Effect of Al on microstructure and mechanical properties of cast CrCoNi medium-entropy alloy

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Abstract: Cast CrCoNiAl_x ($x=0-1.2$) medium-entropy alloys (MEAs) were produced by arc melting and flip cast to investigate the alloying effect of Al addition on the microstructure, phase constituent and mechanical properties. The crystal structure changes from an initial face-centered cubic (FCC) to duplex FCC and body-centered cubic (BCC) and finally a single BCC with increasing Al content. In the duplex region, FCC and BCC phases form under a eutectic reaction in the interdendrite region. In the single BCC region, the dendrites transform to ordered B2 and disordered A2 BCC phases resulting from spinodal decomposition. Corresponding to their phase constituents, yield strength increases accompanied with an elongation reduction with increasing Al addition. A very interesting phenomenon of very weak ordered FCC (001) spots appearing in Al-0.4 alloy was observed, indicating a local ordering of FCC phase. The changes of fracture surfaces after the tensile deformation are also corresponding to the variations in mechanical properties.

Key words: medium-entropy alloy; microstructure; mechanical properties; Al addition

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In 2014, a new class of multi-component alloys with equal or nearly equal atomic elements for each component was put forward and termed as high-entropy alloys (HEAs) or multi-principal-element alloys [1,2]. In the following years, a great number of studies focused on these alloys, among which the typical CrMnFeCoNi HEA, proposed by Cantor et al. [1], was investigated systematically [3-23]. CrMnFeCoNi HEA with a single FCC phase exhibits exceptional damage tolerance with tensile strengths above 1 GPa and fracture toughness values exceeding 200 MPa·m^{1/2} [23]. Soon afterwards, researchers found that the ternary CrCoNi, referred to as a medium-entropy alloy (MEA), even possesses significantly superior mechanical properties to quinary CrMnFeCoNi HEA both at room temperature and 77 K [19, 24]. Along with its simpler composition, it has been considered as a promising alloy for cryogenic engineering.

Although the CrCoNi MEA has good cryogenic fracture toughness, its strength is still relatively low due to its single FCC crystal structure with which the metals generally exhibit good elongation but low yield strength. A number of studies showed that elemental additions (or alloying) into alloys, including these multi-principal-element alloys, could tailor their crystalline structures, microstructures and enhance the mechanical properties [7, 25-31]. For instance, He et al. [7] investigated the effect of Al on the structure and tensile properties of CrMnFeCoNi HEA and found that the crystalline structure changes from the single FCC structure to a duplex FCC and BCC structure and then a single BCC structure when the Al concentration increases. Wang et al. [27] studied the effect of Al addition on the microstructures and mechanical properties of CrFeCoNi alloy, and similar variations of phase constituents were observed, but with different critical Al concentrations which induce the phase transformation from single FCC to FCC and BCC and then single BCC. Stepanov et al. [32] added vanadium into a CrMnFeCoNi HEA and found that the phase constituents change from single FCC phase to FCC and sigma phase, where the sigma-phase volume fraction increases with the increasing vanadium

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content. Mechanical properties, as could be expected, are greatly affected by the sigma phase: the strength is increased whereas the ductility is meanwhile lost. Some criterions^[33], such as valence electron concentration (VEC), atomic size difference, enthalpy of mixing etc., were successfully used to predict the formation of solid solutions in multicomponent alloys. Although there are numerous reports about the alloying in CrMnFeCoNi HEAs, the systematic investigation of alloying effects on CrCoNi MEA is still lacking. Compared with the CrMnFeCoNi system HEAs, the CrCoNi MEA may exhibit differences to a certain extent in phase constituents and mechanical properties when alloying elements were added, which needs to be studied in detail.

In this study, Al was chosen as the alloying element to study its effect on the phase constituents and tensile properties of a CrCoNi MEA. The reason for selecting Al is that Al is a BCC stable element which can introduce BCC phase and enhance the strength of the CrCoNi MEA by tailoring the phase constituents. However, its exact effect on the CrCoNi MEA is still unclear, which, as can be expected, may be somewhat different from alloy to alloy.

A series of different Al contents was added into cast CrCoNi MEA in the current work. Thus, a systematic study was executed including the effect of Al on phase constituents, microstructures and mechanical properties at room temperature. Also, the mechanism of phase formation and evolution, dependence of mechanical properties on microstructures were discussed.

1 Experimental

Alloys with a nominal composition of CrCoNiAl x ($x=0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1$ and 1.2), corresponding to 0, 3.22, 6.25, 9.09, 11.76, 16.67, 21.05, 25, 28.57 at.%, respectively, were prepared by arc-melting a mixture of pure metals (purity >99.5wt.%) under a purity argon atmosphere inside a water-cooled copper crucible. The alloys were expressed as Al-0, Al-0.1, Al-0.2, Al-0.3, Al-0.4, Al-0.6, Al-0.8, Al-1 and Al-1.2 for short hereafter, respectively. After the raw materials were loaded in the arc melter, the chamber was first evacuated and then backfilled with pure Ar and evacuated twice to dilute the residual air inside the chamber, and finally backfilled under a pressure of $\sim 3 \times 10^4$ Pa. Before the materials were melted, a small piece of pure Ti was melted to absorb some residual oxygen or nitrogen that might be present in the chamber. To achieve a homogeneous distribution of elements in the alloys, each alloy was remelted five times and flipped over for each melt, and was kept in a liquid state for about 2 min during each melting process. Melted alloys were eventually flipped and poured into a graphite mold with a dimension of 17 mm $\times$ 8 mm $\times$ 70 mm.

Selected samples with a dimension of 8.5 mm $\times$ 8 mm $\times$ 5 mm were cut from the position (5 mm from bottom) using an electric discharge machine (EDM) for the analysis of microstructures and phase constituents. The cross sections of ingots were ground with SiC paper to a grit size of 7 μ m and polished with a diamond suspension down to 1 μ m. After mechanical polishing,

the microstructures and phase constituents of the alloys were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The XRD analysis was performed using a SHIMADZU XRD-7000S diffractometer using Cu K α radiation ($\lambda=1.5406$ Å) with the range of 20–90° at a speed of 5 °·min⁻¹. The observation of microstructures was conducted utilizing an FEI Quanta 200 microscope operated at the back-scatter electron (BSE) mode equipped with an energy-dispersive (EDS) detector at an accelerating voltage of 20 kV. Thin sheets with a thickness of ~ 400 μ m were carefully extracted from the ingots by a cutting machine and ground down to foils with a thickness of about 100–120 μ m using fine SiC papers. Discs with a diameter of 3 mm were punched out of the foils and electron transparent regions were produced in a twin jet polishing system at 40 V using a mixture consisting of 90vol.% glacial acetic acid and 10vol.% HClO₄ at room temperature. TEM and selected area electron diffraction (SAD) investigations were performed using JEM-2010FEF and 2100F microscopes operated at an accelerating voltage of 200 kV.

Tensile samples with a gauge length of 20 mm, a width of 4 mm and a thickness of ~ 1.1 mm, were cut from the as-cast ingots by EDM. Tensile tests were carried out on a Shimadzu AG-100KN machine with a strain rate of 1×10^{-3} s⁻¹ at room temperature. The fracture morphology of the tensile samples was probed by SEM operated in the secondary electron (SE) mode. Hardness measurements were conducted using a Vickers hardness tester (430SVD) operated at a 136-degree Vickers diamond pyramid with a load of 9.8 N for 15 s; and for each specimen, at least 10 indents were measured to obtain an average value.

2 Results

2.1 Phase constituents

Figure 1 shows the XRD patterns of the as-cast CrCoNiAl x ($x=0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1$ and 1.2) alloys. There is a crystal structure transition from FCC to BCC with the increase of Al content. Low-aluminum alloys (Al-0 to Al-0.2) form a single FCC crystal structure. However, in the Al-0.3 alloy, a minor reflection nearby (111) FCC starts to appear. Afterwards, the relative intensity of the (110) BCC diffraction peak shows up and increases with increasing Al content, and then FCC reflection peaks disappear in the Al-1 alloy. For high-aluminum alloys (Al-1 to Al-1.2), only the BCC diffraction peaks are identified, which indicates that either the FCC phase no longer exists or its amount is inferior to the determinable limit of XRD measurements, similar to that in CrMnFeCoNi high entropy alloy system^[7]. The (111) FCC peak firstly shifts to the lower 2θ angle as $x \leq 0.3$, but then switches towards the higher 2θ angle as $x \geq 0.4$. The shift of (110) BCC peak is more complicated in the current alloys as $x \geq 0.4$ due to the formation of duplex solid solutions. There are three weak peaks in all the alloys around 30°, which is caused by the rubber used for holding our samples. Taking into consideration that these peaks exist in all

Fig. 1: XRD patterns of as-cast CrCoNiAl $_x$ ($x=0-1.2$) alloys

samples with or without the Al addition, it can be understood that they are not caused by the Al addition. More importantly, they are not belonging to FCC or BCC phases according to the crystal diffraction theory. Note that a peak close to $\sim 31^\circ$ appears in high-aluminum alloys, which is pointed out by the inset enlarged image. This peak is corresponding to the ordered (100) BCC crystal plane, which means ordered BCC phase forms. The phase constituent and morphology will be identified further by TEM and SADs afterwards.

Lattice constants of the FCC and BCC as a function of the Al content in the as-cast CoCrNiAl $_x$ MEAs are depicted in Fig. 2, which were calculated based on the XRD data. Increasing the Al content, the lattice constant of FCC phase initially increases and then decreases, while the value of BCC phase gradually decreases with the exception of the Al-0.8 alloy increasing slightly.

2.2 Microstructure evolution

To further investigate the microstructure evolution of CrCoNiAl $_x$ MEAs, SEM BSE images are shown in Fig. 3. The phases with different morphologies or contrasts were selected to be conducted by the EDS analysis, whose results are listed in Table 1. For low-aluminum content MEAs (Al-0 to Al-0.2), the single equiaxed FCC grains (Figs. 3a-c) with the size ranging from tens to hundreds of microns are present. The measured compositions by EDS are reasonably close to the nominal ones of the as-cast alloys. Figures 3d-g display microstructural morphologies of Al-0.3 to Al-0.8 alloys containing duplex phases, respectively. In Fig. 3e (i.e. Al-0.4), long side-plates are

Fig. 2: Lattice constant of FCC and BCC phase as a function of Al content in as-cast CoCrNiAl $_x$ ($x=0-1.2$) alloys

found to be developed from boundaries and grow across the grains. As the Al content is further increased, the long side-plates also expand (Fig. 3f). The EDS results show that these phases along the grain boundaries or interdendrites are enriched in Al and Ni but depleted in Cr and Co; whereas these phases in the interior grains or dendrites are reverse. In Al-0.8, the equiaxed grains are gradually replaced by bright dendrites and the dark blocky phases are spreading in the interdendrite region (Fig. 3g). Along with the XRD data, we can conclude that these phases in the grain boundaries or interdendrites are BCC phases. Finally, the single equiaxed BCC phases are exhibited in Al-1 and Al-1.2 (Fig. 3h and 3i) alloys. Similarly, the dark blocky phases are enriched in Al and Ni. Although only one BCC phase was detected by XRD analysis in Al-1 and Al-1.2 alloys, two kinds of morphologies with different elemental distribution were observed from SEM BSE images. Whether they are the same phases could not be determined by SEM and XRD, which needs further clarification.

In order to clearly observe the morphologies of duplex phases at the grain boundaries, TEM image (Fig. 4a) of Al-0.4 MEA was observed. The microstructure is composed of a dark phase and a bright phase, which is similar to that of BSE image. The TEM EDS maps of the red frame in Fig. 4a are illustrated in Fig. 4c, which indicate that the dark phase is relatively enriched in Al and Ni, whereas the bright phase is enriched in Cr and Co, respectively. To accurately determine these phases with different compositions, SADs were conducted in the white and dark phases. Two patterns in two different zone axes for each phase are shown in Fig. 4b, respectively. The upper two patterns are belonging to the bright phases and the lower two patterns are the dark phases. The bright phase patterns were identified as FCC phase with the zone axes of [013] and [011]. But it is unexpected that very weak ordered (100) spots appear in the two FCC patterns, which means that ordered FCC phase forms in some parts. The SADs of the dark phase with the zone axes of [001] and $[\bar{1}11]$ were identified as ordered BCC phase since the ordered (001) spot appears in the former low index pattern.

Fig. 3: SEM BSE images of as-cast CrCoNiAl_x: (a) Al-0, (b) Al-0.1, (c) Al-0.2, (d) Al-0.3, (e) Al-0.4, (f) Al-0.6, (g) Al-0.8, (h) Al-1 and (i) Al-1.2

Table 1: Nominal composition of designed CrCoNiAl_x alloys and composition analysis of different regions in as-cast CrCoNiAl_x alloys by EDS (^a G: Grain, DR: dendrite, ID: interdendrite; B: bright phase, D: dark phase.)

Alloys	Region ^a	Chemical composition (at.%)			
		Al	Cr	Co	Ni
Al-0	Nominal	0	33.33	33.33	33.33
	G	0	32.10	33.72	34.18
Al-0.1	Nominal	3.22	32.26	32.26	32.26
	G	4.56	30.58	30.57	34.29
Al-0.2	Nominal	6.25	31.25	31.25	31.25
	G	7.02	30.53	29.66	32.79
Al-0.3	Nominal	9.09	30.3	30.3	30.3
	G	8.24	30.83	30.41	30.52
Al-0.4	Nominal	11.76	29.41	29.41	29.41
	DR	12.43	27.23	29.58	30.76
	ID	22.24	24.14	21.58	32.04
Al-0.6	Nominal	16.67	27.78	27.78	27.78
	DR	13.82	31.35	28.76	26.07
	ID	28.98	21.00	22.45	27.57
Al-0.8	Nominal	21.05	26.32	26.32	26.32
	B	18.28	31.64	26.01	24.08
	D	34.50	14.05	21.56	29.89
Al-1	Nominal	25	25	25	25
	B	16.12	37.01	26.15	20.72
	D	36.94	11.20	31.39	30.47
Al-1.2	Nominal	28.57	23.81	23.81	23.81
	B	19.91	34.94	24.78	20.37
	D	39.40	11.04	21.27	28.29

Fig. 4: TEM analysis of as-cast CrCoNiAl_{0.4} MEA: (a) TEM bright field image showing the dark phase and bright phase; (b) SAD patterns of dark and bright phases in different zone axes, which are corresponding to BCC and FCC phases, respectively; (c) TEM EDS maps of red rectangular box in (a) showing that Al and Ni are relatively enriched in dark phases, whereas Cr and Co are enriched in bright phases.

Figure 5(a) shows the TEM image of Al-1 MEA with single BCC phase indicated by XRD patterns. However, two different morphologies with different contrasts could be clearly seen, especially in the enlarged image in Fig. 5(b) which is corresponding to the blue frame in Fig. 5(a). The red frame in Fig. 5(b) was selected to conduct the TEM EDS mapping, whose results are shown in Fig. 5(c). The bright phase is also enriched in Al and Ni, and the dark phase is enriched in Cr and Co, which are consistent with the SEM results. The SADs with the zone axes of [001] and [011] were identified as the disordered BCC phase (A2), which are inserted in Fig. 5(a). Although two BCC phases (A2+B2) were indeed detected, we still term it as single phase here since they have the same crystal structure.

2.3 Mechanical properties

Room temperature tensile tests and hardness measurements were conducted to study the mechanical properties of the as-cast CoCrNiAl_x ($x=0, 0.2, 0.4, 0.6, 0.8, 1$ and 1.2) MEAs. Figure 6(a) shows engineering stress-strain curves of the

Fig. 5: TEM analysis of as-cast CrCoNiAl MEA: (a) TEM bright field image where the insets are SAD patterns of BCC phases in different zone axes; (b) high magnification of blue frame in (a); (c) TEM EDS maps of red rectangular box in (b), showing that Al and Ni are relatively enriched in dark phases, whereas Cr and Co are enriched in bright phases.

CoCrNiAl x MEAs. Yield strength, tensile strength and tensile elongation to failure as a function of Al content are depicted in Fig. 6(b). It should be pointed out that Al-0.8, Al-1 and Al-1.2 alloys are so brittle that they can endure slight deformation (not shown here). The hardness versus Al content is displayed in Fig. 6(c).

Both the tensile and yield strengths, as well as hardness, increase as Al content increases. However, tensile elongation decreases with the increase of Al content. Particularly, tensile and yield strengths, hardness of Al-0 alloy are 616 MPa, 269 MPa and 154.9 HV, respectively, but increase significantly to 1,109

MPa, 544 MPa and 371.74 HV in Al-0.6 alloy. In contrast, tensile elongation reduces obviously from 62% in Al-0 alloy to 14% in Al-0.6 alloy. In parallel, their Vickers hardness values also sharply increase with Al content increasing from Al-0.4 to Al-1 and approaching a value of 657.18 HV in Al-1 alloy. The hardness value of the alloys with more than 25at.% Al (i.e. Al-1) becomes saturated and keeps essentially the same [Fig. 6(c)]. Either the strength or hardness of the low-aluminum alloys (i.e., in single FCC region) with a single phase increases very slightly, indicating the greater strengthening effect of the second BCC phase rather than the solid solution by Al addition.

Fig.6: Mechanical properties of as-cast CrCoNiAl x MEAs at room temperature: (a) engineering stress-strain curves of CrCoNiAl x ($x=0, 0.2, 0.4, 0.6$) alloys; (b) effect of Al content on tensile strength, yield strength and elongation and (c) Vickers hardness variation as a function of Al content

2.4 Fractograph

To further confirm the underlying mechanism of the ductility variation in these alloys, their fracture surfaces after the tensile deformation were observed by SEM in SE mode, as shown in Fig. 7. The obvious morphologies of dimple fracture are found in Al-0, Al-0.2, Al-0.4 and Al-0.6 alloys, and the diameter and depth of the dimples display smaller with the increase of Al content. As the Al content is further increased, a typical brittle fracture and the obvious cleavage planes can be observed. Resulting from the changes of fracture surfaces, there are also corresponding variations in mechanical properties.

3 Discussion

Several physical parameters, derived from Hume-Rothery rules, have been proposed to predict the structural stability and phase formation in multicomponent alloys^[33, 34]. At first, most works

used these criteria in the high entropy alloys according to the initial definition, which are termed as the systems containing five to thirteen metallic elements, with a concentration in the range of 5at.% to 35at.% for each element^[35]. However, whether these criteria are applicable to the current CoCrNiAl x MEA or not is still not clear, thus these parameters will be assessed in the following manner. Among these parameters, both atomic radius difference (δ) and the mixing enthalpy (ΔH_{mix}) are found to act main roles in controlling the phase selection in multicomponent alloys^[33]. It was found that the solid solution tends to form in the region of $-15 \text{ kJ}\cdot\text{mol}^{-1} \leq \Delta H_{\text{AB}}^{\text{mix}} \leq 5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\delta \leq 6.6\%$. A mixture of ordered solid solution and random solid solution is favored in the regions of $-20 \text{ kJ}\cdot\text{mol}^{-1} < \Delta H_{\text{mix}} < 0 \text{ kJ}\cdot\text{mol}^{-1}$ and $5\% < \delta < 6.6\%$. To further consider the mixing entropy effect, an additional parameter Ω was also proposed^[36], which concluded that the criteria for forming simple solid solutions are $\Omega \geq 1.1$ and $\delta < 6.6\%$. Because no intermetallics were detected by either

Fig.7: SEM secondary electron images of fracture surfaces after tensile deformation for as-cast CrCoNiAl_x MEAs: (a) Al-0, (b) and (c) Al-0.2, (d) Al-0.4, (e) and (f) Al-0.6, (g) Al-0.8, (h) Al-1 and (i) Al-1.2

XRD or TEM, the other criteria^[37] have not been considered.

For the current MEAs, δ , ΔH_{mix} and Ω are listed in Table 2. The δ value of the Al- x alloys changes from 0.16% to 6.37%, the ΔH_{mix} value is from $-4.89 \text{ kJ}\cdot\text{mol}^{-1}$ to $-16.37 \text{ kJ}\cdot\text{mol}^{-1}$ and the Ω value is from 1.1 to 3.5. The $\Delta H_{\text{mix}}-\delta$ and $\Omega-\delta$ graphs are plotted in Fig. 8a and 8b, respectively. This indicates that the above criteria can also predict partly the phase evolution of the CrCoNiAl_x MEAs. However, two alloys, Al-1 and Al-1.2, are slightly beyond the solid solution regions probably because of their more negative mixing enthalpy (lower than $-15 \text{ kJ}\cdot\text{mol}^{-1}$).

Besides the above discussed criterions, valence electron concentration (VEC) theory could effectively separate the exact transition of crystal structure of solid solutions. VEC theory was put forward by Guo et al.^[34, 38], which suggested using the VEC to predict the BCC and FCC structured solid solutions of multicomponent alloys. The VEC values of the current CrCoNiAl_x MEAs were calculated and plotted in Fig. 7(c). As seen, the VEC decreases linearly with the increase of Al content, since Al has the lowest VEC value in the system^[7]. The duplex-

phase alloys fall within the predicted region. However, there are still some questions which need to be further studied. First, VEC criterion obviously offers a wider boundary condition for forming the single FCC and BCC solid solution phases, such as Al-0.3 and Al-1 alloys. The Al-0.3 alloy is indeed a duplex-phase alloy indicated by the XRD pattern which detected a BCC (110) peak, however, this alloy is in the two-region boundary. On the other hand, Al-1 alloy, as a single BCC phase indicated by XRD and TEM analysis, is also situated at the boundary. This result is similar to the previous works^[7, 27] which indicated that in addition to atomic bonding, other factors also play an important role in the phase formation caused by the Al addition. Second, these criteria are referred to as simple solid solutions, but no precise criteria have been available for the disordered and ordered phase transition. In a word, these above-mentioned criteria are considered as necessary conditions for forming simple solid solutions but not sufficient conditions^[39], because exceptions have been found for many systems^[37]. However, they are still useful in predicting the phase evolution in some cases.

Fig. 8: Model predictions: (a) $\Delta H_{\text{mix}}-\delta$; (b) $\Omega-\delta$ and (c) VEC as a function of Al content in as-cast CrCoNiAl_x ($x=0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1$ and 1.2) MEAs

Phase structure transition from FCC to BCC is apparently related to the Al addition (Fig. 1). When single FCC just starts to decompose, the ordered Al-Ni-rich B2 phase forms, which was further confirmed by the Al-0.4 alloy (Fig. 5). After the Al addition reaches the single BCC region, disordered Al-Ni-less A2 phase exists apart from the ordered Al-Ni-rich BCC phase (Fig. 6). The similar phenomenon was also found in the previous works^[7, 27, 40-42]. Therefore, Al has been termed as a BCC former^[40]. Combining with the XRD, SEM and TEM results, one can conclude that with the aluminum increasing to the duplex-phase region, a eutectic reaction occurs in the interdendrite region and decomposes into two phases, where a duplex-phase structure was observed. After the Al reaches 1.0, the dendrites transform to two phases (ordered B2 and disordered A2 without clear phase boundaries), resulting from spinodal decomposition

Table 2: Calculated parameters δ , ΔH_{mix} and Ω for current MEAs

Al fraction	δ (%)	ΔH_{mix} (kJ·mol ⁻¹)	Ω
0	0.16	-4.89	3.5
0.1	2.59	-6.70	2.8
0.2	3.53	-8.28	2.3
0.3	4.17	-9.66	2.0
0.4	4.65	-10.87	1.8
0.6	5.34	-12.84	1.5
0.8	5.81	-14.35	1.3
1.0	6.13	-15.50	1.2
1.2	6.37	-16.37	1.1

(Fig. 6). These similar transformations have been reported by the He^[7] and Tong^[42]. The reasons why ordered B2 and disordered A2 phases coexist in the high-Al BCC alloys have not been discussed in the multicomponent alloys. However, Li et al.^[41] studied AlCrCoNiFe based alloys and considered that the BCC structure of the alloys should be a B2 instead of an A2 due to the great difference in electronegativities among the components. The A2 phase is not stable, as long as Al is sufficient, the B2 phase will dominate the structure formation. If considering Al and Ni as essential components due to the most negative mixing enthalpy^[41], they should hold the sites of center and corner in B2, while the other components substitute Al and Ni. Due to the similar electronegativity and atomic radius of Co and Ni, Co could take up the site of Ni in the B2 structure. Meanwhile, the above values of Cr and Al are very close, and Cr may occupy the site of Al. It is known that Cr lowers the ordering energy of NiAl^[43]. Murty et al.^[44] also pointed out that Cr induces the disordering tendency in thermodynamically stable B2 NiAl and the addition of Cr to the extent of ~20 at.% to NiAl can induce complete disorder after mechanical alloying. It can be concluded that the enrichment of Cr in the Al-Ni-less phases leads to the disordering.

Unexpectedly, SAD patterns of Al-0.4 alloy show a very weak ordered FCC spot (001) in two zone axes of $[0\bar{1}3]$ and $[011]$ (Fig. 4), which means FCC phases partly transform to ordered FCC phase. Since the ordered FCC structure was not observed in the XRD pattern, its fraction in the alloy should be less than 5%. The existence of this phase should be related to the inhomogeneous distribution of Al. Although this ordered FCC phase was not mentioned in the previous work, the ordering degree induced by Al has been recognized^[7, 27, 29]. The solid solution of Al with greater atomic radius into CrCoNi MEA is considered to distort the lattice. The enrichment of Al

and Ni in the BCC phases is related to their mixing enthalpy. From the chemical mixing enthalpy of different atom-pairs calculated by Miedema's approach (Table 3), it can be seen that Al and Ni have the most negative value, indicating the strong affinity. These phases also present in CrMnFeCoNiAlx^[7] and CrFeCoNiAlx alloys^[45], which are stable at high temperatures and could retard the grain growth during recrystallization. However, the mixing enthalpy between Al and Co is also very negative, although a little higher than that between Al and Ni. Actually, Al and Co readily form intermetallics in the Ni-free systems^[46, 47]. In addition, the mixing enthalpy between Ni and Co is 0. The values of Cr-Al and Cr-Ni are not as negative as that of Al-Ni. Thus, from the viewpoint of mixing enthalpy, it can be understood that with the increasing Al addition, Al and Ni are enriched at the grain boundaries, where the concentration of Co is higher than Cr (Table 1). The crystal lattice constants of both FCC and BCC phases vary with Al content fluctuation (Fig. 2). Al can be partly dissolved into the as-cast CrCoNi MEA although the Al element has a very negative enthalpy of mixing and larger atomic size compared with the other constituent elements (Table 3)^[25, 48]. Therefore, with the increase of Al content in single FCC MEAs, the crystal lattice constant increases sharply. Then in the duplex phase MEAs, the values of both FCC and BCC phases decrease.

Table 3: Chemical mixing enthalpy (ΔH_{mix} , kJ·mol⁻¹) of different atom-pairs calculated by Miedema's approach^[49]

Element (atomic size, nm)	Al	Cr	Co	Ni
Al (0.1432)	-	-10	-19	-22
Cr (0.1249)	-	-	-4	-7
Co (0.1251)	-	-	-	0
Ni (0.1246)	-	-	-	-

The mechanical properties of the current CrCoNiAlx MEAs are closely related to their microstructures. The hardness, yield and tensile strength all increase as the Al content increases (Fig. 4) in the single FCC region, suggesting a solid solution strengthening effect caused by the enlarged lattice distortion. For the alloys in the FCC+BCC duplex-phase region, it is known that BCC phases are generally more brittle and stronger than FCC phases due to the difference in the number of their available slip systems^[50]. Thus, their yield and tensile strengths increase with the phase fraction of BCC positively related to Al content. Al-0.8, Al-1 and Al-1.2 alloys are too brittle to be deformed under tensile loading. As for the hardness, it is nearly linear to the BCC fraction and becomes steady up to the single BCC region. At the same time, the increase of the strength and hardness sacrifices the elongation, due to the brittle BCC phases. The changes of fracture surfaces after the tensile deformation are also corresponding to variations in the mechanical properties. However, a trade-off of strength and elongation could be obtained by appropriately adjusting the fraction of FCC and BCC phases.

4 Conclusions

- (1) The crystal structure changes from a single FCC crystal structure (Al-0 to Al-0.2), to duplex FCC and BCC (Al-0.3 to Al-0.8) and then a single BCC (Al-1 to Al-1.2) with increasing Al content.
- (2) With increasing aluminum to duplex region, FCC and BCC phases form under a eutectic reaction in the interdendrite region. After Al reaches 1.0, dendrites transform to ordered B2 and disordered A2 BCC phases resulting from spinodal decomposition. It is not clear why ordered FCC phase appears in the duplex region.
- (3) The investigated crystalline phases in the current CrCoNiAlx MEAs cannot be fully predicted using the existing criteria (ΔH_{mix} , δ and VEC), indicating that further work is necessary for understanding phase transition in the CrCoNiAl MEA system.
- (4) The mechanical properties of current CrCoNiAlx alloys are strongly dependent on their microstructures, and hardness and strength both increase as Al content increases, but tensile elongation decreases. Their hardness values increase with the increase of volume fraction of BCC phase, which is positively related to Al content.

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