\text{Fe,V})_{29}$

Satoshi Sugimoto, Tomoyasu Shimono, Hajime Nakamura, Toshio Kagotani,
Masuo Okada and Motofumi Homma

Department of Materials Science, Faculty of Engineering,
Tohoku University, Sendai 980-77, JAPAN

Phase relations in the Sm-Fe-V system, especially around the compound $\text{Sm}_3(\text{Fe,V})_{29}$, have been studied. Isothermal sections of the iron-rich corner of the Sm-Fe-V system were constructed from X-ray diffraction studies and microstructural observations. α -(Fe,V), γ -(Fe,V), $\text{Sm}_2(\text{Fe,V})_{17}$, $\text{Sm}(\text{Fe,V})_{12}$ and liquid phases are present near the $\text{Sm}_3(\text{Fe,V})_{29}$ compound after annealing at 1100°C. However, nearly single phase $\text{Sm}_3(\text{Fe,V})_{29}$ can be obtained with an alloy of composition $\text{Sm}_{9.5}\text{Fe}_{83.5}\text{V}_7$. The solid solubility of Sm in $\text{Sm}_3(\text{Fe,V})_{29}$ compound is very small, but that of V is in the range 5.6 at% to 9.2 at%. The liquid phase region expands to the lower V content with increasing annealing temperature, leading to a decreasing V content in the $\text{Sm}(\text{Fe,V})_{12}$ compound at high temperature.

key words : phase relation, $\text{Sm}_3(\text{Fe,V})_{29}$ compound, isothermal section, microstructure, annealing, X-ray diffraction, SEM-EDX

I. Introduction

After the discovery of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound⁽¹⁾, intermetallic compounds with rare earths (RE) and 3d transition metals were investigated by many researchers. Iron based compounds are very attractive for permanent magnet applications because of their high magnetic moments. At first, attention was paid on the investigation of the magnetic properties of $\text{RE}(\text{Fe,M})_{12}$ (M= Ti, Cr, V, Mn, Si etc.) (1-12) compound with the ThMn_{12} -type structure⁽²⁻⁵⁾. Then the focus moved onto carbon or nitrogen containing $\text{RE}_2\text{Fe}_{17}$ (2-17) compounds⁽⁶⁻⁸⁾. Among $\text{RE}_2\text{Fe}_{17}\text{N}_x$ compounds, $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ compound shows good magnetic properties, comparable to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound, and has been studied by many researchers.

Recently, Collcott et al.⁽⁹⁾ reported a new intermetallic compound near the 1-12 and 2-17 compound. X-ray diffraction reveals that this new intermetallic compounds has a monoclinic structure and a composition of $\text{RE}_3(\text{Fe,M})_{29}$ (3-29)⁽¹⁰⁻¹³⁾. The structure of the 3-29 compound forms by the replacement of 2/5 of the rare earths atoms by Fe-Fe dumb-bells in the CaCu_5 -type structure, and is derived from the alternate stacking of 1-12 and 2-17 segments. In common with $\text{RE}_2\text{Fe}_{17}$ compounds, nitriding greatly increases the magnetic properties of the 3-29 compound. In particular, $\text{Sm}_3(\text{Fe,M})_{29}\text{N}_x$ exhibits good magnetic properties and is an interesting candidate for the next generation of permanent magnets⁽¹⁰⁻¹⁷⁾. Suzuki et al.⁽¹⁸⁾ reported that nitrided $\text{Sm}_3(\text{Fe,M})_{29}$ alloy powders stabilized by V (M=V), exhibit a characteristic magnetization curve of a gentle slope, like that seen in "pinning type"

magnets. Therefore, it can be said that there is a possibility of forming a pinning type magnet, such as $\text{Sm}(\text{Co, Fe, Cu, Zr})_{7-8.5}$ magnets⁽¹⁹⁾, in the Sm-Fe-V-N system.

However, the compositional region where $\text{Sm}_3(\text{Fe,V})_{29}$ exists as a single phase, is not yet clear, and so there is a great need for a basic understanding of the phase relations in the Sm-Fe-V system around the compound $\text{Sm}_3(\text{Fe,V})_{29}$. Only one isothermal phase diagram of 3-29 compound has been reported by Margarian et al.⁽²⁰⁾, but this is for the Nd-Fe-Ti system. Therefore this study aims to construct isothermal sections around the iron rich corner of the Sm-Fe-V system, paying particular attention to the compound $\text{Sm}_3(\text{Fe,V})_{29}$.

II. Experimental Procedures

The compositions of the studied alloys, and a schematic diagram of the experimental procedures, are shown in Fig. 1. Twelve alloys with composition $\text{Sm}_z\text{Fe}_{100-y-z}\text{V}_z$ ($z=7.5-10.5$, $y=5-9$) surrounding the $\text{Sm}_3(\text{Fe,V})_{29}$ (3-29) compound were induction-melted and cast into a Cu mold in an Ar atmosphere. The cast ingots were cut to the size, annealed at 1100 and 1200°C for 20 h in an Ar atmosphere, and then quenched in water.

The compositions of the alloys were verified by inductively coupled plasma atomic emission spectrometry (ICP). Microstructural observations were performed by scanning electron microscopy (SEM) to the specimens after etching the specimens in 2% nital. However, some specimens were observed without etching, in order to observe Sm-rich phases which would otherwise not be retained.

Fig. 1 The compositions of studied alloys and experimental procedures.

The phases present in the ingots were identified by X-ray diffraction (XRD) using Fe-K α radiation, and by an energy dispersive X-ray spectroscopy (EDX).

III. Results and Discussions

Figure 2 shows the X-ray diffraction patterns obtained from $\text{Sm}_{7.5}\text{Fe}_{92.5-y}\text{V}_y$ ($y=5,7,9$) alloys annealed at 1100°C for 20h. All of the alloys show X-ray diffraction peaks around $2\theta=47^\circ$ and 50° , which are typical X-ray diffraction peaks for the $\text{Sm}_3(\text{Fe,V})_{29}$ phase. This suggests that all the alloys contain $\text{Sm}_3(\text{Fe,V})_{29}$ phase. The X-ray intensity of α -Fe becomes stronger with decreasing V content, so it can be said that the volume fraction of α -Fe increases with decreasing V content. The X-ray diffraction peaks besides those of $\text{Sm}_3(\text{Fe,V})_{29}$ phase and α -Fe are mostly likely due to the presence of $\text{Sm}(\text{Fe,V})_{12}$ and $\text{Sm}_2(\text{Fe,V})_{17}$ phases. Judging from the X-ray diffraction peak around $2\theta=39^\circ$, it is possible that the $\text{Sm}_2(\text{Fe,V})_{17}$ phase is present in the 5at%V alloy. However, using only X-ray diffraction, it is difficult to distinguish $\text{Sm}_2(\text{Fe,V})_{17}$, $\text{Sm}_3(\text{Fe,V})_{29}$ and $\text{Sm}(\text{Fe,V})_{12}$ phases clearly, because their diffraction peaks tend to overlap. Therefore microstructural observations using SEM-EDX were carried out.

Figure 3 shows SEM micrograph of (a) $\text{Sm}_{7.5}\text{Fe}_{83.5}\text{V}_9$, (b) $\text{Sm}_{7.5}\text{Fe}_{85.5}\text{V}_7$ and (c) $\text{Sm}_{7.5}\text{Fe}_{86.5}\text{V}_5$ alloys annealed at 1100°C for 20h in an Ar atmosphere. In addition to the matrix phase, a dark and a grey phase were observed in the (a) $\text{Sm}_{7.5}\text{Fe}_{83.5}\text{V}_9$ alloy. The EDX analysis revealed that the matrix, dark and gray phases are $\text{Sm}_3(\text{Fe,V})_{29}$, α -Fe and $\text{Sm}(\text{Fe,V})_{12}$, respectively. It is most likely that the other phase in the $\text{Sm}_{7.5}\text{Fe}_{83.5}\text{V}_9$ alloy, besides

Fig. 2 The X-ray diffraction patterns of $\text{Sm}_{7.5}\text{Fe}_{92.5-y}\text{V}_y$ ($y=5,7,9$) alloys annealed at 1100°C for 20h.

Fig. 3 SEM microstructures of (a) $\text{Sm}_{7.5}\text{Fe}_{83.5}\text{V}_9$, (b) $\text{Sm}_{7.5}\text{Fe}_{85.5}\text{V}_7$ and (c) $\text{Sm}_{7.5}\text{Fe}_{86.5}\text{V}_5$ alloys annealed at 1100°C for 20h.

$\text{Sm}_3(\text{Fe,V})_{29}$ and $\alpha\text{-Fe}$ phases is the $\text{Sm}(\text{Fe,V})_{12}$ phase, which can not be determined by X-ray diffraction alone (Fig. 2 (a)). In the (b) $\text{Sm}_{7.5}\text{Fe}_{85.5}\text{V}_7$ alloy, three phases can be observed, but the $\text{Sm}(\text{Fe,V})_{12}$ phase has disappeared and a small amount of $\text{Sm}_2(\text{Fe,V})_{17}$ phase can also be observed. This alloy has three phases: $\text{Sm}_3(\text{Fe,V})_{29}$ matrix phase; $\alpha\text{-Fe}$; and $\text{Sm}_2(\text{Fe,V})_{17}$ phase. However with decreasing V content, the matrix phase changes from $\text{Sm}_3(\text{Fe,V})_{29}$ to $\text{Sm}_2(\text{Fe,V})_{17}$, as shown in the $\text{Sm}_{7.5}\text{Fe}_{86.5}\text{V}_5$ alloy (Fig. 3 (c)).

Figure 4 shows the SEM photographs of $\text{Sm}_{10.5}\text{Fe}_{89.5-y}\text{V}_y$ alloys annealed at 1100°C for 20h. A small amount of $\alpha\text{-Fe}$ can be observed in the (a) $\text{Sm}_{10.5}\text{Fe}_{80.5}\text{V}_9$ alloy, however, the volume fraction is smaller than the $\text{Sm}_{7.5}\text{Fe}_{92.5-y}\text{V}_y$ alloys shown in Fig. 3. The (a) $\text{Sm}_{10.5}\text{Fe}_{80.5}\text{V}_9$ alloy contains $\alpha\text{-Fe}$, $\text{Sm}_3(\text{Fe,V})_{29}$ and $\text{Sm}_2(\text{Fe,V})_{17}$ phases. Comparing with the $\text{Sm}_{7.5}\text{Fe}_{83.5}\text{V}_9$ alloy (Fig. 3(a)), the $\text{Sm}(\text{Fe,V})_{12}$ phase is replaced by $\text{Sm}_2(\text{Fe,V})_{17}$ phase in the $\text{Sm}_{10.5}\text{Fe}_{80.5}\text{V}_9$ alloy. The main phase of $\text{Sm}_{10.5}\text{Fe}_{82.5}\text{V}_7$ and $\text{Sm}_{10.5}\text{Fe}_{84.5}\text{V}_5$ alloys is $\text{Sm}_2(\text{Fe,V})_{17}$ phase, as shown in Fig. 4 (b) and (c).

In order to investigate the phase change with increasing Sm content, X-ray diffraction studies were carried out on $\text{Sm}_z\text{Fe}_{93-z}\text{V}_7$ ($z=7.5-10.5$) alloys annealed at 1100°C for 20h (Fig. 5). Every alloy shows the X-ray diffraction pattern of the $\text{Sm}_3(\text{Fe,V})_{29}$ phase; in particular the

Fig. 5 The X-ray diffraction patterns taken from $\text{Sm}_z\text{Fe}_{93-z}\text{V}_7$ ($z=7.5-10.5$) alloys annealed at 1100°C for 20h.

Fig. 4 SEM microstructures taken from (a) $\text{Sm}_{10.5}\text{Fe}_{80.5}\text{V}_9$, (b) $\text{Sm}_{10.5}\text{Fe}_{82.5}\text{V}_7$ and (c) $\text{Sm}_{10.5}\text{Fe}_{84.5}\text{V}_5$ alloys annealed at 1100°C for 20h.

characteristic X-ray diffraction peak at $2\theta=47^\circ$ can be observed. This shows that $\text{Sm}_3(\text{Fe,V})_{29}$ exists as a main phase in these four alloys. The X-ray intensity of $\alpha\text{-Fe}$ decreases with increasing Sm content which suggests that the volume fraction of $\alpha\text{-Fe}$ decreases, however clear informations on the other phases cannot be obtained using X-ray diffraction, because of the reasons described before. Therefore, SEM-EDX observation were carried out.

Figure 6 shows the corresponding SEM photographs. Three phases dark, grey and bright grey, can be observed in the $\text{Sm}_{7.5}\text{Fe}_{85.5}\text{V}_7$ and $\text{Sm}_{8.5}\text{Fe}_{84.5}\text{V}_7$ alloys (Fig. 6 (a) and (b)). EDX analysis identifies them as $\alpha\text{-Fe}$, $\text{Sm}_3(\text{Fe,V})_{29}$ and $\text{Sm}_2(\text{Fe,V})_{17}$, respectively. $\text{Sm}_3(\text{Fe,V})_{29}$ exists as a matrix phase and $\text{Sm}_2(\text{Fe,V})_{17}$ can be observed at grain boundaries as a minor phase. The $\alpha\text{-Fe}$ phase is present near the $\text{Sm}_2(\text{Fe,V})_{17}$ phase. In the $\text{Sm}_{9.5}\text{Fe}_{83.5}\text{V}_7$ and $\text{Sm}_{10.5}\text{Fe}_{82.5}\text{V}_7$ alloys (Fig. 6 (c) and (d)), the $\alpha\text{-Fe}$ phase disappears and two phases such as $\text{Sm}_3(\text{Fe,V})_{29}$ and $\text{Sm}_2(\text{Fe,V})_{17}$ phases appear. Small cracks are observed within the $\text{Sm}_3(\text{Fe,V})_{29}$ grains, and the $\text{Sm}_2(\text{Fe,V})_{17}$ phase is surrounded by $\text{Sm}_3(\text{Fe,V})_{29}$. Nearly single phase $\text{Sm}_3(\text{Fe,V})_{29}$ compound can be obtained with these alloys, but from microstructural observations on $\text{Sm}_{10.5}\text{Fe}_{82.5}\text{V}_7$ alloy without etching, a phase with a Sm content of 75-92 at% can be observed, which is most probably liquid at 1100°C . Therefore it can be said that liquid phase is present in this compositional region.

Fig. 6 SEM photographs of $\text{Sm}_z\text{Fe}_{93-z}\text{V}_7$ ($z=7.5-10.5$) alloys annealed at 1100°C for 20h.

The isothermal section of the Sm-Fe-V system at 1100°C , constructed from the experimental results described above, is shown in Fig. 7. The dashed lines in Fig. 7 are expected from both experimental results and binary phase diagrams. The existence of five phases around the $\text{Sm}_3(\text{Fe,V})_{29}$ compound can be confirmed. The phase regions appearing in Sm-Fe-V system are characterized by two-phase and three-phase fields among the compounds $\text{Sm}_3(\text{Fe,V})_{29}$, $\text{Sm}(\text{Fe,V})_{12}$, $\text{Sm}_2(\text{Fe,V})_{17}$, $\alpha\text{-(Fe,V)}$, $\gamma\text{-(Fe,V)}$ and liquid. The EDX analysis suggests that the solid solubility of Sm to $\text{Sm}_3(\text{Fe,V})_{29}$ is very small, however, that of V is in the range 5.6 to 9.2 at%. When the V content increases from that of the $\text{Sm}_3(\text{Fe,V})_{29}$ compound, the $\text{Sm}(\text{Fe,V})_{12}$ compound

coexists in this region. However, with decreasing V content, the $\text{Sm}_2(\text{Fe,V})_{17}$ phase appears. When the Sm concentration decreases from the $\text{Sm}_3(\text{Fe,V})_{29}$ compound, $\alpha\text{-(Fe,V)}$ appears at the expense of $\text{Sm}_3(\text{Fe,V})_{29}$. The $\alpha\text{-(Fe,V)}$ phase exists in a relatively large region, because V is soluble in the $\alpha\text{-(Fe,V)}$ phase to the amount of 30 at% at 1100°C , as shown in Fe-V binary phase diagram. The liquid phase is formed with increasing Sm content from the $\text{Sm}_3(\text{Fe,V})_{29}$ compound.

Figure 8 shows the isothermal sections of the Sm-Fe-V system at 1200°C obtained by the same method described before. The phase relations do not change greatly when compared with those at 1100°C , however the liquid phase region expands to lower V content alloys, resulting in

Fig. 7 Isothermal section of the Sm-Fe-V system at 1100°C .

Fig. 8 Isothermal section of the Sm-Fe-V system at 1200°C .

a decrease of the solid solubility of V in $\text{Sm}(\text{Fe,V})_{12}$.

Acknowledgment

The authors would like to thank Dr. David Book for his helpful discussions and Mr. Yoshihiro Yamazaki for his assistance with many measurements.

References

- (1) M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto and Y. Matsuura, *J. Appl. Phys.*, **55** (1984), 2083.
- (2) K. Ohashi, T. Yokoyama, R. Osugi and Y. Tawara, *IEEE Trans. Magn.*, **MAG-23** (1987), 3101.
- (3) K. Ohashi, Y. Tawara, R. Osugi, J. Sakurai and Y. Komura, *J. Less-Common Met.*, **139** (1988), L1.
- (4) B. D. Mooij and K. H. J. Buschow, *Philips J. Res.*, **42** (1987), 246.
- (5) D. B. Mooij and K. H. Buschow, *J. Less-Common Met.*, **136** (1988), 207.
- (6) T. Iriyama, K. Kobayashi, N. Imaoka, T. Fukuda, H. Kato and Y. Nakagawa, *IEEE Trans. Magn.*, **28** (1992), 2326.
- (7) J. M. D. Coey, H. Sun and Y. Otani, *Proc. 11th Int'l. Workshop on R. E. Magnets & Their Applications*, Pittsburgh, (1990), p. 36.
- (8) Y. Otani, D. P. F. Hurley, H. Sun and J. M. D. Coey, *J. App. Phys.*, **69** (1991), 5584.
- (9) S. J. Collocott, R. K. Day, J. B. Dunlop and R. L. Davis, *Proc. 7th Int. Symposium on Magnetic Anisotropy & Coercivity in RE-TM Alloys*, Cambera, (1992), p. 437.
- (10) H.-S. Li, J. M. Cadogan, R. L. Davis, A. Margarian and J. B. Dunlop, *Solid State Commun.*, **90** (1994), 487.
- (11) J. M. Cadogan, H.S. Li, R. L. Davis, A. Margarian, S. J. Collocott, J. B. Dunlop and P. B. Gwan, *J. Appl. Phys.*, **75** (1994), 7114.
- (12) C. D. Fuerst, F.E. Pinkerton, and J. F. Herbst, *J. Magn. Magn. Mater.*, **129** (1994), L115.
- (13) J. M. Cadogan and H. -S. Li, A. Margarian, J. B. Dunlop, D. H. Ryan, S. J. Collocott, and R. L. Davis, *J. Appl. Phys.*, **76** (1994), 6138.
- (14) J. M. Cadogan, R. K. Day, J. B. Dunlop and A. Margarian, *J. Alloys Compounds*, **201** (1993), L1.
- (15) B. P. Hu, G. C. Liu, Y. Z. Wang, B. Nasunjilegal, R. W. Zhao, F. M. Yang, H. S. Li and J. M. Cadogan, *J. Phys.: Condens. Matter*, **6** (1994), L197.
- (16) J. Hu, F. Yang, B. Nasunjilegal, R. Zhao, H. Pan, Z. Wang, B. P. Hu, Y. Zhong and G. C. Liu, *J. Phys.: Condens. Matter*, **6** (1994), L411.
- (17) B. Nasunjilegal, F.-M. Yang, N. Tang, W. D. Qin, J. L. Wang, J. J. Zhu, H. Q. Guo, B. P. Hu, Y. Z. Wang and H. S. Li, *J. Alloys Compounds*, **222**(1995), 57.
- (18) S. Suzuki, S. Suzuki and M. Kawasaki, *J Appl. Phys.*, **76** (1994), 6708.
- (19) K.J. Strnat, *Ferromagnetic Materials, vol.4*, Ed. by E. P. Wohlfarth and K. H. J. Buschow, Elsevier Science Publishers B.V., Amsterdam, (1988), p. 131.
- (20) A. Margarian, J. B. Dunlop, R. K. Day and W. Kalceff, *J. Appl. Phys.*, **76** (1994), 6153.