

Proposed Definition of Microchemical Inhomogeneity and Application To Characterize Some Selected Miscible/Immiscible Binary Metal Systems

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A new parameter is proposed to quantify the microchemical inhomogeneity (MCI) for a general multicomponent system and is applied to characterize some selected binary metal systems, i.e., the Ag–Ru, Ag–Co, Ni–Ru, and Ni–Hf systems, through molecular dynamics simulations. For the equilibrium immiscible Ag–Ru, Ag–Co, and Ni–Ru systems, *ab initio* calculations are performed to acquire some physical properties for fitting the respective *n*-body potentials. On the basis of the derived potentials, simulations reveal that in the highly immiscible Ag–Ru system, when the solute concentration is less than one of the critical values, i.e., either 6 atom % of Ru or 10 atom % of Ag, in the Ag-based and Ru-based solid solutions, respectively, the MCI is a small positive number and that when the solute concentration exceeds the critical values, i.e., falls in a composition range of 6–90 atom % of Ag, the MCI rises sharply to a large positive value ranging from 0.8 to 0.95, suggesting an incomplete-phase-separation tendency, which may result in forming a nanometer/subnanometer scaled structure. Similar simulations reveal that for the medium immiscible Ag–Co system, the MCI is about +0.7 within a composition range of 10–85 atom % of Ag and that for the Ni–Ru system, characterized by a nearly zero heat of formation, the MCI is nearly zero over the entire composition range, suggesting a possible metastable isomorphous phase diagram for the system, in which amorphous alloy, namely metallic glass, is hardly formed. In the contrast, for the miscible Ni–Hf system featuring a large negative heat of formation, the MCI is negative and is about –0.17 within a composition range of 25–80 atom % Ni, in which a crystalline solid solution prefers to turn into an amorphous state, corresponding almost exactly to the glass-forming range known from experiments as well as from theoretical prediction.

1. Introduction

It is known that the microchemical inhomogeneity (MCI) is referred to the compositional nonuniformity in nanometer or subnanometer scale and often exerts profound effects not only on the chemical and physical processes, but also on the properties and performance of the materials.^{1–4} For example, Rogers et al.³ reported that there was a drastic MCI in a Co₇₈Cr₂₂ film grown epitaxially on Ru substrate by electron beam evaporation, resulting in an enhanced saturation in magnetization, and that the MCI was believed to play an important role in governing the magnetic properties of the Co–Cr alloy thin films. Consequently, the MCI has long been an active topic in condensed-matter physics, chemistry, and materials science. Hence, a relevant definition and quantitative evaluation of the MCI is of vital importance from a scientific as well as a technical point of view. For instance, Warren⁵ and Cargill et al.⁶ proposed two parameters α and η to quantify the “local chemical order”, which were defined as $\alpha = Z_{ij}/\bar{Z}_{ij} - 1$ with $\bar{Z}_{ij} = x_j[x_i(Z_{ii} + Z_{ij}) + x_j(Z_{ji} + Z_{jj})]$ and $\eta = Z_{ij}/\bar{Z}_{ij} - 1$ with $\bar{Z}_{ij} = x_j Z_j Z_i / (x_i Z_i + x_j Z_j)$. Here, x_i is the concentration of the component *i*, Z_i , and Z_{ij} are the average numbers of the nearest neighbors around an *i* atom and of the nearest neighbors of the *j* atoms around the *i* atom, respectively. However, there is a problem with the two proposed parameters in depicting the MCI. Above all, both parameters are only available to deal with the binary system and are not able to describe the MCI involved in the ternary

and multicomponent systems. Besides, either the Warren or Cargill–Spaepen parameter gives two different values for a system, i.e., one refers to the solute atom, while the other is for the solvent atom, thus bringing about an uncertainty and even confusion. Naturally, the MCI should be an intrinsic character of a system and therefore should have a definite value, which is independent of the atomic species referenced in the evaluation. Consequently, a new parameter is proposed in this paper to appropriately and accurately quantify the MCI for a binary system as well as for a general multicomponent system.

As an intrinsic character of a system, the MCI should be governed only by the atomistic configuration of the system, and therefore can be evaluated from an atomistic interaction potential of the system through molecular dynamics (MD) simulation, as the MD simulation can provide some details concerning the atomic configuration by the calculations of the partial radial distribution functions (PRDF). Hence the coordination numbers or the nearest neighbors, i.e., Z_i and Z_{ij} , could be calculated by integrating up to the first minimum in the PRDF, thus enabling one to evaluate the MCI quantitatively. To illustrate the feasibility of acquiring the proposed MCI through MD simulation, four binary metal systems, i.e., the Ag–Ru, Ag–Co, Ni–Ru, and Ni–Hf systems, are selected and investigated in the present study.

According to Miedema’s theory, the heats of mixing of the four selected systems are +35, +28, +1.5, and –63 kJ/mol, respectively.⁷ The Ag–Ru system is equilibrium immiscible in the solid state, while there is a miscibility gap in the liquid state.

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The Ag–Co system is equilibrium immiscible not only in the solid state, but also in the liquid state. For the Ni–Ru system, there is a peritectic reaction, yet there exists no intermetallic compound in its equilibrium phase diagram. In contrast, for the Ni–Hf system characterized by a large negative heat of mixing, there are several intermetallic compounds and four eutectic reactions appearing in its equilibrium phase diagram.^{7,8}

To our knowledge, no n -body Ag–Ru potential has ever been reported in the literature and therefore it is necessary to construct a realistic Ag–Ru potential prior to performing the MD simulations for evaluating the MCI of the Ag–Ru system. As mentioned above, as there is no equilibrium compound existing in the immiscible Ag–Ru system, very few physical data could be used in fitting the Ag–Ru potential. To tackle this problem, we perform first principles calculations using the Vienna ab initio Simulation Package (VASP)^{9–11} to acquire some physical properties of a few possible nonequilibrium compounds in the Ag–Ru system, and then use the calculated properties to derive the cross potential.^{12,13}

2. Definition of the MCI

Consider a multicomponent system consisting of N components, e.g., solid or liquid solution of metals (or amorphous alloys), of which the concentration of each component is c_i with $i = 1, 2, \dots, N$. For a specific component, e.g., the component i , each atom of i has, on an average, Z_{ii} nearest neighbors of a similar species and Z_{ij} nearest neighbors of dissimilar j atoms. Here $j = 1, 2, \dots, N$, and let $Z_i = Z_{ii} + Z_{ij}$. Thus, $p_{ii} = (Z_{ii}/Z_i)$ and $p_{ij} = (Z_{ij}/Z_i)$ ($j \neq i$) are the average probabilities of an i atom to have an atom of similar species and to have an atom of dissimilar species as its nearest neighbor, respectively. The values of Z_i , Z_{ii} , and Z_{ij} are statistical averages, though they may vary somewhat from site to site for a specific component. Apparently, the values of p_{ii} and p_{ij} range from 0 to 1. The MCI of the component i , ζ_i , and the MCI of the system, ζ , are defined as follows, respectively:

$$\zeta_i = p_{ii} - \sum_{j \neq i}^N p_{ji} \quad (1)$$

$$\zeta = \sum_i^N \zeta_i c_i \quad (2)$$

For a binary system, the MCI parameters are simplified as $\zeta = \zeta_1 = \zeta_2$ and $\zeta = p_{11} - p_{21} = p_{22} - p_{12}$. For a monocomponent system, i.e., pure metal, it should be regarded as the limit of a binary dilute solution. Thus the equations of $p_{11} = p_{21} = 1$ and hence $p_{12} = p_{22} = 0$ always hold. The physical meaning of the proposed definition could therefore be well understood as follows. If an atom i occupies the nearest neighbor of atom i in the same probability as it occupies the nearest neighbor of another atom species, the component i is considered to be microchemically homogeneous, and correspondingly, the MCI of component i should be zero. It follows that if every component is microchemically homogeneous, the whole system should be considered as microchemically homogeneous, i.e. the MCI of the system should be zero. Obviously, the value of ζ_i and ζ ranges from -1 to $+1$. Accordingly, $\zeta = 0$ indicates that the average composition at any location in the system is identical with the overall composition of the system.

To appraise the validity of the present definition for the MCI, Table 1 gives the comparison between the Warren parameter α , the Cargill–Spaepen parameter η , and the present MCI

TABLE 1: Comparison between Warren Parameters α , Cargill–Spaepen Parameters η , and the Microchemical Inhomogeneity Parameters ζ for the Ni–Nb System^{14,15}

alloys	Z_{11}	Z_{12}	Z_{22}	Z_{21}	α	η	ζ
Ni ₄₄ Nb ₅₆ (glass)	3.8	8.2	9.0	5.5	−0.02	0.07	−0.063
Ni ₅₀ Nb ₅₀ (glass)	5.0	7.4	7.5	7.4	−0.08	0.09	−0.093
Ni ₆₃ Nb ₃₇	6.6	5.9	5.6	10.0	−0.16	0.11	−0.113
Ni ₆ Nb ₇ (μ phase)	5.15	6.85	7.00	8.00	−0.13	0.10	−0.104

parameter ζ calculated for a representative system, i.e., the Ni–Nb system.^{14,15} It should be noted that only one value for each Warren parameter α or Cargill–Spaepen parameter η is listed in the table, although the values for the solute and solvent are different. According to their definitions, a negative α and a positive η indicate that the Ni and Nb atoms in the system both prefer to have dissimilar atoms as neighbors.^{14,15} From Table 1, one sees that for the five Ni–Nb alloys, the present parameter ζ is always negative, suggesting the Ni and Nb atoms prefer to form some compounds, which are similar to those deduced from η and α . Apparently, under the newly proposed definition, the parameter ζ can be used to quantify the MCI for a mono-component system, a binary system, a ternary system, and even a general multicomponent system.

Concerning the feasibility and uniqueness of the newly defined MCI, we intend to discuss briefly its implication and application in the binary systems. In the case of a binary system with a large positive heat of mixing, there exists a strong repulsion between the two components (i.e., atoms of dissimilar species) and therefore each atom in the system would prefer to have the atoms of similar species as its neighbors, implying that the system has a tendency for clustering, segregation, or phase separation. According to the present definition, one obtains $p_{ii} > p_{ij}$ and $\zeta = \zeta_1 = \zeta_2 > 0$. In other words, the MCI is a positive value for a system with a large positive heat of mixing. Correspondingly, if a system is characterized with a large negative heat of mixing, the MCI would be a negative value, implying that the system has a tendency for ordering or compounding. It is deduced that for a system characterized by a heat of mixing around zero, its MCI should be close to zero. Generally speaking, the binary systems characterized by positive heats of mixing prefer positive MCIs, while the systems featuring negative heats of mixing would probably possess negative MCIs.

3. Calculation of the MCI

3.1. The Ag–Ru and Ag–Co Systems. In the present study, ab initio calculations are carried out to acquire some physical properties of a few possible nonequilibrium compounds in the Ag–Ru system and the calculated properties are then employed to derive the Ag–Ru cross potential. The ab initio calculation is based on the well-established Vienna ab initio simulation package (VASP).^{9–13} The calculations are conducted in a plane-wave basis, using fully nonlocal Vanderbilt-type ultrasoft pseudopotentials to describe the electron–ion interaction, which allows the use of a moderate cutoff for the construction of the plane-wave basis for the transition metals.¹⁶ In the calculations, the exchange and correlation items are described by the generalized-gradient approximation (GGA) proposed by Perdew and Wang.¹⁷ The integration in the Brillouin zone is done in a mesh of $11 \times 11 \times 11$ special k points determined according to the Monkhorst–Pack scheme, as such integration is proved to be sufficient for the computation of simple structures.¹⁸ In the present study, the ab initio calculations are carried out for a few possible nonequilibrium compounds, i.e., the B₂ AgRu and L₁₂ Ag₃Ru and AgRu₃, based on the following consider-

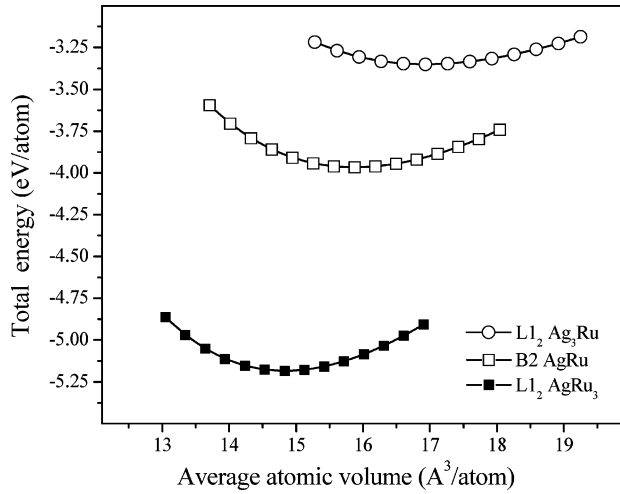


Figure 1. The total energy as a function of average atomic volume for the metastable compounds with different structures in the Ag–Ru system, obtained from the ab initio calculation.

ations. First, the metastable alloy phases obtained so far in experiments are frequently of simple structures, i.e., typically in fcc, bcc, and hcp structures, but not any complicated structure due to the restricted kinetic conditions available in the non-equilibrium producing processes, such as ion beam mixing, vapor deposition, etc.¹⁹ Second, it is feasible and convenient to fit the potential parameters by using the compounds of simple structures. Accordingly, the total energy curves versus the average atomic volume for three nonequilibrium Ag–Ru compounds are obtained by ab initio calculations and are displayed in Figure 1. These calculated results provide the necessary data to fit the cross-potential parameters of the Ag–Ru system.

In the Tight-Binding Second-Moment Approximation (TB-SMA) scheme, the repulsive portion is a Born–Mayer pairwise interaction and the attractive portion is a second-moment approximation of the tight-binding band energy. The cohesive and repulsive items of the total energy are exponential functions of the atomic distance, and the total energy is written as^{20–24}

$$E_{\text{total}} = \sum_i \left\{ \sum_{j \neq i} A_{\alpha\beta} \exp \left[-p_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}} - 1 \right) \right] - \sqrt{\sum_{j \neq i} \xi_{\alpha\beta}^2 \exp \left[-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}} - 1 \right) \right]} \right\} \quad (3)$$

where α and β indicate the atomic species, r_{ij} is the distance between atoms i and j and is calculated up to a distance of r_{cutoff} , whereas $r_{\alpha\beta}$ is taken to be the nearest distance between atoms α and β in the crystal structure. $A_{\alpha\beta}$, $p_{\alpha\beta}$, $\xi_{\alpha\beta}$, and $q_{\alpha\beta}$ are adjustable parameters, which are generally determined by fitting to their respective physical properties. For $\alpha = \beta$, the fitting procedures are performed on the cohesive energies, lattice constants, elastic constants, etc. at 0 K for pure Ag and Ru. For the atomistic interaction in the hcp lattice, the c/a ratio was optimized employing the approach proposed by Willaime et al.²² while keeping the atom volume as a constant, equaling the experimental value. For $\alpha \neq \beta$, the corresponding parameters are fitted to the cohesive energies and lattice constants of three possible metastable compounds, i.e., the B2 AgRu and L1₂ Ag₃Ru and AgRu₃,⁷ acquired by ab initio calculations. The parameter $r_{\alpha\beta}$ is taken to be the average value of the nearest

TABLE 2: Tight Binding Potential Parameters for the Ag–Ru System Constructed in the Present Study^a

	p	q	A	ξ	r_0	r_{cutoff}
Ag–Ag	11.2407	2.8378	0.0839	1.0744	2.89	5.50
Ru–Ru	25.5412	1.3414	0.0335	1.9119	2.68	4.00
Ag–Ru	5.6189	3.2052	0.5133	2.7244	2.80	5.00

^a A and ξ are expressed in eV/atom, r_0 and r_{cutoff} are expressed in Å.

TABLE 3: Properties of Ag and Ru, i.e. Cohesion Energies E_c , Lattice Constants a and c , and Elastic Constants C_{ij} Used in Fitting and the Reproduced Values^a

	experimental ^{7,8,25}		reproduced or fitted	
	Ag	Ru	Ag	Ru
E_c	2.85	6.74	2.85	6.74
a	4.085	2.71	4.085	2.68
c		4.28		4.36
C_{11}	1.240	5.626	1.213	5.834
C_{12}	0.937	1.878	0.859	2.071
C_{13}		1.682		1.651
C_{33}		6.242		6.385
C_{44}	0.461		0.508	
C_{55}		1.806		1.462

^a E_c is expressed in eV/atom, r_0 , a , and c are expressed in Å, and C_{ij} is expressed in Mbar.

TABLE 4: Properties of Metastable Compounds of Ag–Ru Systems Obtained from ab Initio Calculation and the Fitted Results^a

	ab initio calculation		reproduced or fitted	
	a	E_c	a	E_c
Ag ₃ Ru (L1 ₂)	4.08	3.35	4.08	3.41
AgRu (B2)	3.17	3.97	3.17	4.06
AgRu ₃ (L1 ₂)	3.90	5.19	3.89	5.08

^a Cohesion energies E_c are expressed in eV/atom. Lattice constants a are expressed in Å.

atomic distance in the three compounds. The fitted tight binding potential parameters for the Ag–Ru system are listed in Table 2. The experimental data or the ab initio calculated results used in constructing the potentials are listed in Tables 3 and 4 together with the properties reproduced from the derived potential. From these tables, one sees that the reproduced properties match well with the experimental values as well as the ab initio calculated results. More calculations are carried out to further certify the relevance of the derived potentials. For example, the lattice constants of the D0₁₉ AgRu₃ compound⁸ deduced by the derived n -body potential are 5.52 and 4.43 Å, respectively, matching well with the ab initio calculated values of 5.53 and 4.37 Å, respectively. One sees that the maximum error is only about 1.4%, confirming that the potentials are competent for describing the atomistic interaction of the Ag–Ru system.

On the basis of the constructed Ag–Ru potential, MD simulations are carried out at 300 K and 0 Pa for the fcc Ag-based and hcp Ru-based solid solutions with various solute concentrations, respectively. The simulation models consist of $8 \times 8 \times 8 = 512$ unit cells (2048 atoms) for the fcc Ag-based and $10 \times 6 \times 6 = 360$ unit cells (1440 atoms) for the hcp Ru-based solid solutions, respectively. For both solid solution models, the [100] and [001] crystalline directions are parallel to the x - and z -axes, respectively, and the crystalline directions along the y -axis are [010] for the fcc lattice and [120] for the hcp lattice, respectively. The periodic boundary conditions are adopted in all three directions. In setting the solid solution models, the solute atoms are added into the model by randomly substituting a desired number of solvent atoms to obtain the

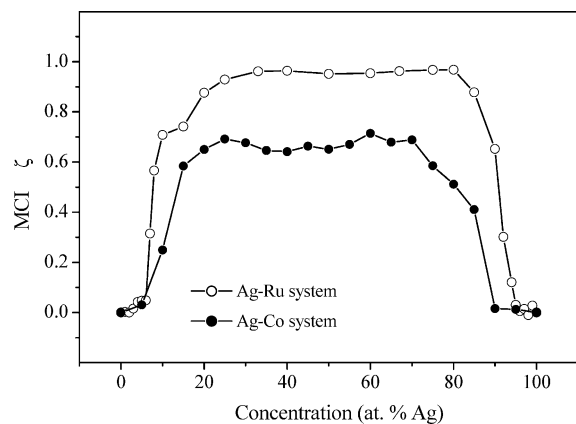


Figure 2. The microchemical inhomogeneity (MCI), ζ , as a function of concentration of Ag for Ag–Co and Ag–Ru systems obtained through molecular dynamics simulations.

initial state of the solid solution models. MD simulations are then carried out with the Parrinello–Rahman constant pressure scheme and the equations of motion are solved by using the second-order four-value predictor–corrector algorithm of Gear with a time step $t = 5 \times 10^{-15}$ s.^{26–28} In the present study, MD simulations are conducted for 50 000 to 150 000 MD time steps to reach a relatively stable (i.e. metastable) state, at which all the related dynamic variables show no secular variation. The process of the structural change in the solid solution models is monitored by the pair-correlation functions $g(r)$. The planar structure factor $S(k, z)$ and density profiles $\rho_a(z)$ of each species along the z direction are also inspected to provide evidence of the structural change.^{29–31} Meanwhile, the MCI defined above are calculated to characterize the microchemical distribution.

Figure 2 illustrates the correlation between the calculated MCI and the Ag concentration in the Ag–Ru system. One sees that when the solute concentration in an alloy is less than a critical value, i.e., either 6 atom % of Ag in the hcp Ru-based solid solution or 10 atom % of Ru in the fcc Ag-based solid solution, the alloy possesses a small positive MCI, indicating a slight tendency of clustering in the alloy. It is of interest to note that when the solute concentrations exceed the respective critical values, namely when the Ag concentration of an alloy falls into the composition range of 6–90 atom % of Ag, the MCI increases rapidly from about 0.1 to about 0.8–0.95, indicating a strong tendency for phase separation in the alloy.

Figure 3 exhibits the projections of atoms of the solid solution model to show the atomic configurations at various solute concentrations. One sees clearly that when the solute concentration is less than the critical value, the solid solution can preserve its original structure with slight clustering of the solute atoms, as shown in Figure 3a for the fcc Ag-based solid solution with 94 atom % of Ag and Figure 3b for the hcp Ru-based solid solution with 5 atom % of Ag, respectively. In contrast, for the solid solution exceeding the critical value, one observes incomplete phase separation, as shown in Figure 3c (75 atom % of Ag) and Figure 3d (35 atom % of Ag). From Figure 3, one may find that the resultant phase is neither an amorphous alloy nor a conventional phase of spinodal decomposition. In fact, the resultant phase interconnects and spreads out in three dimensions and exhibits a nanometer or subnanometer scaled structure. Incidentally, Sheng et al. have also observed such an atomic configuration in the Ag–Cu and Ag–Ni systems, and argued that a large positive heat of mixing and a miscibility gap in the liquid state persisting to a very high temperature are favorable in forming a spinodal-like phase.^{32,33} To determine the spinodal decomposition point, Figure 4 sketches the Gibbs

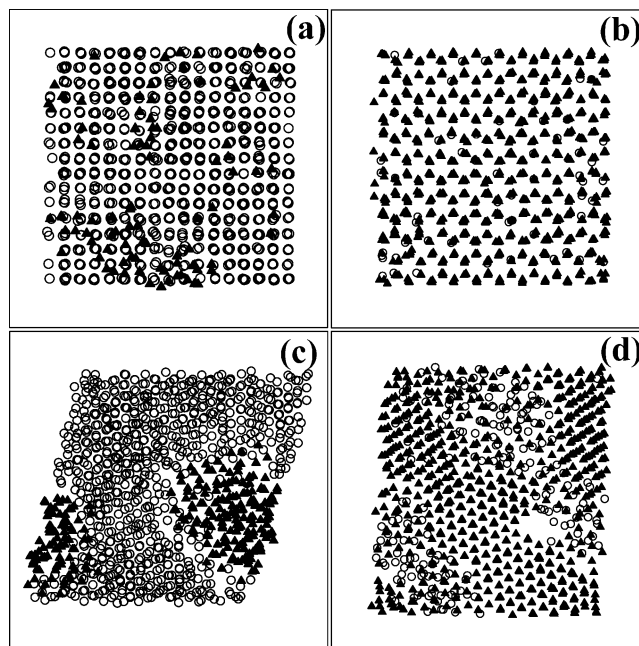


Figure 3. Projections of atoms in the MD box onto the x – y plane for Ag–Ru solid solutions after 53 000 MD steps. The concentrations are (a) 94 atom % of Ag, (b) 5 atom % of Ag, (c) 75 atom % of Ag, and (d) 35 atom % of Ag, respectively. Open circles stand for Ag atoms and solid triangles stand for Ru atoms.

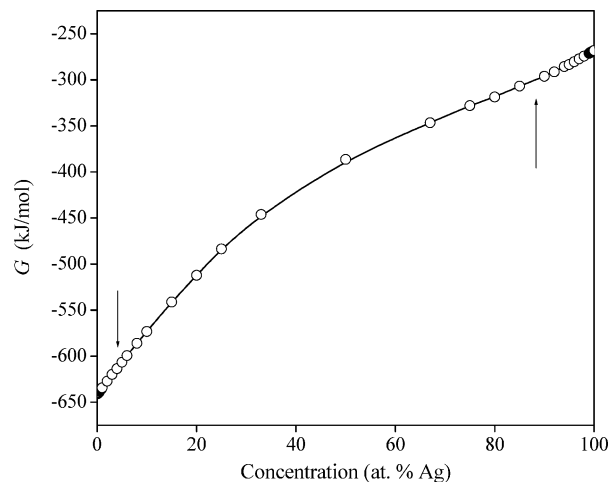


Figure 4. The calculated Gibbs energy as a function of Ag concentration in the hcp ($c_{\text{Ag}} \leq 50$ atom % of Ag) and fcc ($c_{\text{Ag}} \geq 50$ atom % of Ag) Ag–Ru solid solutions; the two inflection points are marked with fine arrows.

energy as a function of alloy concentration for the Ag–Ru system in the initial state. In Figure 4, there appears clearly two inflection points in the energy curve, located at about 6 and 88 atom % of Ag, respectively. According to the phase transformation theory,³⁴ the two inflection points are just the critical points of spontaneous decomposition, lending strong support to the relevance of the MD simulation results. In short, the simulation results suggest that when the MCI is large enough, e.g., about 0.9 in the present case of the Ag–Ru system, phase separation may take place under a nonequilibrium condition.

The Ag–Co system is characterized by a heat of mixing of + 28 kJ/mol, which is slightly smaller than that of the Ag–Ru system. Very recently, Guo et al. have studied the atomic structures of the nonequilibrium Ag–Co alloys by MD simulations based on a derived n -body Ag–Co potential.³⁵ For

TABLE 5: Tight Binding Potential Parameters^a for the Ni–Ru and Ni–Hf Systems Derived by the Authors^{36,38}

	p	q	A	ξ	r_0	r_{cutoff}
Ni–Ni	11.6430	2.1331	0.0913	1.4783	2.49	4.65
Ru–Ru	25.5412	1.3414	0.0335	1.9119	2.68	4.00
Ni–Ru	9.5786	2.6266	0.2956	3.2879	2.57	4.55
Hf–Hf	10.557	1.9610	0.1325	2.1546	3.14	5.20
Ni–Hf	10.9886	1.2829	0.1126	1.7791	2.69	4.70

^a A and ξ are expressed in eV/atom, r_0 and r_{cutoff} are expressed in Å, respectively.

comparison, we calculate the MCI of the Ag–Co system using the derived potential³⁵ and plot the calculated MCI as a function of the Ag concentration in Figure 2 together with the calculated results for the Ag–Ru system. From Figure 2, one can see that for the Co–Ag-based solid solutions, when the concentration falls into the composition range of 10–5 atom % of Ag, the calculated MCI (ξ) increases sharply from about zero to a large positive value being around 0.7, suggesting a strong tendency of segregation or phase separation. In fact, Guo et al. have observed a similar phenomenon where the Co–Ag-based solid solution could retain its atomic homogeneity up to a critical point of 9 atom % of Ag and 12 atom % of Co, beyond which the Ag/Co solute atoms began to segregate and to turn into an amorphous phase with inhomogeneous atomic structure.³⁵ Apparently, the composition ranges determined in the present study by the calculated MCI and those by Guo are quite compatible with each other, implying that the MCI parameter ξ is of relevance in quantitatively characterizing the microchemical distribution.

One may note that the maximum values of the MCIs for the Ag–Ru and Ag–Co systems are about 0.95 and 0.7, respectively, which might indicate that the microchemical distribution in the Ag–Ru system is more inhomogeneous than that in the Ag–Co system. It is believed that two factors, i.e., the difference in the heats of mixing between the Ag–Ru and Ag–Co systems and the difference in the melting points between the Ru and Co, may account for the difference in the maximum MCI values.^{32,33} In this regard, however, further studies are needed to clarify the underlying physics and the detailed mechanism.

3.2. The Ni–Ru and Ni–Hf Systems. As mentioned above, the Ni–Ru system has a small positive heat of mixing (about +1.5 kJ/mol), and according to a recent study by the present authors, nickel and ruthenium may form a metastable isomorphous phase diagram under a nonequilibrium state.³⁶ As a result, the amorphous alloy is hardly formed in the Ni–Ru system, which could therefore be classified as a hardly glass-forming system. In contrast, the Ni–Hf system, due to its large negative heat of mixing (about –63 kJ/mol), is classified as a readily glass-forming system.³⁷ In the present study, we evaluate and compare the MCIs of the Ni–Ru and Ni–Hf systems. The n -body potentials of the Ni–Ru and Ni–Hf systems have been derived under the framework of TB-SMA by the present authors and have been proven to be realistic.^{36,37} For convenience as well as completeness, the parameters of the Ni–Ru and Ni–Hf potentials are directly cited and are listed in Table 5. Employing the derived potentials, similar MD simulations are carried out to reveal the correlations between the MCI and the alloy concentration for the Ni–Ru and Ni–Hf systems, respectively, and the results are plotted in Figure 5. We now discuss what one could observe from the figure.

First, for the Ni–Ru system, the MCI is very small (in absolute value), around zero over the entire composition range, indicating that the microchemical distribution is very much homogeneous in the system. In other words, there exists almost

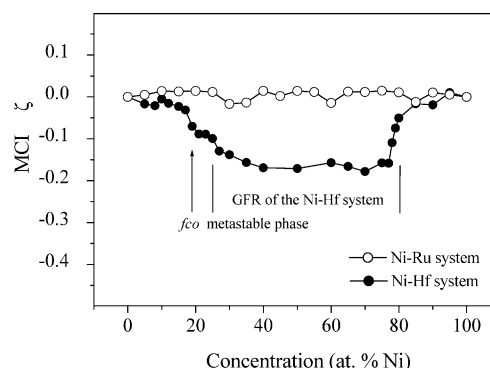


Figure 5. The MCI, ξ , as a function of Ni concentration for the Ni–Ru and Ni–Hf systems obtained through MD simulations. The metastable face-centered orthorhombic (fco) phase and the glass-forming range (GFR) of the Ni–Hf system are marked in the figure for attention.³⁷

no tendency of ordering or clustering in the system. The calculated MCI could also account for the fact that the Ni–Ru system is a hardly glass-forming one and that no amorphous alloy has so far been obtained in the system by any currently available glass-producing techniques.³⁶

Second, for the Ni–Hf system, there appear three critical points in the calculated MCI over the entire composition range, i.e., 16 atom % of Ni and 25 atom % of Ni, for the hcp Hf-based solid solution and 20 atom % of Hf for the fcc Ni-based solid solution, respectively, which coincidentally match well with three specific compositions found previously for the Ni–Hf system, corresponding to a composition for forming a metastable face-centered orthorhombic (fco) phase and another two compositions defining the glass-forming range, respectively.^{37,38} It is obvious that when the solute concentrations are less than the critical points, the MCI of the Ni–Hf system is very small, and that when the alloy compositions fall into the range of 16–80 atom % of Ni, the Ni–Hf alloys prefer to be in an amorphous state, resulting in forming metallic glasses, as the negative MCI means there is a tendency of ordering.³⁹ It is therefore concluded that the composition range determined from the calculated MCI agrees well with that predicated previously as well as with the experiment observations, as the Ni–Hf metallic glasses have readily been produced by some nonequilibrium materials processing techniques within the predicted compositions range.^{40,41}

In summary, the calculations of the MCIs for the four representative binary metal systems show that there exist close correlations among the microchemical distribution, the atomic configuration, and the associated MCI. Once the atomic configuration is known, for instance, through the computer simulation as illustrated in the present study or by experimental analysis, one can use the MCI to quantitatively characterize the microchemical distribution. Besides, one may also use the calculated MCI to compare the degrees of inhomogeneity at different compositions of the same system or the degrees of inhomogeneity of different systems.

4. Concluding Remarks

We have shown the competence of the proposed parameter ξ for a quantitative description of the microchemical inhomogeneity for a binary system and the proposed microchemical inhomogeneity can be calculated directly from the interatomic potential of the system through molecular dynamics simulation. The defined MCI can also be used for a ternary or even a multicomponent system.

On the basis of the calculations for the MCIs of the four selected binary metal systems, i.e., the Ag–Ru, Ag–Co, Ni–Ru, and Ni–Hf systems, three categories are proposed in terms of their respective MCIs, i.e., (i) a system with positive heat of mixing frequently has a positive MCI, which indicates a tendency of clustering, phase segregating, or separating, (ii) a system with a negative heat of mixing frequently has a negative MCI, which suggests a tendency of ordering or compounding, and (iii) a system with a heat of mixing around zero has an MCI also around zero, which may imply a possible metastable isomorphous phase diagram.

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References and Notes

- (1) Sobolev, V. V.; Guilemany, J. M. *Mater. Lett.* **1995**, *25*, 285.
- (2) Wittig, J. E.; Al-Sharab, J. F.; Doerner, M.; Bian, X.; Bentley, J.; Evans, J. D. *Scripta Mater.* **2003**, *48*, 943.
- (3) Rogers, D. J.; Maeda, Y.; Krishnan, K. M. *J. Magn. Magn. Mater.* **1997**, *163*, 393.
- (4) Vasilyeva, I. G. *J. Alloy Compd.* **2001**, *323–324*, 34.
- (5) Warren, B. E.; Averbach, B. L.; Robert, B. W. *J. Appl. Phys.* **1951**, *22*, 1493.
- (6) Cargill, G. S., III; Spaepen, F. *J. Non-Cryst. Solids* **1981**, *43*, 91.
- (7) Miedema, A. R.; Niessen, A. K.; De Boer, F. R.; Boom, R.; Matterns, W. C. M. *Cohesion in Metals: Transition Metal Alloys*; North-Holland: Amsterdam, The Netherlands, 1989.
- (8) Brandes, E. A.; Brook, G. B. *Smithells Metals Reference Book*, 7th ed.; Butterworth-Heinemann: Oxford, UK, 1992.
- (9) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.
- (10) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15.
- (11) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
- (12) Liu, B. X.; Lai, W. S.; Zhang, Z. J. *Adv. Phys.* **2001**, *50*, 367.
- (13) Lai, W. S.; Liu, B. X. *J. Mater. Res.* **2001**, *16*, 446.
- (14) Kreuch, G.; Hafner, J. *J. Non-Cryst. Solids* **1995**, *189*, 227.
- (15) Mendelev, M. I.; Belashchenko, D. K.; Ishmaev, S. N. *J. Non-Cryst. Solids* **1996**, *205–207*, 888.
- (16) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
- (17) Perdew, J.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (18) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.
- (19) Liu, J. B.; Yang, G. W.; Liu, B. X. *Phys. Rev. B* **2000**, *62*, 11277.
- (20) Tomanek, D.; Aligia, A. A.; Balseiro, C. A. *Phys. Rev. B* **1985**, *32*, 5051.
- (21) Rosato, V.; Guillope, M.; Legrand, B. *Philos. Mag. A* **1989**, *59*, 321.
- (22) Willaime, F.; Massobrio, C. *Phys. Rev. B* **1991**, *43*, 11653.
- (23) Cleri, F.; Rosato, V. *Phys. Rev. B* **1993**, *48*, 22.
- (24) Meyer, M.; Pontikis, V. *Computer Simulation in Materials Science*; NATO ASI Ser. E V205; Kluwer: Dordrecht, The Netherlands, 1991.
- (25) David, R.; Lide *Handbook Of Chemistry And Physics: A Ready Reference Book Of Chemical And Physical Data*, 83rd ed.; CRC: New York, 2002.
- (26) Parrinello, M.; Rahman, A. *J. Appl. Phys.* **1981**, *52*, 7182.
- (27) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon: Oxford, UK, 1986.
- (28) Ciccotti, G.; Hoover, W. G. *Molecular-Dynamics Simulation of Statistical-Mechanical Systems*; ASI-NATO: North-Holland: Amsterdam, The Netherlands, 1986.
- (29) Rosato, V.; Ciccotti, G.; Pontikis, V. *Phys. Rev. B* **1986**, *33*, 1860.
- (30) Phillpot, S. R.; Yip, S.; Wolf, D. *Comput. Phys.* **1989**, *3*, 20.
- (31) Liebermann, H. H. *Rapid Solidified Alloys: Processes, Structures, Properties, Applications*; Dekker: New York, 1993.
- (32) Sheng, H. W.; He, J. H.; Ma, E. *Phys. Rev. B* **2002**, *65*, 184203.
- (33) He, J. H.; Sheng, H. W.; Schilling, P. J.; Chien, C. L.; Ma, E. *Phys. Rev. Lett.* **2001**, *86*, 2826.
- (34) Hillert, M. *Phase equilibria, phase diagrams and phase transformations: a thermodynamic basis*; Cambridge University Press: New York, 1998.
- (35) Guo, H. B.; Liu, B. X. *J. Mater. Res.* **2004**, *19*, 1364.
- (36) Li, J. H.; Guo, H. B.; Kong, L. T.; Liu, B. X. Prediction of metastable phase formation in the Ni–Ru system by ab initio and molecular dynamics calculations. *Phys. Rev. B*. Submitted for publication.
- (37) Li, J. H.; Kong, L. T.; Liu, B. X. Structural transition and glass-forming ability of the Ni–Hf system studied by molecular dynamics simulation. *J. Mater. Res.* Submitted for publication.
- (38) Li, J. H.; Guo, H. B.; Liu, B. X. Crystallographic and lattice point correlations of a new hcp-to-fcc martensitic transformation observed in the Ni–Hf system. *ACTA Mater.* Submitted for publication.
- (39) Haasen, P. *Physical Metallurgy*, 3rd ed.; Cambridge University Press: Cambridge, UK, 1996.
- (40) Thomson, J. R.; Politis, C.; Kim, Y. C. *Mater. Sci. Eng.* **1988**, *97*, 31.
- (41) Rossum, M.; Nicolet, M.-A.; Johnson, W. L. *Phys. Rev. B* **1984**, *29*, 5498.