EPJ Web of Conferences **185**, 04026 (2018) https://doi.org/10.1051/epjconf/201818504026
MISM 2017

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

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Abstract. The results of thermomagnetic, metallographic and X-ray diffraction phase analysis as well as the measurements of specific magnetization (σ_s), 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 σ_s = 112.6 emu/g and T_C = 600 ºC are attained in the $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ alloy after its annealing at 1050 ºC 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 – stabilizating 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 $RFe_{(12-x)}Ti_x$ alloys occupies the 8*i* 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 σ_s, 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 – $SmFe_{(12-x)}Ti_x$, x = (0.5, 1.0); No. 2 – $(Sm_{0.8}M_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$, where M = (Sm, Zr, Hf); No. 3 – $(Sm_{(1-x)}Zr_x)(Fe_{0.75}Co_{0.25})_{(11.2+x)}Ti_{(0.8-x)}$, x = (0.05 – 0.25) were melted in an electric arc furnace under a pure helium gas protection. An excess of rare earths metal

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(~ 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} 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 χ(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_α 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 χ(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 $SmFe_{11.5}Ti_{0.5}$ sample. Its T_C value = (210 ± 5) ºC. For alloys where a 25 % of Fe is replaced by Co, the T_C of the main 1-12 phase is increased up to (600 ± 5) °C. A sharp kink in the χ(T) dependences at T = (780 ± 5) °C corresponds to a ferro – paramagnetic phase transition for the second phase which can be identified as α-Fe. Unlike of the above event, the samples of $(Sm_{0.8}M_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ alloys, where M = (Zr, Hf), do not contain the α-Fe phase. Therefore, the substitution of 20 % Sm for Zr or Hf prevents this phase formation.

The results of the thermomagnetic phase analysis (TMA) of the $(Sm_{(1-x)}Zr_x)(Fe_{0.75}Co_{0.25})_{(11.2+x)}Ti_{(0.8-x)}$ homogenized samples showed that in the entire series there is no contribution from the α-Fe phase in the χ(T) dependence. Nevertheless on the χ(T) curves of slowly cooled samples (Fig. 2), the contributions from another 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.

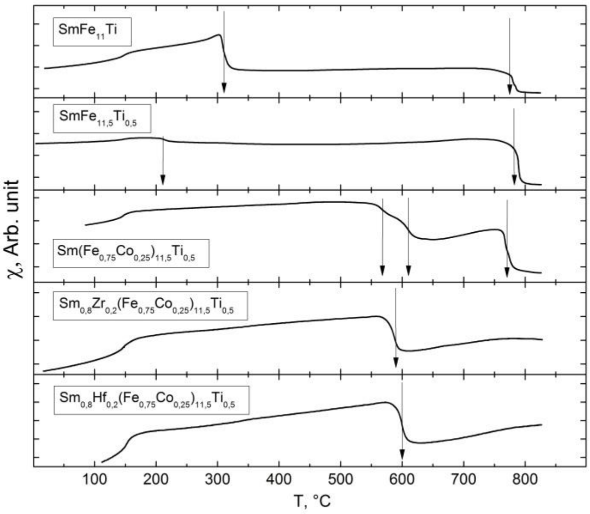

Fig 1. Magnetic susceptibility temperature dependences χ(T) of No. 1 and No. 2 series homogenized samples

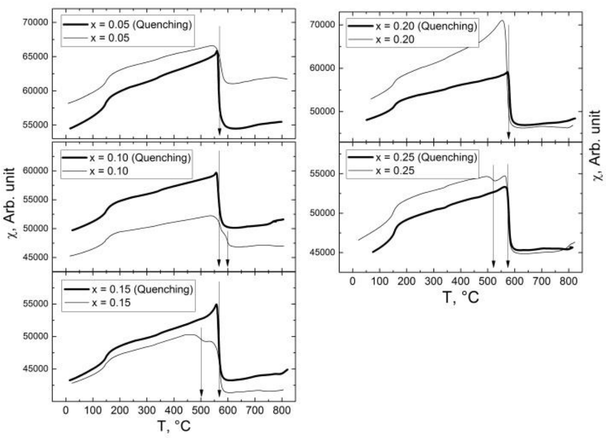

Fig. 2. Magnetic susceptibility temperature dependences – χ(T) of No. 3 series homogenized samples. A wide line corresponds to the rapidly cooled samples, and a thin one for slowly cooled.

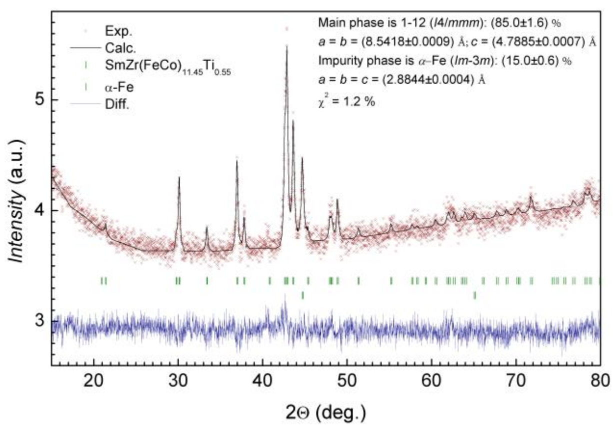

Fig. 3. The X-ray diffraction pattern of $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ after annealing and rapid cooling.

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

($a = b = 8.5418(9)$ Å, $c = 4.7885(7)$ Å) there are peaks from the second α-Fe phase ($a = b = c = 2.8844(4)$ Å), whose fraction is 15 at%, but contribution from it does not observed in χ(T) - dependence (see, Fig. 2).

Comparing the samples specific magnetization values for the No. 1 and No. 2 series alloys before and after the homogenizing annealing (Fig. 4A) we could see that annealing increase one for $Sm(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ and $(Sm_{0.8}Hf_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ alloys. Presumably, in these alloys in addition to α-Fe the Co-metal impurity are formed during the homogenization, as a result of the peretectic reaction. The particular substitution of Sm for Hf prevents the α-Fe phase precipitation and reduces the amount of Co- impurity. A similar substitution of Sm for Zr practically prevents the precipitation of Co-metal also.

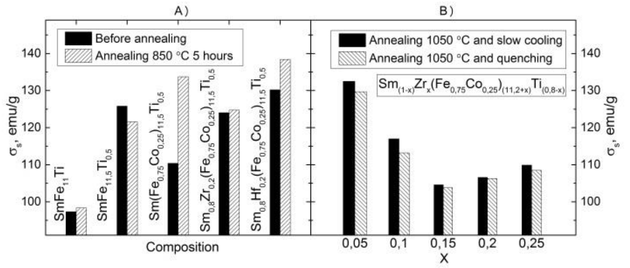

Fig. 4. A) Specific magnetization σ_s values in a magnetic field H = 12 kOe for No. 1 and No. 2 series samples before and after homogenizing annealing. B) The same as in (A) but for No. 3 series as the dependence on the cooling rate.

Comparison of the specific magnetization values for No. 3 series homogenized alloys samples after SC and RC treatments is shown in Fig. 4B. The slowly cooled samples magnetization is higher than that of RC samples, which indirectly indicates to the presence of additional phases with a large magnetization, probubly α-(Fe,Co).

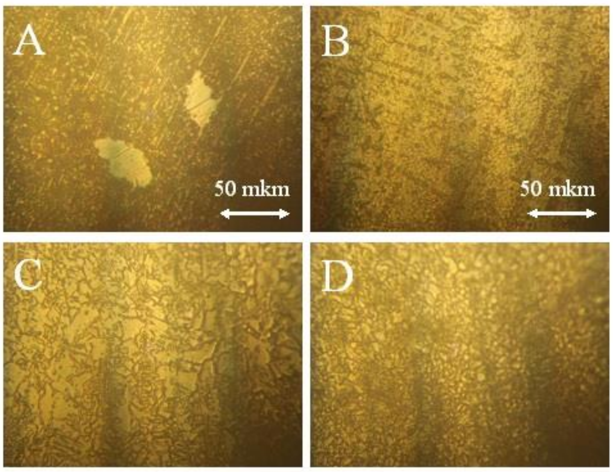

Fig. 5. Micrographs of homogenized samples of the $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ alloy. A and C – material is after a slow cooling. B and D – after rapid cooling in a water.

Figure 5 shows the results of the metallographic analysis of the $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ alloy samples after the homogenizing annealing with slow final cooling to RT (Fig. 5A and Fig. 5C) and after RC (Fig. 5B and Fig. 5D). At the micrograph of Fig. 5A 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 intergrain 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.

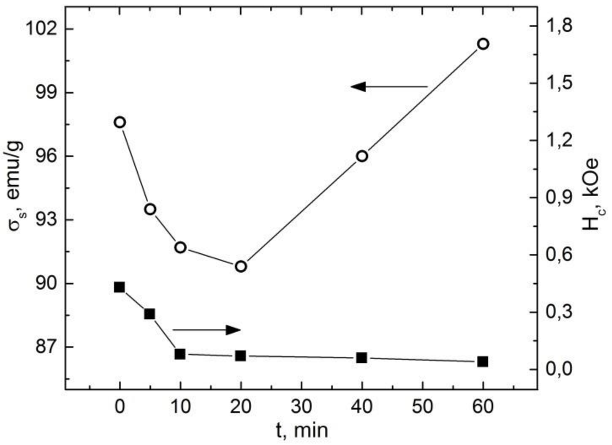

Fig. 6. σ_s (H = 12 kOe) and H_C dependences of the No. 1 series sample (x = 1) on the milling time in the attritor.

For No. 2 and No. 3 series of quenched alloys samples, a slightly different picture is observed. For the $(Sm_{0.85}Zr_{0.15})(Fe_{0.75}Co_{0.25})_{11.35}Ti_{0.65}$ 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 ± 80) Oe, depending on the milling time. What is explained by the way of powders probe taking and testing. It is noted that the σ_s and H_C curves correlate well.

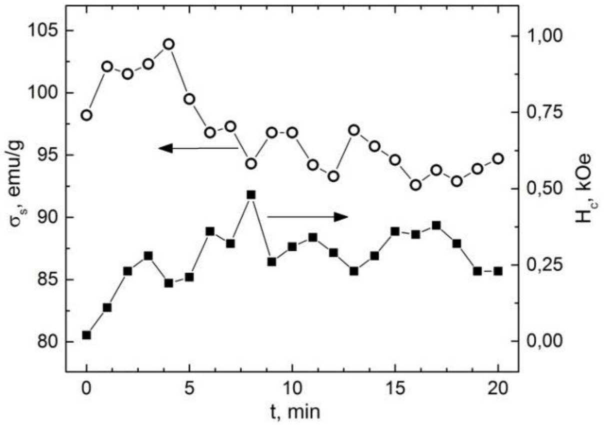

Fig. 7. σ_s (H = 12 kOe) and H_C dependences of series No. 3 sample (x = 0.15) on the milling time in the attritor.

For alloy $(Sm_{0.9}Zr_{0.1})(Fe_{0.75}Co_{0.25})_{11.3}Ti_{0.7}$, 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).

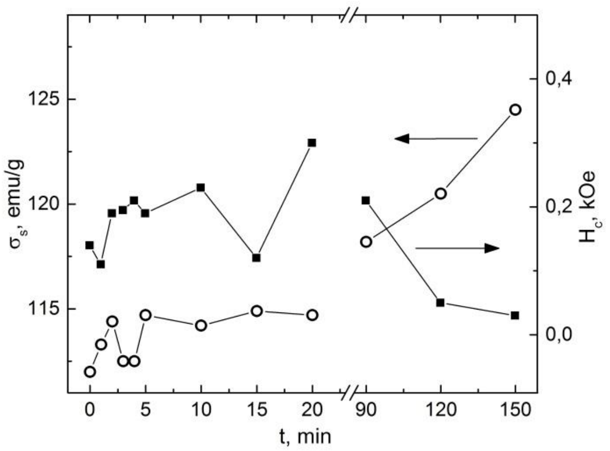

Fig. 8. σ_s (H = 12 kOe) and H_C dependences of the series No. 3 sample (x = 0.10) on the milling time in the attritor.

Figure 9 shows the X-ray diffraction intensity-normalized pattern at room temperatures for $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ 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 σ_s increase, which is explained by the bcc-Fe phase precipitates formation having the higher magnetization.

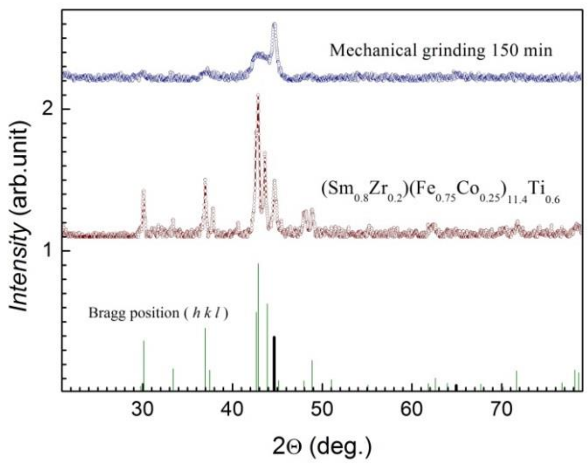

Fig. 9. The X-ray diffraction intensity – normalized pattern of $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.4}Ti_{0.6}$ before and after high-energy 150 minutes milling in the attritor.

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 α-Fe phase precipitation from the melt, and the substitution of 20 % Sm for Zr suppress the precipitation both α-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 $(Sm_{0.8}Zr_{0.2})(Fe,Co)_{11.4}Ti_{0.6}$ sample is found to be 112.6 emu/g in a magnetic field of 12 kOe, which confirms its perspective for a high $(BH)_{max}$ 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.

Acknowledge

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.

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