Materials Letters 15 (1992) 45–48
North-Holland

MATERIALS LETTERS

Thermal analysis of $SmTiFe_{11-x}Co_x$ ($x=0$, 11) and $DyTiCo_{11}$ intermetallic alloys

B.G. Demczyk

North Campus Electron Microbeam Analysis Laboratory, Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109-2143, USA

Received 30 June 1992

Alloys of composition $SmTiFe_{11-x}Co_x$ ($x=0$, 11) and $DyTiCo_{11}$ have been examined via differential thermal analysis. Thermal peaks found in the Sm-containing $TiFe_{11}$ sample were consistent with a 1-12 phase, with additional Fe_2Ti and α-Fe phases present, as found in a previous work. In $SmTiCo_{11}$, evidence for a 1-12, a 2-17 and a primarily Co-containing solid solution was found. When Dy is substituted for Sm in the Co_{11} sample, an additional peak, possibly due to the formation of the hexagonal 2-17 phase from the rhombohedral phase was noted. In addition, peaks corresponding to the ferromagnetic ordering of Fe in $SmTiFe_{11}$ and of Co in $DyTiCo_{11}$ were observed.

1. Introduction

Among permanent magnets, the $Nd_2Fe_{14}B$-based magnets have the highest energy product (in excess of 45 MGOe). However, their Curie temperatures are relatively low, leading to a large temperature coefficient of coercivity that limits the range of their application. Also, corrosion is a problem for these magnets. Ohashi et al. [1] and Stadelmaier et al. [2] have reported a body-centered tetragonal $SmTiFe_{11}$ compound which is isomorphous with $ThMn_{12}$ (I4/mmm). This material has solicited interest due to its high room-temperature anisotropy field (>100 kOe) which renders it a promising candidate for permanent magnet applications. The Curie temperature of this material (≈ 300°C) is comparable to that of $Nd_2Fe_{14}B$ and can be increased by replacing Fe with Co. Therefore, it is of interest to examine the effects of Co substitution on the phase distribution in the $SmTiFe_{11}$ alloy. Also, the effect of replacing Sm by other rare earth atoms (R) is of interest. The magnetic properties, phase and structural characteristics in the $RTiFe_{11-x}Co_x$ system have been examined previously [3–9]. The results of phase analysis using scanning electron microscopy [8] indicate the presence of a R_2(Fe, Co, Ti)$_{17}$ phase and a (Fe, Co, Ti) solid solution in addition to the R(Fe, Co, Ti)$_{12}$ phase with increasing Co content in samples annealed at 1000°C. The reported phase diagrams for these ternary systems are incomplete (see, for example, ref. [10]). Prior transmission electron microscopy/X-ray energy dispersive spectroscopy analyses have identified the predominant phases in these alloys [11]. In this work, the specific transition temperature regimes in the bulk alloys $SmTiFe_{11}$, $SmTiCo_{11}$ and $DyTiCo_{11}$ were examined by differential thermal analysis.

2. Experimental

Samples with the compositions of $SmTiFe_{11}$, $SmTiCo_{11}$ and $DyTiCo_{11}$ were prepared from high-purity constituent elements by induction melting in a 450 kHz water-cooled copper boat furnace in flowing argon. Excess samarium was added to compensate for samarium loss during melting. As-cast ingots were wrapped in Ta foils, sealed in argon filled quartz tubes and annealed at 1000°C for one week. Samples were then broken into approximately 3 mm diameter chunks for analysis. Thermal analysis was performed using a Perkin-Elmer DTA 1700 differential thermal analyzer coupled to a System 7/4 thermal analysis controller. Heating and cooling scans were taken at 10°/min for 200 to 1450°C. The sample was kept in an isothermal state between heating and cooling runs.

3. Results and discussion

Figs. 1a and 1b represent heating and cooling curves, respectively, for the $SmTiFe_{11}$ alloy. From fig. 1a, we observe peaks at approximately 1260 and 1310°C. The higher-temperature peak is most likely due to the decomposition of the Fe_2Ti phase into an Fe–Ti solid solution and possibly α-Fe [12,13]. All three phases have been found in previous transmission electron microscopy/X-ray energy dispersive spectroscopy analyses [11]. In that work, the reported stoichiometries were 75% Fe–25% Co for the Fe_2Ti and 98% Fe–2% Ti for the solid solution. The peak at 1260°C is most likely due to the decomposition of a "1-12" phase, which is not identified as such in ref. [12], but was nevertheless found in ref. [11]. In this case the stoichiometry was 85% Fe–8% Sm–7% Ti. Upon cooling from an isothermal state at 1450°C, two peaks appear at 1440 and 1410°C, respectively. The upper peak is due to the formation of Fe_2Ti, which congruently melts [13]. The lower peak extends over a range of temperatures, down to 1350°C, which is consistent with the published phase diagram [13]. Close examination of fig. 1b reveals a small peak at 747°C, which represents the ferromagnetic ordering of Fe [13].

Figs. 2a and 2b depict the same curves for the $SmTiCo_{11}$ alloy. From fig. 2a, we again note the presence of two peaks. These most likely correspond to the breakdown of the 1-12 (1210°C) and the 2-17 (1250°C) phases. It should be noted that there is no explicit 1-12 phase shown in ref. [14], but this

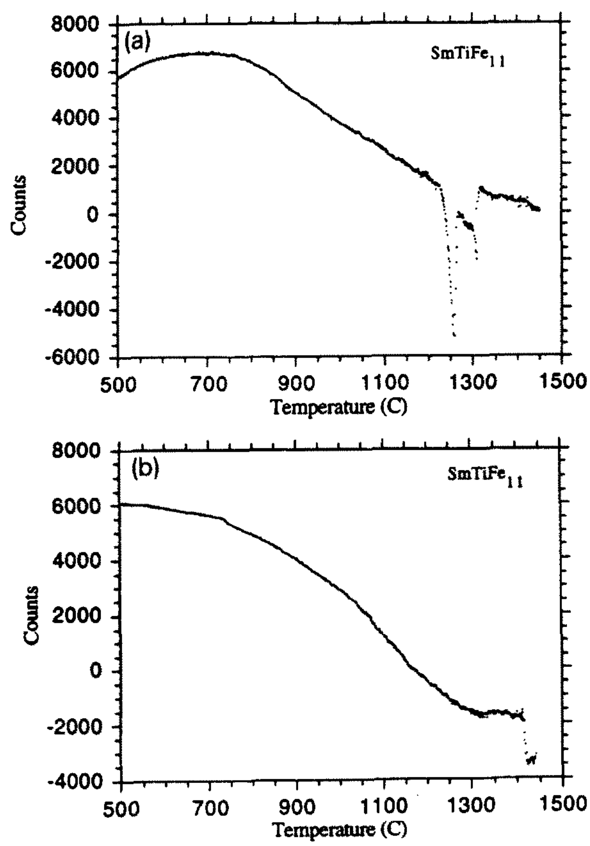

Fig. 1. (a) Heating and (b) cooling curves for $SmTiFe_{11}$ alloy.

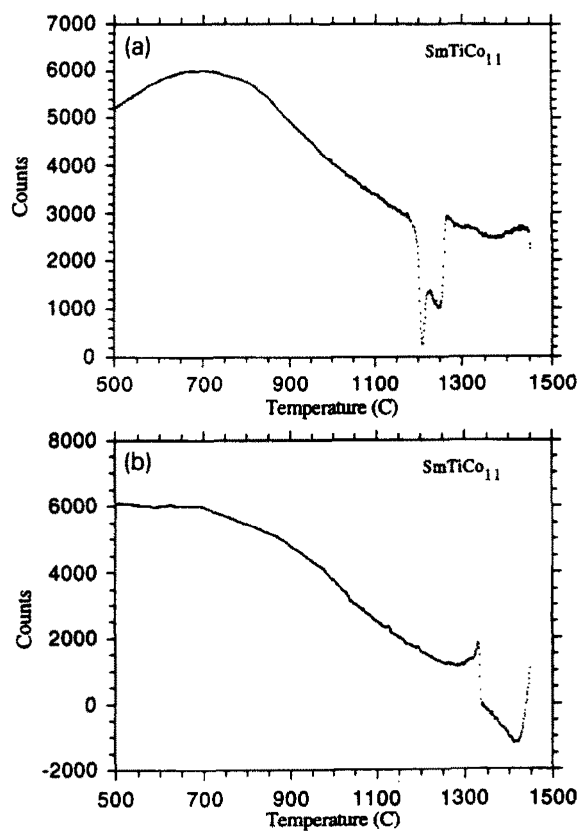

Fig. 2. (a) Heating and (b) cooling curves for $SmTiCo_{11}$ alloy.

phase (84% Co–7% Sm–9% Ti) was found in ref. [11], along with the 2-17 phase (85% Co–9.5% Sm–5% Ti). The highest-temperature peak ($\approx$1450°C) is that of the melting of near-elemental Co [13], which has also been found as a solid solution (90% Co–10% Ti) in a previous work [11]. The cooling curve (fig. 2b) displays a primary peak at 1340°C. However, it is extended over a range of 1250–1340°C, encompassing the reformation of the 2-17 and 1-12 intermetallic phases. We also observe the solidification of Co at 1450°C.

When Sm is replaced by Dy, we obtain qualitatively similar heating/cooling curves to the Sm case (figs. 3a and 3b). Thus we see peaks at 1210 and 1250°C corresponding to the 1-12 and 2-17 phases, respectively. Again, no 1-12 phase is depicted in ref. [15], but such was found in ref. [11] (84.5% Co–8% Dy–7.5% Ti), in addition to 2-17 (85.5% Co–10% Dy–4.5% Ti). Also, there is seen to be an extended melting regime ($\approx$1350–1430°C), possibly corresponding to the partial transformation of the rhombohedral 2-17 form to the hexagonal form, which was reported in ref. [11]. As in the Sm case, near-elemental Co is seen to melt at $\approx$1450°C.

The cooling curve (fig. 3b) is considerably simpler, exhibiting only the Co peak at 1450°C, and a sharp peak at 1225°C, due to the formation of one "2-17" phase, with stoichiometry 24% Dy+Ti, 76% Co, as depicted in ref. [15]. Close examination of fig. 3b also reveals a small peak at $\approx$960°C, which corresponds to the ferromagnetic ordering of Co, as shown in ref. [13].

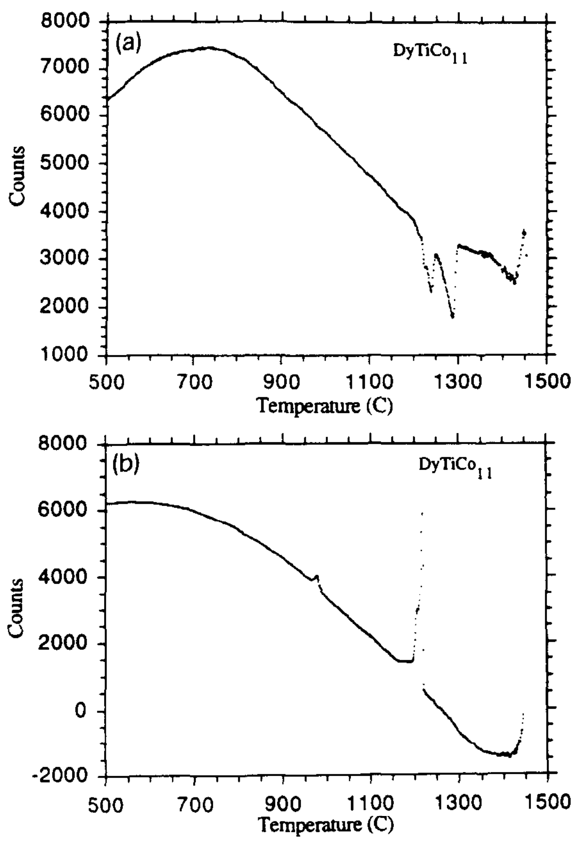

Fig. 3. (a) Heating and (b) cooling curves for $DyTiCo_{11}$ alloy.

4. Summary

Alloys of the composition $SmTiFe_{11}$, $SmTiCo_{11}$ and $DyTiCo_{11}$ have been examined by differential thermal analysis. Thermal peaks found in the Sm-containing $TiFe_{11}$ sample were consistent with a 1-12 phase, with additional Fe_2Ti and α-Fe phases present, as found in a previous work. In $SmTiCo_{11}$, evidence for a 1-12, a 2-17 and a primarily Co-containing solid solution was found. When Dy is substituted for Sm in the Co_{11} sample, an additional peak, possibly due to the formation of the hexagonal 2-17 phase from the rhombohedral phase was found. In addition, peaks corresponding to the ferromagnetic ordering of Fe in $SmTiFe_{11}$ and of Co in $DyTiCo_{11}$ were observed.

Acknowledgement

Samples were supplied by the Advanced Materials Corporation, Pittsburgh, PA.

References

[1] K. Ohashi, Y. Tawara, R. Osugi, J. Sakurai and Y. Komura, J. Less-Common Metals 139 (1988) L1.
[2] H.H. Stadelmaier, F.J. Cadieu and N.C. Liu, Mater. Letters 6 (1988) 80.
[3] S.F. Cheng, V.K. Sinha, Y. Xu, J.M. Elbicki, W.E. Laughlin, S.G. Sankar and D.E. Laughlin, J. Mag. Magn. Mater. 75 (1988) 330.

[4] E.B. Boltich, B.M. Ma, L.Y. Zhang, F. Pouranian, S.K. Malik, S.G. Sankar and W.E. Wallace, J. Mag. Magn. Mater. 78 (1989) 364.
[5] V.K. Sinha, S.K. Malik, D.T. Adroja, J.M. Elbicki, S.G. Sankar and W.E. Wallace, J. Mag. Magn. Mater. 80 (1989) 281.
[6] L.Y. Zhang, E.B. Boltich, V.K. Sinha and W.E. Wallace, IEEE Trans. Magn. 25 (1989) 3303.
[7] V.K. Sinha, S.F. Cheng, W.E. Wallace and S.G. Sankar, J. Mag. Magn. Mater. 81 (1989) 227.
[8] S.F. Cheng, V.K. Sinha, B.G. Demczyk, W.E. Wallace and D.E. Laughlin, unpublished research,
[9] S.F. Cheng, V.K. Sinha, Y. Xu and W.E. Wallace, unpublished research.
[10] T. Massalski, ed., Binary alloy phase diagrams, 2nd Ed. (ASM International, Materials Park, OH, 1990).
[11] S.F. Cheng, B.G. Demczyk and D.E. Laughlin, J. Mag. Magn. Mater. 84 (1990) 162.
[12] O. Kubashewski, Iron binary phase diagram (Springer, Berlin, 1982) p. 105.
[13] J.L. Murray, Phase diagrams of binary titanium alloys (ASM International, Materials Park, OH, 1987).
[14] W.G. Moffatt, ed., Handbook of binary alloy phase diagrams (General Electric Corporation, Schenectedy, NY, 1981).
[15] T. Massalski, in: Binary alloy phase diagrams, 2nd Ed., ed. T. Massalski (ASM International, Materials Park, OH, 1990) p. 1184.