Acta Materialia 153 (2018) 45–52

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Antiphase domains or dispersed clusters? Neutron diffraction study of coherent atomic ordering in Fe_3Al-type alloys

Anatoly M. Balagurov [a, b], Ivan A. Bobrikov [a, *], Sergey V. Sumnikov [a], Igor S. Golovin [c]

[a] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980, Dubna, Russia
[b] Lomonosov Moscow State University, 119991, Moscow, Russia
[c] National University of Science and Technology "MISIS", 119049, Moscow, Russia

ARTICLE INFO

Article history:
Received 24 November 2017
Received in revised form
3 April 2018
Accepted 8 April 2018
Available online 24 April 2018

Keywords:
Fe-27Al
Neutron diffraction
Structural phase transitions
Antiphase domains
Dispersed clusters

ABSTRACT

A combination of high-resolution and *in situ* real-time neutron diffraction was used to collect the experimental data concerning coherent atomic ordering in Fe_3Al-type alloys in a wide temperature range. The analysis of the obtained data was carried out within the framework of two models: antiphase domains and dispersed clusters embedded in matrix. The second model, for which the atomic ordering is organized in the form of clusters of mesoscopic sizes (from ~200 to ~400 Å) randomly distributed inside a less ordered matrix, provides a better fit of the data. For two chemically identical Fe_3Al samples - the first was in the as-cast polycrystalline bulk state, and the second was grown as a single crystal - the initial state can be described as a partially ordered B2 structure (matrix) with dispersed clusters of the $D0_3$ ordered phase. The initial (quenched) state of the $(Fe_{0.88}Cr_{0.12})_3Al$ polycrystalline sample is the disordered A2 phase with clusters of the partially ordered B2 phase. After heating and subsequent slow cooling, the structure of both binary and ternary alloys is B2 matrix with dispersed $D0_3$ clusters, whose dimensions are increased up to ~900 Å.

1. Introduction

The ordering of atoms in a stoichiometric alloy of the composition Fe_3Al (Fe-25Al) has been known since the 1930s. Already in Ref. [1] it was established that during the crystallization of Fe_3Al, a structure is formed, now called $D0_3$, in which the atoms are distributed over 16 possible Wyckoff positions in the cubic space group $Fm3m$ ($a \approx 5.834$ Å), and, as follows from an X-ray analysis, Al atoms occupy mainly (~92%) 4 of these positions. When Fe_3Al is heated, the second-order structural transitions occur: $D0_3 \rightarrow B2 \rightarrow A2$, where B2 is a partially ordered ($Pm3m$), and an A2 is a completely disordered ($Im3m$) phase.

The presence of atomic ordering determines the appearance in the diffraction patterns of superstructure (s) peaks, whose intensities are:

$$I_s \sim |F_s|^2 \sim \xi^2 \cdot (b_{Fe} - b_{Al})^2, \quad (1)$$

where F represents the structure factor, b is the atomic form-factor for X-ray diffraction or coherent scattering length for neutron diffraction, and ξ is the degree of Fe and Al ordering over crystallographic positions ($0 \leq \xi \leq 1$). Intensities of fundamental (f) peaks in diffraction patterns are:

$$I_f \sim \left|F_f\right|^2 \sim (3b_{Fe} + b_{Al})^2, \quad (2)$$

and the so-called contrast $R = F_s/F_f$, at complete ordering is 0.19 for neutrons ($b_{Fe} = 0.945$, $b_{Al} = 0.345$, in 10^{-12} cm units), which is quite acceptable for reliable registration of s-peaks.

An interesting feature of the Bragg diffraction patterns of Fe_3Al is the specific modulation of the widths of the diffraction peaks: they are large for superstructure peaks and comparatively small for fundamental ones. For the first time, a similar phenomenon was observed for the Cu_3Au compound [2], in which atomic ordering also occurs under certain conditions. In the classical paper [3], this effect was explained using a model of antiphase domains (APDs): neighboring regions with the same arrangement of atoms in the unit cell, but shifted to each other by a fraction of some lattice translation vector. The waves diffracted by these domains are coherent and shifted in the phase.

As it follows from the APDs model the width of the f-peaks is

* Corresponding author.
E-mail address: bobrikov@nf.jinr.ru (I.A. Bobrikov).

https://doi.org/10.1016/j.actamat.2018.04.015
1359-6454/

determined by the finite size of coherently scattering areas regardless of their partition onto antiphase domains, whereas the width of *s*-peaks is determined by the average size of individual domain. Accordingly, if the domains with ordered atomic structures are connected by a coherent boundary (antiphase boundary, APB), the *s*-peaks will be broadened relative to the *f*-peaks because of the size effect. This model became generally accepted and was used in numerous articles, monographs, and textbooks (see, e.g., paper [4] and books [5,6]).

The possibility of the appearance of antiphase domains in ordered alloys is confirmed by various observations and calculations. Most of the observations were made using transmission electron microscopy (TEM). For example, in Ref. [7] this method was used for determination of the critical behavior of antiphase boundaries (the correlation length l_c in the Landau-Ginzburg theory was analyzed) in Fe_3Al at a temperature transition between B2 and $D0_3$ structural phases. From the obtained dependence of l_c on $(T_c - T)/T_c$, where T_c is the disorder-order transition temperature, it follows that B2 ↔ $D0_3$ is a second-order transition, and that, near T_c (at $T_c - T < 10$ K), the correlation length can exceed 100 Å (up to 400 Å). In Ref. [8], to visualize APB in $Fe_{65}Al_{35}$ in the B2 structural phase, diffraction of a coherent X-ray beam was used along with electron microscopy. This method confirmed the results of the TEM observations and at the same time allowed the registration of the intensity modulation in the superstructure peak (001) predicted by the APDs model.

A detailed analysis of the TEM data on the formation of the APDs and the motion of the APB in the course of the B2 → $D0_3$ transition was performed in a review article [9]. According to simulations, based on the minimization of the thermodynamic potential, if the initial B2 phase is isothermally annealed, the disperse $D0_3$ domains of a small size appear, which then grow and merge if there is no phase shift between them, or form APDs if the phase shift is present. In parallel with the increase in size, the degree of atomic ordering gradually increases. With prolonged annealing, the B2 regions disappear, becoming APB between the ordered domains. The final stage of the process is the alignment of the APB due to the disappearance of small domains that are absorbed by domains with the opposite ordering phase.

The question about universality of this picture of APDs formation remains an open one. Obviously, the attainability of the final equilibrium state considerably depends upon the conditions of sample preparation, the duration and the temperature of its annealing, and its specific microstructure. Often a TEM analysis is conducted with samples, whose state is far from equilibrium. In the literature, one can easily find many TEM pictures that clearly do not correspond to the state, with the APDs separated by narrow, flat APB. A typical example of such an intermediate state is shown in Fig. 1 [10], where the regions of the ordered $D0_3$ phase of arbitrary size and shape are clearly visible. The interlayers between them also have arbitrary thickness and shape. Nevertheless, even in this case, it is customary to describe the regions of the ordered phase as antiphase domains, although if the interlayers between the adjacent regions are large, it is impossible to say whether their atomic structures are in phase or antiphase. The concept of matrix of a disordered phase with dispersed clusters of an ordered phase is more appropriate for the situation shown in Fig. 1.

The explanation for the nonstandard profiles of the diffraction peaks in ordered alloys based on the APDs model suggested in Ref. [3] is also not universal. Already its author, A.J.C. Wilson, has pointed out that the model based on the "foam structure" proposed by W.L. Bragg [11], can also explain the observed effects. Moreover, for non-equilibrium state, the Bragg model looks much more realistic than Wilson's assumption of antiphase domains of equal volume with flat boundaries. In some papers, both assumptions are used to explain the behavior of the widths of the diffraction peaks

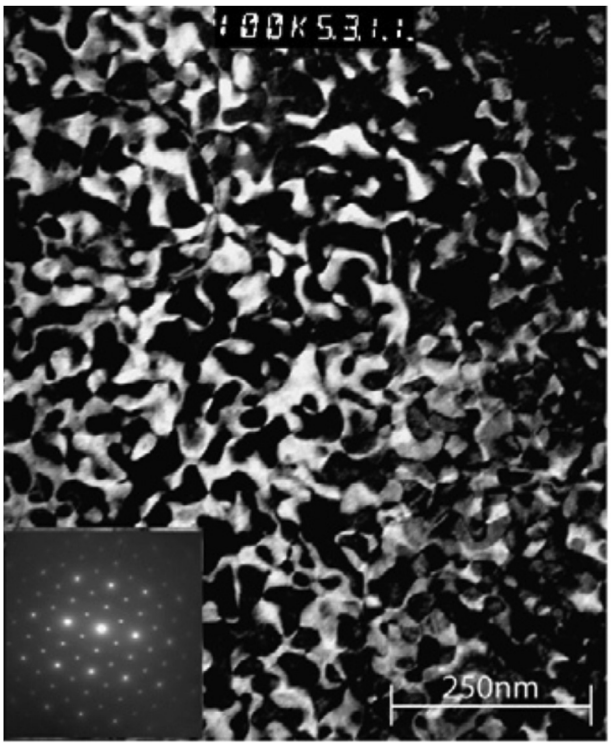

Fig. 1. Dark-field transmission electron microscope image of the structure of Fe–26Al in annealed at 300 °C state: $D0_3$ domains (in white) immerged into B2 matrix (in black). Reprinted from Ref. [10], copyright 2018, with permission from Elsevier.

(e.g. Ref. [12]). In the Fe-Al system with ~20 at. % Al nanodispersed inclusions of the ordered $D0_3$ phase with dimensions from 20 to 50 Å in the disordered A2 matrix were observed by TEM [13,14]. A similar state (nanodispersed $D0_3$ clusters in A2 matrix) was identified for the Fe-19Ga composition using high-resolution transmission electron microscopy (HRTEM) [15]. Moreover, in that paper, this state was used to explain the enhanced magnetostriction in Galfenol alloys. The possibility of the existence of such regions also follows from calculations based on the Atomic Density Field (ADF) theory [16], carried out in Ref. [17] for the Fe-(15–20)Ga compositions.

Thus, one can expect that, for the analysis of non-equilibrium states, including those gradually formed during isothermal annealing treatment, the model of dispersed clusters would be the most adequate, and the question is whether it can explain the effects observed for the widths of the diffraction peaks. Our preliminary results on this subject [18], acquired for the same polycrystalline $Fe_{2.77}Al$ sample, allowed for the assertion that the main volume of the material is filled by a partially ordered B2 phase, whereas the completely ordered $D0_3$ phase is organized in the form of small clusters being coherently incorporated into the B2 matrix. In this paper, the coherent incorporation of the ordered $D0_3$ clusters into a less ordered B2 matrix and the accompanying diffraction effects are discussed in more detail with the use of neutron data concerning a single crystal of $Fe_{2.77}Al$ alloy. Important additional information was obtained with the $(Fe_{0.88}Cr_{0.12})_3Al$ composition in the quenched state. The use of neutrons confirmed the volumetric nature of the measured effects and excluded the effects of surface and local inhomogeneities.

For compactness, the content of this paper is limited with analysis of above-mentioned models for microstructure of the studied compounds. Their physical properties and characteristics are discussed in details in our recent paper [19].