CONTINUUM FIELD MODEL OF DEFECT-INDUCED HETEROGENEITIES IN A STRAINED THIN LAYER

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Abstract We investigate the effect of external stresses on structural and mechanical properties of a strained damaged thin layer by developing a continuum phase-field mesoscale model based on the introduction of an order parameter field, the defect concentration, coupled with a displacement field. We find that even in the case of an initially uniform distribution of point defects external stresses drive the nucleation of local regions with higher concentration of vacancies or self-interstitials than their average value over the film. The effect can explain our experimental findings relating generation of highly heterogeneous regions in cobalt disilicide film fabricated in self-aligned processing on a silicon surface as well as improvement of fracture toughness in a tetragonal zirconia ceramics with oxygen vacancies.

Keywords: Point defects, displacement field, continuum model, thin layer

Introduction Material properties of thin solid layers are often controlled by complex microstructure formed during their fabrication. Let us assume a film with a uniform distribution of point defects that is uniaxially strained. If lattice deformations are small (in experiments discussed below they are limited to a few tenths of a percent), according to naive expectations, the distribution of the defects should remain the same in a strained
state, i.e., homogeneous. The purpose of this paper is to prove that, in general, it is not true and even comparatively small stresses may result in any significant modification of a displacement field as well as the microstructure within the sample that can cause different mechanical and chemical changes on a macroscopic scale. We address this issue by means of a novel phase-field approach for a strained damaged layer based on the introduction of two continuum fields relating the defect concentration and atom displacements. The following section gives an outline of the theoretical approach and in remainder of the paper a simplified one-dimensional quasi-static model is studied numerically. The data obtained are discussed with respect to two our experiments dealing with strained thin layers of cobalt disilicide and zirconia ceramics that exhibit an 'unusual' sensitivity of their material properties to (apparently weak) disorder.

1. The Model

Phase-field methodology has become increasingly recognized as a useful tool for simulating mechanical failure due to external stresses and understanding the role of the underlying physical processes (see the papers [1–4] and references therein). Advantages of the continuum approaches starting from basic theoretical assumptions have been clearly demonstrated: first, they avoid any abrupt interfaces, facilitating numerical convergence and, second, they are dealing with more realistic equations of motion for the material than alternative sharp interface theories. The diffuse interface models consider amorphous solids and are based on the introduction of two fields: that of a local order parameter describing fluctuations in the mass density and a standard displacement field $u(r)$ of mass points measured from their original positions. The latter one representing strain in the material is usually treated within the conventional linear elasticity theory whereas the former field is supposed to obey a double-well Ginzburg-Landau potential with two minima representing vacuum and perfect solid states (it turns out to be hard to realize physical limitations of such an approximation that covers the whole range of the order parameter between two limiting cases). In contrast to the works used two-field fracture models, we focus here on small fluctuations of both parameters when approximations made become more evident and physically clear. We show that in appropriate circumstances (if some scale in the material is comparatively small) the combination of weak disorder and strain may change the system properties dramatically.

In this section we present the basic ideas of the approach similar in philosophy to, but very different in detail from, the works cited above.
Local disorder will be characterized by the relative concentration $c(r)$ of point defects in the material, positive for vacancies and negative for self-interstitials; $|c(r)| < 1$. We start from a non-strained solid with a homogeneous distribution of defects $c(r) = c_0$ produced during its fabrication process when the system passed through a sequence of metastable states. If thermal fluctuations are not relevant, it usually remains in a given configuration as long as the state corresponds to a free energy minimum. The latter condition means that any local deviation from $c_0$ will only increase the energy and for small variations of $c(r)$, we may limit ourselves with a quadratic term in the free energy density of a damage solid, $k(c(r) - c_0)^2/2$, where $k$ is a phenomenological parameter. Following Ginzburg-Landau ideas on phase transitions, we introduce a gradient term $g(\nabla c(r))^2/2$, energetically suppressing spatial fluctuations in the order parameter. Another limiting case is a perfect crystal in a deformed state whose local elastic free energy density is assigned by the strain tensor $u_{ik} = \partial u_i/\partial x_k + \partial u_k/\partial x_i$. Within the linear elasticity theory it is of a quadratic form $\lambda_{iklm}u_{ik}u_{lm}/2$ with parameters $\lambda_{iklm}$ that for a homogeneous, isotropic material are described by two Lamé constants [5] whereas for a system undergoing a first order transition the energy should be taken as a Landau polynomial of strain tensor components.

What is less trivial is the coupling between two fields $c(r)$ and $u(r)$. To give an insight about its form, we shall discuss a crystal containing a mesoscopic dilation center at a point $r_0$ formed by self-interstitials. Its presence is regarded for a solid as an external origin of stresses causing displacements of nearest atoms from their equilibrium positions. Then the stress tensor may be approximated with a simple formula $\sigma_{ik} = K\Omega_{ik}\delta(r - r_0)$, where $K$ is the bulk modulus, a linear combination of two Lamé constants. As $u_{ll} = \sigma_{ll}/3K$, the total change of the solid volume $\delta V$, that can be roughly estimated as the number of interstitials in the dilatation center multiplied by an atomic volume, is equal to $\delta V = \int u_{ll}dV$ [5]. Hence, the trace of the tensor $\Omega_{ik}$ is $\Omega_{ll} = 3\delta V$. For a single dilatation center the interaction energy is equal to $-K\Omega_{ik}u_{ik}(r_0)$ that can be generalized in the common case of a continuous defect distribution as $c(r)\alpha_{ik}u_{ik}(r)$, where $\alpha_{ik}$ is a tensor with components whose values can be very roughly estimated as the bulk modulus $K$. The second effect is related with changes of elastic characteristics $\lambda_{iklm}$ for host-host atom interactions due to their displacements in the vicinity of defect: $\delta\lambda_{iklm} = \Omega^{*}\Lambda_{iklm}\delta(r - r_0)$, where $\Omega^{*}$ is the value of the order of $\delta V$, parameters $\Lambda_{iklm}$ are positive for a dilatation center (host-host atom interactions become stronger in the nearest neighborhood of the defect) and negative for a pore. For a continuous distribution of local defects
we may approximate $\delta \lambda_{iklm}$ as $-c(r)\lambda_{iklm}$. An additional argument for such a substitution is that in the case of $c(r) = 1$ the elastic energy is vanishing. Phase-field equations describing a quasi-static behavior of the system (that is an aim of the paper) can be obtained by minimizing its total free energy.

2. Numerical Simulations and Discussion

To show how our model is working and what can happen with a damage but homogeneous elastic solid under strain, we limit ourselves to a one-dimensional approximation. It means that we shall assume the presence of a wide and thin layer of a finite length $2L$. Collecting all contributions to the free energy together and rescaling $x/L \rightarrow x$, $g/(\lambda L^2) \rightarrow g$, $k/\lambda \rightarrow k$, $\alpha/\lambda \rightarrow \alpha$, we get the following expression for a total free energy of the solid:

$$F = L\lambda \int_{-1}^{1} dx \left[ g\left(\frac{dc(x)}{dx}\right)^2 + k\left(c(x) - c_0\right)^2 + \alpha c(x)\frac{du(x)}{dx} + \frac{1}{2}(1 - c(x))\left(\frac{du(x)}{dx}\right)^2\right].$$

(1)

In a quasi-static case spatial distributions of the defect concentration $c(x)$ and atom displacements $u(x)$ should minimize the free energy, i.e., $\delta F/\delta c(x) = 0$ and $\delta F/\delta u(x) = 0$. It yields the following set of two differential equations:

$$g\frac{d^2c(x)}{dx^2} = k(c(x) - c_0) + \alpha \frac{du(x)}{dx} - \frac{1}{2}(\frac{du(x)}{dx})^2;$$

$$\frac{d^2u(x)}{dx^2} = \frac{1}{1 - c(x)} \frac{dc(x)}{dx}\frac{du(x)}{dx} - \alpha.$$  

(2)

The equations thereby incorporate the physics of the defect subsystem and the macroscopic behavior of a strained solid that follows from the conventional theory of elasticity. Because we are dealing with a finite-size problem, it is very important to formulate correct boundary conditions. First, we suppose that displacements at the boundaries are known: $u(\pm L) = \pm \delta L$ (it is positive when the sample is squeezed and negative for stretching efforts). Second, because of the symmetry of the problem the function $c(x)$ should be symmetrical on $x$. And, last, we assume a conserved order parameter, i.e., the initial number of defects will not be changed in a strained material:

$$\int_{-1}^{1} c(x)dx = 2c_0.$$  

(3)
Such a condition may be applied to a solid layer if defects (vacancies and self-interstitials) are already redistributed within it but the process of their annihilation at boundaries has not started yet.

In Fig. 1a we show both fields \(c(x)\) and \(u(x)\) calculated for a positive value of \(c_0\) and certain other reasonable parameters. It follows that the concentration of vacancies at the center of the layer is larger than at its ends. The displacement field is also inhomogeneous that is more

![Figure 1](image-url)

**Figure 1.** (a) Profiles of the defect distribution \(c(x)\) (solid line) and the displacement field \(u(x)\) (dashed line). (b) The strain \(du(x)/dx\) (solid line) and the local free energy density \(f(x)\) (dashed line); \(\delta L/L=0.005; c_0=0.05; g=1.0; k=3.0, \) and \(\alpha=3.0.\) Corresponding characteristics for a homogeneous film without any defects are shown by relating thin (solid and dashed) lines.
evident from Fig. 1b, where the stress $du(x)/dx$ (which characterizes relative changes of the length along the sample) has maximal negative values in the middle part of the sample. Because the mass of the film is fixed, large squeezing at the center is compensated by the stretch at ends, where local relative changes of the length are positive (see Fig. 1b). The parameters were chosen to be similar to those for experiments described below.

A strong enhancement of the mechanical response induced in a material by a small perturbation at its boundaries can imply 'unusual' phenomena if some scale in the system is comparatively small. To show where and how our model can be useful, we refer to two our experiments with a combination of weak disorder and small stresses. We start with a solid phase reaction that is thermally initiated on a substrate covered by other reagent and results in formation of the layer of a new compound. The reaction rate follows the Arrhenius law $\exp(-W/k_B T)$ with an activation energy $W$, the Boltzmann constant $k_B$ and the temperature $T$, usually $W \gg k_B T$. It should be emphasized that even in the case of tiny variations $\delta W$ of the energy barrier to be overcome, their effect can be observable on a macroscopic scale if $\delta W$ is comparable with the temperature coefficient $k_B T$. In this case significant reaction rate modifications (of several times) may take place in different parts of the heterostructure.

We believe that it can be one of the main sources of the heterogeneity of CoSi$_2$, a practically important material that is usually obtained in self-aligned silicide processing [6]. The layer of cobalt disilicide is formed by depositing a Co layer onto a Si substrate and heating the combination until the two elements react to form Co$_2$Si, then CoSi, and finally the desired phase CoSi$_2$. The cobalt disilicide films obtained by such a way are usually rough, contain a high density of pinholes and even break into islands [7]. It raises a question of either the heterogeneity is a purely technical problem, or there is something more fundamental behind it. In our opinion, the mechanical failure is a sequence of substantial thermal stresses in a defect Co layer due to an essential mismatch of thermal expansion coefficients between silicon and cobalt. It leads to the overall relative Co film contraction of nearly 0.5% at 700°C, the highest processing temperature, that, according to Fig. 1, drives nucleation of regions with higher concentration of defects. Simultaneously, an inhomogeneous displacement field is generated that results in local changes of the free energy (see Fig. 1b). In principal, they are very small comparing with the reaction activation energy but (as our estimates show) are of the same order of magnitude as the temperature scale $k_B T$. And it just may lead to the formation of highly heterogeneous CoSi$_2$ coatings during the silicidation reaction. The ways to avoid it are to reduce external stresses
and/or to get the cobalt film as clean as it is possible. We have performed first experiments which show that the layer-by-layer procedure strongly reducing thermal stresses allows formation of CoSi$_2$ layers of a better quality than those produced by a standard silicidation technique.

Another experimental support for the model has come from our experiments for 4-mol% yttria-stabilized tetragonal zirconia polycrystals with intrinsic oxygen vacancies. The nearly 4% volume expansion during the tetragonal t-ZrO$_2$ to monoclinic m-ZrO$_2$ phase change [8] triggered in the crack vicinity is conventionally regarded as the main mechanism leading to strengthening in zirconias containing tetragonal grains. Our three-point bend measurements for stripes with a significant amount of the vacancies [9] have revealed fracture toughness (resistance to crack propagation) two times higher than the characteristic for a usual tetragonal zirconia without defects. Because the transformation toughening is a process dominated by the volume increase, the effect observed in damaged samples [9] subjected to an external stretching force may be interpreted in terms of an enhanced driving force for the tetragonal to monoclinic inversion. Based on the concepts elaborated above, the latter mechanism could be explained as a generation of m-ZrO$_2$ precipitates inside tetragonal grains. Really, calculations for a negative sign of $\delta L$ (similar to those of Fig. 1 where $\delta L$ is positive) show that in the case of expanded samples the local lengthening of a damaged film is greater in the center than at the ends. Moreover, if to imitate the proximity to a phase transition by taking the local elastic free energy density of the system in a form of a dilational strain Landau polynomial, the effect becomes more pronounced. It means that already at apparently small strains the presence of defects would favor the generation of regions with a significantly larger atomic volume. We believe that just their presence initiates the tetragonal $\rightarrow$ monoclinic transformation and thus improves the mechanical characteristics.

In conclusion, within the framework of a continuum field model we have shown that defects may induce a spatially inhomogeneous strain state in a stressed film. In the light of present results, our experimental findings for damaged layers of cobalt disilicide [7] and 4-mol% yttria-stabilized zirconia [9] are explained qualitatively. We do hope that our approach can be applicable to some other fields of thin film metallurgy and mechanics.

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