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Structural features of Fe–Al-vacancy system

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The influence of structural defects on phase transformation in Fe–Al-vacancies system is considered. It has been shown that, due to existing trend to accumulation of point defects at increasing aluminum content in Fe–Al system alloys, the appearance of ferrite precipitates in Fe_3Al compound becomes thermodynamically favorable in the temperature region of the equilibrium $\alpha_1(Fe_3Al)$-phase existence.

Рассмотрено влияние дефектов структуры на протекание фазовых превращений в системе Fe–Al-вакансии. Показано, что вследствие существующей тенденции накопления дефектов структуры по мере увеличения содержания алюминия в сплавах системы Fe–Al, в интерметаллиде Fe_3Al в области температур существования равновесной $\alpha_1(Fe_3Al)$-фазы термодинамически выгодным становится появление выделений феррита.

The disordered condensed systems are under steady interest for researchers, since it is possible, taking those as examples, to trace the disordering influence on the dynamics of a system containing defects and its macroscopical properties [1]. The important role of vacancies in structure and phase state evolution is emphasized in numerous works. This concerns especially some irradiated metals and alloys. For example, the $\gamma \to \alpha$ martensitic transformations are considered to be a possible ways to relaxation of the stresses arising under irradiation in austenitic stainless steels [2]. Before [3] we have shown the construction possibility of phase diagrams for "iron-carbon-vacancy" (Fe–C–v) alloys in elastic stress fields which provides comparison of the transformation stresses with point defect concentration and can be used to explain the structure and phase transformations in the initial and irradiated materials, as well as in development of new functional materials.

There is a lot of facts on "unexpected" occurrence of "massive ferrite" precipitates in the alloys laying inside the γ phase region of the equilibrium phase diagram as a result of neutron irradiation [4], due to reverse martensitic transformations, as well as occurrence of massive ferrite between voids in strongly swelled austenitic steel [4], etc. A significant attention is given in the scientific literature to quasi-equilibrium conditions of ordered Fe–Al system [5–10], where even the amorphous phase was observed near to interface of the Al–Fe crystal layers which are characterized by considerably different lattice parameters [5]. At the same time, the role of defect concentration change at varying composition of binary ordered Fe–Al alloy in formation of structures untypical of investigated temperature-concentration area of the phase diagram of homogeneous solutions is investigated insufficiently. It is just the internal friction (IF) [5–9] that is especially sensitive to such defects. The form of the mechanical relaxa-

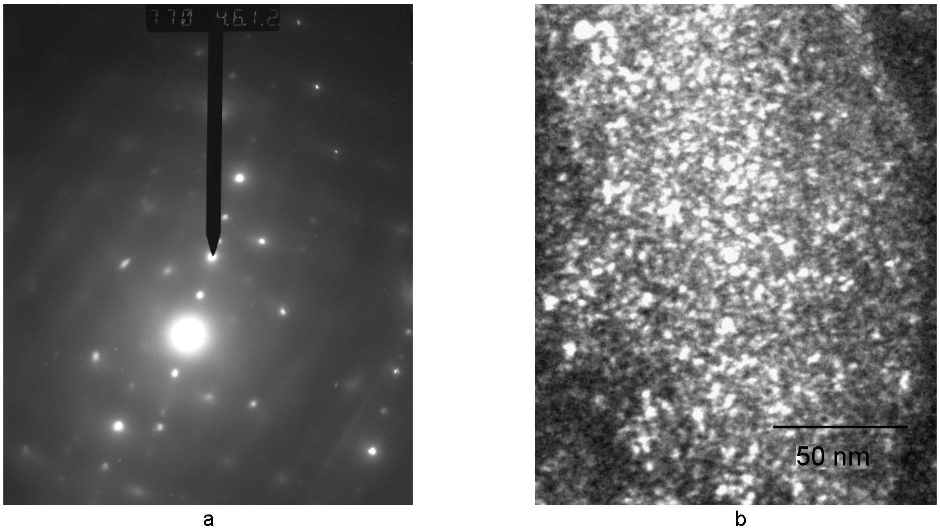


Fig. 1. Electron-diffraction patterns of a Fe_3Al sample cooled in quartz ampoule in air from 1273 K ([111] direction) (a) and view of ordered $D0_3$-structure domains in a superstructural reflex (111) (light areas with d ~ 5–10 nanometers with sharp edges) (b).

tion spectrum in Fe–Al system alloys is substantially connected to varying vacancy concentration due to the large dimensional difference between iron and aluminum atoms. The role of vacancies is so essential that in [7, 9] not binary Fe–Al system, but ternary Fe–Al-vacancy one are considered. However, the structural aspect of the relaxation effects in Fe–Al system, in particular that of so-called X-relaxation, requires a further research [6–8]. In this work, the structural and dissipative properties of ternary Fe–Al–v system have been studied experimentally and analytically basing on the approach offered in [3].

As the study object, Fe-25.0 at. % Al alloy is used (the carbon content did not exceed 0.085 at. %). The specimens were cut out from 1 kg vacuum induction melted ingot of refined GPOO8 iron and A99 aluminum and had the average grain size of 0.6 mm as determined by optical microscopy. The specimens were annealed in evacuated quartz ampoule at 1273 K for 1 hour to eliminate the stresses brought at manufacturing of specimens, and to obtain further the disordered solid solution Al in α-Fe (bcc) by quenching in water to 273 K. Some specimens were cooled in the ampoule to obtain ordered Fe_3Al state. The internal friction and elastic properties measurements were carried out at Kharkiv National University (Ukraine) using the technique described in [6], and at Institute for Metal Physics and Nuclear Physics of Solids, Technical University of Braunschweig (IMNP TU-BS) (Germany) [11] using laser registration system based on a position-sensitive photodiode and an analog-to-digital converter. The measurements carried out using double blade specimens with the working part of 25 mm length and 2.2 mm diameter (twisting at 90 Hz frequency) and plates of $25\times2\times0.2$ mm^3 in 10^{-3} Pa vacuum at the bending vibration frequency of 200–300 Hz. As the IF measure, logarithmic decrement δ was used. The IF temperature dependences were measured within the range from liquid nitrogen boiling point up to 750 K. The transmission electron microscopy (TEM) was done using a LEO-922 device at IMNP TU-BS. The images were prepared also in superstructural reflexes to reveal the medium-sized ordered domains. The samples were oriented along the Kekuchi lines. For an additional defect formation influence on the effects under study, the samples were subjected to γ irradiation (^{60}Co).

A sample of the investigated alloy Fe_3Al quenched in water from 1273 K shows the Kekuchi lines positions in electron diffraction patterns typical of bcc lattices, i.e., those of substitutional solid solution on the basis of α-Fe. After annealing at 623 K (in the field of the ordered α_1-phase) or after cooling in air from 1273 K in an evacuated quartz ampoule, additional lines of superstructure Fe_3Al appear as is illustrated in Fig. 1a (the hexagon typical of DO_3 superstructure is clearly seen, formed by {220} type reflexes at imaging in the [111] direction). After cooling in a quartz ampoule in air, there are also B2 reflexes of

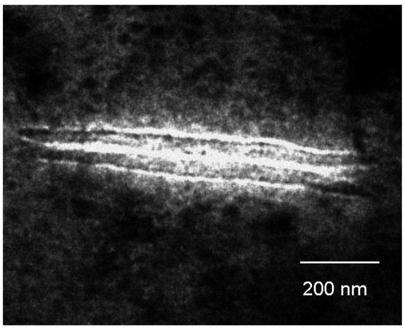


Fig. 2. A pair of extended precipitates in the D0$_3$ ordered matrix of intermetallic compound Fe_3Al (light areas).

FeAl structure (pointed by an arrow), since the ordering occurs according to the known scheme α-Fe → FeAl(B2) → $Fe_3Al(D0_3)$.

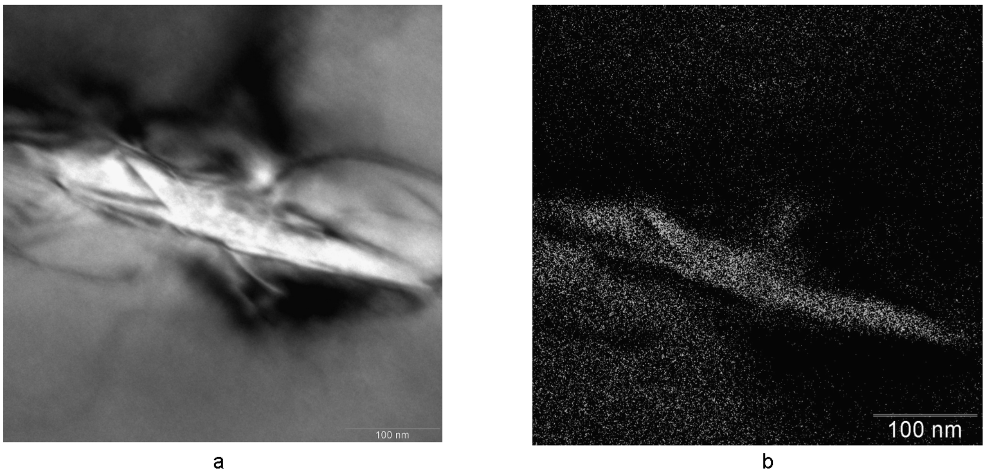
Imaging in the superstructural reflexes (110) for B2 structure (Fig. 1a, pointed by an arrow) and (111) for D0$_3$ structure have shown that at intermediate cooling rates(cooling in a quartz ampoule in air), within relatively large (some hundreds nanometers) domains of B2 structure, nanoscale (5–10 nm, Fig. 1b) structure equiaxial domains are formed, which correspond to D0$_3$ (Fe_3Al) structure that is an equilibrium one in the phase diagram, as it was expected. However, at careful research of the structure, unexpectedly, strongly nonequiaxial (1:15 to 1:35) 25 to 40 nm thick needle-like particles of a phase were observed (Fig. 2) in volume fraction about 1 %.

The analysis of the impurity distribution carried out using EELS technique (analysis of the energy spectrum of electrons passed through a foil in LEO-922 device), testifies unequivocally to the disperse phase enrichment in iron as compared to its content in the alloy (Figs. 3a and 3b). This is evidenced by the fact that the of iron spatial distribution pattern (Fig. 3b) repeats in details the phase contour (Fig. 3a).

The disperse phase enriched in iron contained 87±1 at.% of iron, that is, the aluminum content therein was halved as compared to that in the alloy. Comparing the electron diffraction patterns from the matrix phase of D0$_3$ structure (Fig. 5a), and from the disperse phase (Fig. 5b), additional reflexes of phase α-Fe were revealed, which should not be present after the ordering, according to the equilibrium phase diagram.

Studying the relaxation properties of alloy Fe-25 at. % Al in the states where the discussed considerably anisotropic phase was observed, the presence of so-called "carbon vacancy" IF peak was revealed, which was referred to as the $X(R)$ peak [6–10] (for D0$_3$ structures, it was observed for the first time in Fe-31.5 at.% Al alloy [6]). For the sample cooled in the ampoule, the X-peak is expressed rather well (Fig. 4a).

The X-peak is stable at heating up to 570–620 K; this is believed to be connected with the fact that vacancies may form complexes with carbon [8, 10], the presence of the letter in the solid solution is evidenced by the Snoek peak (C) (Fig. 4a). After heating up to 720 K, as is seen in the Figure (the reverse temperature run), X-peak disappears (the "carbon-vacancy" complexes are decom-



a b

Fig. 3. The light field image of iron-enriched phase (a) and iron distribution in the same site of a Fe_3Al intermetallic compound sample (b) (light areas).

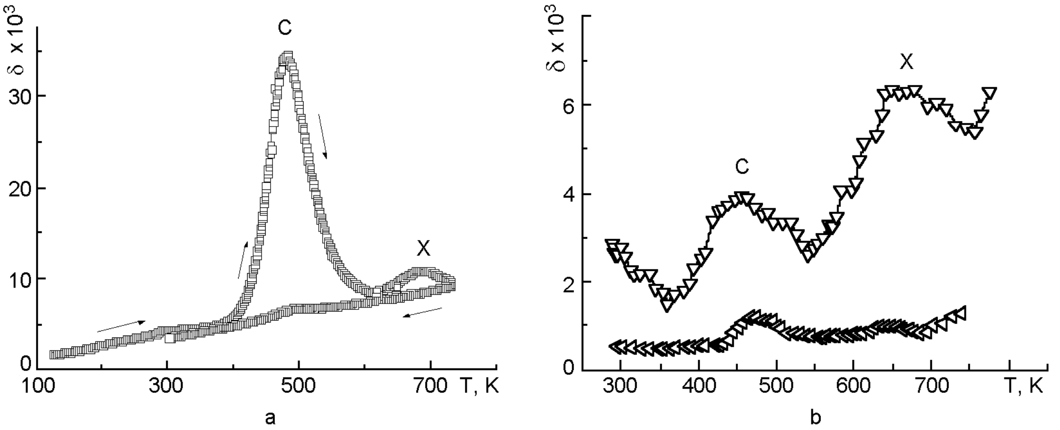


Fig. 4. Temperature dependence of attenuation δ for a Fe_3Al sample quenched in ampoule (bending vibrations, *f* ~ 230 Hz on the X peak) (a) and after quenching in oil from 1273 K, ageing at 573 K for 1 h and gamma irradiation at the dose $2.2\cdot10^5$ Grey (к); the bottom curve corresponds to repeated heating (twisting, *f* ~ 90–120 Hz) (b).

posed), and C-peak decreases (carbon leaves from solid solution into carbides).

We have create artificially conditions where the point defect formation probability increases. To that end, the samples were gamma irradiated. In Fig. 4b, the temperature dependence of internal friction for a sample after heat treatment is presented. No "carbon-vacancy" peak was observed. However, it appears after gamma irradiation (^{60}Co) at $2.2\cdot10^5$ Grey dose (gamma irradiation energy approximately 1.25 MeV). The presence of this peak specifies that the radiation influence favors the formation of point defect complexes. After the first heating up to 800 K, these defects are annealed and at repeated heating (the lower curve), the X peak decreases strongly, while carbon remains in part in the solid solution (the C peak is rather high).

It is known [10, 12, 13], that point defects and complexes thereof play an essential part in relaxation of ordering alloys. In particular, in [12], the role of quenched vacancies and their concentration due to low formation enthalpy in concentrated alloys Fe–Al (from 1.8 eV for Fe-25 %FeAl up to 0.77 eV for Fe–47 %Al) has been analyzed during structurization and formation of relaxation properties. Basing on the enthalpy data, the authors have assumed that vacancy supersaturation arises as in the alloys as a result of quenching. According to the theory [3], in this case, the behavior of point defects should correspond to action of hydrostatic compressing stresses. In fact, however, low formation enthalpy of the vacancies may evidence the vacancy deficit. This is connected with the fact that the "oversized" aluminum in the quenched alloy generates high hydrostatic tensile stresses. Under high hydrostatic tensile stresses, vacancies can survive only when they make volumetric complexes as micropores. Experiments on positrons annihilation in quenched Fe–Al alloys confirm existence such tridimensional vacancy complexes containing from 4 up to 10 vacancies (experimentally determined concentration about 10^{-4} to 10^{-5} [14]). Such vacancy accumulations as such cannot result in formation of mechanical relaxation peaks (in particular X-peak). At the same time, together with formation of vacancy complexes, all-round tensile stresses generate supersaturation of the alloy with iron interstitials.

As is seen from the structural researches, the tensile stress relaxation of the quenched Fe–Al alloy during annealing starts with ordering and formation of the Fe_3Al phase microdispersed precipitates. The volumetric discrepancies between the matrix and the arising new phase generate vacancies which lack in the alloy and which are spent in Al migration and the further ordering. The stress relaxation near to Fe_3Al phase precipitates promotes "displacement" (migration) of interstitial iron atoms into the interphase space (see Fig. 2, Figs. 3a, 3b). In the iron-enriched areas, the tensile stresses are accumulated, that, as it is established, results eventually in phase transformation with formation extended precipitates of α-ferrite. The transformation seems to run according to martensitic type that favors the tensile stress relaxation, since interstitial iron atoms are spent to the new phase formation.

The appearance of X peak under strongly nonequilibrium structural conditions characterized by high mobility of iron atoms and iron "displacement" into interphase space, as well as after radiation stimulation suggests that iron diffusion under applied stresses should be considered in more detail as an element of the X peak formation mechanism. Such a possibility with involvement of vacancies was considered in so-called "four-jumping" B.Damson mechanism [8, 13] which can be further developed.

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Структурні особливості системи Fe–Al-вакансії

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Розглянуто вплив дефектів структури на перебіг фазових перетворень у системі Fe–Al-вакансії. Показано, що внаслідок існуючої тенденції накопичення дефектів структури зі збільшенням вмісту алюмінію у сплавах системи Fe–Al в інтерметаліді Fe_3Al в області температур існування рівноважної $\alpha_1(Fe_3Al)$-фази термодинамічно вигідним стає поява виділень фериту.