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Origin of differences in the excess volume of copper and nickel grain boundaries

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ABSTRACT

The excess volume associated with grain boundaries is one of the primary factors driving defect segregation and diffusion which controls the electronic, mechanical and chemical properties of many polycrystalline materials. Experimental measurements of the grain boundary excess volume of fcc metals Cu and Ni have shown a difference of over 40%. The difference in lattice constant between Cu and Ni is only 3%, therefore this substantial difference is currently lacking explanation. In this article we employ a high throughput computational approach to determine the atomic structure, formation energy and excess volume of a large number of tilt grain boundaries in Cu and Ni. By considering 400 distinct grain boundary orientations we confirm that theoretically there is a systematic difference between the excess volumes in the two materials and we provide atomistic insight into the origin of the effect.

1. Introduction

Grain boundaries play a decisive role in determining the properties and functionality of polycrystalline materials relevant to wide ranging technological applications [1–5]. While grain boundary (GB) phenomena can be varied and complex there are some features that appear to be more universal with general implications for understanding the properties of polycrystalline materials. For example, GBs are almost always associated with an excess volume relative to the corresponding bulk crystal. This additional 'free space' is thought to be one of the main factors responsible for the preferential segregation of defects and impurities towards GBs, which affects key materials properties, such as mechanical strength and electrical resistivity [6–8]. It also helps explain the phenomena of enhanced impurity diffusion along GBs that has been observed in a diverse range of materials [9–11]. While excess volume is recognized as a key materials parameter probing it in real materials remains extremely challenging. A small number of studies have characterized excess volume for specific GBs using high-resolution electron microscopy [12,13]. More recently ensemble average excess volumes have been determined for bulk polycrystalline samples of copper and nickel using high-precision difference dilatometry [14,15]. These experimental studies found that the average excess volume associated with grain boundaries in Cu (0.46 Å) is significantly larger than that in Ni (0.32 Å) – a difference of over 40%. Given that Cu and Ni possess the same fcc crystal structure and fairly similar lattice constants (3.62 Å and 3.52 Å respectively – a difference of less than 3%) the origin of this distinct behavior is not well understood. An atomistic understanding of the nature and origin of GB excess volumes is lacking but could provide invaluable insights to guide the choice of materials for applications. Furthermore, identification of key properties that determine GB excess volumes would be very useful for materials design and optimization.

The structure and properties of GBs in metals have been the focus of many previous experimental and theoretical investigations [8,16–19]. Experimentally, high resolution transmission electron microscopy (TEM) has proven an invaluable probe of GB structure down to the atomic level. Detailed images of the structure of individual tilt GBs have also been acquired [20,21], confirming the existence of a relationship between the GB orientation and the structures of associated dislocation cores. Corresponding GB formation energies have also been estimated by analysis of triple junctions [22,23]. GB excess volumes are more challenging to probe directly but have been studied for both individual GBs and polycrystalline samples, in which case the excess volume corresponds to an average over many GB types [12–15]. Segregation of elements

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to GBs and their modified diffusion is also an issue that has received considerable attention [24–26]. For example, segregation of H and Bi to GBs in palladium and copper has been probed using techniques such as TEM and activity measurements [27,28]. The modified diffusion of impurities along GBs in metals have also been studied using the tracer diffusion method [10,29].

Theoretically, a range of modeling techniques based on both classical potentials and first principles calculations have been developed to predict the structure of GBs on the basis of their formation energy [30–37]. In many cases very good agreement with experiment is obtained for both structure and associated properties (e.g. mechanical, electronic or chemical) [30,33,35,38–40]. A rather general finding is that GBs are often favorable locations for the segregation of defects and impurities which in part has been associated with the additional 'free space' which can more easily accommodate lattice defects [39,41–43]. Often such calculations are performed at the classical potential level but in some cases first principles methods such as density functional theory are employed. For example, the segregation of He to GBs in metals and the resulting embrittlement has received significant attention owing to its relevance to the design of materials for fusion reactors [44–46]. While excess volume differences in otherwise similar metals (like Cu and Ni) have been observed experimentally, theoretical insight into this important issue is currently missing.

In this article we present a detailed theoretical investigation into GB excess volume in the polycrystalline metals Cu and Ni. These materials are chosen to allow comparison with extensive previous theoretical and experimental studies and due to their numerous applications in areas such as spintronics, fusion, fission, power generation and catalysis [47–50]. We focus our study on symmetric tilt GBs and cover a wide range GB orientations in order to draw out trends across both materials. By employing an automated computational approach based on an embedded atom model (EAM) description of interatomic interactions [33,51] we determine the stable structures of over 400 distinct symmetric tilt GBs for both Cu and Ni. We further demonstrate the validity of the approach by comparison to first principles calculations of GB properties using density functional theory. Our results recover a systematic difference in excess volume of between 0.1 and 0.2 Å in very good agreement with experimental data. By analyzing the strain at the atomic level we demonstrate that the excess volume difference is localized in a region of 5–10 Å around the GB plane. We provide a semi-quantitative explanation for the origin of the difference in terms of the differing bulk moduli of Cu and Ni (138 GPa and 186 GPa respectively). Altogether, these results provide much needed atomistic insight into the nature and origin of excess volume differences in Cu and Ni.

The rest of this paper is structured in the following way. In Sec. 2 we describe the computational methods employed to determine the structure, formation energy and excess volume of GBs both at the interatomic potential and first principles levels. In Sec. 3 we discuss results for the structure and excess volume of a wide range of GBs to illustrate the systematic trends and also provide detailed analysis of nature and origin of differences at the atomic level for a selection of GBs. Finally, in Sec. 4 and Sec. 5 the results are discussed and the main findings of the research summarized.

2. Methodology

2.1. General approach

Symmetric tilt GBs are two-dimensional extended defects that form at the interface between two grains symmetrically rotated about a common tilt axis. The crystallographic orientation of the GB can be fully defined by specifying the crystallographic plane parallel to the GB (*hkl*) and the tilt axis [*mno*] and is usually denoted in the form (*hkl*)[*mno*]. Here, we model the atomic structure of such GBs in three-dimensionally periodic supercells as shown in Fig. 1a. To make the supercell periodic in the direction perpendicular to the GB plane two identical GBs are introduced. We ensure that the separation between the GBs is sufficiently large that mutual elastic interactions are small and can be safely neglected in prediction of GB properties (we find GB separations of 30 Å are more than sufficient and this is the minimum separation employed throughout this study).

While the crystallographic orientation of the grains in the supercell are fully defined by the GB type – (*hkl*)[*mno*] – it is not known *a priori* how the grains should be positioned with respect to each other. In particular, it is known that GBs can exhibit rigid body translations where one grain is translated with respect to the other in the plane parallel to the GB (e.g. see Fig. 1b). To find the most stable GB structure we perform total energy calculations on supercells of the type shown in Fig. 1 and fully optimize the structures using the EAM to describe interatomic interactions. First principles calculations within the framework of density functional theory are also performed on a smaller subset of structures identified by the initial EAM screening. Details of both of these approaches are given in the following sections.

To identify the most stable GB structure for a given orientation we systematically generate a large number of initial structures corresponding to different relative translations of one grain with respect to the other. Translations are performed in steps of 1 Å over a range of half of the supercell length in the periodic directions [*mno*] and [*hkl*]×[*mno*] (the vector orthogonal to (*hkl*) and [*mno*]) and between −0.5 and +0.5 Å in the GB normal direction (*hkl*). It has been found that the lowest energy structures can be found using only three translation states in (*hkl*) as all inequivalent interface configurations can be explored via translations in (*hkl*) × [*mno*] and [*mno*]. Following crystal translation, if any two atoms are closer than 0.1*a* (where *a* is the lattice constant) one is deleted to obtain a more realistic starting configuration for geometry optimization. This algorithm generates a large number of initial structures corresponding to different grain terminations, relative grain translations and atom configurations near the

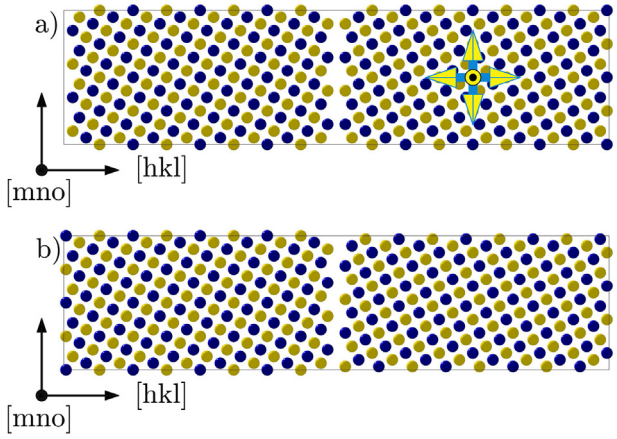

Fig. 1. A typical bicrystal supercell in an fcc material. The yellow and blue atoms indicate atoms in different planes perpendicular to the tilt direction [*mno*]. a) Initially two mirror symmetric grains are placed in the simulation cell. The arrows indicate the directions in which the right grain is to be translated. b) An example of a configuration obtained after one crystal is translated with respect to the other. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)