

Interatomic Potentials for NiZr Alloys from Experimental and *Ab initio* Calculations*

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Received Feb. 27, 2001

We applied an approach to the development of many-body interatomic potentials for NiZr alloys, gaining an improved accuracy and reliability. The functional form of the potential is that of the embedded method, but it has been improved as follows. (1) The database used for the development of the potential includes both experimental data and a large set of energies of different structures of the alloys generated by *Ab initio* calculations. (2) The optimum parametrization of the potential for the given database is obtained by fitting. Using this approach we developed reliable interatomic potentials for Ni and Zr. The potential accurately reproduces basic equilibrium properties of the alloys.

Keywords *Ab initio*, NiZr alloy, Many-body interatomic potential

Article ID 1005-9040(2002)-01-038-04

Introduction

The first solid-state amorphization was observed in 1983 for the Au-La system with a large negative heat of formation^[1]. Since then, many similar results have been reported for other alloys. Various physical processes such as irradiation, interdiffusion annealing, or mechanical alloying can make a crystalline material transform into an amorphous solid, a common feature of these processes is the intimate intermixing of the constituents, resulting in chemical disorder. The Ni-Zr alloys are known to be transformed into amorphous material not only by liquid quenching but also by solid state diffusion. During the last years, a wide variety of computational methods have been developed and used to study the electronic structure and energetics of amorphous alloys, such as order-N locally self-consistent multiple scattering method (LSMS), linear muffin tin orbitals (LMTO). In spite of greatly advanced computer speeds, the application of *ab initio* methods to an atomistic simulation of materials is still limited to large systems. In contrast, the use of empirical or semiempirical potentials makes it possible to simulate much larger systems (up to 10^6 — 10^7 atoms). Therefore, based on *ab initio* calculations, simulations using empirical potential functions can provide efficient and inexpensive means for studying atomic structure and dynamics about amorphous alloys. Although h. c. p metal Zr and f. c. c metal Ni have

many types of potential functions, such as EAM, FS, EMT forms^[2-7], their alloy potentials have seldom been reported. Sabochick and Lam^[8,9] and Lam *et al.*^[10] used embedded-atom potentials to simulate the effects of Frenkel pairs and chemical disorder. Massobrio *et al.*^[11] studied amorphous NiZr₂ by introducing chemical disorder in an MD simulation performed with tight-binding potentials. Most of the constructed potentials were fitted by the cohesive energy, equilibrium volume, and other physical data.

There is an approximate consideration for uniformity electron density. While crystalline-amorphous (CA) transform process occurs, amorphous or liquid phase exhibits heterogeneous electron density, which satisfies the statistical distribution, due to local order and long range disorder. The present paper covers a new potential function from experimental data and *ab initio* calculations. The potentials can be used for the thermodynamics simulation and surface phenomena. Furthermore, this work may help to develop reliable interatomic potentials for the ordered intermetallic compounds of the NiZr system.

General Approach and Theory

The potentials developed in this work are based on the formalism of the embedded atom method (EAM). The total energy of the system is represented as

* Supported by the National Natural Science Foundation of China (No. 29892166, 29803006, 29983001).

$$E_{\text{tot}} = \frac{1}{2} \sum_{ij} V(r_{ij}) + \sum_i F(\bar{\rho}_i), \quad (1)$$

where $V(r_{ij})$ is a pair potential as a function of the distance r_{ij} between atoms i and j , F is the "embedding energy" as a function of the host "density" $\bar{\rho}_i$ induced at site i by all other atoms in the system, which is given by $\bar{\rho}_i \sum_{j \neq i} \rho(r_{ij})$, and $\rho(r_{ij})$ is the "atomic density" function. The second term in eq. (1) is volume dependent and represents, in an approximate manner, many-body interactions in the system. $V_{\text{NiNi}}(R)$, $V_{\text{ZrZr}}(R)$, $\rho_{\text{Ni}}(R)$ and $\rho_{\text{Zr}}(R)$ have been obtained from the existing EAM potentials for pure Ni and Zr. We still need to construct the cross-potential $V_{\text{NiZr}}(R)$ and determine the scaling parameter for the relative ratio of the atomic densities to obtain the best fit to alloy properties. In order to construct the tentative crossing-potential we made use of Johnson's mixing scheme. With this approximation, the interaction of crossing-potential pairs is the only new value which needs to be determined in the case of a binary alloy and is taken as

$$V_{\text{NiZr}}(R) = \frac{1}{2} \left[\frac{\rho_{\text{Ni}}}{\rho_{\text{Zr}}} V_{\text{ZrZr}}(R) + \frac{\rho_{\text{Zr}}}{\rho_{\text{Ni}}} V_{\text{NiNi}}(R) \right] \quad (2)$$

To avoid singularities, the cut-off distance for the electron-density function for a specific element must be equal to or greater than the cut-off distance for the two-body term. Once the general form of the potential is chosen, the important issues become how to choose the data for fitting and how to parametrize and optimize the potential functions.

Ab initio Data and Experimental Data

The *ab initio* calculation data were generated by means of different methods for different structure sizes. For the regions of low density in NiZr microclusters^[12], we calculated the NiZr energy by using the hybrid density functional method^[13], with Becke's 3-parameter exchange functional combined with the correlation potential by Lee, Yang and Parr^[13] (B3LYP), the basis sets used were LANL2DZ, in the GAUSSIAN 98 Program^[14] employed in the computations. We present the calculated energies and geometries of various $(\text{NiZr})_n$ microclusters (n from 1 to 5), the geometry structures are shown in Fig. 1. we defined the cohesive energy per atom, *i. e.*,

$$E_c(\text{Ni}_m\text{Zr}_n) = \frac{1}{m} \{ m[E(\text{Ni}) + E(\text{Zr})] - [E(\text{Ni}_m\text{Zr}_n) + E_{2p}] \} \quad (3)$$

In the above EAM scheme, the cohesive energy of the diatomic was $E_c = V(r_c) + 2F[\rho(r_c)]$ and others were similar to it so as to obtain the related distance expression. They were used for the fitting procedures. For bulk and surface structures, we performed the calculations by using the *ab initio* total energy pseudopotential methods, flhind program, written by Scheffler and coworkers^[15,16], based on density functional theory (DFT), plane-wave basis for the expansion of the single particle Kohn-Sham wavefunction (Norm-conserve potentials), Local density approximation (LDA), Perdew-Wang-Ceperly-Alder form for exchange-correlation potential



Fig. 1 Bimetallic Ni_nZr_n clusters.

Light and dark gray spheres represent Ni and Zr atoms, respectively.

and Generalized gradient approximation (GGA), Becke-Perdew form for exchange-correlation potential. The calculations were made by means of a supercell method and a plane wave basis set with a kinetic energy cut-off 8 Rydbergs and a single Γk point. we selected different three-dimension and two-dimension structures, including FCC, simple cubic, BCC, HCP, vacancy lattice and diamond, meanwhile considered slab structures, for Ni FCC 100, 110,

111 and Zr HCP 0001, $1\bar{1}00$, $11\bar{2}0$.

The structures and their first principle energies are listed in Table 1. According to the above data, we used two types of energies for fitting to or improving each other, *i. e.*, *ab initio* energies of microclusters for a set of low coordination numbers and different structures with a fixed first-neighbor distance.

Table 1 Properties of Ni, Zr in comparison with experimental and *ab initio* data

Ni			Zr		
lattice properties	Experiment	<i>ab initio</i>	lattice properties	Experiment	<i>ab initio</i>
a_0/nm	0.352	0.365	a_0/nm	0.323 2	0.341
$E_0/(\text{eV} \cdot \text{atom}^{-1})$	-4.45	-4.70	$E_0/(\text{eV} \cdot \text{atom}^{-1})$	-6.25	-6.70
$E(\text{hcp})/(\text{eV} \cdot \text{atom}^{-1})$	-4.42	-4.40	$E(\text{fcc})/(\text{eV} \cdot \text{atom}^{-1})$		-6.20
$E(\text{bcc})/(\text{eV} \cdot \text{atom}^{-1})$	-4.30	-4.20	$E(\text{bcc})/(\text{eV} \cdot \text{atom}^{-1})$		-5.90
$E(\text{diamond})$	-2.51	-2.90	$E(\text{diamond})$		-4.30
Surface			Surface		
$r_s(110)/(\text{mJ} \cdot \text{m}^{-2})$	2 280	2 450	$r_s(110)/(\text{mJ} \cdot \text{m}^{-2})$	1 022	1 320
$r_s(100)/(\text{mJ} \cdot \text{m}^{-2})$	2 280	1 876	$r_s(100)/(\text{mJ} \cdot \text{m}^{-2})$	1 086	950
$r_s(111)/(\text{mJ} \cdot \text{m}^{-2})$	2 280	1 657	$r_s(111)/(\text{mJ} \cdot \text{m}^{-2})$	1 230	1 040

Parametrization of Potential Functions

Simple functional forms for the atomic density, pair interaction and embedding function were assumed and several parameters were adjusted to fit the data. The pair interaction $V(r)$ was chosen as Morse potential to the fitting:

$$V(r) = f_e [\exp(-2a\rho) - 2\exp(-a\rho)] \quad (4)$$

where $\rho = r - r_e$, f_e , and a are fitting parameters.

To determine the atomic density function, the following function was found to be the simplest functional form which allowed the better fitting to the data, *i. e.*,

$$\rho(r) = q r^k [\exp(-\xi r) + \gamma \exp(-\eta r)] \quad (5)$$

Given the functional form for pair potential and the atomic electron density, the embedding function is determined by means of the universal scaling function proposed by Rose *et al.*^[17]. Compared with F-S type function, we should use a single polynomial of order eight in the square root of the electron density:

$$F(\bar{\rho}) = \sum_{k=1}^n a_k \bar{\rho}^{k/2} \quad (6)$$

so we need to know V_{ZrNi} , V_{ZrZr} , V_{NiZr} , ρ_{Ni} , ρ_{Zr} , F_{Ni} and F_{Zr} functional forms, eq. (4) involves three adjustable parameters f_e , a and r_e , eq. (6) involves five parameters q , k , ξ , γ and η , eq. (5) has eight parameters.

Table 2 lists all the parameters for Ni, Zr and Ni-Zr potentials. As expected, there is a decreased tendency for the rms deviation with an increasing number of free parameters. For a fixed number of parameters, the minimum rms error saturates at a fairly low number of parameters with an rms error of around 0.32 eV. In fact, the *ab initio* calculation and the experimental data led to an error of up to 0.6 eV per atom.

The calculated elastic constants are compared with the corresponding experimental values and the tight-binding potential parameters for the NiZr systems, listed in Table 3.

Table 2 Parameters of Ni, Zr and Ni-Zr

Parameters	Ni	Zr	Parameters	Ni	Zr	Parameters	Ni	Zr
f_e/eV	2.066	3.130	γ	-0.600 4	-545.8	a_5	3.365×10^5	2.652×10^5
a	1.785 3	1.524	η	2.769 4	7.20	a_6	-5.789×10^6	-4.217×10^6
r_e/nm	0.211	0.239	a_1	1.387×10^3	2.477×10^1	a_7	5.329×10^6	3.614×10^6
q	2.742	1.0	a_2	-2.571×10^4	-9.870×10^2	a_8	-2.038×10^6	-1.211×10^6
k	2.563	6.0	a_3	2.274×10^5	1.527×10^4			
ξ	2.85	3.641	a_4	-1.139×10^6	-8.861×10^4			

Table 3 Elastic results compared with experimental and other calculated values

	Ni			Zr			NiZr ₂		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
10×10 ¹¹ C11/Pa	2.61	2.49	2.57	1.55	1.58	1.53	1.59	1.72	1.61
10×10 ¹¹ C12/Pa	1.51	1.66	1.65	0.67	0.71	0.74	1.34	1.14	1.06
10×10 ¹¹ C13/Pa				0.65	0.67	0.55	0.85	0.98	0.95
10×10 ¹¹ C33/Pa				1.73	1.78	1.68	1.47	1.60	1.68
10×10 ¹¹ C44/Pa	1.32	0.81	0.93	0.36	0.47	0.45	0.24	0.46	0.54
10×10 ¹¹ C66/Pa							0.06	0.50	0.61

a. Experimental values^[16]; *b.* calculated ones; *c.* the results of Massobrio^[19].

Conclusion

As a try of this approach we have constructed EAM potentials for Ni and Zr. The partial *ab initio* data included the energies of different structures (bulk and surface) generated by the density function method. Via fitting, we have obtained the NiZr binary alloy potential form, which has been compared with experimental and other potentials elastic values, the results fit well. The simulation of some thermodynamic and structures properties is in progress.

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