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Stabilization of bcc-born phases in Fe-27Ga by adding Tb: Comparative in situ neutron diffraction study

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ABSTRACT

Significant influence of 0.3 at%Tb on phase transitions in the Fe-27.4Ga alloy in the range of 20–850 °C is observed by in situ neutron diffraction. The conventional transition sequence at heating $D0_3 \rightarrow L1_2 \rightarrow D0_{19} \rightarrow B2 \rightarrow A2$ in binary Fe-27.4Ga is changed for $D0_3 \rightarrow (B2(\sim 75\%) + L1_2(\sim 25\%)) \rightarrow (B2(\sim 85\%) + D0_{19}(\sim 15\%)) \rightarrow B2 \rightarrow A2$ transitions in the Tb-containing alloy. At slow cooling (2 K/min) the mixture of $D0_3(90\%) + L1_2(10\%)$ is recorded in the Tb-containing sample instead of dominating $L1_2(\sim 90\%)$ and very limited amount of $D0_{19}$ and A2 phases in the binary Fe-27.4Ga alloy. We conclude that the addition of a small amount of Tb stabilizes bcc-born phases (A2, B2 and $D0_3$) and prevents appearance of closed packed (fcc ordered $L1_2$ and hcp ordered $D0_{19}$) phases.

1. Introduction

Rare-earth elements (such as Tb, Dy, etc.) exhibit a huge Joule magnetostriction [1] due to their substantial spin-orbit interaction, though only at low temperatures. That is why alloys between rare-earths and 3D-elements are often considered for magnetostrictive applications [2]. Recently rare-earth-free Fe-Ga alloys have also become a focus of research because of their highest magnetostriction among Fe-based alloys [3]. Fe-Ga alloys are also attractive due to relatively low switching field and desirable mechanical properties, allowing potential applications in sensors, actuators, and transducers. Fe-Ga alloys exhibit relatively high damping capacity at low [4] and high frequencies [5] due to irreversible motion of magnetic domain walls and eddy currents, correspondingly. Trace doping with 0.2 at% rare-earth elements increases the magnetocrystalline anisotropy and greatly enhances their magnetostriction [6].

Papers by Jiang et al. [e.g., 7] show that alloying of Fe-Ga alloys by Tb or Dy through rapid cooling remarkably improves the magnetostriction. This research suggests that Fe-Ga-(Tb or Dy) alloys are promising materials for energy harvesting. An increase in magnetostriction from 70 to 160 ppm was recorded in polycrystalline $Fe_{83}Ga_{17}$ alloy doped by 0.2%Tb [8]. First principal calculation reveals that random replacement of Tb for Fe or Ga sites is in favour of the formation of tetragonal symmetry [9]. A 250% increase in magnetostriction is reported for the [110]-textured polycrystalline $Fe_{81}Ga_{19}Tb_x$ (x=0.3) alloy, as compared to the parent compound, $Fe_{81}Ga_{19}$. Tb doping resulted in an increase in magnetization, a reduction of saturation field as well as a decrease in magnitude of the magnetostriction temperature coefficient. These characteristics can have a beneficial effect in practical applications that require operability in wide temperature ranges [10].

Fe-Ga binary alloys have two maxima of magnetostriction at 17–19 and ~27 at% Ga (atomic percentage is used in this paper) [11]. Mechanical and magnetic properties of Fe-(17–19)Ga alloys have been studied much better compared to Fe-27Ga alloys in which several phase transitions take place. The main purpose of this research is to study the effect of Tb on the phase transitions in a Fe-27Ga alloy. We use in situ neutron diffraction to study sequence and kinetics of phase transitions in directly solidified Fe-27.4Ga and Fe-27.4Ga-0.3Tb alloys. The paper focuses on the differences in the phase transformations in bulk samples with and without Tb upon heating and cooling.

2. Materials and methods

Two Fe-27.4 at%Ga alloys without and with ~0.3 at%Tb (denoted in the paper as Fe-27Ga and Fe-27Ga-Tb) were produced by directional solidification in copper mould using pure Fe and Ga by induction melting under protection of high-purity inert argon gas using an Indutherm MC–20V mini furnace. Using energy dispersive spectroscopy, the chemical compositions of the cast

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buttons were measured with ±0.1% accuracy.

The neutron diffraction patterns were measured with a high resolution Fourier diffractometer (HRFD) [12] at the IBR-2 pulsed reactor in JINR (Dubna). The neutron diffraction experiments were performed on rectangular samples with a size of 4 × 8 × 40 mm. The HRFD is a time-of-flight diffractometer with a correlation mode of data acquisition. Its $\Delta d/d$ resolution is determined by the maximum frequency of the fast Fourier chopper. In a routine operation (V_{max}=4000 rpm), $\Delta d/d \approx 0.001$ for d=2 Å, only slightly depends on d_{hkl}, and improves with increasing d_{hkl}. The acquisition time for each diffraction pattern was as short as 1 min. Heating of the samples was carried out in a specialized furnace (ILL standard) with vanadium screens up to 850 °C. Both samples were heated with a temperature rate of ~2.2 K/min. The cooling process was performed with the same rate down to ~300 °C. Further details can be found in [13].

According to the phase diagram, the following phases can be observed in binary Fe-27Ga alloys:

- the $L1_2$ (equilibrium phase below ~615 °C) has a Cu_3Au-type structure with Fe and Ga atoms partially ordered, sp. gr. *Pm*3*m*, $a \approx 3.72$ Å (at 20 °C);
- the $D0_{19}$ (equilibrium phase from ~615 to ~680 °C) has a $MgCd_3$-type structure with Fe and Ga atoms partially ordered, sp. gr. $P6_3/mmc$, $a \approx 5.28$ Å, $c \approx 4.28$ Å (at 20 °C);
- the B2 (equilibrium phase from ~680 to ~825 °C) has a CsCl-type structure with Fe and Ga atoms partially ordered, sp. gr. *Pm*3*m*, $a \approx 2.92$ Å (at 20 °C);
- the A2 (equilibrium phase above ~825 °C) has an α-Fe-type structure with Fe and Ga atoms randomly distributed, sp. gr. *Im*3*m*, $a \approx 2.92$ Å (at 20 °C).
- the $D0_3$ (non-equilibrium phase for Fe-27Ga alloy which appears as a result of fast cooling from A2 range of phase diagram) has a BiF_3-type structure with Fe and Ga atoms partially ordered, sp. gr. *Fm*3*m*, $a \approx 5.83$ Å (at 20 °C);

Phase composition of the samples was also examined at room temperature by XRD (Bruker AXS D8 ADVANCE) with $K_{\alpha 1}$ copper incident radiation of 1.54056 Å wavelength at step size=0.05 deg/s (2θ=20–120 deg).

Microstructure explorations and an EDS analysis of the experimental samples were carried at an electronic scanning microscope (TESCAN VEGA 3 LMH) with a LaB6 cathode and EDS AZtecEnergy Advanced Microanalysis System software (Oxford Instruments). The acceleration voltage used for the EDS was 20 kV. The measurements were carried out with a simultaneous check against standard samples. The error of the measurements did not exceed 0.1 wt%. Both mechanical polishing (Struers Labopol-5) and electrolytic polishing were used for the sample preparation for the microstructural analysis since these methods complement one another and enable a complete observation of the microstructure.

3. Results

The initial state after direct solidification for both studied samples is represented by the bcc-born $D0_3$ structure (ordered A2 phase). The widths of diffraction lines only slightly exceed the contribution from the resolution function, which agrees with our earlier findings [13,14]. Thus, we can conclude that both samples have a single $D0_3$ ordered state. This conclusion is different from the paper [15], though it does not contradict it. Thus, we found a mixture of A2 and $D0_3$ phases in the Fe-26.3Ga alloy by XRD: in contrast with XRD diffractions from most rapidly cooled surfaces of a sample. In this paper we study neutron diffractions from bulk samples.

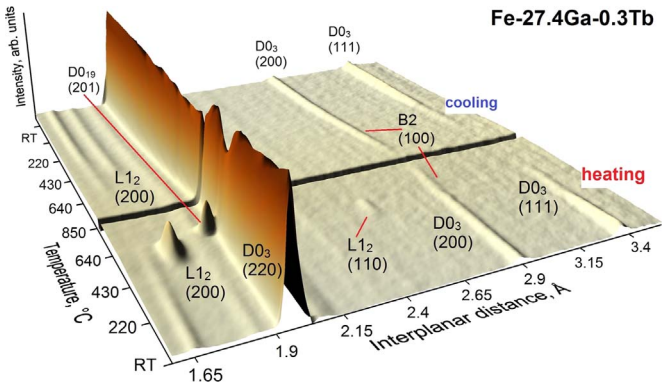

Fig. 1. The 3D visualization of the diffraction pattern upon heating and subsequent cooling the Fe-27Ga-Tb sample after direct solidification. The *d*-spacing range from 1.65 to 3.50 Å is shown. The initial and final states are $D0_3$ phase, which is undoubtedly identified by (200) and (111) lines at d=2.92 Å and 3.37 Å. Vanishing of the (111) line at heating and its subsequent appearance at cooling (both at about 500 °C) means $D0_3 \leftrightarrow$ B2 transformation.

Upon heating and cooling, several phase transitions occur. Fig. 1 shows their 3D representation for ternary Fe-27Ga-Tb sample. This overview of phase transitions is quite different as compared to the representation of phase transitions in binary Fe-27Ga alloy, which can be found in the paper [13]. The main differences between phase transitions in these two alloys are in the amount of intermediate phases appeared between initial ($D0_3$) at room temperature and final (A2) state at 850 °C at heating and also in the final state after cooling. The recorded sequence of phase transitions upon continuous heating in Fe-27Ga alloy is: $D0_3 \rightarrow L1_2$ (up to 100%)→$D0_{19}$ (up to 100%)→B2 (up to 100%)→A2 (100%) (Fig. 2a); whereas in Fe-27Ga-Tb alloy this sequence is $D0_3 \rightarrow$B2 (up to 100%)→$L1_2$ (limited amount coexisting with B2)→$D0_{19}$ (limited amount coexisting with B2)→B2 (up to 100%)→A2 (Fig. 2b).

In the Fe-27Ga sample, continuous cooling (after heating up to 850 °C) leads to the formation of the $L1_2$ phase directly from A2 phase below 550 °C (Fig. 2c). Some limited amount of the $D0_{19}$ appears in the temperature range from 560 and 460 °C. A certain amount of A2 phase remains down to room temperature: high-resolution diffraction evidences that A2 phase gets $D0_3$ order. In contrast, only very limited amount of the $L1_2$ phase appears below 430 °C in ternary Fe-27Ga-Tb alloy at cooling (Fig. 2d), whereas bcc A2 phase remains to be the dominating phase in the structure: it gets some B2 ordering between 700 and 500 °C and $D0_3$ ordering below 500 °C.

Obviously, the volume fraction of phases at heating and cooling significantly depends on both temperature and time. According to our XRD data both alloys after 300 h annealing at 275 °C still have bcc-originated structure ($D0_3$ and A2 phases); in contrast, after 300 h annealing at 330 °C their structure is practically 100% of $L1_2$ phase (Fig. 3).

At heating or isothermal annealing the $L1_2$ phase nucleates mainly at grain boundaries of the $D0_3$ phase and grows into the grain body (Fig. 4a and b). Grain boundaries in directly solidified ternary alloy Fe-27.4Ga-0.3Tb with $D0_3$ structure were found to be decorated by Tb-enriched phase (Fig. 4c). Using energy dispersive spectroscopy, the chemical compositions of Tb-enriched phase after 300 h annealing at 330 °C (volume fraction ~3%) were measured to be 47.9%Fe, 45.2%Ga, 6.9%Tb (in atomic percentage) with ±0.1% accuracy. Possibly, by adding 0.3%Tb we have exceeded solubility limit of Tb in Fe-27Ga solid solution and precipitations of the Tb-enriched phase on the grain boundaries slow down nucleation and growth of the $L1_2$ phase.

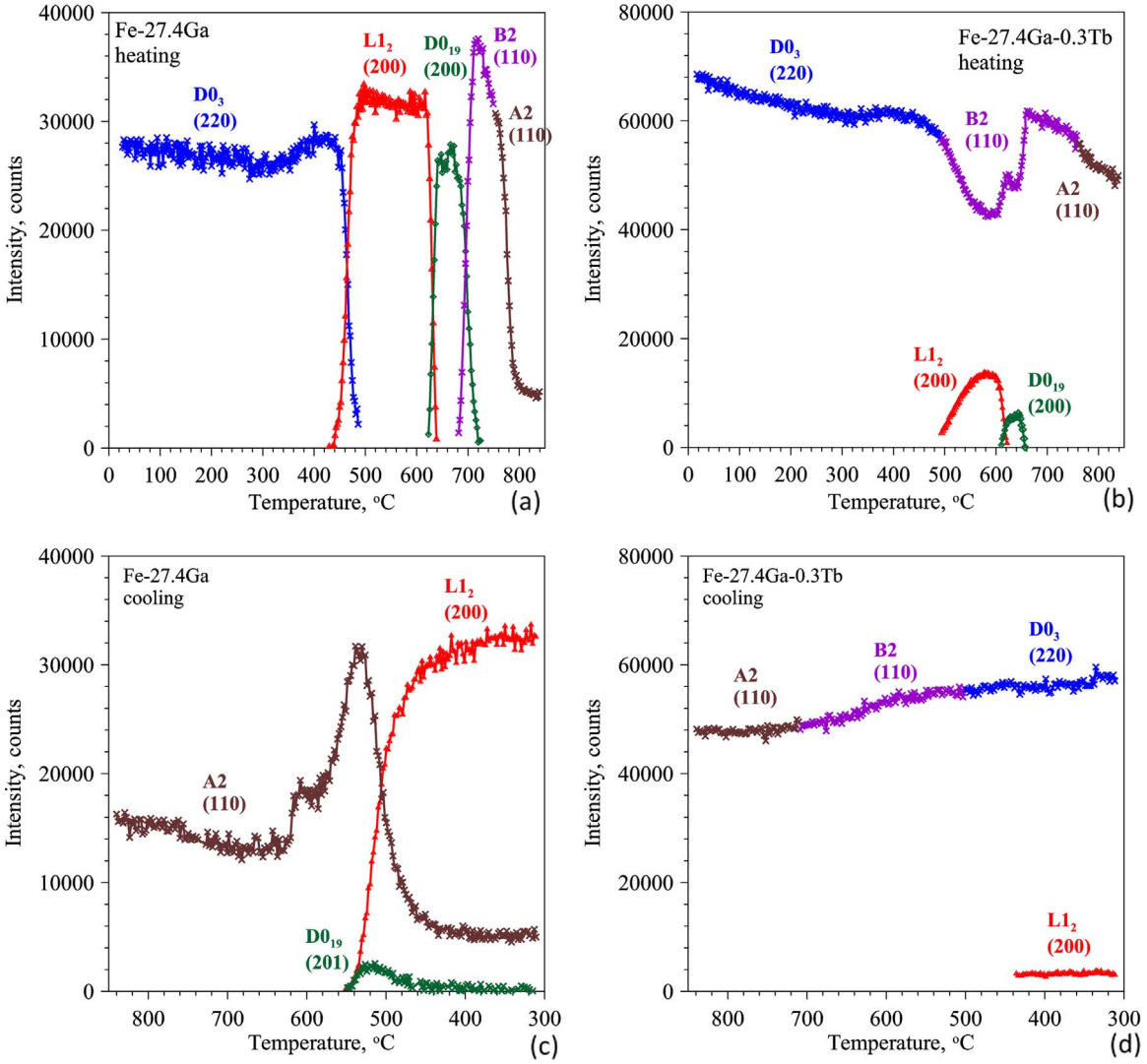

Fig. 2. Phase transitions in the Fe-27Ga (a, c) and Fe-27Ga-0.3Tb (b, d) samples at heating (a, b) and cooling (c, d) with a rate of ~2.2 K/min shown as intensity changes of the characteristic diffraction peaks. The Miller indices of the peaks are indicated nearby the curves.

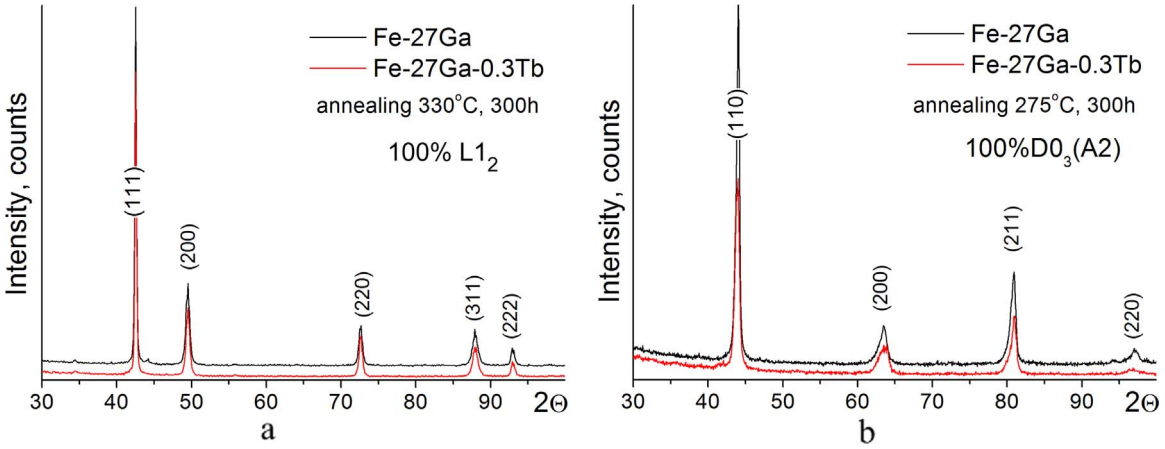

Fig. 3. XRD spectra of Fe-25Ga and Fe-27Ga-Tb samples at room temperature after 300 h annealing at 275 (a) and 330 °C (b).

4. Conclusions

An improvement of the functional properties of Fe-Ga alloy by adding a small amount of terbium has been reported in several papers [2–9]. In this paper we suggest the probable microscopic cause of this phenomenon in Fe-27Ga alloy. Microalloying of Fe-27Ga alloy by 0.3Tb significantly suppresses the appearance of closed packed structures (fcc-based $L1_2$ and hcp-based $D0_{19}$ phases) at continuous heating and continuous cooling and stabilizes the bcc-born $D0_3$ structure at room temperature.

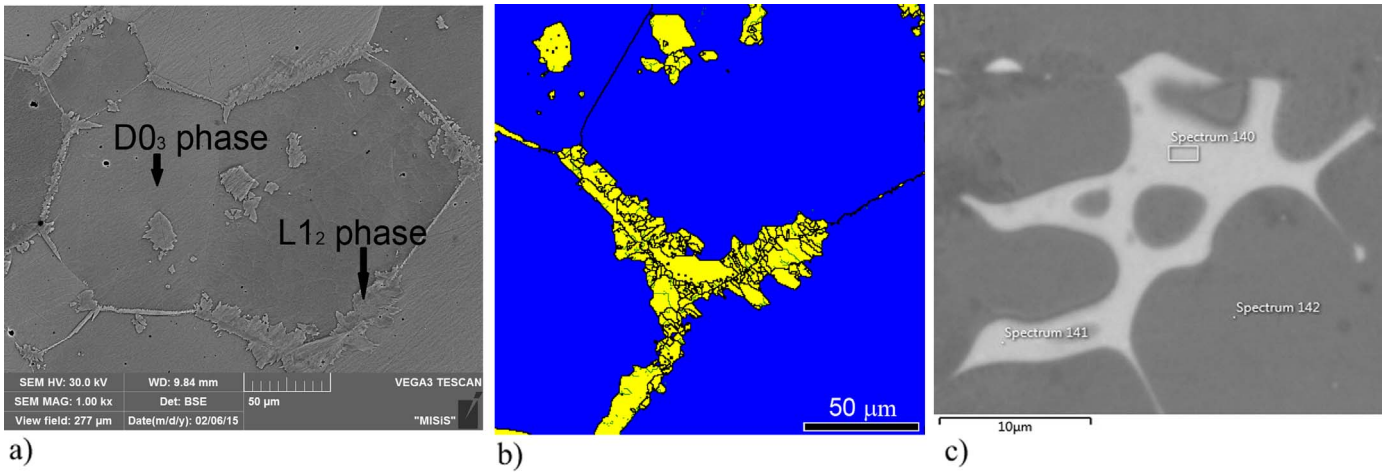

Fig. 4. The microstructures of alloys, SEM: a) microstructure of Fe-27Ga alloy; b) microstructure of Fe-27Ga alloy after EBSD analysis ($L1_2$ phase – yellow color, $D0_3$ phase – blue color); c) allocation Tb-enriched phase (light grey) on the grain boundaries with spectra of EDS analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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