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Precipitation in solids

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The diffusional decomposition mechanism in solid solutions is discussed. The mechanism, despite the great variety of its morphological and kinetic peculiarities for different alloys, remains the same. Fundamental properties of large collections of particles are revealed and the physical aspects of the decomposition process are reported. Therefore, the division of phase transitions in solids into first and second orders, and the division of phase transitions of the first order into those decomposing by spinodal or nucleation-growth mechanisms are, to a certain extent, artificial and do not have adequate experimental confirmation. Proof is given that solid solutions decompose by the spinodal mechanism only, and thus they do not need to overcome the fluctuating energy barrier, as was supposed in nucleation-growth theory. The results given testify to the narrowness and lack of grounding of the generally assumed "linear" concepts of dynamics of phase segregation based on an exponential increase of small fluctuations; they also show that the incubation period before precipitation of a new phase in the solid is a process of "searching" by the system for a correlation distance (that is, the stochastic process being submitted to the laws of dynamic scaling).

1. Introduction

To date a large number of experimental results of studies of the phenomenon of diffusional decomposition of solid solutions have been reported. A few authors, however, have given a unique answer to the question of the decomposition mechanism. It is conditioned by the fact that though the well-known mechanisms of decomposition in alloys (spinodal and nucleation-growth) are theoretical alternatives, the morphology of the alloys supposedly decomposing by these two mechanisms actually does not differ. Even for early stages of decomposition there exist no clear distinctions in morphology. For instance, from Table I it becomes evident that the given "distinctions" in the morphology of the alloys decomposing by the spinodal or by the nucleation-growth mechanism are most likely distinctions between the early and later stages of decomposing, that is between the precipitation process and the process of coarsening. To define which period of decomposing is fixed (a period of nucleation or a period of coarsening) by morphological data, is difficult.

It is known that in a number of alloys, before precipitation of a new phase, Guinier–Preston (GP) zones form. It is generally considered that the existence of the zone stage, if zones are understood as described by Guinier [1], is evidence of the decomposition of an alloy by the spinodal mechanism. Guinier considered the main difference in the zones from the smallest precipitates of a new phase to be, in fact, that they have the same type of lattice as the matrix; the boundaries between the zones and the matrix are diffusional and thus completely coherent. Precipitates which have a different lattice from that of the matrix could also be completely coherent, thus both zones and precipitates can equally distort the matrix and, in a number of cases, lead to similar diffractional effects.

These peculiarities can be observed in the process of ageing of alloys when classical GP zones are precipitated, in Al–Cu, Al–Zn, Al–Ag, Fe–Be, etc. The same zones have been revealed in the decomposition of binary iron alloys, for example, in the systems of Fe–Mo, Fe–W, Fe–Ti, Fe–Cr, and others. It was shown [2–5] that before the precipitation of Fe_2Mo in the structure of Fe–(3.9–20.0) Mo alloys, molybdenum zones were formed. Having discovered modulated structure in the Fe–20 at % Mo alloys, and having found none in the Fe–13 at % Mo and Fe–15 at % Mo alloys, Miyazaki *et al.* and Kozakai *et al.* [6, 7] came to the conclusion that these alloys decompose by different mechanisms (by spinodal and nucleation-growth, respectively), and the change of one mechanism to the other occurs gradually according to Binder's theory [8].

Here we attempt to examine numerous structural results of the second-phase precipitation in solids. The question arises: is it possible to distinguish both spinodal and nucleation-growth mechanisms by structural methods? It appears that there is only one distinguishing feature: cluster (GP zones) formation in the structure before the second phase precipitation. Other structural differences are not proof of either precipitation mechanism. For example, modulated structures are often used as a proof of the spinodal mechanism because of its periodicity predicted by the Cahn's theory [15]. But this structure forms during the later stages of decomposition as a result of high elastic deformation when a new coherent phase precipitates in solids. For example, Kozakai and Miyazaki [7] showed that ageing of Fe–19.2 at % Mo at 570 and

TABLE I Some factors distinguishing the mechanism of nucleation-growth from the spinodal one

Nucleation-growth	Spinodal
From the moment of the critical nucleus formation the composition of the second phase does not change in time.	The continuous change of the composition of both phases takes place with time until equilibrium is not achieved.
From the moment of the critical nucleus formation the boundary between the phases is always sharp and incoherent.	The surface between the phases is initially quite diffusional and completely coherent; with time the boundary becomes gradually sharper, and coherence is broken.
The tendency to random distribution of particles in the matrix takes place.	The regularity in the distribution of the second phase, characterized by modulations, takes place.
The tendency to precipitation of incoherent spherical particles of the second phase takes place.	The tendency to precipitation of nonspherical coherent particles of the second phase takes place.
The incubation period before the critical nucleus formation takes place.	The incubation period is absent.

585 °C results in two very different structures, a typical modulated one and plate-shaped zones, observed along the ⟨1 0 0⟩ matrix direction. But in earlier stages of ageing, microstructural differences are absent: in both cases we were able to observe many fine striations perpendicular to the ⟨1 0 0⟩ direction and diffuse streaking associated with the ⟨2 0 0⟩ main reflection maximum, which results from the irregular periodic modulations of the composition in the matrix. This structure is usually termed "tweed" and occurs in irregular modulation of a composition but not in particles of the second phase.

Therefore, if GP zones are observed in the structure of solids before the second phase, the spinodal mechanism can be considered. However, if they are not observed there is no proof that they are absent, so no conclusions may be drawn. It may be that the structural methods used to find the zones were imperfect or that the ageing temperature was too high to fix this stage for a long time.

There is a great problem in distinguishing clusters (GP zones) and fine coherent particles of the second phase. First of all, we followed Guinier's lead and defined GP zones as clusters with the lattice being the same as solid solution, distorted due to alloy atoms but not having a new phase lattice. Fine coherent particles of both the second phase and GP zones distort conjugated areas of the matrix lattice, resulting in hardening of the alloys. Usually, streaking of the matrix spots, parallel to ⟨1 0 0⟩ directions was clearly visible in the electron diffraction patterns. Thus with the appearance of streaking in the electron diffraction patterns we can conclude only that some very fine particles resulting in strong tetragonal distortions of matrix were formed in the alloys.

To distinguish clusters from fine coherent particles of a new phase at the earlier stages of ageing it may be possible to use the well-known rule formulated by Guinier and Preston: the size of the unit cell in solid solution containing GP zones cannot considerably change if compared with that of the disordered solid solution of the same concentration, because the only difference between the two solutions is that the arrangement of solutes in the solvent is ordered or disordered. Therefore, precise measurement of the unit cell of the solid in the process of ageing is the best method (together with electron and field-ion microscopies) to distinguish clusters from the finest coherent particles of the new phase.

We shall consider two systems which have clear differences in their chemical nature: for example, the Fe–Cr system has positive deviations from Raoult's law and therefore segregation occurs in these alloys. The Fe–Mo system has negative deviations and therefore ordering occurs in it. Our results, and those of other authors are reported here.

2. Experimental procedure

High-purity raw materials were used to produce the alloys in a small induction furnace under an argon atmosphere. The compositions of the iron alloys examined was 10, 15 and 20 at % Mo and 10, 20, 30 and 40 at % Cr. The melts were homogenized at 1300 °C, then forged to 12 mm square bars. Specimens for hardness tests, electron microscopy, field-ion microscopy, X-ray and Mössbauer spectroscopy were cut from the bars. All specimens were austenitized at 1300 °C in a barium salt for 4 h, quenched into iced water and then in liquid nitrogen. They were tempered at 550 and 500 °C for up to 1000 h in a salt bath. Vickers hardness measurements were made after each tempering treatment between 0.1 and 1000 h. The foils were electrolytically thinned for examination by transmission electron microscopy and electron diffraction using an accelerating potential of 100 kV. Field-ion microscopy specimens were prepared by a two-stage process. The first stage involved producing a "neck" in the specimens by a.c. polishing. The second stage involved d.c. polishing through this "neck". Neon was employed as the image gas. Micrographs were obtained on microchannel plates. The lattice parameter of Fe–M solids was determined by X-rays using the 2 1 1, 2 2 0 and 3 1 0 reflections; unit cell dimensions were measured to within ± 0.000 05 nm.

Mössbauer spectra were recorded using a Mössbauer spectrometer and 4.096 multichannel analyser, the source was 20 mCi ^{57}Co in chromium. Each spectrum involving 3×10^5 counts per channel was performed in the regime of constant acceleration. M atom cluster formation within binary Fe–M solid solutions was studied by Mössbauer spectroscopy. For this purpose the parameter α_0 was suggested [9]

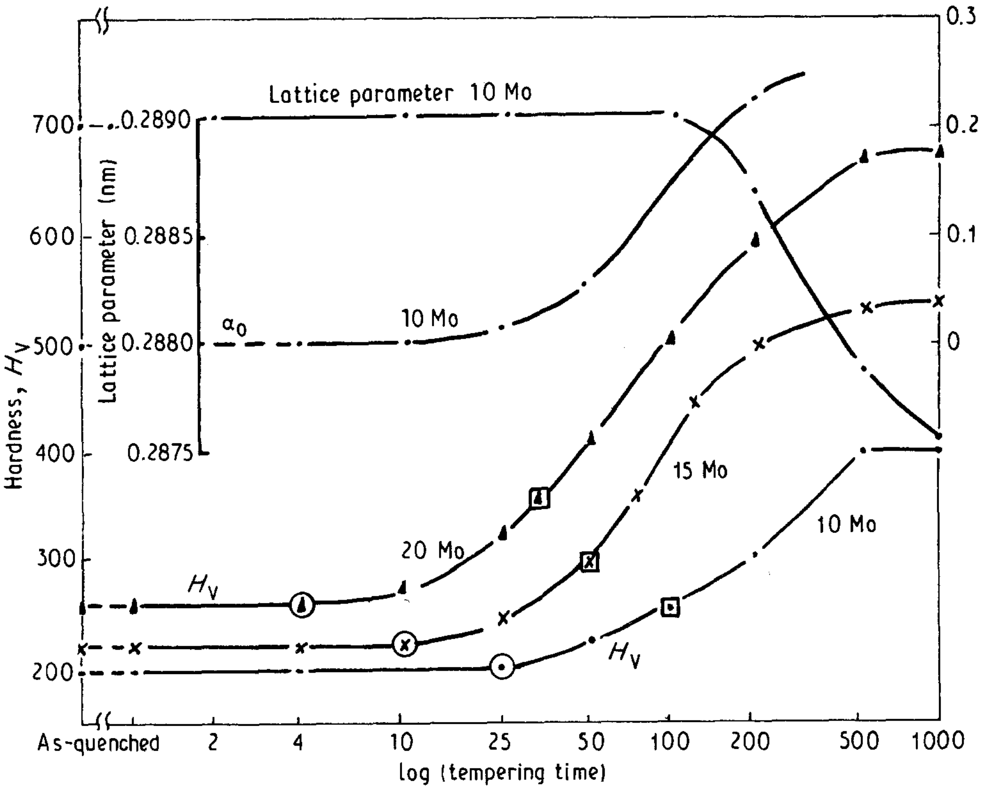

Figure 1 Change in hardness of Fe–10Mo, Fe–15Mo and Fe–20Mo alloys quenched from 1350 °C into water during ageing at 550 °C. (☐) The moment of Fe_2Mo precipitation, (○) formation of tweed structure. The lattice parameter of the solid and α_0 are shown for the Fe–10Mo alloy only.

$$\alpha_0 = 1 - K(n_i = 1, 2, \ldots)/W(n_i = 1, 2, \ldots) \quad (1)$$

where $K(n_i = 1, 2, \ldots)$ and $W(n_i = 1, 2, \ldots)$ are the fractions of iron atoms having no M neighbours in the i coordinate sphere, the former were derived experimentally for the conditions investigated and the latter calculated by statistical distribution of species.

3. Results

3.1. Fe–Mo system

The hardness curves of the alloys investigated are shown in Fig. 1 in the form of ageing time at 550 °C. They look similar to the hardness curves given by Miyazaki *et al.* [6] for the alloys with larger contents of molybdenum atoms. Consider the structural peculiarities of decomposition in the example of an Fe–10 at % Mo alloy as a rather dilute alloy. The lattice parameter of α-solid and α_0 parameter of Fe–10Mo alloy are also shown in Fig. 1.

During the period of ageing when the hardness, the lattice parameter of the solid and α_0 parameter of Fe–10Mo do not change at all, i.e. at an ageing time less than 10 h, field-ion microscopy shows that no clusters of molybdenum solutes in the solid are observed (Fig. 2). The electron diffraction patterns at this period ageing time are without peculiarities too.

With a longer ageing time (10–25 h) the increase in α_0 parameter begins, the hardness and the size of the unit cell of the solid do not change. Increasing α_0 results in the onset of the clustering process. In fact, field-ion microscopy allows observation of very small clusters of molybdenum atoms (Fig. 3). The electron diffraction patterns at these moments are without peculiarities. At the ageing time when hardness begins to increase, and α_0 continues to rise, the lattice parameter of the solid does not change. In the electron diffraction pattern streaking of the iron matrix, spots parallel to ⟨1 0 0⟩ directions were clearly visible, the electron micrographs also showing tweed structures (Fig. 4).

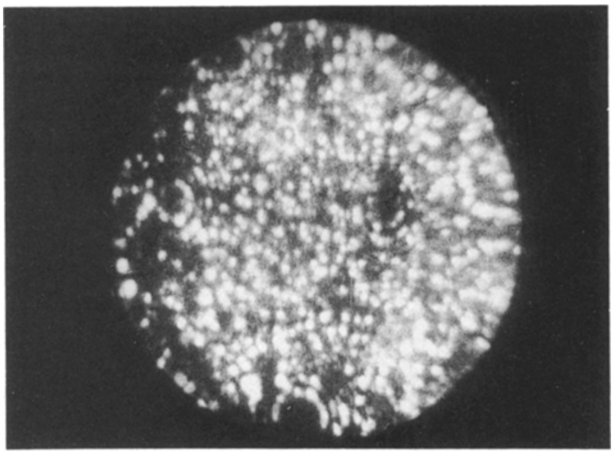

Figure 2 Field-ion micrograph of Fe–15Mo alloy aged at 550 °C for 4 h: no contrast of clusters is evident.

Comparing the experimental evidence from field-ion microscopy and Mössbauer spectroscopy, showing the formation of molybdenum clusters in the solids, and electron microscopy indicating no second phase reflexes from the tweed structure, and if X-ray measurements of the α-Fe lattice parameter are quite unchanged, the conclusion may be drawn that during

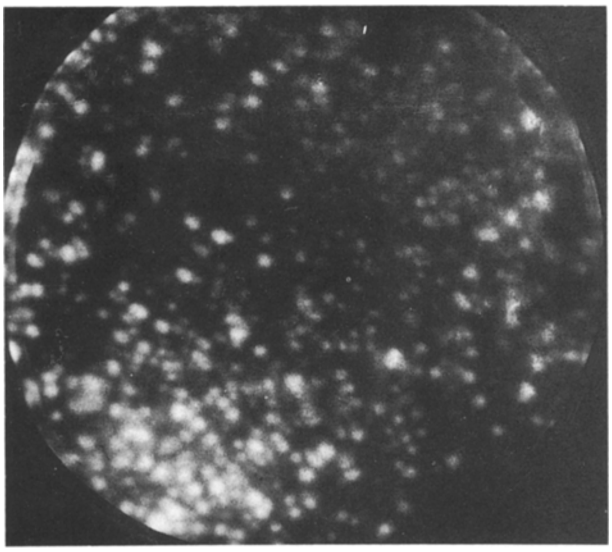

Figure 3 Field-ion micrograph of Fe–15Mo alloy aged at 550 °C for 10 h: a cluster of molybdenum atoms can be seen.

the period from 25–100 h, molybdenum clusters are not the second phase, because they have a lattice similar to that of the matrix, i.e. b c c. Naturally, the lattice inside and around the clusters is distorted resulting in streaking in the electron diffraction patterns.

The moment of ageing when the tweed structure is first observed on the electron micrographs of the alloys investigated is shown on HV curves by circles (Fig. 1). These points coincide with the very beginning of the increase in hardness. At the point of ageing when the hardness curves of Fe–10 at % Mo alloy continue to increase, the lattice parameter of the solid begins to fall. As discussed earlier, this is evidence of second-phase formation in the solid. Plate-shaped particles can be seen in the electron micrographs with their reflections in the electron diffraction patterns (Fig. 5). It becomes clear that the particles are second phase with their own lattice. The moment of ageing at which the lattice parameter of the solid begins to fall and thus second phase formation begins, is shown on the HV curves by squares (Fig. 1).

3.2. Fe–Cr system

It is known that Fe–Cr alloys show positive deviations from Raoult's law at any composition and, therefore, there is a tendency for chromium atoms to surround themselves by chromium atoms only, i.e. segregation occurs. However, in the region of equal composition in the *T–c* diagram, σ-phase forms. This indicates that the chemical relations between iron and chromium atoms are reversed when the composition changes. It

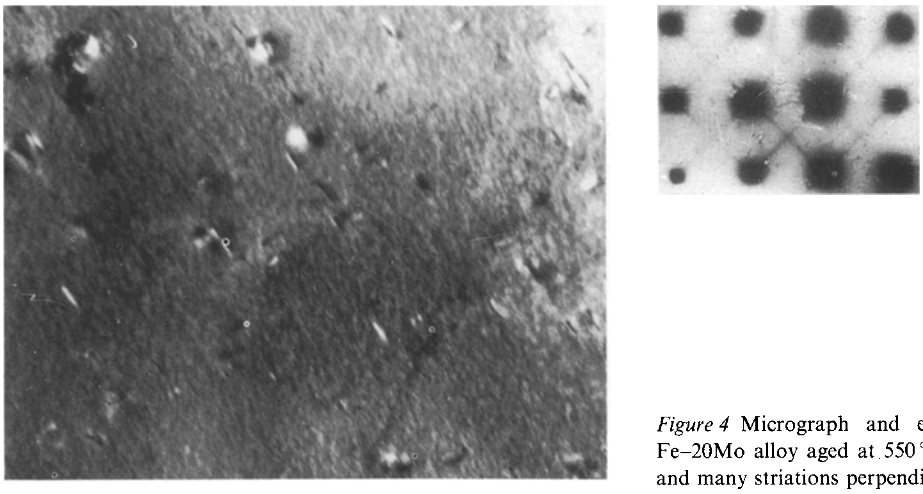

Figure 4 Micrograph and electron diffraction pattern of the Fe–20Mo alloy aged at 550 °C for 25 h, showing tweed structure and many striations perpendicular to the [1 0 0] direction.

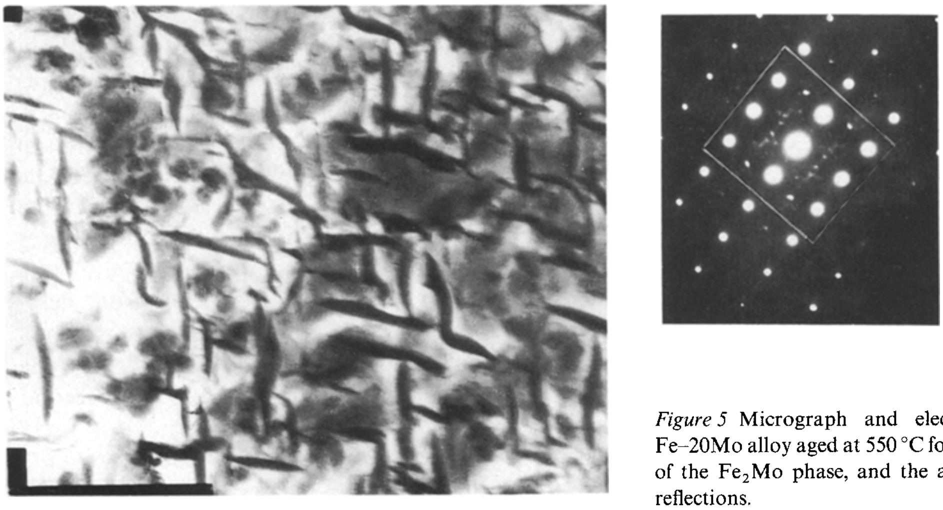

Figure 5 Micrograph and electron diffraction pattern of the Fe–20Mo alloy aged at 550 °C for 100 h, showing plate-like particles of the Fe_2Mo phase, and the additional system of Fe_2Mo phase reflections.

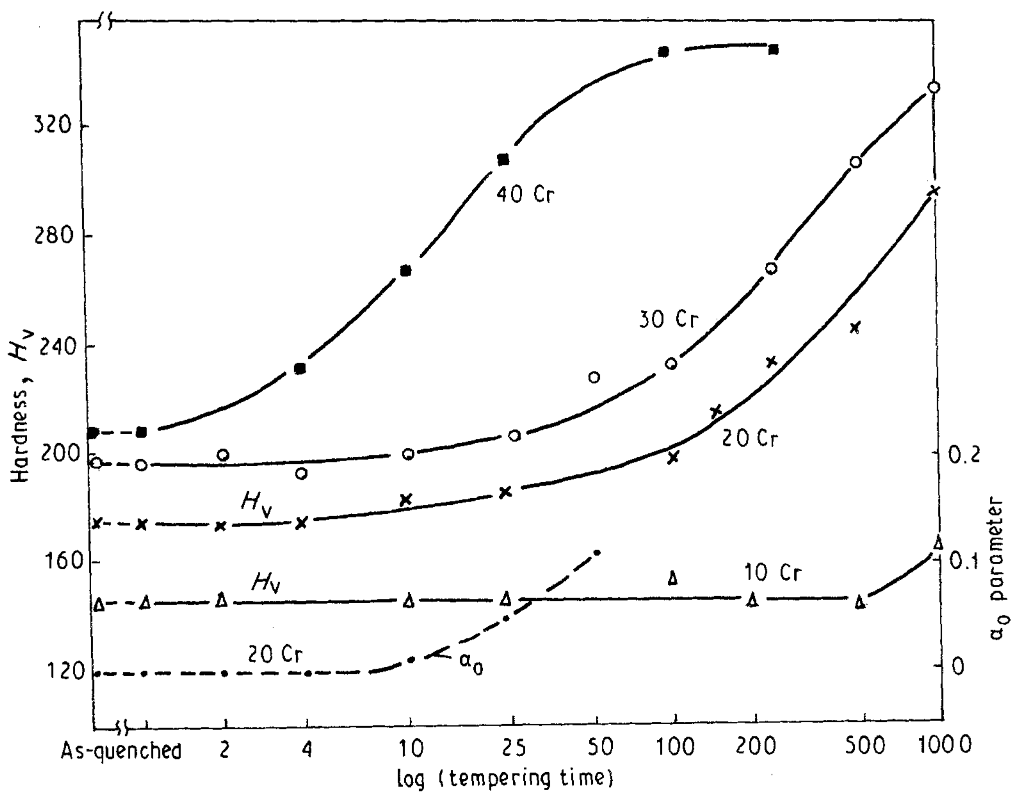

Figure 6 Change in hardness of Fe–10Cr, Fe–20Cr, Fe–30Cr and Fe–40Cr alloys quenched from 1250 °C into water during the process of ageing at 500 °C. α_0 is shown for Fe–20Cr alloy only.

is difficult to believe that it is possible for the chemical nature of the Fe–Cr interaction may be changed from repulsion to attraction. In fact, our structural investigations and those of Lagneborg [10] did not find any σ-phase in the Fe–Cr system.

In Fe–(25%–40%) Cr alloys neutron diffraction analysis showed spherical (radius ~ 2 nm) zones, containing chromium atoms only [11]. With smaller quantities of chromium, the zones consisting of chromium atoms only were not revealed, however, the chromium-rich regions were found by Mössbauer spectroscopy. It was concluded that the zones in the Fe–Cr alloys are formed by the spinodal mechanism [11]. Lagneborg [10] analysed the structure of decomposing Fe–30Cr. His electron diffraction patterns of the structure show that after annealing at 475 °C the shape of the particles is spherical, and at 550 °C they are disc-shaped. Using these data and noticing that the decomposition is a much slower process at 475 °C than at 550 °C (which is quite natural as the temperature is lower), Lagneborg concludes that at 475 °C the decomposition occurs by the spinodal mechanism and at 550 °C by the nucleation-growth mechanism.

The hardness curves of the Fe–Cr alloys investigated are shown in Fig. 6 for 500 °C ageing with time. They appear to be the same as the hardness curves of Lagneborg. α_0 of the Fe–20Cr alloy is also shown in Fig. 6. Increase in α_0 begins after about 8 h 500 °C ageing; increase in the hardness of the Fe–20Cr alloy begins some time later, i.e. ~ 10 h. It is clear that chromium-rich clusters appearing in the solid result in an increase in the hardness.

At present there is no doubt that Fe–Cr alloys decompose by the spinodal mechanism only and, in this case, clusters appear at the very beginning of ageing, resulting in increasing hardness. The delay of 8–10 h ageing time is surprising and unexplained.

4. Discussion

4.1. Ordering and segregation

It is well-known that there are negative deviations from Raoult's law in Fe–Mo solids and consequently they must show a tendency to short-range ordering. In these cases when the composition of Fe–Mo solids is far from stoichiometric, this tendency may result in molybdenum clustering and later in the formation of Fe_2Mo phase in local volumes of alloys only. Fe–Cr alloys have positive deviations from Raoult's law and at a certain ageing temperatures segregation is observed there. Therefore, in both cases, clusters of solutes are formed.

On considering the above results, one can draw a quite definite conclusion: independent of the sign of the deviation from Raoult's law, the decomposition process in all the solids with non-stoichiometric composition begins with clustering of atoms of the second component and occurs by uphill diffusion, that is the following ratio takes place: $D_{ef} < 0$, and, therefore, $\partial^2 f(c)/\partial c^2 < 0$.

In solids of non-stoichiometric composition, the process of new phase precipitation may be divided into two stages: (1) the formation of clusters of solutes by uphill diffusion; (2) if during the process of annealing the composition of the clusters reaches the stoichiometric composition of the new phase, the formation of the lattice of such a phase takes place. When the composition of clusters does not reach the stoichiometric composition of the new phase, the second stage in the process of phase formation is not realized. The first stage of the process (the formation of clusters of solutes) kinetically and morphologically is similar to the segregation process, analogous to the concentration in alloys with positive deviations from Raoult's law, although the final composition of such clusters is different.

There may be a case when the time and temperature of tempering are insufficient for the completion of diffusion resulting in the formation of A_mB_n phase in local volumes of the matrix. Then clusters of solutes only are fixed, and the latter differ insignificantly from the clusters formed as a result of the segregation in solids, having positive deviations from Raoult's law. If diffusional processes bring the system with negative deviations to the equilibrium state, then the composition of clusters gradually approaches the composition of the A_mB_n phase. The lattice in the clusters is increasingly distorted as a result of redoubling the concentration of the solutes in the clusters. Such distortions of the lattice within clusters gradually increase until their structure is described by the new lattice corresponding to the structure of the A_mB_n phase.

In the case when the composition of the alloy, having negative deviations, is in the one-phase region of the phase diagram, clusters may be observed in which the concentration of the solutes will never reach the composition of the A_mB_n phase. Thus the clusters in the structure of such alloys are the final product of decomposition and they differ insignificantly from the clusters formed as a result of segregation.

Thus, in non-ideal binary solids of non-stoichiometric composition, clustering occurs during annealing regardless of the sign of their deviation from Raoult's law. Such clusters may be both the final product of decomposition (we shall call them clusters of the first kind) and intermediate products en route towards second-phase formation (we shall call these clusters of the second kind).

The tendency of alloys to ordering or segregation defined by the sign of deviation (plus or minus) in the behaviour of alloys from Raoult's law is the chemical driving force of decomposition. The final results to which this tendency brings us, depend on the chemical affinity, composition, time and temperature of ageing and that is why it may differ for different situations.

4.1.1. Signs of f(c)

The nucleation-growth mechanism is known to be realized due to fluctuations only, the process of the formation of critical nuclei being possible even if there is no chemical interaction between the elements, that is the latter is possible on condition that there is a tendency neither to segregation nor ordering. In fact practically all binary metallic systems are non-ideal and the signs of their deviations from Raoult's law are constantly preserved over the whole range of compositions. This indicates that when decomposition of such systems occurs the tendencies to either segregations or ordering are realized for any composition including those which are situated in the region where, according to theory, the nucleation-growth mechanism must occur.

At present, $f(c)$ for the decomposition of solids is conventionally presented as a curve with two minima and one maximum. It is considered that the spinodal mechanism takes place in the region where $f(c)$ is convex ($\partial^2 f(c)/\partial c^2 < 0$) and the mechanism of nucleation-growth works where $f(c)$ is concave. At critical points, where $\partial^2 f(c)/\partial c^2 = 0$, the substitution of the decomposition mechanism by another, substitution of the direction of diffusion by the opposite one, takes place.

As shown by Langer [12] in the case where $f(c)$ is described by the curve with convex and concave regions, it cannot represent the true free energy of the system. The true free energy must be a convex function of the composition only [13].

Langer's conclusions about the shape of $f(c)$ are supported by the following points. It is known that in approximation of regular solids the chemical potential, μ_i, is bound with the free energy for a particle of the system, $f(c_i)$

$$\mu_i = [\partial f(c_i)/\partial c_i]_{T,P} \tag{2}$$

Hence, it follows that

$$\begin{aligned} \partial^2 f(c_i)/\partial c_i^2 &= \partial \mu_i/\partial c_i \\ &= k_B T/c_i(1 - c_i) - 4zE_{\text{mix}} \end{aligned} \tag{3}$$

and it is possible to evaluate at what relations between thermodynamic and thermic constituents the sign of the second derivative of the free energy with respect to the concentration will be positive and at what it will be negative.

Three cases are considered.

1. $k_B T < 4zE_{\text{mix}} c_i(1 - c_i)$. Here correlation effects in the distribution of neighbours prevail over heat energy and, therefore, the process of a new phase formation proceeds. All the components in this relation are always positive except E_{mix}, which may be positive (segregation) or negative (short-range ordering). Let us analyse the situation at different signs of energy of mixture.

(a) $E_{\text{mix}} > 0$. In our case above, $k_B T - 4zE_{\text{mix}} c_i (1 - c_i)$ will always be negative; therefore, $\partial^2 f(c_i)/\partial c_i^2 < 0$ and $f(c)$ is a convex function.

(b) $E_{\text{mix}} < 0$. In this case $\partial^2 f(c_i)/\partial c_i^2$ in Equation 3 must be positive and $f(c)$ must be concave.

Thus, we conclude that clustering in non-stoichiometric solids with negative deviations from Raoult's law should take place by the "normal" ($D_{\text{ef}} > 0$) diffusion. In fact, clustering in a random solid is possible by uphill diffusion only, then in this case $\partial^2 f(c_i)/\partial c_i^2$ should be negative and therefore, E_{mix} should not have a negative sign. It is concluded that clustering in non-stoichiometric solids does not depend on the sign of the energy of the mixture, but it does depend on the absolute value of the energy only. Then Equation 3 is

$$\partial \mu_i/\partial c_i = k_B T - 4z|E_{\text{mix}}| c_i (1 - c_i) \tag{4}$$

Consequently, the concentration dependence of non-equilibrium free energy must be convex, if clusters form in a non-stoichiometric solid having negative deviations from Raoult's law. This is a most essential point to our considerations and which has not been regarded properly before.

2. $k_BT > 4zE_{mix}c_i(1 - c_i)$. In this case Brownian motion prevails over the ordering processes (high-temperature region) and irrespective of the E_{mix} sign, $\partial^2 f(c_i)/\partial c_i^2$ will always be positive, i.e. $f(c_i)$ is a concave curve.

3. $k_BT = 4zE_{mix}c_i/(1 - c_i)$. This case refers to the state representing the boundary between the high-temperature region with random distribution of atoms, and the low-temperature region, in which correlation effects in distribution prevail.

4.2. Precipitation kinetics

Let us consider the kinetics of $f(c_i)$ variation for the phase diagram of the AB system, with a negative energy of mixtures. On lowering the temperature the second phase is precipitated from the solid. The T–c diagram is shown in Fig. 7. Below the solidus line all the compositions in the equilibrium state are α-solids. At c_a and $T < T_2$ the equilibrium state of the system represents phase A_mB_n which is formed by long-range ordering of the α-solid in all the bulk alloy. In the range of the compositions limited by c_3ac_1 and c_2ac_4 curves, the final state of the system which is approached at $t \to \infty$, represents an inhomogeneous solid with clusters of solutes having the same type of lattice as the depleted solid. Usually such a state is known as the K-state. By analogy, this is marked on the T–c diagram (Fig. 7).

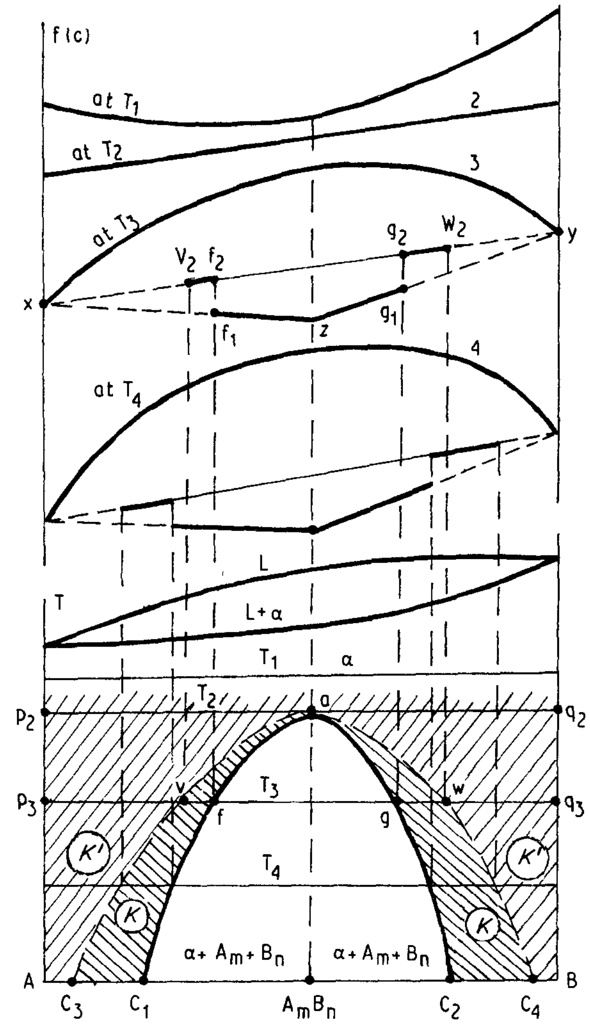

Figure 7 The concentration dependences of non-equilibrium and equilibrium free energies during the decomposition of the alloys of the A–B system with negative deviations from Raoult's law: the phase diagram of the system. All indexing is given in the text.

The final state of the alloys of the A–B system in both ac_3Ap_2 and ac_4Bq_2 segments of the T–c diagram is a homogeneous solid despite the fact that $k_BT < 4z|E_{mix}|c_i(1 - c_i)$. This situation can be understood if we consider clustering formation in solids. Let us analyse Langer's equation of the structure factor

$$\frac{\partial S(\boldsymbol{\beta}, t)}{\partial t} = -2M\beta^2(f'' + x^2Y + K\beta^2)S(\boldsymbol{\beta}, t) + \sum_{n=3}^{\infty} \frac{f}{(n-1)!} S_n(\boldsymbol{\beta}, t) - 2Mk_BT\beta^2 \quad (5)$$

where $S_n(\boldsymbol{\beta}, t)$ is the Fourier representation from

$$G_n(r, t) = \langle \eta^{n-1}(r_0 + r, t)\,\eta(r_0, t)\rangle \quad (6)$$

in which elastic stresses caused by decomposition are also taken into account. In Equation 5, the nucleation-growth mechanism is not described (though all constituents of free energy are considered in it) because when $f''(c_i)$ is positive the sign of $\partial S(\boldsymbol{\beta}, t)/\partial t$ will never be positive. Hence, for the case of nucleation-growth, Equation 5 has no physical meaning.

If a completely random non-stoichiometric solid produced as the result of quenching at high temperatures is heated to a temperature sufficient for the diffusive mobility of substitutes, then the process of uphill diffusion begins in it resulting in the formation of clusters. Here, it should be noted that the system "does not know" the size of clusters and the correlation distance between them (the minimum distance between the precipitates for the given composition of the alloy and temperature of ageing). The decomposition may be irreversible if this distance is reached. Such a size and a distance must be "found" by the system.

As $f''(c_i) < 0$, and all the other terms in brackets in Equation 5 are positive, it means that clustering caused by a chemical potential difference is opposed by elastic and gradient components, and also Brownian motion.

In the initial stage of annealing the atom distribution will be most probably and rapidly obtained when the decrease in ΔF is minimum, i.e. roughly speaking, when two nearest-neighbour identical atoms form a "cluster". The lifetime of such a "cluster" is comparable with the time of its formation, i.e. it is represented as a fluctuation formed, however, not as a result of random Brownian motion of B atoms, but as a result of the tendency of the A–B system to decrease the chemical potential difference between its states with ordered and random distribution of atoms. At that moment there actually appears a sinusoidal distribution of B atoms with the wavelength $\lambda_1 = \lambda_{min} \to 0$. Such a sinusoidal distribution of impurities cannot be homogeneous at the expense of both percolation phenomena, various bifurcations and also because of the fact that it takes place in a real alloy, but not in a structureless continuum. The formation of such fluctuations causes the growth of gradient energy in the alloy at the expense of growth of β, and elastic energy at the expense of growth of x. Therefore, Langer's relation

$$f''(c_i)S(\boldsymbol{\beta},t) > (x^2Y + K\beta^2)S(\boldsymbol{\beta},t) + k_BT \quad (7)$$

satisfaction of which is necessary for the continuation of the decomposition process, for high values of β stops functioning and the initially formed distributions of B atoms with λ_{min} will have to decompose. At such fluctuations in dissolution both the gradient and elastic components in Equation 7 decrease and again conditions appear for realization of Equation 7. The non-uniform character of formation and, as stated above, dissolution of the sinusoidal distribution of atoms will lead to the situation when at the moment Equation 7 is satisfied, a new sinusoidal distribution of B atoms will never be an exact copy of the previous one, the wavelength, λ_2, will be more than λ_1, and the sizes of the fluctuations will be higher. Again during the formation of such a distribution gradient, elastic components will grow in Equation 7, and once more at a certain stage the realization of Equation 7 will be impossible. Atom distribution, having formed at the moment of t_2, will begin dissolving and further in its place a new distribution of atoms B would appear with another wavelength, $\lambda_3 > \lambda_2$, etc. Such cycling (formation–dissolution–formation of fluctuations–, etc.) is repeated, any new distribution being different from the previous one by the growth of the amplitudes and the wavelength of the fluctuations, until at t_m the wavelength reaches λ_m corresponding to the so-called correlation distance. Having reached this distance, the fluctuations can exist as long as possible, i.e. represent clusters which may be fixed by structural methods.

Equation 5 for the structural factor $S(\boldsymbol{\beta},t)$, describing the start of the decomposition process, is invariant when β and t change at the same time. So this equation satisfies the relation of dynamic scaling. It is correct only when the system is in the state of "searching" for the correlation distance which is so much larger than the microscopic length (for example, lattice spacing). Therefore, dynamic scaling may be employed to relax the system over a distance far from equilibration, as first reported by Binder and Stoll [13].

Dynamic scaling is explicitly revealed when a non-ideal solid, random after quenching, is given a chance to relax but it is not shown the way to do it. As a result, a "search" begins for the correlation distance, that is the minimum distance between the clusters of such a composition and such sizes that when this state is reached the structure factor $S(\boldsymbol{\beta},t)$ becomes positive and does not further change its sign, i.e. stable clusters appear in the system.

The correlation distance and its attainment rate are constants for each alloy at the annealing temperature. An increase in temperature leads to an increase of the correlation distance and its attainment rate as the result of the growth of diffusional mobility of the atoms. The increase in B atom concentration in the A–B alloy decreases the correlation distance and the time required for its "search". Hence, the closer the composition of the alloy to stoichiometric and the higher the temperature of annealing (i.e. a two-phase region of the diagram), the shorter is the period of "search"; at certain T and at $c_B \rightarrow c_B^{st}$ the latter may become so short that it will not be found by experimental methods.

4.3. Incubation period

It is known that Mössbauer spectroscopy is able to resolve the smallest deviations of a solid from a fully disordered state and, therefore, if clusters appear in the solid, α_0 must increase. In Figs 1 and 6 it can be seen that the hardness curves of the alloys investigated do not increase for a long ageing time, depending on the composition and temperature. Let us term this period the incubation period. The field-ion micrographs confirm that there are no clusters in the incubation period (see Fig. 2) which is usually considered to be direct proof of such a system's decomposition by the nucleation-growth mechanism, because the presence of the incubation period cannot be explained by Cahn's theory of spinodal decomposition. The tweed structure (Fig. 4) representing irregular modulations of the composition (but not precipitates) first appeared in the electron micrographs after 4, 10 and 25 h ageing for Fe–20Mo, Fe–15Mo and Fe–10Mo alloys, respectively (Fig. 1). The distance between the modulations of composition measured, for example, in the electron micrographs of the Fe–15% Mo was $\sim 5 \times 10^{-6}$ cm. The effective coefficient of diffusion of molybdenum atoms at 550 °C, $D_{eff} \simeq 10^{-11}\ \mathrm{cm^2\,s^{-1}}$, permits atoms of molybdenum to cover half the distance between neighbouring modulations in about 2 s but not for 10 h, as the experiment yields. Therefore, the delay in tweed structure formation cannot be explained by kinetic reasons.

We come to a paradoxical conclusion that alloys decomposing by the spinodal mechanism (there being no doubts about the Fe–Cr alloys) have the incubation period of decomposition. Apparently, the incubation period is the specific state of the alloy, far from equilibrium, in which changes accumulate gradually. Having reached a certain value (the correlation distance), the system is to decompose. It becomes clear why at early stages of clustering we cannot find the sinusoidal distribution of solutes, as predicted by Cahn. Apparently, from the very beginning of ageing, the sinusoidal distribution, aggravated by bifurcations, occurs with an ever increasing wavelength and disappears again, according to scaling laws. So it transforms to a type which in no way resembles Cahn's sinewave.

From the points mentioned above, we can realize why in the ac_3Ap and ac_4Bq portions of the T–c diagram the final state represents a homogeneous solid, despite the fact that in these portions of the diagram $k_BT < 4z|E_{mix}|c_i(1 - c_i)$. The system under consideration seems to be in the fluctuating regime of the correlation distance "search"; although the latter can be reached thermodynamically, practically it turns out to be unachievable. Let us mark these portions in the diagram as the K′-state. We can see that the incubation period in spinodal decomposition has some features resembling those of the nucleation-growth mechanism (fluctuating regime of the correlation distance "search", i.e. in other words, the nuclei of a "critical size") although it does not require overcoming the energy barrier.

4.4. Evolution of $f(c)$

Consider the evolution of $f(c_i)$ under the conditions of transition of the system from a non-equilibrium to an equilibrium state (Fig. 7). Suppose that all the alloys of the system were heated to T_1, corresponding to a one-phase state α-solid. In this case the concentration dependence of the equilibrium free energy is represented by a concave curve 1. On lowering the temperature in the one-phase region of the diagram, the concavity of the $f(c)$ curve diminishes and at $T_2 = T_a$, the $f(c)$ dependence will give a straight line.

Suppose that the alloys of the AB system heated to T_1 were sharply quenched to T_3 (so that at the time of cooling no diffusional processes took place). In this case the concentration dependence of the non-equilibrium free energy at $t = 0$ will be represented by a convex curve 3 with the relation $\partial^2 f(c)/\partial c^2 < 0$. After a prolonged ($t \to \infty$) relaxation at T_3 the concentration dependence of the equilibrium free energy should represent a broken line xzy with the minimum at point z, where A_mB_n is formed throughout the total volume of the alloy. Lines xz and zy imply the concentration dependence of the free energy of the two-phase mixture A_mB_n and the solid. As seen from the T–c diagram, however, the two-phase region at T_3 can exist in the range of c_f–c_g compositions only, the free energy can approximate its equilibrium values at T_3 within the range of these compositions only. The f_1zg_1 part of the xzy line in the $f(c)$ diagram is shown by a solid line. The parts xf_1 and yg_1 are represented by a dotted line in Fig. 7. These parts correspond to the equilibrium values of $f(c)$ which could be reached at c_A–c_f and c_B–c_g if these compositions are presented in the two-phase region of the diagram.

The equilibrium level of free energy represented by xzy at T_3 can be reached through a number of intermediate states. One such state is shown by the straight line xy, the part of which $v_2f_2g_2w_2$ characterizes the free energy of the mixture of enriched and depleted regions, clusters of the second kind being formed in the part c_f–c_g, those of the first kind being formed in parts c_v–c_f and c_g–c_w. Portions c_3ac_1 and c_2ac_4 of the phase diagram in which clusters of the first kind form, present regions of K-state.

c_A–c_v and c_B–c_w compositions of the solid at T_3 are in the oscillation state of the correlation distance "search" as long as possible, because the B atom concentration is low. Under these temperature–concentration conditions the equilibrium state could be achieved thermodynamically, but not kinetically.

Fig. 7 also shows the concentration dependences of non-equilibrium and equilibrium free energies for lower temperature, T_4. As $f(c)$ and T_4 is completely similar to that at T_3, Fig. 7 was not indexed.

Thus, we may conclude that despite the great variety of morphological and kinetic peculiarities of decomposition of solids, the mechanism of decomposition remains the same. Here fundamental properties of large collections of particles are revealed and the physical generality of processes in different alloys is discovered.

Our ideas concerning the process of precipitation of new phases in metallic solids can be summarized as follows: if a non-stoichiometric solid having, for example, negative deviation from Raoult's law, is completely random after quenching, the process of the new phase precipitation starts with the correlation distance "search" (the minimum distance between clusters, when such clusters can exist in the system). It is noted that in the cases when under certain temperature and concentration conditions the system cannot "find" such a distance for any period of time, the solid preserves its structure (K′-state). When that distance is found, two variants are possible: at low concentrations of solutes the formation of clusters of the first kind occurs by the uphill diffusion (K-state, GP zones, local short-range order, grain-boundary segregations, etc.). The lattice of these clusters, being the same as that of the matrix, is distorted as the result of a higher concentration of solutes in clusters (striations in electron diffraction patterns, X-ray diffraction).

At high concentrations of solutes the formation of clusters of the second kind takes place (the same diffusional effects). As the concentration of the solutes in clusters is doubled and tetragonal distortions of the lattice in the clusters grow, the clusters transform into particles of a new phase (satellites in the electron diffraction patterns). If a new type of lattice, produced by the tetragonal distortion of the original one, coincides with the structure of the equilibrium phase, this phase is stable; if no such coincidence occurs the phase is metastable and later, under approximate conditions, it rearranges into a stable one. For the stoichiometric alloys the precipitation of a new phase is the process of ordering of atoms inside the total volume of the alloy which can be correctly described by well-known theories taking into consideration the concept of the parameter of order. If in the systems a considerable part of the mixture energy is composed of its elastic component, the defects of a crystal structure, i.e. dislocations and boundaries, play an important role both in kinetics and thermodynamics of the process [14].

5. Conclusions

The ideas discussed may help to avoid some discrepancies characteristic of previous approaches.

1. We may conclude that solid solutions decompose by the spinodal mechanism only and that is why the decomposition does not require activated nucleation, i.e. the fluctuational surpassing of the energy barrier, as is supposed in the nucleation-growth theory.

2. The mysterious fog around the notion of the spinodal mechanism disappears, as well as the exotic

ideas about spinodal decomposition. If we term the considered mechanism of decomposition the spinodal mechanism (it has, in fact, many features of Cahn's spinodal mechanism) the spinodal curve in the T–c diagram, i.e. the position of points at which $\partial^2 f(c_i)/\partial c_i^2 = 0$ in the $f(c)$ diagram, will not be found, because the specific free energy of decomposition of the solid solution is described only by the convex curve.

3. Thermodynamics and morphology of the ideas such as clustering, formation of GP zones, short-range ordering, segregation, K-state, etc. are revealed. For us all these ideas indicate some unity, having, however, different historically established names. In all cases they are clusters of solutes in the matrix, with the same type of lattice as the matrix, but with a different morphology and chemical composition.

If clusters are formed in the alloy, the composition which corresponds to a one-phase region of the phase diagram, they are then the final product of decomposition (clusters of the first kind). In the case when clusters are formed before the precipitation of a new phase (the alloy has a composition corresponding to the two-phase region), they represent one of the stages of decomposition en route towards the precipitation of a new phase (clusters of the second kind). There is no morphological difference between the former and the latter clusters, the only difference can be in concentration. There seems to be no sufficient grounds for linking such clusters to the particles of a new phase, because some features of the phase are not found in the clusters (at early stages there is no clear-cut demarcation between the clusters and the matrix; the lattice parameter of the solid with or without clusters is just the same).

The conclusions considered testify to the narrowness and lack of grounding of the generally assumed "linear" concepts of dynamics of phase segregation which are based on the exponential increase of small fluctuations. The process of the correlation distance "search", which can be observed due to the incubation period occurring under certain conditions, is actually the stochastic process being submitted to the laws of dynamic scaling.

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