INTERFACES IN NANOSTRUCTURED FILMS AND COATINGS

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1. Introduction

This paper reviews theoretical models of interfaces in nanostructured films and coatings with the special attention being paid to their nano-scale structural features and the properties associated with such features. The paper deals with many models which, however, are discussed briefly, in a non-detailed way.

In general, nanostructured films and coatings exhibit outstanding physical and mechanical properties, in which case they are thought of as advanced materials with wide applications in different areas of technology, e.g. [1-6]. The outstanding properties of nanostructured films and coatings crucially depend on both the structure and the properties of interfaces, that is, intergrain and interphase boundaries whose total volume fraction ranges from 10 to 50 % in such materials. The interfacial structures have been revealed as those ranging rather widely in nanostructured solids. They include the specific interfacial structures that are inherent to only nanostructured solids and conventional interfacial structures that exist also in conventional films and coatings. (Hereinafter, by conventional films and coatings are meant coarse-grained polycrystalline films and multilayer coatings that consist of meso-scale single crystalline or coarse-grained polycrystalline layers.) In this context, the present paper is concerned with not only interfaces in nanostructured films and coatings, but, in part, also with interfaces in conventional films and coatings.

The specific features of interfacial structures in nanostructured films and coatings are caused, in particular, by the following: (1) The volume fraction of the interfacial phase is extremely high in nanostructured films and coatings. (2) Interfaces as structural elements mostly have extremely short dimensions in nanostructured films and coatings, in contrast to the situation with conventional solids. (3) There is a strong elastic interaction between neighbouring interfaces, because (extremely short) distances between them are close to the characteristic scales of their stress fields. (4) In nanocrystalline films and coatings there is a strong effect of triple junctions and nanograins on interfaces and vice versa, in contrast with conventional

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films and coatings, because the volume fraction of triple junctions is extremely high in nanocrystalline solids and because nanograins commonly are more distorted than conventional grains in polycrystalline films and coatings. (5) Formation of nanostructured films and coatings frequently occurs at highly non-equilibrium conditions that essentially influence the interfacial structures.

The aforesaid aspects should be taken into account in theoretical models of the interfacial structures in nanostructured films and coatings, which, in most cases, can not be unambigiously identified with the help of contemporary experimental methods. Below we will briefly review "fresh" models of interfaces in nanostructured films and coatings while focusing on highly defected and non-periodic interfaces whose structural features are related to nano-scale effects.

2. Misfit Disclinations at Interfaces in Nanostructured Films

Let us consider the specific features of misfit defect structures that can exist in systems consisting of a single crystalline substrate and a nanocrystalline film. In general, misfit stresses (that occur in films due to a geometric mismatch between crystalline lattices of films and substrates) essentially contribute to the properties of films. Misfit stresses are commonly viewed to effectively relax via generation of "standard" misfit dislocations with crystal lattice Burgers vectors. Such dislocations commonly form dislocation rows at interphase (film/substrate) boundaries, partly compensate misfit stresses and, therefore, often improve functional physical characteristics of films, e.g. [7-10]. At the same time, misfit dislocation cores are located at interphase boundaries, and, therefore, negatively affect functional physical characteristics of interphase boundaries. This causes high interest in searching for alternative effective micromechanisms for relaxation of misfit stresses.

In nanocrystalline films with their high-density ensembles of grain boundaries, there is an effective alternative to the standard physical micromechanism for relaxation of misfit stresses, namely formation of special interfacial disclinations (Fig. 1) [11]. Such disclinations induce stresses that compensate, in part, misfit stresses in the film and are located at junctions of the interphase boundary and grain boundaries (Fig. 1a). In general, as with disclinations in polycrystalline and nanocrystalline bulk solids synthesized at highly non-equilibrium conditions [12, 13], the discussed disclinations can exist also at triple junctions of grain boundaries in a nanocrystalline film (Fig. 1b). Hereafter we shall call such disclinations (Fig. 1a and 1b) as misfit disclinations.

Following the estimations [11] of energetic characteristics of a nanocrystalline film with misfit disclinations periodically arranged at an interphase boundary between a substrate and the film (Fig. 1a), the existence of misfit disclinations is more energetically favourable than the existence of "standard" planar rows of misfit dislocations with lattice Burgers vectors. More than that, following estimations [11],

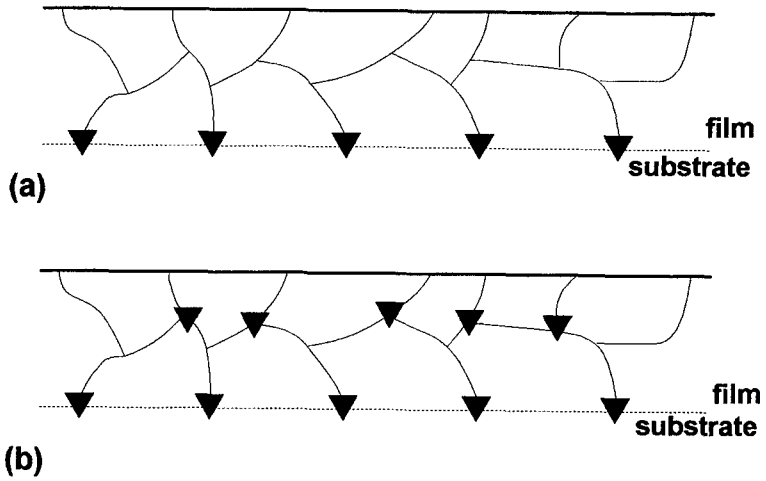


Figure 1. Misfit disclinations at interfaces in nanostructured films. (a) Periodically arranged ensemble of misfit disclinations at nanocrystalline film/substrate interface. (b) Misfit disclinations at interfaces — intergrain and interphase boundaries — in nanocrystalline film.

the critical thickness, h_c, for the generation of misfit disclinations in nanocrystalline films is $h_c = 0$, at least, for characteristic values of misfit parameter ranging from 10^{-4} to 10^{-2}. It means, in particular, that the generation of misfit disclinations is more energetically favourable than the existence of a coherent interphase boundary between a substrate and a nanocrystalline film at any value of its thickness.

Misfit disclinations and their configurations can be formed also in polycrystalline films. The partial case of misfit disclination configurations, namely dipoles of misfit disclinations located at junctions of an interphase boundary and twin boundaries, has been observed experimentally in epitaxial rhombohedral ferroelectric films (see paper [14] and references therein).

Generally speaking, misfit disclinations can also be generated as defects that bound walls of misfit dislocations in single crystalline films and multilayer coatings (Fig. 2) [15]. Such dislocation walls have been observed experimentally in films resulted from convergence of island films [16].

3. Grain Boundary Dislocations and Their Configurations as Misfit Defects in Nano-Film/Substrate Systems

In general, due to the presence of high-density ensembles of grain boundaries, their triple junctions, and junctions of grain boundaries and interphase boundaries in nanocrystalline films and coatings, the generation of grain boundary dislocations

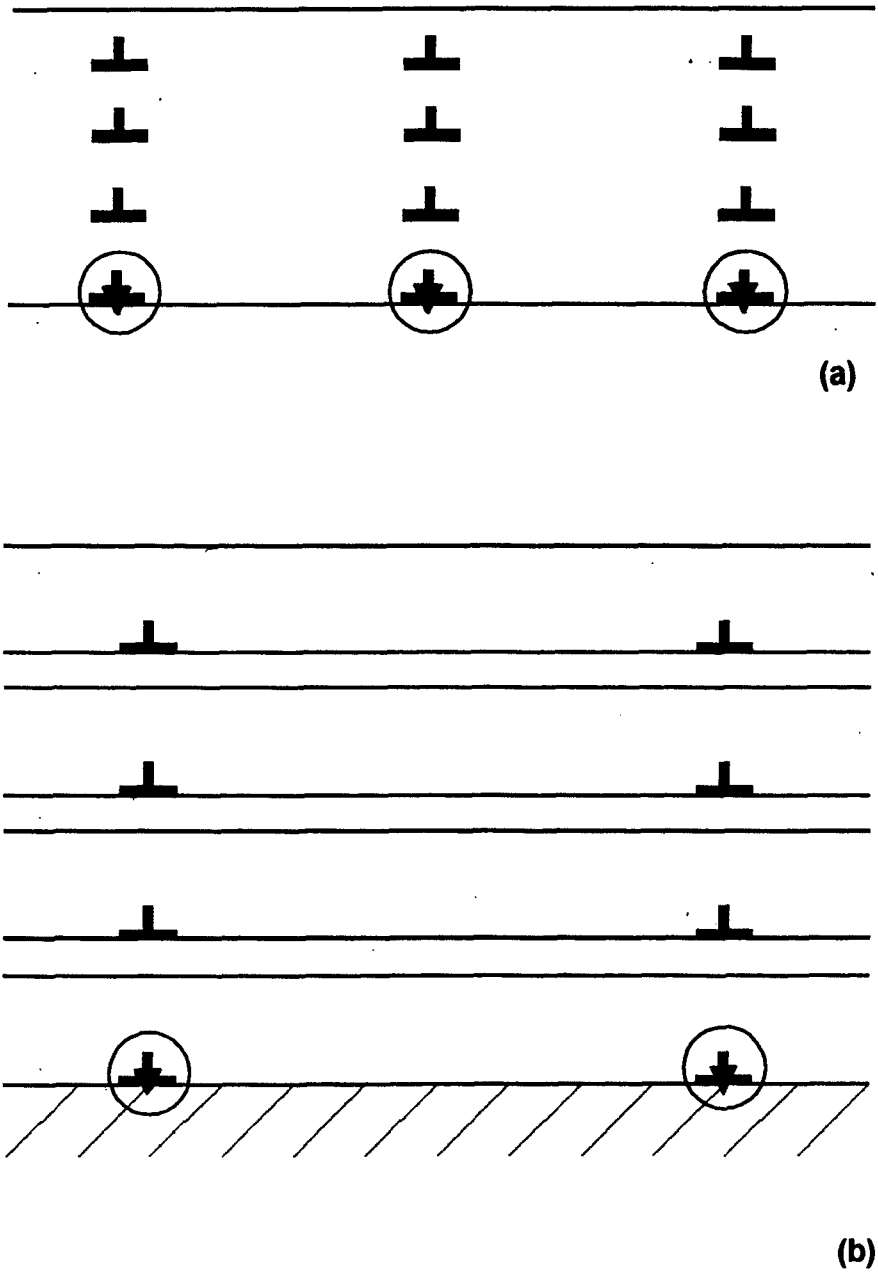


Figure 2. Disclinations (located at open circles) at ragged walls of misfit dislocations in (a) single crystalline film and (b) multilayer coating.

and their configurations as misfit defects, is capable of effectively contributing to relaxation of misfit stresses. For instance, let us consider a periodically arranged ensemble of grain boundary dislocations located at junctions of grain boundaries and the interphase boundary between a single crystalline substrate and a nanocrystalline film (Fig. 3). In context of the general theory of misfit dislocations (e.g., [7-10]), such dislocations create stress fields that compensate misfit stresses generated due to the geometric mismatch between the crystalline phases matched at an interphase boundary. In doing so, the most spatially homogeneous distribution of misfit dislocations is characterized by minimal elastic energy density and, therefore, is most stable.

Grain boundary dislocations are commonly characterized by Burgers vectors being essentially lower than those of "standard" misfit dislocations being crystal lattice dislocations. This specific feature allows grain boundary dislocations to be more homogeneously distributed along an interphase boundary as compared with "standard" misfit dislocations with the proviso that the sum Burgers vectors of the misfit dislocation ensembles are the same per unit of the boundary length. As a corollary, the existence of grain boundary dislocations as misfit dislocations is more energetically favourable than that of "standard" misfit dislocations.

In general, due to the presence of high-density ensembles of grain boundaries in nanocrystalline films, complicately arranged configurations of grain boundary dislocations can be formed as defect configurations causing the effective relaxation of misfit stresses in nanocrystalline film/substrate systems. Examples of such configurations are compensated and non-compensated dipoles of grain boundary dislocations (Fig. 4a), networks of grain boundary dislocations distributed within a nanocrystalline film (Fig. 4b), grain boundary dislocation-dislocation ensembles (Fig. 4c), etc.

4. Partly Incoherent Interfaces

An interphase boundary between a single crystalline substrate and a nanocrystalline film is featured by the existence of many boundary fragments bordered by junctions of the interface boundary and grain boundaries of the nanocrystalline film. In these circumstances, one of the effective micromechanisms for misfit stress relaxation that are specific for nanocrystalline film/substrate systems is the formation of a partly incoherent interface, a partly incoherent interphase boundary. Each such a partly incoherent interface consists of both coherent and incoherent fragments and is characterized, in the first approximation, by a modified misfit parameter, $\tilde{f} = f(1 - \delta)$, depending on the ratio, $\delta = l_i/l_c$, of the sum length, l_i, of the incoherent fragments to the sum length, l_c, of the coherent fragments. In general, when the thickness, h, of a film increases resulting in an increase in the elastic energy, this energy effectively relaxes via generation of new incoherent fragments. In these circumstances, a nanocrystalline film is characterized by two critical values, h_{c1} and h_{c2}, of its thick-

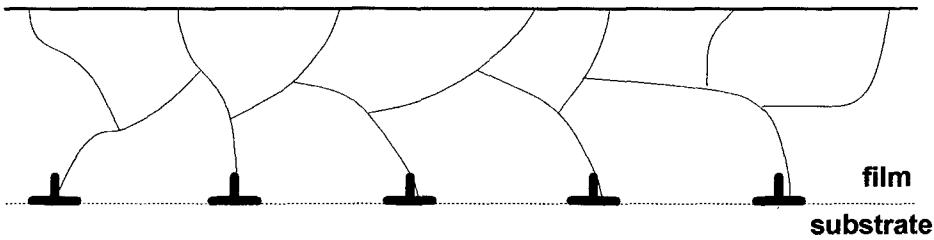
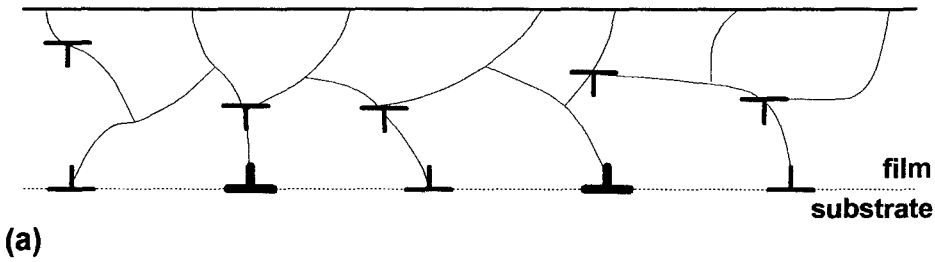
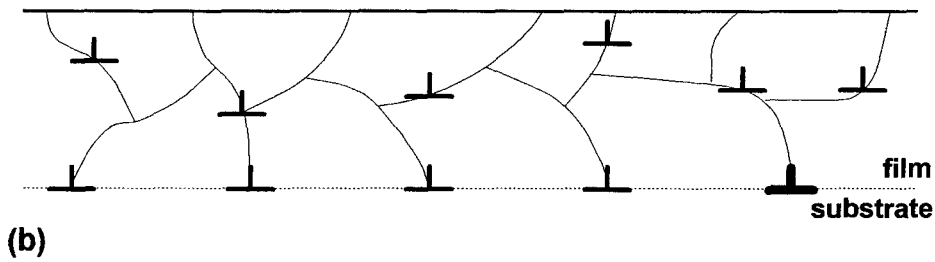


Figure 3. Periodically arranged ensemble of misfit, grain boundary dislocations.





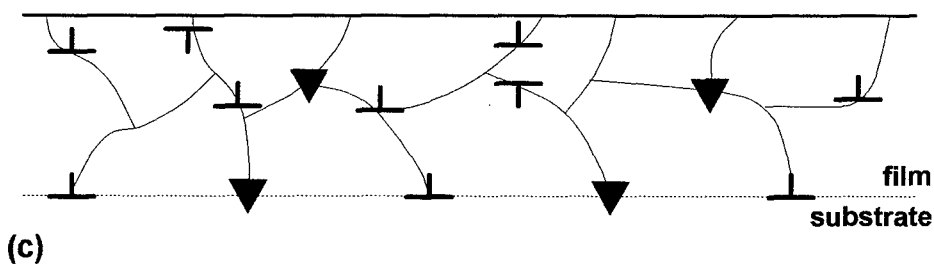


Figure 4. Configurations of interfacial dislocations and disclinations in nanocrystalline films.

ness. Generation of incoherent fragments is energetically favourable in films with thickness above h_{c1} (Fig. 5 a and b). The existence of a totally incoherent interface is energetically favourable in films with thickness above h_{c2} (Fig. 5 c).

5. Crystal/Glass Interfaces

The properties of advanced crystal-glass nanocomposites essentially depend on crystal/glass interfaces, e.g. [17-19], in which case the characteristics of crystal/glass interfaces are of great interest. Recently, a model [11, 20] has been developed describing crystal/glass interfaces as semi-coherent interfaces containing misfit disclinations and dislocations. In the framework of this model, misfit disclinations are generated at crystal/glass interfaces as extensions of disclinations inherent to the adjacent glassy phase. Misfit dislocations at crystal/glass interfaces provide a partial compensation of the so-called dilatation misfit stresses occurring due to the difference between the characteristic interatomic distances in the adjacent crystalline and glassy phases.

Crystal/glass interfaces modeled [11, 20] as semi-coherent interfaces contain coherent fragments, in which case such interfaces have to be sensitive to crystallographic peculiarities of the adjacent crystalline phase. In this context, experimental observations of facetted crystal/glass interfaces [17, 21] and pronounced textures in polycrystalline films on glassy substrates [19] support the theoretical model [11, 20].

In the framework of the model [11, 20], the total elastic energy density of a crystal/glass interface (calculated as the elastic energy density of misfit disclinations and dislocations) is as follows:

$$W \approx k G a , \tag{1}$$

where k ranges from 0.06 to 0.18, G denotes the shear modulus, and a the mean interatomic distance in the glassy phase. In general, W is either larger or smaller than values of the energy density (per unit area) of high-angle grain boundaries in crystals (for example, [22]), depending on parameters of grain boundaries and crystal/glass interfaces.

6. Amorphization at Interphase Boundaries in Multilayer Coatings

Solid state amorphizing transformations occur in multilayer coatings consisting of alternate layers, say, α and β [23, 24]. In these circumstances, layers of the new amorphous alloyed phase $\alpha - \beta$ nucleate at α/β interfaces due to diffusional mixing of atoms α and β (Fig. 6). Recently, it has been experimentally revealed that the solid state amorphization does not occur in Ni/Ti multilayer composites having the crystalline layer thickness in a composite below some critical thickness h_c^{am} (being several nanometers) [23].

Solid state amorphizing transformations in layered composites have been theo-

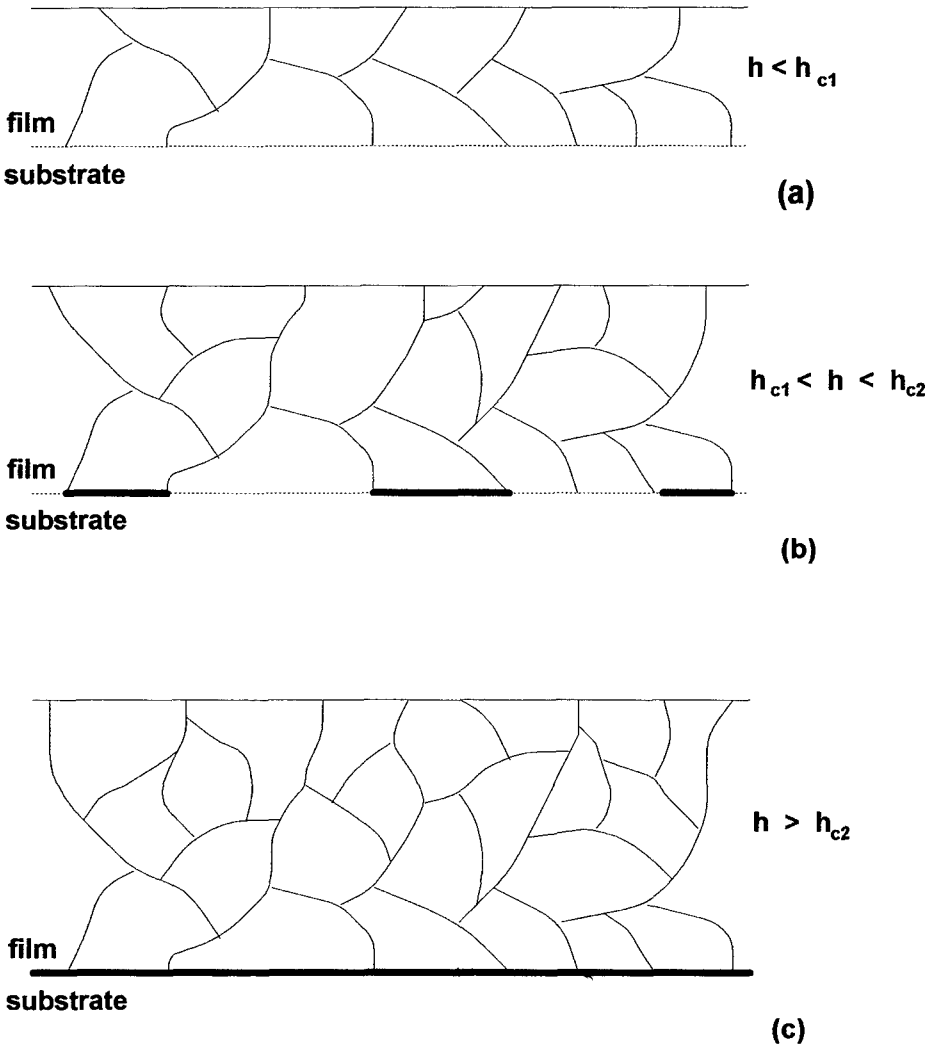


Figure 5. Coherent-to-incoherent transformation of interphase boundary as a micromechanism for misfit stress relaxation.

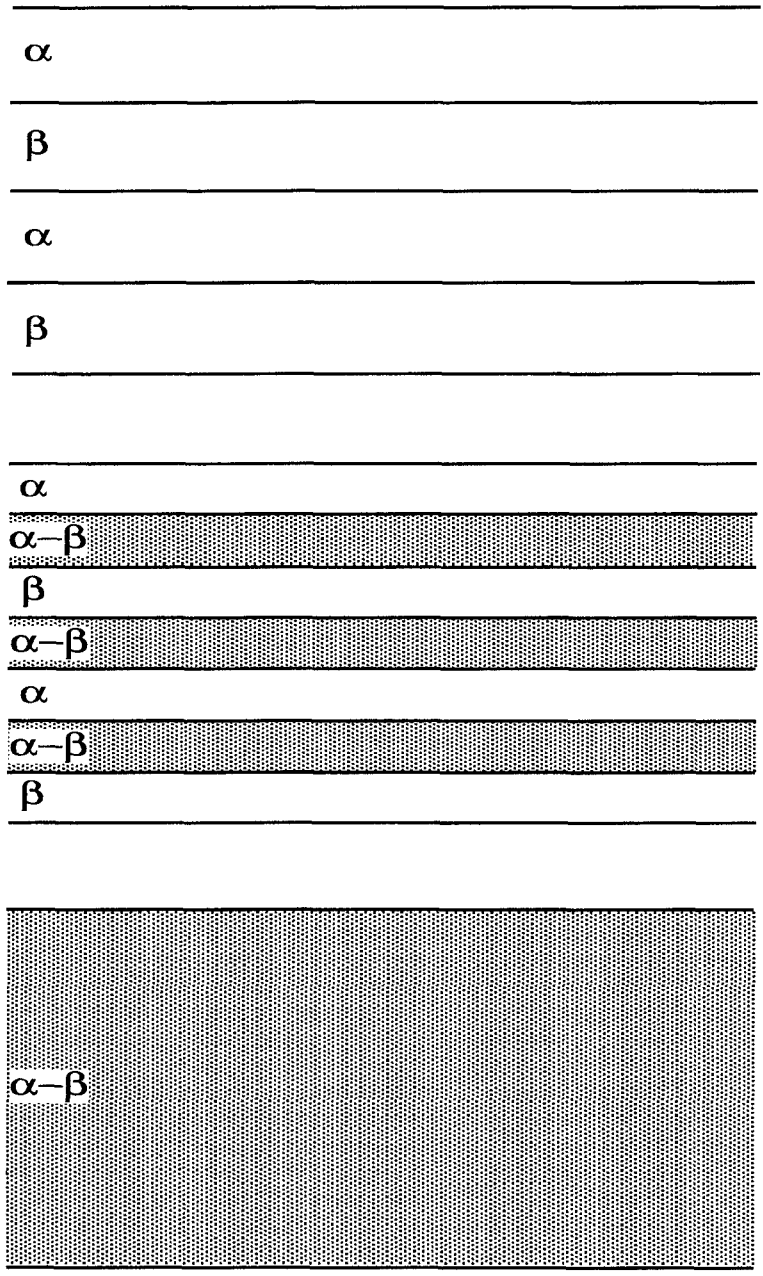


Figure 6. Solid state amorphization in multilayer coatings.

retically described in [25] as phase transformations affected by misfit straines. It has been found that there is a misfit-stress-induced minimal critical thickness h_c^{am} which characterizes the solid state amorphization in layered composites: composites consisting of layers with thickness whose values are above h_c^{am}, are amorphized, whereas below are not amorphized.

7. Amorphous and Quasioperiodic Grain Boundaries

Let us briefly outline models that describe amorphous and quasiperiodic interfaces in nanostructured films and coatings. These models are beyond the applicability of the standard concept [22] of periodic interfaces in solids.

Grain boundaries in nanostructured materials are characterized by extremely short lengths, in which case tilt boundaries of finite extent are theoretically recognized to be more often quasiperiodic than periodic [10, 26, 27]. The presence of such quasiperiodic tilt boundaries in nanostructured materials, in particular, is capable of effectively contributing to the experimentally observed deviations of the yield stress dependence on grain size from the standard Hall-Petch relationship [10, 26].

Amorphous grain boundaries are often experimentally observed in nanocrystalline and polycrystalline ceramics [28, 29]. Following computer experiments (see [30, 31] and references therein), such boundaries can exist also in nanostructured metals and silicon. The elastic energy and stress fields of amorphous grain boundaries are effectively calculated as those of special ensembles of grain boundary dislocations.

8. Technological Aspects

The above representations on new interfacial defect structures potentially can be used in both optimization of conventional technologies and design of new technologies for synthesis of nanostructured films and coatings with desired properties. So, in the light of the representations of new interfacial defect structures, interphase boundaries in nanostructured films and coatings strongly affect grain boundaries within nanocrystalline films and vice versa. As a corollary, one can use technologies that control interphase boundary parameters in order to form grain boundary structures with desired properties in nanocrystalline layers. And, on the contrary, one can use technologies that control grain boundaries in order to form interphase boundaries with desired properties in nanostructured coatings.

In particular, the effect of relaxation of misfit stresses via formation of grain boundary defects on nanocrystalline films potentially allows one to design films and coatings with spatially variable stable structure which consists of single crystalline

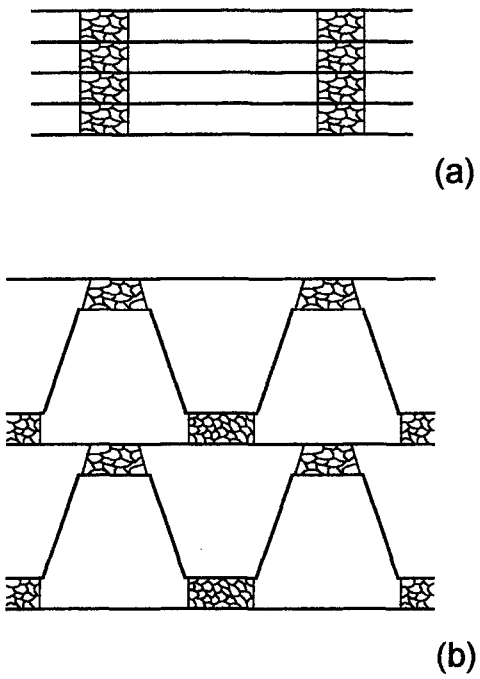


Figure 7. Coatings with spatially variable structures containing single crystalline and nanocrystalline regions.

regions divided by ideal coherent boundaries and nanocrystalline regions causing effective relaxation of misfit stresses. In these circumstances, single crystalline regions with ideal coherent matching exhibit desired functional properties, while nanocrystalline regions play the role of structural elements that provide misfit stress relaxation. Some illustrations of the coatings with spatially variable structures and various geometries are shown in Fig. 7.

The coatings with spatially variable structures potentially can be synthesized, for instance, in a two-step manner. At the first step, a coating with the completely nanocrystalline structure is synthesized by conventional methods. At the second step, local heating can be used to induce local recrystallization processes that result in a desired spatially variable structure. This method can serve as a kind of nanolithography.

Also, local regions with the nanocrystalline structure in either film or substrate of a heteroepitaxial system are capable of effectively contributing to misfit stress relaxation in the system, even if such nanocrystalline regions are located far from

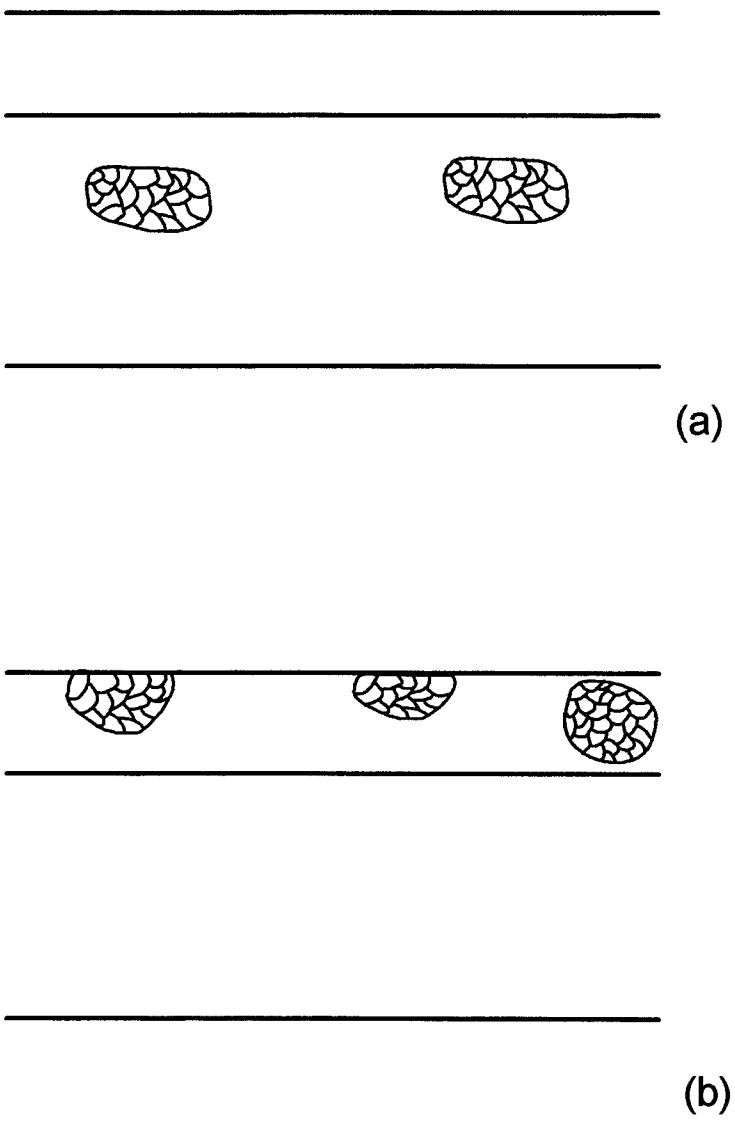


Figure 8. Local nanocrystalline regions in film/substrate systems. Nanocrystalline regions are located in either (a) substrate or (b) film.

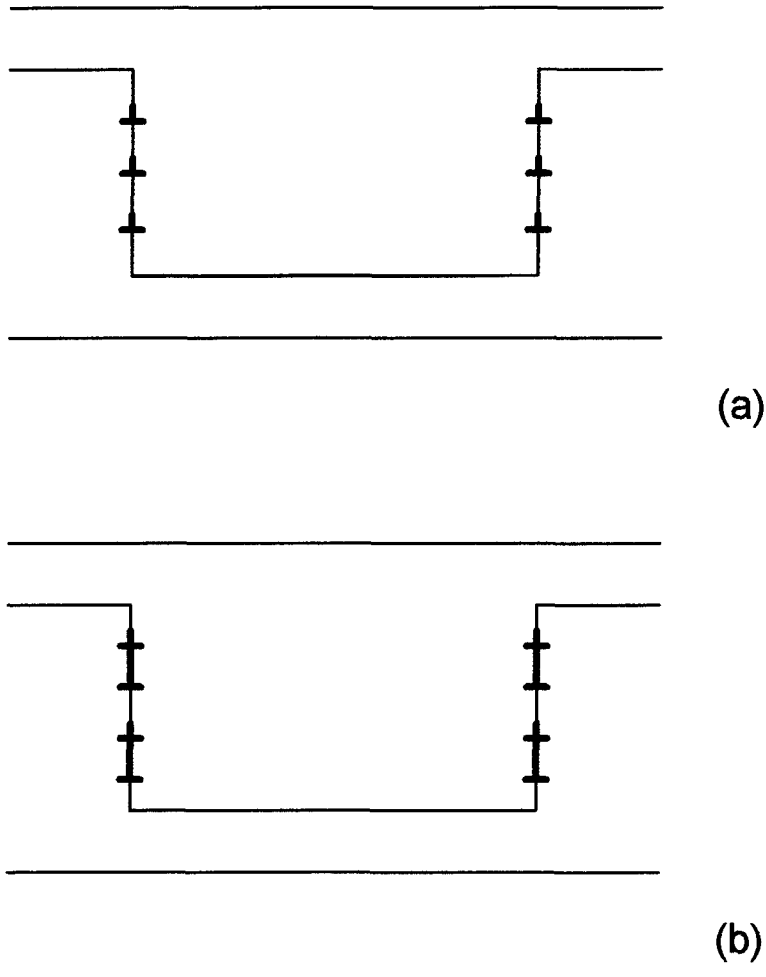


Figure 9. Film/substrate systems with interface containing walls of (a) perfect and (b) partial misfit diclocations.

the interphase boundary (Fig. 8). This effect can be potentially used in technologies, too.

Also, multilayer coatings with single crystalline layers divided by interfaces having a complicated geometry and containing walls of either perfect or partial misfit dislocations (Fig. 9) potentially can be synthesized as coatings with unusually wide areas of the ideal coherent matching. This is important for applications of coatings with the functional properties dependent on the coherent matching of thick single crystalline layers.

9. Concluding Remarks

Thus, such defected and non-periodic interfaces as quasiperiodic tilt boundaries, partly incoherent interfaces, interphase boundaries with misfit disclinations, misfit grain boundary dislocations, and misfit partial dislocations, crystal/glass interfaces, quasiperiodic and amorphous interfaces between crystalline phases are inherent structural elements of nanostructured films and coatings. Both the specific structure and the specific properties of defected and non-periodic interfaces in nanostructured films and coatings cause the specific effects of such interfaces on the macroscopic properties of nanostructured films and coatings. These effects should definitely be taken into account in experimental research and theoretical description of the structure and behavior of advanced nanostructured materials.

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