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Journal of Alloys and Compounds 224 (1995) 29–32

Journal of
ALLOYS
AND COMPOUNDS

The formation of Z-phase $Sm(Fe,Ti)_{8.5}$

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Received 24 May 1994

Abstract

The high-temperature modification $Sm_2(Fe,Ti)_{17}$ of Th_2Ni_{17} type was found to exist in the $Sm(Fe_{1-x}Ti_x)_y$ alloy system ($0.04 \leqslant x \leqslant 0.07$ and $8.0 \leqslant y \leqslant 9.0$) at $T \geqslant 1250$ °C. More low-temperature phases $Sm(Fe,Ti)_{12}$ and $Sm_2(Fe,Ti)_{17}$ of Th_2Zn_{17} type form from this modification. A ternary $Sm(Fe_{0.935}Ti_{0.065})_{8.5}$ compound analogous to the Z-phase $Sm(Fe_{0.91}V_{0.09})_{8.5}$ is obtained in the interval 1150–1250 °C. It can be considered to have a new type of a superstructure based on the $CaCu_5$-type structure with a monoclinic unit cell having parameters $a = 0.972$ nm, $b = 0.856$ nm, $c = 1.063$ nm, $\beta = 96° \, 50'$.

Keywords: Hard magnetic materials; Rare-earth intermetallics

1. Introduction

During recent years, R–M–T systems (R is a rare earth metal; M ≡ Fe, Co, T is an element of groups IV–VI of Mendeleev's periodic table) in the M-rich regions have been intensively studied as they might serve as starting materials for permanent magnets. The iron-rich corner of the Sm–Fe–Ti diagram has been investigated [1–3]. A ternary $ThMn_{12}$-type compound $Sm(Fe,Ti)_{12}$ as well as $Sm(Fe,Ti)_{11}$ with $Ce(Mn_{0.55}Ni_{0.45})_{11}$-type structure have been found. The $Sm(Fe,Ti)_9$ compound with proposed $TbCu_7$-type structure has also been discovered.

Our investigations [4] and recently published paper [5] have shown that a new compound analogous to Z-phase $R(Fe_{0.91}V_{0.09})_{8.5}$ (R ≡ Y,Nd,Sm,Gd,Tb) [6–8] exists in this system. The Z-phase can be identified as a superstructure of a new type based on the $CaCu_5$ structure. Initially [6], its structure was described as hexagonal with parameters approximately five times larger than those of $CaCu_5$. However [7], it was established that the lattice differed from hexagonal: one of the ⟨11.0⟩ axes was slightly shorter than the other two (the ratio was close to 0.98). The lattice was described as orthorhombic with parameters $a = 4.260$ nm, $b = 2.427$ nm, $c = 2.099$ nm. Further comprehensive electron diffraction investigation [8] allowed determination of the extinction rules. According to these the unit cell cannot be considered orthorhombic because in this case the reflections with indexes hkl are often allowed, while $hk\bar{l}$ reflections are forbidden. A model of the arrangement of atoms in the Z-phase, in agreement with these extinction rules, has been proposed. The monoclinic unit cell with parameters $a = 0.970$ nm, $b = 0.852$ nm, $c = 1.058$ nm, $\beta = 96° \, 39'$ corresponds to this model.

Here, we report the formation of the Z-phase in the Sm–Fe–Ti system, its composition and magnetic properties.

2. Experimental details

$Sm(Fe_{1-x}Ti_x)_y$ alloys, where $0.03 \leqslant x \leqslant 0.08$ and $7.0 \leqslant y \leqslant 9.0$, were prepared by induction melting from the elemental constituents of purities 99.80% for Sm, 99.98% for Fe and 99.95% for Ti. Our starting compositions contained 10%–12% excess Sm relative to $R(Fe,Ti)_{8.5}$ stoichiometry. The samples were annealed at 900–1250 °C in a pure helium atmosphere.

The crystal lattice was investigated in RKU-114M and RKV-86A chambers or with a DRON-type diffractometer using Cr radiation. The samples for X-ray studies were powder or single-grain fragments of size 0.1–0.2 mm. The easy magnetization direction (EMD) was found from X-ray photographs of oscillations of magnetically oriented powders.

The magnetic moment was measured with a vibrating sample magnetometer on powders in magnetic fields up to 1.6 MA m^{-1} in an electromagnet. The Curie temperatures T_c were obtained from the temperature

SSDI 0925-8388(94)01483-3

dependences of the a.c. susceptibility in fields less than 100 A m^{-1} at a frequency of 80 Hz.

3. Results and discussion

X-ray diffraction patterns of $Sm(Fe_{0.935}Ti_{0.065})_{8.5}$ annealed at 1150 °C are shown in Fig. 1(a). They are very similar to those of the Z-phase [7] and $R_3(Fe,Ti)_{29}$ (R ≡ Nd, Pr, Ce) [5,9]. Diffraction peaks are indicated assuming that the unit cell is monoclinic with parameters $a = 0.972$ nm, $b = 0.856$ nm, $c = 1.063$ nm, $\beta = 96° \ 50'$. In brackets, indexes corresponding to an orthorhombic cell are also displayed because this cell was initially assumed for $Sm(Fe_{0.91}V_{0.09})_{8.5}$ in Ref. [7].

The data on single-grain fragments $Sm(Fe_{0.94}Ti_{0.06})_{8.5}$ [4] are strong evidence for its being the Z-phase. Comprehensive analysis of X-ray photographs of oscillations was carried out in this paper. All reflections not relating to any previously known compounds were found to be exactly the same as those from single-grain fragments of the Z-phase $Y(Fe_{0.91}V_{0.09})_{8.5}$ [6]. However, the photographs can only be understood under the assumption that there are regions of several orientations related to each other. The formation of such regions is possible if the Z-phase forms from a more high-temperature phase, with the lattices of both phases being related by a certain mutual orientation.

To clarify this problem and to refine the concentration and temperature regions of the Z-phase, we investigated the phase content of as-cast alloys as well as alloys annealed at different temperatures. Some of these results are listed in Table 1. The Z-phase is the only phase in $Sm(Fe_{1-x}Ti_x)_y$ alloys annealed at 1150 °C for $x = 0.065$–0.070 and $y = 8.0$–8.5. After annealing for prolonged times at 900 and 1000 °C, many of the alloys investigated were found to contain $Sm_2(Fe,Ti)_{17}$ and $Sm(Fe,Ti)_{12}$ along with the Z-phase. Obviously, the Z-phase exists in a very narrow interval of concentrations x and y at these temperatures. The Z-phase is not detected in as-cast alloys or alloys annealed at 1250 °C. Thus, the upper boundary of existence of the Z-phase lies between 1150 and 1250 °C.

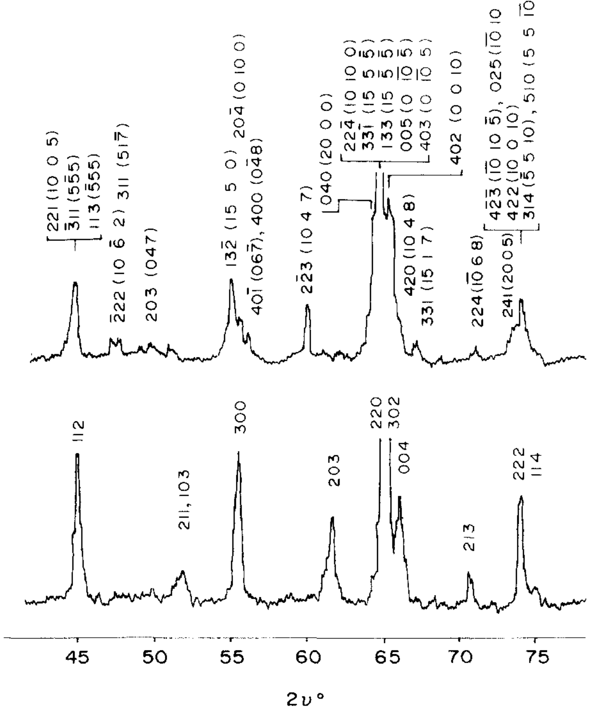

Fig. 1. X-ray diffraction patterns: (a) the Z-phase $Sm(Fe_{0.935}Ti_{0.065})_{8.5}$; (b) high-temperature modification $Sm_2(Fe,Ti)_{17}$ of Th_2Ni_{17}-type.

The Th_2Ni_{17}-type phase with parameters $a = 0.851$ nm and $c = 0.838$ nm (denoted $Sm_2(Fe,Ti)_{17}$–H in Table 1) is observed in as-cast alloys or alloys annealed at 1250 °C. Its X-ray diagram is shown in Fig. 1(b). The Th_2Zn_{17}-type low temperature modification $Sm_2(Fe,Ti)_{17}$ (denoted $Sm_2(Fe,Ti)_{17}$–R) has parameters $a = 0.856$ nm and $c = 1.247$ nm. Reducing to the $CaCu_5$-type unit cell gives the value $c/a = 0.8528$ for $Sm_2(Fe,Ti)_{17}$–H, noticeably larger than the value $c/a = 0.8412$ for $Sm_2(Fe,Ti)_{17}$–R.

As is seen from Table 1, the $Sm(Fe,Ti)_{12}$ compound is present in many as-cast alloys or alloys annealed at 1250 °C. It is found that in the X-ray photographs of oscillations, the reflections from large grains of $Sm_2(Fe,Ti)_{17}$–H and $Sm(Fe,Ti)_{12}$-containing alloys are as a rule ternary. One of these belongs to $Sm_2(Fe,Ti)_{17}$–H and the other two belong to $Sm(Fe,Ti)_{12}$ (for example, the reflection groups $420_{1:12}$–$22.2_{2:17}$–$222_{1:12}$ or $602_{1:12}$–$60.0_{2:17}$–$004_{1:12}$ and others are observed). After

Table 1
Phase content of $Sm(Fe_{1-x}Ti_x)_y$ alloys annealed at different temperatures

T (°C)	$x = 0.05$ $y = 9.0$	$x = 0.05$ $y = 8.5$	$x = 0.05$ $y = 8.0$	$x = 0.065$ $y = 8.5$	$x = 0.04$ $y = 8.0$
As-cast	2:17-H 1:12 α-Fe	2:17-H 1:12	2:17-H 2:17-R 1:12 *	1:12 1:2 2:17-H *	2:17-H 2:17-R 1:2 *
1250	2:17-H 1:12	2:17-H 1:12 *	2:17-H α-Fe 1:12 *	1:12 2:17-H α-Fe *	2:17-H α-Fe *
1150	1:12 Z α-Fe	Z 2:17-R	2:17-R	Z 1:12 *	2:17-R
1000	1:12	Z 2:17-R 1:12 *	2:17-R	2:17-R Z 1:12 *	2:17-R

2:17-R, $Sm_2(Fe,Ti)_{17}$ of Th_2Zn_{17}-type, $a = 0.856$ nm, $c = 1.247$ nm.
2:17-H, $Sm_2(Fe,Ti)_{17}$ of Th_2Ni_{17}-type, $a = 0.851$ nm, $c = 0.838$ nm.
1:12, $Sm(Fe,Ti)_{12}$.
Z, the Z-phase.
1:2, $Sm(Fe,Ti)_2$.
*, very small amount.

annealing the alloys at lower temperatures, 900–1150 °C, the $Sm(Fe,Ti)_{12}$ reflections remain double; the third $Sm_2(Fe,Ti)_{17}$ reflection disappears. This means that the $Sm(Fe,Ti)_{12}$ regions have different orientations. It is believed that $Sm_2(Fe,Ti)_{17}$–H is the most high-temperature phase and the other phases form from it. The emergence of the Z-phase is preceded by the formation of $Sm(Fe,Ti)_{12}$.

The Z-phase can be considered as a superstructure based on $CaCu_5$, as well as R_2M_{17} and RM_{12}. The (00.1) and (10.0) planes of the $CaCu_5$-type hexagonal lattice are shown in Fig. 2. It is seen how the R_2M_{17}, RM_{12} and Z-phase lattices are oriented with respect to $CaCu_5$. It is apparent that an orientation relation between the lattices of any these two compounds may exist. Our data support the conclusion that the indexes of the aforementioned reflection groups $Sm_2(Fe,Ti)_{17}$ and $Sm(Fe,Ti)_{12}$ as well as the relative positions of the Z-phase, $Sm_2(Fe,Ti)_{17}$–R and $Sm(Fe,Ti)_{12}$ reflections in the photographs from single-grain fragments (for example, see Fig. 2 [4]) agree with the orientation relations between the phases, resulting from Fig. 2. Thus, the formation of $Sm_2(Fe,Ti)_{17}$–H and $Sm(Fe,Ti)_{12}$ with subsequent appearance of the Z-phase, can lead to the emergence of regions with several orientations in every grain. As seen from Fig. 2, regions of three $Sm(Fe,Ti)_{12}$ and six Z-phase orientations can coexist.

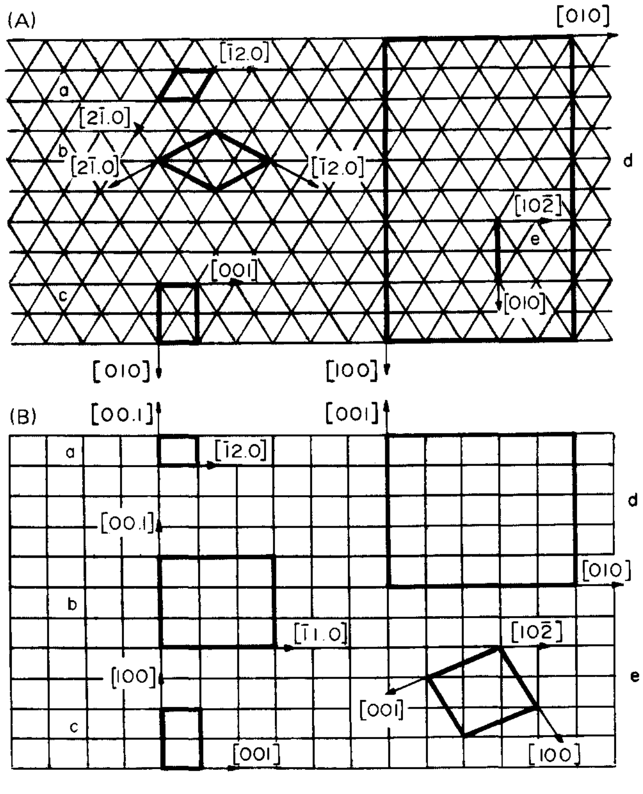

Fig. 2. The planes (00.1) (A) and {10.0} (B) of the $CaCu_5$-type hexagonal lattice. Mutual orientations of the $CaCu_5$ (a), Th_2Zn_{17} (b), $ThMn_{12}$ (c), Z-phase (d, an orthorhombic cell; e, a monoclinic cell) type unit cells are shown.

The Z-phase and $Sm_2(Fe,Ti)_{17}$–H are ferromagnets at room temperature. The Curie temperatures are 453–471 K and 453 K respectively. The scatter in T_c values is likely to be connected with the existence of a homogeneity region of the Z-phase. The highest T_c value for $Sm_2(Fe,Ti)_{17}$–R in the alloys investigated does not exceed 434 K.

The X-ray study of the magnetically oriented powders showed that the Z-phase $Sm(Fe,Ti)_{8.5}$ is magneto-uniaxial at room temperature, as well as $Sm(Fe_{0.91}V_{0.09})_{8.5}$ [7]. Its EMD coincides with the [10$\bar{2}$] axis of the monoclinic cell (the [010] axis of the orthorhombic cell). It is seen from Fig. 2 that this axis is one of three ⟨11.0⟩ axes of the $CaCu_5$ cell and it is shorter than the other two axes. In this respect the Z-phase does not stand out among known compounds which can be regarded as superstructures on the basis of $CaCu_5$ (RM_3, R_2M_7, R_2M_{17} and RM_{12}). All of these have the EMD parallel to the [00.1] axis or lying in the basal plane of the $CaCu_5$ lattice. So the monoclinic unit cell is inconvenient for perceiving this fact. The $Sm_2(Fe,Ti)_{17}$–H compound has the EMD lying in the basal plane.

The magnetization curves $\sigma(H)$ for oriented powders of the Z-phase and both modifications $Sm_2(Fe,Ti)_{17}$ measured in a magnetic field parallel or perpendicular to the EMD are illustrated in Fig. 3. The Z-phase is seen to have a sufficiently high value of anisotropy field in comparison with those of $Sm_2(Fe,Ti)_{17}$ which possesses plane anisotropy.

A correlation between our data and those for $Sm(Fe,Ti)_9$ [2] leads to the conclusion that this compound is identical to the Z-phase. Indeed, the compounds have almost the same composition: the composition of the Z-phase corresponds to the formula $Sm(Fe_{0.965}Ti_{0.035})_{8.5}$ and the composition of '$Sm(Fe,Ti)_9$' in fact corresponds to $Sm(Fe_{0.968}Ti_{0.032})_{8.58}$. The compound $Sm(Fe,Ti)_9$ has $T_c = 465$ K falling within the foregoing T_c interval of the Z-phase. The magnetic domain patterns [2] reveal that $Sm(Fe,Ti)_9$ should be uniaxial and have a high value of anisotropy field. The authors also noticed that the magnetic domains in neighbouring $Sm(Fe,Ti)_9$ and $Sm(Fe,Ti)_{12}$ grains were mostly coupled. The Z-phase is uniaxial high-anisotropic ferromagnet and the EMD of the Z-phase and $Sm(Fe,Ti)_{12}$ may be parallel because they form from the same initial high-temperature $Sm_2(Fe,Ti)_{17}$–H compound. Hence, the magnetic domains in grains of both compounds can be coupled. Thus, the peculiarities of the domain patterns are more likely to correlate with the supposition that '$Sm(Fe,Ti)_9$' is the Z-phase rather then the $TbCu_7$-type structure.

We have also found the Z-phase in $R(Fe,Ti)_{8.5}$ alloys where R ≡ Y, Nd, Gd. As mentioned above, a phase with the same monoclinic unit cell in R–Fe–M systems with R ≡ Ce, Pr, Nd, Sm and M ≡ Ti, Cr, Mn was

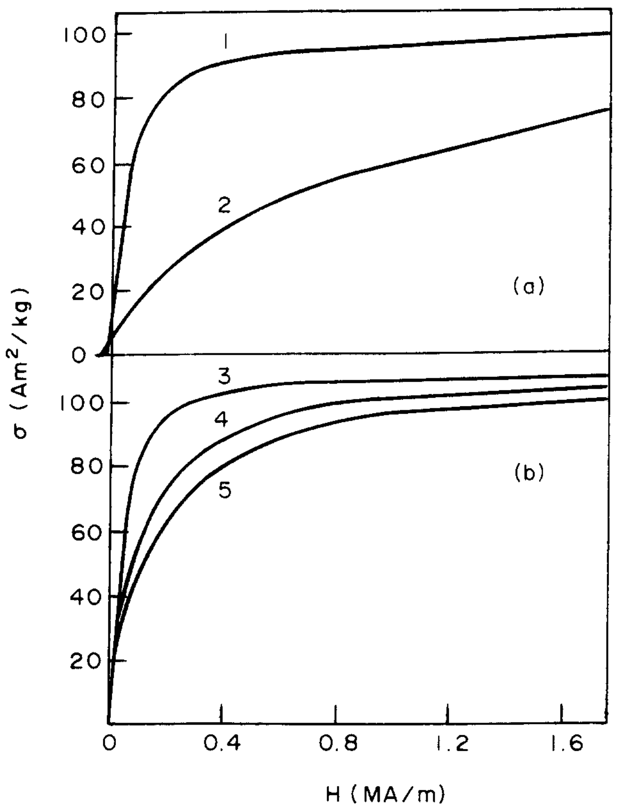

Fig. 3. Room temperature magnetization curves for oriented powders of the Z-phase Sm(Fe$_{0.935}$Ti$_{0.065}$)$_{8.5}$ (a) and Sm$_2$(Fe,Ti)$_{17}$ (b) measured in a magnetic field parallel (curves 1,3) or perpendicular (curves 2,4,5) to the easy magnetization direction: curves 3,4, Sm$_2$(Fe,Ti)$_{17}$–R; curves 3,5, Sm$_2$(Fe,Ti)$_{17}$–H.

discovered in Refs. [5,9]. According to these, the composition of the compounds corresponds to R$_3$(Fe,M)$_{29}$ stoichiometry. Earlier [8], we proposed three models for formation of the Z-phase by substitution of Fe or M for part of the R atoms in the CaCu$_5$-type structure. The alloy compositions and densities calculated for each model for R≡Sm were compared with experimental values. Only ten Sm atoms fall within a selected monoclinic unit cell. The model of substitution of four (Fe,V) atoms for four R atoms was preferable. In this case, the composition will be Sm(Fe,V)$_9$ and the density will be 7.447 g cm^{-3}. On the assumption of substitution of eight (Fe,V) atoms for the same four R atoms, the corresponding values will be Sm(Fe,V)$_{9.667}$= Sm$_3$(Fe,V)$_{29}$ and 7.87 g cm^{-3}. The experimental density is (7.6±0.1) g cm^{-3}. This value falls in the range between 7.447 and 7.87 g cm^{-3} and is closer to 7.447 g cm^{-3}. Notice that the experimental density may be an underestimate because of the presence of micropores and cracks in the alloys. We give the composition of the Z-phase as the composition of the starting charge for alloys containing only the Z-phase. Evidently, the above composition may be in error. However, in our opinion the Z-phase is identical with the 'Sm(Fe,Ti)$_9$' compound for which the composition was determined by EDAX. It is clear that supplementary work on the composition of the Z-phase is needed.

In the course of this study, the Sm$_2$(Fe,Ti)$_{17}$ compound of Th$_2$Ni$_{17}$-type with lattice parameters $a=0.851$ nm and $c=0.838$ nm was found. In the literature there is some information on the Th$_2$Ni$_{17}$ modification which may be obtained as a result of melt-quenching of Sm$_2$Fe$_{17}$ [10]. It is believed that substitution of Ti for part of the Fe atoms stabilizes this modification. It is stable at $T \geqslant 1250$ °C and is the most high-temperature phase in Sm(Fe$_{1-x}$Ti$_x$)$_y$ with $0.04 \leqslant x \leqslant 0.07$ and $8.0 \leqslant y \leqslant 9.0$. The rest of the phases form from Sm$_2$(Fe,Ti)$_{17}$–H. The Z-phase exists between 1150 and 1250 °C and its emergence is preceded by the formation of Sm(Fe,Ti)$_{12}$. The orientation of the crystal lattices of these phases are related. As a result, the Z-phase and Sm(Fe,Ti)$_{12}$ of several orientations are observed in the grains.

Acknowledgment

This work was supported by the Russian Science Foundation under Grant 93-02-2076.

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