Effect of alloying elements (Zr, Hf, Co), heat and mechanical treatment conditions on the phase composition and magnetic properties of SmFe$_{11}$Ti compounds with ThMn$_{12}$ structure

Andrey Urzhumtsev$^{1,2}$, Maksim Anikin$^1$, Evgeniy Tarasov$^1$, Mikhail Semkin$^{1,2}$, Maksim Cherepkov$^1$, Nikolay Kudrevatykh$^1$, Aleksandr Zinin$^1$, and Vladimir Moskalev$^3$

$^1$Ural Federal University, Ekaterinburg, Russia
$^2$M.N. Mikheev Institute of Metal Physics of Ural Division of RAS, Ekaterinburg, Russia
$^3$POZ - Progress Co, Verkhnaya Pushma, Sverdlovsk region, Russia

Abstract. The results of thermomagnetic, metallographic and X-ray diffraction phase analysis as well as the measurements of specific magnetization ($\sigma$), Curie temperature ($T_C$), coercive force ($H_C$) of (Sm,M)(Fe,M)$_{12-x}$Ti$_x$ alloys samples, where M = Zr, Hf, Co with the ThMn$_{12}$ main phase structure (1-12) are presented. The effect of the annealing temperature and the cooling rate on the formation of 1-12 phase and its magnetic properties, including the effect of high-energy milling on the magnetic hysteresis properties and alloys structure are described. It was found that the highest magnetic characteristics such as $\sigma$ = 112.6 emu/g and $T_C$ = 600 °C are attained in the (Sm$_{0.6}$Zr$_{0.2}$)(Fe$_{0.75}$Co$_{0.25}$)$_{11.4}$Ti$_{0.6}$ alloy after its annealing at 1050 °C and rapid cooling. It is noted that a mechanical milling of the alloy leads to 1-12 phase amorphization which accompanied by an α-(Fe) or metal Co phases impurity formation.

1 Introduction

Rare Earth – 3d-metal intermetallic compounds with the ThMn$_{12}$ crystal structure are considered as a promising material for high magnetic energy product permanent magnets due to the favorable potential magnetic parameters for several of them [1]. However, the Fe-containing 1-12 phase is formed only with some amount of another 3d-transition metals (Cr, V, Ti – stabilizing elements (SE)), which prevents to attain the high magnetization value and Curie temperature $T_C$ of this phase [2]. The average magnetic moment per 3d-ion is inversely proportional to the concentration of SE and monotonously decreases [3]. Neutron diffraction and Mossbauer spectroscopy studies show that the SE in the ThMn$_{12}$ type structure of RFC($\alpha$)$_{12}$Ti$_x$ alloys occupies the 8i positions without forming its own sublattice, since the values of $x$ in the homogeneity region are smaller than the fraction of 3d-metal atoms in each of the sublattices [4]. In connection with this, the main tasks in the development of hard magnetic materials based on this class of compounds are the stabilizing element amount reduction in the alloy and technological methods finding to keep in the alloy the 1-12 phase presence in a highest volume [5].

The dependence of $T_C$ value on the R – metal type in 1-12 phases is common for R – 3d intermetallics with a large 3d-atoms molar portion. The difference between the maximal and minimal $T_C$ values in the R-series does not exceed 25 %, indicating that the Fe – Fe exchange interaction is dominating. The contribution from the R – Fe interaction is proportional to the spin of the R-ion in the first approximation [4].

Despite the high values of $\sigma$, $T_C$ and the anisotropy field ($H_a$) of the SmFe$_{11}$Ti type compounds, the value of their coercive force ($H_C$) is still very far from the theoretical limit (~ 50 kOe). For sintered magnets the highest $H_C$ value of 1.8 kOe is reported, for samples obtained by mechanical alloying – 4.4 kOe, for thin films is 3.9 kOe and 5.8 kOe – for rapidly quenched materials [3, 6]. The reasons of the large discrepancy between the theoretical and experimentally obtained $H_C$ values presumably lie not only in the presence of secondary phases in these type alloys (besides 1-12), but also in the fact that their coercivity nature is not fully understood and requires the further studies [5, 7]. Thus, the task of this work was to investigate the effect of alloying elements and a heat treatment conditions on the structure and magnetic properties of (Sm,M)(Fe,Co)$_{12-x}$Ti$_x$ type alloys with ThMn$_{12}$ main phase as in the bulk and powdered states prepared by its mechanical milling.

2 Experimental details

Samples of the following series: No. 1 – SmFe$_{11.4}$Ti$_{0.6}$, $x$ = (0.5, 1.0); No. 2 – (Sm$_{0.6}$Zr$_{0.2}$)(Fe$_{0.75}$Co$_{0.25}$)$_{11.4}$Ti$_{0.6}$, where M = (Sm, Zr, Hf); No. 3 – (Sm$_{0.6}$Zr$_{0.2}$)(Fe$_{0.75}$Co$_{0.25}$)$_{11.2-1.4}$Ti$_{0.8-0.4}$, $x$ = (0.05 – 0.25) were melted in an electric arc furnace under a pure helium gas protection. An excess of rare earths metal...
(~ 20 wt %) was added to the starting compositions for the formation preventing of α-(Fe,Co) phases. After the melting, each sample was sealed in to a quartz ampoules, which pumped to the pressure P = 10^{-3} \text{ torr} and subjected to the further annealing. For alloys samples of No. 1 and No. 2 series it was made in a furnace at temperature (T) 850 °C during 5 hours. The samples of No. 3 system were split into two parts, each of them was also placed in an ampoule with the following pumping and sealing. Annealing of these samples was carried out at T = 1050 °C for 8 hours, after that a one ampoule with the sample was rapidly cooled (RC) by dropping into a water, and the other one was slowly cooled (SC) to a room temperature in the furnace.

Magnetic susceptibility temperature dependence measurements $\chi(T)$ of the samples were carried out in an alternating magnetic field of 50 Oe amplitude in the temperature range from 25 up to 800 °C. The samples crystalline structure was determined using X-ray diffraction technique (D8 Advance, Bruker with Cu K\(_\alpha\) radiation source). The morphological structure of the alloys was revealed with a help of MIM-7 optical microscope. For that aim prepared by mechanical polishing a flat surface of the studied sample was treated with 3 % nitric acid for 10 seconds.

Magnetization was measured using the vibrating sample magnetometer of VM-114 type at room temperature in a magnetic field up to 12 kOe. Mechanical milling of the alloys was carried out in a ball mill of the attritor type in ethyl alcohol media at the ratio of the milling balls to the material sample masses of 500/8, and rotational speed of the impeller blade – 4000 rpm.

3 Results

The $\chi(T)$ dependences plotting of the No. 1 and No. 2 series (Fig. 1) shown to the presence of a several specific places which correspond to the temperatures of magnetic phase transition close to $T_C$ values. As it is seen, the homogenized samples of SmFe\(_{11}\)Ti, SmFe\(_{11.5}\)Ti\(_{0.5}\) and Sm(Fe\(_{0.75}\)Co\(_{0.25}\))\(_{11.5}\)Ti\(_{0.5}\) alloys contain at least two magnetic phases.

The lowest temperature Curie, corresponding to the ThMn\(_{12}\) type phase is observed for SmFe\(_{11}\)Ti, SmFe\(_{11.5}\)Ti\(_{0.5}\) and Sm(Fe\(_{0.75}\)Co\(_{0.25}\))\(_{11.5}\)Ti\(_{0.5}\) alloys contain at least two magnetic phases.

The X-ray diffraction analysis of the (Sm\(_{0.8}\)Zr\(_{0.2}\))(Fe\(_{0.75}\)Co\(_{0.25}\))\(_{11.4}\)Ti\(_{0.6}\) RC alloy sample (pattern in Fig. 3) shows, that in addition to the main 1-12 phase 2 magnetic phases with $T_C$ close to the main 1-12 phase are observed. As it seen, the rapid alloy cooling treatment prevents their formation.

**Fig. 1.** Magnetic susceptibility temperature dependences $\chi(T)$ of No. 1 and No. 2 series homogenized samples

**Fig. 2.** Magnetic susceptibility temperature dependences $\chi(T)$ of No. 3 series homogenized samples. A wide line corresponds to the rapidly cooled samples, and a thin one for slowly cooled.

**Fig. 3.** The X-ray diffraction pattern of (Sm\(_{0.8}\)Zr\(_{0.2}\))(Fe\(_{0.75}\)Co\(_{0.25}\))\(_{11.4}\)Ti\(_{0.6}\) after annealing and rapid cooling.
there are two large white spots which present the inclusions of additional phase, while in Fig. 5B there are no them. Figures 5C and 5D show a matrix of dark fine lines presumably being an intergran boundaries.

Figures 6, 7 and 8 show the coercive force changes of the studied alloys powders on the milling time. As a result for No. 1 sample \((x = 1)\) the coercive force is monotonously reduced from 450 Oe to 50 Oe during the first 10 minutes of milling (Fig. 6) and remains unchanged up to the 60 minutes treatment.

For No. 2 and No. 3 series of quenched alloys samples, a slightly different picture is observed. For the \((\text{Sm}_{0.88}\text{Zr}_{0.15})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.35}\text{Ti}_{0.65}\) alloy \(H_C\) value increases from 30 Oe up to 500 Oe during the first 8 minutes of the process (Fig. 7). Then in the interval from 8 up to 20 minutes it oscillates in the interval of \((300 \pm 80)\) Oe, depending on the milling time. What is explained by the way of powders probe taking and testing. It is noted that the \(\sigma_s\) and \(H_C\) curves correlate well.

For alloy \((\text{Sm}_{0.9}\text{Zr}_{0.1})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.3}\text{Ti}_{0.7}\), the increment of \(H_C\) value from 100 Oe up to 330 Oe in the first 20 minutes milling and a smooth drop from 250 Oe up to 50 Oe in the interval \((90 – 120)\) minutes are found (Fig. 8).
Fig. 8. $\sigma_s$ (H = 12 kOe) and $H_c$ dependences of the series No. 3 sample (x = 0.10) on the milling time in the attritor.

Figure 9 shows the X-ray diffraction intensity-normalized pattern at room temperatures for $(\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.4}\text{Ti}_{0.6}$ alloy before and after its 150 minutes mechanical milling. A significant broadening of the peaks is observed on the X-ray pattern of the sample, which indicates to a main 1-12 phase transformation to the amorphous state. It accompanies by $\sigma_s$ increase, which is explained by the bcc-Fe phase precipitates formation having the higher magnetization.

4 Conclusions

Based on the results of the work, the effect of the composition and processing conditions on the crystal structure and magnetic properties of SmFe$_{11}$Ti type alloys, with the ThMn$_{12}$ (1-12) main phase structure were studied.

Substitution of the 25% Fe atomic fraction by Co raises the Curie temperature of 1-12 phase from 300 up to 600 °C. The substitution of 20% Sm for Hf prevents the $\alpha$-Fe phase precipitation from the melt, and the substitution of 20% Sm for Zr suppress the precipitation both $\alpha$-Fe and Co-metal phases.

The alloys rapid cooling after annealing significantly reduces the content of the secondary phases giving raise the main 1-12 phase volume. The specific saturation magnetization of the most homogeneous polycrystalline $(\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{1-\varepsilon}\text{Co}_{\varepsilon})_{11.4}\text{Ti}_{0.6}$ sample is found to be 112.6 emu/g in a magnetic field of 12 kOe, which confirms its perspective for a high (BH)$_{\text{max}}$ permanent magnets manufacturing from them.

Mechanical milling amorphizes the crystal structure of 1-12 compounds and does not allow to achieve the higher coercive force values.

Acknowledgements

The work was supported by the State contracts No. 3.6121.2017/8.9 between UrFU and the Ministry of Education and Science of Russian Federation and by the Fund of assistance to development of small enterprises in scientific-technical sphere No. 11996GU/2017.

References