

Fe-rich portion of the Fe-Cr phase diagram: electron microscopy study

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Transmission electron microscopy and the corresponding selected-area electron diffraction patterns of Fe-(10;20;30;40;47) wt. pct. Cr alloys heat treated isothermally from 500°C up to 1500°C at 100°C was employed to construct the equilibrium Fe-rich portion of the Fe-Cr phase diagram. It has been found to be quite different from the generally accepted one. Two regions of phase separation are in the diagram at low and high temperatures. Two lines of the second-order phase transition “ordering-separation” are pointed also. The σ -phase region in the diagram is considered as a region containing two phases, namely, the σ -phase surface layer and the solid solution bulk. © 2002 Kluwer Academic Publishers

1. Introduction

The binary Fe-Cr system has been intensively investigated. It may appear that there have been no open questions and that the existing knowledge of the thermodynamic properties of the Fe-Cr system is fully consistent with the usually accepted phase diagram [1]. However, in recent papers [2, 3], some structural features which are not accounted for by the phase diagram of the Fe-Cr system have been reported. These features are the following:

(A) Many investigators believe the high-temperature (1200–1400°C) region of the Fe-Cr diagram to be a region of disordered solid solutions. However, the thermodynamic studies [4, 5] carried out at high (1040–1400°C) temperatures showed the Fe-Cr solid solutions to have positive deviations from Raoult’s law in all the compositions studied and, therefore, to exhibit a tendency toward separation. In fact, different types of microstructures formed under phase separation were found by electron microscopy for all the compositions [2, 3]. All of them are Cr-enriched clusters situated in a Cr-depleted matrix. These clusters are of different morphology depending on the heat treatment and compositions. For the Fe-20Cr and Fe-30Cr compositions the clusters have a periodic distribution in the form of so-called tweedlike microstructure oriented along the strain-soft directions of the matrix. For the Fe-40Cr and Fe-47Cr compositions the clusters are of two kinds:

- an $\alpha_1 + \alpha_2$ mixture consisting of small separated nonoriented dark α_2 particles (a Cr-enriched solid solution) in a bright α_1 matrix (a Fe-rich solid solution);
- very coarse particles consisting of alternating multiatomic layers of strong Cr-enriched (dark layers) and strong Cr-depleted (bright layers) solid solutions. Sometimes the particles are oriented along the $\langle 100 \rangle$ directions of the matrix. The electron

diffraction pattern selected from such a particle shows that the reflection maxima split into two spots. Such a doublet is observed in each main reflection maximum including the zero one. These particles were called first the σ -phase [2] and then the J-phase [3]. The J-phase is not an intermetallic chemical compound of the Fe_xM_y type (Laves phase), it forms as a consequence of a phase-separation process and consists of alternating solid solution layers enriched in Cr or Fe atoms, having the same type of the lattice but different lattice parameters [3].

(B) When the Fe-(30-47)wt%Cr alloys are first heat treated in the high-temperature separation region (1200–1400°C) and water-quenched, and then heat treated in the temperature region of the σ -phase formation (600–830°C) for different times and also water-quenched, both kinds of the high-temperature separation microstructures ($\alpha_1 + \alpha_2$ and the J-phase) dissolve almost completely, and coarse wide lathes are observed along some crystallographic directions of the matrix in electron micrographs obtained by defocusing. The electron diffraction patterns selected from these lathes give no additional reflections from the lathes. Therefore, there is no reasons to consider the lathes as particles of a new phase. The authors of Ref. [3] supposed them to be domains formed as the result of an “*in situ*” transformation of the electron configuration with $E_{\text{mix}} > 0$ (separation) into an electron configuration with $E_{\text{mix}} < 0$ (ordering). This transformation begins at local points of the alloy in the form of so-called “e-domains” observed as lathes, and then gradually spreads over the whole space between the domains. In order to understand the causes of the e-domains formation, it is necessary to specify the conditions accompanying their formation. The e-domains are formed only when the high-temperature separation microstructure fixed by water-quenching from

1200–1400°C is heat treated in a temperature range of the tendency toward ordering (at 600–800°C, where the σ -phase can precipitate), and moreover, only at that stage of the 600–800°C heat treatment when the separation microstructure is almost dissolved but the σ -phase is not yet formed.

The microstructural results mentioned above were represented as the Fe-rich portion of the metastable Fe-Cr phase diagram [3]. This diagram has some shortcomings. The boundaries between different regions on the diagram mentioned were not defined with a sufficient degree of accuracy. The e-domains region was shown on the diagram, although the e-domains are known to be non-equilibrium and to form only under specific conditions of heat treatment.

The results of Refs. [2, 3] give the impression that the high-temperature separation occurs over the whole temperature range of the solid solution existence right up to the melting points, at least, for the Fe-40Cr and Fe-47Cr compositions. Besides, the existence of two types of separation microstructures ($\alpha_1 + \alpha_2$ and the J-phase) provoke some questions like: What is the role of each of them in the process of phase separation, and why this process cannot be limited to the formation of a single type of separation microstructure. The representation of the e-domains region on the metastable diagram [3] raises other questions, for example: Is it possible to consider the e-domains (as well as the ferromagnetic and ferroelectrical domains) as a new phase (maybe, a metastable one), or are they structural peculiarities (maybe, defects of the stacking fault or twins type).

The existence of two separation regions (high-temperature and low-temperature) in the metastable phase diagram [3] brings up the question in what differ these two types of separation microstructures. So, in the present paper we have made an attempt to answer all these and some other questions and to construct the Fe-rich portion of the equilibrium Fe-Cr phase diagram.

2. Experimental procedure

The iron-chromium alloys were prepared by melting pure Fe and Cr together in an induction furnace and were forged into 12 × 12 mm square bars. The composition of the alloys was defined by chemical analysis and presented in Table I. The content of C and N impurities in the alloys studied is so small that even though all interstitial atoms take part in the formation of chromium carbides and nitrides during isothermal treatment from 500°C and up, a fraction of interstitial phases in volume of an alloy will not exceed 0.5 vol% and these

TABLE I Chemical composition of the alloys studied, wt%

Alloy	Element		
	Cr	C	N
Fe-10Cr	10.3	0.02	Traces
Fe-20Cr	20.1	0.03	Traces
Fe-30Cr	29.7	0.03	Traces
Fe-40Cr	39.7	0.02	0.002
Fe-47Cr	47.3	0.03	0.002

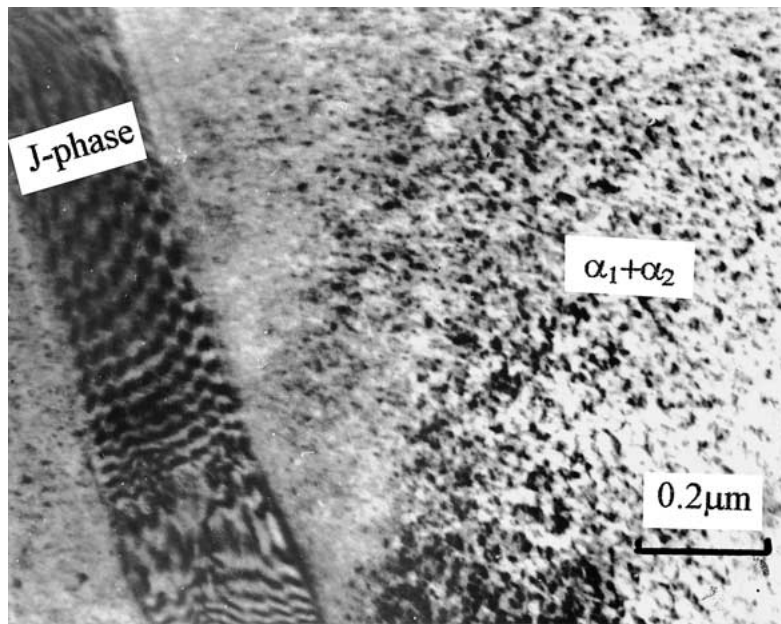
Fe-balance.

phases will form well before the ordering process is completed. The isothermal treatments were carried out beginning from 500°C up to 1500°C at 100°C intervals. The duration of each heat treatment was 1 h to 22 h. After each isothermal heat treatment the forgings were water quenched to preserve the structure characteristics for the temperature studied. Foils for the transmission electron microscopy and specimens for the X-ray and Vickers hardness measurements were cut from the heat-treated forgings. Micrographs and electron diffraction patterns were obtained using a TESLA-BS500 electron microscope operating at 90 kV. Field-ion microscopy images were obtained using Ne as the imaging gas with a pressure of 5×10^{-5} Pa (the background pressure was about 10^{-7} Pa). The specimen temperature was kept at that of liquid nitrogen.

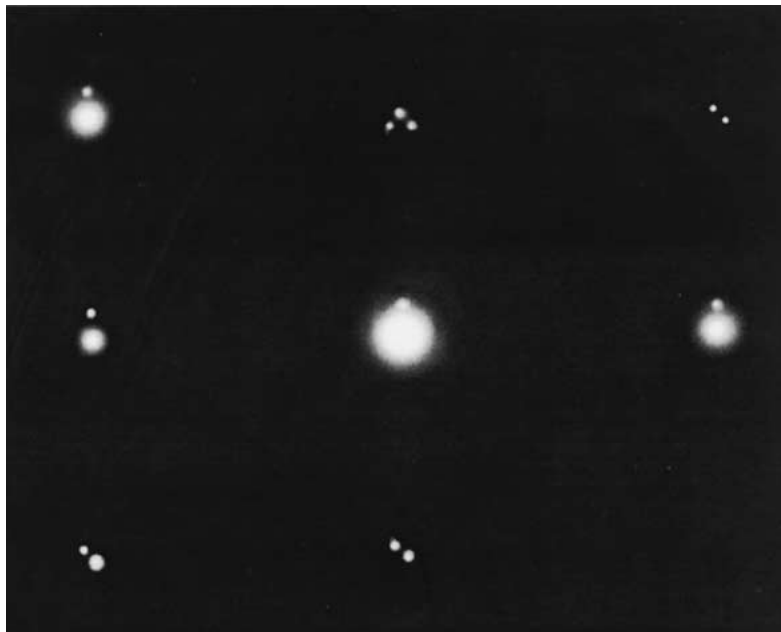
3. Results and discussion

Fig. 1a demonstrates a typical bright-field image of the microstructure characteristic of the Fe-47Cr alloy as-quenched from 1200°C–1 h in water. A flat elongated particle called the J-phase [3] is visible in the electron micrograph. Inside the J-phase particle, alternation of dark (Cr-enriched) and bright (Cr-depleted) layers is observed. A selected-area electron diffraction pattern taken from the J-phase particle consists of two systems of reflections (Fig. 1b). A dark-field analysis shows that the main reflections are formed by the bright layers of the J-phase particle, and by the bright precipitate-free zones around the particle; the satellite reflections are formed by the dark layers of the J-phase particle. This splitting of each reflection (including the zero one) into two satellites is a result of the solid solution separation into a highly Cr-enriched and a highly Cr-depleted clusters. The Cr-enriched and Cr-depleted solid solutions have different b.c.c. lattice parameters close to those of pure Cr and pure Fe. Fig. 1a shows also the regions of nonoriented, chaotically arranged particles enriched in Cr (α_2) in a Cr-depleted matrix (α_1). The selected-area electron diffraction pattern taken from the $\alpha_1 + \alpha_2$ mixture gives no split reflections, which suggests that a smaller chromium concentration in the Cr-enriched regions (α_2) takes place in comparison with the Cr-enriched layers of the J-phase. If the time of the 1200°C heat treatment is prolonged up to 22 h or if the heat-treatment temperature is increased up to 1400°C, the number of J-phase particles increases (Fig. 1c) and the length of the $\alpha_1 + \alpha_2$ region decreases as compared with the 1200°C–1 h heat treatment, while the size of α_2 particles increases (Fig. 2a). Within some J-phase particles oriented perpendicularly to the electron beam, the alternation of dark (Cr-enriched) and bright (Cr-depleted) layers is visible only at the periphery of the particles (Fig. 2b).

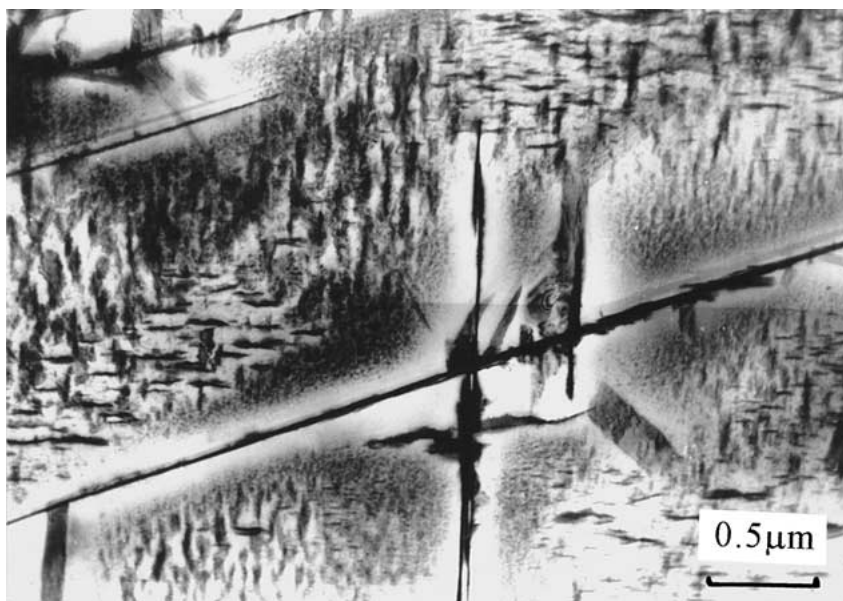
In this connection a question arises as to why the high-temperature separation in the Fe-47Cr alloy results in two different types of structures: an $\alpha_1 + \alpha_2$ mixture and the J-phase particles. A comparison of Fig. 1a with Fig. 1c and Fig. 2a allows us to conclude that the separation process in the alloy starts mainly with the formation of a mixture of α_2 and α_1 solid solutions where the enrichment and depletion in Cr are



(a)

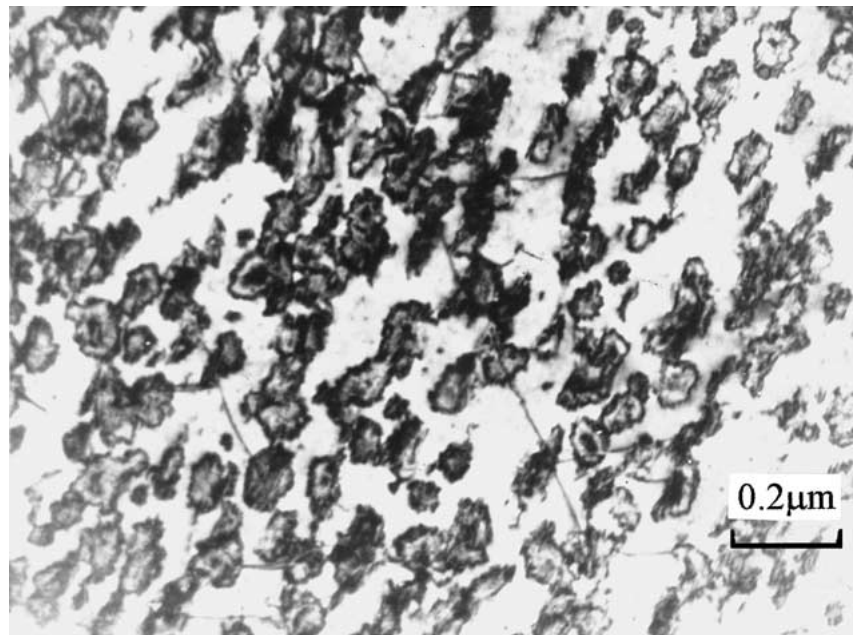


(b)

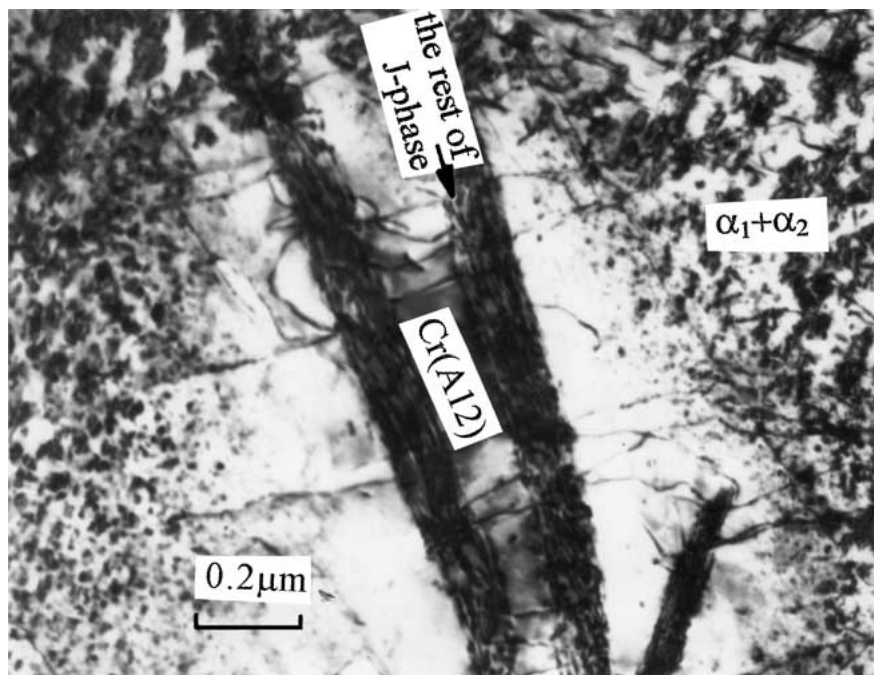


(c)

Figure 1 Fe-47Cr alloy heat treated at (a,b) 1200°C for 1 h and (c) 1200°C for 22 h and then water-quenched; (a,c) bright-field electron microscopy pictures; (b) electron diffraction pattern selected from the J-phase particle in (a).



(a)



(b)

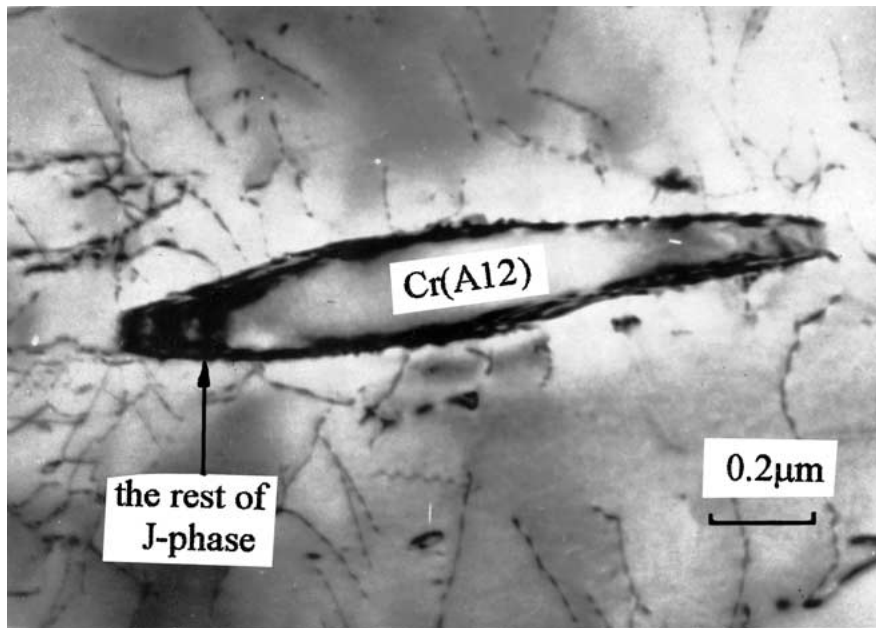
Figure 2 Fe-47Cr alloy heat treated at 1400°C for 1 h and then water-quenched: (a) $\alpha_1 + \alpha_2$; (b) a portion of pure Cr inside J-phase particle.

not so strong as in the J-phase particles. As mentioned above, some particles of the J-phase have the periodic arrangement of Cr-enriched and Cr-depleted layers only at their periphery. At the center of the J-phase particles, bright regions free of periodicity are observed (Fig. 2b). Their identification will be made in Fig. 3 (see below).

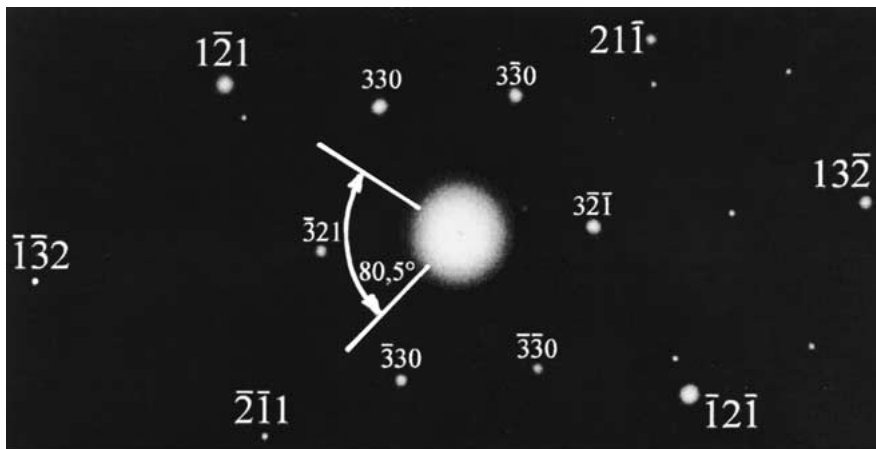
To find out whether the region of high-temperature separation extends to 900 and 1000°C temperatures, the specimens of the Fe-47Cr alloy, preliminarily water-quenched from 1200°C, were repeatedly water-quenched from 1000°C for 8 h and 24 h, and from 900°C for 24 h. The microstructure of the Fe-47Cr alloy as-quenched from 900°C for 24 h and from 1000°C for 24 h is a solid solution, i.e. the separation microstructures formed earlier at 1200°C and fixed by water quench-

ing totally dissolve during a 900–1000°C heat treatment for 24 h. After a 1000°C-8 h heat treatment the separation microstructures are not entirely dissolved; certain nondissolved particles are sometimes observed in electron micrographs (see Fig. 3a). A selected-area electron diffraction pattern (Fig. 3b) taken from the particle (Fig. 3a) shows that the particle has an A12 crystal structure. The question arises: Which phase of the Fe-Cr system can have an A12 lattice?

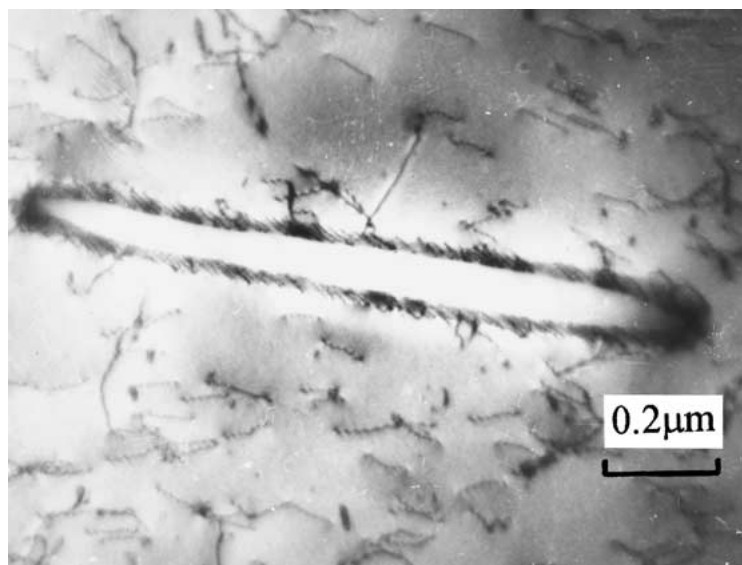
It is well known that the crystal structures of the γ - and α -solid solutions of the Fe-Cr system are A1 and A2 respectively, and the crystal structure of the σ -phase is tetragonal, the space group being $D_{4h}^{14} - P4_2/mnm$ [6]. In accordance with the Fe-Cr phase diagram, there are no other phases in the Fe-Cr system. However, turning back to the discussion about the Cr allotropy in the



(a)



(b)



(c)

Figure 3 Fe-47Cr alloy heat treated at 1200°C for 1 h, water-quenched, repeatedly heat treated at 1000°C for 8 h, water-quenched: (a) bright-field image of Cr(A12) particle; “The rest of J-phase” is a periodical structure characteristic for J-phase and preserved at the periphery of the particle; (b) the selected-area electron diffraction pattern from the particle; all spots are indexed (the matrix spots are marked by numerals of larger size); (c) Cr particle dissolving.

50s and early 60s, it should be recalled that the A12 lattice of Cr was detected as one of the allotropic modifications of chromium and entered in all the X-ray handbooks. Therefore, we have no choice but to consider the A12 lattice of the particles in Fig. 3 as a possible crystal structure of pure Cr, probably, in the non-equilibrium state. Analogous cases when the particles precipitated from the matrix by way of diffusion have a lattice different from that of the equilibrium state have been sometimes observed. As an example, the precipitation of the Mo₂C carbide [7] and AlN nitride [8] in the Fe-Mo-C and Fe-Al-N systems could be mentioned. These precipitates have hexagonal crystal structures at equilibrium, their non-equilibrium crystal structure at initial stages of aging being f.c.c. of the B1 type [7, 8]. Apparently, a similar situation arises in the case of the formation of pure Cr particles during the high-temperature separation, but this fact does not mean at all that Cr has more than one allotropic modification in the equilibrium state.

In some cases, a thick forest of dislocations, the external contour of which repeats the initial shape of the Cr particle, is observed (Fig. 3c). As well known, the thick dislocation network forms always in the place of newly dissolved particles of the second phase, therefore, it can be said that the state of particle dissolution is fixed in Fig. 3c. Comparing the high-temperature separation microstructures (the mixture of α_1 and α_2 solid solutions, the J-phase particles, and the J-phase particles, at the center of which a pure Cr region is gradually forming), one can conclude that all of them are consecutive intermediate stages of the solid-solution separation into a mixture of pure components grains. Now it becomes clear why such a variety of separation microstructures, including the J-phase, is observed. All these microstructures have a peculiar morphology and differ from each other in Cr content.

Isothermal 1100°C heat treatment for 24 h (with subsequent water quenching) results in the formation of an $\alpha_1 + \alpha_2$ microstructure only (the J-phase does not form). Since the separation microstructure formed earlier during a high-temperature (1200°C) heat treatment dissolves completely at 1000°C for 24 h, it may be inferred that the lower boundary of the high-temperature separation region lies somewhere in the temperature range between 1000 and 1100°C, closer to 1100°C. Probably, the high-temperature separation region was not revealed earlier in numerous studies by other authors, because the heat treatment before water quenching was usually carried out at temperatures close to 1000°C. It was supposed that it would make no special sense to increase the temperature of heat treatment, because a temperature of 1000°C was high enough for the disordered Fe-Cr solid solution formation.

Vintaikin [4], using the Knudsen effusion method for the determination of the vapor pressure of iron over solid Fe-Cr at 1100–1400°C, Jeannin *et al.* [5], using the method of the equilibrium between Fe-Cr alloy, chromic oxide, hydrogen, and water at 1040–1300°C, revealed substantial positive deviations from the ideality in the α and γ phases, suggesting a tendency toward separation in Fe-Cr alloys. Mazandarany and Pehlke

[9], using the latter method, demonstrated that in the range from 900 to 1200°C the Cr activity has positive deviations in both γ and α phases for Fe-Cr alloys up to 63 at.%Cr. Therefore, even when the activity of the components has a positive sign, Fe-Cr alloys can exist in the form of a disordered solid solution.

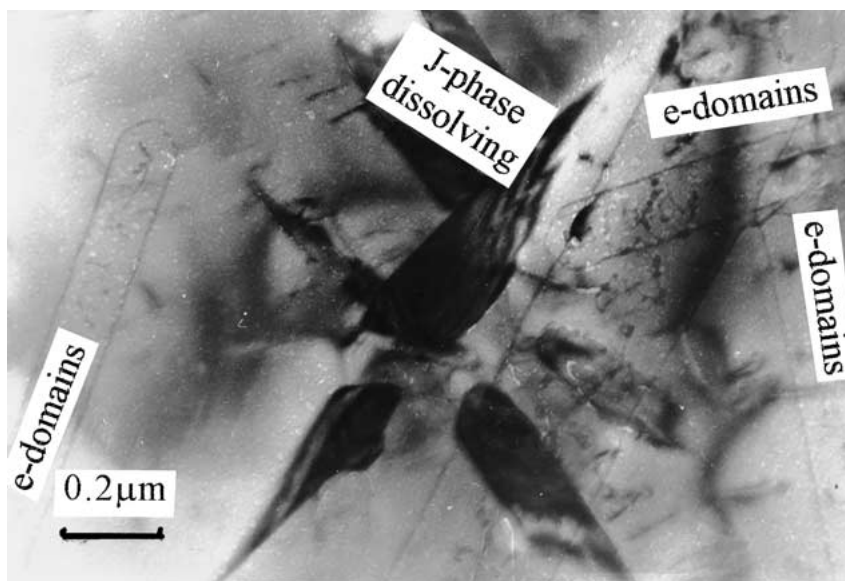
As shown above, the tendency toward separation results in the formation of coarse microstructures of high-temperature separation at 1200 and 1400°C. This raises the question of what is the maximum temperature at which the separation of Fe-Cr alloys is possible. To answer this question, the Fe-40Cr and Fe-47Cr alloys were water-quenched from 1500 and 1550°C. The electron micrographs obtained after the heat treatments mentioned show the microstructure of the alloys studied to be a solid solution. This means that the upper boundary of high-temperature separation lies somewhere in the temperature range of 1400–1500°C for the alloys Fe-(40,47)wt%Cr and, as was shown earlier [3], close to 1300°C for the alloys Fe-(20,30)wt%Cr.

So, the solid-solution microstructure observed in Fe-(40,47)%Cr at 900, 1000 and above 1400°C, as well as in Fe-(20,30)%Cr at temperatures below 1100°C and above 1300°C does not necessarily mean that at the temperatures mentioned the tendency toward separation disappears. As known, in the approximation of regular solutions, the chemical and thermal terms of the free energy for the case of separation are related by the expression:

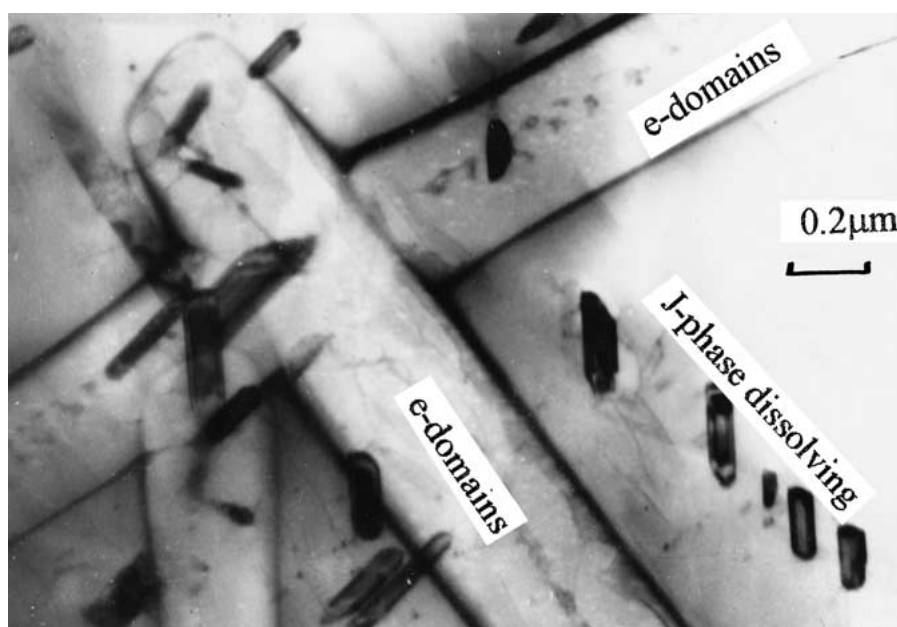
$$\partial^2 f(c_i) / \partial c_i^2 = \partial \mu_i / \partial c_i = \kappa_B T - 2z E_{\text{sep}} c_i (1 - c_i)$$

If $\kappa_B T < 2z E_{\text{sep}} c_i (1 - c_i)$ the chemical energy prevails over the thermal one, and therefore the process of phase separation takes place. In the case of the inverse relation the Brownian motion prevails over the separation process, which is observed at very high temperatures (above 1400°C for Fe-(40,47)%Cr). At 900 and 1000°C the separation energy diminishes progressively and vanishes as the temperature approaches 830°C and, as a result, the relation $\kappa_B T > 2z E_{\text{sep}} c_i (1 - c_i)$ holds true and a solid solution forms.

When Fe-(40,47)%Cr alloys preliminarily water-quenched from 1200°C for 1 h are heat treated in the temperature range of the σ -phase formation (with subsequent water-quenching), the high-temperature separation microstructures dissolve. In their place, flat long lathes oriented along the strain-soft directions of the matrix can be observed in the electron micrographs obtained after a 700°C–8 h heat treatment (Fig. 4). The electron diffraction pattern taken from these lathes does not show any peculiarities characteristic of twins, stacking faults or new phase particles. The contrast from these lathes is analogous to that from ferromagnetic and ferroelectric domains. With the image focused, the domain walls are observed in the electron micrographs as very thin lines (Fig. 4a). On defocusing, the domain walls can be seen in the form of thick blurred dark or bright lines, moreover, the width of blurring depends on the degree of defocusing (Fig. 4b). The authors of Ref. [3] consider the electron domains formed after a 1200°C–1 h heat treatment (quenching in water)



(a)



(b)

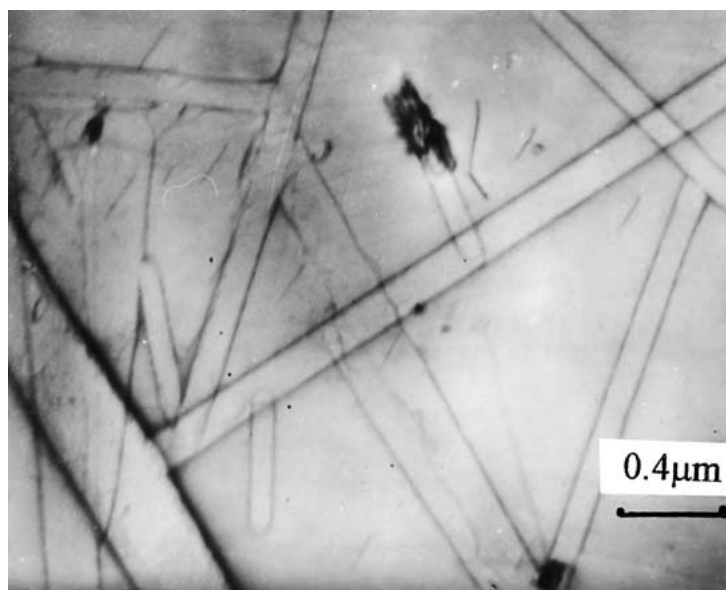
Figure 4 Fe-47Cr alloy heat treated at 1200°C for 1 h, water-quenched, repeatedly heat treated at: (a) 800°C for 4 h; (b) 700°C for 1 h. Bright-field images: (a) focussed; (b) defocussed.

+700°C for 8 h (quenching in water) as some regions where the ordering energy reverses its sign to negative, contrary to the rest of the matrix where the ordering energy remains positive. The reversal of the ordering-energy sign leads to a change in localization of the valence d-electrons. This circumstance allows us to call these lathes the electron domains (e-domains). The electron domains, like ferromagnetic and ferroelectric domains, can be visualized in the electron microscope due to different deflection of the electron beam by regions with different electron structures.

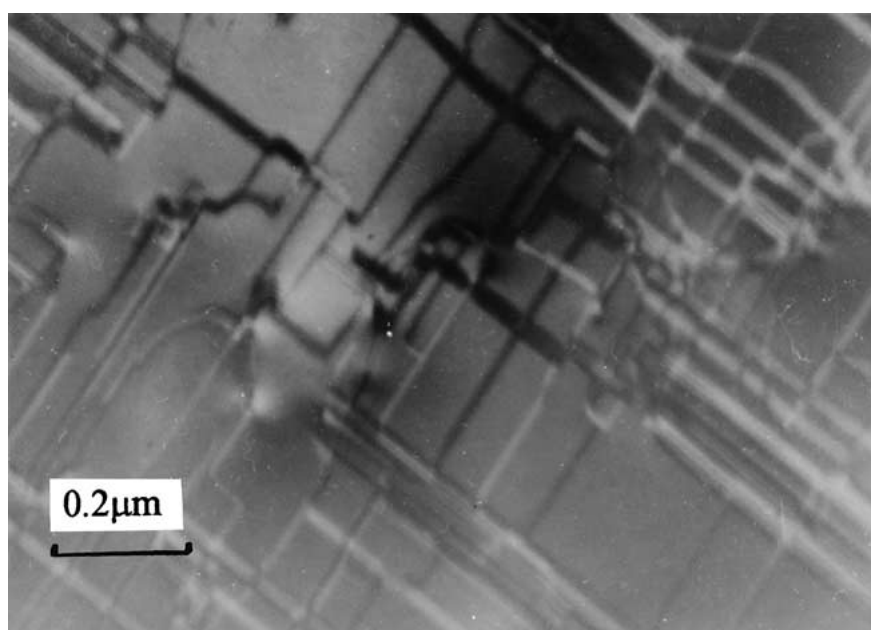
The electron domains form not only in the high-Cr Fe-alloys, but also in the Fe-(20,30)%Cr ones in which, as known, the σ -phase does not precipitate. For example, Fig. 5a shows these domains in the Fe-30Cr alloy water quenched from 1200°C for 1 h and then heat treated at 800°C for 8 h with subsequent water cooling. This means that the ordering energy changes sign in the range of the compositions studied.

If the alloys are first heat treated for the σ -phase precipitation to take place, and then aged at 500–550°C, the sign of the ordering energy is expected to change from minus to plus and, as a consequence, the electron domains should be observable in the electron micrographs. Indeed, the e-domains are observed (Fig. 5b), and they form as the regions where the sign of the ordering energy changes to positive in contrast to the surrounding matrix, where the sign remains negative. Thus, it is possible to consider the electron domains as regions of similar electron structure corresponding to one or another sign of the ordering energy, separated by domain walls. These domains are a visual confirmation of the phase transition occurring when the tendency toward separation changes to the one toward ordering, and vice versa.

As known, there is a great variety of order parameters [11]. If a phase transition is accompanied by a continuously vanishing order parameter at the transition



(a)



(b)

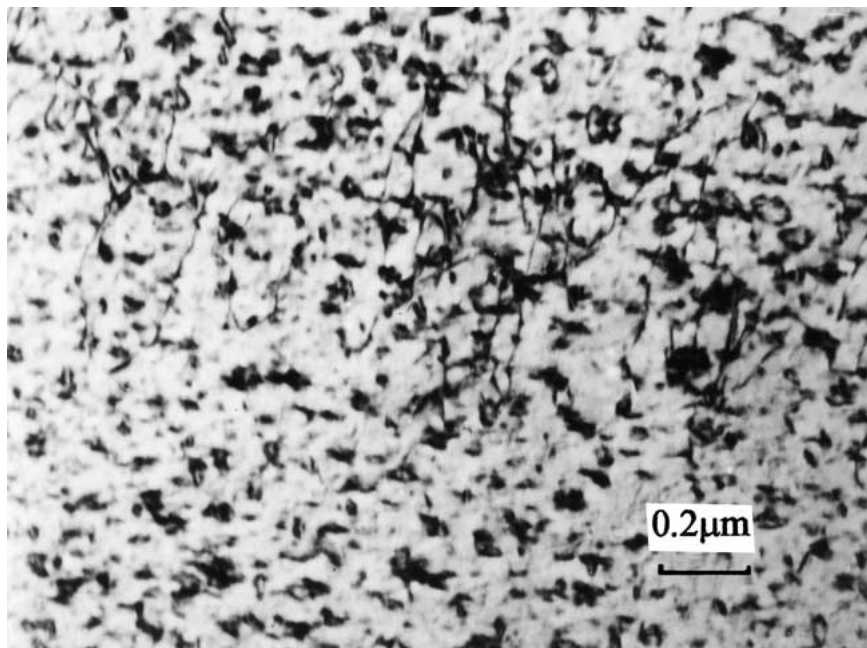
Figure 5 (a) Fe-30Cr alloy heat treated at 1200°C for 1 h, water-quenched, repeatedly heat treated at 800°C for 8 h; e-domains; (b) Fe-47Cr alloy heat treated at 700°C for 8 h, water-quenched, repeatedly heat treated at 550°C for 4 h; e-domains.

point, this is a second-order transformation [11]. If in equilibrium configurations the order parameter varies in space, this usually leads to the appearance of a domain structure, in the domain walls of which the order parameter always goes to zero. This circumstance allows us to classify the ordering-separation phase transition, like other analogous phase transitions associated with the formation of domains (ferromagnetic and ferroelectric), as a second-order transition. The e-domains are retained in the microstructure of the alloy for rather short time at room temperature (about 1 month), i.e. with time the ordering energy takes the same sign in all the bulk.

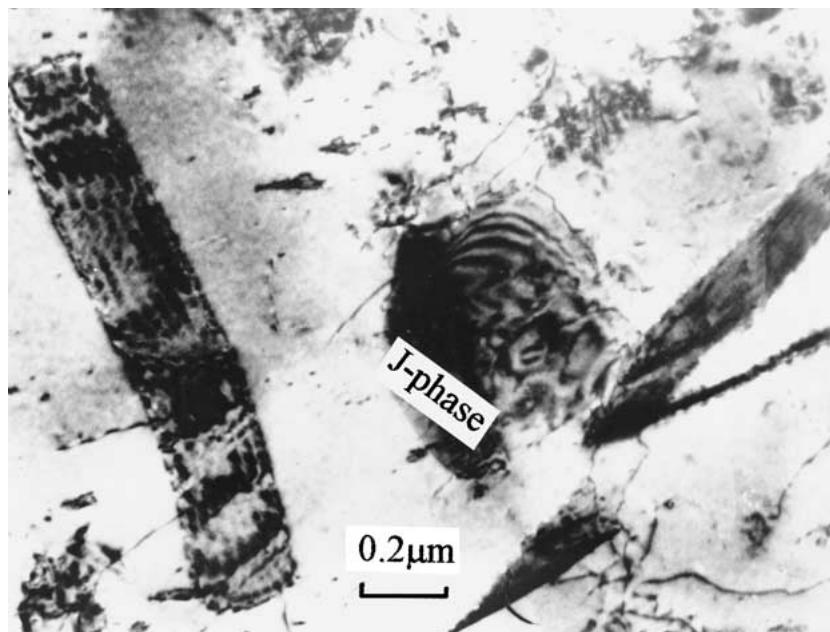
If a tendency toward separation reveals itself structurally in the temperature ranges 1100–1450°C and 20–600°C, one should expect that the coarse structure of high-temperature separation fixed by water quench-

ing from 1200°C will not change during the subsequent prolonged 550°C aging. In fact, Fig. 6a and b demonstrates two types of microstructures formed at 1200°C and fixed by water quenching, which are still retained after a 550°C aging during 75 h (a—the $\alpha_1 + \alpha_2$ mixture; b—the J-phase particles).

When the Fe-47Cr alloy preliminary heat treated in the temperature range of the σ -phase formation (700°C for 8 h, the microstructure in the bulk is a solid solution) is aged at 550°C for 15 h, the precipitates oriented along the strain-soft directions of the matrix are observed (Fig. 7a). This picture is characteristic of the precipitation from disordered solid solutions. An electron diffraction pattern taken from the precipitates shows two identical b.c.c. lattices (Fig. 7b). Apparently, the particles visible in Fig. 7a are very enriched in Cr. Their lattice parameter essentially differs from that of



(a)



(b)

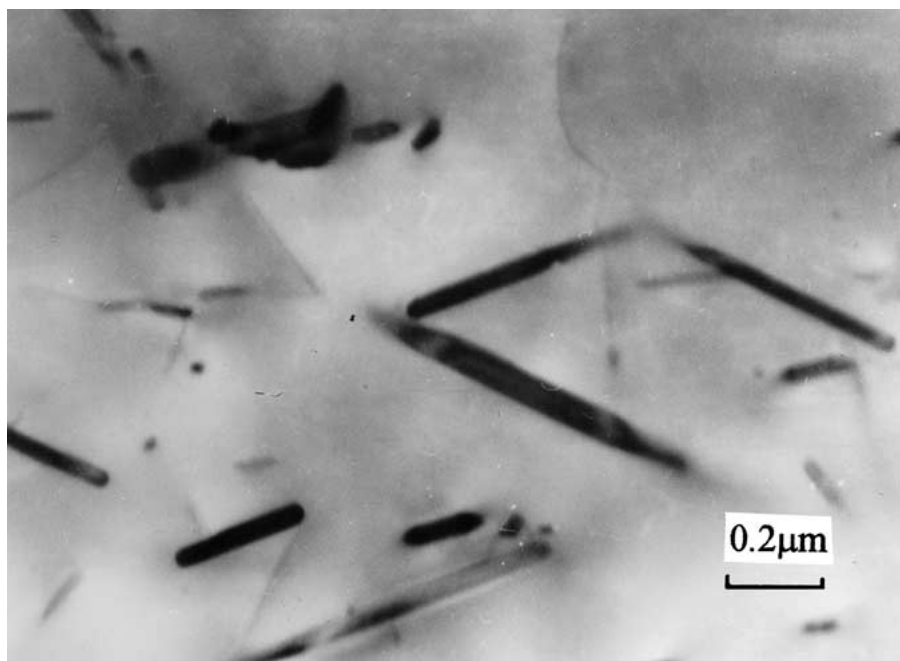
Figure 6 Fe-47Cr alloy heat treated at (a) 1200°C for 1 h ($\alpha_1 + \alpha_2$) and (b) 1200°C for 2 h (the J-phase particles) and then water-quenched. The subsequent heat treatment was at 550°C for 75 h in both cases.

the Cr-depleted matrix, which results in splitting of the reflections in the electron diffraction pattern.

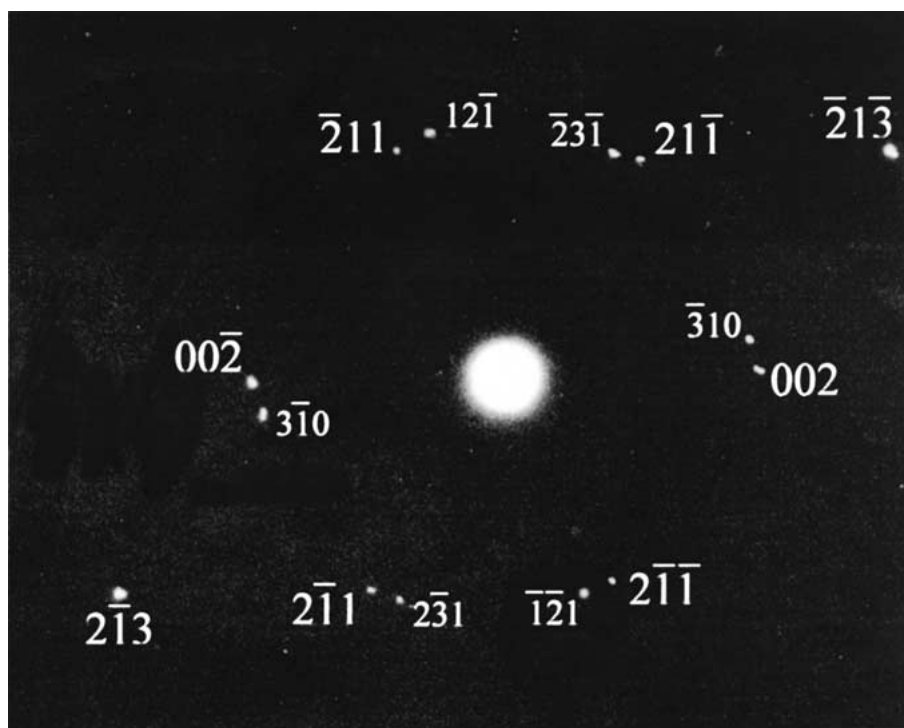
For alloys with a smaller Cr content (20 and 30%) the correlation between the high- and low-temperature separation microstructures somewhat differs from that in high-Cr alloys. A periodic tweed microstructure forms in these alloys at 1200°C. Electron microscopy pictures of tweed microstructure are presented in Refs. [2, 3]. A field-ion microscopy image of the tweed microstructure for the Fe-20Cr alloy water-quenched from 1200°C for 1 h is shown in Fig. 8a. Cr-enriched particles α_2 are well visible in the form of darkly-imaging isolated islands; they form as a result of preferential evaporation of Cr atoms. The detection of the high-temperature separation microstructure with the help of one more

high-resolution investigation technique should dispel any doubts upon the existence of high-temperature separation in Fe-Cr alloys. If the Fe-(20,30)%Cr alloys water-quenched from 1200°C are aged at 550°C the periodic microstructure of high-temperature separation transforms into a microstructure consisting of small dark α_2 points (Cr-enriched clusters) against bright α_1 background (Fig. 8b). Miller [12] used the field-ion microscopy to study the Fe-(17,19,24)%Cr alloys aged in the temperature range 500 to 540°C and also detected Cr-enriched clusters in the form of darkly-imaging isolated islands.

Using the results obtained in this work and in Ref. [3], we represented the equilibrium Fe-Cr phase diagram in the form shown in Fig. 9. Since all the morphological



(a)



(b)

Figure 7 Fe-47Cr alloy heat treated at 700°C for 8 h, water-quenched, subsequent aging at 550°C for 15 h: (a) bright-field image, (b) the selected-area electron diffraction pattern, $(240)_{\alpha 1} || (137)_{\alpha 2}$.

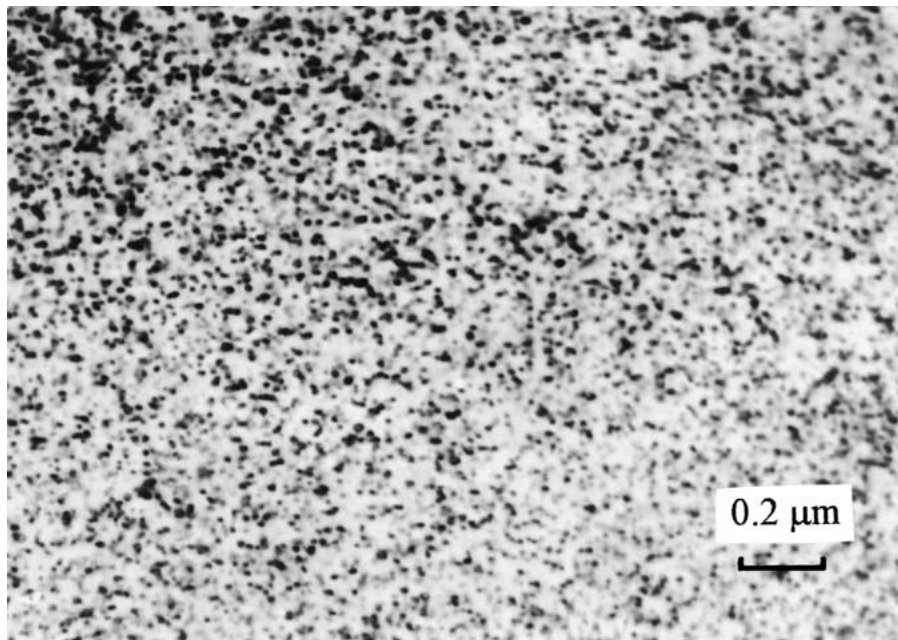
features of the high-temperature separation of the Fe-Cr alloys (tweed microstructure for Fe-20Cr and Fe-30Cr [3], J-phase particles, $\alpha_1 + \alpha_2$ mixture, the particles of pure Cr (A12) for the Fe-40Cr and Fe-47Cr compositions) are a consequence of the same tendency toward separation, and as these features depend only on the alloy composition and the temperature of heat treatment, it is possible to present them in the phase diagram as a certain region which is referred to as phase-separation region.

The phase diagram in Fig. 9 was constructed on the basis of electron microscopy studies only. The exper-

imental methods usually applied to the phase diagram construction are questionable in the case of diagrams in which the boundaries between the one- and two-phase regions are strongly blurred. Using the current concept of a phase, it is rather difficult to define at which stage of ordering the composition inhomogeneities can be considered as a two-phase mixture. Due to the blurring the accuracy of location of the boundaries between the solid solution regions and the regions of separation and ordering is not so high and can be assessed within $\pm 50^\circ\text{C}$ on the temperature axis and within $\pm 5.0\%$ on the composition axis. The σ -phase region is represented in our



(a)



(b)

Figure 8 (a) Fe-20Cr alloy heat treated at 1200°C for 1 h and water-quenched. Field-ion microscopy image of Cr-enriched clusters; (b) Fe-30Cr alloy heat treated at 1200°C for 1 h and water-quenched; the subsequent heat treatment at 550°C for 8 h; low-temperature separation microstructure.

diagram (Fig. 9) as a region of coexistence of the surface σ -phase layer and the bulk α solid solution (σ_{surf} and α_{bulk}). As was shown earlier [3, 13], a very thin continuous layer (0.007 mm) of σ -phase is formed at the surface of a Fe-Cr alloy after a 700°C–0.25 h aging, and then it grows into the depth with a velocity of about 0.03 mm/h. Fig. 10 shows the profile of Vickers hardness vs. the depth under the surface of Fe-47Cr alloy heat treated at 700°C for 8 h.

As shown in Ref. [1], the σ -phase region is shaped like ellipse with the lowest point at 440°C. Actually,

however, this region exists down to 600°C only and cannot overlap with the region of low-temperature separation (Fig. 9).

The second-order ordering-separation phase transition is shown on the phase diagram by two dot-and-dash lines, which becomes possible due to the detection of the electron domains in the micrographs. The lines of the second-order phase transition, for example, the Curie point are usually showed on the phase diagrams, therefore, it seems reasonable to plot also the lines of the ordering-separation transition in the Fe-Cr diagram.

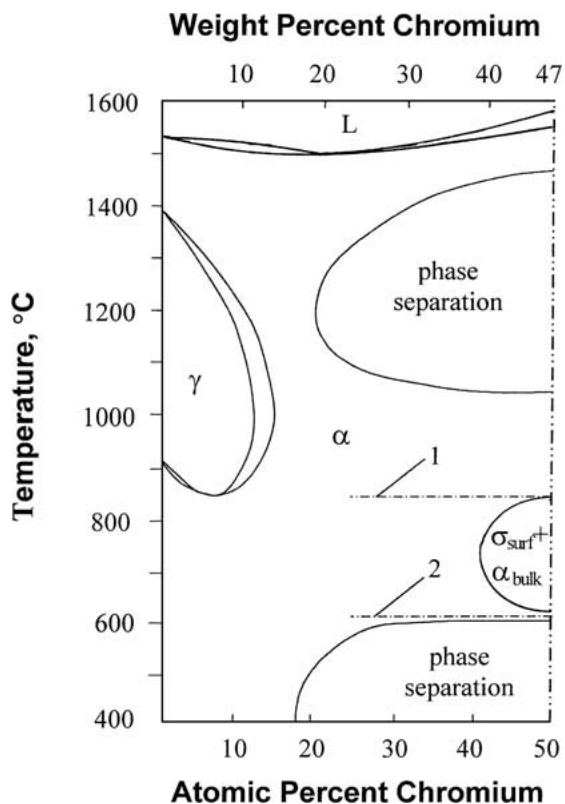


Figure 9 Fe-rich portion of the Fe-Cr phase diagram. The lines of two second-order phase transitions "ordering-separation" are marked by numerals.

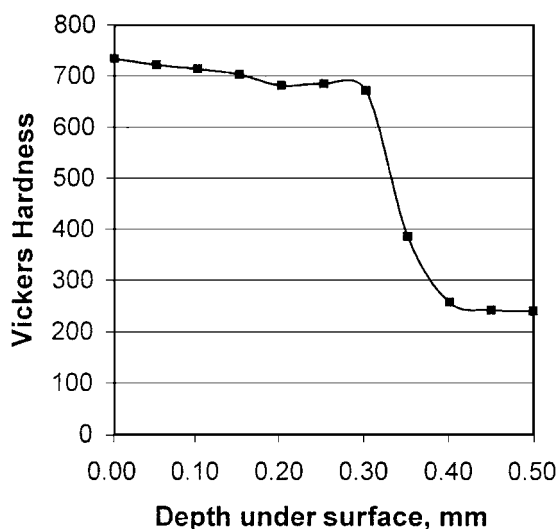


Figure 10 Fe-47Cr alloy heat treated at 700°C for 8 h, water-quenched. Vickers hardness vs. depth under surface.

4. Conclusion

The high-temperature separation of Fe-Cr alloys occurs in a rather wide range of temperatures and compositions and reveals itself in different morphologies depending on temperature and composition: a tweed microstruc-

ture for the Fe-(20,30)%Cr at 1100–1300°C; $\alpha_1 + \alpha_2$ mixture, particles of the intermediate J-phase forming as a result of separation and particles of pure Cr for the Fe-(40,47)%Cr at 1100–1450°C. The structures of high-temperature separation do not change their morphology during subsequent prolonged heat treatment in the region of low-temperature separation. This implies that the difference in morphology between the high- and low-temperature separation arises as a result of kinetic causes. The electron domains are a visual confirmation of the second-order ordering-separation phase transition happening upon the change of the tendency from separation to ordering, and vice versa. On the basis of the electron microscopy data obtained in this work, the Fe-rich portion of the Fe-Cr phase diagram was constructed, which turned out to be substantially different from the generally accepted one. These differences include: two regions of the high- and low-temperature phase separation; two lines of the second-order ordering-separation phase transition; the region of coexistence of the surface σ -phase layer and the bulk α solid solution.

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