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Editors

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Preface

This volume contains two articles on topics in materials science of great importance: the thermodynamics of stressed solids, a fundamental problem that goes back to Gibbs, and hydrogen in materials, an area that is both scientifically rich and of great current technological importance.

The article on Thermodynamics of Elastically Stresses Solids by Peter Voorhees and William Johnson is a scholarly and pedagogical treatise on a deep, fundamental problem. Even though the thermodynamics of fluids applies to large, hydrostatically stressed solids in equilibrium, its extension to solids not in equilibrium, to non-hydrostatically stressed solids and to small particles where capillary effects become important, is far from straightforward.

Since Gibbs's initial work more than 100 year ago, our understanding of the solid has changed. We now know that diffusion occurs in the solid state and that solids can sustain non-dilatational stresses during diffusion. Over the years, this at times quite controversial problem has attracted some of the best minds in the field, including C. Herring, W. W. Mullins, J. W. Cahn, F. Larché, and M. E. Gurtin.

The present authors continue this tradition: they point out that much of the confusion in the field arises from a failure to distinguish two different thermodynamic approaches, in which either the vacancy concentration or the total number of lattice sites is treated as the independent variable. Using Gibbs's variational approach, they carefully track these descriptions while they develop the thermodynamics of small particles and non-hydrostatically stresses solids.

The subject is not just of academic importance. It is essential, for example, for a precise understanding of phase equilibria and surface morphologies in epitaxial alloy thin films. Much of the thermodynamics used in the current whirlwind of activity in nanoscience would be greatly improved by the rigor this article brings to the study of nanometer-size particles.

The article is deliberately pedagogical. It can be used to introduce graduate students to the subject, as the authors do in their own courses.

Hydrogen has a long history in materials science: as a reducing agent, as a highly mobile solute, as an embrittling agent, and as a structural probe. The resurgent interest in hydrogen as a fuel has prompted new research into the use of metals for its storage. In his article, Reiner Kirchheim focuses on solid solutions of hydrogen in complex materials, such as defective crystals and amorphous materials.

After a review of the basics of solubility of hydrogen in metals, the author starts with a fundamental treatment of how the hydrogen atoms are distributed according to Fermi-Dirac statistics over a complex energy landscape described by a density of site energies. He then lays out the implications for the diffusion of the hydrogen through such a landscape. The results are applied to the interaction with other solutes, vacancies, dislocations, grain boundaries and interfaces. The application to amorphous metals is particularly interesting, since hydrogen proves to be a remarkable tool to test the uniquely complex structure of these materials.

Even though the emphasis of the article is on metals, polymers, oxide glasses and metal-oxide interfaces are considered as well, as are systems with at least one small dimension, such as thin films and clusters.

HENRY EHRENREICH
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The Thermodynamics of Elastically Stressed Crystals

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I. Introduction

Elastic stresses arise naturally in crystals, even in the absence of external forces acting on the material. Solid-state phase transformations and the heteroepitaxial growth of thin films on a substrate are just two technologically important examples where self-stresses arise owing to a difference in the lattice parameters between the two crystals. Compositional heterogeneity, which develops during diffusional phase transformations, can engender stress when the crystal's lattice parameters are a function of the composition. Nonhydrostatic stresses are a natural byproduct of displacive transformations, where the lattices of the parent and product phase possess different lattice parameters and symmetries, and also occur during various second-order magnetic, ferroelectric, and order–disorder transitions. The deposition of a film with a different lattice parameter than the substrate often results in significant stresses, in some cases far in excess of the bulk yield stress of the film.

There is a significant body of experimental evidence that shows stresses can affect the evolution of a crystalline microstructure in several ways. One example, shown in Figure 1, illustrates the effect of a precipitate misfit strain resulting from the difference in lattice parameter between the precipitate and matrix, on the equilibrium precipitate shape as the precipitate size increases for a Ni-Al binary alloy. The precipitates evolve and grow by the diffusion of atoms through the matrix. In this alloy, the interfacial energy density is essentially isotropic, and the equilibrium precipitate shape in the absence of stress is given by the classical Wulff construction as a sphere. However, the elastic properties of the alloy reflect the anisotropic cubic symmetry of the the two crystals, with the elastically soft directions parallel to the $\langle 100 \rangle$ directions. Even though the misfit strain of the γ' precipitate is isotropic, the elastic energy of the precipitate is usually minimized when the precipitate assumes a plate-like shape.[1–3] The equilibrium shape of the precipitate is determined by minimizing the sum of the elastic and interfacial energies. Because the elastic energy scales with the volume of the precipitate, and the interfacial energy scales with the surface area of the precipitate, interfacial energy should be the dominant contribution to the system energy at sufficiently small particle sizes and, conversely, elastic energy should be the dominant energy contribution at large particle sizes. This behavior is similar to that observed in Figure 1. Equiaxed particles are observed at small particle sizes in Figure 1(a). With increasing particle radius, the precipitate shape begins to display some of the symmetry of the elastic field, developing regions of low curvature along the soft

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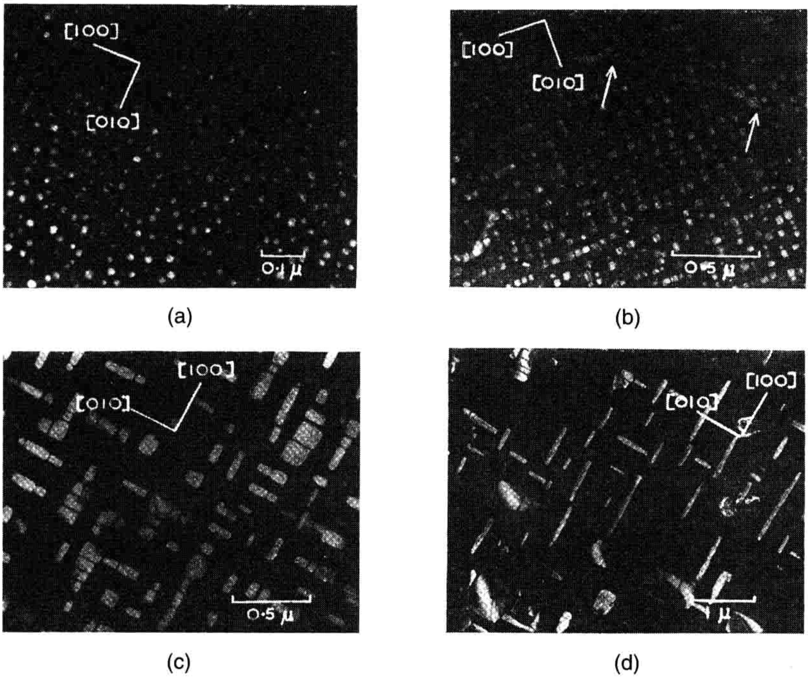
[1] J. K. Lee, D. M. Barnett, and H. I. Aaronson, *Metall. Trans.* **8A**, 973 (1977).

[2] A. G. Khachaturyan, *Theory of Structural Phase Transformations in Solids*, John Wiley, New York (1983).

[3] T. Mura, *Micromechanics of Defects in Solids*, Kluwer Academic Publishers, Dordrecht, The Netherlands (1987).



(a) (b)

(c) (d)

FIG. 1. Centered dark-field images show precipitate shape evolution in a Ni-6.71w%Al alloy aged for various times at 750°C: (a) 15 min, equiaxed γ' (Ni_3Al) precipitates; (b) 4h, cube-shaped precipitates; (c) 72h, cubical precipitates become plate-shaped and aligned along $\langle 100 \rangle$ elastically soft directions; and (d) 450 h. Precipitate shape transitions occur with increasing precipitate size in coherent systems owing to the different scaling of the elastic strain and interfacial energies with the precipitate radius: The interfacial energy dominates at small precipitate radii giving equiaxed precipitate shapes in this example, while the elastic energy dominates at large precipitate radii. Micrographs courtesy of A. J. Ardell.

$\langle 100 \rangle$ directions and assuming a shape that resembles cubes, as seen in Figure 1(b). At yet larger sizes the elastic energy contribution to the total energy becomes still more important, leading to a breaking of the four-fold symmetry of the precipitate in the (001) projection and development of plate-shaped or rod-shaped precipitates (Figure 1(c)); the aspect ratio increases with increasing particle size (Figure 1(d)).

Elastic stresses also influence the spatial correlation between particles as illustrated in the three-dimensional reconstruction of a $\gamma - \gamma'$ alloy.[4] These micrographs show that the particles are arranged in sheet-like arrays. In order to display this correlation, the microstructure has been separated into three regions: A, B, and C.

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[4] A. C. Lund and P. W. Voorhees, *Acta mater.* **50**, 2585 (2002).

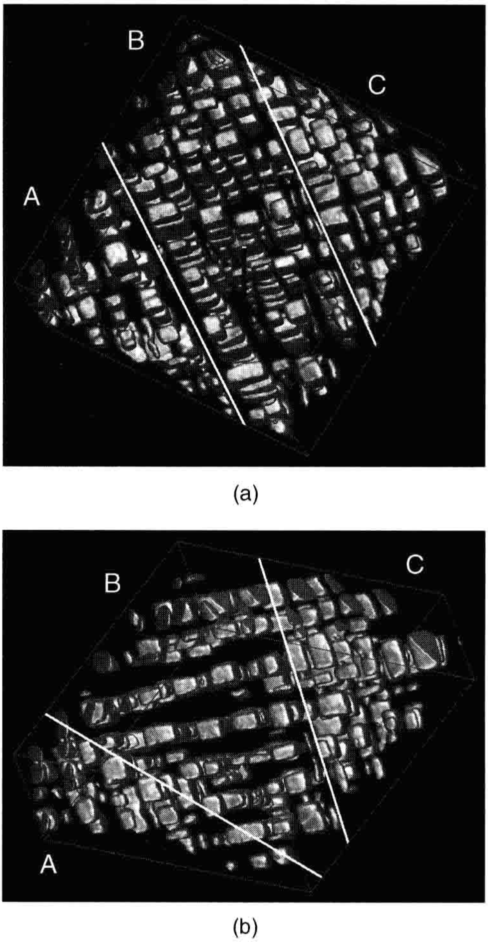

FIG. 2. A 10 × 10 × 3.6 μm portion of a $\gamma - \gamma'$ microstructure showing two different views of the microstructure. In (b), the microstructure shown in (a) has been rotated, and the same regions A, B, and C are again labeled. There is a strong alignment of particles within each sheet along the two $\langle 100 \rangle$ directions, but not between sheets.

In all three regions, particles align along the $\langle 100 \rangle$ crystallographic directions. In region B in particular, most of this alignment occurs along two of the $\langle 100 \rangle$ directions while there is very little alignment along the third $\langle 100 \rangle$ direction. In Figure 2(b) the microstructure shown in Figure 2(a) has been rotated, and the same regions A, B, and C are again labeled. From this viewing angle it becomes obvious that the particles in region B are aligned in two-dimensional sheets, which are perpendicular to the $\langle 100 \rangle$ direction along which no alignment appears to be

TABLE 1. MATERIALS PARAMETERS FOR EXPERIMENTAL NI-AL-MO ALLOYS: FIGURES 2 AND 3

Alloy	Al [$at\%$]	Mo [$at\%$]	$f_{\gamma'}[\%]$	γ' solvus °C	ϵ^T (misfit)
A1	12.5	2.0	15 ± 5	≈ 1000	+0.65%
A2	9.9	5.0	19 ± 6	≈ 1000	+0.40%
A3	7.7	7.9	15 ± 5	≈ 950	<0.10%
A4	5.7	10.9	7 ± 2	?	−0.15%
A5	5.3	13.0	8 ± 2	≈ 900	−0.30%

occurring in Figure 2(a). The separation distances between the sheets are far larger than the interparticle separation distances within the sheets, and appear to be relatively constant. The strong alignment of particles within each sheet into lines of particles is also clear from Figure 2(a). This alignment is due to an attractive force between the corners of particles and a repulsive force between the faces of particles.[5]

The centered dark-field micrographs appearing in Figure 3 show the influence of the sign and magnitude of the misfit strain on the development of microstructure in a nickel-based alloy similar to that shown in Figure 2. The five microstructures correspond to five different ($\gamma + \gamma'$) Ni-Al-Mo ternary alloys after heat treating each alloy for 67h at 775°C. The compositions of each alloy, given by Table I, are chosen so that the volume fraction of the γ' precipitates in each alloy is roughly 10% but the misfit strain, ϵ^T, becomes progressively more negative with increasing Mo content.

The alloys of Figure 3 exhibit distinctive microstructures. The alloys with the largest magnitude of misfit, A1 (a) and A2 (b), display microstructures in which the precipitates are aligned along the elastically soft $\langle 100 \rangle$ directions of the matrix phase. The lowest misfit alloys, A3 (c) and A4 (d), show a more uniform dispersion of spherical precipitates while some of the precipitates of alloy A5 (e) are just beginning to assume a cube-like shape. After 430h of aging at 775°C, the precipitates of alloys A1 (a) and A2 (b) have lost their four-fold symmetric shapes and those of alloy A4 (d) have begun to assume a more cube-like morphology. The precipitates of alloy A3 (c), which have a vanishingly small misfit strain with respect to the matrix phase, still remain spherical and uniformly distributed. These results demonstrate that the long-range elastic stress engendered by the misfit strain strongly influences both the shape and the spatial distribution of precipitates of these alloys. This is particularly important as the Ni-Al system is the base alloy for the superalloys used in many high-temperature applications and the microstructure has a strong influence on the mechanical properties.

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[5] C. H. Su and P. W. Voorhees, *Acta mater.* **44**, 1987 (1996).

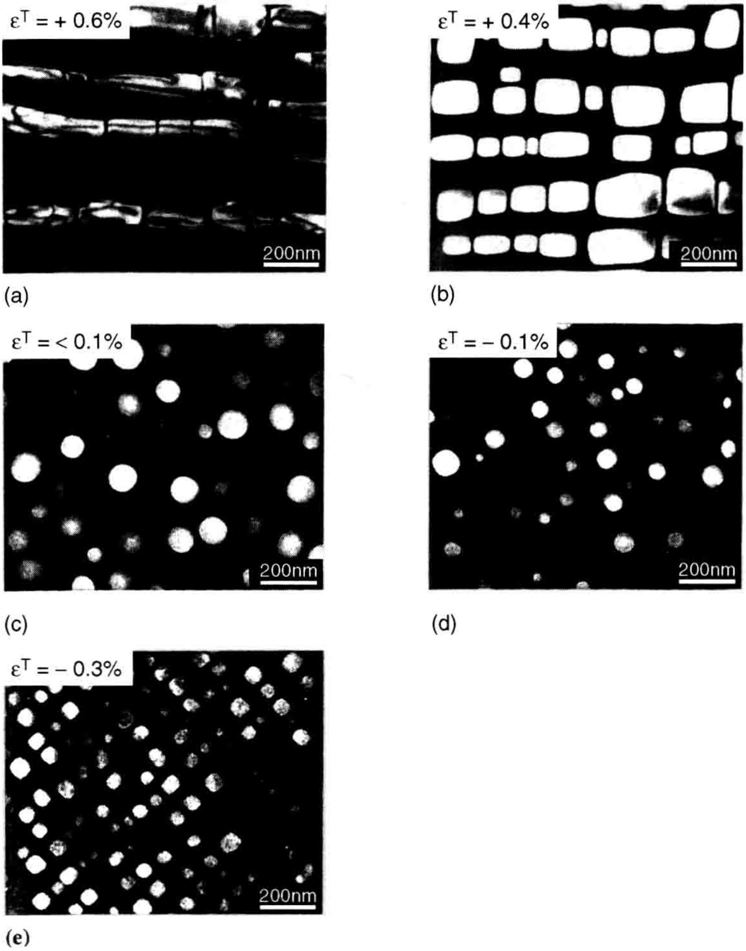

FIG. 3. Centered dark-field images show microstructural evolution in five Ni-Mo-Al alloys possessing roughly equal volume fractions of the γ' precipitates with misfit strains (a) $\epsilon^T = +0.6\%$; (b) $\epsilon^T = +0.4\%$; (c) $\epsilon^T \approx 0$; (d) $\epsilon^T = -0.15\%$; and (e) $\epsilon^T = -0.3\%$ after 67 h of aging at 775°C. Micrographs courtesy of M. Fährmann.

The morphological development of films deposited or grown on a substrate is also strongly influenced by stress.[6] Films deposited on a substrate are known to grow in many modes. If there is no difference in lattice parameter between the film and substrate, and the film wets the substrate, the film grows in a planar, layer-by-layer fashion. At the other extreme, in which the film does not wet the

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[6] V. A. Shchukin and D. Bimberg, *Rev. Mod. Phys.* **71**, 1125 (1999).

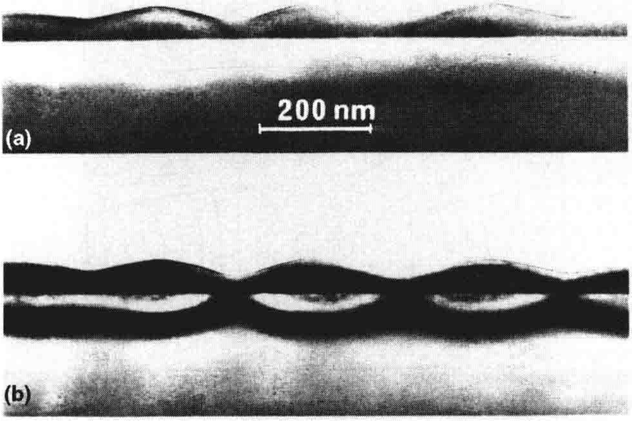

FIG. 4. Ripple formation in a $Si_{0.79}Ge_{0.21}$ alloy grown at 750°C on a (001) Si substrate. (a) bright field image, (b) dark field image showing strain.[7]

substrate, small islands of film form immediately on deposition. The intermediate case, Stranski-Kranstanow growth, occurs when the film wets the substrate and the film and substrate have different lattice parameters. In this case the film grows initially in a layer-by-layer mode and then forms islands at some later time in order to relieve the strain energy.

For many years it was thought that, during Stranski-Kranstanow growth, islands formed as a result of stress-relaxing dislocations forming at the interface of the substrate and film. However, more recently it has become clear that islands can form even in the absence of dislocations. As the film grows, the stress of this planar film can be reduced if the film undergoes a morphological instability. This process begins by the planar film becoming unstable to ripples on the surface, as seen in Figure 4.[7]

Figure 4(a) is the rippled surface of a nominally 40nm-thick Si-Ge film deposited on a Si substrate. There are no dislocations present in the film, as shown in Figure 4(b), yet there is clear evidence of strain. The undulations develop because the stress is relaxed at the peaks and concentrated at the troughs, similar to the stress concentration at the tip of a crack. The stress relaxation at the peaks and concentration at the troughs is illustrated in Figure 5. In this case the stress-free film has a larger lattice parameter than that of the substrate. The lack of lateral constraint near the peaks, as compared to a planar film, results in a splaying of the lattice planes near the peaks. This results in a film lattice parameter in this region that is closer to its natural lattice parameter. The converse is true at the

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[7] A. G. Cullis, D. J. Robbins, A. J. Pidduck, and P. W. Smith, *J. Cryst. Grwth.* **123**, 333 (1992).

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