Functional Materials 11, No.2 (2004)

Dilatometric study of ordered structures in Fe–Al alloys

M.Boufenghour, A.Hayoune, N.Ya.Rokhmanov, M.Bouchear, D.Hamana*

Phases Transformations Laboratory, Faculty of Sciences,
Mentouri University of Constantine, Algeria
*Department of Experimental Physics,
V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

The order-disorder transformations in iron based alloys containing 21.5 and 25 at. % Al have been studied. Consideration of results obtained using dilatometry allowed us to assert that the ordering reaction in Fe–Al alloys after quenching from disordered state is a rather rapid process and ageing at moderate temperatures results in increased extent of the DO_3 type ordering.

Изучено превращение порядок-беспорядок в сплавах на основе железа, содержащих 21.5 и 25 ат. % Al. Анализ результатов, полученных путем дилатометрии, позволяет утверждать, что реакция упорядочения в Fe–Al сплавах после закалки из области неупорядоченного состояния является довольно быстрым процессом и старение при умеренных температурах приводит к повышению степени дальнего порядка типа DO_3.

The intermetallic compounds of iron aluminides are an interesting structural material for high-temperature applications due to their favorable properties, in particular, high strength and good corrosion resistance [1–3]. The structural changes associated with ordering in the Fe–Al system were first elucidated in 1932 by the classical X-ray work of Bradley and Jay [4], who showed how the two different kinds of atoms can occupy the different positions in the lattice as the composition is varied. Although slight correstions have been made, their results have been largely confirmed in [5]. In alloys containing from 0 up to 23 at. % Al, the two kinds of atoms are arranged randomly within the common lattice whether they are quenched from a high temperature (600 or 700°C) or slowly cooled, although slowly cooled alloys have been shown to exhibit short-range order. For slowly cooled alloys in the range 23 to 25 at. % Al, aluminum atoms begin to segregate to the *b*-type sites, until at 25 at. % Al (Fe_3Al), the ordering becomes almost perfect, with aluminum atoms occupying almost all the *b* positions and the aluminum population of the *a*, *c* and *d* positions being nearly zero, so that the centers of alternate small cubes are mainly occupied by aluminum atoms (Fig. 1). At 28 at. % Al, the occupation of the *b* positions with aluminum is complete, but then aluminum atoms start also to re-

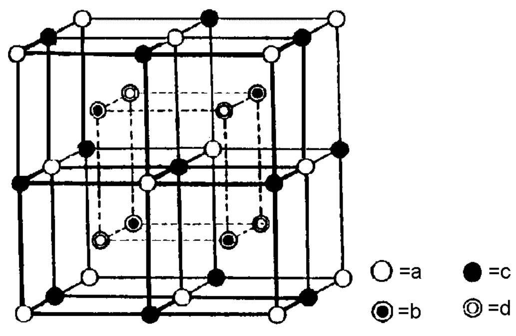

Fig. 1. Fe_3Al structure with Al atoms occupying the *b* sites [7].

enter the *d* positions which at the composition Fe_3Al were occupied almost entirely by iron atoms. In slowly cooled alloys, this process continues, the aluminum occupancy of the *b* sites decreasing slowly as aluminum atoms continue to re-enter *d* sites until at 40 at. % Al the two positions are equally occupied.

The resulting structure has been referred to as the "pseudo-FeAl" type of ordering, and is in fact the CsCl type of superlattice in which the ordering is imperfect because of lack of stoichiometry, since the *b* and *d* positions, in addition to containing all the aluminum atoms, must also accommodate the iron atoms remaining when the *a* and *c* positions are fully occupied. For alloys quenched from higher temperatures, it has been found that alloys with compositions exceeding ~25 at. % Al retain the "pseudo-FeAl" ordered structure up to temperatures near the melting point. Interesting lattice-parameter changes associated with the ordering onset in this system are observed. Up to ~ 18 at. % Al, there is an approximately linear lattice parameter vs. composition relationship, the iron lattice being expanded due to addition of aluminum. From about 18 up to 30 at. % Al, the lattice parameter of slowly cooled alloys (or of alloys that have been quenched after a low-temperature annealing treatment) shows very little change with composition, then decreases to a minimum at about 34 at. % Al before increasing again in a normal way with addition of aluminum. It is very likely that the almost constant parameter values between 18 and ~ 30 at. % Al correspond to a two-phase field on either side of the almost stoichiometric phase Fe_3Al region.

This interpretation is supported by [6] where thin-film electron microscopy was used providing a clear evidence for the existence of two phases in alloys containing just less than 25 at. % Al. For such alloys, equilibrium between an α solid solution and the almost stoichiometric ordered Fe_3Al phase at temperatures below ~ 550°C has been proved. The very slight minimum that may be present in the parameter values at the Fe_3Al composition may correspond to perfect ordering in the single-phase alloy at this composition. The more pronounced minima at ~ 34 at. % Al and at ~ 40 at. % Al are associated with the formation of the pseudo-FeAl type of ordering: at compositions > 30 at. %, this type of ordering exists at low and high temperatures, but it is believed that between 23 and 30 at. % Al, there is a random solid solution at 1000°C and the ordering reaction can only be partially suppressed by quenching [7]. The aim of this work is to follow the structural evolutions engendered by the ordering process, using dilatometric analysis which is sensitive to the volume changes.

Fe-21.5 and 25 at. % Al alloys were used in this work. The samples were cut out of an ingot prepared in a Balcers vacuum-induction furnace, using refined iron and pure aluminum (99.99 %). The samples were annealed for 2 h at 1100°C, quenched in water and aged at 300°C during various times (1 h, 10 h, 20 h, and 200 h). For dilatometric measurements, a DI24 Adamel Lhomargy dilatometer connected to a computer has been used. The samples were in a cylindrical shape (25×5 mm^2). A suitable software (Logidil) allowed the data processing and the determination of critical points on the recorded curves at heating-cooling cycles under controlled atmosphere. The thermal cycle applied in the dilatometer consists of heating from 25 to 1100°C, followed by holding for 5 min at this temperature and cooling to 25°C at the same rate (5°C/min). It is necessary to recall that the "ordering" process (appearance of ordered phases DO_3 and B2) is accompanied by a remarkable decrease of the lattice parameter value, consequently, ordering and disordering reactions must show contraction or expansion effects in the dilatometric curves. As a rule, the dilatometric curve of the complete cycle gives a general idea on the behaviour of the material during the whole thermal cycle, while the derivative curves for different segments (heating, holding, cooling) puts in evidence any dilatometric anomaly or effect.

Study of the Fe-21.5 at. % Al alloy

As-quenched state. The derivative curve of the heating branch for a sample homogenized for 2 h at 1100°C and quenched in water presents (Fig. 2a) an important anomaly in the temperature interval [200–500°C] including:

— an important contraction between 200 and 340°C with a peak situated about 280°C certainly relating to the formation of ordered DO_3 particles and to increase of the ordering extent starting from a completely disordered state in accordance with [8–11];

— an important expansion within the temperature interval 340–500°C peaked at 410°C, associated with the decrease in the

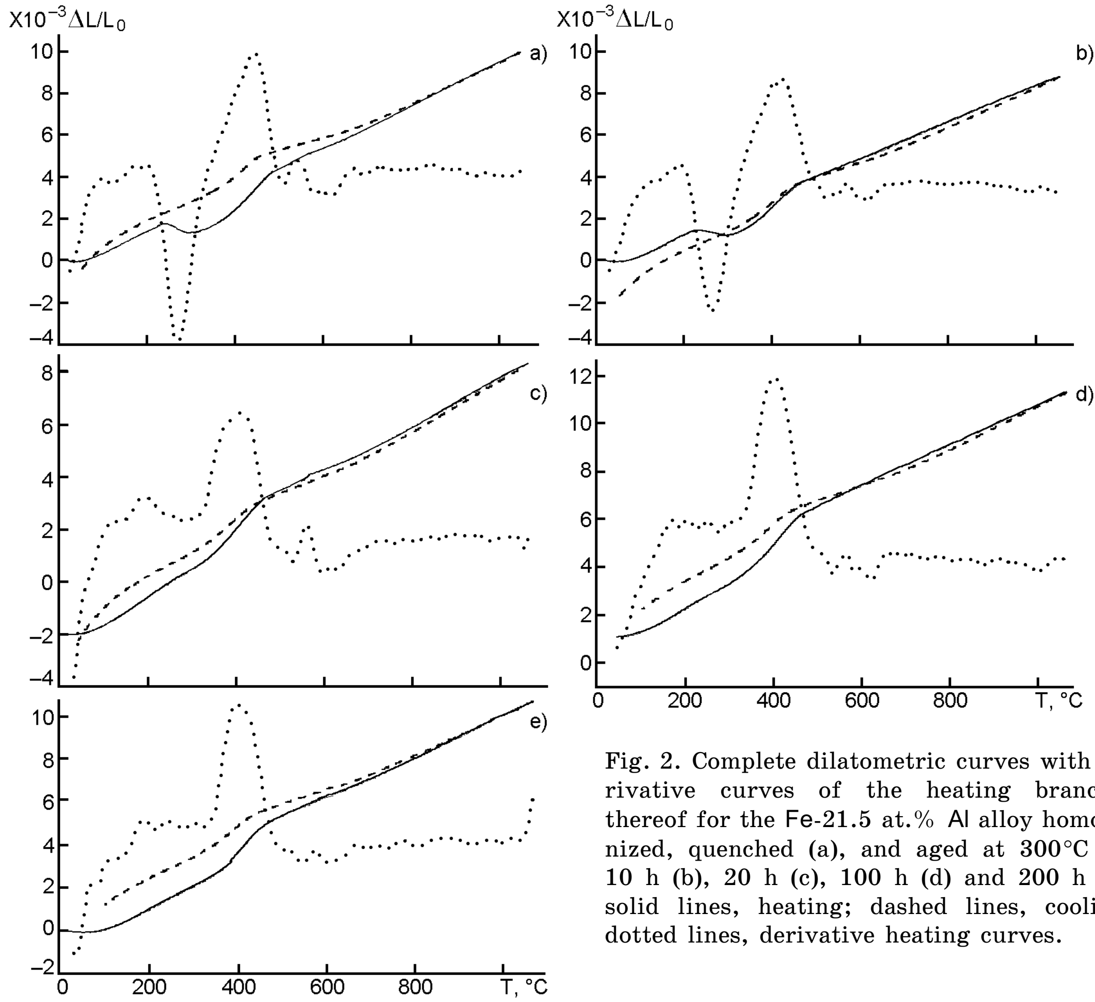

Fig. 2. Complete dilatometric curves with derivative curves of the heating branches thereof for the Fe-21.5 at.% Al alloy homogenized, quenched (a), and aged at 300°C for 10 h (b), 20 h (c), 100 h (d) and 200 h (e): solid lines, heating; dashed lines, cooling: dotted lines, derivative heating curves.

of DO_3 particle ordering extent followed by their dissolution in the disordered matrix [5–8] by approaching the $\alpha + DO_3 \rightarrow \alpha$ transformation line.

Ageing state. The dilatometric curves of the samples homogenized, quenched and aged at 300°C present effects almost identical to those of the as-quenched state. The derivative curve of the heating branch for the sample aged for 10 h (Fig. 2b) has a shape similar to that of the as-quenched state: one observes an important contraction between 200°C and 320°C with a maximum at 280°C. However, it is lower as compared to as-quenched state. This contraction is followed immediately by an important expansion in the temperature interval 320–500°C with a peak near 423°C. The observed contraction amplitude decrease in comparison with the as-quenched state is always associated with an improvement of the DO_3 particle ordering extent during this aging.

After 20 h of aging, the derivative curve of the heating branch (Fig. 2c) presents a shape almost similar to that of the sample aged for 10 h. However, a decrease of the contraction amplitude is observed certainly related to the increase of the DO_3 phase ordering extent. The aging time increase up to 100 h (Fig. 2d) results in a considerable decrease in the contraction amplitude, due to the increase of the DO_3 particle ordering extent [12]. However, the dilatometric curve of the sample aged for 200 h presents (Fig. 2e) a somewhat different anomaly in comparison with the previous states: only an expansion appears in the temperature interval 327–500°C with a maximum near 400°C, related to the decrease of the DO_3 particle ordering extent followed by their dissolution in the disordered phase; the disappearance of the contraction is certainly due to the state of perfect order of DO_3 particles achieved after this long aging.

Thus, the progressive decrease of the contraction amplitude with aging time is observed. This relation is well intelligible because the ordering reaction can be summarized as follows: first, the transforma-

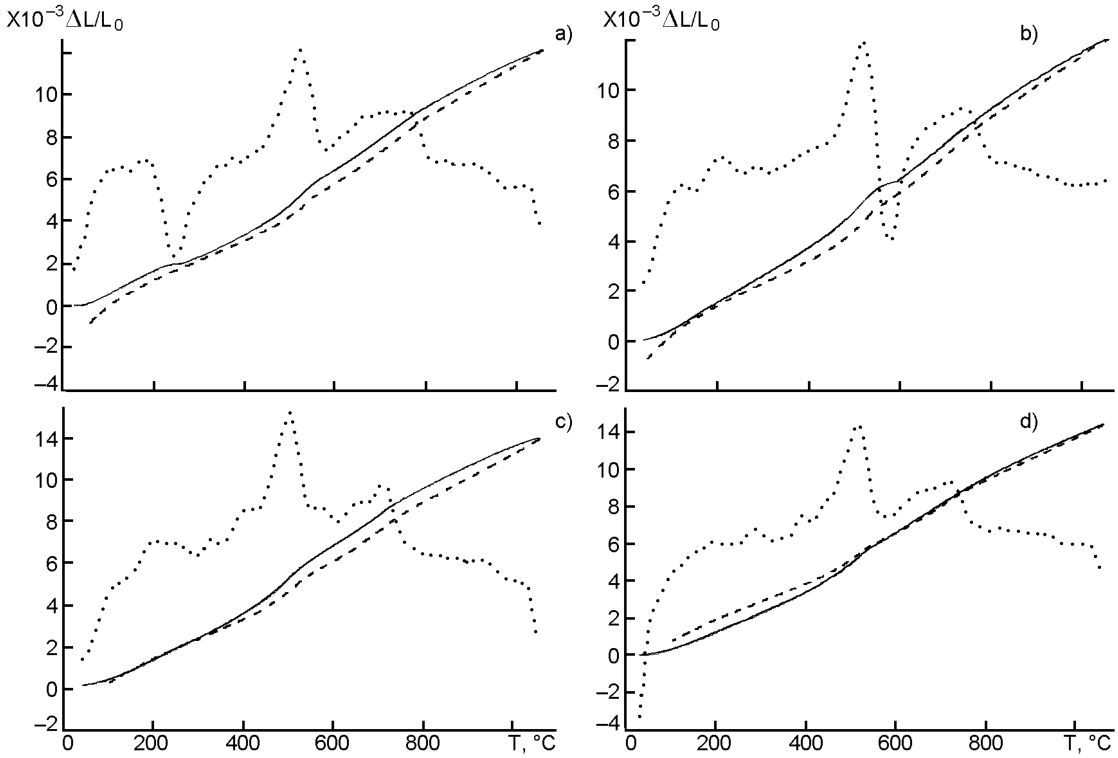

Fig. 3. Complete dilatometric curves with derivative curves of the heating branches thereof for the Fe-25 at.% Al alloy homogenized, quenched (a), and aged at 300°C for 20 h (b), 100 h (c), and 200 h (d): solid lines, heating; dashed lines, cooling: dotted lines, derivative heating curves.

tion of all the disordered material into DO_3 phase occurs, which is a very rapid process finished in one minute [8] because it requires only short-range redistribution, then, as the the aging time increases, the ordered DO_3 regions split off into several particles by segregation of Fe atoms at antiphase boundaries (APB) by forming disordered α-phase and increasing, as a consequence, the ordering degree of these particles. This process requires long-range diffusion through the APB [12].

Study of Fe-25 at. % Al alloy

As-quenched state. The dilatometric curve of the homogenized and quenched Fe-25 at. % Al alloy (Fig. 3a) exhibits during the heating an important anomaly between 190°C and 800°C totally different from those of the previous samples, including an important contraction in the temperature interval 190–325°C with a peak at 245°C, attributed to the ordered DO_3 phase formation from a completely disordered state; it is probable that the critical nuclei of the transformation are those of the B2 phase because the transformation $\alpha \rightarrow B2$ is difficult to avoid at a rapid quenching. The B2 phase appears in the shape of scattered points in the disordered matrix because, in bcc materials, vacancies are strongly bound to the interface between ordered and disordered phases in such a way that these points grow by vacancy-migration until they reach a state in which they become unstable. They will undergo a $B2 \rightarrow DO_3$ transformation.

The general transformation sequence is:

— $\alpha \rightarrow B2 \rightarrow DO_3$ [9];

— an important expansion between 438°C and 562°C with a peak at 520°C certainly related to a decrease in the DO_3 phase ordering extent followed by formation of B2 domains;

— a second contraction in the temperature interval 562–632°C with a peak at 578°C, due to an increase in the B2 phase ordering extent [9–11];

— a second expansion in the temperature interval 632–800°C with a peak difficult to identify, related to the $B2 \rightarrow \alpha$ transformation [9–11].

Ageing state. The derivative curve of the sample homogenized, quenched and aged 20 h (Fig. 2b) has a shape practically identical to that of the as-quenched sample. Indeed, it exhibits an important anomaly in the temperature interval 200–800°C, including a contraction between 200°C and 460°C with a peak difficult to determine, related to an increase in the ordering extent of the DO_3 phase formed during the aging [9–11]. This contraction is followed by an important expansion in the temperature interval 460–550°C with a well pronounced peak at 530°C, attributed to the processes of the DO_3 phase disordering and the B2 phase formation [9–11]. It is immediately followed by a second fairly important contraction situated in the temperature interval 550–620°C with a peak near 600°C, linked to the increase of the degree of ordering of the B2 phase [9–11]. This second contraction is followed by a second expansion between 620°C and 800°C with a peak difficult to determine, attributed to the process of disordering of the B2 phase and the formation of the disordered phase. After 100 h of aging, the derivative of the heating branch (Fig. 3c) keeps almost the same shape as that of the sample aged for 20 h. However, a remarkable amplitude decrease of the first contraction is observed due certainly to an increase in the DO_3 phase ordering extent [12]. Ageing for 200 h (Fig. 3d) results in the disappearance of the first contraction. However, all the other effects are present. The disappearance of the contraction is due certainly to the perfect order of the DO_3 phase reached after this long ageing.

The results obtained allowed us to draw the following conclusions. In the studied alloys, a rapid quenching in water from high temperatures (1100°C) provides conservation of the disordered phase. A prolonged ageing at 300°C results in an increased DO_3 phase ordering extent because of a chemical composition modification in the ordered domains due to Fe atoms segregation at antiphase boundaries, resulting in the disordered phase. During the aging at 300°C, the ordering starts with the conversion of all the sample to the DO_3 phase; then the continued ageing results in precipitation of the disordered phase by separating the sample into small DO_3 domains with an almost perfect ordering. Finally, dilatometry constitutes a very important experimental method for study of ordered solid solutions. However, to refine the obtained results, transmission electronic microscopy study would be necessary.

References

1. H.Neuhauser, *Mat. Sci. and Eng.*, **A324**, 43 (2002).
2. M.H.Yoo, K.Yoshimi, S.Hanada, *Acta Mater.*, **47**, 3579 (1999).
3. N.Ya.Rokhmanov, *Functional Materials*, **7**, 235 (2000).
4. A.J.Bradley, A.H.Jay, *Proc. Roy. Soc. A*, **136**, 210 (1932); *J. Iron Steel Inst.*, **125**, 339 (1932).
5. A.Taylor, R.M.Jones, *Phys. Chem. Solids*, **6**, 16 (1958); A.Lawley, R.W.Cahn, *Ibid*, **20**, 204 (1961).
6. G.Lutjering, H.Warlimont, *Z. Metallkunde*, **56**, 1 (1965).
7. W.H.Rothery, R.E.Smallmon, C.W.Haworth, in: The Structure of Metals and Alloys, 5th Ed., Richard Clay Ltd.,New York, 171 (1969).
8. D.G.Morris, S.Gunther, *Acta Mater.*, **44**, 2847 (1996).
9. A.Lowley, R.W.Cahn, *J. Phys. Chem. Solids*, **20**, 204 (1961).
10. K.Oki, M.Hasaka, T.Egushi, *Japan. J. Appl. Phys.*, **12**, 1522 (1973).
11. K.Oki, M.Hasaka, T.Egushi, *Trans. JIM.*, **14**, 8 (1973).
12. S.M.Allen, *Phil. Mag.*, **36**, 181 (1977).

Дилатометричні дослідження впорядкованих структур в Fe–Al сплавах

М.Буфенгур, А.Хайюн, М.Я.Рохманов, М.Бушар, Д.Хамана

Досліджено перетворення порядок-невпорядкованість у сплавах на основі заліза, що містили 21.5 та 25 at. % Al. Аналіз результатів, одержаних методом дилатометрії, дозволяє стверджувати, що реакція впорядкування в Fe–Al сплавах після загартування з області невпорядкованого стану є досить швидким процесом, а старіння при помірних температурах спричиняє підвищення ступеня дальнього порядку типу DO_3.