Phonon Dispersion Curves and Structural Stability for CuZr Alloys using a New Modified Embedded Atom Method Potential

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For the purpose of developing interatomic potentials for the simulation of Cu-Zr amorphous alloys, determination of parameters in the modified embedded atom method (MEAM) potential is studied. The procedure which determines the potential parameters for Cu-Zr system consists of two stages. First, the fundamental parameters are fixed as to represent the basic properties of both Cu and Zr crystals. The phonon dispersion curves as well as typical structural properties are used for parameter fitting. Secondly, the other parameters which are concerning to a reference structure of binary alloy and screening functions are examined. It is found that the stability of crystal structure of alloy depends sensitively on the choice of the parameters of screening function. Only the first neighbour interaction is basically considered in the MEAM framework. Nevertheless, it is found that it can represent the difference in energy between fcc and hcp. Because it is said that the first neighbor interaction concerning with the atomic radius is important to form the amorphous alloys, according to the feature of MEAM, it is expected that the MEAM potential has an advantage in studying systems far from a reference structures, such as amorphous alloys.

Key words: Computational Mechanics, Molecular dynamics, Amorphous, CuZr alloy, MEAM potential

1. INTRODUCTION

Amorphous alloys show unique mechanical properties. The origin of these properties is related to their special atomic structure. Therefore, atomic-level simulation is useful to clarify the mechanism. Our motivation is to create an interatomic potential that can be applied to actual amorphous alloys. Zr-based amorphous alloys are focused on and previous studies of Zr-based amorphous alloys are addressed.

Kobayashi et al. studied CuZr systems using a pair potential [1]. Gaukel *et al.* [2, 3] have proposed a unique interatomic potential for Ni-Zr using a similar framework to the modified embedded method (MEAM) originally proposed by Baskes [4]. Massobrio *et al.* [5] investigated Ni-Zr amorphous alloys by using a Finnis-Sinclair type N-body potential.

There are two common assumptions in most previous studies, including those referred to above. One is that long-range interactions are used to represent the lower energy of the hcp phase relative to the fcc phase for pure Zr. The other is that the parameters of pair interaction between two different species of atoms are assumed to be the average value of each atom. The first assumption is introduced because the first neighbor interaction cannot show the difference in energy between fcc and hcp, using pair and EAM-type potentials.

However, the first neighbor interaction is important for a correct description of the amorphous alloy structure, but the physical meaning of the second neighbor interaction is no longer clear. Therefore, its accuracy is not necessarily guaranteed for an amorphous system. If the modified, embedded atom method, in which only the first neighbor interaction is considered, shows the difference in energy between fcc and hcp, a feasible interatomic potential for an amorphous system may be constructed.

The second assumption is an assumption of average pa-

rameters. The ratio of atomic radius is an important factor in amorphous alloys. Consequently, it might be too straightforward for the determination of the interatomic interaction between different species of atoms to use a simple averaging method. In MEAM theory, the information on formation enthalpy of a reference alloy structure is considered. Therefore, MEAM is more meaningful [6].

2. METHOD AND PROCEDURE

2.1 Modified embedded atom method

The object of this paper is to determine parameters for the modified embedded atom method (MEAM), which was originally proposed by Baskes in 1994. MEAM has three features: 1) only the first neighbor interaction is used, 2) there are unified formulations for many atomic elements, and 3) there is flexibility in the choice of screening functions. Our strategy is to represent the properties of "Cu", "Zr", and "CuZr" systems by using MEAM. This should be done as preparation for application to CuZr amorphous alloys in the future.

2.2 Determination of potential

The procedure to determine the potential parameters for the CuZr system consists of two stages.

Firstly, several of the known properties of Cu and Zr perfect crystals are identified as references. Corresponding property values, calculated for selected parameter sets, are shown in Tables I and II. Because Zr transforms from hcp to bcc at elevated temperatures, information about the bcc phase is also included.

The parameter sets of MEAM potential for Cu and Zr considered are shown in the Table III. The parameter set for Cu, 'Cu1', was proposed by Baskes in his original paper about MEAM [4]. The parameter set for Zr, 'Zr1',

Table I	Quantities used in the determination of the
	parameter sets for fcc Cu

Lattice constant	<i>a</i>
Cohesive energy	E ^{fcc} _{sub}
Elastic constants	$B, (C_{11} - C_{12})/2, C_{44}$
Vacancy formation energy	Evf

 Table II
 Quantities used in the determination of the parameter sets for Zr

Element (Phase)	Zr (hcp)	Zr (bcc / fcc)
Lattice constant(s)	$a_{\rm hcp}, c/a_{\rm hcp}$	$a_{\rm bcc}/a_{\rm hcp}$
Elastic constants	<i>B</i> , <i>C</i> ₄₄ ,	Β,Δ,
	$(C_{11} - C_{12})/2$	C_a, C_b, C_c
Cohesive energy	$E_{\rm sub}^{\rm ncp}$	$E_{\rm sub}^{\rm bcc}(E_{\rm sub}^{\rm fcc})$
Vacancy formation energy	\vec{E}_{vf}	
Stacking fault energy	$E_{ m sf}$	_
Surface energy	$E_{\text{surf1}}, E_{\text{surf2}}$	
Points at which	K(L), M(L),	$\Gamma(L), \Gamma(U),$
phonon dispersion	A(L), A(U)	N(L),N(U),
frequency is fit		H(U), P(U)

was proposed by Baskes and Johnson in 1994 [7]. The other three sets are proposed in the present study.

Table III The parameter sets of MEAM potentials for Cu and Zr

Param. set	Ref. lat.	β_0	β_1	β_2	β3	<i>t</i> ₁	<i>t</i> ₂	<i>t</i> ₃	A _{sub}
Cu1	fcc	3.634	2.20	6	2.20	3.14	2.49	2.95	1.07
Zrl	hcp	2.10	-0.0	1.74	7.0	6.1	6.1	-2.0	1.15
Zr2	hcp	2.40	0.0	2.30	1.0	9.0	2.0	-4.0	1.13
Zr3	hcp	2.40	3.0	2.30	2.0	2.0	2.0	-4.0	1.13
Zr4	hcp	2.85	2.24	0.41	1.56	10.57	5.39	-8.01	1.119

Secondly, two known lattice structure types, C11 and B2, are used as reference structures for parameter sets. These are evaluated against the parameter sets previously established for the properties shown in Tables I and II. The better parameter sets for Cu and Zr are used for further evaluation. The stability of the crystal structure depends on temperature and reference is made to a phase diagram of the CuZr binary system described by Kneller [8]. At elevated temperatures above 985 K, the simplest structure of CuZr, a B2 structure, is stable. At low temperature, $Cu_{10}Zr_7$ and $CuZr_2$, which has a C11 structure, appear by a eutectoid reaction. They are the neighbor equilibrium phases. In this work, the B2 structure for CuZr, or the C11 structure for $CuZr_2$, is used as a reference. The stability of the crystal structure, the lattice constants and formation enthalpy are considered.

3. RESULTS AND DISCUSSION

3.1 Single elements Cu, Zr

The phonon dispersion curves were calculated using the parameter set 'Cu1'. The properties of the phonon frequency in the low frequency region, where phonon dispersion is closely related to elastic properties, agree with experiment.

The phonon dispersion curves for hcp Zr were calculated using the original parameter sets 'Zr1'. There are some unstable regions and the discrepancy from experiment is large.

Table IV shows the lattice constants structures and sublimation energy of the hcp, fcc and bcc phases. They are presented for the parameter sets 'Zr2', 'Zr3' and 'Zr4'. MEAM succeeded in representing the difference in energy between the hcp and fcc phases. The difference obtained using 'Zr2' and 'Zr3' is smaller than that from using 'Zr4'.

Table IV Lattice constants and sublimation energy of Zr

Property		Γ		
	Zr2	Zr3	Zr4	Ref.[10]
	(hcp)			
Lattice constant a [Å]	3.219	3.222	3.246	3.237
Lattice constant c [Å]	5.164	5.153	5.077	5.153
E_{sub} [eV]	6.361	6.362	6.367	6.36
	(fcc)			
Lattice constant a Å	4.528	4.530	4.533	1
E_{sub} [eV]	6.327	6.327	6.294	
	(bcc)			
Lattice constant a [Å]	3.512	3.514	3.481	
E _{sub} [eV]	6.284	6.281	6.289	
$E_{sub}(hcp) - E_{sub}(fcc) [eV]$	0.034	0.035	0.073	

The phonon dispersion curves for hcp/bcc Zr are shown in Fig. 1. For the hcp phase, the results using both 'Zr3' and 'Zr4' agree with experiment. For the bcc phase Zr, the negative frequency region near the point N for the T_1 mode appears for both 'Zr3' and 'Zr4'. This tendency is reported in other previous works [9], in which it is mentioned that instability is closely related with the bcc-hcp phase transition at low temperature. From a comprehensive viewpoint, 'Zr4' may be effective and become another choice. More detailed evaluations are necessary to determine which parameter set is best.



3.2 CuZr binary alloy

The fitting procedures for the binary system are as follows. The parameter sets 'Cu1' and 'Zr4' are adopted for each single component system and for two reference structures. In this study, one is the CuZr (B2 structure) system and the other is the $CuZr_2$ (C11 structure) system. The parameters in the screening function are the original sets proposed by Baskes [4] and a modified set developed in the present study. Therefore, four parameter sets 'A1', 'A2', 'A3' and 'A4' are studied, which are combinations of the two screening functions and the two reference structures.

Structure and energy: Table V shows the structure and energy of CuZr alloys. The distance between layers of the C11 structure is spacings c_1 and c_2 , are closely related to the atomic size neighboring each other. Because the C11 structure is more complex than B2 structure and it includes not only Cu-Zr but Zr-Zr neighboring pair. 'A2' and 'A4' which represent the lattice constants of stable C11 structure have an advantage to apply to amorphous structure which also closely related to the nearest neighbor distance.

Table V Structure and energy of Cu-Zr alloy system (Cu1, Zr4)

Sets	Al	A2	A3	A4	Experi-	
Reference	CuZr	CuZr	CuZr ₂	CuZr ₂	ment	
lattice	(B2)	(B2)	(C11)	(C11)		
Angular - screening factors	homo. *1)	inhomo. *2)	homo. *1)	inhomo. *2)		
CuZr						
Lattice	3.26	3.32	2.97	3.09	3.26	
$E_{sub}[eV]$	5.20	5.84	5.28	5.62	5.20	
CuZr ₂						
Lattice constant a [Å]	3.07	3.60	2.89	3.23	3.22	
Lattice constant c [Å]	12.37	9.13	11.94	10.03	11.18	
E_{sub} [eV]	5.93	6.22	5.77	5.86	5.60	
Spacing c_1^{*3} [Å]	1.90	1.39	1.71	1.47	1.7	
ratio c_2/c_1^{*3}	1.24	1.18	1.46	1.40	1.35	
*1) $C_{max}(i i k) = 2.8$, $C_{min}(i i k) = 2.0$ (for $i i k = Cu, Zr$)						

*1) C_{max}(1, i, i) = 2.6, C_{min}(1, i, i) = 2.6 (for i, j, i) = 2.6, C_{min}(2r, i, Zr) = 0.8 (for i = Cu, Zr) The other components are the same as in the homogeneous case.

*3) The distances between layers in CuZr₂ (C11).

 c_1 : spacing between neighboring Cu and Zr layers c_2 : spacing between neighboring Zr and Zr layers

Potential energy of the uniformly deformed lattice: Figure 2 shows a change in the potential energy under uniform expansion and contraction of the lattice constants in the vicinity of the stationary point for CuZr. While there is not stable point but a saddle point for 'A1' and 'A3', stable points appear in 'A2' and 'A4' cases. According to the above discussion, if the screening function is chosen suitably, it is possible to represent alloy structures accurately. The change in potential energy under uniform expansion and contraction of the lattice constants near the stationary point for C11 structure of CuZr₂ is considered. The stable points appear in the 'A2' and 'A4' cases.

However 'A2' has a negative value for the vacancy formation energy. Therefore, 'A4' is more adequate for the purpose than the others.

4. MOLECULAR DYNAMICS SIMULATION OF HEATING-COOLING PROCESS

According to the above study on the structure of binary alloy crystals, the interatomic potential using parameter sets of 'Cu1'-'Zr4' with 'A4'-condition is the most preferable for the simulation of amorphous phase.

Molecular dynamics simulations of heating-cooling process of Cu-Zr alloy are conducted using the interatomic











Fig.2 Potential energy of deformed lattice CuZr (B2) structure

potential.

We examine three models with different initial structures: (i) CuZr, (ii) CuZr₂, (iii) expanded CuZr. Models (i) and (ii) are initially set with stress free at zero temperature, i.e. the lattice constants are a = 3.09Åfor model (i) and a = 3.23Å, c = 10.03Å for model (ii) (see Table V. On the other hand, model (iii) isotropically expanded until a = 3.26Å which corresponds to the experiment.

First, initial temperature is set 300K. Then temperature increment, 100K is given for every 1 ps. When temperature reach to 1500K, then, the temperature increment is inverted to -100K. Finally, we obtain the structure obtained through heating-cooling process.

Temperature is controlled every time increment by using the velocity scaling method. The simulation is carried out under constant volume condition. The relationship between potential energy and time for each model is shown in Fig.3. Figure 4 shows snap shot of the atomic configuration at initial step and final step.



Fig.3 Potential energy change in heating-cooling process



Fig.4 Atomic configuration of initial and final stages

Any melting phenomenon is not observed in the model (i) which corresponds to CuZr and change of potential energy is symmetry between heating process and cooling process. On the other hand, the potential energy suddenly goes down around 6ps in the model (iii) which corresponds to extended CuZr. We obtain an amorphous-like structure at final stage. In the model (ii) which corresponds to $CuZr_2$, there is no discontinuity in the change of potential energy. We also obtain, however, an amorphouslike structure at final stage. In this model, the absolute value of slope of potential energy change under cooling with respect to time that is proportional to the temperature is larger than that under heating. Then final value of potential energy is smaller than initial value. This implies the $CuZr_2$ structure is metastable at 300K at least and it is impossible to obtain the $CuZr_2$ crystal structure by cooling process from the liquid state.

The final value of potential energy is also smaller than initial value in model (iii). However, the final value in model (iii) is larger than that in model (i). The result suggest a possibility of the existence of metastable amorphous phase in which the potential energy is larger than that of the crystal phase. Simulations under pressurecontrolled condition are needed for an verification of it in future.

5. CONCLUSIONS

The determination of parameters in the modified embedded atom method, for the purpose of developing interatomic potentials for the simulation of CuZr amorphous alloys has been described.

MEAM, which assumes only first-neighbor interactions, has an advantage in studying systems far from a reference structure, such as amorphous alloys.

It is found that we can obtain some metastable amorphous structures using molecular dynamics simulations of heating-cooling process of Cu-Zr alloy system in which the interatomic interaction is described by the MEAM framework.

At this present stage, the search of the parameter space has not necessarily been sufficient, and an optimal parameter set was not found. However, it is concluded that many physical properties, especially phonon dispersion properties of various structures, can be represented in the MEAM framework.

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REFERENCES

[1] S. Kobayashi, K. Maeda and S. Takeuchi, *J.Phys. Soc.*, *Jpn.*, **48**, 1147-1152 (1980).

[2] C. Gaukel, M. Kluge and H. R. Schober, J. Non-Cryst. Sol., 250-252, 664-668 (1999).

[3] C. Oligschleger, C. Gaukel and H. R. Schober, J. Non-Cryst. Sol., **250**-252, 660-663 (1999).

[4] M. I. Baskes, Phys. Rev., B, 46, 2727-2742 (1992).

[5] C. Massobrio and V. Pontikis and G. Martin, *Phys. Rev., B*, **40**-15, 10486 - 10497 (1990).

[6] K. Nakatani *et al.*, Proc. of Int. Conf. on Computational Engineering & Sciences, (2002), CD-ROM,

[7] M. I. Baskes and R. A. Johnson, Model. Simul. Mater. Sci. Eng., 2, 147-163 (1994).

[8] E. Kneller, Y. Khan and U. Gorres, Zeitschrift für Metallkunde, 77, 43-48 (1986).

[9] U. Pinsook and G. J. Ackland, *Physical Review B*, **59** 13642-13649, (1999)

[10] C. J. Smithells, "Metals Reference Book fifth edition", Butterworths London and Boston (1976) p.117.

[11] U. Pinsook and G. J. Ackland, *Phys. Rev.B*, **59**-21, 13642-13649, (1999).

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