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PALS Investigation of Structural Vacancies During Phase Transitions in Fe-27Ga and Fe-27Ga-0.1Tb Alloys

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Abstract. Good mechanical properties and relatively low switching magnetic field make Fe-Ga alloys very useful magnetostrictive material for wide range of practical applications. Doping with rare-earth elements (such as Tb) can significantly increase magnetostriction, because Tb rearranges vacancy structure during phase transitions in Fe-27Ga alloys. It was found that A2 and $D0_3$ structures in Fe-27Ga have high density of Fe-monovacancies with the positron lifetime ≈180 ps regardless of the presence of Tb. Transition into L12 structure is accompanied by formation of a significant number of larger vacancy defects, which increases the e+ lifetime by 5 %. Addition of 0.2% Tb suppress formation of these large defects at annealing temperatures of 400–550 °C. Presence of Tb also decreases concentration of vacancies in $D0_{19}$ structure. After annealing at 650 °C $D0_{19}$ volume fraction in Fe-27Ga-0.2Tb decreases to 60 % , (according to the positron measurements) against 95 % in Fe-27Ga. In both alloys at 700 °C number of monovacancies increases dramatically during formation of the bcc B2 phase.

INTRODUCTION

During the last decade Fe-Ga alloys (Galfenols) have become an object of intensive investigations because of their highest magnetostriction among Fe-based alloys [1]. In addition to a good saturated magnetostrictive response (up to 400 ppm) under very low magnetic fields, Fe-Ga alloys possess good mechanical properties making them a sustainable alternative especially to conventional Terfenol-D that suffers from brittleness and low yield stress under shock and tensile loads. Desirable mechanical properties and relatively low switching field have introduced Fe-Ga alloys as a promising class of smart magnetostrictive materials for acoustic sensors and transducers, actuators, positioning devices, torque sensors, and recently developed magnetoelectric (or multiferroic) sensors [2,3]. Fe-Ga alloys exhibit a relatively high damping capacity at low and high frequencies of vibrations due to irreversible motion of magnetic domain walls and eddy currents, correspondingly [4].

Fe-Ga binary alloys have two maxima of magnetostriction at ~19 and ~27 at.% Ga [5]. Fe-27Ga alloys have more complicated kinetics of phase transitions compared to Fe-19Ga, so it is studied not so thoroughly. In this work we study the effect of Tb on changing of the vacancy structure during phase transitions in Fe-27Ga alloys and search correlations with phase composition and magnetic properties of the alloys. To investigate vacancy behavior upon the annealing in the temperature range from 20 °C to 750 °C we use positron annihilation lifetime spectroscopy (PALS).

MATERIALS AND TECHNIQUES

Fe-27.6Ga and Fe-27.4Ga-0.1Tb alloys 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 buttons were measured with

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± 0.2 % accuracy. The samples were cut from the plate using a cutting machine and underwent thermal treatments. The samples were annealed for 40 minutes at 1273 K (1000 °C) in a furnace and then they were cooled in water. As-quenched alloys were subjected to isochronal annealing for 60 min with a step-by-step increase of annealing temperature. After each step of annealing, the samples were water quenched. The annealing temperature points were chosen according to the data on phase transitions obtained earlier [6, 7] in situ neutron diffraction on Fe-27Ga and Fe-27Ga-0.15Tb alloys.

The positron lifetime measurements were performed at room temperature by means of a conventional coincidence spectrometer with two BaF_2 detectors. They were arranged at the angle of 90° between their axes. As a positron source we used $^{22}NaCl$ (2 MBq) packed in between two 8 μm kapton films. Each measurement contained about 10 million counts. Source contribution to the lifetime spectra was 19 %. The time resolution of the system was 240 ps. The positron lifetime data were analyzed by using the LT10 program [8].

RESULTS AND DISCUSSION

Possible structure types of Fe-27Ga are presented in Fig. 1a. According to the equilibrium phase diagrams (Fig. 1b), during initial cooling from 1000 °C Fe-Ga alloys undergo ordering from A2 high temperature phase. Formation of equilibrium phases is rather slow and for high cooling rates ordering proceeds according to the metastable phase diagram (Fig. 1b), which suggests that at room temperature the studied alloys belong to a mixture of A2 and $D0_3$ phases.

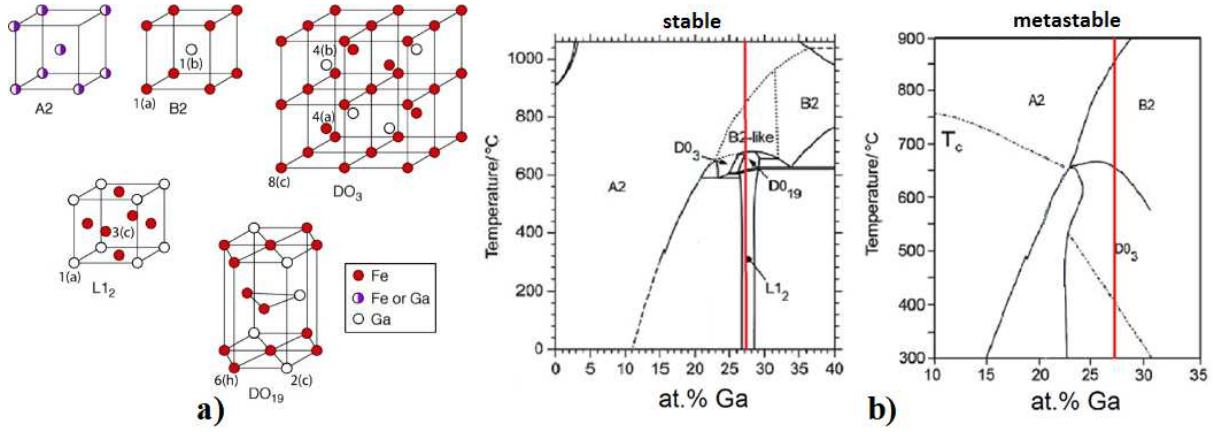

Fig. 1. (a) Structure types of Fe-27Ga alloys [9]; (b) Stable and metastable Fe-Ga phase diagrams (red line corresponds to 27 at% of Ga) [9]

According to neutron diffractions, the initial state after direct solidification for the Fe-27Ga [7] and the Fe-27Ga-0.15Tb [6] samples is represented by the bcc-born $D0_3$ structure (ordered A2 phase), which has a BiF_3-type structure with Fe and Ga atoms partially ordered, spatial group Fm3m, $a \approx 5.83$ Å at 20 °C. Using XRD it was also established that thin surface area (the most rapidly cooled part of the samples) has a disordered A2 structure. Investigating the samples by PALS we need to take into account that part of positrons annihilate in the near surface area. The main difference between the phase transitions in the binary and ternary alloys is in the amount of intermediate phases appeared between the initial ($A2+D0_3$) at room temperature and the final (A2) state at 850 °C at heating. The recorded sequence of the phase transitions upon continuous heating in the Fe-27Ga alloy is: $D0_3 \rightarrow L1_2 \rightarrow D0_{19} \rightarrow B2 \rightarrow A2$; whereas in the Fe-27Ga-0.15Tb alloys, this sequence is $D0_3 \rightarrow L1_2 + A2 \rightarrow D0_{19} + A2 \rightarrow B2 \rightarrow A2$.

Experimental PALS spectra for the initial as-quenched samples can be fitted by one exponential component very well, though in the spectra obtained for annealing temperatures near 650 °C it is possible to distinguish two lifetime components. Positron lifetime spectra for the as-quenched samples of both alloys can be fitted by monoexponential function with lifetime of about 175 ps. It indicates that positrons annihilate mainly in the open volume defects with lifetime typical for monovacancies in α-Fe lattice and that the defects concentration lies above the saturation limit ($>2 \cdot 10^{-4}$ atom^{-1}). Initial samples according to the neutron diffraction data contain predominantly the partially ordered $D0_3$ structure. High vacancy concentration in $D0_3$ phase of Fe-27Ga is in contrast to the alloys with lower Ga-

content (less than 25 %) [9]. Most probably Fe-vacancies appear in the lattice of Fe-27Ga as constitutional defects to compensate the excess of gallium with respect to the stochiometric composition of fully ordered $D0_3$ phase (Fe_3Ga).

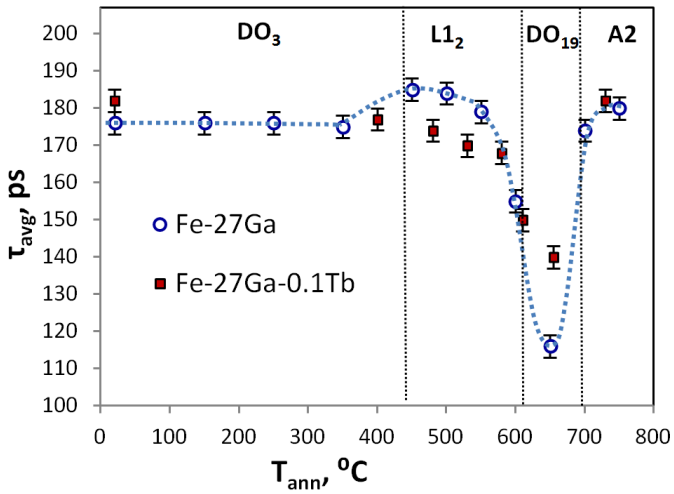

Fig. 2. Dependence of the average positron lifetime in Fe-27Ga and Fe-27Ga-0.1Tb on the annealing temperature (identification of the structural types is based on the neutron diffraction data)

Fig. 2 shows that the average positron lifetime (τ) in Fe-27Ga remains unchanged during annealing up to 450 °C. Then, simultaneously with the formation of the $L1_2$ structure, lifetime increased by 8-10 ps and remained so until the transition of $L1_2$ to the $D0_{19}$ structure began at 600 °C (according to the phase diagram). There is no increase on the curve corresponding to the Fe-27Ga-0.1Tb. It is consistent with the fact that the formation of $L1_2$ is partially suppressed by Tb and we have the mixture of $L1_2$ and $D0_3$ instead of pure fcc structure. Possibly such a mixture or the presence of fcc lattice distortions due to Tb atoms makes the appearance of larger defects not so necessary as in pure $L1_2$ phase.

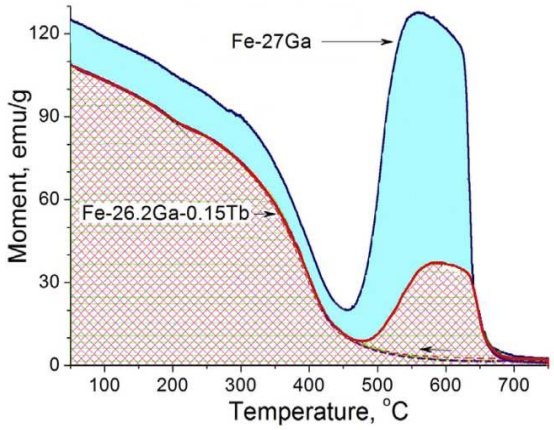

Fig. 3. Temperature dependent magnetization with a heating rate of 6 K/min for the Fe-27Ga and Fe-26.2Ga-0.15 Tb as cast alloys [6]

Above 600 °C, average e^+ lifetime τ strongly decreases and its minimal lifetime (≈115 ps) is reached at 650 °C. The decrease of τ may be caused by two processes: (i) recovery of quenched thermally equilibrium vacancies or (ii) growing of the phase with low vacancy concentration. Since we could not detect the component with lifetime shorter than 112 ps we believe that the trapping model is not applicable in this case, and we must use simple two-exponential deconvolution of the positron lifetime spectra. The shortest component (112 ps) is associated with the defect-free $D0_{19}$ structure, and the long-lived component (176 ps) characterizes the structures with high concentration of monovacancies ($>2\cdot10^{-4}$ atom^{-1}). Intensities of these components equal to the fractions of

corresponding phases in the alloy. Intensity of the shortest component (corresponding to the defect-free $D0_{19}$ phase) is equal to 95 % at 650 °C for Fe-27Ga and 60 % for Fe-27Ga-0.1Tb. Further annealing above 700 °C leads to transition of $D0_{19}$ to A2 or B2 having higher vacancy concentration. So the average e^+ lifetime again increases up to 180 ps.

It should be noted that formation of the vacancy-free $D0_{19}$ structure leads to a rapid decrease of the magnetic susceptibility of the investigated alloys, Fig. 3. The materials in this phase become paramagnetic. Probably it is related with the packing density of the crystal lattice, which does not require structural vacancies to compensate for the excess of gallium. It is easy to see in Fig. 3 that magnetization disappears when the structure of the alloy changes from $L1_2$ to $D0_{19}$ at about 650 °C.

CONCLUSIONS

1. The e+ lifetime (175-180 ps) in Fe-27Ga and Fe-27Ga-0.2Tb samples after quenching from 1000 °C corresponds to the positron lifetime in Fe monovacancies and indicates on their high concentration ($> 2 \cdot 10^{-4}$ $atom^{-1}$) in $D0_3$ structure. Apparently, these Fe vacancies compensate an excess of Ga (in comparison with the stochiometric Fe_3Ga composition) and stabilize the $D0_3$ phase. Annealing of the $D0_3$ structure at T<550 °C does not lead to a variation of the average positron lifetime and accordingly to a decrease of the vacancy concentration.

2. Formation of the $L1_2$ structure at 450 °C in Fe-27Ga leads to an increase in the positron lifetime by 8-10 ps. Addition of Tb suppresses formation of the $L1_2$ structure, so e+ lifetime does not increase at 450-600 °C.

3. Decrease in the mean positron lifetime in Fe-27Ga and Fe-27Ga-0.2Tb samples correlates with the formation of the $D0_{19}$ structure at 650 °C. Presence of terbium in the alloy weakens this effect. Volume fraction of $D0_{19}$ structure in Fe-27Ga-0.2Tb, estimated from PALS data, reaches 60 % against 95 % in Fe-27Ga.

4. Transition $D0_{19} \rightarrow$ A2 in Fe-27Ga and $D0_{19} \rightarrow$ B2 in Fe-27Ga-0.2Tb at 700 °C results in increase of the e+ lifetime up to 175-180 ps, which indicates the restoration of a high vacancy concentration, irrespective of the terbium presence. Thus, we can assume that structural stabilization of A2 and B2 also requires constitutional vacancies.

5. Thus $D0_{19}$ is the only structure of Fe-27Ga, which does not require Fe vacancies to compensate internal stresses in the crystal lattice associated with excess of gallium. It should be noted that the $D0_{19}$ structure is also the only one of Fe-Ga structure, which is not ferromagnetic.

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REFERENCES

1. Clark A.E., Hathaway K.B., Wun-Fogle M. et al., J. Appl. Phys. **93**, 8621-8623 (2003).
2. Atulasimha J. and Flatau A.B., Smart Mater. Struct. **20**, 043001 (2011).
3. Srisukhumbowornchai N., S. Guruswamy, J. Appl. Phys. **90**, 5680 (2001).
4. Golovin I.S., Palacheva V.V., Zadorozhnyy V.Yu et al., Acta Mater. **78**, 93-102 (2014).
5. Xing Q., Du Y., McQueeney R.J., Lograsso T.A., Acta Mater. **56**, 4536-4546 (2008).
6. Golovin I.S. et al., Journal of Alloys and Compounds **707**, 51-56 (2017).
7. Golovin I.S., Balagurov A.M., Palacheva V.V. et al., Mater. Des. **98**, 113-119 (2016).
8. Giebel D. and Kansy J., Phys. Procedia **35**, 122-127 (2012).
9. Dubov L.Yu. et al., Materials Letters **171**, 46-49 (2016).