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Empirical design of single phase high-entropy alloys with high hardness

Fuyang Tian [a, b, *], Lajos K. Varga [c], Nanxian Chen [b, d], Jiang Shen [b], Levente Vitos [a, c, e]

[a] Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm SE-100 44, Sweden
[b] Institute for Applied Physics, University of Science and Technology Beijing, Beijing 100083, China
[c] Wigner Research Centre for Physics, Institute for Solid State Physics and Optics, P.O. Box 49, H-1525 Budapest, Hungary
[d] Department of Physics, Tsinghua University, Beijing 100084, China
[e] Department of Physics and Astronomy, Division of Materials Theory, Uppsala University, Box 516, SE-751210 Uppsala, Sweden

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ABSTRACT

We collect the available basic properties of nearly 100 high-entropy alloys (HEAs) with a single face centered cubic (fcc) or body centered cubic (bcc) phase. HEAs crystallizing in the fcc structure are mainly composed of the late 3*d* elements (LTM-HEAs), whereas HEAs consisting of the early (refractory) transition elements and the LTM-HEAs containing an increased level of bcc stabilizer form the bcc structure. Guided by the solid solution theory, we investigate the structure and hardness of HEAs as a function of the valence electron concentration (VEC) and the atomic size difference (δ). The fcc structure is found for VEC between 7.80 and 9.50, whereas the structure is bcc for VEC between 4.33 and 7.55. High strength is obtained for an average valence electron number VEC ~ 6.80 and for an average atomic size difference $\delta \approx 6\%$. Based on these empirical correlations, one can design the high-entropy alloys with desired hardness.

1. Introduction

High-entropy alloys (HEAs) proposed by Yeh *et al.* are multi-component solid solutions consisting of more than four equimolar or near equimolar elements [1]. The large number of weakly interactive components stabilizes a single-phase solid solution structure via the mixing entropy (ΔS_{mix}) [1]. Due to the unique microstructures and special performances, different types of HEAs have been reported since 2004 [1–39].

In this promising new class of engineering materials, the stabilization of the simple solid-solution phase is very significant for the appropriate microstructure and properties. There were many attempts trying to reveal the rules of single phase formation. The sluggish diffusion of atoms derived from the high ΔS_{mix} is responsible for the stability of the simple solid solutions rather than a mixture of ordered intermetallic compounds [40–42]. Zhang *et al.* summarized the microstructure characteristics in terms of their atomic-size difference (δ) and mixing enthalpy (ΔH_{mix}), to predict the solid-solution formation in the reported HEAs [10]. The combinations of δ and ΔH_{mix} were used to capture the phase selection mechanism for solid solution or amorphous phase [43]. The reason of a single solid solution has being discussed since the solid-solution phase formation rules for multi-component alloys were reported [10]. Others predicted the formation rule of HEAs based on the solid solution theory [44–46]. Guo *et al.* divided the multicomponent alloys into amorphous phase, solid solution, intermetallic compound, and discussed the relations between structure and valence electron concentration (VEC), ΔH_{mix}, ΔS_{mix}, and δ as well as the electronegativity difference [44,45]. Formation of solid solution was found for $-22 \leq \Delta H_{mix} \leq 7$ kJ/mol, $0 \leq \delta \leq 8.5\%$, and $11 \leq \Delta S_{mix} \leq 19.5$ J/(K mol). Furthermore Yang and Zhang [46] discussed the formation ability of HEAs as a function of $T_m\Delta S_{mix}/|\Delta H_{mix}|$ and δ and predicted the values $T_m\Delta S_{mix}/|\Delta H_{mix}| \geq 1.1$ (herein T_m is the mole averaged melting point) and $\delta \leq 6.6\%$ for the solid solution formation.

Besides the formations ability of HEAs, little attention has been paid for the structural properties dependence on the simple parameters like VEC and δ. In this paper, we collect these simple parameters, the corresponding structures and hardness in order to find empirical correlations between them which are useful in designing high-entropy alloys with optimal properties. The established correlations will also serve as reference for future theoretical studies based on *ab initio* quantum mechanics.

The structure of the paper is as follows. In Section 2, we review the physical parameters used in the theoretical analysis. The

* Corresponding author. Royal Institute of Technology Applied Materials Physics, Department of Materials Science and Engineering 100 44 Stockholm Sweden.
E-mail addresses: fuytian@gmail.com, fuyang@kth.se (F. Tian).

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Table 1
List of HEAs crystallizing in fcc or bcc structure (str.); w is the Wigner-Seitz radius (in bohr) converted from experimental lattice parameters via $4\frac{4}{3}\pi w^3 = a^3$ for fcc structure and $2\frac{4}{3}\pi w^3 = a^3$ for bcc structure, a is the cubic lattice parameter; w_{mix} is the average Wigner-Seitz radius (in bohr); VEC stands for the average valence electron concentration (in e/a); δ is the atomic size difference (%), δ_1 is calculated based on the data from Ref. [49], δ_2 is calculated from Ref. [50]; the mixing enthalpy ΔH_{mix} (in kJ/mol); the mixing entropy ΔS_{mix} (in J/K mol); Vickers hardness Hv (in HV). The corresponding sources are listed in the last column.

HEAs	Str.	w	w_{mix}	VEC	δ_1	δ_2	ΔH_{mix}	ΔS_{mix}	Hv	Ref.
CuNiCoFeCr	fcc	2.643	2.647	8.80	1.07	1.07	3.20	13.38	133	[1–3]
$CuNiCoFeCrAl_{0.3}$	fcc	2.646	2.666	8.47	3.42	3.15	1.56	14.43	185	[1,2]
$CuNiCoFeCrAl_{0.5}$	fcc	2.647	2.667	8.27	4.17	3.82	−1.52	14.70	208/212	[1,2,4]
$CuNiCoFeCrAl_{2.8}$	bcc	2.700	2.770	6.72	6.57	5.99	−10.28	14.01	655	[1,2]
$CuNiCoFeCrAl_{3.0}$	bcc	2.696	2.776	6.63	6.61	6.09	−10.56	13.86	635	[1,2]
$CuNiCoFeCrTi_{0.5}$	fcc	2.667	2.670	8.36	4.82	4.46	−3.70	14.70	–	[3,5]
$CuNiCoFeCrAl_{0.5}$ $V_{0.2}$	fcc	–	2.683	8.16	4.15	3.87	−2.50	15.54	202	[6]
CuNiFeCr	fcc	2.651	2.656	8.75	1.15	0.96	4.75	11.53	–	[7]
CuNiFeCrMo	fcc	–	2.710	8.20	3.58	4.10	4.64	13.38	263	[8]
CuNiCoFe	fcc	2.648	2.638	9.50	1.14	1.03	5.00	11.53	–	[9]
CuNiCoFeV	fcc	–	2.673	8.60	2.20	2.88	−1.78	13.38	–	[10]

HEAs	Phase	w	w_{mix}	VEC	δ_1	δ_2	ΔH_{mix}	ΔS_{mix}	Hv	Ref.
CuNiCoFeTi	fcc	–	2.721	8.40	6.50	6.13	−11.04	13.38	–	[11]
CuNiCoFeMn	fcc	–	–	9.00	3.18	0.92	−1.76	13.38	–	[12]
$CuNi_2$ $FeMn_2$ Cr	fcc	2.667	–	8.43	3.57	0.99	0.44	12.89	–	[13]
$CuNi_2$ $FeCrAl_{0.2}$	fcc	–	2.658	8.77	2.94	2.69	0.12	12.01	160	[14]
$CuNi_2$ $FeCrAl_{0.4}$	fcc	–	2.670	8.56	3.84	3.48	−1.70	12.45	172	[14]
$CuNi_2$ $FeCrAl_{0.5}$	fcc	–	2.676	8.45	4.20	3.82	−2.51	12.60	200	[14]
$CuNi_2$ $FeCrAl_{0.7}$	fcc	–	2.687	8.26	4.74	4.30	−3.96	12.81	240	[14]
$CuNi_2$ $FeCrAl_{1.6}$	bcc	–	2.729	7.55	6.02	5.46	−8.41	13.00	557	[14]
$CuNi_2$ $FeCrAl_{1.8}$	bcc	–	2.736	7.41	6.17	5.60	−9.07	12.95	550	[14]
$CuNi_2$ $FeCrAl_{2.0}$	bcc	–	2.744	7.29	6.30	5.71	−9.63	12.89	570	[14]
$CuNi_2$ $FeCrAl_{2.2}$	bcc	–	2.751	7.17	6.40	5.80	−10.12	12.81	580	[14]
$CuNi_2$ $FeCrAl_{2.5}$	bcc	–	2.760	7.00	6.52	5.91	−10.74	12.68	600	[14]
$Cu_{0.75}$ $NiCoFeCrTi_{0.5}$ $Al_{0.25}$	fcc	2.676	2.699	8.00	5.40	5.03	−7.28	15.55	–	[5]
$Cu_{0.75}$ $NiCoFeCrAl_{0.25}$	fcc	2.653	2.663	8.40	3.43	3.00	−0.71	14.32	–	[15]
$Cu_{0.5}$ $NiCoFeAl_{0.5}$ Cr	fcc	2.661	2.679	8.00	4.37	4.00	−4.60	14.54	–	[15,16]
$Cu_{0.5}$ $NiCoFeAl_{0.5}$ Cr_3	bcc	–	2.681	7.43	3.77	3.38	−2.99	13.09	–	[16]
$Cu_{0.5}$ $NiCoCrAl_{0.5}$ Fe_2	fcc	–	2.677	8.00	4.08	3.67	−2.55	13.94	–	[16]
$Cu_{0.5}$ $NiCoCrAl_{0.5}$ Fe_3	fcc	–	2.676	8.00	3.84	3.41	−2.06	13.09	–	[16]
$Cu_{0.5}$ $NiCoCrAl_{0.5}$ $Fe_{3.5}$	fcc	–	2.675	8.00	3.74	3.30	−1.87	12.66	–	[16]
$Cu_{0.5}$ NiCoFeCr	fcc	2.648	2.645	8.56	0.84	1.06	0.49	13.15	174	[16–18]
$Cu_{0.5}$ $NiCoFeCrAl_{1.5}$	bcc	–	2.731	7.17	6.11	5.56	−10.14	14.53	–	[16]
$Cu_{0.5}$ $NiCoFeCrAl_{2.0}$	bcc	–	2.751	6.92	6.46	5.87	−11.60	14.23	–	[16]
$Cu_{0.5}$ $NiCoFeAlCr_{1.5}$	bcc	–	2.706	7.42	5.34	4.82	−6.22	14.53	–	[16]
$Cu_{0.5}$ $NiCoFeAlCr_{2.0}$	bcc	–	2.704	7.31	5.18	4.64	−5.68	14.23	–	[16]
$Cu_{0.5}$ NiFeCrAl	bcc	–	2.729	7.22	5.92	5.21	−12.94	13.15	–	[16]
$Cu_{0.5}$ $NiFeCrAlCo_{0.5}$	bcc	–	2.717	7.40	5.71	5.12	−7.92	14.54	–	[16]
$Cu_{0.5}$ $NiFeCrAlCo_{1.0}$	bcc	–	2.708	7.55	5.51	5.02	−7.93	14.70	458	[16,19]
$Cu_{0.5}$ $NiFeCrAlCo_{3.0}$	fcc	–	2.682	7.93	4.88	4.60	−7.25	13.48	–	[16]

HEAs	Phase	w	w_{mix}	VEC	δ_1	δ_2	ΔH_{mix}	ΔS_{mix}	Hv	Ref.
$Cu_{0.5}$ $NiFeCrAlCo_{3.5}$	fcc	–	2.678	8.00	4.75	4.51	−7.03	13.09	–	[16]
$Cu_{0.5}$ CoFeCrAl	bcc	–	2.731	7.00	5.86	5.21	−10.67	13.15	–	[16]
$Cu_{0.5}$ $CoFeCrAlNi_{0.5}$	bcc	–	2.718	7.30	5.68	5.12	−7.28	14.54	–	[16]
$Cu_{0.5}$ $CoFeCrAlNi_{3.0}$	fcc	–	2.679	8.20	4.93	4.60	−8.39	13.48	–	[16]
$Cu_{0.5}$ NiCoCrAl	bcc	2.683	2.717	6.09	2.81	5.44	−10.17	13.15	496	[20]
$Cu_{0.25}$ NiCoFeCrAl	bcc	–	2.709	7.38	5.65	5.13	−9.94	14.34	–	[10]
NiCoFe	fcc	–	2.627	9.00	0.33	0.75	−1.33	9.13	124	[11,21]
$NiCoFeCr_{0.5}$	fcc	2.638	2.635	8.57	0.31	0.95	−2.94	11.24	–	[22]
$NiCoFeCr_{0.6}$	fcc	2.639	2.637	8.50	0.31	0.97	−3.15	11.36	–	[22]
$NiCoFeCr_{0.7}$	fcc	2.639	2.638	8.43	0.31	0.99	−3.33	11.44	–	[22]
$NiCoFeCr_{0.8}$	fcc	2.640	2.639	8.37	0.30	1.00	−3.49	11.49	–	[22]
$NiCoFeCr_{0.9}$	fcc	2.641	2.640	8.31	0.30	1.02	−3.63	11.52	–	[22]
$NiCoFeCr_{0.95}$	fcc	2.641	2.641	8.28	0.30	1.02	−3.69	11.52	–	[22]
$NiCoFeCr_{1.05}$	fcc	2.642	2.642	8.22	0.30	1.03	−3.80	11.52	–	[22]
$NiCoFeCr_{1.10}$	fcc	2.642	2.643	8.20	0.30	1.04	−3.85	11.52	–	[22]
$NiCoFeCr_{1.15}$	fcc	2.642	2.643	8.17	0.30	1.04	−3.90	11.51	–	[22]
NiCoFeCr	fcc	3.642	2.642	8.25	0.30	1.03	−3.75	11.53	116	[22–24]
$NiCoFeCrMo_{0.3}$	fcc	2.659	2.661	8.09	2.38	2.92	−4.15	12.83	210	[25,26]
$NiCoFeCrMo_{0.1}$ $Al_{0.3}$	fcc	2.659	2.672	7.84	3.90	3.74	−7.26	13.44	–	[25]
$NiCoFeCrTi_{0.3}$	fcc	2.658	2.670	7.88	3.76	3.49	2.00	12.83	350	[27]
$NiCoFeCrTi_{0.1}$ $Al_{0.3}$	fcc	–	2.675	7.80	4.40	4.06	−8.93	13.44	–	[28]
$NiCoFeCrAl_{0.25}$	fcc	2.653	2.662	7.94	3.47	3.25	−6.75	12.71	110	[23]
$NiCoFeCrAl_{0.3}$	fcc	2.659	2.666	7.88	3.76	3.49	2.00	12.83	–	[25]
$NiCoFeCrAl_{0.375}$	fcc	2.656	2.671	7.80	4.08	3.80	−7.99	12.97	131	[23]
$NiCoFeCrAl_{1.25}$	bcc	2.673	2.725	7.00	5.95	5.55	−13.42	13.34	487	[23]
$NiCoFeCrAl_{1.5}$	bcc	2.684	2.737	6.82	6.16	5.77	−14.28	13.25	403/580	[23,29]
$NiCoFeCrAl_{2.0}$	bcc	2.686	2.758	6.50	6.41	6.04	−15.44	12.98	432/615	[23,29]