

## Molecular-dynamics calculations of thermodynamic properties of metastable alloys

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(Received 22 April 1996; revised manuscript received 24 July 1996)

In order to improve our current understanding of the microscopic structure of metastable alloys of immiscible elements such as Ag-Cu and Co-Cu, the Helmholtz free energy of several microstructures based on an fcc unit cell has been calculated and compared with that of a reference state. The microstructures considered for the free energy calculations at fixed volume are (1) a structure formed by alternating layers of fixed thickness of metal 1 and metal 2 separated by coherent interfaces; (2) an atomically disordered solid solution; (3) a structure comprising a random distribution of elemental cubic grains separated by coherent interfaces. Numerical results show that the Helmholtz free energy of structure (3) decreases with increasing grain size and that its value calculated for a sufficiently large grain size approaches the free energy of structure (1). Further molecular-dynamics simulations for the Ag-Cu system have allowed the calculation of the enthalpy at the equilibrium volume of several microstructures including some of those listed above. A comparison of the calculated values of the enthalpy with the heat release observed experimentally allows the advancement of an hypothesis concerning the reaction path and the structure of the equiatomic Ag-Cu alloy obtained by ball milling. [S0163-1829(97)08901-7]

### I. INTRODUCTION

The formation of metastable alloys upon high-energy ball milling of mixtures of elemental powders having a large positive enthalpy of mixing and, therefore, limited mutual solubility in the solid state, has been the subject of several studies concerned with both the structure and the thermodynamics of these phases.<sup>1-4</sup> Still, the nature of the driving force leading to the alloy formation and the atomic level structure of these phases are the subject of an ongoing debate. In essence, in order to describe the alloying process, two different explanations have been advanced. The first<sup>3</sup> is concerned with the accumulation of structural defects and dishomogeneities during ball milling, and with their annihilation during the alloy formation once the free energy associated with these defects exceeds the free energy of mixing. The second<sup>4</sup> is concerned with the occurrence of a transient supersaturation of point defects and with the mechanical energy supplied by the stress field of the plastic deformation, both of which are supposed to allow nonequilibrium interdiffusion of the atomic species.

On the basis of the above considerations it appears particularly relevant to follow the evolution of the microstructure of the alloyed phase and to define its details at the atomic level. To this purpose, in the case of the Cu-Fe system, several techniques, such as transmission electron microscopy,<sup>4</sup> Mossbauer spectroscopy,<sup>5</sup> and extended x-ray absorption fine structure<sup>6</sup> have been employed, in an attempt to complement the structural characterization by conventional x-ray diffraction, whose limits for investigating com-

positional dishomogeneities have been recently discussed.<sup>7</sup> The application of these techniques suggests that mixing of the two components occurs in the Cu-Fe system at the atomic level, even if there is an indication of local compositional fluctuations<sup>5</sup> and, to a limited extent, of modulated structures with a periodicity of a few nm.<sup>4</sup>

No investigations at the same level of detail have been performed for other immiscible systems such as Co-Cu and Ag-Cu, so that in these cases the knowledge of the microscopic structure of the metastable alloys obtained by ball milling is very limited and based only on conventional diffractometry which shows the existence of a single crystallographic phase (within the limits mentioned above) and on differential calorimetry which evidences a heat release of several kJ/mol when these alloys are heated to  $\sim 1000$  K.<sup>1-3,8</sup> Another difficulty in understanding the mechanism of alloying in these systems arises from the lack of accurate information (both experimental and calculated) concerning the enthalpy and the free energy of the different microstructures which could develop during the process of ball milling, including the ideal solid solution which, of course, is not experimentally accessible in the whole range of composition. The enthalpy and the free energy of the ideal solid solution can be calculated<sup>2,3</sup> with the calculation of the phase diagram (CALPHAD) method or with other more sophisticated approaches such as the free-energy minimization method<sup>9</sup> (FEMM) or the second-order expansion<sup>10</sup> (SOE), all of which are of static nature and, therefore, less accurate than a molecular-dynamics (MD) calculation.

The ability of thermodynamic methods to calculate the

enthalpy and the free energy of the metastable phase is restricted to those structures for which some experimental results are available. This limitation can be overcome by the use, in an MD calculation, of interaction potentials having good transferability, that is, depending only weakly on the particular crystal structure whose properties have been used for a fit of the free parameters appearing in the potential.

In view of these considerations we have decided to calculate the free energy and the enthalpy of a number of phases and microstructures of equiatomic Ag-Cu and Co-Cu alloys which could play a role in the alloying process of systems with a positive enthalpy of mixing, using an MD approach based on a  $n$ -body empirical potential.<sup>11</sup>

## II. ENERGY CALCULATIONS

### A. Structural models

Two different types of MD calculations, relative to Helmholtz free energy and to enthalpy, have been performed. In the first case, for which the Ag-Cu and the Co-Cu systems have been considered, the Bennet method<sup>12</sup> has been used to calculate the free energy difference between several microstructures of an equiatomic alloy, all of which are constrained to have the same density of the corresponding alloy obtained by ball milling. In the second case, relative only to the Ag-Cu system, constant-pressure, constant-temperature MD simulations have been performed to relax to their equilibrium configuration some of the microstructures considered for the free-energy calculations, and other structures for which the free energy could not be calculated using the Bennet method.

In order to apply Bennet prescription for the calculation of the free energy, it is necessary to consider only those microstructures which are defined by a common set of coordinates  $\{R_j\}$ , where  $R_j$  is the position vector of the  $j$ th atom, independent of the particular microstructure, so that the only difference between two microstructures tractable with this method is relative to the distribution of atomic species among the  $R_j$ s. With this limitation, the following microstructures have been considered for the free-energy calculations:

(1) A cube containing  $12 \times 12 \times 12$  fcc unit cells, the upper half of which is composed of metal 1 and the lower half of metal 2. The two halves are constrained to have the same lattice parameter and are thus separated by a coherent interface parallel to a (001) plane. Periodic boundary conditions have been applied along the three coordinate axes so that the system is composed of alternated slices, six unit cells thick, stacked along  $z$  and extending indefinitely in the  $x, y$  directions. This phase, labeled as structure 1, according to the requirements of the Bennet method<sup>12</sup> has been retained as the reference phase for the free-energy calculations.

(2) An equiatomic fcc solid solution, structure 2, disordered at the atomic level and, therefore, characterized by the absence of any conventional interface, whose atoms are arranged in the same lattice of those of structure 1.

(3) A coarse grained disordered structure made of pure cubic grains of the two elements, the side of each grain being equal to  $d$  fcc unit cells. The individual grains, separated by coherent interfaces, are distributed at random in a cubic volume equal to that of the reference structure. Several different

sizes with increasing values of  $d$  ( $d=2,3,6$ ) have been analyzed. These structures have been collectively labeled structure 3.

In addition to the free-energy calculations, enthalpy calculations have been performed for structure 1, structure 2, and structure 3 with  $d=6$  and  $d=8$ , for a three-dimensionally ordered arrangement of alternating cubic grains of the pure elements, for the undercooled liquid alloy, for the ordered  $L1_0$  structure, and for a system with no periodic boundary conditions composed by two large grains of Cu and Ag, separated by an incoherent (001) interface, whose dimensions along the directions parallel to the interface are very close to a perfect match between the crystal edges. Using a  $23 \times 23 \times 8$  Ag crystal and a  $26 \times 26 \times 8$  Cu crystal, one has that the edges of the square (001) faces of the two crystals are equal to better than 0.1%. The reference state for the enthalpy calculations is the weighted average of the constituent elements.

### B. Method outline

For over a decade, computer simulations have handled metallic systems with satisfactory accuracy making use of empirical  $n$ -body potentials.<sup>13,14</sup> MD simulations based on these potential schemes have been extensively used to obtain relevant information about the structure and the stability of different phases.<sup>15,16</sup> Of course, the equilibrium configuration of a system can be investigated also by means of free-energy calculations (this subject is extensively reviewed in Refs. 17–19). To this purpose the equilibrium value of the free energy of a system can be evaluated by a minimization of the Gibbs free-energy functional. In this scheme the enthalpy of the system can be calculated from a MD simulation, the configurational entropy can be evaluated with the use of the cluster variation method, and the vibrational entropy evaluated in the quasiharmonic approximation.<sup>16</sup>

Another approach to the stability problem is based on the calculation of free-energy differences. These differences are usually calculated with respect to a state which can be either a phase whose free energy can be estimated by some means<sup>20</sup> or simply a phase which represents a common reference state, even if its free energy is not known.<sup>12,21</sup>

As stated above, the present approach compares the free energy of systems which differ only in the “chemical order,” i.e., in the arrangement of the atomic species in the structure. In classical statistical mechanics, thermodynamic potentials are determined from the configurational integral which defines the partition function. MD simulations, however, are not able to evaluate accurately the  $3N$ -dimensional configurational integral so that the evaluation of the thermodynamic potentials is not reliable. Several methods have been proposed to overcome this difficulty. One of them, usually referred to as the method of “overlapping energy distributions,”<sup>12,21</sup> makes use of a convenient manipulation of the exponential probability distribution of states to obtain an equation determining the ratio of the configurational integrals for systems with different potential-energy functions.

With reference to the canonical (NVT) ensemble (number-density, volume, and temperature), the Helmholtz free energy  $F$  can be written in terms of the configurational integral  $Q$  as,<sup>21</sup>

TABLE I. Potential parameters of the different atomic species used in the simulations [Eq. (7)].

	$A$ (kJ/mol)	$\xi$ (kJ/mol)	$p$	$q$	$r_0$ (Å)
Ag-Ag	9.9364	113.7498	10.9093	3.1410	2.888
Cu-Cu	8.2495	118.0989	10.9600	2.2780	2.556
Co-Co	9.1662	143.5712	11.6040	2.2860	2.502
Ag-Cu	7.2297	107.7832	11.0000	3.5000	2.888
Co-Cu	8.6837	128.3350	11.2820	2.2820	2.540

$$F = -\frac{1}{\beta} \ln Q, \quad (1)$$

where  $\beta = (k_B T)^{-1}$  and

$$Q = \int_{\Omega} e^{-\beta U(q^N)} dq^N. \quad (2)$$

The integration of Eq. (2) extends over the volume  $\Omega$  of the coordinate space occupied by the  $N$  particles of the system. If two systems are at the same temperature and volume, the free-energy difference  $\Delta F$  can be written as

$$\beta(F_1 - F_2) = \beta \Delta F = \ln \left( \frac{Q_2}{Q_1} \right) \quad (3)$$

with  $Q_1$  and  $Q_2$  integrated over the same volume of the coordinate space. One can, in principle, define the energy difference distribution functions  $h_1(\Delta)$  and  $h_2(\Delta)$  as

$$h_1(\Delta) = \frac{\int_{\Omega} \delta(U_1 - U_2 - \Delta) e^{-\beta U_1} dq^N}{Q_1} = \langle \delta(U_1 - U_2 - \Delta) \rangle_1, \quad (4)$$

$$h_2(\Delta) = \frac{\int_{\Omega} \delta(U_1 - U_2 - \Delta) e^{-\beta U_2} dq^N}{Q_2} = \langle \delta(U_1 - U_2 - \Delta) \rangle_2, \quad (5)$$

where  $\delta(x)$  is Dirac's delta,  $U_1$  and  $U_2$  represent the potential energy of phase 1 and phase 2, and the angular bracket  $\langle \rangle_i$  ( $i=1,2$ ) as defined by Eqs. (4) and (5), represents the ensemble average of  $\delta(U_1 - U_2 - \Delta)$  in the canonical ensemble generated by  $U_i$ . By simple algebraic manipulations, one gets

$$\frac{Q_1}{Q_2} = e^{-\beta \Delta} \frac{h_2(\Delta)}{h_1(\Delta)}. \quad (6)$$

As the left-hand side of Eq. (6) is independent of  $\Delta$ , one can evaluate the right-hand side of Eq. (6) at any value of  $\Delta$ . Particularly convenient is the value  $\Delta'$  such that  $h_1(\Delta') = h_2(\Delta')$ . With this choice one obtains  $Q_1/Q_2 = e^{-\beta \Delta'} = e^{-\beta(F_1 - F_2)}$  so that, in practice, one interpolates the numerical functions describing  $h_1(\Delta)$  and  $h_2(\Delta)$  in order to find the intersection value  $\Delta'$  which, as shown above, equals the free-energy difference between the two states.

### C. Calculations

The model system used for the free-energy computations is an fcc structure with 6912 atoms with a lattice parameter

equal to the experimental value of the alloy that is 3.590 Å for Cu-Co and 3.887 Å for Ag-Cu.

The interactions between the atomic species have been described with a  $n$ -body potential derived from a second-moment approximation of a tight-binding Hamiltonian.<sup>11</sup> In this scheme the cohesive energy can be written as

$$E_c = \sum_{i=1}^N \left\{ \sum_{j=1}^N A_{\alpha\beta} e^{-p_{\alpha\beta}(-r_{ij}/r_{\alpha\beta}^0)} - \sqrt{\sum_{j=1}^N \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}(-r_{ij}/r_{\alpha\beta}^0)}} \right\}, \quad (7)$$

where  $A_{\alpha\beta}$ ,  $\xi_{\alpha\beta}$ ,  $p_{\alpha\beta}$ , and  $q_{\alpha\beta}$  are potential parameters referring to the interactions between pairs of atoms of species  $\alpha$  and  $\beta$ . The potential cutoff has been extended up to fifth neighbors for Ag-Cu and up to ninth neighbors for Co-Cu. While the potential parameters for the pure species are available in the literature,<sup>11</sup> the cross parameters (Ag-Cu and Co-Cu) have been evaluated using a fitting procedure slightly modified with respect to that currently used. In fact, the experimental quantities commonly used for the fitting procedure of cross terms are the cohesive energy and the elastic constants, with the boundary condition of vanishing external pressure at the equilibrium volume of the intermetallic phase at a given stoichiometry. In the absence of any intermetallic compound (as it happens for systems with positive heat of mixing), we have used the values of the enthalpy of mixing for liquid alloys reported by Hultgren *et al.*,<sup>22</sup> that is  $\Delta H_m(\text{Ag}_{50}\text{Cu}_{50}) = 4.58$  kJ/mol at  $T = 1423$  K and  $\Delta H_m(\text{Co}_{95}\text{Cu}_5) = 1.565$  kJ/mol at  $T = 1473$  K. Assuming a vanishingly small volume change upon mixing of the liquid metals, we have assigned arbitrary initial values to the cross parameters. These values have been adjusted in successive constant-volume MD simulation runs until the cohesive energy of the liquid alloy at zero external pressure reached the desired value. The cross parameters deduced for the liquid alloy using both an attractive and a repulsive term have been used for the solid-state calculations. Table I reports the parameters used in Eq. (7) for the computations.

In the free-energy calculations, the simulations have been performed in the canonical (NVT) ensemble (number-density, pressure, and temperature), as prescribed by the theoretical layout. For the enthalpy calculations the system has been relaxed in the constant pressure, constant temperature (NPT) ensemble. All calculations have been performed at  $T = 300$  K, with a time step for the integration of the equations of motion of  $10^{-15}$  s.

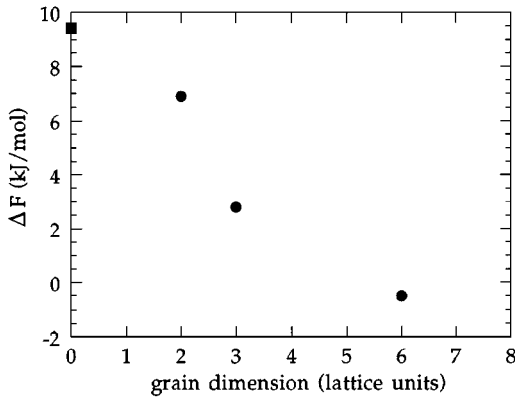


FIG. 1. Calculated values of  $\Delta F$  between structure 1 and structures 2 and 3 for equiatomic Ag-Cu. Dots refer to structure 3 with  $d=2,3,6$ ; the square to random solid solution.

### III. RESULTS AND DISCUSSION

The  $\Delta F$  values calculated between the reference structure (which in the case of Co-Cu contains Co in the high-temperature fcc phase) and the other structures are shown in Figs. 1 and 2 as a function of grain size  $d$ . In order to include in these figures the results relative to the solid solution, we have assigned to this structure the value  $d=0$  as a reasonable approximation to the effective value of the “grain size” in this case. Actually, Figs. 1 and 2 show that the calculated  $\Delta F$ 's can be interpolated by a smooth decreasing function of the grain size. The deviations of the actual  $\Delta F$  values from the interpolated curve are due to the small number of grains used in the simulations which does not exactly reproduce a random distribution. With respect to structure 1 the values of the free energy of structure 3 calculated for  $d=6$  are negative by a few tenths of kJ/mol, which is of the order of the statistical fluctuations affecting each calculated value. Considering that the free energy of structure 1 and of structure 3 must approach the same asymptotic value for increasing layer thickness and for increasing grain size, it appears that in the case of both Ag-Cu and Co-Cu the free energy of a system composed of coherent domains with size  $>2$  nm is only weakly dependent on the geometrical details of the microstructure. On the other hand, the free energy of the solid solution is considerably higher than that of the reference structure.

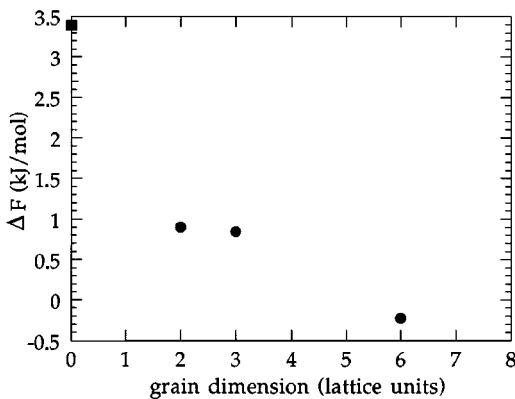


FIG. 2. Same as in Fig. 1 for Co-Cu.

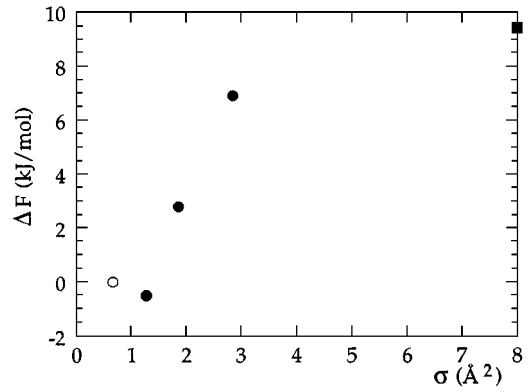


FIG. 3. Same  $\Delta F$  values of Fig. 1, shown as a function of  $\sigma$ . The open circle corresponds to structure 1.

At constant volume, the contribution to the free-energy difference between structures 1 and 3 arising from the presence of coherent interfaces can be thought of as composed of two parts: the first is of chemical origin and for systems having a positive heat of mixing is positive; the second is of entropic nature and, for a coherent interface, contains almost exclusively a vibrational contribution, which, in the present conditions, depends very little on the topology of the interface. Accordingly, the free-energy differences at 300 K should be dominated by the chemical contribution. This qualitative feature is apparent in Fig. 3, which shows a plot of the free energy of Ag-Cu as a function of the density of interface area defined as the ratio between the sum of all the metal 1–metal 2 interface areas actually present in a given structure (irrespective of the interface topology) and the number of atoms. These considerations, apart from a relatively small configurational term easy to evaluate in the Bragg-Williams approximation, apply also to the random solid solution for which  $\sigma$  has been defined as  $\Sigma/4$ , where  $\Sigma$  is the surface area of the Wigner-Seitz cell of the fcc structure.

For the enthalpy calculations of the Ag-Cu system, some of the structures described above (namely structure 1, structure 2, and structure 3 with  $d=6$  and 8) have been relaxed at  $T=300$  K and vanishing external pressure. The three-dimensionally ordered arrangement of alternating cubic grains with  $d=6$  (three-dimensional chess board), the ordered  $L1_0$  phase, the undercooled liquid, and the two-grain system have been also relaxed at the same temperature for comparison purposes. In the case of the two-grain system we have not calculated the enthalpy of the whole structure, which is bounded by free surfaces, but only the energy of a small inner core. The dimensions of the core, comprising two adjoining blocks of  $9 \times 9 \times 4$  Cu unit cells and  $8 \times 8 \times 4$  Ag unit cells are such that the free surfaces of the two grains contribute a negligible amount to the enthalpy of the core atoms. On the other hand, in order to be sure to include all the perturbation arising from the interface, the thickness of the core (four unit cells on each side of the interface) has been chosen to be about twice as large as the range of the interaction potential.

The enthalpy, the molar volume, and the density of interface area calculated for each of the above structures are reported in Table II. Listed in Table II are also the results of a

TABLE II. Thermodynamic data for different structures of Ag-Cu (see text). The density  $\sigma$  of metal 1-metal 2 interfaces has been given (wherever available) before (unrel) and after (rel) the relaxation at vanishing external pressure. The reference structure corresponds to the weighted average of the constituent elements.

	Structure	$\langle H \rangle$ (kJ/mol)	$\Delta H$ (kJ/mol)	$V$ (cm <sup>3</sup> /mol)	$\sigma_{\text{unrel}}$ ( $\sigma_{\text{rel}}$ ) (Å <sup>2</sup> )
1	Reference	-309.81	0	8.85	0
2	Incoherent interface	-305.78	4.03		0.48
3	Structure 1	-303.57	6.25	8.89	0.62 (0.63)
4	Structure 2	-296.60	13.21	9.08	8.00 (8.15)
5	Structure 3 ( $d=6$ )	-301.00	8.81	8.98	1.26 (1.27)
6	Three-dimensional chess board ( $d=6$ )	-299.65	10.16	8.99	1.89 (1.91)
7	Structure 3 ( $d=8$ )	-302.00	7.81		0.94
8	Undercooled liquid	-295.29	14.50	9.24	8.27
9	$L1_0$	-297.90	11.9		7.55
10	$L1_0$ (Ref. 23)		10.0	8.58	7.40

first-principles calculation for the  $L1_0$  structure<sup>23</sup> performed at  $T=0$  K in reasonable agreement with the present MD values.

In accordance with the arguments advanced with regard to free energy, Fig. 4 shows the enthalpy difference between each of the above microstructures and the reference state as a function of  $\sigma$ , including the inner core of the two-grain system and the undercooled liquid for which we have used the density of interface area of the solid solution scaled to the two-thirds power of the volume. Notwithstanding the difference between the structures considered in Fig. 4 the excess enthalpy appears to depend only slightly on the details of each microstructure.

In the case of the solid solutions we have repeated the calculations for a number of configurations in order to have an estimate of the statistical fluctuation. The resulting error bar is of the order of 0.1 kJ/mol and, if reported in the figure, would be smaller than the dot size.

Comparing with the reference state the enthalpy of structure 1 and of the inner core of the two-grain system, the enthalpy of the (001) interface has been calculated as 1.38 J/m<sup>2</sup> for the incoherent case and 1.89 J/m<sup>2</sup> for the coherent

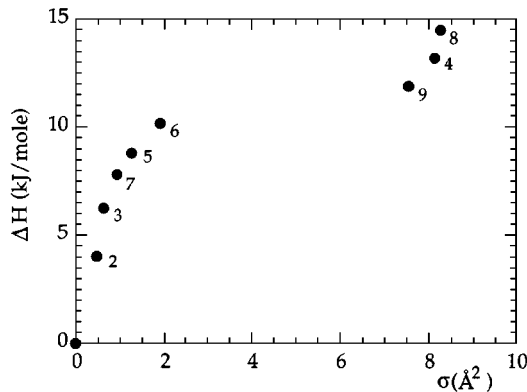


FIG. 4. Calculated values of  $\Delta H$  for equiatomic Ag-Cu. Each dot is numbered as the corresponding structure in the first column of Table II.

one. The energy of a certain microstructure will therefore depend on both the type and the density of interface area. For instance, in the case of the inner core of the two-grain system, the substitution of the incoherent interface with a coherent one would increase the energy of the inner core by about 1.5 kJ/mol.

The behavior of  $\Delta H$  as a function of  $\sigma$  can be easily reproduced, at least for the geometry of structure 3, on the basis of a simple model based on a pair interaction scheme. Consider a large cube of side  $L$  comprising  $n^3$  elemental cubic grains of side  $l$  arranged as in structure 3. Let us assume that at each  $A/B$  interface the interaction extends over a range  $\Delta l$  so that the enthalpy increase of each grain, due to the interaction with the adjoining grains of a different atomic species, is proportional to the volume fraction of each grain comprised within a distance  $\Delta l$  from the interfaces. The calculation of the relevant volume fraction is particularly easy with the condition  $\Delta l \leq l$ , in which case each grain interacts only with its nearest neighbors. With this restriction, if  $H$  is the total enthalpy due to the interfaces and  $N$  is the total number of atoms of the large cube, one can write

$$h = \frac{H}{N} \propto n^3 \frac{[l^3 - (l - \Delta l)^3]}{N}, \quad (8)$$

where the quantity between square brackets is proportional to the volume fraction of each grain defined above. From the definition of  $n$  as  $L/l$  one has

$$h \propto \frac{[l^3 - (l - \Delta l)^3]}{l^3} = 3 \frac{\Delta l}{l} - 3 \left( \frac{\Delta l}{l} \right)^2 + \left( \frac{\Delta l}{l} \right)^3. \quad (9)$$

Defining  $S$  as the total interface area contained in the large cube one has

$$\sigma = \frac{S}{N} \propto n^3 l^2 \propto \frac{1}{l} \quad (10)$$

so that if we define  $x = \Delta l/l$  we have that  $x$  is proportional to  $\sigma$ . In summary,

$$h \propto x^3 - 3x^2 + 3x, \quad (11)$$

with  $0 \leq x \leq 1$ . Recalling that  $x$  is proportional to  $\sigma$ , one can compare the parabolic behavior exhibited by Eq. (11) with the behavior of  $\Delta H$  as a function of  $\sigma$  shown in Fig. 4.

The essence of the model, as shown by Eq. (8), is that when a volume element belongs to more than one interface it is counted only once. Even admitting that this assumption is too simplistic, it appears nonetheless that the hypothesis of nonadditivity of the interface effects gives a clue for modeling the results of the enthalpy calculations.

The computed values of the enthalpy can be compared with the heat released by the Ag-Cu alloys upon heating, corrected for the enthalpy of formation of the terminal solutions and for the heat release due to recovery and grain growth. These corrected values are reported in Ref. 9 and, for the equimolar composition, the heat release amounts to  $\sim 5$  kJ/mol. Adding to this value the interface enthalpy (estimated as  $1 \text{ J/m}^2$  according to the present computations) calculated for a grain size ranging between 20 and 40 nm, one obtains that the experimental value of the enthalpy difference between the Ag-Cu alloy and the reference state is of the order of 6 kJ/mol.

A comparison of this result with the values shown in Fig. 4 suggests that the Ag-Cu alloys obtained by high-energy ball milling are not atomically disordered solid solutions but contain coherent regions which, at least in one direction, have a thickness of the individual layers of the order of a few nm. This result is independent of the uncertainties affecting the corrected values of the heat release which, in any case, is smaller by a factor of 2 than the computed enthalpy difference between the reference state and the solid solution. Of course, this conclusion does not rule out the possibility that this partially decomposed structure is the result of the trans-

formation of a higher-energy microstructure which could grow during the short-time interval typical of the ball impact and then relax quickly to a less energetic state. Actually, it has been already pointed out with reference to the Fe-Cu case<sup>4</sup> that the mechanical energy supplied by the stress field and the transient enhancement of the defect concentration during the plastic deformation may be able to induce the formation of a solid solution. In the same case it was also observed that the density of extended defects was relatively low, thus suggesting that some recovery of the defects created by the plastic deformation had occurred. All these observations point to the presence of some excess mobility and therefore to the occurrence of a microstructural evolution of the samples for a certain time after the deformation.

The above remarks may be generalized saying that all transformations undergone by the system after the primary alloying process must correspond to a free-energy decrease.

As a consequence it appears that, in the Ag-Cu system, while a transformation from the solid solution to a modulated coherent structure containing more or less pure layers of the elements is energetically possible, the reverse transformation is not allowed unless the refinement of the coherent modulated microstructure continues down almost to atomic level. In this case, however, the formation of the solid solution from the pure elements as a result of the injection in the system of a considerable amount of mechanical energy appears much more realistic.

#### ACKNOWLEDGMENTS

The authors acknowledge Dr. Massimo Celino (ENEA) for helping with the calculations. Dr. M. Vittori Antisari is also acknowledged for helpful discussions and comments.

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