

Fluctuationless mechanism for martensitic transformations

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(Received 18 January 1993)

A fluctuationless mechanism for martensitic transformations consisting of the appearance and development of a lattice instability triggered by defects is presented. A number of properties associated with martensitic transformations are qualitatively explained. As a quantitative example, the theory of the displacive β - ω transformation is constructed. It is argued that this transformation is triggered by interstitial impurities (O,N,C).

The problem of nucleation and growth of a new phase is a central one in the theory of martensitic transformations (MT) since these processes are the key to understanding many of the unique and unusual features of these transformations.¹ A classical mechanism of first-order transformation supposes a fluctuation or thermally activated nature for these processes.^{2,3} As applied to diffusionless structural transformations, at the stage of nucleation it is the thermal formation (homogeneous or heterogeneous) of critical nuclei of the product phase by means of heterophase fluctuations which starts the transformation. During growth, it is fluctuation jumps of atoms at an interphase boundary from their positions in one structure to another. This mechanism is realized in many metals and alloys undergoing structural transformations without long-range diffusion. In metallurgical literature such transformations are called massive⁴ (or polymorphic² for pure metals).

While MT are also diffusionless structural transformations, they display significantly different features that indicate another mechanism for development. Unlike the classical mechanism, the growth of a low-temperature phase in MT proceeds without thermal activation. An individual martensitic crystal grows at a velocity approaching the speed of sound and stops very rapidly (the reasons for that are discussed below). After that, at a constant temperature, the martensitic crystal does not experience further changes. The absence of thermally activated growth, as in the case of massive transformations, can be explained if at a given temperature, atomic fluctuation jumps across the interface have too high an activation barrier which blocks these jumps. So, thermally activated growth at this temperature is impossible and the system will remain in a thermodynamically nonequilibrium state, i.e., part of the crystal will remain in the high-temperature metastable phase, as long as temperature, pressure, stress, etc. remain constant.

The problem of nucleation of a martensite is usually treated in the framework of the classical thermal mechanism.⁵ In spite of a great number of different models of thermal nucleation (homogeneous or on lattice imperfections), the details of nucleation are still quite unclear. So, it is of interest to consider the possibility of a formation of a new structure without thermal activation, i.e., not requiring heterophase fluctuations. Such a fluctuationless

appearance of a new phase is consistent with the growth mode which does not require fluctuations. Moreover, unlike massive transformations, MT may proceed at very low temperatures (for instance, the transition temperature for sodium is 35 K), where fluctuation processes are hindered or even completely frozen. The purpose of this paper is to present a specific fluctuationless mechanism for MT and to suggest how the predictions of the theory might be tested experimentally.

A distinguishing characteristic of MT is the cooperative or "military" movement of atoms during the transformation. This fact is an indication of some kind of instability of a lattice with respect to atomic displacements along definite directions. But experimental data⁶ have shown that elastic moduli and phonon frequencies remain positive down to the transition temperature and, hence, a harmonic instability of the bulk lattice is absent. However, there is another possibility for a lattice instability, namely, an instability that is initiated by a defect.⁷ The instability arises at finite deformations caused by the defect as a result of different anomalies in a phonon system and strong anharmonicity of a lattice (i.e., this is essentially a nonlinear effect).

The defect causes local lattice deformations whose magnitude depends on the interatomic forces. The largest displacements from the periodic lattice correspond to those with the weakest restoring forces, usually revealed in the phonon-dispersion curves as low-lying vibrational modes. As a result of such a partial phonon softening for definite wave vectors above the transition temperature, a defect created instability will cause lattice distortions along the transformation path toward the low-temperature structure. These distortions are the reason for premartensitic effects observed in many alloys⁸ because, to a certain extent, they resemble a product structure.

The distortions will increase with decreasing temperature due to the temperature dependence of elastic coefficients (elastic moduli, phonon frequencies, anharmonic parameters, and other coefficients in the free-energy expansion in powers of static atomic displacements). At the transition point, the distortions become large enough to overcome the energy barrier between product and parent phases along the transformation path i.e., the high-temperature structure turns locally unstable

and the MT starts on the defect.

The transformation begins in the region nearest to the defect where atomic displacements are largest. The transformation in this region pulls behind itself atoms in adjacent regions and causes them to transform. There arises a transformation wave spread out from the defect. The driving force of the transformation is the great elastic stresses at the interface which cause adjacent portions of the untransformed crystal to become unstable. The development of this instability is the growth process for the piece of martensite.

The growth of martensitic crystal stops when the interphase boundary will be in a state of mechanical equilibrium. The form and volume of the transformed crystal depend on elastic coefficients, i.e., they will be different at different temperatures. Hence, decreasing or increasing temperature results in a reversible change of the transformed region. This effect is called the thermoelastic behavior of martensite with a coherent interphase boundary. The growth of the crystal may stop earlier if during development of the instability the interphase boundary has lost its coherency. In this case we will get nonthermoelastic martensite.

More detail and quantitative analysis of MT requires, primarily, knowledge of the defect that triggers the transformation and the description of the nature of defect-driven instability. For a concrete example, we present the theory⁹ worked out for the displacive transformation in Zr and Ti alloys from the bcc β phase to the hexagonal ω phase^{10,11} that will be shown to be initiated by interstitial impurities (O,N,C). During quenching, the β - ω transformation is accompanied by a formation of small (typically less than 50 Å) ω particles elongated in $\langle 111 \rangle$ directions. The transformation can be represented as a collapse of each first and second (111) atomic planes of the bcc crystal while each third plane remains at rest. Such a lattice reconstruction is given by the static displacement wave along the [111] direction with the wave vector $\mathbf{q}_0 = 2/3(111)$ (Ref. 12),

$$u(\mathbf{R}_s) = (a/6)\eta \sin(\mathbf{q}_0 \cdot \mathbf{R}_s), \quad (1)$$

where a is a lattice constant, and an order parameter $\eta = 1$ corresponds to a full transformation into the ω phase.

A free-energy expansion in powers of atomic displacements along the [111] axis has the form

$$F = \frac{N}{2} \sum_{\mathbf{q}} M \omega^2(\mathbf{q}) |u(\mathbf{q})|^2 + \frac{N}{3!} \sum_{\mathbf{q}_1, \mathbf{q}_2} g(\mathbf{q}_1, \mathbf{q}_2) u(\mathbf{q}_1) u(\mathbf{q}_2) u(-\mathbf{q}_1 - \mathbf{q}_2) + \dots \quad (2)$$

Here M is the atomic mass and $\omega(\mathbf{q})$ is the phonon frequency for longitudinal mode L [111] with wave vector \mathbf{q} . Inserting Eq. (1) in Eq. (2) we obtain the Landau expansion for the β - ω transformation,

$$\frac{F}{N} = \frac{M \omega_0^2}{2} \left[\frac{a}{6} \right]^2 \left[\frac{\eta^2}{2} - \frac{\lambda \eta^3}{3} + \frac{(\lambda - 1)\eta^4}{4} \right]. \quad (3)$$

Here $\omega_0 = \omega(\mathbf{q}_0)$, $\lambda = -ag(\mathbf{q}_0, \mathbf{q}_0)/24M\omega_0^2$ is a dimensionless anharmonic parameter. The coefficient at η^4 is found from the condition that the free energy has an extremum in the ω phase at $\eta = 1$.

In order for the ω phase to be stable at low temperatures, we should assume that $\lambda = \lambda(T)$ is positive and increases with decreasing temperature. This temperature dependence of λ is caused by the coefficient $g(\mathbf{q}_0, \mathbf{q}_0)$ because ω_0 in the systems under consideration is almost temperature independent.^{13,14} Then the ω phase is metastable within the temperature interval with $2 < \lambda(T) < 3$ and stable at $\lambda(T) > 3$. The equilibrium temperature T_0 between the β and ω phases is given by the condition $\lambda(T_0) = 3$.

In the presence of a point defect we should add to the free energy [Eq. (2)] the term $-\sum W(\mathbf{q})u(\mathbf{q})$, where $W(\mathbf{q})$ is the Fourier transform of defect-host atom forces. Within the harmonic approximation minimization of F at $\mathbf{q} \approx \mathbf{q}_0$ gives the usual result of the Kanzaki model for atomic displacements around a point defect,^{15,16}

$$u_0(\mathbf{q}) = W(\mathbf{q}_0)/NM\omega^2(\mathbf{q}). \quad (4)$$

In Zr, Ti, and their alloys, the phonon branch $\omega(\mathbf{q})$ has a pronounced dip at the ω point $\mathbf{q} = \mathbf{q}_0$.^{13,17} Near \mathbf{q}_0 , the dispersion law is almost one dimensional. The frequency $\omega(\mathbf{q})$ sharply depends on the longitudinal component q_{\parallel} of the vector $\mathbf{q} - \mathbf{q}_0$ and is almost constant on the section of area $S_{\perp} \approx (\pi/a)^2$ for the perpendicular directions. In this region $\omega(\mathbf{q})$ can be approximated by the two-parameter function,

$$\omega(\mathbf{q}) = \omega_0 + \omega' \ln(1 + q_{\parallel}^2/\alpha^2). \quad (5)$$

Since $u_0(\mathbf{q})$ has a sharp extremum at $\mathbf{q} = \mathbf{q}_0$, in position space the atomic displacements $u(\mathbf{R})$ around a defect will have a longitudinal oscillating component with the wave vector \mathbf{q}_0 . These oscillations have the form of Eq. (1) but with local order parameter $\eta(\mathbf{R}) \propto \omega_0^{-3}$ decreasing with a distance R from the defect. The oscillations mainly exist in rod-shaped regions elongated in the [111] direction with the length $2/\alpha \approx 20$ Å and the width $\sim a$.

In the case of a positive magnitude of $W(\mathbf{q}_0)$, the oscillations have ω character [$\eta(\mathbf{R}) > 0$] and atoms around a defect are displaced toward the ω structure. For a substitutional defect, $W(\mathbf{q}_0) = (a^2/4)(c_{11} + 2c_{12})L$, and for an interstitial impurity in the octahedral position (001/2), we have

$$W(\mathbf{q}_0) = (a^2/2)(c_{11} - c_{12})(L_z - L_x),$$

where parameters $L_i = a^{-1} da_i/dc$ define changes of lattice constants when defects of this type are introduced in a lattice. Therefore, ω -like distortions are created by either interstitial impurities (O,N,C) or substitutional defects expanding the lattice ($L > 0$). In the first case their magnitudes are usually much greater because a substitutional defect with large atomic radius cannot fit in the lattice. These distortions from interstitial impurities can be large near a defect and imitate real ω particles, producing anomalies in the elastic diffuse scattering^{9,18} and high-resolution electron microscopy (HREM) images¹⁹ above

the transition temperature.

Consider now atomic displacements around a defect taking into account the third-order term in the free energy [Eq. (2)]. Minimization of F leads to the nonlinear integral equation for $u(\mathbf{q})$ at $\mathbf{q} \approx \mathbf{q}_0$,

$$u_0(\mathbf{q}) = u(\mathbf{q}) - \frac{g(\mathbf{q}_0, \mathbf{q}_0)}{2M\omega^2(\mathbf{q})} \sum_{\mathbf{q}_1 \approx \mathbf{q}_0} u(\mathbf{q}_1)u(\mathbf{q} + \mathbf{q}_1). \quad (6)$$

The greatest difference between $u(\mathbf{q})$ and the result of the harmonic approximation $u_0(\mathbf{q})$ is in the region $q_{\parallel} \ll \alpha$ when the coefficient at the nonlinear term is maximum. In this region, according to Eqs. (4) and (5), $u_0(\mathbf{q}) \propto \omega_0^{-2}$. At $q_{\parallel} \gg \alpha$, when $u_0(\mathbf{q})$ does not depend on ω_0 , the coefficient in Eq. (6) is small and $u(\mathbf{q}) \approx u_0(\mathbf{q})$. For this reason, the solution of the integral equation can be sought in the form of Eqs. (4) and (5) but with the effective frequency ω_0^{eff} instead of ω_0 . The transcendental equation for the frequency ω_0^{eff} is obtained from Eq. (6) at $\mathbf{q} = \mathbf{q}_0$ and can be written as follows:

$$t^2 = 1 + Dt^{7/2}, \quad t = \frac{\omega_0}{\omega_0^{\text{eff}}}, \quad D = \lambda W(\mathbf{q}_0) \frac{15\alpha a^2 S_{\perp}}{64\pi^2 M \omega_0^{3/2} \sqrt{\omega'}}, \quad (7)$$

where $\lambda = \lambda(T)$ is defined in Eq. (3).

For interstitial impurities $D(T) > 0$ and Eq. (7) has the solution $t > 1$ (i.e., it gives an effective decrease of the frequency, $\omega_0^{\text{eff}} < \omega_0$). Therefore, due to anharmonic effects the local order parameter $\eta(\mathbf{R})$ or the amplitude of static oscillations around a defect increases with temperature decreasing (i.e., locally atoms are displaced more and more toward the ω structure).

With continued decreasing temperature, at a critical point, $T = T_{\omega}$, with $D_{\text{cr}} = (4/7)(3/7)^{3/4} = 0.303$ and $t_{\text{cr}} = \sqrt{7/3} = 1.53$, the solution of Eq. (7) disappears. No solution at $T < T_{\omega}$ ($D(T) > D_{\text{cr}}$) means that we cannot find atomic positions in the bcc crystal around the impurity that would satisfy mechanical stability. In other words, at the temperature $T = T_{\omega}$, when $D(T_{\omega}) = D_{\text{cr}}$, the β phase becomes unstable and the local displacive β - ω transition occurs. The transformation results in the formation of the real ω particles centered on interstitial impurities with uniform order parameter $\eta \approx 1$. For example, for O in Zr, we obtain $\lambda(T_{\omega}) = 4.1$, i.e., the instability temperature T_{ω} lies below the equilibrium temperature, for which $\lambda(T_0) = 3$. In principle, the instability may arise also on substitutional defects with $L > 0$, but the transition temperature for them is much lower (maybe, even negative) than in the case of interstitial impurities.

The process of development of this instability is a separate problem and has not been analyzed here. Nevertheless, it is clear that the form of ω particles formed will inherit that of distorted regions above the transition temperature, i.e., will be elongated in $\langle 111 \rangle$ directions. Because of coherency of the β - ω interface,²⁰ this transformation is an analog of thermoelastic martensite.

The proposed theory proves a fluctuationless character of the β - ω transformation initiated by interstitial impurities. Preliminary results obtained by the authors suggest

the possibility that classical MT in many cases are also triggered by interstitial impurities (O,N,C). This fact is consistent with a lens-shaped form of martensitic crystals on the early stage of a transformation that indicates a point center of their nucleation. The wonderful feature of interstitial impurities is their small size and, hence, great gradients of elastic stresses, which facilitates the instability. Besides, unlike other point defects, interstitial impurities are very effective in producing atomic distortions in a proper direction. Apparently, without interstitial impurities the martensitic transformation would not proceed at all. In an experiment,²¹ the density of martensitic crystals was estimated as 10^6 cm^{-3} . The minimal concentration of interstitial impurities needed to nucleate these crystals is about 10^{-16} at. %. Of course, such a tiny amount of impurities exists in any "pure" sample.

Since a transformation occurs locally on an individual impurity, its transition temperature will depend on specific conditions for this defect. Particularly, elastic stresses from external sources or from other defects may raise the temperature of instability. For this reason, the beginning of the MT usually proceeds near different crystal imperfections where the transition temperature is higher than that for an impurity in the free-stress parts of the sample. The first martensitic crystals formed produce elastic stresses around themselves and thereby increase the instability temperature for impurities situated close to these crystals. It may cause stress-induced transitions on the impurities and the process will be developed autocatalytically at constant temperature. Such transformation kinetics are called isothermal. In the case of athermal kinetics, elastic fields from transformed regions do not cause an instability on new impurities and to continue the transformation, additional cooling is required. Whether the kinetics is isothermal or athermal depends on a great number of factors: temperature, concentration and distribution of impurities and other defects, applied stresses, and so on.

The reverse transformation for nonthermoelastic martensite proceeds similar to the direct one. The impurity situated inside a martensitic crystal causes a lattice instability and the high-temperature structure appears, develops, and swallows up a martensite region. We see that the above fluctuationless mechanism makes it possible to understand qualitatively many features of MT without resorting to additional physical processes.

Since heterophase fluctuations and atomic jumps between two phases are blocked or are insignificant due to the very fast kinetics of a martensitic reaction, a system has no possibility to establish thermodynamic equilibrium between the two phases, nor even to compare their free energies. Hence, MT are essentially nonequilibrium and even nonthermodynamic. For this reason, the difference between free energies of the two phases is not a driving force of the transformation and the position of their equilibrium temperature is, in principle, unimportant for this transformation. The role of temperature is simply to change the elastic coefficients which determine the instability of the lattice surrounding the point defect. This picture is unusual since with a lack of fluctuations it corresponds to a mechanical rather than a thermodynam-

ic phase transformation. And the problem of nucleation and growth for martensite turns into a very complicated and very interesting problem of nonlinear physics, the appearance and development of defect-driven instabilities in a crystal. This paper is only the first step in this direction. Mechanical determinism of the transformation (the absence of random thermal fluctuations) is responsible for reversibility of a structure on heating and cooling and for the definite orientation relations between product and parent structures. All these features are absent in massive transformations⁴ which develop by the classical mechanism.

Experimentally, it may be possible to test the idea that interstitial impurities can, in certain materials, act as the nucleation centers for MT. The theory presented above

predicts large, temperature-dependent distortions toward the low-temperature phase around the interstitial atom. A local probe of the defect atom and its immediate environment might be accomplished with NMR or extended x-ray-absorption fine-structure experiments, although with O, N, and C atoms neither of these experiments is straightforward.

One of the authors (D.A.V.) is very grateful to V. Fradkov for the discussion of the kinetics of fluctuations. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences of the U.S. Department of Energy.

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