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Separation in solid solutions of Fe-W system

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The microstructure of Fe-15 wt% W and Fe-18 wt% W alloys has been studied using methods of transmission electron microscopy and X-ray diffraction. It has been shown that in the region of a solid solution the separation microstructure is formed. During isothermal aging at 600°C the separation microstructure is dissolved and before precipitation of the stable Fe_2W phase an unknown metastable phase is formed and then dissolved. The conclusion has been made that a solid solution region in the Fe-W system is actually the region in which a tendency toward separation takes place.

1. Introduction

Since the transmission electron microscopy (TEM) has been used for studying phase transformations during aging, many authors have noticed that a microstructure of some alloys water-quenched from the region of a solid solution does not always correspond to the microstructure of a solid solution; more often it represents the products of its decomposition. After high-temperature water-quenching a microstructure having a periodic morphology is observed on electron micrographs in many cases; electron diffraction patterns show satellites in the vicinity of the main reflections. Alloys of such systems as Au-Ni [1], Ni-Mo [2], Fe-Be [3], Al-Zn [4], Cu-Be [5], Nb-Zr [6] and some others are considered as classical examples of formation of that microstructures in the region of a solid solution at high temperatures. Sometimes the decomposition microstructures forming after quenching from the region of a solid solution has been explained by the fact that the boundaries of the solid solution region on some phase diagrams were determined inexactly [6], however in most cases it has been believed that decomposition occurring by spinodal mechanism takes place in a very short time interval and has a chance to complete in a time of cooling of an alloy into water [1–6]. The latter conclusion contradicts the theory of spinodal decomposition of Cahn (Cahn solved an ordinary diffusion equation) [7] and the known magnitudes of diffusion coefficients, which indicate that on quenching into water the time for the formation of the relatively coarse microstructures which were found using TEM [1–6] is insufficient.

Similar microstructures have been recently obtained after quenching into water from the region of a solid solution for some alloys of Fe-Cr, Fe-Ti, Fe-Co and Fe-Mo systems. For instance, Fe-(20÷47)%Cr alloys quenched from the temperature range 1200–1400°C, demonstrate on the electron micrographs rather coarse precipitates called the J-phase, and on the electron diffraction patterns there are satellite reflections in the vicinity of every main reflection [8]. With increasing high-temperature exposure in the range from 1200 to 1400°C (with the subsequent quenching into water) these precipitates become coarser and gradually transform into particles of chromium having a metastable lattice A12 [9]. These chromium particles have their origin in the fact that a tendency toward separation takes place in a Fe-Cr solid solution. The same conclusion has been made by Jeannin *et al.* [10], who observed positive deviations from ideality in some alloys of the Fe-Cr system at 1100–1400°C.

The separation microstructures are not formed in all the solid solution region of the Fe-Cr phase diagram. As it was shown in [11] the separation region occupies only some part of the region of a solid solution and extends from 1100 to 1450°C and from 20%Cr and higher. These limitations are caused by the fact that above 1450°C the thermal component of free energy becomes more than an ordering energy component, but below 1100°C the absolute magnitude of the ordering energy diminishes progressively (at 830°C the ordering energy changes its sign to the opposite, i.e., it passes through zero) [11].

In the whole region of the solid solution of Fe-Ti system, including very low concentrations of titanium (down to 0.3%), a modulated microstructure has been revealed [12]. Using the atom probe it has been shown that the enriched modulations of composition in the Fe-5%Ti alloy contain about 15%Ti, whereas the depleted ones contain about 2%Ti [12]. Prolonged 600°C aging of a Fe-5%Ti alloy leads to the complete dissolution of the modulated microstructure and the formation of the Fe_2Ti particles. As far as the Fe_2Ti phase formation is only possible if a tendency toward ordering occurs, it has been concluded that the modulated microstructure is a result of an opposite tendency—a tendency toward separation, which takes place in the region of a solid solution [12].

In some alloys of a Fe-Co system as-quenched from the A2 solid solution region, the separation of the A2

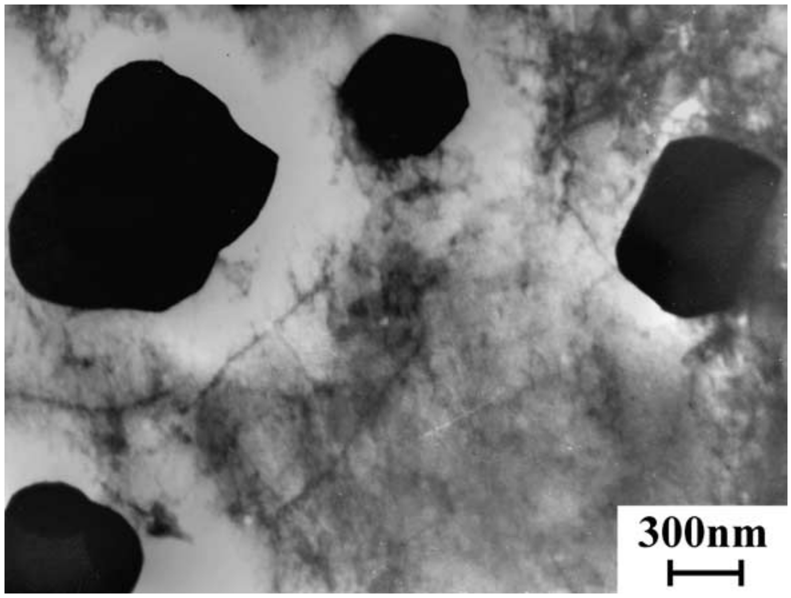
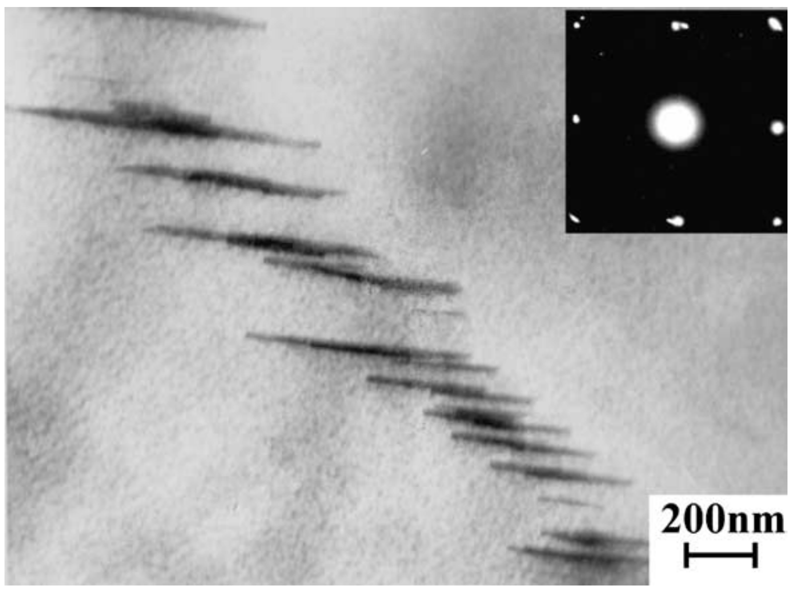
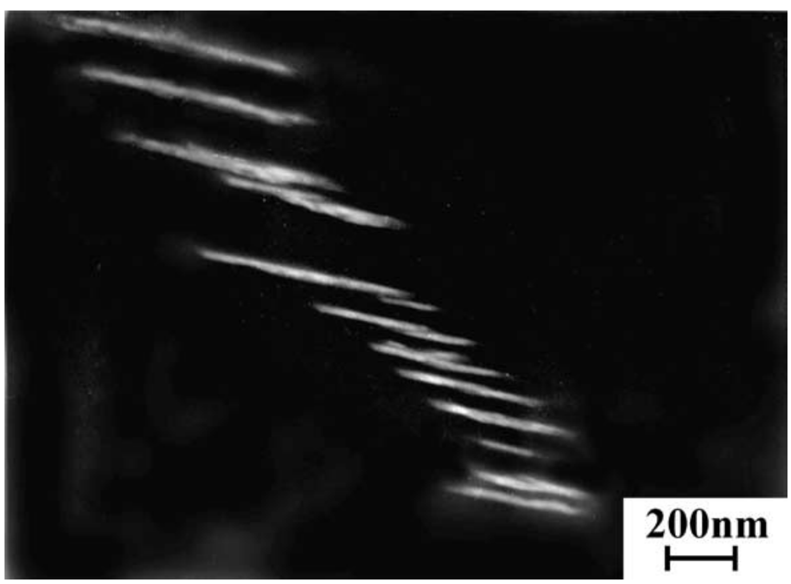


Figure 1 Microstructure of Fe-15 W alloy heat treated at 1300°C for 0.5 h, furnace cooling. Visible large particles of Fe_2W phase. Initial state.



(a)

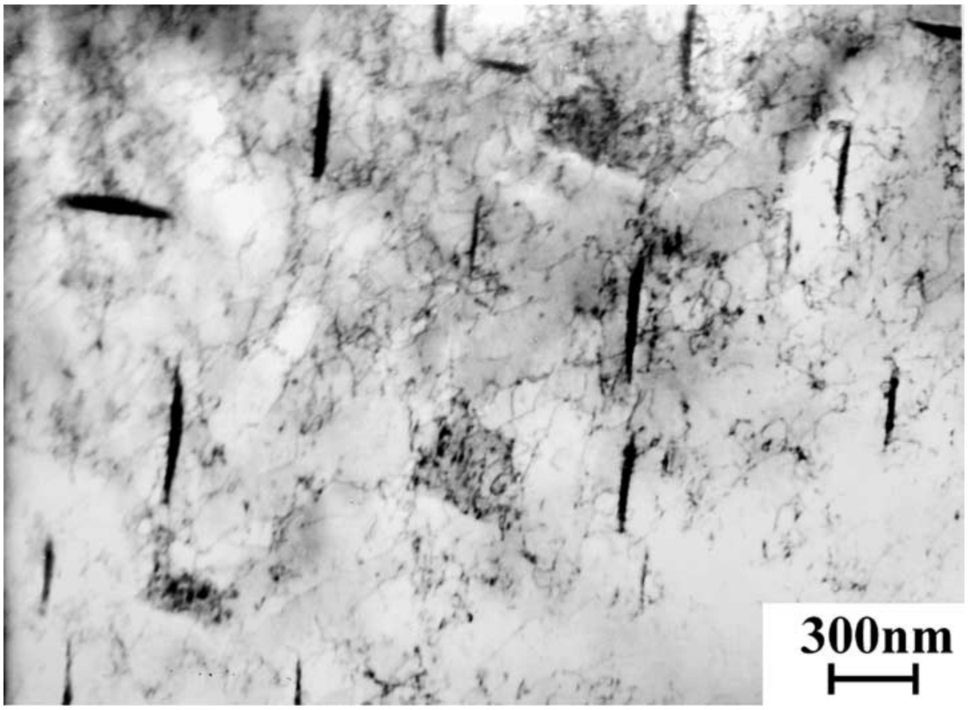


(b)

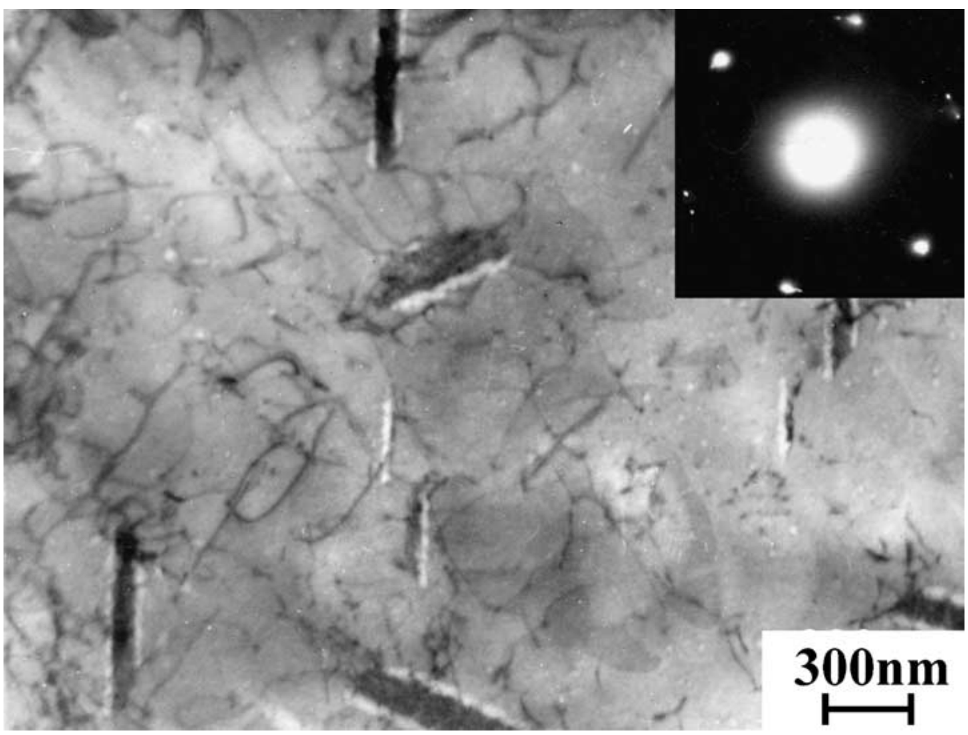
Figure 2 TEM images of Fe-15 W alloy re-heated up to 1300°C during 0.5 h and cooled in water: (a) a bright-field image of a separation microstructure (inset: selected area electron diffraction pattern from precipitates) and (b) a dark-field image in the light of the satellite reflection (020).

solid solution is observed in the bulk; the volume fraction of the particles enriched with Co and having fcc crystal structure represents about 10% [13]. In the surface layer down to 70 μm in depth, these alloys are separated totally into the bcc Fe(Co) and fcc Co(Fe) grains and for the $Fe_{50}Co_{50}$ alloy, for example, the intensities of the X-ray lines $(110)_\alpha$ and $(111)_\gamma$ are approximately equivalent [13].

So, from the preceding [1–6, 8–13] it is seen that in the regions of a solid solution the products of separation ranging in morphology from clusters enriched in an alloying component to the particles with the crystal structure characteristic of the alloying component are formed at high temperatures. Hence, it is possible to make a conclusion that the solid solution regions on phase diagrams are in fact the regions where a tendency toward separation takes place. In a certain part of the solid solution region (and sometimes in the all region) the microstructures of separation are formed. Indeed, according to thermodynamics, practically all

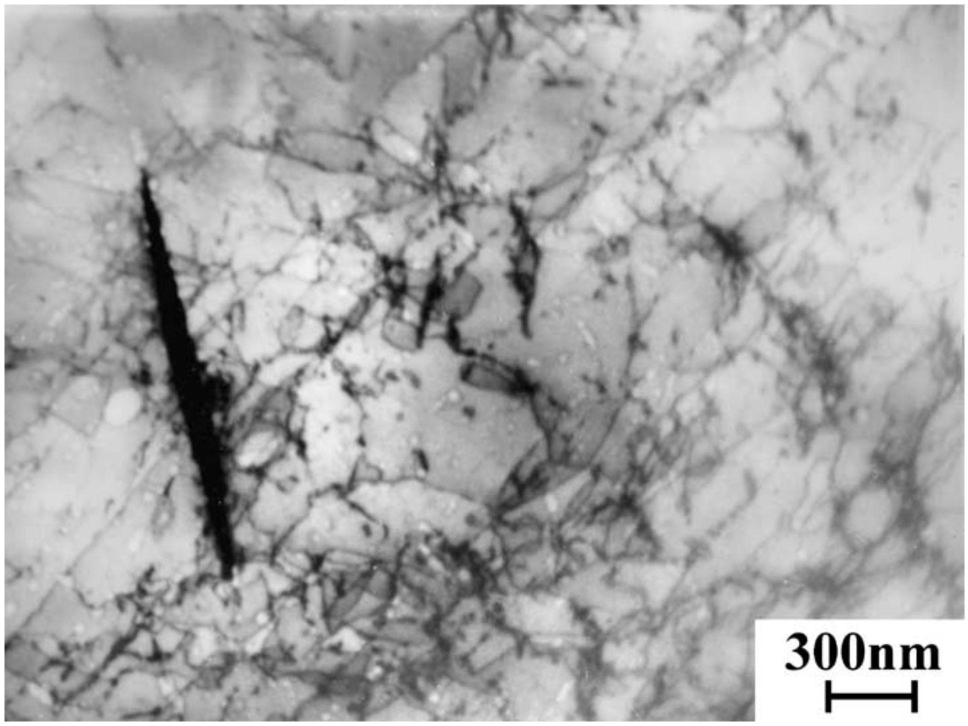


(a)



(b)

Figure 3 TEM images of Fe-15 W alloy re-heated up to 1300°C during 1 h and cooled in water: (a) (001) orientation (b) (111) orientation; bright-field image of a separation microstructure (inset: selected area electron diffraction pattern from precipitates) and (c) water-quenching from 1400°C for 1 h. (*Continued*)



(c)

Figure 3 (*Continued*)

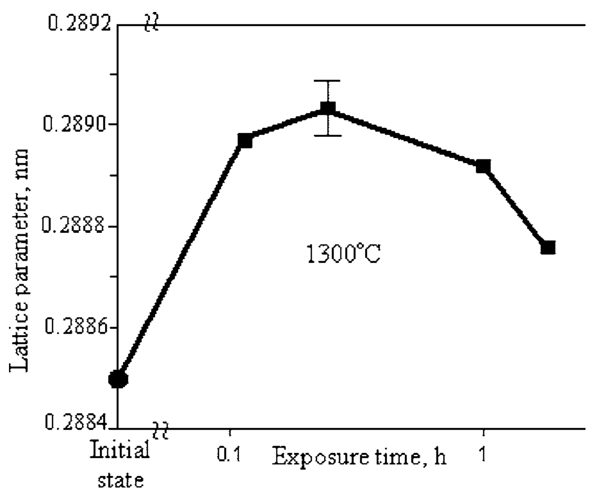


Figure 4 Lattice parameter of a Fe-15 W solid solution vs. time of exposure at 1300°C; ●—value in an initial state.

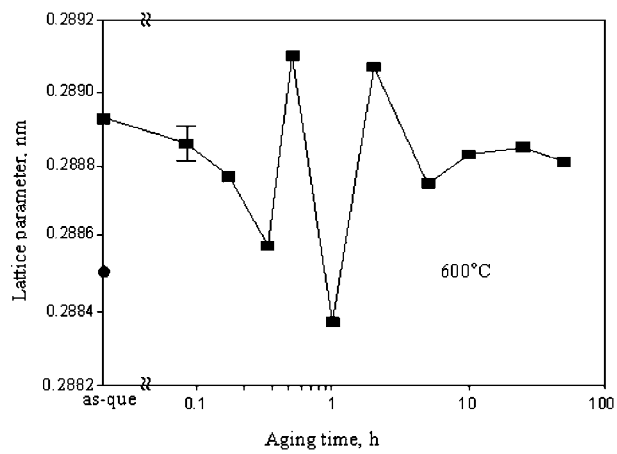


Figure 5 Lattice parameter of a Fe-15 W solid solution vs. 600°C aging time.

solid solutions are not ideal; therefore, when the system approaches equilibrium, they should decompose. It means that the equilibrium phase diagrams must not contain the regions of a solid solution, as far as the latter is not an equilibrium phase. However, such regions are observed almost on each phase diagrams. Perhaps, it is due to the fact that microstructure investigation methods are rarely used for the construction of phase diagrams, and this renders to distinguish a microstructure of a disordered solid solution and a microstructure consisting of enriched and depleted clusters impossible.

The region of a solid solution in the Fe-W system is rather narrow and it widens only at pre-melting temperatures; the maximum content of tungsten represents about 6.6 at% at 1300°C, while tungsten practically does not dissolve in Fe lattice at room temperature [14]. In these conditions a tendency towards separation, even if it is present in the solid solution region, would not seemingly lead to the formation of separation microstructures (a temperature is high, W concentration is low). Therefore, even if it has been possible in those conditions to reveal a separation microstructure, there is bound to be a potent argument in the use of the existence of a tendency toward separation in the solid solution regions of a lot of systems.

2. Experimental

The alloys labeled Fe-15 W and Fe-18 W were prepared from pure components in a vacuum induction furnace and forged at high temperatures. The chemical analysis of the alloys showed the following compositions (in the weight percentages): 14.8%W; 0.02%C; 0.003%N (Fe-15 W) and 18.0%W; 0.03%C; 0.006%N (Fe-18 W). At high temperatures the alloys were in the region of solid solutions, and at temperatures below 1200°C (Fe-15 W) and 1280°C (Fe-18 W) were in a suitable two-phase region. The Fe-15 W alloy was quenched into water from the temperatures of 1100, 1200, 1300 and 1400°C, while Fe-18 W alloy—from 1400°C. The isothermal aging at 600°C also was conducted. The X-ray diffraction phase analysis was performed by means of a diffractometer with the use of Co K_{α} radiation. Unit cell dimensions were corrected by the Nelson–Riley extrapolation method using the (211), (220) and (310) lines, and are believed to be accurate to ±0.00005 nm. The microstructure was studied with the help of a transmission electron microscope TESLA BS-500 operating at 90 kV. Thin foils were prepared by electropolishing in a chromium-orthophosphoric acid solution.

3. Results and discussion

The TEM studies have been mainly performed on the Fe-15 W alloy. A microstructure formed in the alloy after annealing at 1300°C for 0.5 h with subsequent furnace cooling has been taken as an initial microstructure (Fig. 1). As far as the particles of a phase shown in Fig. 1 are too massive and an electron beam cannot pass through them, the X-ray diffraction phase analysis has been used. It shows that these particles are the Fe_2W phase. In order to investigate a microstructure corresponding to the high-temperature state of the alloy, the specimens have been heated in evacuated quartz ampoules up to 1100, 1200, 1300 and 1400°C and then cooled in water with fracture of ampoules. After water-quenching from 1100°C (i.e., from $\alpha + Fe_7W_6$ region), the microstructure is similar to the morphology displayed in Fig. 1. The X-ray diffraction phase analysis evidences that these particles have a crystal structure of the Fe_7W_6 phase. With increasing quenching temperature up to 1200°C (exposure during 1 h), the microstructure of a solid solution is observed on the electron micrographs. Further increasing temperature of heat treatment up to 1300°C also should seemingly bring about the solid solution microstructure. However, after quenching from 1300°C during 0.5 h in water some precipitates arranged in rows parallel to each other are observed on the electron micrographs (Fig. 2a). These rows do not occupy the entire area of the micrograph and are situated at a certain distance from each other. The selected-area electron diffraction pattern taken from the precipitates shows the main reflections with satellites (inset in Fig. 2a). The dark-field analysis detects the rows of the precipitates in the light of these satellites (Fig. 2b). This means that the precipitates have the bcc lattice; however, their lattice parameter is different than that of the matrix.

A similar electron diffraction pattern with the satellites has been previously observed in the Fe-Cr alloys as-quenched from 1200°C-1 h. It has been shown [11] that these satellites are decisive evidence of the separation of a solid solution. These satellites have been appeared in the electron diffraction patterns from J-phase particles, which represent a periodic distribution of strongly Cr-enriched and strongly Cr-depleted clusters [11]. The comparison of the data mentioned in this work with the results in [11] leads to the conclusion that the precipitates in Fig. 2 are the clusters strongly enriched with W and they are formed as a result of a tendency of a Fe-15 W solid solution toward separation.

Heat treatment for a longer time at 1300°C up to 1 h changes the arrangement of the W-enriched clusters and the clusters line up along the elastically soft directions of the matrix {100} (Fig. 3a). When the orientation of the foil is (111), it is possible to observe the internal microstructure of the clusters (Fig. 3b),

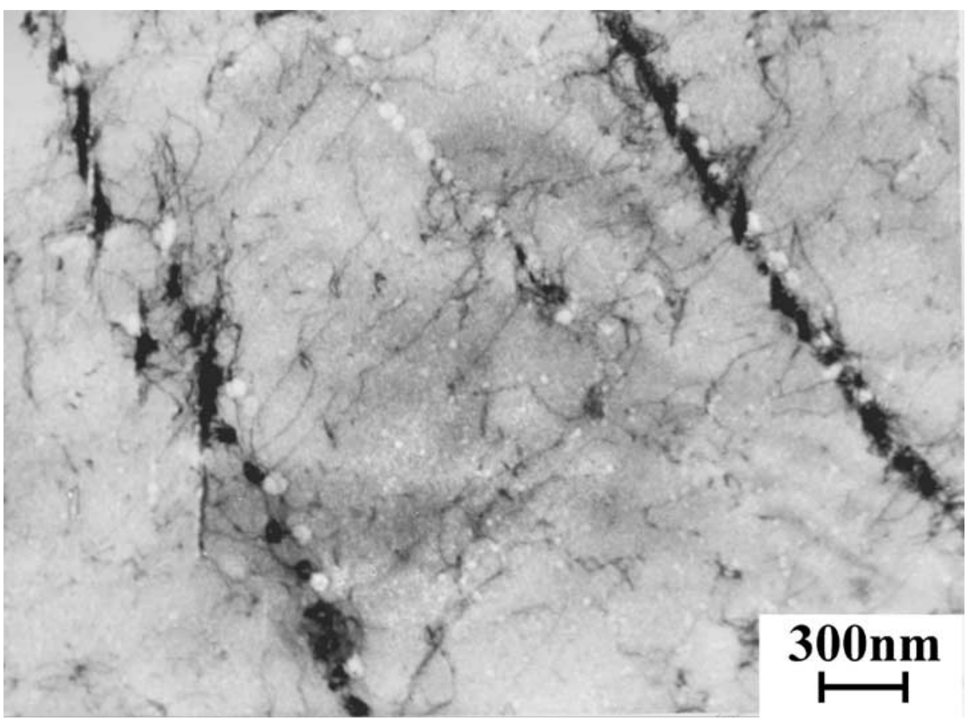
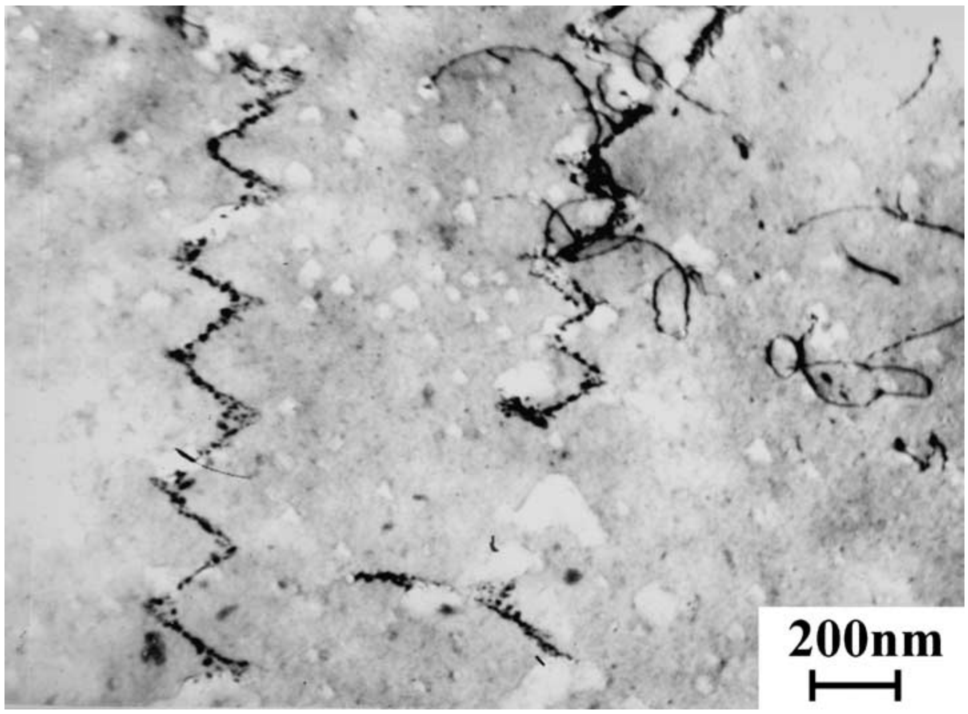


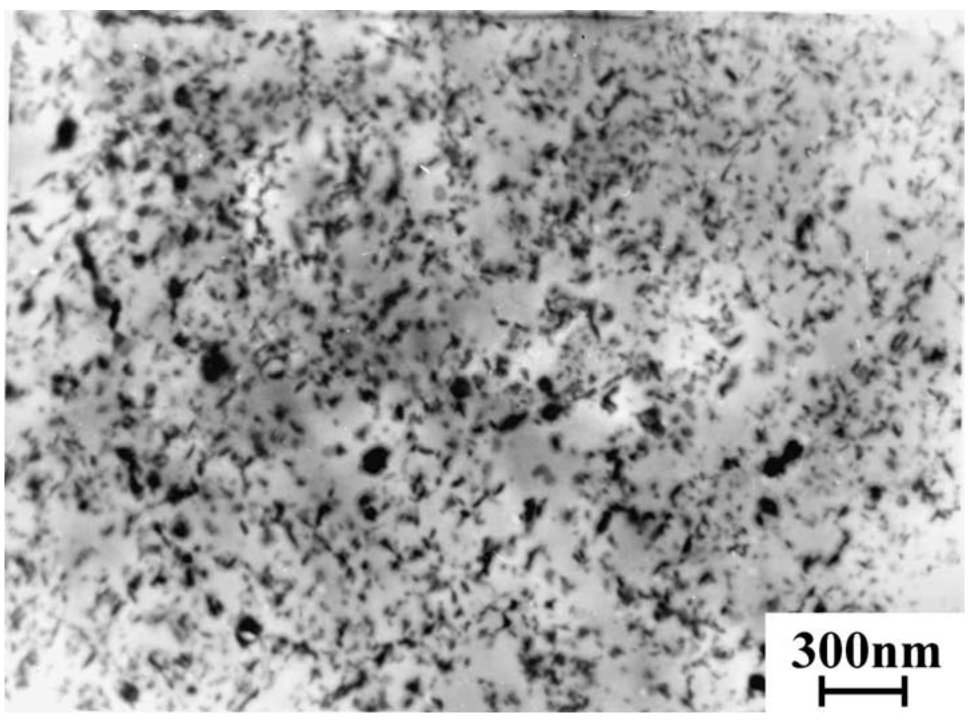
Figure 6 TEM image of Fe-15 W alloy; aging at 600°C for 20 min. A bright-field image of a separation microstructure.

which represent small globular particles lying compactly in the planes {100}. The further increase of the quenching temperature up to 1400°C significantly decreases the number of the W-enriched clusters; however, their arrangement and shape are similar to those displayed in Fig. 3a, whereas their sizes grow (Fig. 3c).

The change of the lattice parameter of a Fe-15 W solid solution is shown in comparison with the initial state (Fig. 4). It can be seen that when the coarse particles of Fe_2W (Fig. 1) completely dissolve during heating up to 1300°C and exposure for 0.25 h the lattice parameter increases due to the participation of the W atoms in a solid solution formation. Since the sizes of the W atoms are significantly larger than those of the Fe atoms, their dissolution in the lattice of Fe will lead to an increase of the lattice parameter of a solid solution, and their departure from the Fe lattice with the formation of various precipitates will result in a decrease of the parameter. Exposure during 1 h at 1300°C leads to

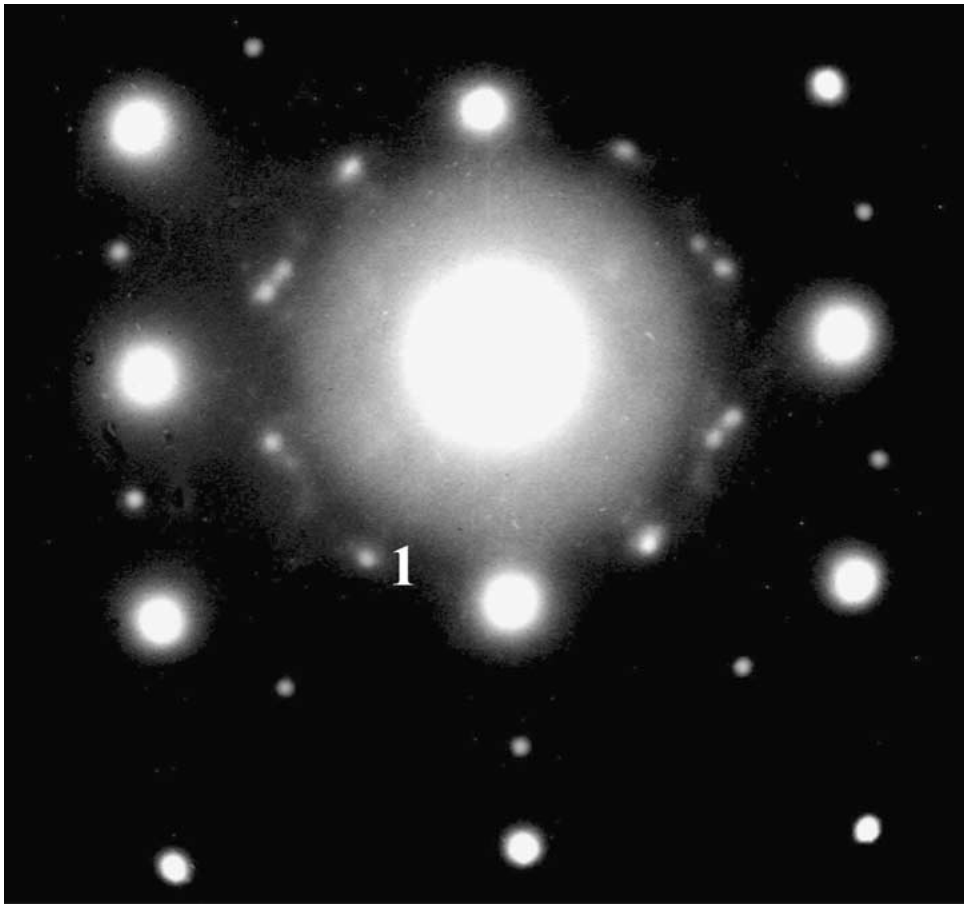


(a)



(b)

Figure 7 TEM image of Fe-15 W alloy; aging at 600°C for 1 h: (a, b) bright-field images of precipitates, (c) electron diffraction pattern from (b), (d) a dark-field image in the light of an additional reflection marked by numeral 1 in the electron diffraction pattern (c). (*Continued*)



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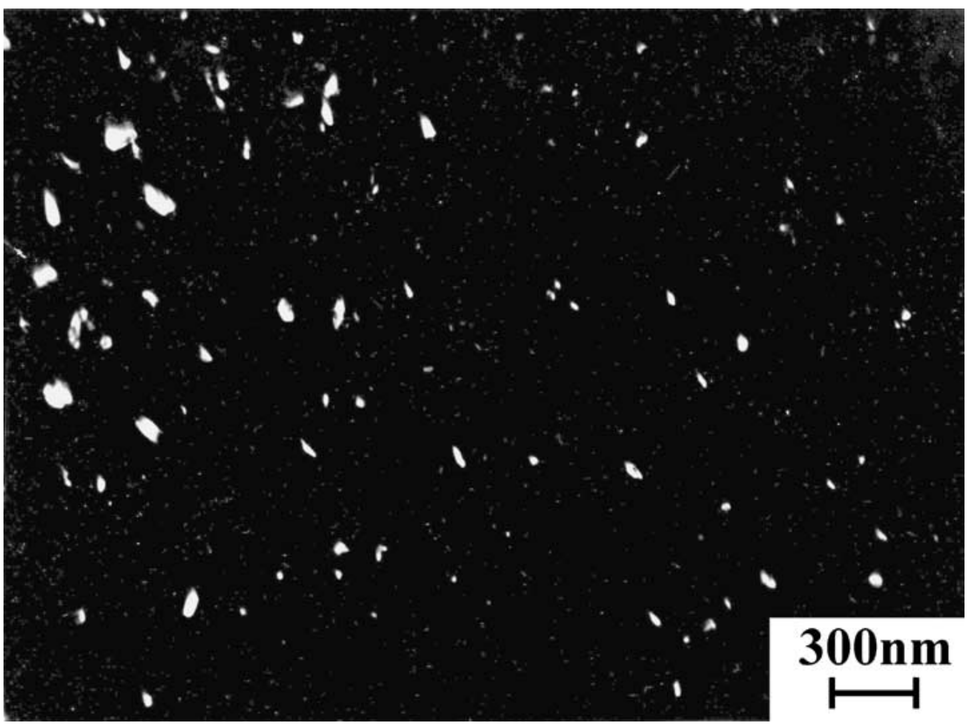
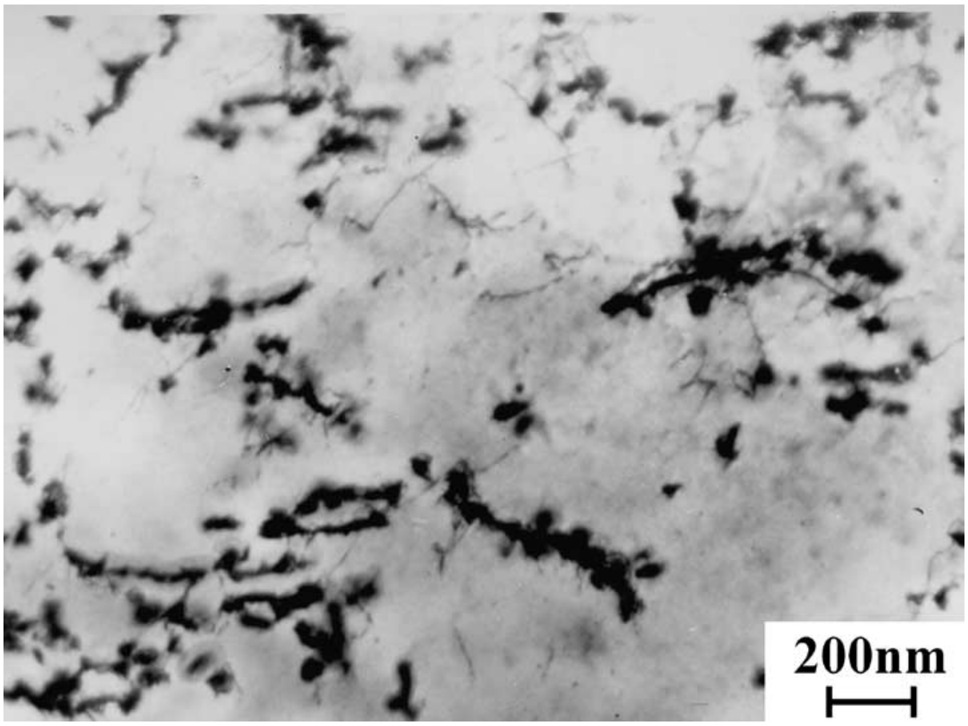


(d)

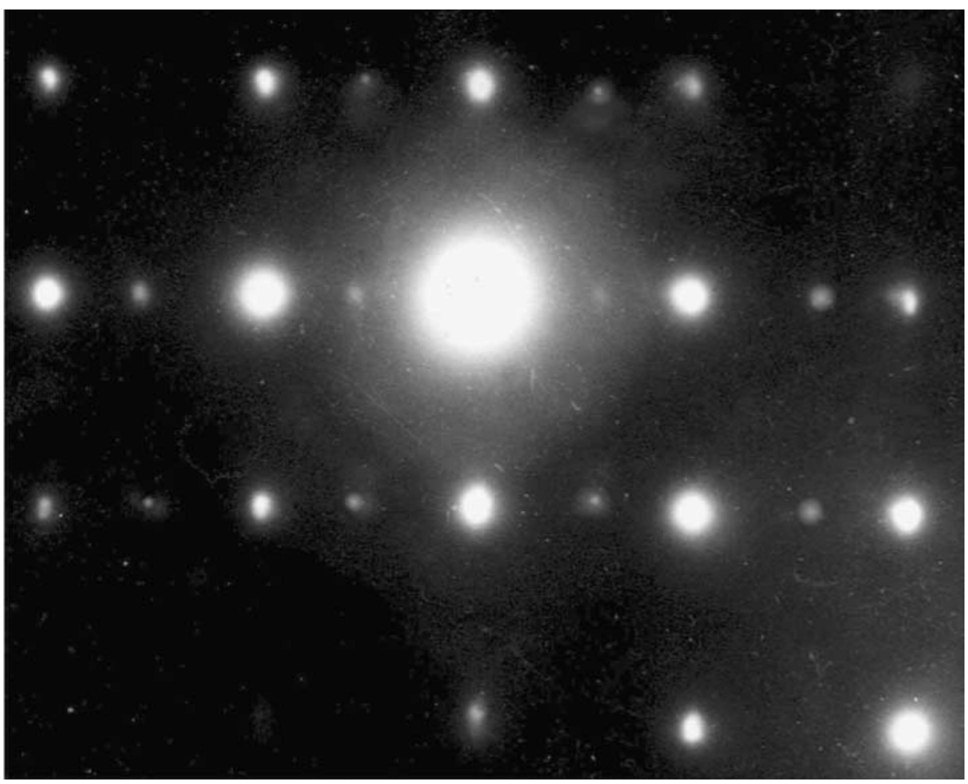
Figure 7 (*Continued*)

the formation of the separation microstructure (Fig. 3), some part of the W atoms depart from the solid solution forming the particles enriched with tungsten, and the lattice parameter decreases (Fig. 4).

Since tendencies toward separation or ordering are alternative (in the first case: $u_{AA} + u_{BB} > u_{AB}$, and in the second case: $u_{AA} + u_{BB} < u_{AB}$, where u_{AA}, u_{BB} and u_{AB} represent an effective pair interactions between A and B atoms) the transition from the microstructures formed due to a tendency toward separation to the microstructures of ordering should necessarily be accompanied by dissolution of the separation microstructures, and vice versa. Really, as it was shown experimentally [9, 11], the transition from the region where the microstructure of separation is formed to the region of ordering microstructures leads to the dissolution of the separation microstructure and the formation of the microstructure characteristic for a tendency toward ordering. In order to clarify how the separation-ordering transition occurs in the Fe-15 W alloy the lattice parameter of a solid solution has been determined after quenching from 1300°C–0.5 h and after subsequent aging at 600°C for different times (the measurements were performed on the same specimen). The results are shown in Fig. 5. When exposure of 600°C aging is about 20 min, a lattice parameter decreases, indicating that in the beginning of aging more and more quantity of the W atoms escape from the solid solution causing significant

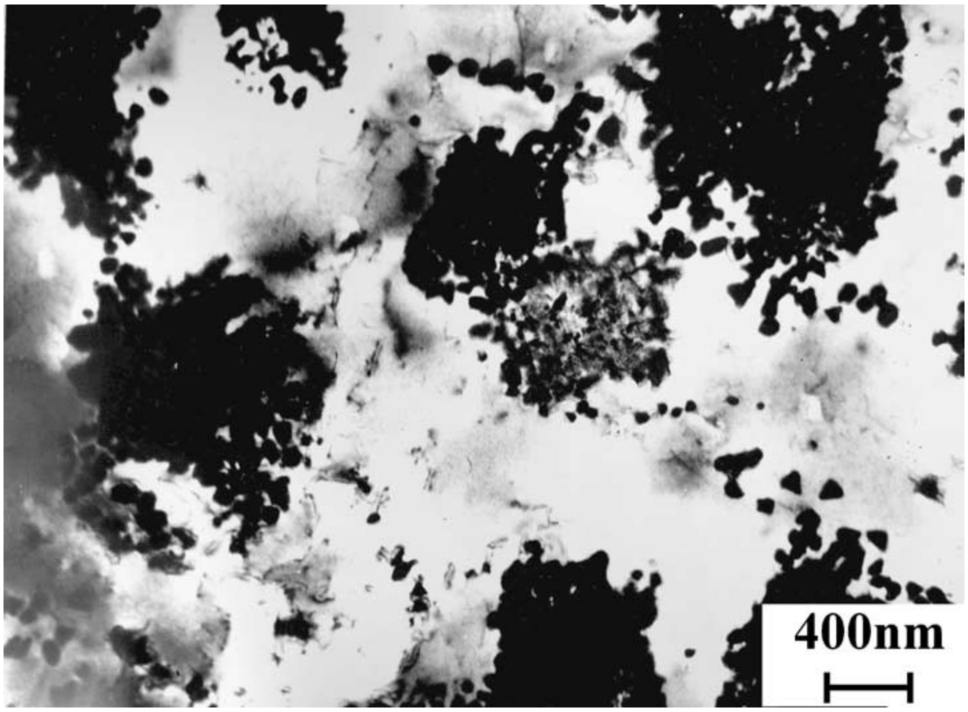


(a)

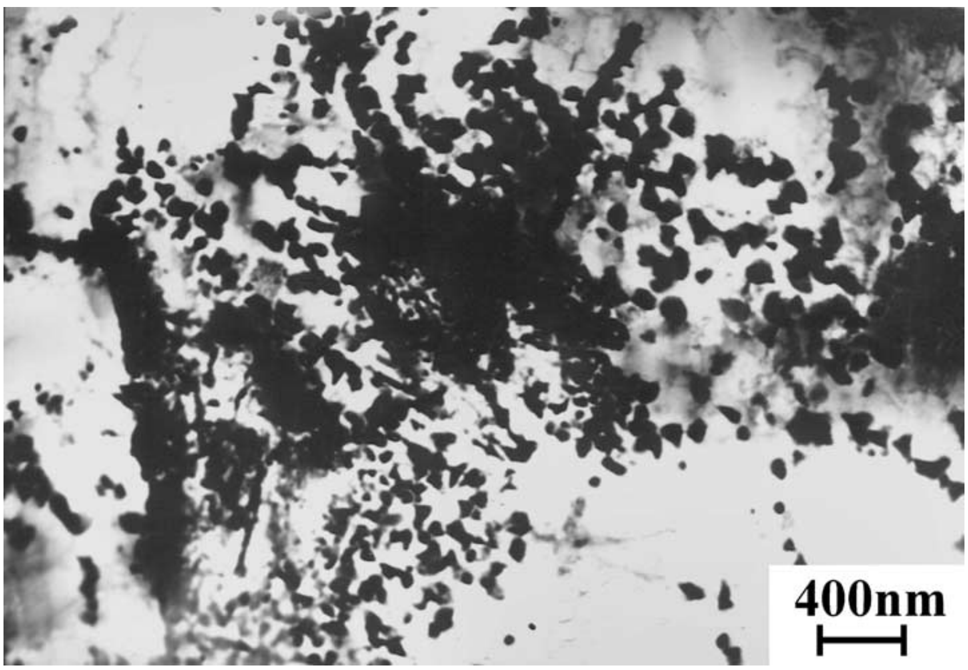


(b)

Figure 8 Microstructure $\alpha + Fe_2W$: (a) aging at 600°C for 5 h, (b) the same, electron diffraction pattern, (c) aging at 600°C for 10 h, and (d) aging at 600°C for 25 h. (*Continued*)



(c)



(d)

Figure 8 (*Continued*)

coarsening of the previously formed at 1300° for 1 h precipitates, which are arranged as long parallel rods consisting of separate round particles (Fig. 6). Though the aging temperature of 600°C is in the two-phase region ($\alpha + Fe_2W$) of the diagram, one can say that at the very first periods of aging the separation microstructure formed at 1300°C coarsens more and more. It is hard to tell now why that coarsening of separation microstructures takes place in the region of ordering.

However, when the exposure at 600°C increases up to 30 min, the separation microstructure completely dissolves, as would be expected, causing the formation of a solid solution, and, as a result, the lattice parameter sharply increases (Fig. 5). Further exposure at 600°C for 1 h leads to a sharp decrease in the lattice parameter, which could be interpreted as the precipitation of the Fe_2W phase from the solid solution. Indeed, after 600°C aging for 1 h it can be seen that a large number of fine precipitates are situated first along dislocations (Fig. 7a) and then uniformly over all the bulk of the matrix (Fig. 7b). The particles in Fig. 7b are of irregular shape. Selected area of the electron diffraction pattern taken from the particles shows a system of additional reflections (Fig. 7c). It corresponds none of the known phases of the Fe-W system. In the additional reflection designated by numeral 1 on the electron diffraction pattern,

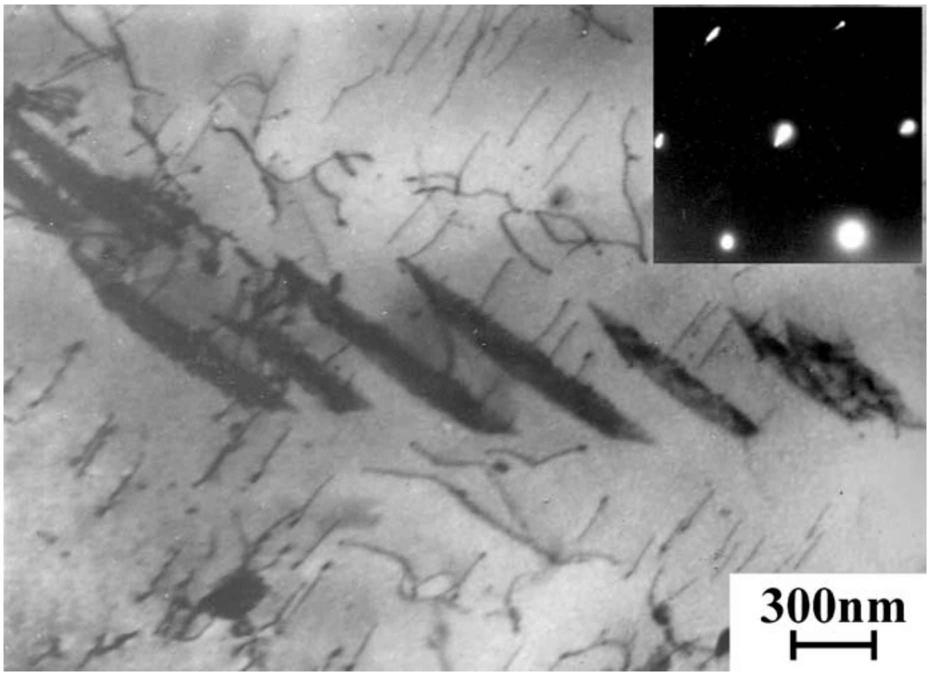


Figure 9 TEM image of Fe-18 W alloy heated up to 1400°C during 1 h and cooled in water; inset: selected area electron diffraction pattern from precipitates.

the particles of an unknown phase mentioned are glowing (Fig. 7d). In accordance with Fig. 5, a larger number of tungsten atoms escape from the solid solution and participate in the formation of this unknown phase.

The particles observed in Fig. 7 are not an equilibrium phase for the temperature of 600°C, and after 2 h aging at 600°C they dissolve (the microstructure of a solid solution is seen on the electron micrographs for this time of aging). As a result of this dissolving, the lattice parameter reaches maximum magnitude as in the case of dissolution of the separation microstructure.

With further aging at 600°C the lattice parameter decreases again (Fig. 5) and the electron micrographs show separate precipitates of irregular shape and clusters of these precipitates which are at times arranged along dislocations (Fig. 8a). The sizes of these precipitates are significantly larger than displayed in Fig. 7. Selected area of an electron diffraction pattern from these particles is presented in Fig. 8b. Its identification evidences that the Fe_2W particles are presented in microstructure as a precipitated phase. Aging for 10 h has resulted in coagulation of these precipitates into massive particles (Fig. 8c). Fig. 8d shows further evolution of a microstructure with time of 600°C aging.

Thus, it can be concluded that the transition from the microstructures of separation to the equilibrium $\alpha+$ Fe_2W microstructure happens at aging in two stages: the microstructure of separation first dissolves, and the particles of some metastable phase precipitate from a solid solution. With further aging these particles dissolve as well, and in their place the particles of a stable Fe_2W phase precipitate.

The microstructure of separation of the Fe-18 W alloy water-quenched from 1400°C for 1 h is shown on Fig. 9. The selected-area electron diffraction pattern taken from the precipitates shows the main reflections with satellites (inset in Fig. 9).

4. Conclusions

Microstructures of separation found in the region of a solid solution of the Fe-W system can be added to the earlier discovered microstructures of separation in the Fe-Cr and Fe-Co systems having extensive regions of a solid solution and in the Fe-Ti system having a limited region of a solid solution. The results received confirm the assumption made earlier that the regions which have got the name 'the solid solution regions' are actually the regions in which a tendency toward separation takes place and the microstructure of separation is formed.

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