Current Opinion in Solid State and Materials Science 20 (2016) 240–246

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms

Surface and grain boundary complexions in transition metal – Bismuth alloys

Qin Gao *, Michael Widom

Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA

ARTICLE INFO

Article history:
Received 24 November 2015
Revised 8 May 2016
Accepted 15 May 2016
Available online 14 October 2016

Keywords:
Complexion
Bismuth
Surface
Grain boundary
Liquid metal embrittlement

ABSTRACT

This article reviews experimental and theoretical work related to grain boundary complexions in transition metals, especially bismuth alloy complexions on nickel and copper surfaces and grain boundaries. One-, three-, five-, and seven-layer bismuth complexions are observed on the Ni(1 1 1) surface. Recent experiments suggest that Bi impurities segregate to form bilayer complexions on Ni and Cu grain boundaries which could possibly explain liquid metal embrittlement. Density functional theory calculations of Bi films on transition metal grain boundaries confirm that Bi bilayer complexions (actually a pair of monolayers bound to the metal surfaces) are thermodynamically stable. Meanwhile, complexion transitions have been demonstrated with molecular dynamics and Monte Carlo simulations and are supported by analytical thermodynamic models.

1. Introduction

Bismuth replaces lead in solder alloys due to its low melting temperature and non-toxicity [1]. Bismuth naphthenate is used as environmentally friendly lubricant additives in extreme pressure applications [2]. Moreover, liquid Bi is used as a spallation target to generate neutrons due to its high neutron production rate [3]. However, liquid Bi is known to embrittle its solid container through grain boundary (GB) penetration. To understand and ultimately solve the liquid metal embrittlement problem, extensive theoretical and experimental studies were performed on Bi at metal GBs. The Micron-scale Bi penetration tips, nanometer-scale intergranular films and bilayer complexions were discovered in experiments with Ni and Cu [4–6].

Analytical thermodynamic models based on ideal solution [7] and critical wetting theory [8–10] explain the complexion wetting and prewetting transitions [11]. First principles studies with density functional theory (DFT) calculations confirmed the stability of bilayer films and explained the difference between transition metals [12,13]. Molecular dynamics (MD) simulation demonstrates complexion transitions in pure Cu [14] and Ag segregated Cu [15], and agreed well with the diffusion experiments [16]. People debate over whether liquid metal embrittlement (LME) is due to an electronic effect [17] or atomic size effect [18] based on monolayer segregation models.

This review will first cover Bi surface complexions and then concentrate on Bi complexions at transition metal (TM) GBs from the aspects of experiments, DFT calculations, analytical models and MD simulations. Some perspectives about future directions will also be discussed.

2. Surface complexion

Bulk Bi takes the rhombohedral structure of Pearson type hR2 (prototype α-As) common to group-V semimetals, which is distorted from the simple cubic structure by a Jones-Peierls mechanism [19]. The bulk Bi structure is best described as a stacking of bilayers in the [0 0 1] direction [20] (3-index hexagonal indexing). Three strong covalent bonds of length 3.06 Å link each Bi atom to others within each bilayer, while three weak metallic bonds of length 3.51 Å connect each Bi atom to others in the adjacent bilayer. The (0 0 1) plane is thus a natural cleavage plane, with divisions expected between bilayers. Additional high pressure forms are also known.

Bi forms various monolayer structures on Ni and Cu surfaces [21–28]. In multilayer surface complexions (~1 nm), Bi exhibits allotropic transformations from puckered pseudocubic films to bulk-like rhombohedral films on Si(1 1 1) and on some quasicrystal surfaces [29,30]. Experiments and first-principles calculations concur that both film types exhibit bilayer growth due to the exotic bonding character of Bi, rather than free-electron like quantum size effect [31]. In contrast, the initial growth of Bi films on metallic substrates has not been well studied until a recent experiment [32]

* Corresponding author.
E-mail address: gaoqins@gmail.com (Q. Gao).

http://dx.doi.org/10.1016/j.cossms.2016.05.007
1359-0286/

reported the formation of Bi-Ni surface alloy, and one-, three-, five- and seven-layer Bi hexagonal films of Bi on the Ni(1 1 1) surface. The authors proposed atomic structures and explained their stabilities based on free-electron-like quantum size effect [32].

DFT calculations were performed within the PBE generalized gradient approximation [33] to verify the stability of the proposed structures and its mechanism [20]. Consider a slab consisting of several layers of elemental Ni in its FCC structure, with two free surfaces each of area A. Define the energy of this structure as $E_{\mathrm{Ni}}^{\mathrm{Slab}}$. Now place N_{Bi} atoms on one surface of this slab resulting in a total energy E_{Tot}. The formation enthalpy of Bi on the surface, relative to the bare slab and bulk bismuth, is

$$\Delta H = E_{\mathrm{Tot}} - E_{\mathrm{Ni}}^{\mathrm{Slab}} - E_{\mathrm{Bi}}^{\mathrm{Bulk}} N_{\mathrm{Bi}}. \quad (1)$$

The surface free energy per area, γ_{surf} (shown in Fig. 1), is defined as

$$\gamma_{\mathrm{surf}} = \Delta H / A \gamma_{\mathrm{surf}} = (\Delta H - \Delta\mu_{\mathrm{Bi}} N_{\mathrm{Bi}})/A. \quad (2)$$

Here we choose to measure the chemical potential of Bi relative to its bulk value $\Delta\mu_{\mathrm{Bi}} = \mu_{\mathrm{Bi}} - \mu_{\mathrm{Bi}}^{\mathrm{Bulk}}$. Finally, if we replace δN_{Ni} atoms in the slab with Bi atoms (most likely on the outer layer of the slab), then we must replace $E_{\mathrm{Ni}}^{\mathrm{Slab}}$ with $E_{\mathrm{Ni}}^{\mathrm{Slab}} - \delta N_{\mathrm{Ni}} E_{\mathrm{Ni}}^{\mathrm{Bulk}}$. Stable structures minimize γ_{surf} at certain $\Delta\mu_{\mathrm{Bi}}$.

Fig. 1 suggests the stable sequence: a bare Ni(1 1 1) transforms to a dilute surface alloy (1 Bi in (3×3) cell) at $\Delta\mu_{\mathrm{Bi}} = -1.34$ eV, the observed $\sqrt{3} \times \sqrt{3}$ surface alloy [32] at $\Delta\mu_{\mathrm{Bi}} = -1.10$ eV, the observed (3×3) monolayer [32] at $\Delta\mu_{\mathrm{Bi}} = -0.70$ eV, a [2012] monolayer like that observed in Bi on Cu(1 1 1) [24] at $\Delta\mu_{\mathrm{Bi}} = -0.34$ eV, an infinite-height bulk-like hR2 film. DFT study thus found a surface monolayer strongly interacting with Ni, ultimately followed by a bulk-like (0 0 1) bilayer films as illustrated in Fig. 2 [20] at $\Delta\mu_{\mathrm{Bi}} = +0.06$ eV (this is slightly positive rather than zero owing to the energy cost of the Ni-Bi interface). These structures are much more stable than the previously proposed hexagonal films and are due to the exotic bonding character of Bi rather than free-electron like quantum size effect.

Formation of bulk Bi on the Ni surface is of course a nonequilibrium structure created by deposition of Bi on the Ni surface. In thermodynamic equilibrium bulk Ni-Bi compounds can form at intermediate $\Delta\mu_{\mathrm{Bi}}$. DFT calculations of the bulk phase diagram reveal coexistence of FCC Ni with monoclinic BiNi at $\mu_{\mathrm{Bi}} - \mu_{\mathrm{Ni}} = -0.07$ eV. Assuming $\mu_{\mathrm{Ni}} = 0$ in the Ni-rich limit of equilibrium with bulk Ni, we see that formation of this compound occurs in equilibrium after the [2012] monolayer but, of course, before growth of bulk Bi.

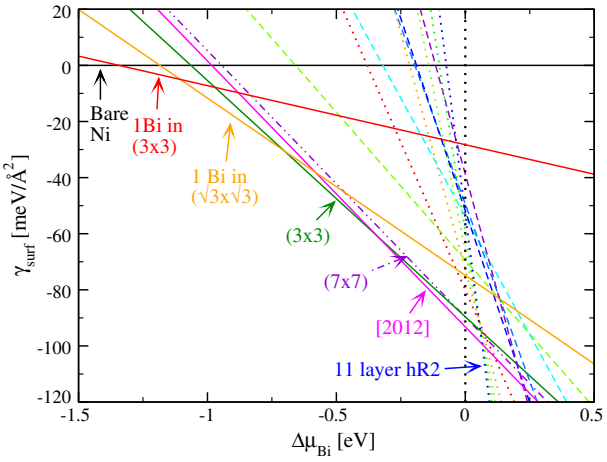

Fig. 1. Surface free energy of Bi on (or in the surface layer of) Ni(1 1 1) surface [20]. The black solid line is bare Ni(1 1 1) surface and other solid lines are stable monolayer structures. The dot-dashed line is the (7×7) structure proposed in [32], which is predicted not stable. Black dotted line stands for infinite bulk-like Bi films. Other dotted lines are Bi bulk-like (0 0 1) films on Ni(1 1 1). Dashed lines are the hexagonal films proposed in [32].

Bi surface complexions also exhibit exotic electronic properties. Bi bulk-like hR2 bilayers have been shown to act as two-dimensional topological insulators [34,35]. A Bi(20 nm)/Ni(3 nm) film has been demonstrated to be a p-wave superconductor [36].

3. Grain boundary complexion

3.1. Experiments

Liquid metal embrittlement (LME) is a long standing puzzle for physics and material science community. Severe embrittlement occurs when ductile metals like Ni and Cu contact liquid metals like Bi. Experimental studies using Auger Electron Spectroscopy (AES) and scanning electron microscopy (SEM) focused on the properties of the liquid metal penetration tip, which is tens or hundreds of microns long and several microns thick liquid Bi formed by wetting [4] the transition metal GB as shown in Fig. 3(A). The penetration tip dissociates the GB by forming two solid-liquid interfaces which are regarded as complexions [11], with bulk liquid Bi-Ni alloy in-between. The region in front of the penetration tip is believed to be a plastic deformation zone [39,40]. Recent experiments found Mn, Sn, and Fe impurities in solid Ni enhance the intergranular penetration 10–20-fold [41]. Based on thermodynamic models, it is inferred that Mn and Sn segregate to the Ni GB and change the penetration morphologies. While Fe in solid Ni is expected to have no effect due to its large solubility, Fe in a liquid Bi-Ni alloy precipitates, consumes Ni, causes dissolution of Ni from the Ni GB, and thus enhance the intergranular penetration.

Besides the penetration tip, SEM and AES measurements indicate a nanometer-thick quasi-liquid Bi intergranular film (IGF) extends hundreds micrometers ahead the penetration tip when Ni is in contact with liquid Bi-Ni alloy [42], extending the crack depth to several times the length of the penetration tip in bending or tensile tests [39,5] as shown in Fig. 3(A) and (B). By observing an abrupt change in GB grooving angle [43] and in the temperature dependence of the Bi adsorption [44], people inferred the existence of complexion prewetting transition as shown in Fig. 3(C). Moreover, a Bi monolayer complexion on a special Cu GB was observed [17].

Recently, using aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), Bi (sub) nanometer thick complexions were directly observed at Ni general grain boundaries [6], as shown in Fig. 4(A)-(D). The Bi complexions are mostly bilayers and are ubiquitous at Ni high energy GBs around the penetration tip. Besides the bilayer complexion, a trilayer complexion coexists with a bilayer complexion as shown in Fig. 4(E), on a single GB near the penetration tip indicates complexion prewetting transition. The two layers in the Bi bilayer complexions are coherent with the Ni GB planes, but not coherent with each other and have large layer spacing (3.9 Å, Fig. 4(F)), which indicates strong Bi-Ni interaction and weak Bi-Bi interlayer interaction. The weak Bi-Bi interlayer interaction could significantly reduce GB cohesion thus lead to embrittlement. The penetration tip and IGF together with the Bi bilayer complexion, could thus explain the LME. Moreover, similar Bi bilayer complexions were observed on Cu general GBs [45]. Besides forming bilayer complexions at GBs, Bi also alters the structure of triple junctions due to the strong reduction of GB energies by segregation [46,47].

3.2. Analytic thermodynamic models

Analytical thermodynamics models of segregation can explain and predict the complexion transitions. Based on the assumption