Hydrogen solution in high-entropy alloys

X. L. Ren[1,4], P. H. Shi[1], B. D. Yao[2], L. Wu[3], X.Y. Wu[3], Y. X. Wang[1]*

1. Key Laboratory of Nuclear Physics and Ion-beam Application (MOE), Institute of Modern Physics, Department of Nuclear Science and Technology, Fudan University, Shanghai, 200433, China

2. Shandong Peninisula Engineering Research Center of Comprehensive Brine Unitilzation, Weifang University of Science and Technology, Shouguang 262700, Shandong, China

3. The First Sub-Institute, Nuclear Power Institute of China, Chengdu, 610005, China

4. College of Material and Metallurgy, Guizhou University, Guiyang 550025, China

S1. The structure of HEAs

The disordered structures for the examined alloys were created using SQS code by optimization of pair correlation functions up to third neighbor shell. The details of the SQS cells are list in Table S1.

Table S1. The unrelaxed SQS lattices for the examined alloys

FeCrCoNi				NbMoTaW				FeCuCrMnMo			
108-atom FCC				128-atom BCC				90-atom BCC			
Lattice vectors				Lattice vectors				Lattice vectors			
10.72	0	0		12.9	0	0		14.6	0	0	
0	10.72	0		0	12.9	0		0	8.76	0	
0	0	10.72		0	0	12.9		0	0	8.76	
Atomic position				Atomic position				Atomic position			
0	0	0	Ni	0	0	0	Nb	0	0	0	Cu
0.83333	0.83333	0	Ni	0	0	0.75	Nb	0.1	0.16667	0.83333	Cu
0	0.83333	0.5	Ni	0.875	0.875	0.625	Nb	0	0.33333	0.66667	Cu
0	0	0.33333	Ni	0.875	0.875	0.375	Nb	0.1	0.16667	0.16667	Cu
0	0.83333	0.16667	Ni	0.875	0.875	0.125	Nb	0.4	0	0	Cu
0.83333	0.66667	0.83333	Ni	0	0.75	0.25	Nb	0.4	0.66667	0	Cu
0	0.66667	0.33333	Ni	0	0.5	0.25	Nb	0.5	0.5	0.5	Cu
0	0.5	0.16667	Ni	0.875	0.125	0.875	Nb	0.4	0.66667	0.33333	Cu
0.83333	0.33333	0.5	Ni	0.625	0.875	0.625	Nb	0.5	0.16667	0.83333	Cu
0.66667	0	0	Ni	0.75	0	0.25	Nb	0.5	0.16667	0.16667	Cu

* Corresponding authors. E-mail: yxwang@fudan.edu.cn

0.66667	0	0.33333	Ni	0.75	0.75	0.75	Nb	0.6	0	0.33333	Cu
0.5	0	0.16667	Ni	0.75	0.5	0	Nb	0.7	0.5	0.16667	Cu
0.5	0.5	0	Ni	0.75	0.5	0.5	Nb	0.6	0.33333	0	Cu
0.66667	0.66667	0.66667	Ni	0.625	0.375	0.375	Nb	0.9	0.83333	0.16667	Cu
0.5	0.66667	0.16667	Ni	0.75	0.5	0.25	Nb	0.8	0.66667	0	Cu
0.66667	0.33333	0	Ni	0.75	0.25	0	Nb	0.9	0.5	0.16667	Cu
0.5	0.33333	0.16667	Ni	0.625	0.125	0.875	Nb	0.8	0.33333	0.66667	Cu
0.66667	0.16667	0.16667	Ni	0.625	0.125	0.125	Nb	0.9	0.16667	0.16667	Cu
0.16667	0	0.83333	Ni	0.5	0	0	Nb	0.1	0.83333	0.83333	Cr
0.33333	0.83333	0.83333	Ni	0.5	0	0.25	Nb	0	0	0.33333	Cr
0.16667	0.5	0	Ni	0.375	0.875	0.125	Nb	0.2	0	0	Cr
0.16667	0.66667	0.83333	Ni	0.375	0.625	0.625	Nb	0.2	0.66667	0.66667	Cr
0.33333	0.5	0.5	Ni	0.5	0.5	0	Nb	0.3	0.5	0.5	Cr
0.16667	0.5	0.33333	Ni	0.375	0.375	0.875	Nb	0.2	0.66667	0.33333	Cr
0.33333	0.5	0.16667	Ni	0.5	0.5	0.75	Nb	0.2	0.33333	0.66667	Cr
0.33333	0.16667	0.83333	Ni	0.375	0.375	0.625	Nb	0.2	0.33333	0.33333	Cr
0.33333	0.33333	0.33333	Ni	0.5	0.5	0.25	Nb	0.4	0.33333	0.33333	Cr
0.83333	0	0.83333	Cr	0.375	0.125	0.875	Nb	0.6	0	0	Cr
0.83333	0.83333	0.66667	Cr	0.5	0.25	0.5	Nb	0.6	0.66667	0	Cr
0.83333	0	0.5	Cr	0.5	0.25	0.25	Nb	0.7	0.16667	0.83333	Cr
0.83333	0.83333	0.33333	Cr	0.125	0.625	0.875	Nb	0.7	0.16667	0.5	Cr
0	0.5	0.83333	Cr	0.125	0.375	0.375	Nb	0.8	0	0.33333	Cr
0.83333	0.5	0.66667	Cr	0.875	0.875	0.875	Mo	0.9	0.5	0.83333	Cr
0	0.5	0.5	Cr	0	0	0.25	Mo	0.8	0.66667	0.66667	Cr
0.83333	0.5	0.33333	Cr	0	0.75	0	Mo	0.9	0.16667	0.5	Cr
0	0.33333	0	Cr	0	0.75	0.5	Mo	0.8	0.33333	0.33333	Cr
0.83333	0.16667	0.33333	Cr	0.875	0.375	0.625	Mo	0	0	0.66667	Fe
0.66667	0	0.66667	Cr	0	0.25	0	Mo	0.1	0.83333	0.5	Fe
0.5	0.83333	0.66667	Cr	0	0.25	0.5	Mo	0.1	0.5	0.83333	Fe
0.66667	0.83333	0.5	Cr	0.875	0.125	0.375	Mo	0	0.66667	0.33333	Fe
0.66667	0.83333	0.16667	Cr	0	0.25	0.25	Mo	0.1	0.5	0.16667	Fe
0.5	0.66667	0.83333	Cr	0.75	0	0	Mo	0	0.33333	0	Fe
0.66667	0.5	0.83333	Cr	0.75	0.75	0	Mo	0.1	0.16667	0.5	Fe
0.5	0.5	0.66667	Cr	0.625	0.625	0.875	Mo	0.3	0.83333	0.83333	Fe
0.66667	0.33333	0.66667	Cr	0.75	0.75	0.5	Mo	0.2	0	0.66667	Fe
0.5	0.16667	0.66667	Cr	0.625	0.625	0.375	Mo	0.2	0.66667	0	Fe
0.16667	0.83333	0	Cr	0.625	0.375	0.875	Mo	0.3	0.16667	0.5	Fe
0.16667	0.83333	0.33333	Cr	0.75	0.5	0.75	Mo	0.3	0.16667	0.16667	Fe
0.33333	0.5	0.83333	Cr	0.625	0.375	0.125	Mo	0.5	0.83333	0.83333	Fe
0.16667	0.66667	0.5	Cr	0.375	0.875	0.625	Mo	0.5	0.83333	0.5	Fe
0.16667	0.66667	0.16667	Cr	0.375	0.625	0.875	Mo	0.6	0.66667	0.33333	Fe
0.33333	0.33333	0	Cr	0.5	0.75	0.75	Mo	0.6	0.33333	0.33333	Fe
0.16667	0.33333	0.83333	Cr	0.5	0.75	0.5	Mo	0.7	0.16667	0.16667	Fe
0.33333	0.16667	0.5	Cr	0.5	0.5	0.5	Mo	0.8	0.66667	0.33333	Fe
0	0.83333	0.83333	Fe	0.375	0.125	0.125	Mo	0.1	0.83333	0.16667	Mo
0	0	0.66667	Fe	0.25	0	0	Mo	0	0.66667	0.66667	Mo
0	0.66667	0	Fe	0.25	0	0.5	Mo	0	0.33333	0.33333	Mo
0.83333	0.5	0	Fe	0.125	0.625	0.625	Mo	0.3	0.83333	0.16667	Mo
0.83333	0.66667	0.16667	Fe	0.25	0.5	0	Mo	0.3	0.5	0.83333	Mo
0	0.33333	0.66667	Fe	0.25	0.5	0.75	Mo	0.3	0.5	0.16667	Mo
0.83333	0.16667	0.66667	Fe	0.25	0.5	0.25	Mo	0.2	0.33333	0	Mo
0	0.33333	0.33333	Fe	0.25	0.25	0	Mo	0.4	0	0.66667	Mo
0	0.16667	0.16667	Fe	0.125	0.125	0.875	Mo	0.5	0.5	0.83333	Mo
0.5	0.83333	0	Fe	0.125	0.125	0.375	Mo	0.4	0.33333	0	Mo

0.66667	0.83333	0.83333	Fe
0.5	0.83333	0.33333	Fe
0.66667	0.66667	0	Fe
0.66667	0.5	0.5	Fe
0.66667	0.33333	0.33333	Fe
0.33333	0	0.66667	Fe
0.16667	0	0.5	Fe
0.33333	0.83333	0.5	Fe
0.16667	0	0.16667	Fe
0.33333	0.66667	0	Fe
0.33333	0.66667	0.66667	Fe
0.16667	0.5	0.66667	Fe
0.33333	0.66667	0.33333	Fe
0.16667	0.16667	0	Fe
0.16667	0.16667	0.66667	Fe
0.16667	0.16667	0.33333	Fe
0.16667	0.33333	0.16667	Fe
0.83333	0	0.16667	Co
0	0.66667	0.66667	Co
0.83333	0.66667	0.5	Co
0.83333	0.16667	0	Co
0.83333	0.33333	0.83333	Co
0	0.16667	0.83333	Co
0	0.16667	0.5	Co
0.83333	0.33333	0.16667	Co
0.5	0	0.83333	Co
0.5	0	0.5	Co
0.5	0.66667	0.5	Co
0.66667	0.66667	0.33333	Co
0.5	0.5	0.33333	Co
0.66667	0.5	0.16667	Co
0.5	0.16667	0	Co
0.5	0.33333	0.83333	Co
0.66667	0.16667	0.83333	Co
0.5	0.33333	0.5	Co
0.66667	0.16667	0.5	Co
0.5	0.16667	0.33333	Co
0.33333	0	0	Co
0.16667	0.83333	0.66667	Co
0.33333	0	0.33333	Co
0.33333	0.83333	0.16667	Co
0.33333	0.33333	0.66667	Co
0.16667	0.33333	0.5	Co
0.33333	0.16667	0.16667	Co

0	0	0.5	Ta
0	0.75	0.75	Ta
0.875	0.625	0.625	Ta
0.875	0.625	0.375	Ta
0.875	0.375	0.875	Ta
0	0.5	0.5	Ta
0.875	0.125	0.125	Ta
0.75	0	0.75	Ta
0.75	0	0.5	Ta
0.625	0.875	0.375	Ta
0.625	0.875	0.125	Ta
0.625	0.625	0.625	Ta
0.625	0.125	0.625	Ta
0.75	0.25	0.5	Ta
0.625	0.125	0.375	Ta
0.75	0.25	0.25	Ta
0.375	0.875	0.875	Ta
0.5	0	0.75	Ta
0.5	0	0.5	Ta
0.375	0.875	0.375	Ta
0.375	0.625	0.125	Ta
0.5	0.25	0.75	Ta
0.375	0.125	0.625	Ta
0.125	0.875	0.375	Ta
0.25	0	0.25	Ta
0.25	0.75	0	Ta
0.125	0.625	0.125	Ta
0.125	0.375	0.875	Ta
0.125	0.375	0.625	Ta
0.25	0.5	0.5	Ta
0.25	0.25	0.5	Ta
0.125	0.125	0.125	Ta
0.875	0.625	0.875	W
0.875	0.625	0.125	W
0	0.5	0	W
0	0.5	0.75	W
0.875	0.375	0.375	W
0.875	0.375	0.125	W
0	0.25	0.75	W
0.875	0.125	0.625	W
0.625	0.875	0.875	W
0.75	0.75	0.25	W
0.625	0.625	0.125	W
0.625	0.375	0.625	W
0.75	0.25	0.75	W
0.5	0.75	0	W
0.375	0.625	0.375	W
0.5	0.75	0.25	W
0.375	0.375	0.375	W
0.375	0.375	0.125	W
0.5	0.25	0	W
0.375	0.125	0.375	W
0.125	0.875	0.875	W
0.25	0	0.75	W

0.5	0.16667	0.5	Mo
0.7	0.83333	0.5	Mo
0.7	0.5	0.83333	Mo
0.7	0.5	0.5	Mo
0.6	0.33333	0.66667	Mo
0.9	0.83333	0.5	Mo
0.9	0.5	0.5	Mo
0.8	0.33333	0	Mo
0	0.66667	0	Mn
0.1	0.5	0.5	Mn
0.3	0.83333	0.5	Mn
0.2	0	0.33333	Mn
0.3	0.16667	0.83333	Mn
0.4	0	0.33333	Mn
0.5	0.83333	0.16667	Mn
0.4	0.66667	0.66667	Mn
0.5	0.5	0.16667	Mn
0.4	0.33333	0.66667	Mn
0.7	0.83333	0.83333	Mn
0.6	0	0.66667	Mn
0.7	0.83333	0.16667	Mn
0.6	0.66667	0.66667	Mn
0.8	0	0	Mn
0.9	0.83333	0.83333	Mn
0.8	0	0.66667	Mn
0.9	0.16667	0.83333	Mn

0.125	0.875	0.625	W
0.125	0.875	0.125	W
0.25	0.75	0.75	W
0.25	0.75	0.5	W
0.125	0.625	0.375	W
0.25	0.75	0.25	W
0.125	0.375	0.125	W
0.25	0.25	0.75	W
0.125	0.125	0.625	W
0.25	0.25	0.25	W

Table S2. Pair correction functions $\Pi_{2,n}$ (n up to the 3th nearest neighbor) for the random structures of the three HEAs.

Structure	$\Pi_{2,1}$	$\Pi_{2,2}$	$\Pi_{2,3}$
108-atom FCC (FeCrCoNi)	1/648	0	1/32
128-atom BCC (NbMoTaW)	0	5/101	1/50
90-atom BCC (FeCuCrMnMo)	1/26	25/818	1/165

Table S3. Order parameter for each atomic pair in the examined alloys.

FeCrCoNi		NbMoTaW		FeCuCrMnMo	
Pair	Order	Pair	Order	Pair	Order
FeFe	0.0123	NbNb	0.0	FeFe	-0.0417
FeCr	0.0	NbMo	0.0	FeCu	0.0278
FeCo	0.0	NbTa	0.0	FeCr	0.0278
FeNi	-0.0123	NbW	0.0	FeMn	-0.0069
CrCr	0.0123	MoMo	0.0	FeMo	-0.0069
CrCo	0.0	MoTa	0.0	CuCu	-0.0417
CrNi	-0.0123	MoW	0.0	CuCr	-0.0069
CoCo	-0.0123	TaTa	0.0	CuMn	0.0278
CoNi	0.0123	TaW	0.0	CuMo	-0.0069
NiNi	0.0123	WW	0.0	CrCr	0.0278
				CrMn	-0.0069

	CrMo	-0.0417
	MnMn	-0.0417
	MnMo	0.0278
	MoMo	0.0278

In our calculations, we paid more attention to the distribution of the first nearest neighbor atoms of the H-embedding interstitial polyhedron. Thus, the disordered distribution of the first neighbor shell is more critical. A Warren-Cowley order parameter was used to estimate the chemical ordering of atomic pairs in alloys, $\alpha_{ij}^{n} = 1 - p_{ij}^{n} / x_j$, where p_{ij}^{n} is the probability of finding an atom of *j* type around an atom of *i* type in the *n*-th neighboring shell (here, we chose n = 1) and x_j is the atomic proportion of type *j*. $\alpha_{ij} = 0$ corresponds a random state of *i-j* atom pair. $\alpha_{ij} > 0$ or $\alpha < 0$ corresponds the poor or rich of *i-j* atom pair, respectively. The order parameters of the atomic pairs in the three HEAs are listed in Table S3 with all of values less than 0.05, which indicates the good performance of random state of these SQS cells.

S2. Solution energies (SEs) for H in pure metals

Table S4. Solution energies (eV) for H in pure metals. The solution energies for H in Ni were computed in its spin-polarized form [37]. Other metals were calculated in the nonmagnetic structures. Ni and γ-Fe [38] are FCC structures. Cr [34], Nb[36], Mo [34], Ta [36], W [35], and α-Fe [30] are computed in BCC structures.

Metals	Ni	γ-Fe	Cr	Nb	Mo	Ta	W	α-Fe
TIs	0.32	0.49	0.79	-0.39	0.78	-0.41	0.88	0.20
OIs	0.07	0.04	0.92	-0.10	1.03	-0.08	1.26	0.33

S3. Correlation between SE and the coordination environment of H atom

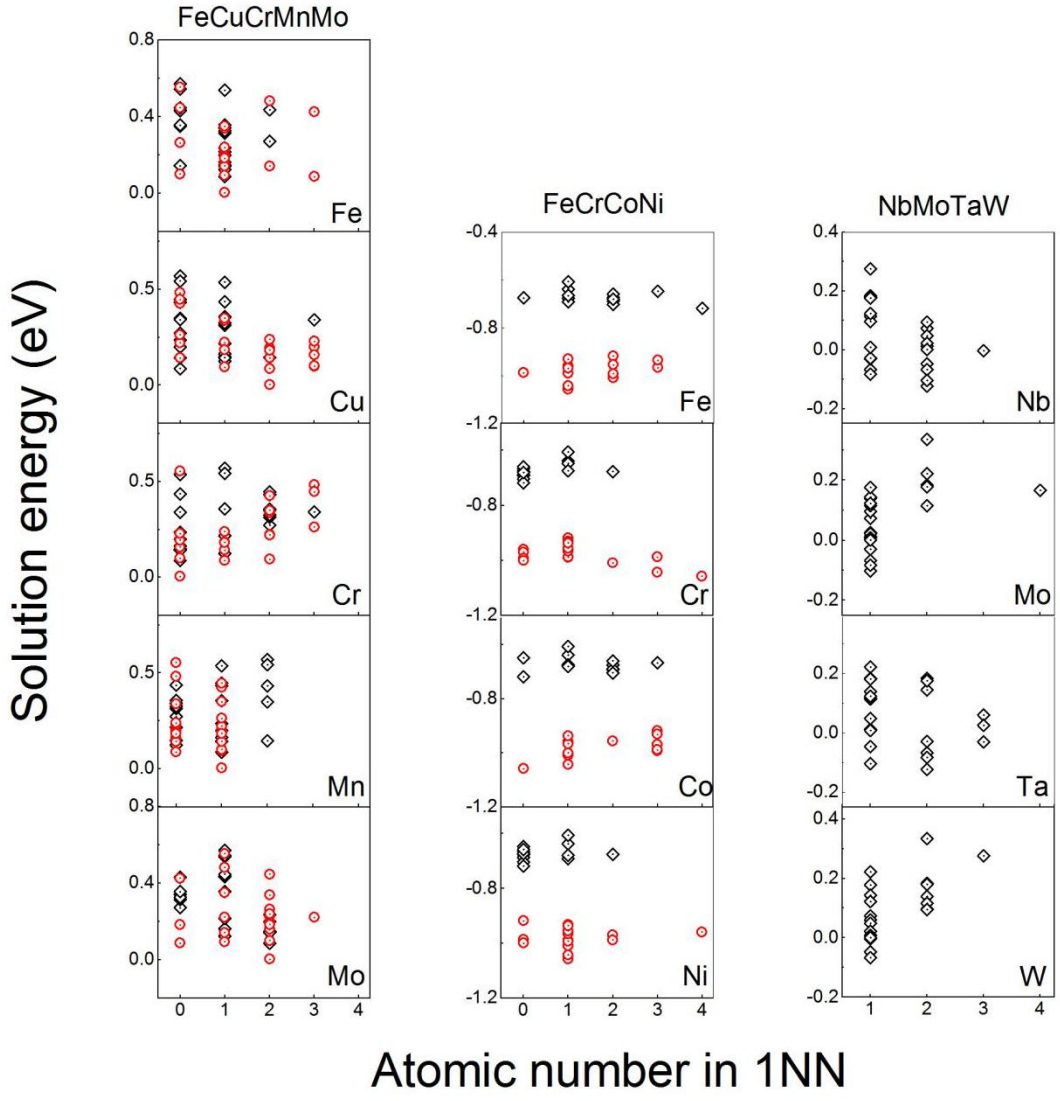

Fig. S1. Dependence of solute energies on the atomic types in the first nearest neighbor shell (1NN). The number of different metal atoms in the first nearest neighbor shell for each solute H atom was counted. From Fig. S1, little correlation has been found out. For instance, in FeCuCrMnMo, the variation of solute energy with the coordinated Cr atoms is non-obvious. The maximum (minimum) value of solute energy coordinated by one Cr atom is larger (smaller) than those values coordinated by multi-atom Cr. Similar phenomenon occurs in previous studies, which is attributed to the inherent chemical complexity in the HEAs. For this reason, we focused on another factors, such as the volume of interstitial polyhedron, to elaborate the mechanism of effect on the solute energy.