ATOMISTIC SIMULATION OF NANOCRYSTALLINE MATERIALS

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DISCLAIMER

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ABSTRACT

Atomistic simulations show that high-energy grain boundaries in nanocrystalline copper and nanocrystalline silicon are highly disordered. In the case of silicon the structures of the grain boundaries are essentially indistinguishable from that of bulk amorphous silicon. Based on a free-energy argument, we suggest that below a critical grain size nanocrystalline materials should be unstable with respect to the amorphous phase.

INTRODUCTION

Atomistic simulations can provide unique insights into the structure and properties of nanocrystalline materials (NCMs), not available by other means. Here we briefly summarize the results of some recent simulations on the growth from the melt of nanocrystalline copper, the relationship between NCMs and the glass, and the structure of grain boundaries (GBs) in nanocrystalline silicon.

A STRUCTURAL MODEL OF NANOCRYSTALLINE MATERIALS

The nature of grain boundaries in nanocrystalline materials has been the subject of extensive discussion ever since the first ultrafine-grained polycrystals were synthesized a decade ago.[1,2] At issue is the question as to whether a novel, "frozen-gas" like state of matter exists in polycrystalline materials with a grain size typically below 10 nm or whether the structure and properties of NCMs can be extrapolated from those of coarse-grained polycrystals.[3,4] In spite of much experimental work attempting to address this issue, a structural model consistent with the observations and one that permits some of the anomalous properties of these materials to be predicted, has not evolved. Our goal has been to develop a molecular-dynamics simulation method to grow space-filling, fully dense three-dimensional polycrystals. It was hoped that by characterizing the underlying atomic structure of the GBs and grain junctions, a structural model for nanocrystalline materials could be developed.

To address the question of the structure of grain boundaries in NCMs, atomic-level computer simulations were used to grow fully dense nanocrystalline fcc copper from a melt into which small crystalline nuclei with more or less random, but well-defined, orientations were inserted.[5] In spite of some striking similarities to the well-known structures of the interfaces in coarse-grained materials, the atomic structures of the grain boundaries were observed to be neither frozen-gas like nor could they be obtained simply by extrapolation from those determined in the coarse-grained compounds. The key observation was a complete lack of strict long-range structural periodicity parallel to the interfaces because many short segments with locally different atomic structures can coexist in these highly constrained microstructures.[6] Moreover, the structures and energies of the grain boundaries in the NCM were much more similar to each other than are those of the corresponding GBs in bicrystals. Based on these observations, we suggested that historic models viewing the grain boundaries as an "amorphous-cement" like phase (Rosenhain, 1913) with a more or less uniform width, density and energy density appear to describe the interfaces more aptly than structural models derived from atomic-resolution experiments on coarse-grained materials [6].

RELATIONSHIP BETWEEN NANOCRYSTALLINE MATERIALS AND GLASSES

The rather isotropic structures and energies of the GBs observed in the above NCM suggested that it should be possible to formulate a simple structural model that is consistent with the MD simulations. In addition to isotropic GB properties, such a model should capture, as a minimum, two additional essential structural features of NCMs, namely geometrical constraints (i.e., a finite grain size) and structural inhomogeneity (due to the GBs and grain junctions). Apart from incorporating a finite grain size, our model [7, 8] was designed to focus less on microstructural features than on a realistic physical description of the nature of the GB-induced inhomogeneities in the material. We found that it is geometrically possible to construct a space-filling three-dimensional polycrystal with a uniform (and unique) rhombohedral grain shape in which all GBs are crystallographically equivalent and all grain boundaries are identical asymmetric tilt boundaries (in our case (111)(115) tilts).[7] Having eliminated the distributions in the types of grain boundaries and the grain shapes, our simulations of this model focused entirely on the effect of the grain size, i.e., on the role of the geometrical constraints on the atomic structure and physical properties of a well-defined GB.

We constructed a series of such model NCMs with grain sizes ranging from ~8Å to ~27Å. The GBs in our monodisperse model NCMs were clearly identifiable, with an atomic structure, energy, volume expansion and width (of about $1.5a_0$) differing remarkably little from those of the corresponding GBs in bicrystals.[7, 8] Using the fully relaxed zero-temperature structures as starting points, lattice-dynamics simulations were then performed to determine the phonon spectrum, which displayed low-energy and high-energy modes not present in the perfect crystal. The low-temperature thermodynamic properties of the material were determined from the phonon spectrum.[7, 8] We found that there is a pronounced low-temperature peak in the specific heat, with a height that decreases with increasing grain size, in qualitative agreement with the experimental results [9, 10].

We also produced a metastable glass by means of a rapid quench from the melt.[11] This was also found to display low-energy and high-energy phonon modes, and a low-temperature peak in the specific heat similar to that seen in the NCMs. A comparison of the calculated vibrational free energies of the NCMs and the glass showed that for grain sizes greater than ~15Å, the NCM is energetically favored with respect to the amorphous phase at all temperatures, while for grain sizes less than ~15Å, the amorphous phase is energetically favored.[11] This suggests that there should be a free-energy based structural transition between the two phases. The existence of such a transition appears physically reasonable, given the common origin of the observed effects in the atomic-level structural disorder and in the related phonon spectra. Indeed, a transition of this nature has been reported for nanocrystalline silicon when the grain size is reduced below about 20Å.[12] The possibility of a reversible, free-energy based transition between the nanocrystalline material and the glass further suggests that their atomic structures may share common elements; these may kinetically enable local amorphous-phase formation in NCMs and, conversely, give the glass an NCM-like intermediate-range structure.

AMORPHOUS GRAIN-BOUNDARY PHASES IN NANOCRYSTALLINE SILICON

In the above-described study of the melt-growth of an fcc-metal NCM it was concluded that the grain boundaries are amorphous. This conclusion, however, was somewhat tentative since, as is well-known, a monatomic fcc metal cannot be amorphized experimentally. Silicon is a much more suitable material in that, while monatomic (and thereby not being complicated by chemical effects), it has a stable bulk amorphous phase. Using a simulation method similar to that described above, and using the well-tested Stillinger-Weber potential [13] to describe the interatomic interactions, fully dense nanocrystalline Si was grown from the melt.[14] The structures and energies of the grain boundaries, line junctions where three grains meet, and the point junctions where four or more meet were analyzed in detail. The structures were found to be essentially indistinguishable from those of bulk amorphous Si.[14] Related simulations of bicrystalline interfaces showed that while low-energy grain boundaries show crystalline order all the way up to the GB, the thermodynamic ground state of all high-energy grain boundaries in Si have a highly disordered structure.[15] Moreover, it was found that this structure is the same for a variety of high-energy grain boundaries on different planes, and that it is very similar to that of the bulk amorphous phase.[15]

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