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Solid–solid transformations via nanoscale intermediate interfacial phase: Multiple structures, scale and mechanics effects

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Abstract

Solid–solid (*SS*) phase transformations via nanometer-size intermediate melts (*IMs*) within the *SS* interface, hundreds of degrees below melting temperature, were predicted thermodynamically and are consistent with experiments for various materials. A necessary condition for the appearance of *IMs*, using a sharp interface approach, was that the ratio of the energies of *SS* and solid–melt (*SM*) interfaces, k_E, were >2. Here, an advanced phase-field approach coupled with mechanics is developed that reveals various new scale and interaction effects and phenomena. Various types of *IM* are found: (i) continuous and reversible premelting and melting; (ii) jump-like barrierless transformation to *IMs*, which can be kept at much lower temperature even for $k_E < 2$; (iii) unstable *IMs*, i.e. a critical nucleus between the *SS* interface and the *IM*. A surprising scale effect related to the ratio of widths of *SS* and *SM* interfaces is found: it suppresses barrierless *IMs* but allows *IMs* to be kept at much lower temperatures even for $k_E < 2$. Relaxation of elastic stresses strongly promotes *IMs*, which can appear even at $k_E < 2$ and be retained at $k_E = 1$. The theory developed here can be tailored for diffusive phase transformations, formation of intergranular and interfacial phases, and surface-induced phase transformations.

Keywords: Intermediate melt; Phase field; Phase transformation; Ginzburg–Landau

1. Introduction

Recently, phase transformations between two solid phases through a nanometer-size molten layer, hundreds of degrees below melting temperature, were predicted thermodynamically [1–4] and confirmed in experiments for β–δ phase transformation in HMX energetic crystals [1–3], $PbTiO_3$ nanowires [4] (Fig. 1), and for amorphization in avandia [5] and materials which exhibit a reduced melting temperature under pressure (e.g. ice, Si, Ge, geological and other materials) [3]. As a moving solid 1–melt–solid 2 (S_1MS_2) interface propagates through the sample, one solid phase melts and resolidifies into another phase. The thermodynamic condition for the formation of an intermediate melt (*IM*) is [4]:

$$E^{21} - E^{10} - E^{20} - E^{e} > (G^0 - G^s)\delta^*, \tag{1}$$

where E^{10}, E^{20} and E^{21} are the energies of the S_1M, S_2M and *SS* interfaces, E^e is the elastic energy of the coherent *SS* interface, and G^0 and G^s are the bulk thermal energies of the melt and solid phase with the lower melting temperature θ_e^m. Thus, melting significantly below θ_e^m can be brought about by a reduction in total interface energy and a relaxation of the elastic energy.

For $E^{10} = E^{20} = E^{s0}$, neglecting elastic energy, and close to θ_e^m (i.e. for $(G^0 \simeq G^s)$), the necessary thermodynamic condition for the formation of an *IM* reduces to $k_E = E^{21}/E^{s0} > 2$. It is clear that for hundreds of degrees below θ_e^m, k_E should significantly exceed 2. However, thermodynamic treatment with sharp interfaces [1–4,6] is an

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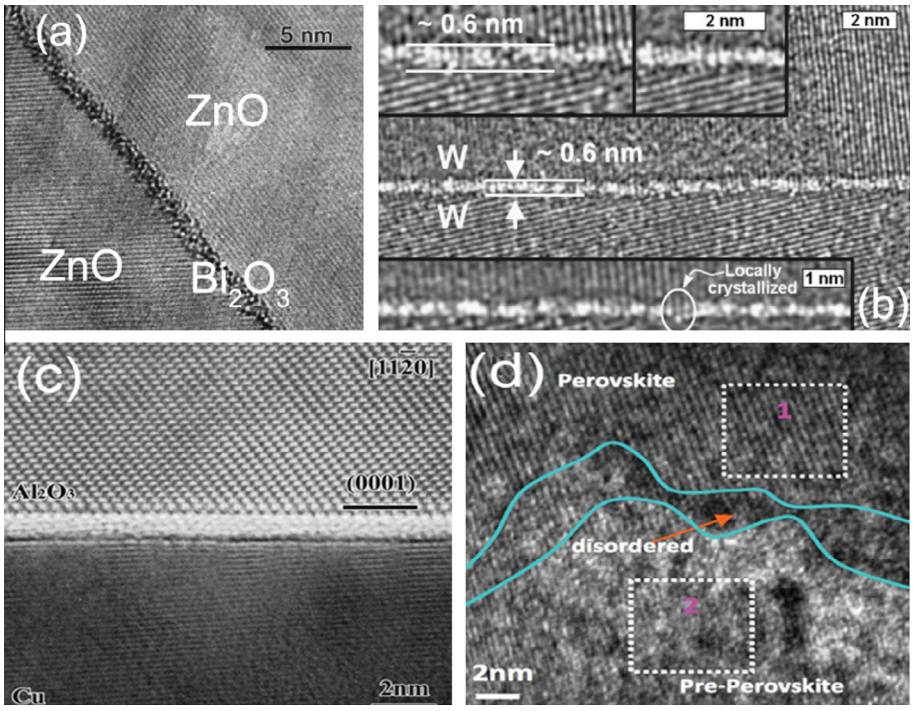

Fig. 1. Experimental evidence of the existence for nanosize intermediate interphase phases: (a) intergranular amorphous films in bismuth-doped zinc oxide (reprinted from [17]; copyright (1998) with permission from John Wiley and Sons); (b) grain boundary premelting in nickel-doped tungsten (reprinted with permission from [18]; copyright (2005), AIP Publishing LLC.); (c) intergranular films at copper–alumina interface (reprinted with permission from [19]; copyright (2005), with permission from Elsevier); and (d) solidified intermediate melt (disordered layer) at the moving perovskite–pre-perovskite interface in $PbTiO_3$ nanowire (reprinted figure with permission from [4]; copyright (2012) by the American Physical Society).

oversimplification and cannot be considered as a strict proof of the phenomena. Melting may not be complete (i.e. premelting) during the *SS* phase transformation and the width of the *IM*, δ^*, is comparable with the widths δ^{21} and δ^{s0} of *SS* and *SM* interfaces. Furthermore, kinetic effects and alternative nanostructures may play a key role in the formation of *IMs*. Therefore, in this paper a phase-field approach is developed, which led to a much more precise proof of the existence of *IMs* and provided the corresponding conditions, as well as revealing new phases, effects and phenomena. We are not aware of any previous phase-field approaches to solid–solid phase transformations via *IMs*. The most similar phase-field approaches reported are for premelting in grain boundaries [7–9], but due to different phenomena they are quite different from what we suggest below and do not include mechanical stresses. Premelting at the external surface [10,11] and surface-induced martensitic phase transformation [12,13] include mechanics but utilize two phases only and do not include a moving *SS* interface. In addition, the premelting discussed in Refs. [7,8,10,11,14] occurs a few degrees below θ_e^m, while the formation of *IM* observed experimentally [1–5] takes places several hundreds of degrees below θ_e^m; prior to this, there was no evidence that the phase-field approach could reproduce these phenomena.

One of the advantages of the approach developed here is that, in contrast to multiphase models [12,13,15,16], each of three phase transformations is described by a single-order parameter, without additional constraints on the order parameters. One of the nontrivial points in the theory is the introduction of the gradient energy for an *SS* interface within an *IM* (governed by a parameter a_0), which describes the interaction between two *SM* interfaces. The effect of two unexplored parameters, namely a_0 and the ratio $k_\delta = \delta^{21}/\delta^{s0}$ of the widths of the *SS* and *SM* interfaces, along with the ratio $k_E = E^{21}/E^{s0}$, temperature θ, and elastic stresses, is examined in detail. Several types of *IMs* are found: (i) continuous and reversible premelting and melting for small k_δ; (ii) jump-like (i.e. first-order) barrierless transformation to *IMs* for larger k_δ; (iii) persistence of *IMs* as a metastable phase at lower temperatures without barrierless resolidification, even for $k_E < 2$, i.e. when the necessary condition for thermodynamically equilibrated *IMs* is not satisfied even for θ_e^m; and (iv) an unstable *IM*, which represents a critical nucleus between the *SS* interface and *IM* and provides a thermally activated transition between them. A surprising scale effect related to k_δ is revealed: increasing k_δ suppresses barrierless *IMs* but allows one to maintain *IMs* at much lower temperatures and even for $k_E < 2$. For $2 < k_E \leqslant 2.5$, a nontrivial nonmonotonous effect of k_δ is revealed, including an *IM* gap (i.e. lack of intermediate melting) for a certain range of k_δ. Crossover from the expected increasing dependence of the width of the *IM* δ^* on parameter a_0 to decreasing dependence at very low temperature is revealed. The