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AND MODULATED STRUCTURES IN DECOMPOSITION REACTIONS

MASTER

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ABSTRACT

A model of coarsening in a heterogeneous cubic alloy with cubic or tetragonal precipitates is proposed. According to the model the coarsening is controlled by the relaxation of the elastic strain energy. The computer simulation of coarsening demonstrates good agreement with electron microscopic observation of the structure and diffraction pattern.

INTRODUCTION

Electron microscopic observations of the decomposition of alloys very often reveal regular substructures which arise during the aging process. These substructures are formed by new phase precipitates whose positions are correlated with one another. Regular structures have been observed in cubic alloys containing precipitates having either cubic or tetragonal structures. The morphology depends on the structure of the precipitate. When the precipitates are tetragonal the so-called "tweed" structure is formed which involves an alignment along $[110]$ directions of the cubic parent phase. The "tweed" structure has been found in many systems such as Cu-Bel, dental Cu-Au based alloy², Nb-O₃, Ni-V⁴ and others. A typical example of the "tweed" structure is presented in Fig. 1. Modulated structures formed by cubic precipitates in cubic matrices have been also observed in many papers. Unlike the "tweed" structure, modulated structures in this case display an alignment along $[100]$ directions with pseudoperiodical spatial distributions along these directions. In this case, the regularity in the precipitate distribution can be so high that the diffraction pattern shows extra spots along $[100]$ directions on either side of the fundamental reflections, which arise from the pseudoperiod of the precipitate distribution. An example of a modulated structure and its diffraction pattern for Cu-Mn-Al alloy⁵ is shown in Fig. 2.

The development of a regular distribution of precipitates during the aging process is presumed to begin from a random distribution in the as-quenched state. The coarsening process which occurs during aging results in the aggregation of the initial precipitates through diffusional movement to yield the spatially correlated distributions, i.e., the formation of either "tweed" or modulated structure. This process is controlled primarily by the relaxation of the elastic strain energy which depends on precipitate distribution.

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Fig. 1: The Tweed structure in a Cu-2% Be alloy (Rioja & Laughlin¹²)

Fig. 2: The modulated structure in a Cu-Mn-Al alloy (Bouchard & Thomas)

Previous work¹⁰ has proceeded from consideration of the elastic energy of specific periodical distributions of precipitates and has chosen those distributions which correspond to minimum elastic energy. This approach is, however, limited in two ways: (1) There may be other distributions (periodical or non-periodical) which have not been considered but which provide still lower elastic strain energy. (2) Even if the preferred metastable periodical distribution is found, it is not certain that this metastable state can be reached through the coarsening process. Below we consider a model of a coarsening process which is free from these disadvantages and which may offer a quantitative treatment of the formation of those regular structures obtainable through a simple coarsening process.

MODEL OF THE COARSENING PROCESS

A coarsening process which is controlled by the relaxation of elastic strain energy can be described if we can find an appropriate method for the quantitative treatment of an arbitrary distribution of precipitates with arbitrary shape. This is accomplished by introducing the concept of an elementary particle of the new phase- the minimum size "brick" of the new phase. Using these "bricks" as a "construction material", we can always build up any desirable spatial distribution of arbitrary precipitates of the new phase. To do this we also have to introduce some grid lattice whose Wigner-Seitz cell coincides with the elementary particles in size and shape. This grid now becomes a framework whose Wigner-Seitz cells can be filled by the elementary particles in any desired order. Since the total volume of a new phase does not change during the coarsening, the total number of elementary particles is conserved and the coarsening influences only the spatial redistribution of elementary particles over the grid lattice.

If the symmetry of the precipitate differs from that of the matrix there will be several distinguishable precipitate types which differ from one another through their orientation relative to the matrix. In the context of the elastic theory of inclusions these carry stress-free strains $\epsilon_{ij}^0(1), \epsilon_{ij}^0(2), \dots, \epsilon_{ij}^0(p), \dots$ which are connected to one another by the symmetry operations of the matrix phase. Any arbitrary configuration (arbitrary substructure) of elementary particles (EP) can be described by the function $\tau_p(\mathbf{r})$ which takes the value one if an (EP) of

type p is at site R , and is zero otherwise. During coarsening the (EP) are assumed to redistribute by diffusion. We assume that each elementary step in the reconfiguration of the EP is one of three events: (i) translation of one of the EPs to the nearest neighbor vacant site of the grid without change of kind, (ii) translation with a change in the kind of EP, (iii) change of the kind of EP without translation. It will be easily seen that each of these events is equivalent to the annihilation of an EP and the subsequent creation of an EP modified in kind or location.

To treat the coarsening process we introduce the concept of a thermoelastic potential $\phi(R)$ —the change of the total free energy (the sum of the bulk chemical free energy, interphase energy and elastic strain energy) due to the creation of an EP of the kind of p at the point R . Any elementary event in the evolution of the system consisting of the annihilation of an EP of the kind of q at site R' and creation of the new EP of kind p at site R (the transition $(q, R') \rightarrow (p, R)$) results in the energy change:

$$\Delta\phi(p, R; q, R') = \phi(p, R) - \phi(q, R') \quad (1)$$

where R is either equal to R' or differs from R' by a nearest neighbor distance. The elementary act is thermodynamically favorable if the thermoelastic potential is negative and unfavorable if the thermoelastic potential is positive. We model the step-by-step evolution of the alloy due to coarsening by choosing the sequence of elementary events which provides the maximum possible decrease of the total free energy, i.e. by selecting each to give the minimum possible value of the thermoelastic potential.

If we assume uniform elastic constants and ignore anharmonic effects the thermoelastic potential for the event (p, R) given an arbitrary distribution of EP may be found in the real-space form⁷

$$\phi(p, R) = \Delta\mu(p, T) + \phi^0 + \sum_{q, R'} \omega_{pq}(R-R') \zeta_q(R') \quad (2)$$

where $\Delta\mu(p, T)$ is the chemical free energy change on formation of an EP of type p , ϕ^0 is the elastic self-energy of the EP, and $\omega_{pq}(R-R')$ is a two-body elastic interaction between an EP of type p at R and an EP of type q at R' . The elastic energy terms in equation (1) depend on the elastic constants of the matrix, the stress-free strains of the precipitates, and the size and shape of the EP, and may be easily calculated in the long-wavelength approximation through the use of Fourier transform techniques⁸.

COMPUTER SIMULATION OF COARSENING

For simplicity our initial computer simulation studies have treated coarsening in a quasi-two-dimensional system. The term, quasi-two-dimensional, means that we assume that all precipitates are infinite rods normal to the planar lattice simulated whose cross sections are coincident with the two-dimensional Wigner-Seitz cells.

The coarsening of either tetragonal or cubic inclusions may be treated by making an appropriate choice of the stress-free strains $\epsilon_{ij}^0(p)$. The strains $\epsilon_{ij}^0(p)$ for tetragonal precipitates in a cubic matrix are, in the quasi-two-dimensional case, 2×2 tensors with non-equal principal strains ϵ_1^0 and ϵ_3^0 ($> \epsilon_1^0$) along the $[10]$ and $[01]$ directions in the plane. Two

variants exist, differing in the direction associated with the strain ϵ_3 (the tetragonal axis) which may be along $[10]$ or $[01]$. The strains for a cubic precipitate in a cubic matrix is simpler: $\epsilon = \epsilon^0 \mathbf{l}$, where $\mathbf{l}$ is the 2×2 unit tensor and ϵ^0 is the magnitude of the strain. In this case the precipitate is a simple center of dilatation and only one variant exists.

In the cubic-cubic and cubic-tetragonal cases the computer has generated random distributions of EPs which are taken to be the initial, "as-quenched" state. Figures 3a, 3b, 3c demonstrate the development of the alignment along (110) directions, i.e. the development of the "tweed" structure during coarsening in a cubic alloy with tetragonal precipitates. The comparison of Fig. 3c with Fig. 1 shows excellent agreement between the calculated and the observed "tweed" structure. It is interesting to note that the calculated diffraction patterns (Fig. 3d) associated with elastic strain closely resemble diffraction patterns observed in selected area electron diffraction from the "tweed" structure. Figures 4a, 4b, 4c demonstrate the development of the modulated structure during coarsening in a cubic alloy with cubic precipitates. Comparison of Fig. 4c with Fig. 2 establishes the agreement between the computer simulation results and the electron microscopic observations. The computed diffraction patterns (Fig. 4a', 4b', 4c') corresponding to the structures presented in Fig. 4a to 4c demonstrate the most typical feature of the modulated structure: the development of side bands on the diffraction pattern (extra spots situated in the directions $[100]$ on both sides of the fundamental reflections).

We conclude that the observed morphology of two-phase alloys arising during aging can be reasonably well modeled as due to the relaxation of the elastic strain energy caused by the mismatch between the crystal lattices of the matrix and precipitates. It is particularly important to note that the spinodal-like structure obtained in the cubic-cubic case (Fig. 4) is obtained from the initial random distribution of precipitates through direct coarsening. It does not require the continuous development of periodic concentration waves as is accepted in the conventional approach of the theory of spinodal decomposition.

Fig. 3: Computer simulation of the development of the tweed structure. (a), (b), (c) microstructures, (d) diffraction pattern.

Fig. 4: Computer simulation of the development of the modulated structure. (a), (b), (c) microstructures. (a'), (b'), (c') diffraction patterns.

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