Phase Stability and Grain Boundary Structure in the Cu-Bi System

R. Siegl, V. Vitek, and D.E. Luzzi
Department of Materials Science and Engineering
University of Pennsylvania, 3231 Walnut St.
Philadelphia, PA 19104
and
M. Yan
Theoretical Division, Los Alamos National Laboratory
Los Alamos, NM 87545

Cu-Bi system is a model system for studies of interfacial phenomena, such as segregation and segregation induced faceting. In previous studies it was found that there is a strong preference for $\Sigma = 3\{111\}-\{111\}$ type facets, and their atomic structure was successfully resolved by combining high-resolution electron microscopy and computer simulation using Finnis-Sinclair type interatomic potential. The resolved grain-boundary structure was examined using *ab initio* full-potential linear muffin-tin orbital method by calculating formation enthalpies of several (hypothetical) Cu-Bi compounds under pressure. It was found that there is no driving force for the ordered alloy formed at the boundary to grow into a three-dimensional phase and thus specific interfacial phases are formed in this system. The range of applicability of Finnis-Sinclair potential used in the previous studies was also investigated by comparison with *ab initio* calculations, and it was shown that the potential is entirely appropriate when Cu concentration is higher than about 66 at.%. In those cases the Cu-Bi system exhibits metallic behavior.

Introduction

Motivation for studies of grain-boundary (GB) phenomena in Cu-Bi alloys is that they are a very suitable model system for investigation of several significant phenomena common to all alloys. These are segregation of minority species and associated embrittlement of boundaries, segregation-induced faceting, and, possibly, formation of two-dimensional interfacial phases. This paper concentrates on the latter, which is, however, intimately linked with faceting.

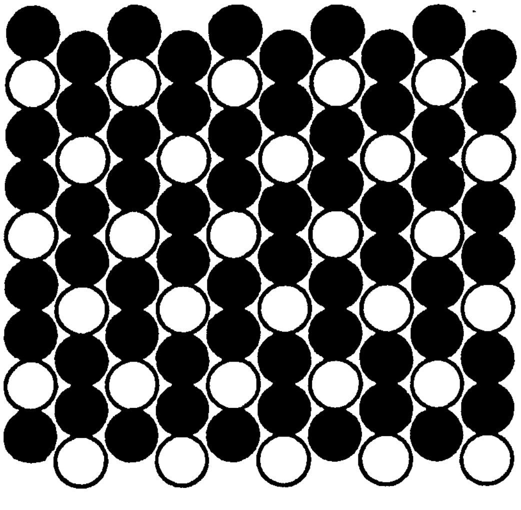

Fig. 1 The ordered Cu-Bi structure in the $\Sigma = 3(111)/(11\bar{1})$ GB (layers C'–C_{Bi}) viewed along the [111] direction. Dark circles represent Cu atoms and white circles Cu vacancies. Bi atoms forming a layer C_{Bi} are positioned on the top of these vacancies.

The segregation-induced faceting in Cu-Bi was recently investigated experimentally, and the major conclusion of these studies is that $\Sigma = 3\{111\}/\{111\}$ is the dominant type of facet (Ref 1-3). At the same time, fracture studies revealed that these facets are very brittle because fracture along them was accompanied by very little plastic deformation (Ref 4, 5). In contrast, in pure Cu there are no pronounced $\Sigma = 3\{111\}/\{111\}$ facets and the most common type of facet among $\Sigma = 3$ GBs found in recent studies (Ref 6-9) was an asymmetrical boundary with the boundary plane inclined by about 82° relative to the $\{111\}/\{111\}$. This unusual feature was explained by the formation of the 9*R* structure in the boundary region that has been confirmed by the high-resolution electron microscopy (HREM) not only for Cu, but also for Ag (Ref 6-10). Comparison of the faceting in pure Cu and Cu-Bi clearly points toward importance of the presence of Bi in the faceting process and, presumably, in the structure of the facets.

For this reason the atomic structure of the $\Sigma = 3(111)/(11\bar{1})$ facets in Cu-Bi was studied by HREM (Ref 11, 12) and by computer modeling. Structure was successfully resolved: crystallographic model based on the HREM image was relaxed using molecular statics and a Finnis-Sinclair type central force many-body potential and was found to be stable. It also reproduced the GB expansion correctly. An excellent agreement has been obtained between the image simulated on the basis of the calculated structure (using a multislice method) and the observed image as well as between calculated and observed expansion at the boundary (Ref 13, 14).

The structure obtained in these studies is shown in Fig. 1. It can be described in terms of stacking of {111} planes in the following way:

$$-A-B-C-A-B-C'-C_{\mathrm{Bi}}-B-A-C-B-A- \qquad \text{(Eq 1)}$$

The double layer $C'-C_{\mathrm{Bi}}$, present in the boundary, is ordered. C' is a pure Cu layer with vacancies arranged in a hexagonal fashion. Bismuth atoms are positioned above these vacancies and form the layer C_{Bi}.

The present work concerns this ordered GB structure and its formation. In particular, the authors wanted to see if they could gain a better understanding of this structure through the study of several ordered Cu-Bi compounds derived from the GB structure by calculating their formation enthalpies under various applied hydrostatic pressures. The reason for including the stress into the considerations is that in polycrystals grains cannot expand freely and, as a consequence, the GB structure is constrained by the adjacent grains. If formation of a three-dimensional Cu-Bi compound derived from the GB structure is favorable under pressure, then this structure might grow into a three-dimensional Cu-Bi phase coherent with the GB. This question is especially interesting because no bulk Cu-Bi compounds exist. The *ab initio* full-potential linear muffin-tin orbital method (FP-LMTO) has been used in these calculations (Ref 15-17).

At the same time, a database of equilibrium lattice parameters and formation enthalpies of several Cu-Bi compounds is generated in the above-mentioned calculations that can be used for further, more detailed assessment of the validity of the Finnis-Sinclair potential that was used in the original study of the GB structure (Ref 14). The range of applicability of the Finnis-Sinclair scheme in Cu-Bi system is particularly interesting because Bi itself is a semimetal with rhombohedral crystal structure, while Finnis-Sinclair scheme, similarly as other analogous approaches, such as embedded-atom method (EAM), describes best close-packed metallic systems.

Ab Initio Calculations

While in a polycrystal, the stress exerted on the GB structure due to adjacent grains has both hydrostatic pressure component and uniaxial stress component, a simple model is used as the first approximation for such complex situations—only hydrostatic pressure is considered. The following ordered Cu-Bi compounds have been considered:

- A trigonal Cu_5Bi compound that is created as a periodic repetition of layers $-C'-C_{\mathrm{Bi}}-B-$ from the GB. This structure is shown in Fig. 2(a).
- A Cu_2Bi compound in $C32$ structure that is generated by periodic repetition of layers $-C'-C_{\mathrm{Bi}}-$ from the GB. This structure is shown in Fig. 2(b).

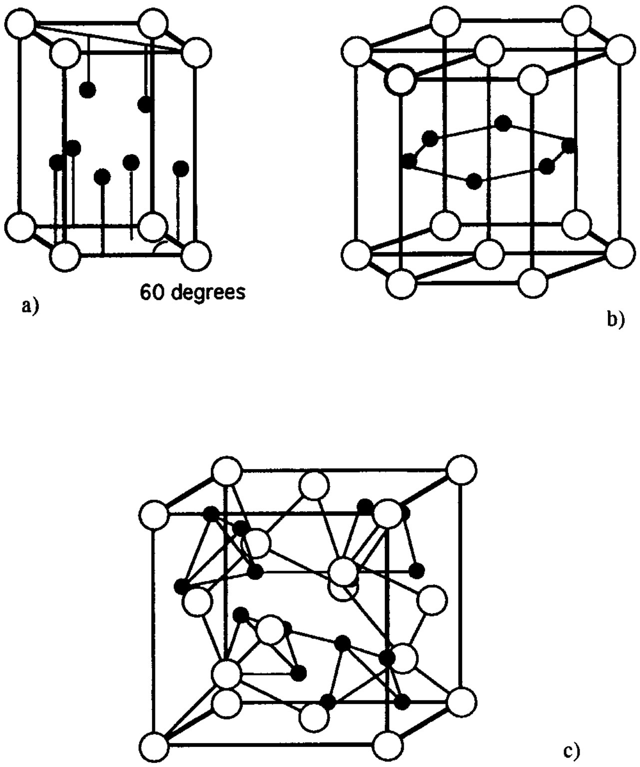

Fig. 2 Cu-Bi compounds studied. **(a)** Cu_5Bi generated by repetition of layers $-C'-C_{\mathrm{Bi}}-B-$ from the GB. **(b)** Cu_2Bi in $C32$ structure; repetition of layers $-C'-C_{\mathrm{Bi}}-$ from the GB. **(c)** Cu_2Bi in $C15$ structure. Large circles represent Bi atoms and small circles Cu atoms.

- A Cu_2Bi compound in $C15$ structure. This structure, shown in Fig. 2(c), is not a repetition of the layers from the GB, but rather the local atomic environment of Bi is similar in $C15$ and in the GB.

The FP-LMTO method, which is an all-electron band-structure method, has been used within the local density approximation of the exchange and correlation. The basis functions are linear muffin-tin orbitals (LMTOs) (Ref 15). No assumption about the crystalline potential is made (Ref 16, 17).

When calculating formation enthalpies of alloys by *ab initio* methods, one has to pay special attention to the precision of calculations because the energy differences can be quite small. Within the FP-LMTO scheme the number of **k**-points, number of orbitals per atom and the cutoff of the charge density expansion are crucial (Ref 18). In their calculations the authors have used typically 300 **k**-points in the irreducible wedge of the Brillouin zone, 22 orbitals per atom and the charge density expansion cutoff $l = 4$. Total energy convergence was 0.7 mev/0.05 mRy per atom with these parameters.

The formation enthalpy ΔH of a compound is defined as:

$$\Delta H = \Delta E + p\Delta V \qquad \text{(Eq 2)}$$

Here ΔE is the formation energy:

$$\Delta E(\text{Cu-Bi}) = E(\text{Cu-Bi}) - c(\text{Cu})E(\text{Cu}) - c(\text{Bi})E(\text{Bi}) \qquad \text{(Eq 3)}$$

where E(Cu-Bi), E(Cu), E(Bi) are cohesive energies of the Cu-Bi compound, Cu, and Bi, respectively, and c(Cu) and c(Bi) are atomic concentrations of Cu and Bi, respectively.

$$\Delta V(\text{Cu-Bi}) = V(\text{Cu-Bi}) - c(\text{Cu})V(\text{Cu}) - c(\text{Bi})V(\text{Bi}) \qquad \text{(Eq 4)}$$

where V(Cu-Bi), V(Cu), and V(Bi) are equilibrium volumes of the Cu-Bi compound, Cu, and Bi, respectively. All these quantities are considered at some particular pressure p.

The energy-volume curves were calculated for each of the three compounds studied, as well as for pure fcc Cu and Bi in rhombohedral and high-pressure bcc structures. This allows one to find energies and volumes at some particular pressure p based on thermodynamical formula:

$$p = -\frac{\partial E}{\partial V}\Big|_{T=\text{const.}} \qquad \text{(Eq 5)}$$

In cases of Cu_5Bi and $C32$ Cu_2Bi c/a ratio was relaxed prior to the energy-volume curve calculation and then kept constant. After finishing the energy-volume curve calculation c/a was relaxed once more and compared to the original one. In both cases, the difference was less than 0.5%. Formation enthalpies (Eq 2) have been calculated for several values of pressure. It was found that influence of the $p\Delta V$ term is a maximum at approximately 25 kbar. The results for this value of pressure are summarized in Table 1.

It is seen that formation enthalpies for all the Cu-Bi compounds studied are positive, and thus none of these compounds form spontaneously. This implies that the two-dimensional ordered compounds formed in the GB will not grow into a three-dimensional Cu-Bi phase coherent with the boundary. Formation of such a phase is not favored even when strained by the adjacent grains (within the authors' approximation of the strain tensor).

Finnis-Sinclair Potential Calculations

Finnis-Sinclair interatomic potential (Ref 19) belongs to the EAM potential family (Ref 20). Within this scheme the energy has the following functional form:

$$E = \sum_{i=1}^{N} \left\{ \sum_{j \neq i} \frac{V_{s_i s_j}(R_{ij})}{2} - \sqrt{\sum_{j \neq i} \Phi_{s_i s_j}(R_{ij})} \right\} \qquad \text{(Eq 6)}$$

Table 1 Formation Energy, $p\Delta V$ term, and formation enthalpy of Cu-Bi compounds studied

	ΔE, eV/atom	ΔV, A^3/atom	$p\Delta V$, eV/atom	ΔH, eV/atom
Cu_5Bi	+0.317	−3.159	−0.050	+0.267
Cu_2Bi $C32$	+0.338	−1.394	−0.022	+0.316
Cu_2Bi $C15$	+0.182	−2.189	−0.034	+0.148

Table 2 Comparison of Lattice Constants and Cohesive Energies Obtained by FP-LMTO and by Finnis-Sinclair Interatomic Potential

	Lattice constant (a), A		c/a ratio		ΔH (0 kbar),	eV/atom
	FS	*Ab initio*	FS	*Ab initio*	FS	*Ab initio*
Cu_5Bi	4.39	4.31	1.37	1.33	+0.293	+0.320
Cu_2Bi $C32$	4.31	4.19	0.83	0.81	+0.309	+0.340
Cu_2Bi $C15$	7.36	7.32	...	...	−0.001	+0.180

FS, Finnis-Sinclair.

where $V_{S_iS_j}, \Phi_{S_iS_j}$ are pair potentials that depend only on the species S_i, S_j involved in the interaction and their interatomic distance R_{ij} (Ref 14).

The Cu-Bi potential was fitted for purpose of the combined HREM and computer modeling study of $\Sigma = 3(111)/(11\bar{1})$ GB (Ref 14). It reproduces lattice constants and elastic constants of pure fcc Cu, bcc Bi, and (hypothetical) $L1_2$ Cu_3Bi compound. Body-centered cubic Bi was chosen because it is a stable metallic phase at 90 kbar pressure. Potential fitted in this way could reproduce the atomic size of Bi in Cu more realistically because Bi atoms are highly pressurized in Cu. Data for $L1_2$ Cu_3Bi compound were obtained by *ab initio* FP-LMTO calculations and were used for the fit of the Cu-Bi cross-potential terms. The potential also reproduces the enthalpy of mixing for the liquid Cu-Bi solution at 1200 K. It was further tested on (hypothetical) CuBi compound in *B*2 structure that was also studied by *ab initio* FP-LMTO. Some discrepancies were already found at such high concentrations of Bi (Ref 14).

In this study, all three Cu-Bi compounds studied were relaxed using this potential. Then the lattice parameters and formation enthalpies (at zero pressure) were compared to the values obtained by FP-LMTO. Values for bcc Bi were used in formulas 3 and 4 because of the construction of Finnis-Sinclair potential. Results are summarized in Table 2.

The agreement in the values of lattice constants is excellent. Not only are the values obtained by both methods almost identical, but the trend is the same: Finnis-Sinclair interatomic potential gives slightly higher lattice constants than FP-LMTO method for all of the compounds.

Relative stabilities of the compounds are also well reproduced by the Finnis-Sinclair potential. This is important because it enables one to distinguish the stable structures from the metastable ones using the potential. Absolute values of the formation enthalpies of Cu_5Bi and *C*32 Cu_2Bi calculated by Finnis-Sinclair potential are in a reasonable agreement with *ab initio* results; the difference is of the order of 30 to 40 meV/atom. There is a larger difference—approximately 180 meV/atom—in the case of *C*15 Cu_2Bi. Small negative value of the formation enthalpy of *C*15 Cu_2Bi calculated by the potential is a little disturbing. However, recall that bcc Bi was used as a reference state and this is not a stable Bi structure at zero pressure. Hence, this small negative value of ΔH does not imply that *C*15 compound formation is favored by the Finnis-Sinclair potential.

The Finnis-Sinclair interatomic potential for Cu-Bi system reproduces the *ab initio* lattice constants with great accuracy over a range of structures and composition. It also gives the correct relative stability of the compounds, though, the absolute values of energy are not exact. It can be concluded, therefore, that the potential can be used with a high confidence in determination of structures and relative structural stability. This is particularly interesting because pure Bi is a semimetal that forms rhombohedral lattice. Results suggest that for alloys of composition Cu_XBi, $X \geq 2$, the system exhibits metallic behavior. Furthermore, the potential determines correctly the atomic size of Bi in such Cu-Bi alloys, and corresponding structures can be described in terms of close packing of small Cu atoms and large Bi atoms.

Conclusions

This paper discusses several ordered phases in the Cu-Bi system derived from the previously observed structure of the $\Sigma = 3(111)/(111)$ GB. Their formation enthalpies under hydrostatic pressure were calculated by *ab initio* FP-LMTO method. It was found that none of these compounds form spontaneously. Based on a simple model of the GB (approximation of the stress of the adjacent grains by hydrostatic pressure) it can be concluded that the compound formed in the GB will not grow into a three-dimensional phase coherent with the GB.

The *ab initio* data (namely, lattice constants and formation enthalpies) were compared to the data obtained by Finnis-Sinclair interatomic potential for Cu-Bi system. The agreement is very good considering that this is a relatively simple scheme. These results mean that Cu-Bi alloys (with Bi concentration lower than 33 at.%) exhibit metallic behavior and that the potential describes well the sizes of Cu and Bi atoms in such alloys.

Acknowledgment

The authors would like to thank Dr. M. Methfessel for providing the FP-LMTO code. The research was supported by DOE, Office of Basic Energy Sciences, Grant No. DE-FG02-87ER45295.

Cited References

1. B. Blum, M. Menyhard, D.E. Luzzi, and C.J. McMahon, Jr., "TEM Investigation of Bismuth Induced Faceting of $\Sigma = 3$ and Near $\Sigma = 3$ Grain Boundaries in Copper," *Scr. Met. Mater., 24,* 2169-2173 (1990).
2. E.C. Urdaneta, D.E. Luzzi, and C.J. McMahon, Jr., "Grain Boundary Transformations in Bi-Doped Copper," *Structure and Properties of Interfaces in Materials,* W.A.T. Clark, U. Dahmen, and C.L. Briant, Ed., Vol. 238, Materials Research Society, Pittsburgh, PA, 201-205 (1992).
3. E.C. Urdaneta, "Grain Boundary Transformations: A Crystallographic Study of Boundary Faceting in Bismuth-Doped Copper Polycrystals," Ph.D. thesis, University of Pennsylvania, 157-169 (1993).
4. M. Menyhard, B. Blum, C.J. McMahon, Jr., S. Chikwambani, and J. Weertman, "Bismuth Segregation in Cu-Bi Bicrystals," *J. Phys., 49,* C5-457 - C5-462 (1988).
5. M. Menyhard, B. Blum, and C.J. McMahon, Jr., "Grain Boundary Segregation and Transformations in Bi-Doped Polycrystalline Copper," *Acta Metall. Mater., 37,* 549-557 (1989).
6. U. Wolf, F. Ernst, T. Muschik, M.W. Finnis, and H.F. Fischmeister, "The Influence of Grain Boundary Inclination on the Structure and Energy of E3 Twin Boundaries in Copper," *Structure and Properties of Interfaces in Materials,* W.A.T. Clark, U. Dahmen, and C.L. Briant, Ed., Vol. 238, Materials Research Society, Pittsburgh, PA, 177-182 (1992).
7. U. Wolf, F. Ernst, T. Muschik, M.W. Finnis, and H.F. Fischmeister, "The Influence of Grain Boundary Inclination on the Structure and Energy of $\Sigma = 3$ Grain Boundaries in Copper," *Philos. Mag. A, 66,* 991-1016 (1992).

8. F. Ernst, M.W. Finnis, D. Hofmann, T. Muschik, U. Schönberger, and U. Wolf, "Theoretical Prediction and Direct Observation of the 9R Structure in Ag," *Phys. Rev. Lett., 69,* 620-623 (1992).
9. T. Muschik, W. Laub, M.W. Finnis, and W. Gust, "Thermodynamics of Faceting of Σ3 Grain Boundaries in Cu," *Z. Metallkd., 84,* 596-604 (1993).
10. D. Hofmann and M.W. Finnis, "Theoretical and Experimental Analysis of Near Σ 3 (211) Boundaries in Silver," *Acta Metall. Mater., 42,* 3555-3567 (1994).
11. D.E. Luzzi, "High-Resolution Electron Microscopy Observations of Faceted Grain Boundaries and Twins in Bismuth-Doped Copper," *Ultramicroscopy, 37,* 180-190 (1991).
12. D.E. Luzzi, "Direct Imaging of Ordered Segregation Layers in Copper Doped with Bismuth," *Philos. Mag. Lett., 63,* 281-287 (1991).
13. D.E. Luzzi, M. Yan, M. Sob, and V. Vitek, "Atomic Structure of a Grain Boundary in a Metallic Alloy: Combined Electron Microscope and Theoretical Study," *Phys. Rev. Lett., 67,* 1894-1897 (1991).
14. M. Yan, M. Sob, D.E. Luzzi, V. Vitek, G.J. Ackland, M. Methfessel, and C.O. Rodriguez, "Interatomic Forces and Atomic Structure of Grain Boundaries in Copper-Bismuth Alloys," *Phys. Rev. B, 47,* 5571-5582 (1993).
15. O.K. Andersen, O. Jepsen, and D. Glotzel, "Canonical Description of the Band Structure of Metals," *Highlights of Condensed Matter Theory,* F. Bassani, F. Fumi, and M.P. Tosi, Ed., North Holland, Amsterdam, 59-176 (1985).
16. M. Methfessel, "Elastic Constants and Phonon Frequencies of Si Calculated By a Fast Full-Potential Linear-Muffin-Tin-Orbital Method," *Phys. Rev. B, 38,* 1537-1540 (1988).
17. M. Methfessel, C.O. Rodriguez, and O.K. Andersen, "Fast Full-Potential Calculations with a Converged Basis of Atom-Centered Linear Muffin-Tin Orbitals: Structural and Dynamic Properties of Silicon," *Phys. Rev. B, 40,* 2009-2012 (1989).
18. M. Asta, D. de Fontaine, M. van Schilfgaarde, M. Sluiter, and M. Methfessel, "First-Principles Phase Stability Study of FCC Alloys in the Ti-Al System," *Phys. Rev. B, 46,* 5055-5072 (1992).
19. M.W. Finnis and J.E. Sinclair, "A Simple Empirical N-Body Potential for Transition Metals," *Philos. Mag. A, 50,* 45-55 (1984).
20. M.S. Daw and M.I. Baskes, "Embedded-Atom Method: Derivation and Application to Impurities, Surfaces, and Other Defects in Metals," *Phys. Rev. B, 29,* 6443-6453 (1984).