A mechanism for the deformation of disordered states of matter

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ABSTRACT

As the frontier in advanced materials development has shifted into highly disordered systems, concepts of deformation based on crystal lattice dislocations often become too coarse to be of relevance. Therefore, a new deformation process, localized to dimensions smaller than those involved in dislocation mechanisms, was proposed sometime ago. Some of its important features are discussed here to suggest that this mechanism is likely to be of use in understanding the superplastic deformation of metals and alloys, ceramics, metal-matrix- and ceramic-matrix-composites, dispersion hardened materials, intermetallics, geological materials, metallic glasses and poly-glasses of grain sizes in the μm-, sub-μm- or nm-range – a much wider area of application than originally anticipated. This will allow one to define "superplasticity" as due to a unique physical mechanism, rather than by the extreme elongations obtainable in tensile testing or the strain rate sensitivity index being more than ∼0.30.

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1. Introduction

Advanced materials development has moved on from slightly imperfect materials to highly disordered systems, e.g., glassy alloys, vapor-quenched or rapidly solidified materials, sputtered films, superplastic alloys, micro-, sub-micro- and nano-crystalline materials. "The concept of a crystal dislocation loses much of its value once there is no longer a good long-range crystal structure in which to define it. For breach of order, there must first be a framework of order" [1].

The phenomenon of superplasticity, during the occurrence of which specimens subjected to a small tensile stress can be stretched by several hundred percent, has emerged as a near-ubiquitous phenomenon, present within well-defined grain size – strain rate – temperature domains in metals and alloys, ceramics, metal-matrix- and ceramic-matrix-composites, dispersion hardened materials, intermetallics, geological materials and metallic glasses. The phenomenon is also present in microcrystalline, submicrocrystalline and nanocrystalline forms of these classes of materials. There is near-universal agreement that bulk of the superplastic deformation is traceable to grain boundary/interphase interface sliding [2–7].

The aim of this paper is to highlight some of the features of a mechanism proposed earlier [8–20] to suggest that that mechanism could be important in all situations where concepts based on dislocations are of limited use. Therefore, an attempt will be made to explain the phenomenon of superplasticity in terms of a single mechanism of deformation, which applies equally well to the different kinds of disordered states of matter listed above. Needless to say, under unfavorable experimental conditions, less strain-rate sensitive mechanisms would intervene and superplastic elongations may not result even in materials that are known to exhibit superplasticity.

In the present viewpoint, the atomistic details of a unit boundary sliding event are considered to be the same regardless of whether one is concerned with a material of grain size in the micrometer, sub-micrometer or nanometer range in the different classes of materials. The distribution/arrangement of atoms and free volume fraction within the basic unit of sliding, the presence of free volume sites along the boundary and the propagation of deformation along the interfaces in a given material, however, will depend on the atomic configurations present in the basic unit of sliding (which are governed, among other things, by the interatomic forces) and its neighborhood in the boundary. To advocate the strength in our arguments, we use the mathematical proof provided by Hutter [21] that "shorter computable theories have more weight when calculating the expected value of an action across all computable theories which perfectly describe previous observations". The applicability of the physics underlying the model to all the classes of materials listed of grain size in the μm-, sub-μm or nm range, in which the phenomenon of superplasticity is observed, is claimed to be its major strength. We have adopted this line of argument because then even after conceding that there could be other explanations, which may be able to explain the phenomenon of superplasticity well, one can claim superiority for the present approach because of its universality. As will be seen later,

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the present approach also will help rationalize what Trelewicz and Schuh [22] have stated on the nanocrystalline–metallic glass transition.

A proper description of boundary sliding pre-supposes a clear understanding of the structure of general high-angle boundaries[1] and the interfaces present in severe plastic deformed materials, metallic glasses, poly-glasses etc., in addition to the boundaries of metallic materials. Our knowledge about the structure of grain boundaries and interfaces in non-metallic materials, metallic glasses and poly-glasses is rather limited. Therefore, the usefulness of the present mechanism for understanding the deformation of the boundaries of the latter classes of materials is due to the rate equation developed being able to fit experimental data pertaining to the different classes of materials equally well, i.e., the justification is based on empirical validation and verification.

2. Structure of high-angle grain boundaries and interfaces

The ideas concerning the structure of high-angle grain boundaries have been derived mostly based on work related to metallic materials. As similar superplastic flow is observed in the other classes of materials also, in the absence of evidence to the contrary, these ideas are considered to be relevant to all the classes of materials that exhibit superplasticity.

Several reviews have examined the models used to describe high-angle grain boundaries for two early reviews, see [23,24]. Of the different approaches, the amorphous boundary model was found to be inadequate,[2] while the dislocation models were useful for understanding the behavior of small-angle boundaries. Island models were incomplete. The coincidence site lattice model [25–28], which is based on the original suggestion of Kronberg and Wilson [29], considers only geometry. This is surprising because, long before this model was proposed, it was known that all elements of a given structure, e.g., FCC, are not identical and that CSL being purely geometrical, does not even require grain boundaries [23,24]. The structural unit model, in contrast, takes into account geometry and the inter-atomic forces present among the boundary atoms. The latter model suggests that the most stable boundaries are known by minimizing the total free energy of the system [23,24,30–32]. However, there are also situations in which thermodynamic non-equilibrium introduces selection rules where it is not the free energy, but the fast reaction rate, that determines the structure of grain boundaries. Such structures must be related to the maximization of entropy dissipation rate [33,34]. In such cases metastable grain boundary structures will result. It will be seen below that the analysis presented in this paper applies equally well to such boundaries also. Geometrical elegance, often seen in crystalline materials is, therefore, a consequence of thermodynamic/kinetic causes.

Using computer simulations, Gleiter, Chalmers and Weins [23,24,30–32] showed that there were actually no coincidence atoms, but that the parameter that characterized the coincidence boundaries was their periodicity. Even in non-coincidence boundaries, the same atomic groups that characterized the adjacent coincidence boundaries appeared in an alternating sequence. These groups formed two-dimensional arrays of groups of atoms, known as the "structural units". The atomic structure of any high-angle grain boundary was suggested to comprise a two-dimensional arrangement of these units mixed in a form that corresponds to the orientation relationship of the two crystals that form the

boundary. Needless to say, the accuracy of prediction of the boundary structure in terms of this model will improve significantly if precise inter-atomic potentials are used. While such potentials are available for some elements, which are then used as model materials to test the validity of the theory, the situation is rather bad for engineering materials, often consisting of several alloy elements. Focused research for obtaining precise potentials for the engineering materials will be extremely useful.

The coincidence site lattice (CSL) concept does not also tell one which of the short periodic boundaries is a "special" one, i.e., a low energy boundary. The rotating sphere experiments [35,36] demonstrated that for two materials with identical CSL, the special boundaries could be different. Crystal structure and a consideration of the geometry of grain boundaries alone do not tell one about the thermodynamic stability of a boundary. For example, without knowing the inter-atomic forces, one cannot understand why Ge with diamond structure is brittle, while FCC Ge is ductile or indeed why the same element Ge should crystallize in two different forms. As with crystals, one may compare the properties and structures of boundaries in materials of similar inter-atomic forces. The rotating sphere experiments revealed the same low energy boundaries in Ag, Au, Cu and even Ni.

The approach of combining the CSL concept and the dislocation model of grain boundaries to describe high-angle boundaries [37,38] suggests that when the orientation relationship of the two grains deviates from the ideal coincidence relationship, in analogy with the Read-Shockley dislocation model for small-angle boundaries [39], off-coincidence high-angle boundary is describable as a network of dislocations superimposed on the corresponding ideal coincidence boundary. This idea of describing the "bad fit" regions of the high-angle grain boundary in terms of misfit-dislocations (whose density increases significantly with increasing deviation from ideal coincidence relationship) has been abandoned since 1977 for the following reasons. (a) The suggestion that in some cases the dislocation could dissociate into DSC (displace-shift-coincide) dislocations with Burgers vectors too small to be observable using TEM [40] has not been followed up since the 1970s. (b) By postulating that in general high-angle grain boundaries and metallic glasses there is no long range order and so at infinite time the shear modulus would fall off to zero [20], it could be predicted using the Peierls–Nabarro equation that the width of the dislocation (defined by its core) will become infinite (Eqs. (5)–(9) of [41]). This prediction is confirmed by the TEM observation [42,43] that when a lattice dislocation enters a high-angle grain boundary, the dislocation image gradually becomes fainter and disappears. This has been interpreted in terms of splitting of dislocation, spreading and overlap of dislocation cores. (c) It could be shown that solitons, e.g. dislocations, vacancies, get delocalized in high-angle boundaries and metallic glasses [44] and therefore, the presence of dislocations in high-angle boundaries is an unsustainable concept. (d) To the best of our knowledge, MD simulations also have provided no evidence during grain boundary sliding along general high-angle grain boundaries for the presence and glide of grain boundary dislocations. As a result, since 1977 descriptions of high-angle grain boundaries, e.g., [45–59], use only free volume to describe the regions of poor fit.

Thus, in contemporary view, the general high-angle boundary does not have long-range order. It is made of numerous structural units and free volume to give rise to the myriads of general high-angle grain boundaries of different orientations. As already mentioned, the inter-atomic forces present in each case will determine the size, combination and distribution of such short- and intermediate-range ordering of atoms, which is a consequence of the tendency of grain boundaries to minimize the total free energy. The structure becomes less orderly, when one considers metallic glasses and poly-glasses. In these latter cases, the need to preserve

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[1] It has been known that grain boundary sliding is the easiest at high-angle boundaries and in fact during the development of superplastic aluminum-lithium alloys, when thermomechanical processing led to microstructures of small-angle grain boundaries only, superplasticity could not be induced (for details, see [20]).

[2] However, in case of ceramic materials in which strong segregation of glass forming solutes is present, the grain boundary structure could be amorphous.