Phase transition induced anelasticity in Fe–Ga alloys with 25 and 27% Ga

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Neutron diffraction and mechanical spectroscopy techniques were applied to study phase transitions in Fe–Ga alloys with 25 and 27 at.% Ga. The following sequences of phase transitions at continuous heating and subsequent cooling in the 20–900 °C temperature range were recorded: D03 → L12 (limited amount) → A2(B2) was recorded at heating and A2(B2) → D03 at cooling for Fe-24.8Ga alloy, and the D03 → L12 → D019 → A2(B2) was recorded at heating and A2(B2) → L12 at cooling for Fe-27.4Ga alloy. Thus, the difference in 2.6 at.%Ga between two studied compositions with D03 structure leads to their different structures after heating to 900 °C. These transition sequences determine different temperature dependencies of elastic and anelastic properties. The D03 → A2(B2) transition (in Fe-25Ga) does not lead to a well-pronounced anelastic effect, in contrast the D03 → L12 transition (in Fe-27Ga) generates internal stresses due to a different rate of an increase in the lattice parameter with temperature and leads to a well-pronounced transient internal friction effect.

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1. Introduction

Due to their magnetostriction, rare-earth-free materials offer great potential for various applications in sensors, actuators, energy-harvesting applications and spintronic devices. The tetragonal magnetostriction of polycrystalline Fe–Ga is maximal for compositions around 19 and 27 at.% Ga [1,2], which makes these alloys attractive for energy-harvesting applications. Alloys with 17–20%Ga are well studied; their structure is rather simple: solid solution of Ga in α–Fe (A2 range of phase diagram) partly D03 ordered in case of slow (furnace) cooling, and alloys with 17–20%Ga have already found some practical applications.

Studies of phase transitions in quenched Fe–Ga alloys under different annealing conditions have been reported for several cases [1–6]. Sometimes, results related to temperature intervals and kinetics of phase transitions differ from paper to paper greatly. It should be noted, that recently a diffusionless character of the D03 to L12 transition has been reported by TEM [6] and internal friction [4,7,8]. This type of phase transition in Fe–Ga was predicted earlier by Khachaturyan et al. [9,10]. Their model suggests the transformation of D03 nanoclusters to an intermediate tetragonal D022 phase via a Bain distortion that shifts the atomic positions in closer to their final positions in the L12 structure, and finally, the precipitation of L12 (Fe3Ga) phase.

An in situ XRD study demonstrated D03 → L12 → D019 − B2 phase transitions in the Fe-27Ga alloy [4]. Unfortunately, X-rays provide insufficient resolution between phases, especially at small volume fractions, owing to the structure similarity of A2, B2, and D03, the coherency of precipitates, and similar X-ray atomic scattering factors of Fe and Ga. Another limitation for XRD studies is that they give information only from the surface of the sample whose structure can be different from bulk samples.

Thus, in situ neutron diffraction studies have some advantages in that case. They can easily be performed in an in situ and real-time mode with a reasonable temporal resolution. The difference between coherent neutron scattering lengths for Fe and Ga is sufficient for reliable observations of the ordering effects. High penetration of thermal neutrons allows analyzing bulk effects unlike XRD. The number of neutron diffraction studies of Fe–Ga alloys is still limited. We are aware of the papers [11,12] in which phase transformations in Fe–Ga ribbons were studied depending on the...
Fe/Ga ratio in the Ga concentration range from 15 to 22.5% and [13,14], where compositional variation of phonons was investigated by means of inelastic neutron scattering. Most recently we have successfully applied neutron diffraction tests to study bulk Fe-27Ga alloy at continuous heating and cooling [15].

In this paper we use neutron diffraction along an internal friction method to study sequence and kinetics of phase transitions in directly solidified Fe–Ga alloys with positive and negative deviations from stoichiometric Fe2Ga compositions (24.3–24.8%Ga and 27.4–27.8%Ga). The paper mainly focuses on the phase transformations in bulk samples upon heating. Additionally, we show how these transitions affect elastic and anelastic properties of the studied alloys.

2. Materials and methods

Two types of Fe–Ga alloys with Ga amounts (1) 24.3–24.8 and 27.4% (Fe-25Ga and Fe-27Ga hereafter) were produced by directional solidification in copper mold using pure Fe and Ga by induction melting under protection of high-purity inert argon gas using an Indutherm MC–20 V mini furnace (Table 1). Using energy dispersive spectroscopy, the chemical compositions of the cast buttons were measured with accuracy within ±0.2%. The location of these alloys in Fe–Ga phase diagram [16] is shown in Fig. 1. At room temperature the studied compositions belong to a two-phase A2 + L12 (Fe-25Ga) and a L12 single-phase (Fe-27Ga) structure according to the equilibrium phase diagram [16].

The neutron diffraction patterns were measured with a high resolution Fourier diffractometer (HRFD) [17] at the IBR-2 pulsed reactor in JINR (Dubna). The neutron diffraction experiments were performed on rectangular samples with a size of 4 × 8 × 50 mm. The HRFD is a time-of-flight diffractometer with a correlation mode of data acquisition. Its Δd/d resolution is determined by the maximum frequency of the fast Fourier chopper. In routine operation (Vmax = 4000 rpm), Δd/d ≈ 0.001 for d = 2 Å, only slightly depends on d_{bkl} and improves with increasing d_{bkl}. Further information can be found in Ref. [15].

The acquisition time for each diffraction pattern was 1 min short. Heating of the samples was carried out in a specialized furnace (ILL standard) with vanadium screens up to ~900 °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.

Simultaneous testing of anelastic (internal friction, Q⁻¹) and elastic (Young’s modulus, E) properties were carried out using forced bending vibrations on a commercial dynamical mechanical analyzer (Q800 TA Instruments) in the temperature range from 0 to 600 °C. The internal friction was measured as tanθ = (Q⁻¹), where θ is the phase lag between the applied cyclic stress, σ, and the resulting strain, ε = ε₀cos(ωt) and ε = ε₀cos(ωt + φ); φ = 2πf; and ε₀ = 5 × 10⁻⁵.

Table 1

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>At.% Ga</th>
<th>Used for:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-25Ga</td>
<td>24.3</td>
<td>DMA tests</td>
</tr>
<tr>
<td>Fe-27Ga</td>
<td>27.4</td>
<td>DMA tests and Neutron diffraction study</td>
</tr>
</tbody>
</table>

1 In this paper we use atomic %.

3. Results

3.1. Neutron diffraction

The initial state after direct solidification for both studied samples is undoubtedly represented by a D0₃ structure: the (111) and (311) diffraction lines, which are clearly seen in the high-resolution diffraction pattern, belong only to the D0₃ ordered phase (Fig. 2). The widths of diffraction lines only slightly exceed the contribution from the resolution function. Thus, we conclude that both samples have a single D0₃ ordered state.

According to the phase diagram, the following phases can be observed in the studied alloys at heating:

- the L1₂ (equilibrium phase below ~600 °C in Fe-25Ga and below ~615 °C in Fe-27Ga alloy) has a CsCl-type structure with Fe and Ga atoms partially ordered, sp. gr. Pn3m, a ≈ 3.72 Å (at 20 °C);
- the D0₃ (equilibrium phase for Fe-25Ga in the temperature range from ~590 to ~670 °C, and for Fe-27Ga from ~680 to ~825 °C) has a BiF₃-type structure with Fe and Ga atoms partially ordered, sp. gr. Fm3m, a ≈ 5.83 Å (at 20 °C);
- the D0₁₉ (equilibrium phase for Fe-27Ga from ~615 to ~680 °C) has a MgCd₃-type structure with Fe and Ga atoms partially ordered, sp. gr. P6₃/mmc, a ≈ 5.28 Å, c ≈ 4.28 Å (at 20 °C);
- the B2 (equilibrium phase for Fe-27Ga from ~680 to ~825 °C) which was not really observed in our tests has a CsCl-type structure with Fe and Ga atoms randomly distributed, sp. gr. Im3m, a ≈ 2.92 Å (at 20 °C);
- the A2 (equilibrium phase in two-phases A2 + L1₂ Fe-25Ga alloy below ~590 °C) has an α-Fe-type structure with Fe and Ga atoms randomly distributed, sp. gr. Im3m, a ≈ 2.92 Å (at 20 °C).

The D0₃ and B2 ordered phases appear in this system as a result of Ga atoms ordering in bcc Fe–Ga (A2) solid solution. The same concerns the D0₁₉ ordered and A3 disordered phases. At continuous heating ordering needs some time: that is why it is not always easy to define if, for example, the A2 phase has got B2 ordering or not. In some of our experiments discussed below we cannot recognize B2 ordering if we use heating rate 2 K/min but it is visible if heating.

Fig. 1. Fe–Ga equilibrium diagram [16] with compositions of studied alloys.
rate is 1 K/min. That is why in several cases we wrote \(A_2(B_2)\) to underline the existing tendency of the \(A_2\) phase to \(B_2\) ordering, which is nevertheless still weak. In most cases we simply skipped mentioning this tendency.

Upon continuous heating several phase transitions occur (Fig. 3), the differences in structural transformations between Fe-25Ga and Fe-27Ga alloys are presented in the 3D schemes. The recorded sequence of phase transitions upon heating with 2.25 K/min in Fe-25Ga is as follows: \(D_0^3 \rightarrow L_{12}\) (limited amount) \(\rightarrow A_2(B_2)\), while in the Fe-27Ga alloy this sequence is \(D_0^3 \rightarrow L_{12}(100\%) \rightarrow D_0(100\%) \rightarrow A_2(B_2)\).

The temperature dependences of neutron diffraction intensities obtained for the studied samples for the heating rate of ~2.2 K/min are shown in Fig. 4. Some minor changes in intensities of reflections from \(D_0^3\) phase are most probably linked with changes in vacancy concentration in this phase and first nucleations of the \(L_{12}\) phase discussed in [18,19] for alloys with 21–27\% Ga. Main volume fraction of the \(D_0^3\) phase in the Fe-25Ga alloy remains up to ~670 °C, where the \(D_0^3\) phase turns to \(A_2(B_2)\) phase simply by disordering of Ga atoms in the \(D_0^3\) lattice. In addition, a limited volume fraction of the \(D_0^3\) phase transforms to the \(L_{12}\) phase above 450 °C. Above 590 °C the \(L_{12}\) phase begins to dissolve and disappears completely at about 700 °C.

In contrast, in the Fe-27Ga alloy the \(D_0^3\) phase completely transforms to the \(L_{12}\) phase in the temperature range from 440 to 510 °C. The single \(L_{12}\) phase exists up to 615–620 °C, where \(D_0^3\) phase transforms to the \(L_{12}\) phase above 450 °C. Above 590 °C the \(L_{12}\) phase begins to dissolve and disappears completely at about 700 °C.

According to the equilibrium phase diagrams, the \(D_0^3\)/\(A_2\) (in Fe-25Ga) and \(D_0(100\%)\)/\(A_2\) (in Fe-27Ga) transformations at heating should go through a partially ordered \(B_2\) phase. The \(B_2\) phase is characterized by a diffraction peak (100) at \(d = 2.95\) Å for \(T > 600\) °C (and some other diffraction peaks with \((h+k+l) = 2n+1\)), but in our diffraction patterns, there were so weak signs of such peaks of the \(B_2\) phase that we preferred not to insist on the presence of this phase if heating rate is 2.25 K/min. The \(B_2\) ordering is better recorded if heating rate is 1 K/min. The same results were received in Ref. [15] where we did not discuss the influence of heating rate on \(B_2\) ordering in high temperature \(A_2\) phase.

Phase transitions in Fe–Ga leads to a noticeable difference in thermal expansion coefficients of different phases. These results are shown in Fig. 5 in terms of normalized volume of unit cell of corresponding phases per one atom. Temperature dependent changes of unit cell volume for Fe-25Ga (left) and Fe-27Ga (right) samples were calculated by corresponding changes in interplanar distances by diffraction peaks both at heating (bottom scale, red curves, the \(D_0(100\%)\) phase is marked green in web version) and cooling (top scale, blue points in web version). The sharpest change in the volume of the elementary cell occurs at heating due to \(D_0^3 \rightarrow L_{12}\) and \(D_0(100\%) \rightarrow A_2(B_2)\) transitions. At cooling, this transition is smeared in a wide temperature range where both phases (\(A_2\) and \(L_{12}\)) coexist. Some consequences of these effects are discussed below in terms of elastic and anelastic behavior of the alloy at heating (Fig. 6).

Kinetics for the isothermal \(D_0^3 \rightarrow L_{12}\) transition at step heating...
of the Fe-27Ga sample is presented in Fig. 6. Step heating means that the sample was quickly heated up (heating rate of about 20 K/min) to 470 °C14C and kept at this temperature about 60 min. Isothermal kinetic shows a transition from D03 to L12 phase: a decrease of the normalized intensities from (220) plane of D03 phase (blue curve in web version) and an increase in the normalized intensities from (200) plane of L12 phase (red curve in web version). One can see that the D03 to L12 transition at 470 °C14C is practically over after 40 min of annealing.

For comparison we added two more curves to this figure: (i) an internal friction level (PTr1 peak) as a function of annealing time at 470 °C14C discussed in detail in the next section and (ii) a similar kinetic of the same phase transition from D03 to L12 structure at 390 °C14C received using in situ XRD tests [Di4]. Kinetic at lower temperature is slower, as it can be expected from general diffusion laws.

3.2. Temperature dependent internal friction

Fig. 7 represents a temperature dependent internal friction (TDIF) and elastic modulus in arbitrary units (TDEM) DMA test of the directly solidified Fe-25Ga (left column) and Fe-27Ga (right column) alloys at heating up to 600 °C. The advantage of this commercial equipment (DMA Q800 TA Instruments) is that it can measure a sample using several frequencies in one heating run. By using six frequencies from 0.1 to 30 Hz, we can easily distinguish between thermally activated effects, which peak position increases with an increase in the frequency of forced vibrations, and effects related to different phase transitions. In this later case, it is the peak height (or relaxation strength) rather than the peak temperature that depends on frequency. Quite similar TDIF curves are recorded on the same samples after being annealed 30 min at 1000 °C and water quenched (the results are not shown in this paper).

Thermally activated effect at 95 e170 °C (denoted as the P1 peak) is common for both alloys. At higher temperatures (325 e500 °C) there is another thermally activated anelastic effect that is better pronounced in Fe-27Ga as compared to Fe-25Ga alloy where it is smeared and masked by the beginning of a high temperature background growth. The activation parameters are also doubtful in this later case. Temperatures of thermally activated P1 and P2 peaks
...corresponding Arhenius treatment provides the activation parameters of these peaks (Table 2).

The P1 peak was interpreted as the Snoek-type relaxation [4,7,8], the activation parameters presented in Table 2 are in agreement with this statement. The Snoek-type relaxation occurs due to stress-induced jumps of interstitial atoms (C) in a random A2 bcc solid solution or bcc-based D03-ordered lattice of Fe–Ga alloys. Approximately 0.2 eV increase in the activation energy for C-atom jumps in Fe–Ga with respect to ‘pure’ $\gamma$-Fe is due to the ‘elastic’ interaction of Ga with C atoms in solid solution. The P1 peak is not recorded at cooling from the range of equilibrium fcc L12 phase, it is also in agreement with the main statement of the Snoek theory that is applicable only for bcc solid solutions but not for the fcc lattice. Fast relaxation time for the P2 peak at least for Fe-27Ga alloy depend on the measuring frequency of the forced vibrations. Corresponding Arhenius treatment provides the activation parameters of these peaks (Table 2).

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\begin{table}[h]
\centering
\caption{Activation parameters of thermally activated internal friction peaks shown in Fig. 7.}
\begin{tabular}{|c|c|c|c|}
\hline
Alloy & P1 & $\tau_0$ & P2 & $\tau_0$
\hline
Fe-25Ga & 1.05 ± 0.02 & 7 × 10$^{-15}$ & 3.12 ± 0.31 & 1 × 10$^{-21}$
Fe-27Ga & 1.08 ± 0.01 & 3 × 10$^{-15}$ & 1.91 ± 0.07 & 1 × 10$^{-16}$
\hline
\end{tabular}
\end{table}

The main difference between TDIF curves for these two alloys is the frequency independent peak at about 470 °C, which is recorded only in Fe-27Ga (Fig. 7b). Transient internal friction $P_{Tr}$ peak temperature, which is accompanied with an increase of the Young’s modulus does not depend on the frequency, whereas its height is strongly affected by the measurement frequency and the heating rate. If heating is stopped at the temperature of the $P_{Tr}$ peak (i.e. at 470 °C), the $P_{Tr}$ peak gradually decreases along with isothermal character of the D03 → L12 transition at a constant temperature. These data are shown in Fig. 7 and they underline the same rate of a decrease in IF and the completeness (сплошный характер) of the phase transition both measured at the same temperature (470 °C).

It should be noted, that a different rate of growth of the lattice parameter of D03 and L12 phase was recorded by neutron scattering at heating, which is likely to be the main source for the transient internal friction peak. The anelastic deformation that gives rise to an internal friction is proportional to the transformed volume fraction of L12 phase and arises from the lattice deformation. This transient peak is recorded neither in Fe-25Ga alloy where amount of the D03 to L12 transition is very limited nor at cooling or subsequent heating in both alloys, i.e. in the cases when the D03 to L12 transition does not take place. Phase transitions from one type of lattice to another one at higher temperatures (e.g., L12 to D019 and D019 to B2 phase) might also lead to anelastic effects but to prove this we need internal friction tests up to 850 °C.

4. Conclusions

Using neutron scattering technique, we have defined ranges of phase transitions in the bulk samples of Fe–Ga alloys with 24.8 and 27.4 at.% Ga under continuous heating. These structural studies allow interpreting anelastic effects recorded in the same conditions in the same materials using mechanical spectroscopy. Different rates of lattice parameters increase in the temperature range of their co-existing lead to significant changes in elastic (E) and anelastic (Q$^{-1}$fi) characteristics of the alloy. We proved that the transient internal friction $P_{Tr}$ peak accompanies the D03 to L12 phase transition.
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