Laves phase formation in solids

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Structural changes of the Fe–Mo, Fe–Ti and Fe–Nb binary alloys have been investigated by means of electron microscopy and X-ray diffraction. A tweed structure representing modulation of the composition always precedes the Laves phase precipitation. The latter fact allows confirmation that the Laves phase precipitation proceeds by the spinodal mechanism. A tweed structure formation results in softening of the Fe–Ti and Fe–Nb alloys; the hardness of the Fe–Mo alloys is unchangeable.

1. Introduction

The modulated structure in which the new phase particles are periodically distributed along the orthogonal < 100 > directions has been observed in many fcc and bcc alloys, such as Au–Pt [1], Au–Ni [2], Ni–Al [3], Cu–Ti [4], Cu–Ni–Fe [5] and Cu–Ni–Co [5]. In the most common iron alloys, the modulated structure has been found only in Fe–Be [6], Fe–Si [7] and Fe–Mo [8, 9] alloys as far as is known. The distribution of the precipitates along the orthogonal < 100 > cubic directions leads to specific diffraction effects, namely satellites appear in the electron and X-ray diffraction patterns.

Cahn's spinodal theory [10] predicts formation of the sinusoidal wave of concentration at the early stages of ageing. In this case, morphological changes are similar to modulated structure formation. The formation of modulated structures has been considered as one of "the most interesting and beautiful consequences" of Cahn's theory [11], although a modulated structure represents a periodic distribution of the coherent particles of a new phase rather than a sinusoidal distribution of the composition.

A modulated structure is formed at the later stages of decomposition as a result of coarsening of the precipitates due to the increase of the coherent stresses in the boundaries of the coexisting phases, namely, solids and particles of the precipitates. Therefore the presence of the modulated structures in the alloy cannot be proof of decomposition proceeding due to the spinodal mechanism [12].

Many reports show the striations in the electron micrographs to be found at the early stages of decomposition. Usually this structure is called tweed. The tweed structure represents a sinusoidal distribution of composition but not precipitates (as in the case of modulated structures) along the < 100 > matrix directions. The distribution results in deformation fields along the < 110 > directions. In the case of the tweed structure, the satellites have not been found in the electron and X-ray diffraction patterns, however it is possible to see sidehand or diffuse scattering around the matrix reflections, but only at high solute concentrations.

Investigating the ageing process of the Fe–(13–20) at % Mo alloys by electron diffraction microscopy, Miyazaki and collaborators [8, 9] have found different types of structures in the alloys at the later stages of ageing. In their opinion, a modulated structure was formed as a result of spinodal decomposition, but the disc-shaped precipitates lying on the {100} matrix planes were formed as a consequence of the nucleation growth decomposition. As both a modulated structure and the disc-shaped precipitates can coexist at some stages of ageing, these authors have concluded that a gradual transition from spinodal decomposition to nucleation growth occurs. The tweed structure has always been observed at early stages of ageing of the alloys investigated, and preceded formation of modulated or disc-shaped structures [8, 9]. Therefore formation of modulated and disc-shaped structures cannot be proof of decomposition by that or another mechanism [12]. Usually the tweed structure formation, as well as the precipitation of the second phase particles, is considered to be a cause of hardening of the alloys. The hardening level depends on many factors, in particular on the mechanism of overcoming the particles by dislocations, i.e. cutting off or bending. Such hardening takes place in many iron alloys, for example the Fe–Mo system [8, 9], the Fe–Cr system [13, 14], etc., independent of the type of decomposition process of solid–new phase precipitation; formation of Guinier-Preston (GP) zones; K-state; tweed or modulated structure; ordering, etc. There are many theories concerning this hardening process, all of which consider interactions between dislocations and obstacles in the solid. However, none of these theories considers the interactions leading to the softening of the alloys in the process of decomposition.

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Microstructural changes in some alloys of the Fe–Mo, Fe–Ti and Fe–Nb systems at the earlier stages of ageing are investigated, and the dependences between the tweed structure and the hardness of alloys are discussed in this paper.

2. Experimental procedure

Binary iron alloys with 10, 15, 20 and 26 wt % Mo; 1.5, 2.5 and 5.0 wt % Ti; 3.5 and 5.0 wt % Nb have been investigated. The alloys were produced from pure components melted in an induction furnace, with an argon atmosphere. Ingots (2 kg) were annealed for 3 h at 1250 °C and then forged at high temperature over 1300 °C in a plate approx. 2 mm thick. The alloys were solution-treated for 2 h at 1250–1350 °C in an argon atmosphere, and quenched into 10% water solution of NaOH. Ageing for various durations was isothermally performed at 550 or 600 °C. Vickers hardness determinations and precise X-ray measurements of the lattice parameter of the solids were made. The structural changes were mainly investigated by means of transmission electron microscopy (TEM), operating at 200 kV.

3. Results and discussion

3.1. Fe–Mo alloys

Changes of hardness with 550 and 600 °C ageing for the alloys investigated are shown in Figs 1 and 2, respectively. For the Fe–10, 15 and 20 % Mo alloys, no hardening was observed at the early stages of ageing, whereas the Fe–26 % Mo alloy shows a rapid growth of hardness at the beginning of ageing. The maximum hardness of the alloys investigated is reached after approximately 500 h at 550 °C ageing, with the exception of Fe–26 % Mo: for the latter, maximum hardness was reached after 10 h and corresponded to the hardness which was possible to measure without failure of the specimen. A process of hardening began after 25, 10 and 4 h ageing at 550 °C for Fe–10, 15 and 20 wt % Mo alloys, respectively. Before these periods of ageing the tweed (striation) structure was observed in the electron micrographs of the alloys (Fig. 3). No streaks or satellite spots appeared in the electron diffraction patterns. No changes of α–Fe lattice parameters determined by X-ray diffraction were observed at these periods of ageing (Fig. 1 shows the lattice parameter of Fe–10 % Mo alloy as an example). These two facts demonstrate that the tweed structure is not a two-phase structure, but is a solid solution with periodic distribution of clusters enriched and depleted by solutes. According to the well-known rule formulated by Guinier [16] that the unit cell dimensions of the solid solution are invariant with respect to the distribution and arrangement of its solute atoms, and so the lattice parameter of a non-random, clustered solid solution is the same as that of a random solid solution of the same concentration.

With a longer period of ageing, the tweed structure becomes less distinct and particles of a new phase appear at first in the local points of tweed structure

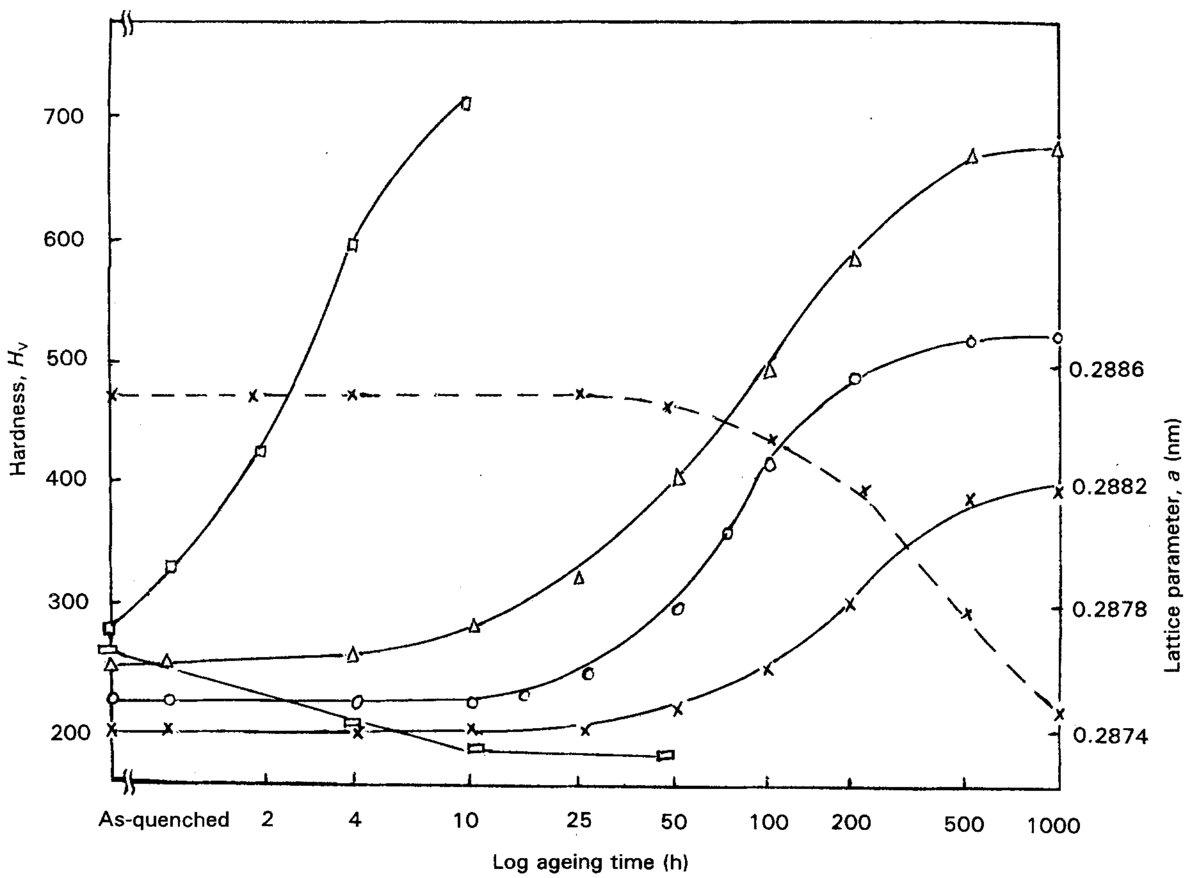

Figure 1 Age-hardening curves (H_v) of Fe– ×,10; ○,15; △,20; □,26 wt % Mo and ▭, Fe–5 wt % Ti alloys, and lattice parameter curve – – × – – Fe–10 wt % Mo alloy against time of ageing at 550 °C (mean-square errors of H_v curves are from $\sigma = \pm 1.75$ to ± 2.08).

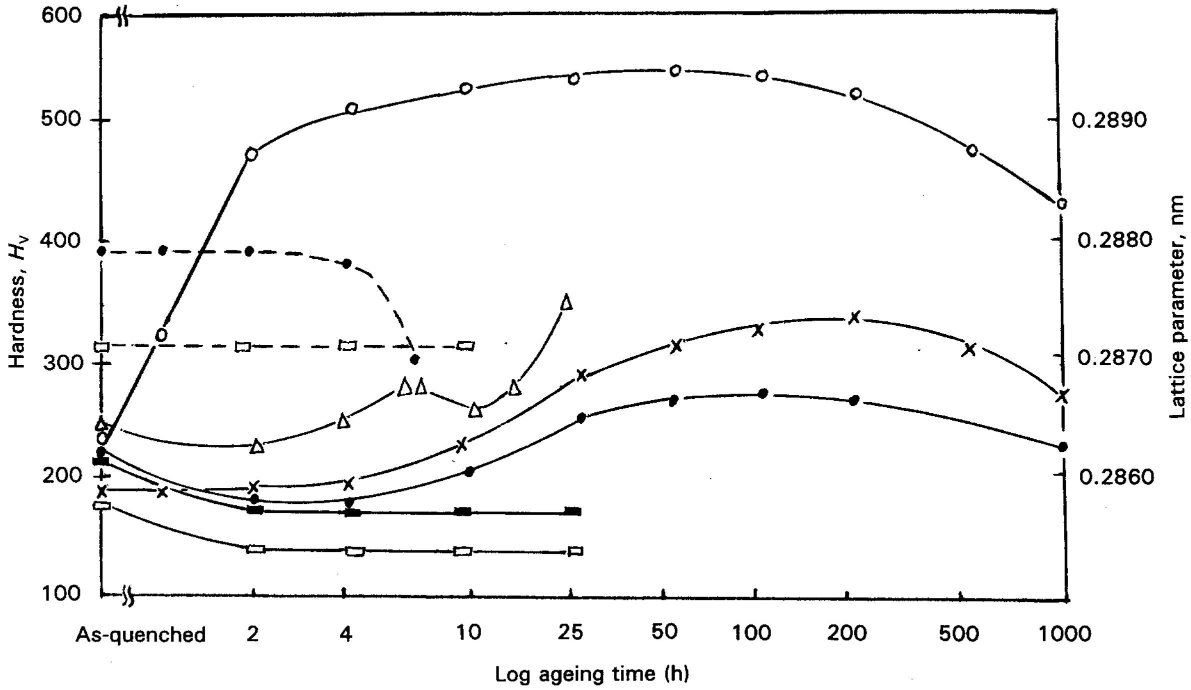

Figure 2 Age-hardening curves of Fe–×,10; ○,15 wt % Mo; Fe–□,1.5; ■,2.5; ●,5.0 wt % Ti and Fe–△,3.5 wt % Nb alloys, and lattice parameter curves of Fe---□--1.5; --●--,5.0 wt % Ti alloys against time of ageing at 600 °C (mean-square errors of H_v, curves are from $\sigma = \pm 1.41$ to ± 2.14).

(Fig. 4) and then in the bulk of the alloy (Fig. 5). It is likely that the Fe_2Mo particles nucleated heterogeneously either on dislocation, at the start of the ageing reaction or at the incipient interfaces in the tweed structure. The tweed structure eventually disappears completely. At the first appearance of Fe_2Mo particles, the lattice parameter of α–Fe begins to fall (see Fig. 1 for Fe–10 % Mo alloy) and the hardness curves begin to rise. Therefore hardening at ageing of the Fe–10, 15 and 20 % Mo alloys is the result of the process of Fe–Mo particle precipitation, rather than tweed structure formation.

With the increase of ageing temperature up to 600 °C, the maximum hardness of Fe–15 % Mo alloy is the same, but for Fe–10 % Mo, much lower than at 550 °C.

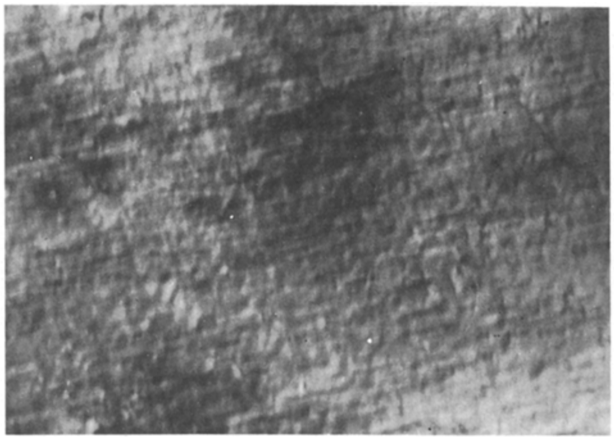

Figure 3 Tweed structure of Fe–15 wt % Mo alloy aged for 0.5 h at 550 °C (×80 000 with foil normal to [1 1 1]).

3.2. Fe–Ti alloys

At the early stages of ageing, the hardness of Fe–5Ti alloy at 550 °C, and Fe–2.5Ti, Fe–1.5Ti at 600 °C, is observed to decrease (Figs 1 and 2). With further ageing the hardness curves of Fe–2.5Ti and Fe–1.5Ti become parallel to the axis of ageing time (Fig. 1), but the curve of Fe–5Ti begins to rise and achieves the maximum after 50 h ageing (Fig 2).

Fig. 6 shows a typical microstructure of the alloys investigated at the stage of decrease in hardness. Many striations perpendicular to the < 1 0 0 > direction are observed. As this micrograph was taken at $\boldsymbol{g} = 200$, the striations are observed only along one direction perpendicular to the $\boldsymbol{g}$ vector. The period corresponding to hardness decrease and the tweed structure may be rather prolonged (for example, for Fe–2.5Ti and Fe–1.5Ti alloys up to 25 h). No streaks or satellite spots are seen in the electron diffraction patterns. A

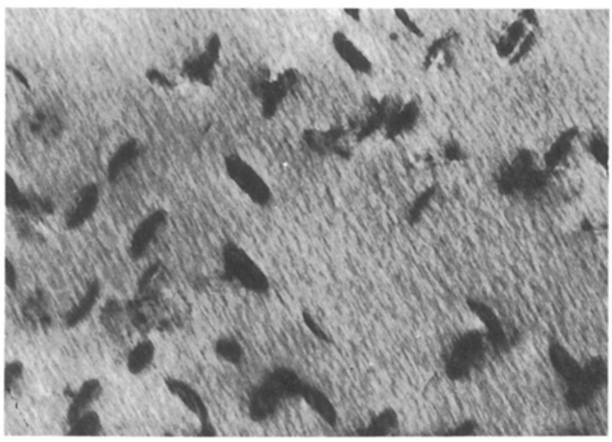

Figure 4 Tweed structure with Fe_2Mo particles. Fe–15 wt % Mo alloy aged for 15 h at 550 °C (×64 000 with foil normal to [1 1 3]).

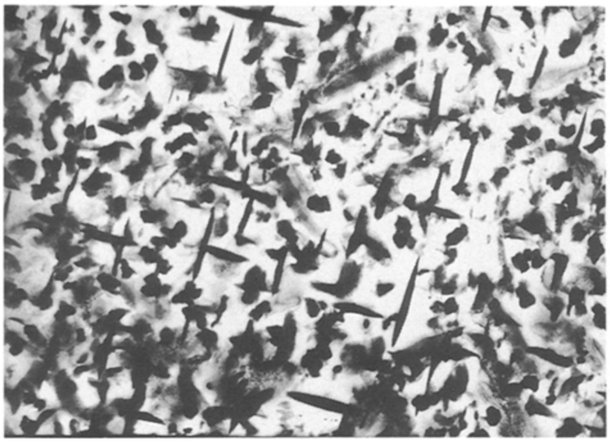

Figure 5 Fe_2Mo particles in the structure of Fe–15 wt % Mo alloy aged for 20 h at 550 °C (× 32 000 with foil normal to [0 0 1]).

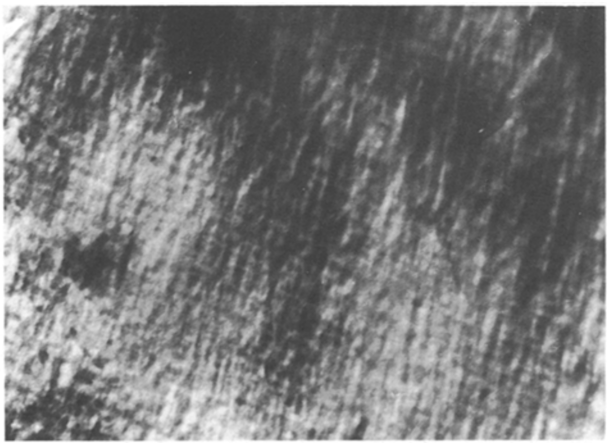

Figure 6 Tweed structure of Fe–2.5 wt % Ti alloy aged for 15 h at 600 °C (× 60 000 with foil normal to [0 0 1]).

lattice parameter of the solid solution determined by X-ray diffraction has no changes at the stage of hardness decrease (as an example, see the lattice parameter curve for Fe–1.5Ti alloy in Fig. 2). The two latter facts show that the tweed structure at the hardness decrease stage is not a two-phase structure, but is a solid solution with alloy-enriched and depleted clusters. Therefore the alloys of the Fe–Ti system, as well as the Fe–Mo system, decompose through the tweed structure stage, i.e. by a spinodal mechanism.

The microstructure of the Fe–5Ti alloy at the hardness increase stage is shown in Fig. 7a (the ageing temperature is 600 °C). Precipitate reflections in the electron diffraction patterns (Fig. 7b), identified as from the Fe_2Ti structure (Fig. 7c), are observed after 7 h ageing. The lattice parameter of the Fe–5Ti solid solution begins to fall at the moment when the hardness curve begins to rise. Therefore Fe_2Ti particle precipitation results in hardening, but a tweed structure formation results in softening. With further ageing the Fe_2Ti particles are gradually coarsened and the hardness curve rises up to its maximum and then begins to fall. Existing theories of hardening as a result of the precipitation process consider very fine precipitates as effective obstacles for dislocation movement in solids. Hardening by spinodal structures is

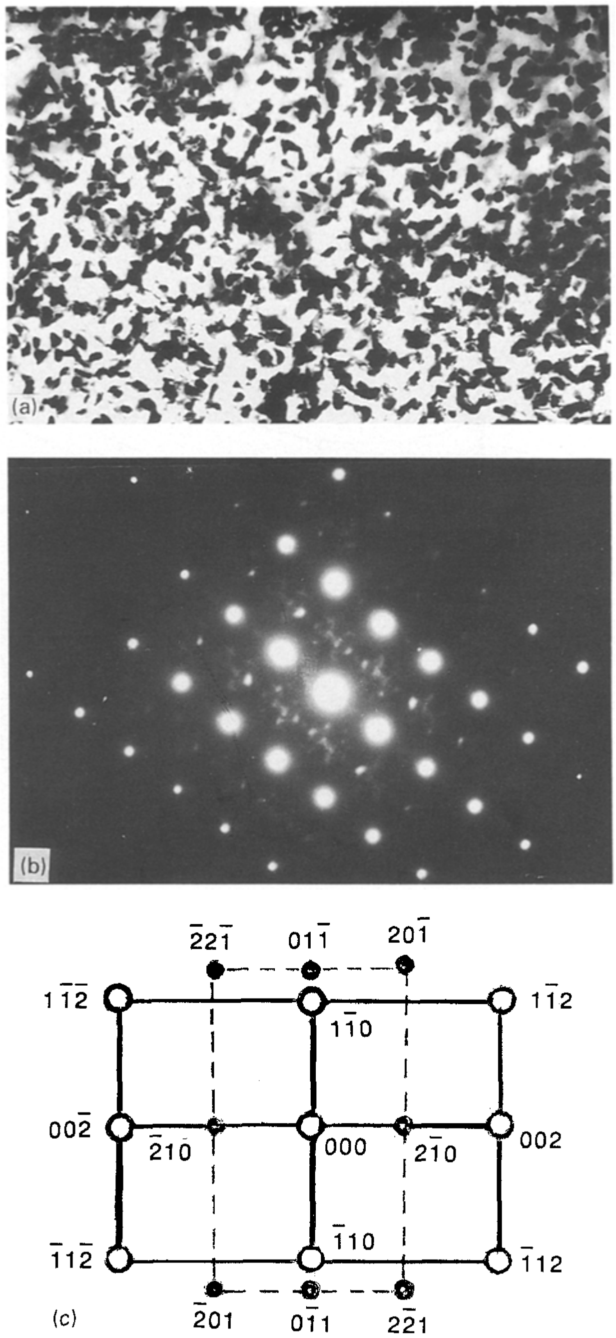

Figure 7 Fe_2Ti particles in (a) the structure (× 40 000) and (b) electron diffraction pattern of Fe–5 wt % Ti alloy aged for 7 h at 600 °C; (c) indexed schematic representation.

associated with the internal stress field, as well as lattice mismatch, the contribution of elastic inhomogeneity, the effect of interfacial energy and a mixed dislocation lying mainly on the positive regions of the internal stress [15]. There is no theory explaining the causes of hardness decrease at decomposition of solids as well as at the tweed structure formation. The tweed structure is an ordered, solid solution with periodic distribution of alloy-enriched and depleted clusters. It is known that any cluster is an obstacle for dislocation movement, and therefore must lead to hardening of a solid, as for example in Fe–Cr alloys aged at 475 °C. However, for Fe-Ti alloys the opposite is true: the clusters in a variety of tweed structures facilitate dislocation movement in the solid solution. This experimental fact requires theoretical explanation. This behaviour of the Fe–Ti alloys is not unique, but is also seen for the Fe–Nb system.

3.3. Fe–Nb alloys

The decomposition kinetics of Fe–3.5Nb and Fe–5Nb alloys are more complicated than in the case of the Fe–Ti alloys. A hardness curve shown only for Fe–3.5Nb has narrow and small maximum after 7 h ageing at 600 °C (Fig. 2). The structure at this moment of ageing represents solid and Nb-enriched disk-shaped dispersed particles creating around themselves fields of elastic stresses (Fig. 8). No streaks or satellite spots are observed in the electron diffraction patterns, confirming that the precipitates in Fig. 8 are clusters. Clusters are overcome by dislocations by the cutting-off mechanism, which is the reason why the maximum of hardness after 7 h ageing is not so high.

With further ageing, a short minimum of hardness takes place at 10 h of 600 °C ageing (Fig. 2). A tweed microstructure is observed at this period of ageing (Fig. 9). No streaks or satellite spots are observed in the electron diffraction patterns. This is identical in the Fe–Ti alloys: a tweed structure formation results in hardness decrease. Therefore the tweed structure facilitates dislocation movement in solid solutions of Fe–Nb alloys. With further progress of ageing at 600 °C, a tweed structure is decomposed and particles of the precipitates which lead to the hardening of alloys are formed (Fig. 10a). Indexing of the set of reflections on the electron diffraction patterns (Fig. 10b) shows that the precipitates are particles of the Fe_2Nb h c p phase.

Figure 8 Clusters of niobium atoms in the structure of Fe–3.5 wt % Nb alloy aged for 7 h at 600 °C (× 150 000 with foil normal to [0 0 1]).

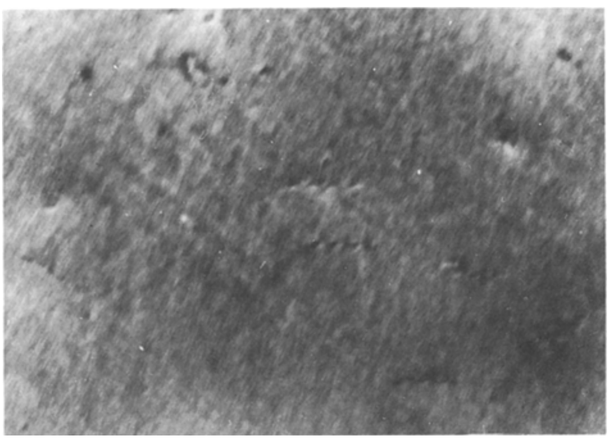

Figure 9 Tweed structure of Fe–3.5 wt % Nb alloy aged for 10 h at 600 °C (× 75 000 with foil normal to [1 1 0]).

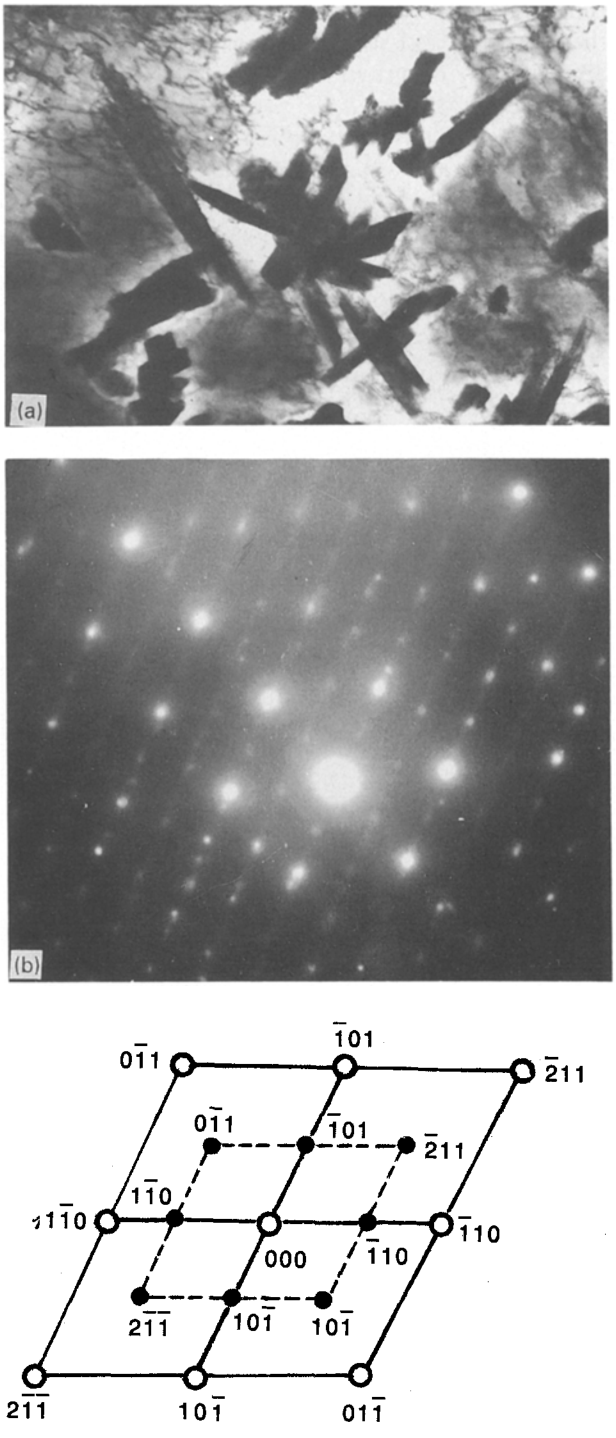

Figure 10 Fe_2Nb particles in (a) the structure (× 15 000) and (b) electron diffraction pattern of Fe–3.5 wt % Nb alloy aged for 25 h at 600 °C; (c) schematic representation.

4. Conclusion

The process of Laves phase precipitation at ageing of Fe–transition elements alloys always passes through the stage of tweed structure formation. The tweed structure is an ordered solid solution with periodic distributions of alloy-enriched and alloy-depleted clusters. Formation of the tweed structure before precipitation of the Laves phase is a proof of decomposition of the alloys by the spinodal mechanism.

A tweed structure formation at ageing of Fe–Mo alloys does not result in a change of hardness of the alloys, but in the case of Fe–Ti and Fe–Nb alloys it results in some decrease of hardness in comparison with the preceding state. Therefore a tweed structure is not an obstacle for dislocation movement any more than a disordered solid solution. The opposite situation usually occurs in the case of formation of another type of cluster — GP zones. Many experiments show that Guinier-Preston (GP) zones, being separate clusters on the $\{100\}$ matrix plane, result in hardening of the alloys. Thus the form of the clusters (either GP zones or tweed structure) has a great influence on their resistance to dislocation movement, and therefore on the hardness of the alloys.

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Received 18 March 1992
and accepted 9 September 1993