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Study of the ordered structures in Fe-Al alloys using dilatometric and calorimetric analysis

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The aim of the present work is to study order-disorder transformation in some alloys of the Fe-Al system (with 9.8, 21.5 and 25 at.% Al). The synthesis and the analysis of numerous and interesting results obtained by dilatometric and calorimetric analysis have allowed us to assert that the ordering reaction is a rapid process and that long ageing at 300°C leads to an increase in the degree of ordering of the DO_3 phase.

1. Introduction

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 [1], who showed how the two different kinds of atom can enter different positions in the lattice as the composition is varied. Although slight changes have been made, their results have been largely confirmed by more recent work [2]. In alloys containing from 0 to ∼23 at.% Al the two kinds of atom are arranged at random on 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 23–25 at.% Al, the aluminium atoms begin to segregate to B sites, until at 25 at.% Al (Fe_3Al) the ordering is almost perfect, with the aluminium atoms occupying almost all the B positions and the aluminium population of the A, C and D positions being nearly zero, so that the centres of alternate small cubes are mainly occupied by aluminium atoms. At 28 at.% Al the occupation of the B positions by aluminium is complete, but by then aluminium atoms have also begun to enter the D positions which at the composition Fe_3Al were occupied almost entirely by iron atoms. For slowly cooled alloys this process continues, the aluminium occupancy of the B sites decreasing slowly as aluminium 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 [3], 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 aluminium 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 onset of ordering in this system are present. Up to ∼18 at.% Al there is an approximately linear lattice—parameter/composition relation, the iron lattice being expanded by addition of aluminium. From ∼18 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 ∼34 at.% Al before increasing again in a normal way with addition of aluminium. 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 [3]. This interpretation is supported by a work using thin-film electron microscopy, where clear evidence for the existence of two phases in alloys containing just less than 25 at.% Al has been obtained [4]. 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 composition >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 [3].

The aim of this work is to follow the structural evolutions engendered by the ordering process, using two methods, one sensitive to the volumes changes (dilatometry) and the second to the heat flow (calorimetric analysis).

2. Experimental procedure

Alloys of the Fe-Al system with 9.8, 21.5 and 25 at.% Al 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 aluminium (99.99%). The samples were annealed 2 h at 1100°C, quenched in water and aged at 300°C during various times (1, 10, 20 and 200 h).

For the dilatometric analysis a DI24 Adamel Lhomargy dilatometer connected to a computer has been used. The samples were in a cylindrical shape (25 mm in length and 5 mm in diameter). A suitable software (Logidil) allows the analysis and the determination of the critical points on the recorded curves. For the differential calorimetric analysis (DSC) a SETARAM DSC 92 analyzer connected to a computer has been used. The samples were in a cylindrical shape (5×5 mm^2) corresponding to a weight of approximately 250 mg. In both cases one can work under a protective atmosphere of pure Argon.

The thermal cycle applied in the dilatometer consists of a heating from 25 to 1100°C, followed by a holding of 5 min at this temperature and a cooling to 25°C with the same rate (5°C/min). The thermal cycle applied for the calorimetric analysis includes a heating from 25 to 550°C, a holding of 5 min at this temperature and a cooling to 25°C with the same rate (5°C/min).

3. Experimental results and discussion

3.1. Dilatometric study

3.1.1. Study of the Fe-9.8 at.% Al alloy

3.1.1.1. As-quenched state. The quenched states will be used as a reference to our subsequent studies. The dilatometric curve of the Fe-9.8 at.% Al alloy homogenised 2 h at 1100°C and quenched in water (Fig. 1a), except an appreciable swelling between 70 and 300°C, does not present any other anomaly due to the lack of any phase transformation, as showed by the phase diagram.

3.1.1.2. Ageing at 300°C state. The derivative curve of the heating segment for the sample homogenised, quenched and aged 1 h presents (Fig. 1b) a shape similar to that of the as-quenched state (Fig. 1a).

The absence of any anomaly on the dilatometric curves for aged samples at 300°C, means that they did not undergo any phase transformation, what is in a good agreement with the phase diagram. However, the swelling noted at the beginning of the heating in the interval [70–300°C], is related to the atomic rearrangement of the structure: after a rapid quenching the latter changes during the heating in the dilatometer.

3.1.2. Study of the Fe-21.5 at.% Al alloy

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

– an important contraction between 200 and 340°C with a peak situated towards 280°C certainly linked to the formation of the ordered particles DO_3 and to the increase of the degree of ordering from a completely disordered state [5–8].

– an important expansion extending in the temperature interval [340–500°C] with a peak at 410°C, linked to the decrease in the degree of ordering of DO_3 particles then to their dissolution in the disordered matrix [5–8] by approaching the line of transformation $\alpha + DO_3 \longrightarrow \alpha$.

3.1.2.2. Ageing at 300°C state. The dilatometric curves of the samples homogenised, quenched and aged at 300°C present effects almost identical to those of the as-quenched state.

The derivative curve of the heating segment for the sample aged 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 situated at 280°C; however, it is less important compared to the as-quenched state. This contraction is followed immediately by an important expansion in the temperature interval [320–500°C] with a peak situated towards 423°C. The observed contraction amplitude decrease in comparison with the as-quenched state, is always linked to the improvement of the degree of ordering of DO_3 particles during this ageing.

After 20 h of ageing, the derivative curve of the heating segment (Fig. 2c) presents a shape almost similar to that of the sample aged for 10 h. However, one notes a decrease of the contraction amplitude certainly linked to the increase of the degree of ordering of the DO_3 phase.

The extending of the ageing time to 100 h (Fig. 2d) leads to a considerable decrease in the contraction

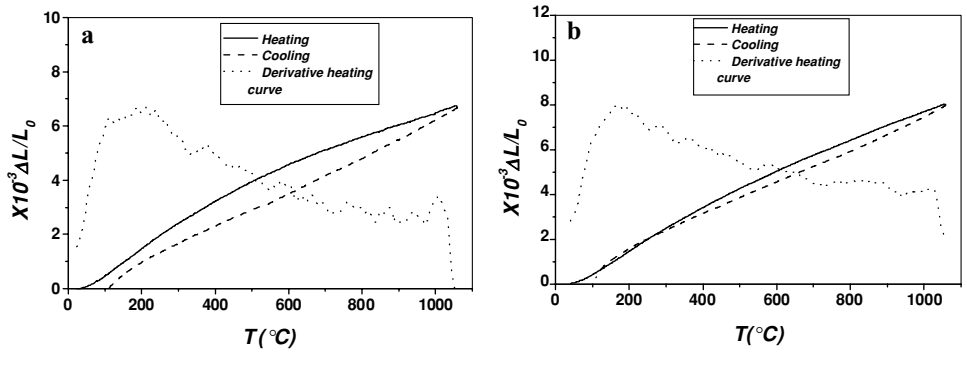

Figure 1 The complete dilatometric curves with the derived curves of the heating ones for the Fe-9.8 at.% Al alloy homogenised, quenched (a) and aged 1 h at 300°C (b).

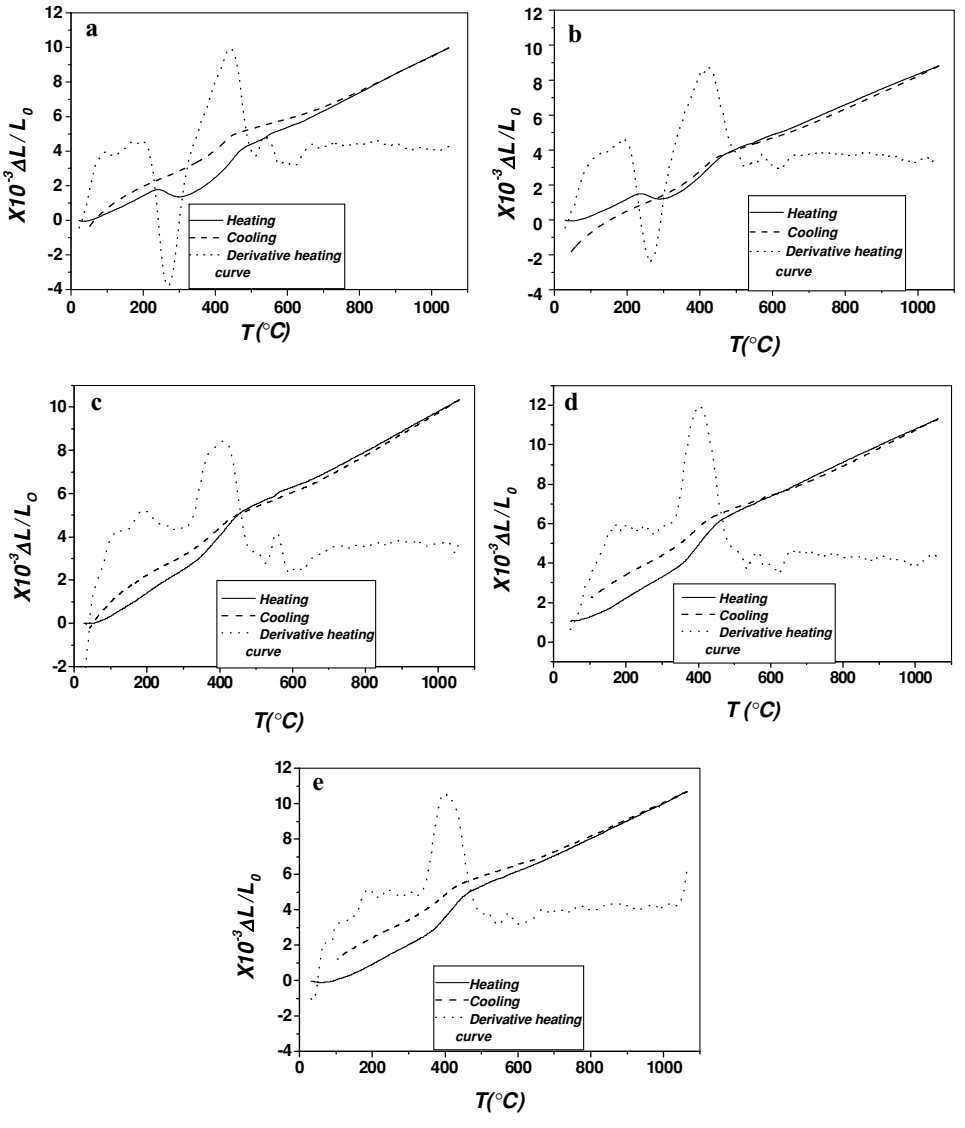

Figure 2 The complete dilatometric curves with the derived curves of the heating ones for the Fe-21.5 at.% Al alloy homogenised, quenched (a) and aged at 300°C during 10 h (b), 20 h (c), 100 h (d) and 200 h (e).

amplitude, due to the increase of the degree of ordering of DO_3 particles [9].

However, the dilatometric curve of the sample aged 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 situated towards 400°C, linked to the decrease of the degree of ordering of DO_3 particles then to 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 ageing.

Thus one observes the progressive decrease of the contraction amplitude with ageing time. This relation is well understood because the reaction of ordering can be summed up as follows: first occurs the conversion of all the disordered material in DO_3 phase, which is a very rapid process finished in one minute [5] because it requires only short-range distribution, then with the increase of the ageing time, 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, consequently, the degree of ordering of these particles; this process requires long-range diffusion through the APB [9].

3.1.3. Study of Fe-25 at.% Al alloy

3.1.3.1. As-quenched state. On the dilatometric curve of the Fe-25 at.% Al alloy homogenised and quenched (Fig. 3a) one observes during the heating, an important anomaly between 190 and 800°C totally different from those of the previous samples, constituted respectively of:

– an important contraction in the temperature interval [190–325°C] with a peak situated at 245°C, attributed to the formation of the ordered DO_3 phase from a completely disordered state; it is probable that the critical nuclei of the transformation are those of the B2 phase because the transformation $\alpha \longrightarrow$ B2 is difficult to prevent during 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

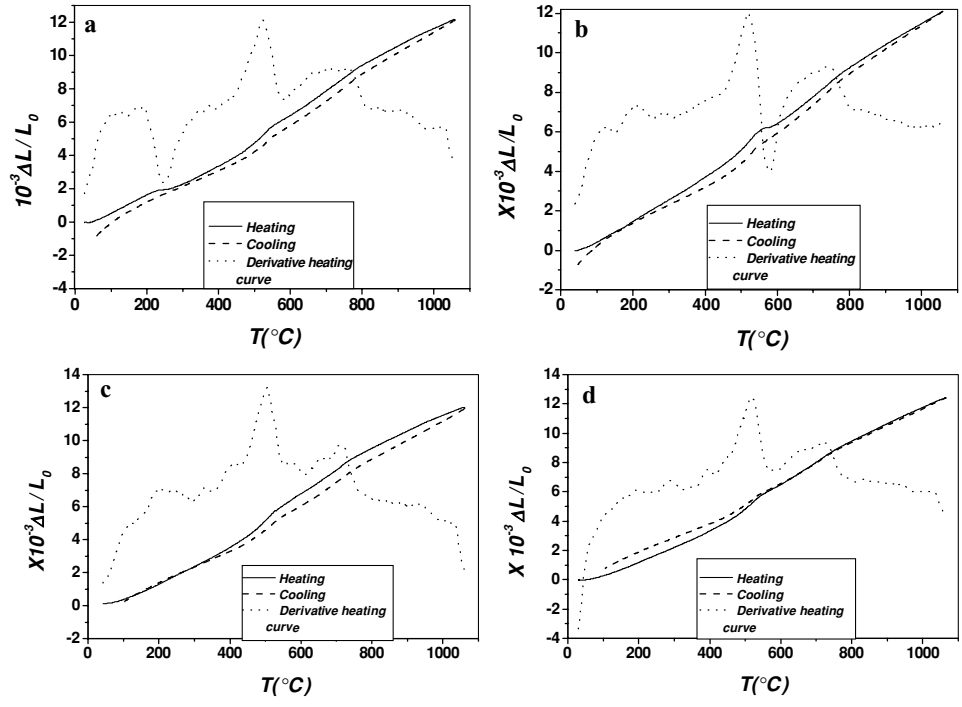

Figure 3 The complete dilatometric curves with the derived curves of the heating ones for the Fe-25 at.% Al alloy homogenised, quenched (a) and aged at 300°C during 20 h (b), 100 h (c) and 200 h (d).

by vacancy-migration until they reach a state in which they become unstable. They will undergo a B2 ⟶ DO_3 transformation. Globally the transformation sequence is: α ⟶ B2 ⟶ DO_3 [9],

– an important expansion between 438 and 562°C with a peak situated at 520°C, certainly linked to the decrease in the order degree of the DO_3 phase then to the formation of B2 domains,

– a second contraction in the temperature interval [562–632°C] with a peak situated at 578°C, due to the increase in the degree of ordering of the B2 phase [6–8],

– a second expansion situated in the temperature interval [632–800°C] with a peak difficult to identify, linked to the transformation B2 ⟶ α [6–8].

3.1.3.2. Ageing at 300°C state. The derivative curve of the sample homogenised, quenched and aged 20 h (Fig. 3b) has a shape practically identical to that of the as-quenched sample; indeed, it presents an important anomaly in the temperature interval [200–800°C], constituted of a contraction between 200°C and 460°C with a peak difficult to determine, linked to the increase in the degree of ordering of the DO_3 phase formed during the ageing [6–8]. 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 disordering of the DO_3 phase and the formation of the B2 phase [6–8]. It is immediately followed by a second fairly important contraction situated in the temperature interval [550–620°C] with a peak situated towards 600°C linked to the increase of the degree of ordering of the B2 phase [6–8]. This second contraction is followed by a second expansion between 620 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 ageing the derivative of the heating segment (Fig. 3c) keeps almost the same shape as that of the sample aged for 20 h; however one notes a remarkable amplitude decrease of the first contraction due certainly to the increase in the degree of ordering of the DO_3 phase [9].

Ageing of 200 h (Fig. 3d) leads to 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.

3.2. DSC study

The same heating and cooling rates have been used, as in the case of the dilatometric study.

3.2.1. Study of the Fe-21.5 at.% Al alloy

3.2.1.1. As-quenched state. The DSC curve recorded during the heating of the sample homogenised and quenched in water (Fig. 4a) shows two peaks of different natures:

– an important exothermic peak in the temperature interval [200–360°C] with a maximum situated at 270°C (P_1), linked to the formation of DO_3 particles then to the increase in their degree of ordering from a totally disordered state [5].

– an endothermic peak in the temperature interval [360–500°C] with a minimum situated at 440°C (P_2) certainly due to the decrease in the degree of ordering of DO_3 particles until their dissolution [5].

3.2.1.2. Ageing at 300°C state. After the ageing of 1 h at 300°C (Fig. 4b), the DSC curve keeps the same shape; however one notes a decrease in the amplitude of the exothermic peak (P_1), which is probably due to the fact

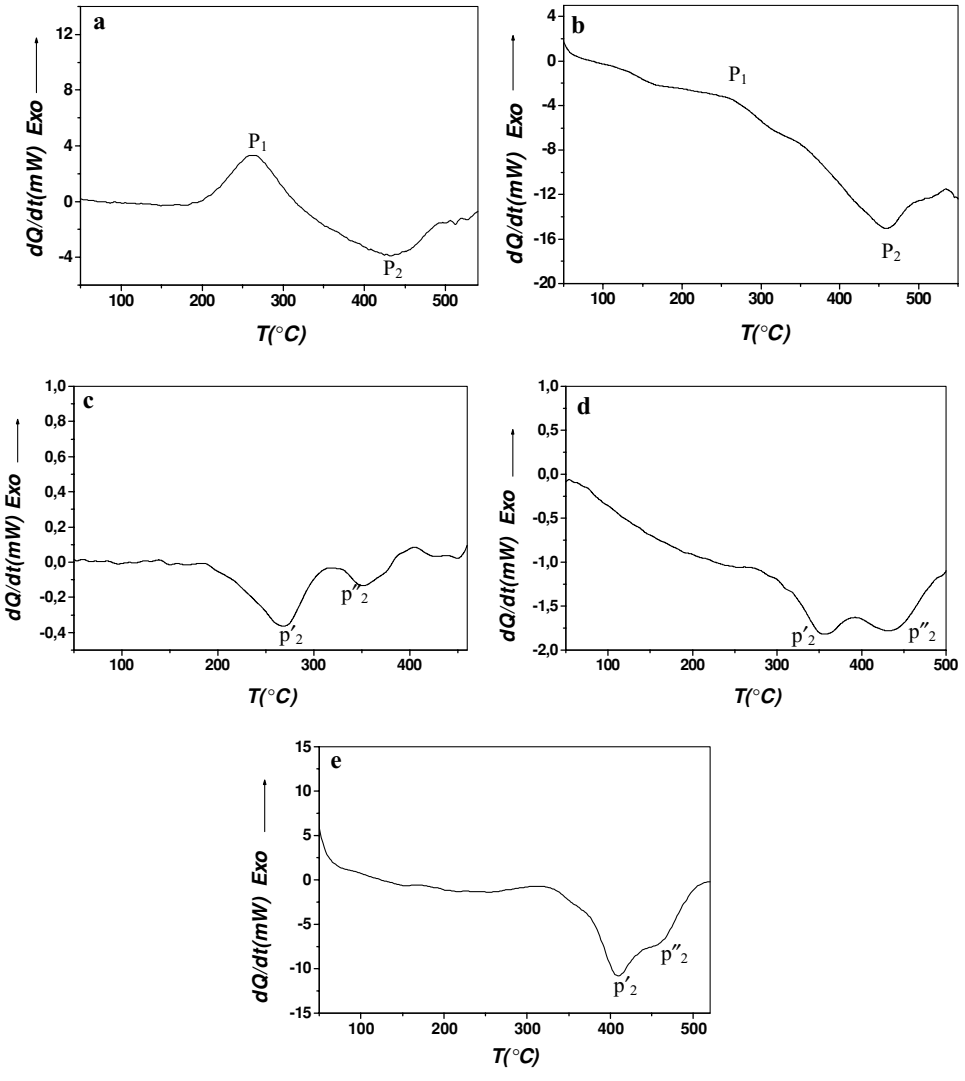

Figure 4 DSC curves for the Fe-21.5 at.% Al sample homogenised, quenched (a) and aged at 300°C during 1 h (b), 10 h (c), 20 h (d) and 100 h (e).

that during this ageing ordered DO_3 particles form but with an imperfect order, in such a way that the heating in the DSC leads only to an increase in the degree of ordering of these particles [5].

Starting from 10 h ageing (Fig. 4c), one notes on the heating segment of DSC curve the absence of the exothermic peak and the appearance of an endothermic peak split into two (P'_2, P''_2). This latter begins at 200°C and finishes at 410°C. The disappearance of the exothermic peak is due probably to the almost perfect order that the DO_3 particles achieve after this ageing. The two-minimum endothermic peak is certainly linked to the decrease in the degree of ordering of DO_3 particles (first minimum) then to its dissolution (second minimum).

One makes the same observations after 20 and 100 h of ageing (Fig. 4d and e). Moreover, with an increase in the amplitude of the first endothermic peak (P'_2), which means that the degree of ordering reached after these ageings is very high and its decrease requires an important energy.

3.2.2. Study of the Fe-25 at.% Al alloy

3.2.2.1. As-quenched state. The heating segment of DSC curve recorded for a sample homogenised 2 h at 1100°C and quenched in water (Fig. 5a) presents two peaks: an important exothermic peak situated in the temperature interval [200–350°C] with a maximum towards 280°C (P_1), corresponding certainly to the formation of the ordered phase DO_3 from a disordered state containing points of the ordered B2 phase, distributed randomly in the disordered phase because the $\alpha \longrightarrow$ B2 transition is so difficult to suppress during rapid quenching. The nature of the critical nuclei for the transformation $\alpha \longrightarrow DO_3$ can be of the B2 type so that the transformation proceeds as follows: $\alpha \longrightarrow$ B2 $\longrightarrow DO_3$ [9]. The endothermic peak is split into two and situated in the temperature interval [350–530°C], with a first peak between 350 and 420°C with a minimum difficult to determine, due certainly to the decrease in the degree of ordering of the DO_3 phase [5], and a second peak in the temperature interval [420–530°C] linked certainly to the transformation $DO_3 \longrightarrow$ B2 [5].

3.2.2.2. Ageing at 300°C state. The heating segment of the DSC curve for the sample homogenised, quenched and aged during 200 h presents (Fig. 5b) a single endothermic peak in the temperature interval [320–490°C] with a minimum situated towards 420°C (P_2),

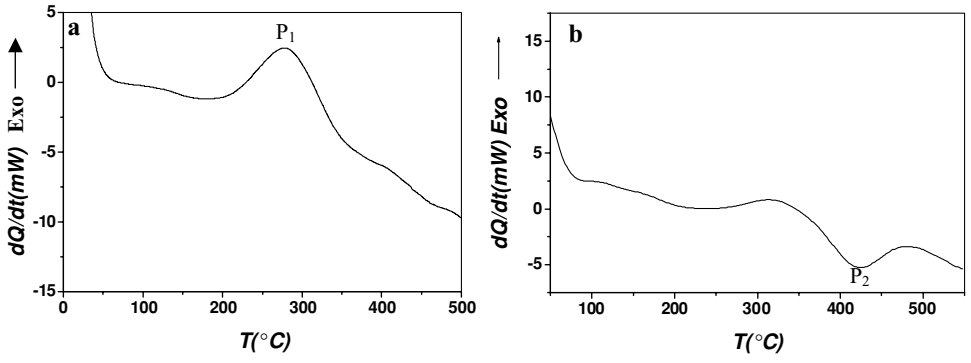

Figure 5 DSC curves for the Fe-25 at.% Al alloy homogenised, quenched (a) and aged 200 h at 300°C (b).

due certainly to the decrease in the degree of ordering of the DO_3 phase formed during this ageing. The absence of the exothermic peak indicates that the formed DO_3 phase has a perfect order.

4. Conclusion

One can affirm that dilatometry and differential scanning calorimetry constitute very important experimental methods for the study of ordered solid solutions. They reveal the $\alpha \longrightarrow \alpha + DO_3$ transformation in Fe-21.5 at.% Al alloy and the $\alpha \longrightarrow DO_3$, B2 $\longrightarrow \alpha$ and the $DO_3 \longrightarrow$ B2 transformations in Fe-25 at.% Al alloy and show the effect of the ageing time on the reactions products. However, to refine the obtained results, x-ray diffraction and particularly, transmission electronic microscopy (TEM) studies would be necessary.

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