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Microchemical inhomogeneity of multicomponent systems and its evaluation from interatomic potentials

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We propose to redefine the microchemical inhomogeneity parameter for a general multicomponent system and illustrate the evaluation of the parameter in a highly immiscible Ag-Ru system from an *ab initio* derived *n*-body potential via molecular dynamics simulations. It is found that the Ag-Ru system is characterized by a large positive value which is responsible for the observed phase separation behavior. Further calculations indicate a small negative value for a miscible Ni-Hf system, whereas it is around zero for a slightly immiscible Ni-Ru system, also matching well with experimental observations.

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Microchemical inhomogeneity (MCI) is a ubiquitous phenomenon in condensed matter and materials physics. It often has complex and profound effects on the properties and performance of the materials, hence strict precautions are always implemented into the synthesizing process, especially, for instance, in the process of fabricating the electronic, optic, and superconductive devices, etc. Meanwhile, MCI is frequently correlated with a number of chemical and physical processes, e.g., solidification of alloys, spinodal decomposition, clustering, etc. Consequently, a relevant description as well as a quantitative evaluation of MCI is of vital importance from a scientific as well as a technical point of view. In the 1950's and 1980's, Warren[1] and Cargill and Spaepen[2] proposed two parameters α and η as an attempt to quantify the ''local chemical order,'' which were defined as $\alpha = Z_{ij}/\widetilde{Z_{ij}} - 1$ with $\widetilde{Z_{ij}} = x_j[x_i(Z_{ii}+Z_{ij}) + x_j(Z_{jj}+Z_{ji})]$ and $\eta = Z_{ij}/\widetilde{Z_{ij}} - 1$ with $\widetilde{Z_{ij}} = x_j Z_j Z_i/(x_i Z_i + x_j Z_j)$. Here, x_i is the concentration of the component i, Z_i and Z_{ij} are the nearest neighbors around an i atom and the nearest neighbors of j atoms around an i atom, respectively. However, there is a problem with the two defined parameters in depicting the MCI. One can see, from their definitions, that either the Warren or Cargill-Spaepen parameter gives two different values of MCI, i.e., one refers to the solute atom, while the other is for the solvent atom, thus bringing about an uncertainty and even confusion. In addition, both parameters are only available to deal with the binary system and are not able to describe the MCI involved in ternary and multicomponent systems. Naturally, the MCI is an intrinsic character of a system and should therefore have a definite value. Moreover, the MCI value of the system should be independent of the atomic species referenced in the evaluation. Consequently, in order to give prominence of the MCI, we propose a general definition for a multicomponent system. We illustrate, in this paper, the superiority as well as feasibility of the proposed definition by a detailed evaluation of the MCI of a representative system, i.e., a highly equilibrium immiscible Ag-Ru system, together with some other binary systems of different characteristics known from thermodynamics.

Suppose a multicomponent system, e.g., solid or liquid solution of metals or amorphous alloys, is constituted of N components and the concentrations are c_i, $i = 1,2,...,N$, respectively. The number of nearest neighbors of an atom i (for amorphous or liquid alloy, or its coordination number for solid solution) is Z_i and Z_{ij} is the number of atoms j in the nearest neighbors around an atom i. $p_{ij} = Z_{ij}/Z_i$ is called the occupying probability of nearest neighbors. It is easily understood that the p value ranges from 0–1. The MCI parameter of components i, ζ_i and the MCI parameter of the system ζ are defined as follows, respectively:

$$\zeta_i = p_{ii} - \sum_{j \neq i}^{N} p_{ji} ,$$

$$\zeta = \sum_{i}^{N} \zeta_i c_i .$$

In the case of the 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 ζ_i is that if the atom i occupies the nearest neighbor of atom i in the same probability as that it occupies the nearest neighbor of other atom species, the component i is considered as microchemically homogenous and, correspondingly, the MCI parameter of this component should be zero. Similarly, if each component is microchemically homogenous, the system should be considered as microchemically homogenous, i.e., the MCI of the system should be zero. Obviously, the value of ζ_i or ζ ranges from -1 to $+1$. Under the present definition, a positive ζ_i or ζ indicates that the system has the tendency of clustering, segregation, and phase separation, whereas a negative ζ_i or ζ represents ordering or even compounding. When $\zeta = 0$, the system is considered as a microchemically homogeneous one, in which the average composition at any location in the system equals to the overall composition of the system.

As stated above, the MCI is an intrinsic character of a system and, therefore, is governed by the atomic interaction involved in the system. Once a realistic n-body potential is known, the MCI parameters of the system can be deter-

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TABLE I. Tight-binding potential parameters used in this study. A and ξ are expressed in 10^{-19} J/atom. r_0 and r_{cutoff} are expressed in Å.

	A	ξ	p	q	r_0	r_{cutoff}
Ag-Ag	0.1343	1.7191	11.2407	2.8378	2.89	5.5
Hf-Hf[a]	0.2120	3.4473	10.557	1.9610	3.14	5.2
Ni-Ni[a]	0.1461	2.3653	11.6430	2.1331	2.49	4.65
Ru-Ru[b]	0.0535	1.4763	25.5412	1.3414	2.68	4.00
Ag-Ru	0.8213	4.3591	5.6189	3.2052	2.80	5.00
Ni-Hf[a]	0.1801	2.8465	10.9886	1.2829	2.69	4.70
Ni-Ru[b]	0.4730	5.2606	9.5786	2.6266	2.57	4.55

[a] Reference 15.

[b] Reference 16.

mined, for example, through computer simulations. In order to illustrate the method of calculating MCI directly from an n-body potential through molecular dynamics (MD) simulations, three representative binary systems, i.e., Ag-Ru, Ni-Ru, and Ni-Hf systems are selected for the present study. The heats of mixing are $+35$, $+1.5$, and -63 kJ/mol for the Ag-Ru, Ni-Ru, and Ni-Hf systems, respectively. The feature of the Ag-Ru system is that it is immiscible in solid state and there is miscibility gap in liquid state. For the Ni-Ru system, there is only one peritectic reaction and no intermetallic compound exists. For the Ni-Hf system, however, several intermetallic compounds and four eutectic reactions exist.[3,4]

It is known that the molecular dynamics (MD) simulation is a powerful method to investigate the structural evolvement at an atomic scale. It can provide details of the atomic configuration, such as the partial radial distribution functions (RDF's). Hence the coordination numbers or the nearest neighbors, i.e., Z_i and Z_{ij}, may be calculated by integrating up to the first minimum in the RDF, thus evaluating the MCI. Naturally, whether or not the calculation gives reasonable results depends on how good the interatomic potentials are. In the present study, the second-moment approximation (SMA) of the tight-binding (TB) scheme[5–7] is adopted in construction of the n-body potentials. It should be noted that no equilibrium compound in the Ni-Ru and Ag-Ru systems exists and, therefore, very few physical data are available for fitting the cross potential. To overcome the problem, we perform the first principles or *ab initio* calculations to acquire some physical properties of the possible nonequilibrium compounds. Some of the calculated properties are then employed to derive the cross potentials. The *ab initio* calculation is carried out using the Vienna *ab initio* simulation package.[7–10] The MD simulation is performed with Parrinello-Rahman constant pressure scheme employing solid solution models at 300 K and 0 Pa.[11–13] The equations of motion are solved adopting a second-order predictor-corrector algorithm of Gear with a time step $t=5\times10^{-15}$ s.[12,14] The MD simulation runs about 50 000 to 150 000 MD time steps to reach a relatively equilibrium (metastable) state, at which all the related dynamic variables show no secular variation. All potential parameters used in the present study are listed in Table I. Concerning the detailed procedure of the *ab initio* calculation and the potential fitting and molecular dynamics simulations, the readers are referred to some recent publications in the literature.[17–21]

We now present and discuss the calculation results. Figure 1 illustrates the correlation between the calculated MCI parameters and the concentration in the three systems. The curve for the Ag-Ru system in Fig. 1 is quite attractive and one can see that when the concentration of the solute is less than a critical value, i.e., either 6 at. % of Ag or 10 at. % of Ru, the alloy possesses a small positive inhomogeneity parameter, which indicates that the alloy tends to clustering. When the concentration of the solute exceeds the critical value, namely, when the concentration of Ag falls into the composition range from 6 to 90 at. %, the alloys feature a large positive MCI, which causes phase separation to take place. From Fig. 1, the MCI of the Ni-Hf alloys is negative and the value is quite small, indicating that a tendency of ordering exists.[22] In addition, the calculated curve shapes into an erose basin ranging from 16 to 80 at. % Ni, which coincidently agrees with the glass-forming range of the system determined previously.[15] Contrastively, the calculated curve of the Ni-Ru systems is quite smooth and its value is nearly zero over the entire composition range, suggesting that almost no tendency of ordering or clustering exists.

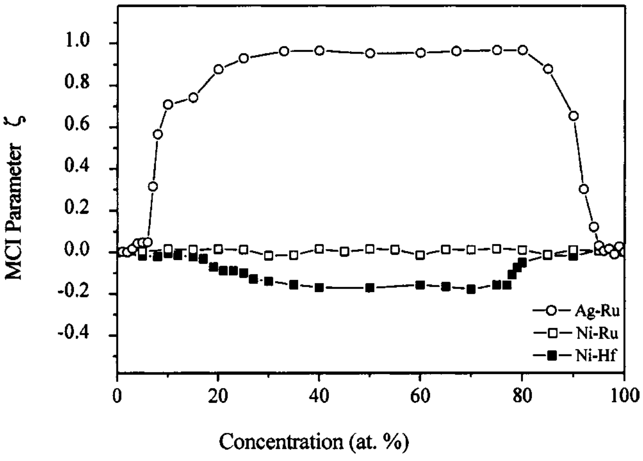

FIG. 1. The microchemical inhomogeneity parameters ζ as a function of concentration of Ag for the Ag-Ru system and Ni for the Ni-Hf and Ni-Ru systems, respectively, obtained through molecular dynamics simulations.

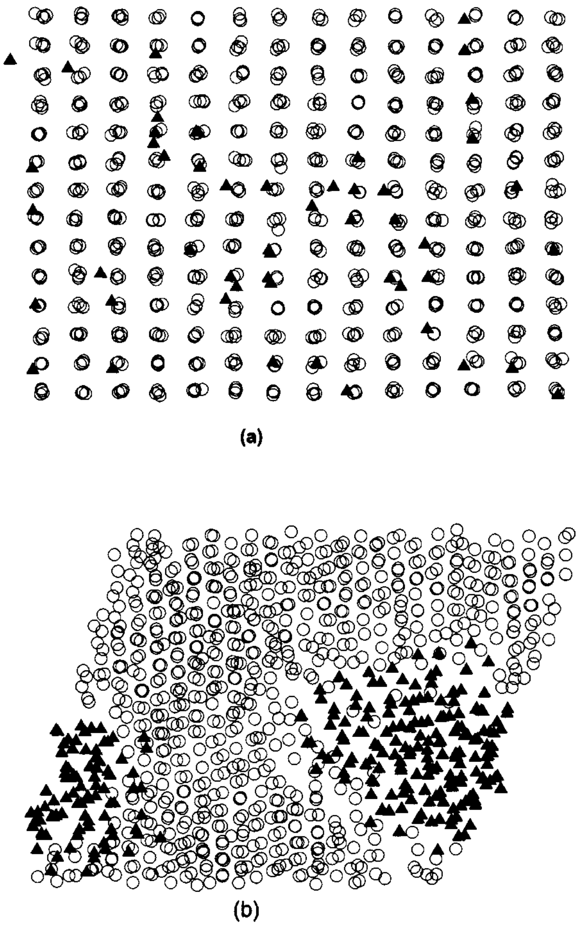

FIG. 2. Projection of all atoms in the MD box onto the *x-y* plane for Ag-based fcc solid solutions after 53 000 MD steps. The concentration are 94 at. % Ag for (a) and 75 at. % Ag for (b), respectively.

The different tendency of ordering between the Ni-Hf and Ni-Ru alloys can probably account for the fact that the former is proven to be, by both experimental studies and theoretical modeling, a readily glass-forming system, and the latter is known as a hardly glass-forming system.[15,16,22]

In order to access the atomic configuration in a system with a high inhomogeneity, Fig. 2 gives two projections of atoms in a MD box, which vividly shows the variation of the MCI with composition for the Ag-Ru system. Fig. 3 sketches the function of Gibbs energy vs the concentration for Ag-Ru system, which is obtained from the supersaturated solid solution model. In the figure, two inflexion points in the curve appear clearly located at about 6 and 88 at. % of Ag, respectively. According to the theory of phase transform,[23] the two inflexion points are just the critical points of spontaneously decomposition, leading strong support to the relevance of the MD simulation results. In fact, for the systems with positive heat of mixing, clustering or phase separation is a common phenomenon observed in experiments and therefore the systems should feature a positive MCI. However, for the systems with negative heat of mixing, especially with a large negative heat of mixing, the tendency of ordering or compounding is very intense and thus the systems should feature a negative MCI.

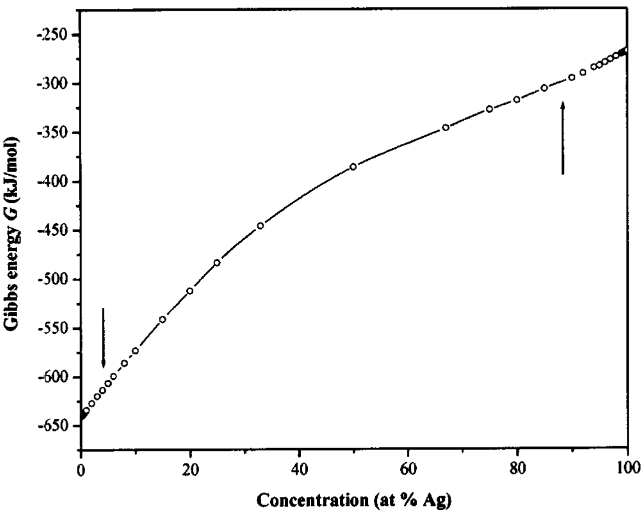

FIG. 3. The Gibbs energy as a function of concentration of Ag in supersaturated hcp ($c_{\mathrm{Ag}} \leqslant 50$ at. % Ag) and fcc ($c_{\mathrm{Ag}} \geqslant 50$ at. % Ag) solid solution, in which the two inflexion points are marked with fine arrows.

Table II gives the comparison between Warren parameter α, Cargill-Spaepen parameter η, and the present MCI parameter ζ. It should be noted that only one value for each α or η is listed in the table although the value is different for the solute and solvent. Table II shows that the absolute value of ζ is close to η. In fact, ζ approximates numerically to the average of the value of η for the solute and the value of η for the solvent. Under the present definition, the parameter ζ can also be used to quantify the MCI for the multicomponent systems.

In summary, the parameter ζ proposed in this paper should be competent to quantificationally characterize the microchemically inhomogeneity intrinsic to a binary, a ter-

TABLE II. Comparison between Warren parameters α, Cargill-Spaepen parameters η and the microchemically inhomogeneity parameters ζ.

Alloys (Refs. 24, 25)	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
$Ni_{62}Nb_{38}$ (glass)	6.74	5.37	5.56	8.76			−0.055
$Ni_{63}Nb_{37}$	6.6	5.9	5.6	10.0	−0.16	0.11	−0.113
Ni_6Nb_7 (μ phase)	5.15	6.85	7.00	8.00	−0.13	0.10	−0.104

nary, or even a multicomponent system. As an intrinsic character of a system, it can be determined by the interatomic potential of the system through molecular dynamics simulation.

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