

On the flickering of disperse particles of a non-isomorphically decomposing alloy when observed in a dark field

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Basic experimental data are reported on effects associated with a reorientation of disperse particles which form in a nonisomorphically decomposing alloy as the result of a transition from a tetragonal crystal structure. A mechanism for this reorientation is hypothesized.

In a fairly large number of systems, a nonisomorphic phase transition results in the formation of disperse particles of a new phase. Examples are Ni–Be, Cu–Be, CoPt, ZrO_2 – Y_2O_3 , the YBCO high- T_c superconductors, Mn–Cu, and other materials with premartensitic states. In the simplest case of a nonisomorphic phase transition—in the case of a tetragonal crystal structure—the strain tensor describing the restructuring of the host lattice into the lattice of the new phase is $\epsilon'_{ij} = 0$, $\epsilon'_{ii} = \epsilon'_{jj} = \epsilon'_{ll}/t$; $i, j, l = 1, 2, 3$. Since the tetragonal axis l can run along any of the three axes of the coordinate system, particles with three distinct orientations can form in a phase transition with this crystal structure.

Electron microscopy of some of these alloys reveals diffraction features formed by particles of only one orientation. Correspondingly, only the particles of this one orientation “shine” on a “dark-field image” recorded in such a feature, and the particles “flicker” during repeated changes in the orientation.

Dark-field electron microscopy of the alloys Cu–2% Be, Ni–2% Be, and CoPt has revealed^{1–3} that the system of disperse particles which form in the course of this phase transition undergoes an extremely complex evolution under the influence of an elastic interaction.

First, a uniform random spatial distribution of particles of the three orientations forms. The tetragonal axis for each particle is oriented in a random way along one of the coordinate axes. The system of particles then loses its uniformity in terms of the distribution of particles with respect to orientation and also in terms of the spatial distribution: Large regions, 1–10 μm in size, form. In these regions there are particles of only two orientations (“TO blocks”). The spatial distribution of the particles in the TO blocks has a clearly expressed periodicity. In a first approximation it can be described by a body-centered tetragonal or base-centered tetragonal² macroscopic lattice. In the final stage of the structural development, the TO blocks decompose into “OO blocks,” i.e., regions occupied by particles of only one orientation. The spatial distribution of these particles can be described by a body-centered orthorhombic⁴ or base-centered orthorhombic³ macroscopic lattice.

In order to form in the position of the original random distribution of TO and OO

blocks, the disperse particles must be able to move in space and change orientation. The first mechanism—diffusive creep—has been described extremely thoroughly; the second has not been studied previously, so we will take a more detailed look at it.

There are at least two known phenomena in which the ability of particles to change orientation repeatedly is seen extremely clearly. First, there is the sequential structural evolution in aging alloys such as beryllium bronze.¹⁻³ If the particles are unable to undergo changes in orientation, the TO and OO blocks cannot form in the position of the original uniform distribution. Second, there is the “flickering” of particles at a frequency of 1–10 Hz, caused by a “random process,” which has been observed directly in an *in situ* study of an Mn–Cu–Al alloy.⁵ In both cases, a reorientation is possible either by virtue of elastic energy stored in the system of particles or by virtue of some external force which performs work on the particle in the course of the reorientation. To choose one mechanism or the other, it is necessary to calculate the change in the energy of the particle in the course of its reorientation.

In order to change the orientation of a particle, we need to deform its lattice. In the course of this deformation, the total elastic energy of the particle will have three terms:

$$E^{\text{particle}} = E^{\text{deformation}} + E^{\text{self}} + E^{\text{interaction}}. \quad (1)$$

In this calculation, in studying problems involving the elastic interaction of the disperse particles, we use the approximation that the elastic constants of the host and the new phase are equal. We also use the approximation of spherical particles.⁶⁻⁸

In the case of a tetragonal strain tensor we would have

$$E^{\text{deformation}} = (1/2)VC_{11}(\epsilon^P)^2 [(t^P)^2 + 4t^P(\kappa - 1) + 2\kappa], \quad (2)$$

where $\kappa = 1 + C_{12}/C_{11}$, C_{12} , and C_{11} are elastic constants; t^P is the degree of tetragonal deformation of the lattice of the new phase; ϵ^P is a component of the corresponding strain tensor; and V is the volume of the particle. An expression for the self-energy in this case follows from the general expression:⁶

$$E^{\text{self}} = (1/2)VC_{11}(\epsilon^i)^2(1-P) \iiint \{ [t^2 + 4t(\kappa - 1) + 2\kappa] - \Phi(\mathbf{v}) \} \sin(\theta) d\theta d\psi. \quad (3)$$

Here $\Phi(\mathbf{v})$ is a complicated function⁷ which depends on the elastic constants, on the degree to which the deformation of the transition is tetragonal, and on the directions of the coordinate system; \mathbf{v} is a unit vector of the coordinate system; t is the extent to which the deformation of the transition is tetragonal; ϵ^i is a component of this tensor; and P is the volume fraction of the particles.

The energy of the elastic interaction between particles is given by⁶

$$E^{\text{interaction}} = (-1/2)VC_{11}(\epsilon^i)^2 \iiint \Phi(\mathbf{v}) F_1(\mathbf{k}) F_2(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3k / (2\pi)^3, \quad (4)$$

where $F_i(\mathbf{k})$ is a Fourier transform of the shape of the particle, and the vector \mathbf{r} joins the centers of the particles. Expression (4) is extremely unwieldy for calculations, so we resort to approximate analytic expressions for a binary potential.^{7,8}

To find quantitative estimates of the elastic energy we consider the well-studied alloy Ni-2% Be. During aging, the B2 phase of NiBe separates out of the fcc solid solution. The lattice of this new phase is related to the host lattice by a Baine orientational relation. As a result, we have $t = -4.76$ and $\epsilon^t = 0.056$, as was shown in Refs. 1 and 3. The volume fraction of this phase is⁹ $\sim 20\%$. In the calculation we assign the elastic constants the values for Ni (Ref. 10): $\kappa = 1.63$ and $C_{11} = 251.2$ GPa. The disperse particles of the NiBe phase have a spheroidal shape with a principal axis 1.2 nm long and with an axis ratio $\sim 1/2$ (Ref. 9). Substituting the corresponding values into the expression for the common factor in Eqs. (2)–(4), we find $(1/2)VC_{11}(\epsilon^t)^2 = 5.27 \times 10^{-2}$ eV/atom or 7.5 eV per particle of the phase. The other terms in Eqs. (2)–(4) are dimensionless.

In the original state, in which the lattice of a particle is distorted solely by its interaction with the host lattice or with other particles, the strain energy is zero. A numerical integration of (3) yields $E^{\text{self}} = 55.65$ eV. Using a binary potential^{7,8} and taking an average over ~ 8000 particles, one finds that the energy of the elastic interaction of the particles of a uniform random spatial distribution is -4.99 eV (Ref. 8), while the minimum and maximum energies are $+11.7$ and -18.45 eV, respectively. In the original state we thus have $E_{\text{average}}^{\text{particle}} = 50.66$, $E_{\text{max}}^{\text{particle}} = 67.35$, and $E_{\text{min}}^{\text{particle}} = 37.2$ eV.

Let us assume that the strain tensor corresponding to the deformation which reorients the particles has a tetragonal symmetry. The particle then goes through an “isomorphic” state, in which its lattice is related to the host lattice by a strain tensor with $t = 1$. From this state, the particle can go into a state with any of three possible orientations of the tetragonal axis.

A strain tensor with $\epsilon^p = -0.1310$ and $t^p = -1.89$ corresponds to a minimum of the sum of the self-energy of a particle in the isomorphic state and the energy of the deformation of this particle to this state (this value of t^p is close to the value of t for pure lead: -2). The magnitude of the strain is measured in comparison with the state of the undeformed particle. In this isomorphic state the particle has $E^{\text{particle}} = 85.05$ eV, which is $\sim 70\%$ larger than the average value of the total elastic energy of the particle in the initial state, and $\sim 25\%$ and $\sim 130\%$ larger than the maximum and minimum values.

These estimates show that along its reorientation path the particle is confronted by an extremely high activation barrier which cannot be surmounted solely by means of the elastic interaction. The flickering of the particles is thus caused by some external force or external object—external with respect to the system of elastically interacting particles.

On the basis of the experimental data reported above, we can offer some suggestions about certain properties of this object.

1. If the particle is to be able to reach a transitional state and then complete the reorientation as the result of an interaction with the object, this object must perform a three-dimensional deformation of the crystal lattice of the particle.

2. The experiments of Ref. 5 revealed that the particles flicker individually, rather

than in groups. The size of this object must therefore not exceed the average distance between particles, which is ~ 1.5 – 2 diameters of the particle or ~ 5 – 10 lattice constants.

3. The objects must be highly mobile, and there must be a fairly large number of them in the material, for otherwise the particles would not be able to flicker at a frequency of 1 – 10 Hz (Ref. 5).

4. The data of Refs. 1–3 on the formation of extremely stable regular structures consisting of particles of two orientations and of one orientation in alloys of the beryllium bronze type make it possible to estimate the energy of these objects.

Using Refs. 7 and 8 and the estimate of the elastic self-energy of the particle found above, we find that in Ni–2% Be the minimum elastic energy of the particles combined into a macroscopic lattice with a minimum interaction energy is about 32.5 eV. If an alloy contained many objects capable of reorienting particles with this energy, the regular structure of the TO and OO blocks would be unstable, and we would not observe a clearly defined tweed contrast on dark-field images of the structure. A value of 50–52 eV can apparently serve as an upper estimate of the spectrum of energies of the objects. On the other hand, if the reorientation process is to be able to proceed, there must be many objects which can easily reorient most of the particles of the random spatial distribution, i.e., with an energy above 30–35 eV.

As a result, the energy spectrum of interest here in the case of a nickel-based alloy is in the interval 30–50 eV for the entire volume of the particle of the new phase or 0.21–0.35 eV per atom. By way of comparison we note that phonons with the Debye frequency in nickel have an energy of 0.04 eV. The elastic energy density of the core of a screw dislocation can be estimated to be 0.02–0.03 eV/atom, and the energy of a vacancy in nickel is 1.6 eV (Ref. 11). The energy of this hypothetical object is thus not the same as the energies of other known entities which are capable of deforming a crystal lattice.

5. It is possible that these hypothetical objects are of the same nature as some entities which have been detected in experiments on diffuse x-ray scattering in single crystals of KMnF_3 , V_3Si , Mo, Nb, KCl, LiF, NaCl, and Fe-31.2at.%Ni. Those other entities were described as extended mobile objects of atoms, namely, chains or planes whose atoms move in a correlated way in the course of thermal vibrations; the coherence of the atomic structure is preserved within an object.^{12–14} Unfortunately, the method of Refs. 12–14 is not applicable for observing corresponding 3D objects, while the hypothetical objects must perform a bulk deformation of the surrounding lattice.

In order to explain the mechanism for the reorientation of the disperse particles formed in an alloy which undergoes a nonisomorphic decomposition as the result of a transition from a tetragonal crystal structure, we must advance the following hypothesis.

Deformation objects (“D-objects”) exist in a solid which is undergoing a phase transition from a tetragonal crystal structure. These objects are regions of a localized deformation of the crystal lattice of the host. Their size is on the order of ten atomic spacings. They are capable of moving through the crystal and of interacting with the disperse particles of the new phase. A primary characteristic of a D-object is the strain

tensor of the crystal lattice corresponding to the deformation which the D-object causes in its vicinity.

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