Functional Materials 11, No.3 (2004)

Kinetics of spinodal ordering in Ni–Mo solid solutions

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The kinetics of spinodal ordering for Ni–Mo solid solutions (Ni-11.8 at.% Mo) has been investigated by residual electric resistance and diffuse X-ray scattering methods. It is shown that during isothermal annealing (at 373 K), the behavior of residual electric resistance, diffuse scattering intensity, and short-range order parameters depends heavily on the initial spinodal ordering state which is obtained by quenching from various temperatures (1223 and 573 K). Such behavior of the specified quantities is caused by origination and mutual transformation of spinodal ordering clusters of N_2M_2 and N_3M types.

Методами остаточного электросопротивления и диффузного рассеяния рентгеновских лучей изучена кинетика спиноидального упорядочения твердых растворов Ni–Mo (Ni-11.8 ат.% Mo). Показано, что с течением времени изотермического отжига (373 K) поведение остаточного электросопротивления, интенсивности диффузного рассеяния, параметров ближнего порядка существенно зависит от исходного состояния спиноидального упорядочения, которое достигается закалкой от различных температур (1223 и 573 K). Такое поведение указанных величин обусловлено зарождением и взаимной трансформацией кластеров спиноидального упорядочения N_2M_2 и N_3M.

Ni–Mo alloys belong to systems where spinodal ordering can be described by a concentration wave with a wave vector $\langle 1\frac{1}{2}0\rangle$ which differs from wave vectors peculiar to long-range ordered (LRO) structures observable under stoichiometry conditions. The study of short-range to long-range order transition thermodynamics and kinetics [1–7] in various Ni_4Mo and Ni_3Mo alloys evidences the presence of various ordering stages. The electron diffraction study results, theoretical stability calculations of various phases, and computer simulation of structure show that at various temperatures, the clusters are formed in time which correspond to the certain long-range ordered structures. Such clusters are considered as those resulting from interference of $\langle 1\frac{1}{2}0\rangle$ concentration waves and/or their interaction with the same waves of $\langle 100\rangle$ type. Only at high temperatures close to those of phase transformations, the formation of discrete microdomains Ni_4Mo for 20 at. % Mo alloys or Ni_4Mo and Ni_2Mo for Ni_3Mo alloys is observed [1–3]. At low concentrations, in the solid solutions region of Ni–Mo alloys, it is natural to expect the presence of spinodal ordering, however, the kinetics of this process and its mechanisms are not investigated. Only short-range ordering in Ni–Mo alloy with 11.8 at.% Mo in annealed state has been investigated in detail using diffuse X-ray scattering method were. Such a state was obtained by slow cooling of a single crystal sample from high temperatures up to room one. It has been shown that in this state, the diffuse $\langle 1\frac{1}{2}0\rangle$ peak is blurred and short-range order of Ni_4Mo type is observed, though no obvious peak in the $\frac{1}{5}\langle 420\rangle$ position is formed [8, 9].

In this work, the kinetics of spinodal ordering processes for a single crystal Ni–Mo (Ni-11.8 at.% Mo) sample was investigated using isotherms of residual electric resistance and diffuse X-ray scattering technique. In the latter case, the intensity ki-

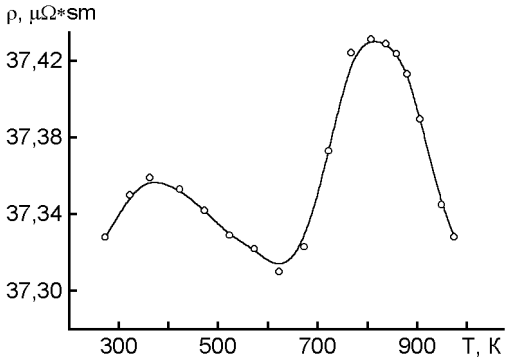

Fig. 1. Temperature dependence of residual electric resistance of Ni-11.8 at.% Mo alloy quenched from 1223 K.

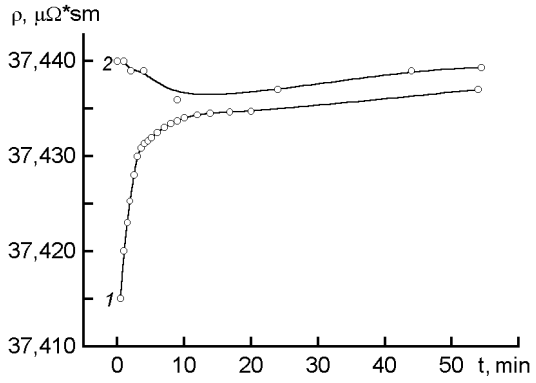

Fig. 2. Kinetics of residual electric resistance for Ni-11.8 at.% Mo alloy, quenched from 1223 (*1*) and 573 K (*2*).

netics caused by the short-range order and linear static distortions separated according to known methods [8, 9] was studied. The diffuse scattering intensity was measured on the (001)* plane of reciprocal space in the region covering $\langle 1\frac{1}{2}0\rangle$ diffuse peak and superstructural maximums $\frac{1}{5}\langle 420\rangle$ of β-Ni_4Mo ($D1_a$) phase and $\frac{1}{3}\langle 420\rangle$ of Ni_2Mo (Pt_2Mo) one. The residual electric resistance was measured for thin polycrystalline samples that of the same composition in liquid nitrogen after isothermal annealing at 373 K for various times for samples quenched from 1223 and 573 K.

It is to note that the study of residual electric resistance for the sample quenched from 1223 K in initial state under isochronous annealing, Fig. 1, testifies to complex behavior of electric resistance with increasing temperature. The change of this electric resistance cannot be attributed to any factor, except for short-range ordering that is observed in alloy. Thus, the complex character of electric resistance unequivocally testifies to a variety of short-range ordering processes in Ni–Mo solid solutions. The value of electric resistance in initial state after quenching from 1223 K is much less than that for annealed sample. It is seen from the electric resistance curve that a change of its behavior occurs at temperatures ~373 and 573 K. Therefore, it was of interest to compare relaxation processes of spinodal ordering at 373 K for various initial states (1223 and 573 K).

The kinetics of residual electric resistance is quite different for the mentioned initial states. So, for a sample quenched from 1223 K, the electric resistance increase sharply at first (Fig. 2) , and then the increase is slowed down. In contrast, for the state obtained by quenching from 573 K, electric resistance decreases at short isothermal annealing (T_a = 373 K) and, passing a minimum, starts to increase slowly, Fig. 2. The study of short-range order kinetics using the time dependence of diffuse scattering intensity in various points of reciprocal space for sample quenched from 1223 K allows to conclude that at the initial stage, the spinodal ordering due to a concentration wave with $\langle 1\frac{1}{2}0\rangle$ type vectors is decayed. The decay of these concentration waves is accompanied in time by intensity increase near superstructural $\frac{1}{5}\langle 420\rangle$ and $\frac{1}{3}\langle 420\rangle$ reflections that testifies to formation of N_3M structure. The presence of such structure, as it was noted, results from superpositions of $\langle 1\frac{1}{2}0\rangle$ waves [7]. Thus, in a temperature interval close to 373 K, the ordering state tends to coexistence of clusters of hypothetical N_2M_2 and N_3M structures. The appearance and growth of the latter one reduces in time the sharp increase of electric resistance.

The decrease of electric resistance observed on isochronous curve in temperature interval between 373 and 573 K (Fig. 1), allows to assume that in this interval, the revival of the $\langle 1\frac{1}{2}0\rangle$ concentration wave occurs. Only in this case the residual electric resistance should decrease. The increase of the $\langle 1\frac{1}{2}0\rangle$ concentration wave amplitude seems to be due to decay of N_3M clusters, therefore, it is natural to expect that it is just an increase of diffuse scattering inten-

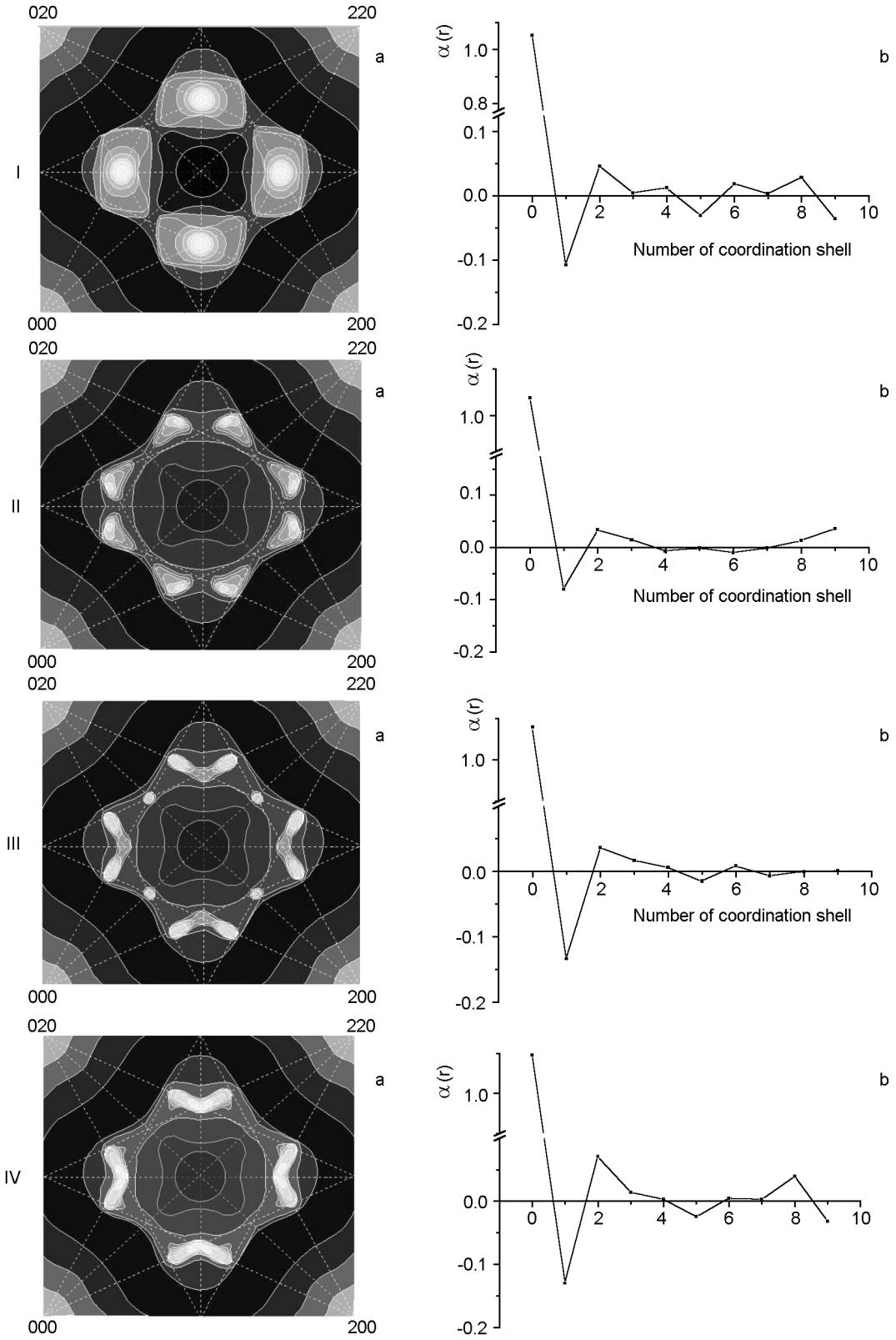

Fig. 3. Distribution of the short-range order intensity $I_{SRO}(h_1h_20)$ (a) and short-range order parameters $\alpha(r)$ (b) for Ni-11.8 at.% Mo alloy quenched from T_q = 573 K and annealed at T_a = 373 K during (min): 0 (I), 0.5 (II), 13 (III), 60 (IV).

sity in $\langle 1\frac{1}{2}0\rangle$ position at its insignificant magnitude in $\frac{1}{5}\langle 420\rangle$ and $\frac{1}{3}\langle 420\rangle$ points that should correspond to the quenched state from 573 K. Really, in the initial state (quenching from T_q = 573 K), the short-range order intensity distribution $I_{SRO}(h_1h_20)$ in reciprocal space, Fig. 3, I(a), and the set of short-range order parameters $\alpha(r)$, Fig. 3, I(b), indicate that $\langle 1\frac{1}{2}0\rangle$ concentration wave, i.e. clusters of N_2M_2 type, prevail in the alloy. At short annealing times at 373 K, Fig. 2, the electric resistance decreases, i.e. an insignificant additional ordering proceeds described by a $\langle 1\frac{1}{2}0\rangle$ wave.

The subsequent increase of annealing duration, even insignificant, Fig. 3, II (a), results in an appreciable redistribution of intensity which becomes concentrated mainly in superstructural positions $\frac{1}{5}\langle 420\rangle$ and $\frac{1}{3}\langle 420\rangle$, and also in bars from point $\langle 1\frac{1}{2}0\rangle$ to $\frac{1}{5}\langle 420\rangle$. The short-range parameters $\alpha(r)$, Fig. 3, II(b), also testify to origination of spinodal-ordered structures of N_4M and N_2M types. At increasing annealing duration, Fig. 3 (III, IV) and Fig. 4, an appreciable formation of N_3M clusters at the expense of destruction spinodal ordering described by a $\langle 1\frac{1}{2}0\rangle$ wave is observable. The generation of N_3M clusters at 373 K is accompanied, as well as in the case of quenching from 1223 K, by a slow increase of electric resistance, Fig. 2.

Thus, in Ni–Mo solid solutions, depending on obtaining conditions of one or other state, a set of wave vectors occurs, to which the spinodal ordering processes correspond. These processes at low-temperature isothermal annealing (T_a = 373 K) are accompanied by mutual transformation of short-range order clusters between structures described by concentration waves $\langle 1\frac{1}{2}0\rangle$, $\frac{1}{5}\langle 420\rangle$ and $\frac{1}{3}\langle 420\rangle$.

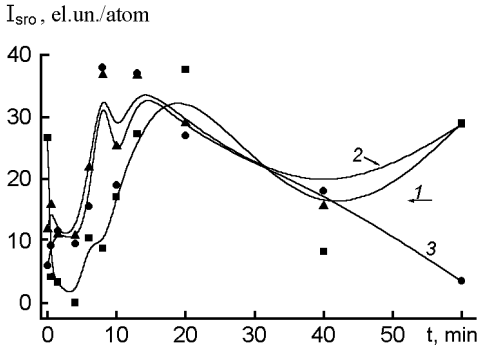

Fig. 4. Kinetics of short-range order intensity $I_{SRO}(h_1h_20)$ at isothermal annealing (T_a = 373 K) in positions N_2M_2 ($\langle 1\frac{1}{2}0\rangle$) (*1*), N_4M ($\frac{1}{5}\langle 420\rangle$) (*2*) and N_2M ($\frac{1}{3}\langle 420\rangle$) (*3*) for Ni-11.8 at.% Mo alloy quenched from T_q = 573 K.

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Кінетика спінодального впорядкування у твердих розчинах Ni–Mo

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Методами залишкового електроопору та дифузного розсіяння рентгенівських променів вивчено кінетику спінодального впорядкування для твердих розчинів Ni–Mo (Ni-11.8 ат.% Mo). Показано, що з часом ізотермічного відпалу (373 К) поведінка залишкового електроопору, інтенсивності дифузного розсіяння, параметрів ближнього порядку суттєво залежить від вихідного стану спінодального впорядкування, яке досягається загартуванням від різних температур (1223 та 573 К). Така поведінка згаданих величин обумовлена зародженням та взаємною трансформацією кластерів спінодального впорядкування N_2M_2 та N_3M.