

Local structural evolution of Fe₅₄C₁₈Cr₁₆Mo₁₂ bulk metallic glass during tensile deformation and a temperature elevation process: A molecular dynamics study

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The Fe, C, Cr, and Mo parameters of 2NN MEAM potentials listed in Table S1 [1] were used for modeling the interaction between pure elements, and these parameters are modified from those of original MEAM [1] by Greg Wagner for LAMMPS MEAM library. The potential form and the parameters of 2NN MEAM can be seen in Lee *et al.* study [2-7] and we decide not to repeat the introduction here. By using these parameters, the predicted lattice constants, binding energies, elastic constants of Fe, C, Cr, and Mo materials as listed in Table S2 are very close to the corresponding experimental values.[8-10] For the cross-element interactions, the force-matching method (FMM) [11] was used to determine the 2nn MEAM parameters for Fe-C, Fe-

Cr, Fe-Mo, Cr-C, Cr-Mo and Mo-C pairs. FMM is based on the variable optimization process of an objective function, which is constructed by the summation of squares of differences between the atomic forces obtained by a potential function and the corresponding atomic forces by *ab initio* or density functional theory (DFT) calculations. The original FMM minimizes the following objective function, $Z(\alpha)$ [12]:

$$Z(\alpha) = \left(3 \sum_{k=1}^M N_k \right)^{-1} \sum_{k=1}^M \sum_{i=1}^{N_k} \left(F_{ki}(\alpha) - F_{ki}^0 \right)^2$$

Where α , M and N_k are the entire set of potential parameters, the number of atomic configurations, and the number of atoms in a configuration k . $F_{ki}(\alpha)$ is the force acting on atom i of the configuration k , which is computed from the potential parameters α . F_{ki}^0 is the corresponding referenced force calculated from the *ab initio* or density functional theory (DFT) calculation approach. Except for atomic forces of all optimized structures, the binding energy, the compression and tension potential energy surfaces of crystal reference structures were also included in our object function.

Six crystal configurations for binary-element systems (Fe_3C_1 , Fe_1Cr_1 , Fe_1Mo_1 , Cr_1C_1 , Cr_1Mo_1 , Mo_1C_1) and one hypothetical four-element unit cell ($\text{Fe}_3\text{Cr}_1\text{Mo}_2\text{C}_2$) were used to provide the reference energies and structures of the potential surfaces by DFT calculation. The unit cells of these configurations can be seen in Fig. 1.

The Dmol3 package [13] was used for the DFT calculation, and the generalized gradient approximation (GGA) with the parameterization of Perdew-Wang generalized-gradient approximation (PW91) [14] was used. Three different functionals (PW91, PBE, and RPBE) were respectively examined, and it was found that the discrepancies (binding energy, lattice constants, bulk and shear moduli)

between the calculation results from PW91 and the corresponding experimental data are relatively lower for Fe, Cr, Mo, and C elements at the same time, which is the main reason for using PW91 in this study. For the DFT settings, all electron calculation with a double numeric plus polarization basis set DNP [15] was used for the spin unrestricted calculation. The energy tolerance in the self-consistent field calculations was 2.72×10^{-5} eV, and the energy, force and atomic displacement tolerances for the ionic step were 2.72×10^{-4} eV, 5.44×10^{-2} eV/Å and 5.00×10^{-3} Å.

For Fe, Cr, Mo and C crystal structures, Table S3 lists the lattice constants as well as the binding energies by Dmol3 optimization calculations and the corresponding experimental data [8] (also in Table. S3). It can be seen that the lattice constants and binding energies obtained by Dmol3 are very close to the experimental values. Besides the lattice constants and the binding energies, Table S4 illustrates the DFT predicted values of lattice constants, elastic constants, bulk moduli and shear moduli of Fe, Cr, Mo and C unit cells, and the corresponding experimental data are also shown in this table [9, 10]. All calculation results about the mechanical properties are in good agreement with the experimental values. Consequently, the current Dmol3 settings can be regarded accurate enough to get the FMM reference data of Fe-Cr-Mo-C system for cross-element 2NN MEAM parameter fitting. The respective DFT optimized unit cell shown in Fig.1 was scaled from 0.9 to 1.1 times for constructing 20 configurations to get the potential energy surface profile. A total of 140 configurations with their corresponding energies were used for FMM.

The idea of basin-hopping (BH) method [16] was used to randomly change the values of MEAM cross-element parameters As follows, target function is applied to estimate the error between the DFT results and those from 2NN MEAM. By repeating the BH search, the best MEAM cross-element parameter set which contains the minimal target function value was obtained. Figures.2 (a)-(g) show the potential

energy surfaces obtained by the 2NN MEAM potentials with the fitted cross-element parameters and those from DFT calculations. It can be seen that the potential energy surfaces from 2NN MEAM are almost identical with the DFT calculations, indicating the 2NN MEAM potential with the fitted parameters can be used to predict the material properties of a Fe-Cr-Mo-C system.

Table S1. The parameters of MEAM potential for Fe, Cr, Mo, C

	Fe	C	Cr	Mo
E_c	4.29	7.37	4.1	6.81
r_e	2.85	3.567	2.885	3.15
B	1.73	4.42	1.6	2.3
A	0.585	1.49	0.94	0.99
$\beta^{(0)}$	3.8	4.26	3.224	4.481
$\beta^{(1)}$	2.0	5.0	1.0	1.0
$\beta^{(2)}$	0.9	3.2	1.0005	1.0006
$\beta^{(3)}$	0.0	3.98	1.0	1.0
$t^{(1)}$	-0.8	7.5	-0.2075	3.4773
$t^{(2)}$	12.3	1.04	12.26	9.486
$t^{(3)}$	2.0	-1.01	-1.9	-2.9
C_{max}	2.8	2.8	2.8	2.8
C_{min}	2.0	2.0	2.0	2.0

Table S2. The experimental and LAMMPS calculation values of binding energies, lattice constants, elastic constants (C_{11} , C_{12} , C_{44}), for Fe, Cr, Mo and C unit cells.

<i>Element</i>	<i>Property</i>	<i>EXP[8-10]</i>	<i>LAMMPS</i>	<i>Error(%)</i>
<i>Fe (BCC)</i>	<i>Binding energy</i>	-4.290	-4.289	-0.023
	<i>Lattice constants</i>	2.866	2.866	0
	<i>C11</i>	226	230.42	1.96
	<i>C12</i>	140	135.25	-3.39
	<i>C44</i>	116	117.23	1.06
<i>Cr (BCC)</i>	<i>Binding energy</i>	-4.100	-4.099	-0.024
	<i>Lattice constants</i>	2.885	2.885	0
	<i>C11</i>	350	346.29	-1.06
	<i>C12</i>	67	66.056	-1.41
	<i>C44</i>	100	100.07	0.07
<i>Mo (BCC)</i>	<i>Binding energy</i>	-6.810	-6.809	-0.015
	<i>Lattice constants</i>	3.147	3.147	0
	<i>C11</i>	463.7	459.62	-0.88
	<i>C12</i>	157.8	168.22	6.60
	<i>C44</i>	109.2	111.15	1.79
<i>C (DIA)</i>	<i>Binding energy</i>	-7.370	-7.369	-0.014
	<i>Lattice constants</i>	3.567	3.567	0
	<i>C11</i>	1080	999.68	-7.4
	<i>C12</i>	127	135.67	6.8
	<i>C44</i>	557	557.64	0.1

Table S3. Comparisons between experimental and Dmol3 DFT calculation results for bcc Fe, bcc Cr, bcc Mo and diamond structure C. The values of a and E are the lattice constant, and the binding energy, respectively.

<i>Element</i>	<i>Function</i>	<i>a (Å)</i>	<i>E (eV/atom)</i>
<i>Fe (BCC)</i>	<i>EXP.[8]</i>	2.866	-4.28
	<i>DFT</i>	2.853	-4.414
	<i>Error (%)</i>	-0.454	-3.14
<i>Cr (BCC)</i>	<i>Exp.[8]</i>	2.885	-4.1
	<i>DFT</i>	2.855	-3.959
	<i>Error (%)</i>	-1.04	-3.42
<i>Mo (BCC)</i>	<i>Exp.[8]</i>	3.147	-6.82
	<i>DFT</i>	3.177	-6.91
	<i>Error (%)</i>	0.953	-1.39
<i>C (DIA)</i>	<i>Exp.[8]</i>	3.567	-7.37
	<i>DFT</i>	3.571	-7.82
	<i>Error (%)</i>	0.112	-6.15

Table S4. The experimental and DFT calculation values (by Dmol3) of lattice constant, elastic constants (C_{11} , C_{12} , C_{44}), bulk modulus (B) and shear modulus (S) for Fe, Cr, Mo and C unit cells.

<i>Element</i>	<i>Property</i>	<i>Exp[9,10](GPa)</i>	<i>DFT(GPa)</i>	<i>Error(%)</i>
Fe (BCC)	C_{11}	226	237	4.87
	C_{12}	140	119	15
	C_{44}	116	107.36	-7.45
	<i>Bulk module</i>	170	190.55	12.09
	<i>Shear module</i>	82	87.95	7.26
Cr (BCC)	C_{11}	350	375.26	7.22
	C_{12}	67	72.63	8.4
	C_{44}	100	94.58	-5.42
	<i>Bulk module</i>	160	173.5	8.44
	<i>Shear module</i>	115	117.24	1.95
Mo (BCC)	C_{11}	463.7	407.45	-12.13
	C_{12}	157.8	172.47	9.3
	C_{44}	109.2	100.56	-7.91
	<i>Bulk module</i>	230	250.8	9.04
	<i>Shear module</i>	126	107.33	-14.81
C (DIA)	C_{11}	1080	1089.42	0.87
	C_{12}	127	137.72	8.44
	C_{44}	557	560.51	0.63
	<i>Bulk module</i>	442	480.43	8.69
	<i>Shear module</i>	478	516.18	7.99

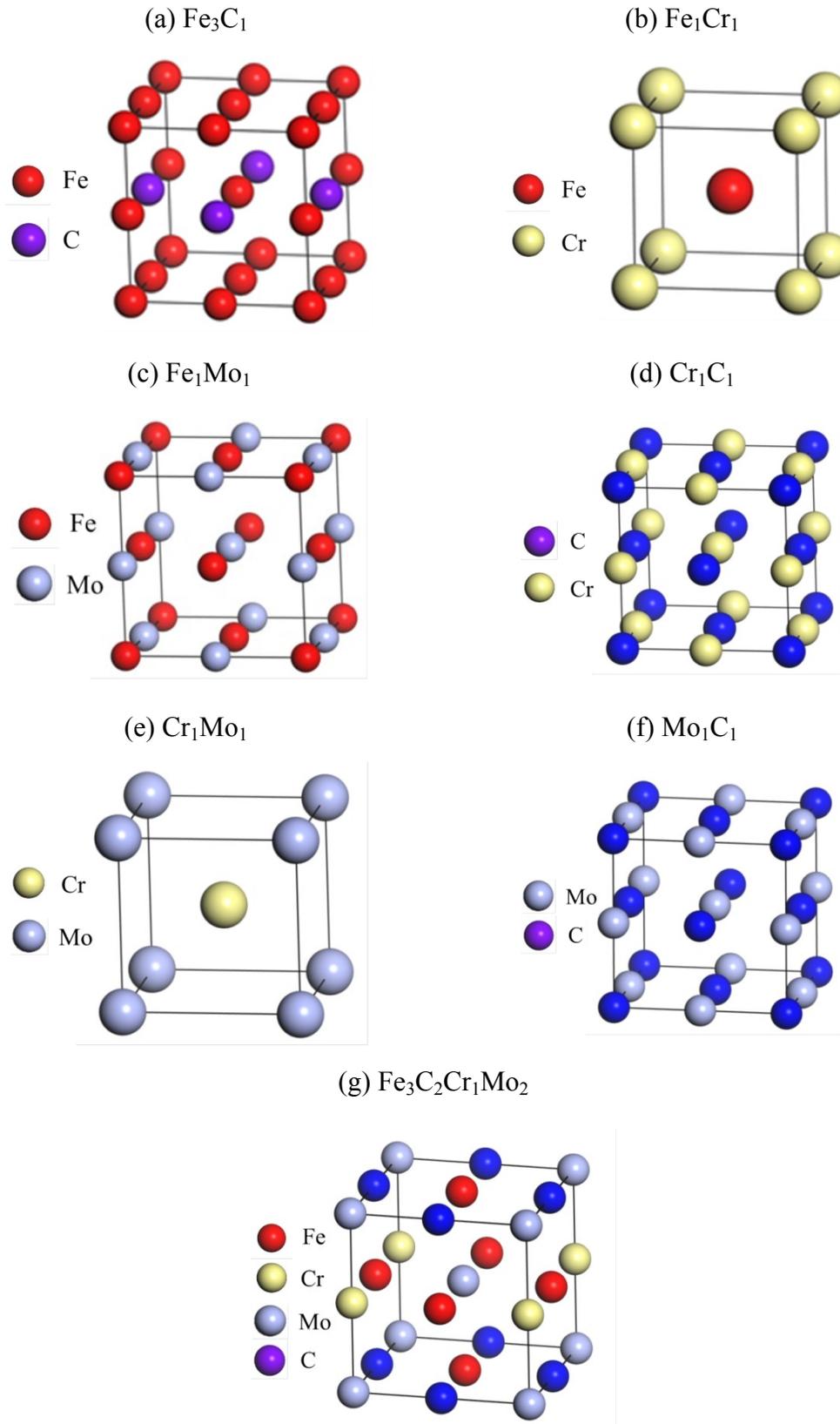
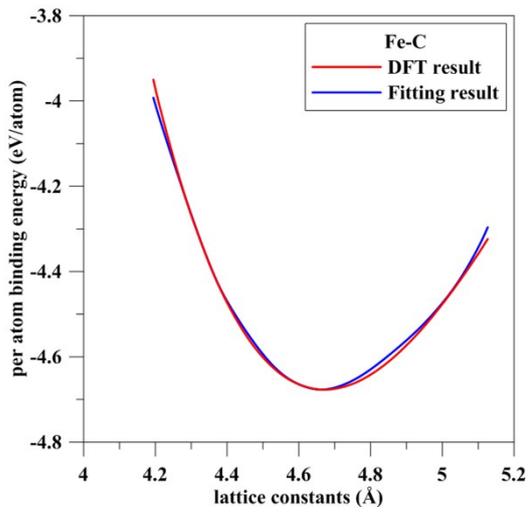
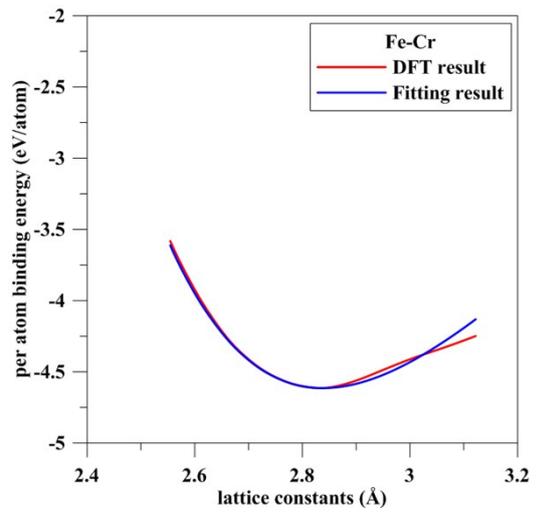


Fig 1. The unit cell of binary-element and hypothetical four-element

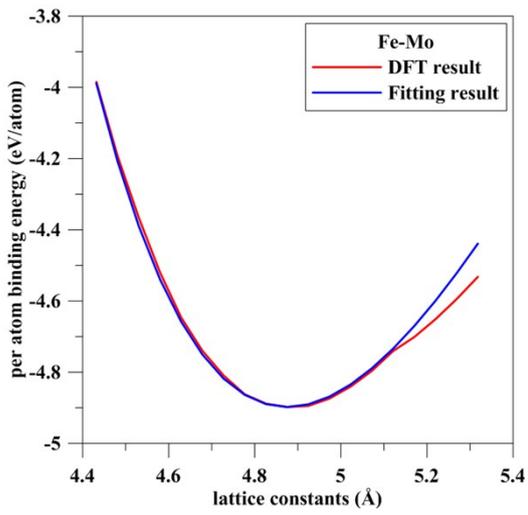
(a)



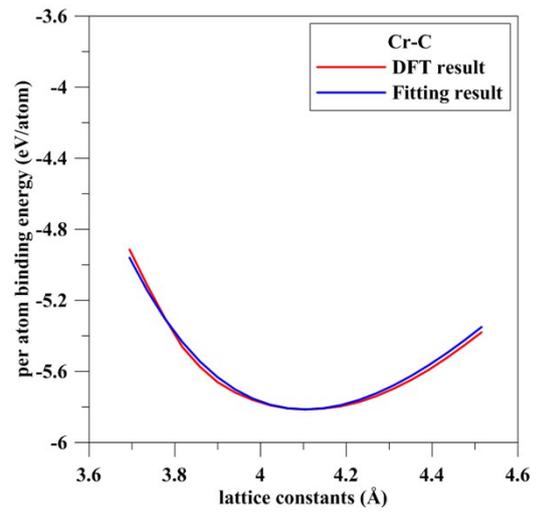
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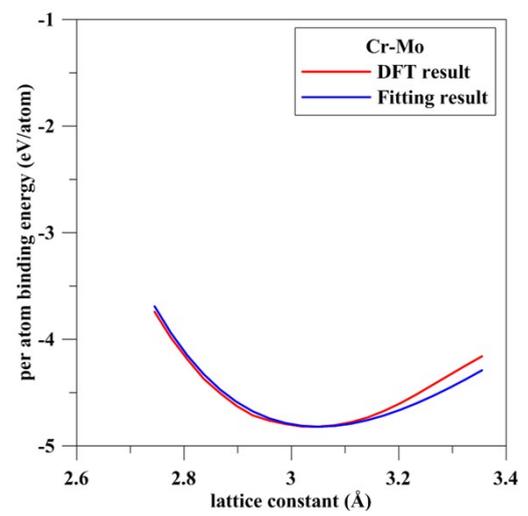
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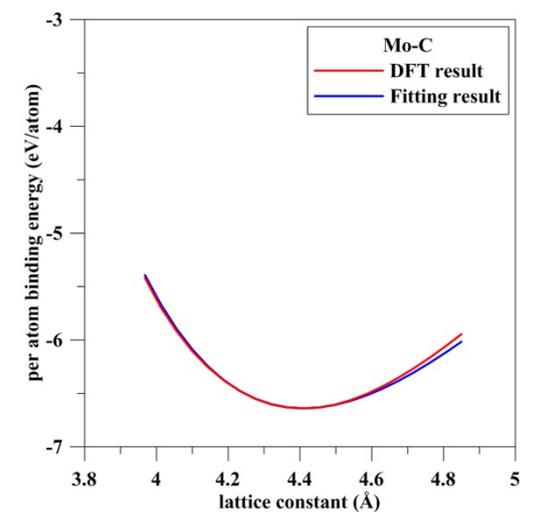
(d)



(e)



(f)



(g)

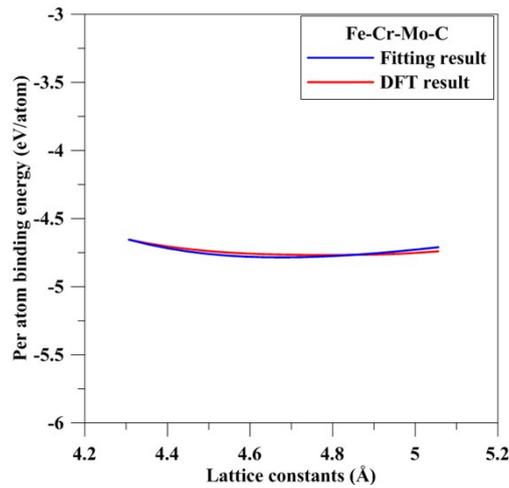


Fig. 2 The curve of per atom binding energy versus lattice constants of cross-element and all element system.(a) Fe-C,(b) Fe-Cr,(c) Fe-Mo,(d) Cr-C,(e) Cr-Mo,(f) Mo-C,and (g) Fe-Cr-Mo-C.

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