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Chemical short-range orders and the induced structural transition in high-entropy alloys

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ABSTRACT

The present work verifies the existence of chemical short-range orders (CSROs) in high-entropy alloys (HEAs) using a cluster-plus-glue-atom model. Two HEAs with a composition of Al_2M_{14} (M = $Ni_4Co_4Fe_3Cr_3$ or $Ni_1Co_1Fe_2Cr_1$) are designed, which is derived from the cluster model of $[Al-M_{12}](M_2Al_1)$ in face-centered-cubic structure or $[Al-M_{14}]Al_1$ in body-centered-cubic structure. It is found that the calculated pair-distribution functions (PDFs) at short inter-atomic distances by these cluster models can describe the neutron PDFs better than the ones by the average crystal structures. It is due to the different CSROs characterized by cluster units that induce the structural transition of HEAs.

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Despite containing multiple-principal elements in equimolar or near-equimolar proportions, high entropy alloys (HEAs) [1–5] generally possess simple crystal structures, such as face-centered cubic (FCC), body-centered-cubic (BCC), and their corresponding ordered derivatives of $L1_2$ (Cu_3Au-type) and B2 (CsCl-type) [6–10]. It is due to the formation of simple structures that HEAs are classified as a special kind of solid solutions, similar to the conventional alloys based on one or two atomic species. They could be formed in diverse alloy systems, typically in those containing Al and transition metals (TMs) [11–15]. Atomic species and their contents can produce different crystal structures, which result in the significant changes in mechanical properties [11–15].

For conventional solid-solution alloys, the most distinguished structural characteristic is the chemical short-range orders (CSROs), which plays an important role to the abnormal mechanical and physical properties of alloys [16–18]. Generally, the CSROs represent the local structural heterogeneities with respect to the average crystal structure, forming some certain preferential inter-atomic neighborhoods. CSROs in HEAs have also attracted much attention recently [19–24]. It is found that the local atomic structure of the BCC ZrNbHf HEA is indeed different from the average one due to the local lattice distortion caused by the atomic sizes, since the first two peaks of the neutron pair-

distribution function (PDF) showed significant deviations from the calculated PDF based on the average crystal structure [20]. The PDF can determine the real-space distribution of atoms in the lattice that is characterized by the inter-atomic distances. In an Al-containing $Al_{1.3}CoCrCuFeNi$ HEA, both neutron-scattering measurements and simulations have identified that Al tends to be nearest-neighbored with TMs, and the Al-TM bond lengths are also different [22–23]. It would certainly produce a relatively-severe lattice distortion in Al-TM HEAs due to the differences in both atomic sizes and interactions between Al and TMs [24]. Finally, the FCC structure would be destabilized with increasing the Al content [11–15,25]. Such a structural transition from FCC to BCC can relax the lattice-distortion energy, since the BCC structure has a lower atomic-packing density than the FCC.

Actually, it is not easy to characterize the CSROs due to the multi-component-induced chemical complexity. To address this key problem, we developed a new structural approach, the cluster-plus-glue-atom model, in which the cluster is the nearest-neighbor polyhedron centered by a solute atom having strong interaction with the base solvent atoms to represent the strongest CSRO, and some other solute atoms (i.e. glue atoms) with weak interactions are certainly required to fill the space between the clusters to balance atomic-packing density [26–27]. Thus, a universal composition formula of [cluster](glue)$_m$ (m being the glue atom number to match one cluster) could be obtained from this model. For the FCC and BCC solid solutions, the nearest-

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neighbor clusters are cuboctahedrons with a coordination number (CN) of 12 and rhombi-dodecahedron with CN14 (the 1st-shell CN8 + 2nd-shell CN6), respectively. This cluster-formula approach has been successfully applied into multi-component complex systems to design solid solution alloys with desired performance [28–29]. It was then used to explore the $Al_xNiCoFeCr$ HEA series [26], in which all the TMs were treated as an averaged virtual element, M, to serve as the base solvent, and Al was regarded as the solute since Al has similarly strong interactions with all TMs. Thus, this $Al_xNiCoFeCr$ series could be expressed with Al_xM_4, where $M = Ni_1Co_1Fe_1Cr_1$ is an equimolar mixing of TMs, similar to the conventional solid-solution alloys. It was found that the composition of Al_2M_{14} ($Al_{12.5}M_{87.5}$, atomic percent), given by both the cluster formulas of the $[Al-M_{12}](M_2Al_1)$ in FCC and the $[Al-M_{14}]Al_1$ in BCC, is close to the upper limit of a single FCC region from experiments, i.e., $Al_{0.5}M_4$ ($Al_{11.1}M_{88.9}$ at.%) [11]. Exceeding this limit, the BCC phase will appear from the FCC matrix. Further changing M from an equimolar mixing to a non-equimolar mixing can render the Al_2M_{14} ($M = Ni_1Co_1Fe_2Cr_1$) HEA with a BCC matrix, instead of a FCC [30]. Thereof, different combinations of TMs can also induce a structural transition, similar to the change of Al.

However, the cluster-plus-glue-atom model for the characterization of CSROs in solid solutions has not been experimentally proven. Therefore, the primary aim of the present work is to validate the CSRO cluster units in HEAs by the evidence that the calculated PDF by the cluster model can reproduce reliably the experimental PDF obtained by neutron scattering at a short inter-atomic distance covering the first two nearest peaks. Second, it will show that the structural transition of HEAs is indeed originated from different CSROs, i.e., different local cluster structural units.

Two HEAs with the same composition formula of Al_2M_{14} but different M were synthesized, in which the A1 alloy ($Al_{12.5}Ni_{25}Co_{25}Fe_{18.75}Cr_{18.75}$ at.%) is $M = Ni_4Co_4Fe_3Cr_3$ with a much more amount of Ni/Co than Fe/Cr to form a FCC phase, and the A2 alloy ($Al_{12.5}Ni_{17.5}Co_{17.5}Fe_{35}Cr_{17.5}$ at.%) is $M = Ni_1Co_1Fe_2Cr_1$ with a more amount of Fe to form a BCC phase. These two alloys were prepared by means of arc-melting and copper-mold suction casting into 3 mm or 6 mm cylindrical rods under an argon atmosphere, where the preparation details are same as that in Ref. [30]. The structural characterization of these as-cast alloys were carried out, using a Bruker D8 X-ray diffractometer (XRD). The microstructures of alloys were observed by the Zeiss Supra 55 scanning electron microscopy (SEM), and Philips Tecnai G^2 transmission electron microscopy (TEM). To understand the local CSRO structures of HEAs, the room-temperature neutron-scattering experiments (3-mm-diameter rods) were performed at the Spallation Neutron Source (SNS) [Oak Ridge National Laboratory (ORNL)] using Nanoscale-Ordered Materials Diffractometer (NOMAD) instrument optimized for studies of local structures [31–32].

As expected, the XRD results (Fig. S1, in supplementary file) show that the A1 alloy exhibits a dual-phase structure of a primary FCC phase plus a small amount of BCC phase, while the A2 possesses a primary BCC/B2 phase plus minor FCC. The lattice constants (a) of these phases were calculated from the XRD results (Table 1) and will be used as the input data for retrieving the neutron-scattering results using Rietveld refinements with the GSAS (General Structure Analysis System) software [33]. The morphology observations also verified the XRD results. The matrix of the A1 presents bright FCC dendrites, and the dark BCC phase is distributed in the inter-dendritic regions with a volume fraction of about 15% [Fig. S2(a)]. On the contrary, the matrix morphology of the A2 alloy exhibits coarse columnar BCC dendrites, and a small amount of FCC is in the inter-dendritic regions with a volume fraction of about 25% [Fig. S2(b)]. It is noted that in the BCC-related regions, the BCC phase is always coherent with its ordered B2 phase.

Neutron-scattering experiments were then carried out in order to understand the variations of CSROs in these two Al_2M_{14} HEAs with different crystal structures. The diffraction patterns were analyzed with the GSAS, in which the composition information of all elements was

Table 1
Parameters related to the crystal lattices of Al_2M_{14} HEAs, including the lattice constants of BCC (a_{BCC}), B2 (a_{B2}), and FCC (a_{FCC}) phases, the lengths of the super-cell for BCC and FCC structures (l_{BCC}, l_{FCC}), and the peak positions of BCC and FCC phases at short inter-atomic distances (P_{BCC}, P_{FCC}), which were output from the XRD, GSAS, PDFgui, and Gaussian fitting, respectively.

	A1 (M = $Ni_4Co_4Fe_3Cr_3$)			A2 (M = $Ni_1Co_1Fe_2Cr_1$)		
	a_{BCC} (Å)	a_{B2} (Å)	a_{FCC} (Å)	a_{BCC} (Å)	a_{B2} (Å)	a_{FCC} (Å)
XRD	2.874	–	3.593	2.862	2.851	3.587
GSAS	2.874	2.884	3.603	2.860	2.849	3.572

		A1 (M = $Ni_4Co_4Fe_3Cr_3$)		A2 (M = $Ni_1Co_1Fe_2Cr_1$)	
		l_{BCC} (Å)	l_{FCC} (Å)	l_{BCC} (Å)	l_{FCC} (Å)
PDFgui	Input[a]	8.662	7.206	8.580	7.144
	Output	8.553	7.176	8.610	7.212

	A1 (M = $Ni_4Co_4Fe_3Cr_3$)			A2 (M = $Ni_1Co_1Fe_2Cr_1$)		
	$P1_{BCC}$ (Å)	$P2_{BCC}$ (Å)	$P1_{FCC}$ (Å)	$P1_{BCC}$ (Å)	$P2_{BCC}$ (Å)	$P1_{FCC}$ (Å)
Gaussian fitting	2.469	2.852	2.533	2.481	2.864	2.557

[a] The input data of the lengths of the super-unit cell (l) were calculated from the lattice constants obtained from GSAS, in which $l_{BCC} = 3 \times a_{BCC}$ and $l_{FCC} = 2 \times a_{FCC}$.

input into the atomic sites of crystal structures. The average crystal structure obtained from the Rietveld refinements was the starting model for the PDF data. The results of Rietveld refinements are summarized in Fig. 1, in which the BCC and B2 phases could be detected precisely. The obtained lattice constants were listed in Table 1, which agrees well with the XRD results. Then the PDF analysis of the neutron-scattering data were carried out using the PDFgui software package [34]. As shown in Fig. 2(a, b), the measured PDFs of these two HEAs match well with the periodic atomic arrangement associated with their respective crystal structures exported from the GSAS results at long distances (A1: $R_w = 0.128$; A2: $R_w = 0.107$, in which R_w is a reliability factor obtained from PDFgui.). The minor difference between the average structural and experimental data at long distances in these two HEAs might result from the crystallographic orientation or texture as the alloy samples were prepared by suction casting. However, at a short distance covering the first two nearest neighbors (less than a lattice-constant distance), the peak shape and position are closely related to the local atomic structures [22–23,35], i.e., local CSROs, as shown in Fig. 2(c, d). Obviously, these first two peaks of the measured PDFs could not be fitted well with the average crystal structures due to the existence of CSROs.

To demonstrate the CSRO distribution of solute atoms in solid solutions, two kinds of cluster-packing modes given by the cluster-glue-atom model were introduced, as seen in Fig. 2(e, f). The model of the Al-centered CN12 cluster $[Al-M_{12}]$ plus three glue atoms of M_2Al_1 in the FCC lattice is used to understand the CSROs of the FCC-based A1 HEA [Fig. 2(e)]. The $[Al-M_{12}]$ cluster is taken from a local atomic configuration of the ordered $L1_2$-Ni_3Al phase of the disordered FCC structure, in line with that the short-range order of crystalline alloys could be described clearly with the Clapp atomic configurations in long-range ordered structures [36]. The other model, being associated with the Al-centered CN14 cluster $[Al-M_{14}]$ plus one glue atom Al_1 in the BCC lattice, is constructed for the BCC-based A2 HEA [Fig. 2(f)]. It is noted that the existing results of both experiments and simulations on the BCC $Al_{1.3}CoCrCuFeNi$ HEA [22] have shown that the lengths of Al-TM bonds around the Al atom are in the sequence of Al-Ni (2.448 Å) < Al-Co (2.461 Å) < Al-Cu (2.577 Å) < Al-Fe (2.577 Å) < Al-Cr (2.719 Å) < Al-Al (2.899 Å), indicating that there indeed exist obvious differences among Al-TM bonds due to the different interactions between Al-Ni/Co and Al-Fe/Cr/Al. Therefore, the atomic positions in the cluster models should be arranged according to the existing evidence for dissimilar bond lengths and non-random pair correlations.