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Structure of Grain Boundaries in Nanocrystalline and Quasicrystalline Materials

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Abstract

The study of the structure of interfaces assume importance in understanding and predicting material behaviour. Of the various types of interfaces, grain boundaries are most important because of their crucial role in polycrystalline materials. The availability of transmission electron microscopes with a point resolution of 0.2 nm or better has made it possible to study atomic configurations at grain boundaries. Research on interfaces in two classes of materials, namely, nanocrystalline phases and quasicrystalline systems have been of much contemporary interest. In the former, the grain boundary atom fraction is significant and can be as high as fifty percent. In the latter we have interesting possibilities of lattice matching between a quasicrystalline phase and a structurally related crystalline phase. The translational order in the crystalline phase is replaced by quasiperiodic order across the interface. Nanocrystalline phases are those with grain sizes of the order of a few nanometres. Structure of grain boundaries and triple line junctions in nanocrystalline metals palladium and titanium, and ceramics thorium dioxide and zirconium dioxide have been extensively studied at our Centre. These studies have helped in a detailed understanding of the nature of defects and the relaxation effects. The results indicate less disorder in the structure of grain boundaries than indicated by other techniques. Images of triple line junctions and of the grain boundaries have been interpreted in terms of the disclination model. The study of the nanocrystalline state is relevant since the nanocrystalline state has been indicated to be a desirable microstructural state for such processes as solid state amorphization reactions. A surprising finding is that no specific structural features could be related to the nature of chemical bonding in the two classes of nanocrystalline materials studied. Structural relations between quasicrystalline and related crystalline rational approximant phases have been of interest for some time now. Such relations are now being used to understand interface structures. Interfaces between structurally related, but dissimilarly periodic phases are expected to show a degree of lattice match. Our HREM studies of interfaces in A–Cu–Fe and Al–Pd–Mn systems have revealed well defined structural ledges. They have been explained in terms of the common structural motifs of the two phases and their geometrical matching across the interface plane. The structural studies in quasicrystal phases while not directly capable of revealing their structure, can indirectly help in finding a solution to their structures.

INTRODUCTION

The study of interfaces in materials is important in understanding and predicting the behaviour of materials. Of the various kinds of interfaces encountered in materials, grain boundaries are the most important both because of their role in interfacial reactions and because of the variety of possible configurations. The significance of the grain boundary triple junctions and the role of disclinations at the triple junctions in interfacial processes is now being recognized, especially in nanocrystalline materials [1]. Elucidation of the atomic structures of grain boundaries in nanocrystalline materials is more difficult than in conventional materials. Many of the physical and mechanical properties of nanocrystalline solids are widely different from conventional solids, resulting from the difference in the nature and type of defects present in them. A discussion on the stability of various defects in nanocrystalline solids has been given by Sundararaman [2].

The problem of locating the atoms in an icosahedral phase remains. Recent studies have noted useful structural relations between the quasicrystalline phase and coexisting crystalline phases [3]. Emphasis has been on the cluster and motif approach in recent times since the projection formalism is successful in explaining the two related lattices but cannot generate the atomic positions. The abundant quasicrystal literature includes a small collection of reports of interface studies in quasicrystals. In the absence of information on the atomic positions or lattice point decorations in quasicrystalline systems, approaches based on projection formalism are of limited value in understanding the observed interface structures at the atomic scale.

In the present work, HREM investigations carried out at our Centre on interfaces in nanocrystalline and quasicrystalline systems are reported.

INTERFACES IN NANOCRYSTALLINE SYSTEMS

HREM studies of thin film nanocrystalline palladium and bulk nanocrystalline thorium dioxide prepared by direct denitration were studied with special reference to the structure of interfaces. A brief account of our findings is given below.

HREM image of nanocrystalline Palladium is shown as Fig. 1, *a*. The grain size is 3–5 nm. Regions with brighter contrast of size in the range of 2–3 nm are seen at many of the grain junctions. Other features of interest in the HREM images are that the character of some grain boundaries seems to vary along the length, changing from sharp to diffuse. The interplanar spacing was measured in a large number of grains and the spacings are always larger than that for the bulk alloy. There is also a wide variation in lattice spacing among the different nanocrystalline grains. Another notable feature is that while some boundaries appear sharp, others are diffuse. The maximum disorder measured perpendicular to the grain boundary is about 2 nm. A few boundaries were also seen to have a continuously varying structure: while some regions of the boundary are sharp, adjacent regions along the same boundary appear disordered. These features can be reconciled with the various relaxation modes of the grain boundaries in nanocrystalline materials, as highlighted in the discussion below.

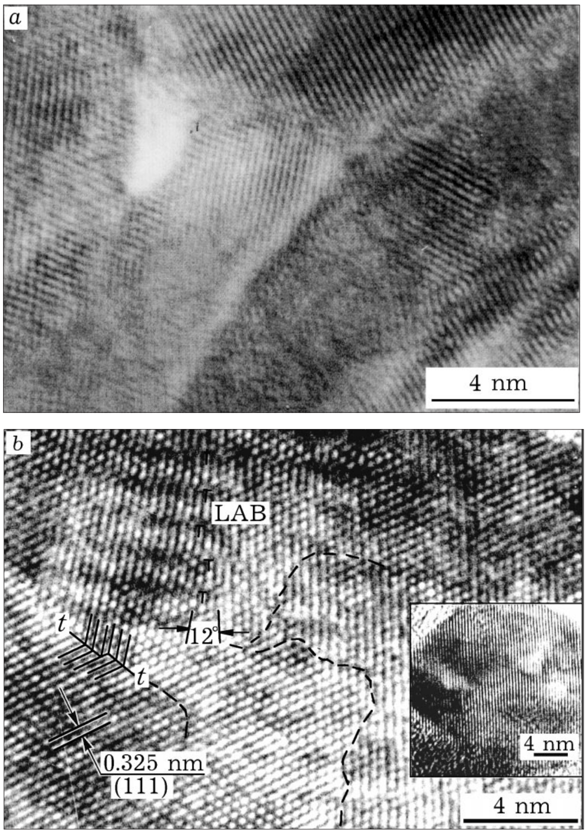

Fig. 1. HREM of nanocrystalline palladium (*a*) and thorium dioxide (*b*).

A HREM image of a thorium dioxide, obtained through direct denitration, is shown in Fig. 1, *b*. After sintered lattice is strain free, as seen in the figure. A variety of grain boundary structures including some low angle boundaries are seen. Due to sintering at high temperatures, the grain boundary structures are relaxed. Hence bright contrast features seen so frequently at the triple junctions in physical vapour deposited nanocrystalline phases are rarely seen. However, that the grain boundary character seems to change along it's length is true in this case as in the case of nanocrystalline palladium.

The structure of nanocrystalline grain boundaries has continued to remain a strongly debated topic, with relevance to its similarities with conventional boundary structures. Birringer [4] has reported a gas-like disordered grain boundaries in nanocrystalline materials, based on extended X-ray absorption fine structure analysis results. However, Siegel *et al.* [5] have reported that nanocrystalline grain boundaries are sharp looking and are not different from the coarse grained boundary structures, based on their HREM results.

Grain boundaries have been described using the disclination model since both of them are rotational defects, unlike dislocations. The equivalent of the Burger's vector of a dislocation is the rotation vector for a disclination. The continuously varying curvature of the boundary is split into regions of high misfit and low misfit regions by the proper choices of disclination rotation vector. The boundary itself is thus constituted of regions of low and high energy. This picture of a grain boundary helps one to realize the presence of varying degrees of disorder in nanocrystalline materials that are generally the outcome due to the different levels of relaxation of the disclination arrays in the boundary. The role of disclinations gains more importance in nanocrystalline solids owing to the high density of grain boundaries.

Bollmann's early work [6] has showed that where the dislocation balance at a triple line is not satisfied, disclinations result. Such triple lines have been named U-lines. It was hypothesized that "a physical difference" should exist at such triple lines. The formation of amorphous packets has been stated in a separate work to be one of the relaxation modes for unbalanced triple lines. Subsequent experimental work on the pitting corrosion in high purity nickel has shown enhanced corrosion rates at U-lines [1]. Energy considerations preclude existence of perfect disclinations in crystals. Partial disclinations have lesser energy. Screening of these disclinations by formation of dipoles or splitting to smaller powers, reduces their energy further. External screening by boundaries or surfaces has a greater effect in energy minimization for disclinations than dislocations. Screened partial disclinations have energies comparable to individual lattice dislocations and can thus be present in engineering materials, for example, as dipoles at grain boundaries. Even so, not all triple junctions show disclination character, the volume fraction of triple lines and of disclinations increasing as grain size decreases to the nanocrystalline range.

Our HREM results are seen to support the disclination model in the light of the above discussion. Formation of amorphous packets is a strong relaxation mode of triple junction disclinations [2]. The amorphous packets represent U-line triple junctions. A highly nonuniform state of stress should exist in the films because of the varying screening effect of disclinations. This should result in variations in the interplanar spacings in the different nanograins. A crystal to amorphous transition can be considered to be associated with an increase in disclination content. Splitting of a triple junction disclination in a nanocrystalline into smaller power partials can lead to the formation of amorphous regions at the core of the initial defects [7]. The driving forces for this process are decrease in elastic energy on splitting and screening of disclinations and the negative free energy of mixing in systems exhibiting solid state amorphization. The nanocrystalline state is thus a desirable microstructural precursor for solid state amorphization.

INTERFACES IN QUASICRYSTALLINE SYSTEMS

While we have studied a number of quasicrystalline systems, the highlights of interface studies are illustrated using our researches into Al−Cu−Fe and Al−Pd−Mn systems. Figure 2 shows a quasicrystal − quasicrystal interface in a melt spun $Al_{65}Cu_{20}Fe_{15}$. The interface plane is approximately twofold. The interface shows frequent, irregularly spaced ledges of length varying from 2.5 to 4 nm separated by height of ~ 1 nm. The ledges are atomically flat with little disorder. On a larger scale, the interface is curved. Figure 3 shows the HREM image of an interface between the icosahedral phase and the orthorhombic R-phase in melt spun $Al_{68}Pd_{23}Mn_9$ alloy. Orientation of the icosahedral phase is approximately twofold along the beam direction. Ledges are clearly seen. The ledge lengths are longer in this case, ~ 7 nm. Again, the ledges are atomically flat.

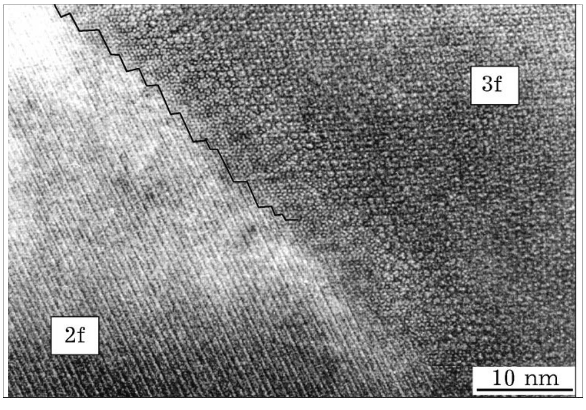

Fig. 2. Quasicrystal − quasicrystal interface in Al−Cu−Fe.

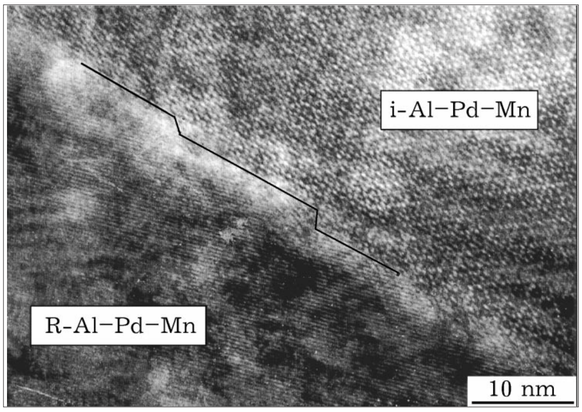

Fig. 3. Quasicrystal − quasicrystal interface in Al−Pd−Mn.

Ledge structure at interfaces between crystalline phases can be differentiated as being structural ledge or growth ledge. Growth ledges at interfaces in crystalline materials extend over longer lengths than the structural ledges. In the present case of the quasicrystal − quasicrystal and the crystal − quasicrystal interface, we argue that the ledge structures are structural ledges and are geometrically necessary. That the ledge faces appear atomically flat and that there is very little disorder suggest that the atomic coordination in the interface plane match to some extent. Ledges appear where the mismatch can no more be accommodated by matching of positions of common motifs across the interface. Icosahedral coordinations exist around two of the Al and Mn atoms in $Al_{31}Mn_6Ni_2$, which is the structure type for the orthorhombic R-phase in the Al−Pd−Mn system. The Mn atom icosahedron is more distorted than the Al icosahedron. The Pd and Mn atoms in the $Al_{68}Pd_{23}Mn_9$ are distributed over the Mn and Ni sites in $Al_{31}Mn_6Ni_2$. Icosahedral clusters in the icosahedral phase thus have similar environments in the R-phase atoms close to the interface. Due to this, a degree of lattice match can be envisioned across the i-phase − R-phase interface. Even in this simplistic picture, it is easy to see that the different types of icosahedral clusters present in the two structures will lead to a variety of possible lattice matches. Depending on which types actually coordinate across the interface, we can have ledge length variations.

SUMMARY

In the case of nanocrystalline boundaries we note the existence of following characteristics:

(i) boundaries with large amounts of disorder upto 2 nm are present;

(ii) low angle boundaries with straight edges and twins are found to coexist;

(iii) triple junctions with amorphous packets and disorder are seen;

(iv) no evidence for "gas-like" disorder have been noticed.

In the case of quasicrystals, the results and ideas presented here suggest that the observed interface structures can be correlated with the known structural relations between the quasicrystalline and the related crystalline phase. Detailed study of the existing atomic coordination in the quasicrystalline phase will provide further input to modelling the interface structure in terms of a finite number of matching motifs in the two related structures somewhat analogous to the conventional structural unit models.

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