



# Effects of Sc addition on microstructure, phase evolution and mechanical properties of $\text{Al}_{0.2}\text{CoCrFeNi}$ high-entropy alloys



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Received 4 January 2023; accepted 10 August 2023

**Abstract:**  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  ( $x=0, 0.1, 0.2$  and  $0.3$ , molar fraction) alloys were prepared by arc melting. The effects of Sc addition on the microstructure, phase evolution and mechanical properties of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys were investigated. The results showed that Sc could refine grain size, change phase type and improve mechanical properties. The grain size of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloy ( $8.5\ \mu\text{m}$ ) was reduced by approximately 50.6% compared to that of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy ( $17.2\ \mu\text{m}$ ). The crystal structure evolved from a single FCC phase to a mixed phase including two types of FCC phases and one type of BCC phase. The FCC phase mainly appeared in the regions of (Co, Cr, Fe)-rich dendrites and (Ni, Sc)-rich interdendrites; while the BCC phase was mainly located in the region of (Al, Ni)-rich interdendrites. The yield strength increased from 167 to 717 MPa as the  $x$  value in  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloy increased from 0 to 0.3, improved by 329.3%, which could be attributed to grain size strengthening, solid solution strengthening and phase evolution.

**Key words:** high-entropy alloy; phase evolution; microstructure; grain refinement; yield strength

## 1 Introduction

High-entropy alloys (HEAs) exhibit high mechanical strength and/or ductility [1], superior compressive or extensive properties [2], high hardness [3], excellent impact toughness [4], special electrical and magnetic properties [5], and good catalytic performance [6], which makes them potential candidates for engineering applications. To date, many HEA systems have been exploited, e.g.,  $\text{Al}_x\text{CoCrFeNi}$  [7,8],  $\text{CoCrFe}(\text{Mn}, \text{Cu}, \text{Nb})\text{-Ni}$  [9,10],  $\text{AlCoCuFeNi}$  [11], and  $\text{AlCoCrFeNi}(\text{Cu}, \text{Mn}, \text{Si}, \text{Ti}, \text{V})$  [12–14]. In particular,  $\text{Al}_x\text{CoCrFeNi}$  has been comprehensively researched because it combines high compressive strength and hardness, excellent fracture toughness and work hardenability coupled with low cost and abundant constituent elements.

The effects of alloying elements, such as Al, Cu, Ti, V, Nb, Y, B, and Si, on the structure and properties of  $\text{AlCoCrFeNi}$  alloys have attracted extensive attention from researchers. Adding Al to an  $\text{Al}_x\text{CoCrFeNi}$  alloy changes the crystal structure [15]. Specifically, the  $\text{Al}_x\text{CoCrFeNi}$  alloy transforms from a single FCC structure to an FCC+BCC structure and finally to a single BCC structure for  $0 \leq x < 0.5$ ,  $0.5 \leq x < 0.9$  and  $0.9 \leq x < 3.0$ , respectively. Changes in the crystal structure consequently vary the material properties [16]. Adding Cu to the as-cast  $\text{AlCoCrFeNi}$  could improve the wear resistance, but it decreased the corrosion resistance of the alloy [17]. The addition of Ti [18], V [19] and Y [20] to HEA alloys could improve the mechanical properties due to the formation of BCC structure and new phase. The addition of Nb and Si could modify the phase compositions and properties of the  $\text{AlCoCrFeNi}$

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DOI: 10.1016/S1003-6326(23)66368-X

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alloys [21,22]. The addition of B improved the hardness and wear resistance of the  $Al_{0.5}CoCrCuFeNi$  alloy but decreased the toughness [23].

Sc is located in the IIIB group and the fourth period of the periodic table, the same period as Ti, V, Cr, Fe, Co, and Ni. It is usually added to aluminium alloys, e.g., 2xxx series, 5xxx series, 7xxx series, Al–Mg–Li and Al–Li–Cu–Mg alloys, as a microalloying element to refine the grain [24,25], improve the mechanical properties [26], corrosion resistance [27–29] and welding performance [30]. The improvement in these properties is due to the formation of coherent  $Al_3Sc$  nanoparticles with  $L1_2$  structure, which significantly affect the grain refinement, precipitation strengthening and recrystallization inhibition [31]. In addition to effectively improving the properties of aluminium alloy, the addition of Sc can improve the mechanical properties of TiAl alloy [32,33], creep resistance of magnesium alloy [34], and mechanical properties of steels [35]. The effect of Sc addition to HEA alloys has been investigated recently. Alloying 0.3–0.5 wt.% Sc addition to the  $Al_2CoCrFeNi$ ,  $Al_{0.5}CoCrCuFeNi$  and  $AlCoCrCu_{0.5}FeNi$  causes the grain refinement, and the increase of the hardness and electrical conductivity [36]. In addition, adding 3 wt.% Sc to  $Al_2CoCrFeNi$  alloy leads to the precipitation of  $Al_2Cu_3Sc$  intermetallic, which has significantly improved the hardness and thermal stability of the alloy [37]. Sc has also been incorporated as one of the principal elements into  $AlCrCuScTi$  [38],  $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$  [39],  $CoGdYScTiZr$  [40],  $ScYLaTiZrHf$  [41], and  $ScHfNbTaTiZr$  [42] alloys. Sc is not only used as a trace element but also as a major alloying element, for Al alloys first and increasingly now to HEA alloys. It is clear that more fundamental research is

required to extend the investigation about the influence of Sc on the microstructure and properties of HEA alloys.

In the present study, a series of  $Al_{0.2}CoCrFeNiSc_x$  ( $x=0, 0.1, 0.2, 0.3$ , molar fraction) alloys were prepared using arc melting method. The purpose of this work was to investigate the effects of Sc addition on the microstructure, phase evolution and mechanical properties of the studied alloys. This work will be of great significance for enriching the composition design of HEA alloys and further providing a new perspective for exploring the potential properties of HEA alloys.

## 2 Experimental

Ingots with nominal  $Al_{0.2}CoCrFeNiSc_x$  compositions were prepared by arc melting in an argon atmosphere. The purities of the metal particles were 99.9% for Al, 99.95% for Co, 99.99% for Cr, 99.99% for Fe, 99.995% for Ni and 99.99% for Sc. The ingot was remelted at least four times to ensure chemical homogeneity, and all samples were tested under as-cast conditions. Table 1 shows the measured chemical compositions of the nominal  $Al_{0.2}CoCrFeNiSc_x$  alloys using the SPECTRO BLUE SOP ICP test. The measured composition of each ingot is close to its nominal composition.

X-ray diffraction (XRD), metallographic microscopy (OM), scanning electron microscopy (SEM), electron back-scattered diffraction (EBSD) and scanning transmission electron microscopy (STEM) were chosen to observe and analyze the microstructure. The specimens for XRD, OM and SEM observation were prepared by mechanical polishing. The polished faces were etched in a mixed solution of 75 vol.% HCl and 25 vol.%

**Table 1** Measured chemical compositions of nominal  $Al_{0.2}CoCrFeNiSc_x$  alloys

Alloy	Composition	Content/wt.%					
		Al	Co	Cr	Fe	Ni	Sc
$Al_{0.2}CoCrFeNi$	Nominal	2.34	25.53	22.52	24.19	25.42	
	Measured	2.41	25.7	22.7	23.5	25.4	
$Al_{0.2}CoCrFeNiSc_{0.1}$	Nominal	2.29	25.04	22.09	23.73	24.94	1.91
	Measured	2.36	25.3	22.3	23.5	24.6	1.81
$Al_{0.2}CoCrFeNiSc_{0.2}$	Nominal	2.25	24.57	21.68	23.28	24.47	3.75
	Measured	2.39	24.4	21.8	23.3	24.2	3.71
$Al_{0.2}CoCrFeNiSc_{0.3}$	Nominal	2.21	24.12	21.28	22.86	24.02	5.52
	Measured	2.32	24.3	21.5	22.1	24.1	5.63

HNO<sub>3</sub> for OM and SEM observation. XRD data were collected on a Bruker D8 Advance diffractometer with Cu K<sub>α1</sub> radiation in the 2θ range from 10° to 80° with a scanning rate of 2 (°)/min to identify the crystal structure of the alloy. OM images were taken using an Axio Observer microscope. A JSM–7610F microscope was used to observe the microstructure, and energy dispersive X-ray spectroscopy (EDS) was used to detect the chemical composition. The Oxford Symmetry EBSD detector was used to detect the crystal structure. STEM investigations were carried out on a Talos F200X G2 microscope at 200 kV to observe the microstructure and analyze the chemical composition. The specimens for the TEM measurements were prepared using a Fischione 1051 ion thinning instrument.

Hardness tests were performed on an HV–1000A type digital Vickers micro-sclerometer under a load of 500 g for 10 s. The mean value of at least six measurements was taken as the final value. Compression samples with a diameter of 4 mm and a height of 6 mm were cut from the as-cast ingot. A UTM5105X electronic universal testing machine was used for compression tests at a constant rate of 0.5 mm/min. Three tests were needed for the sample for each composition.

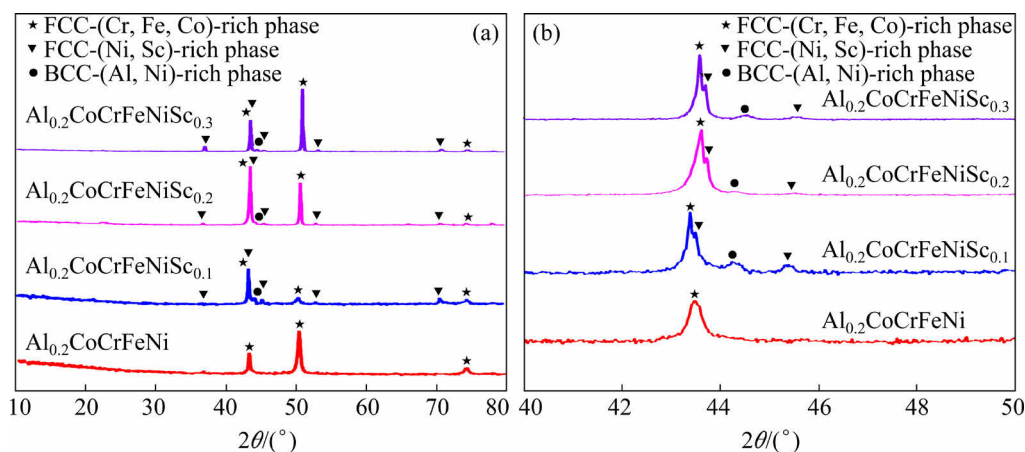
### 3 Results

#### 3.1 Microstructure and phase evolution

Figure 1 shows the X-ray diffraction patterns of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys. For the Al<sub>0.2</sub>CoCrFeNi alloy, only FCC diffraction peaks were observed, which indicated that the crystal structure of the

Al<sub>0.2</sub>CoCrFeNi alloy was a single FCC. When Sc was added to the Al<sub>0.2</sub>CoCrFeNi alloy, another set of FCC diffraction peaks and BCC diffraction peaks appeared, as clearly seen in Fig. 1(b). This finding implies that the crystal structure of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys evolves from a single FCC structure for x=0 to a mixed FCC+BCC structure for x=0.1, 0.2, 0.3. The addition of Sc modified the crystal structure of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys, which will have an important effect on the mechanical properties.

Figure 2 shows the metallographic structure of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys. As shown in Fig. 2(a), the Al<sub>0.2</sub>CoCrFeNi alloy exhibited a wicker-shaped morphology, and the wicker-shaped trunks grew parallel and closely along a specific crystal orientation. The microstructure displayed a columnar dendritic structure after the addition of Sc to Al<sub>0.2</sub>CoCrFeNi alloys. With increasing Sc content, the number of dendrites increased, whereas the arm width and length decreased. Accordingly, the arm width and length of the interdendrite increased, which indicated that the negative mixing enthalpy and the large difference in atomic size caused component supercooling due to the Sc addition [43]. The dendritic and interdendritic regions consisted of alternating bright and dark phases. Each columnar dendritic and interdendritic structure grew along a specific crystal orientation. In the Al<sub>0.2</sub>CoCrFeNiSc<sub>0.1</sub> alloy, the arm widths of the primary and secondary dendrites were large (marked by red arrows in Fig. 2(b)), approximately 18 and 10 μm, respectively. As the content of Sc increased to 0.2, the arm widths of the primary and secondary dendrites decreased (Fig. 2(c)). When the



**Fig. 1** XRD patterns of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys with different Sc contents: (a) XRD patterns in 2θ range of 10°–80°; (b) Enlarged view of XRD patterns in 2θ range of 40°–50°

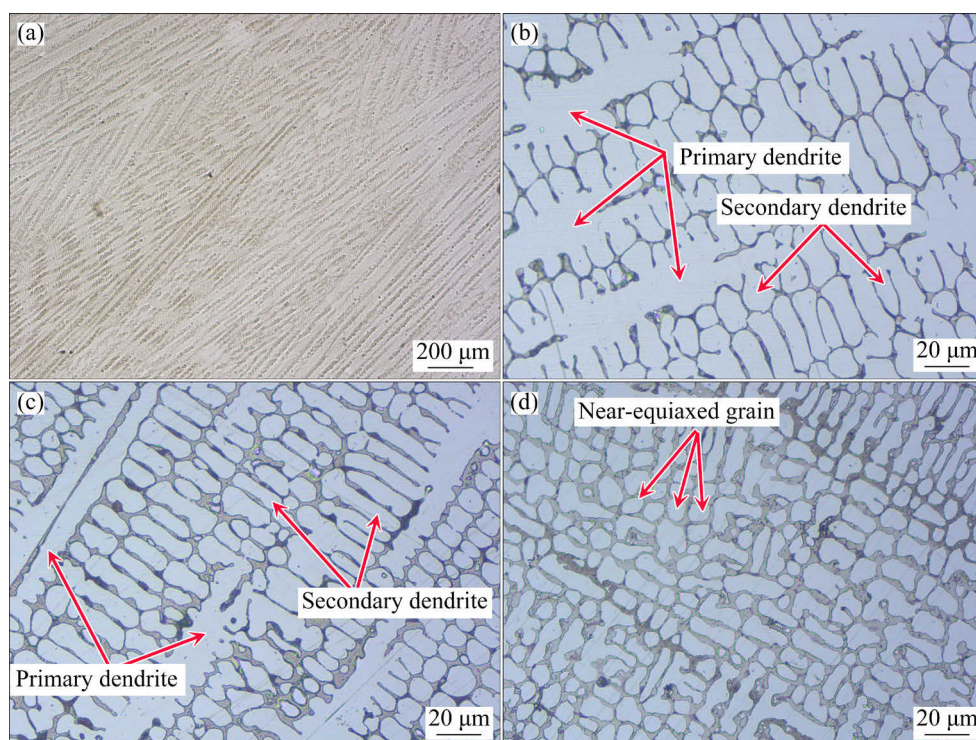
content of Sc increased to 0.3, almost no primary dendrites were observed, and some secondary dendrites were transformed into near-equiaxed grains, as shown in Fig. 2(d). This finding implied that the addition of Sc had a grain-refining effect on the studied alloy.

The grain sizes of the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$ ,  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloys were obtained with the Image Pro-Plus software based on the OM images to better clarify the refining effect of Sc. During the calculation, the secondary dendrite arm spacing was used for measuring the grain size [24,44]. As listed in Table 2, the grain sizes of the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$ ,  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloys were 17.2, 10.2 and 8.5  $\mu\text{m}$ , respectively. As the Sc content increased, the grain size decreased. The grain size of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloy was reduced by approximately 50.6% compared to that of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy.

Figure 3 shows SEM images of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys. The  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy with a single FCC structure had a columnar cellular micro-

structure (see Fig. 3(a)). The  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$ ,  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloys consisted of dendritic and interdendritic microstructures (Figs. 3(b–d)). The interdendritic regions *B* and *C* in Fig. 3(b), i.e., grey interdendritic regions and black interdendritic regions, had different morphologies. The black interdendrite exhibited a stripe shape (see the enlarged view in Fig. 3(b)). EDS measurement was performed to test the chemical compositions of dendrites and interdendrites, and the results are shown in Fig. 4. Specifically, the dendritic region was a (Co, Cr, Fe)-rich phase (Position *A* in Fig. 4(a)), and the grey-coloured interdendritic region was a (Ni, Sc)-rich phase (Position *B* in Fig. 4(a)).

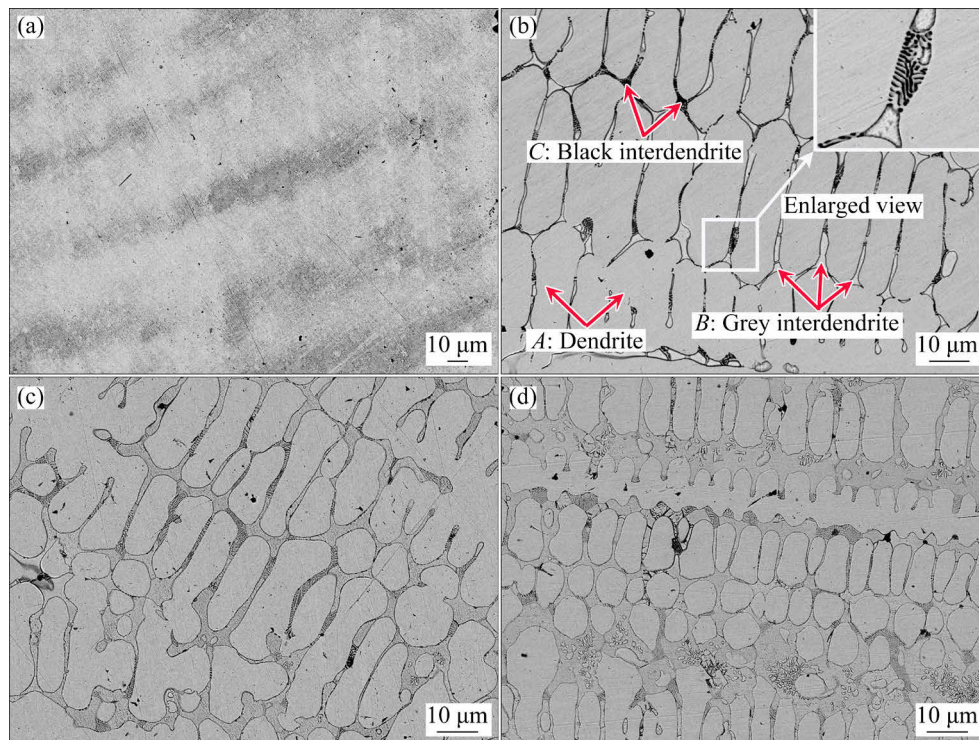
The stripe-shaped interdendritic region was an (Al, Ni)-rich phase (marked by Position *C* in Fig. 4(a)). In addition, Sc was mainly distributed in the interdendritic region, especially the grey interdendritic region *B* in Fig. 4(a). As the Sc content increased, the (Co, Cr, Fe)-rich phases decreased, and the (Ni, Sc)-rich and (Al, Ni)-rich phases increased.



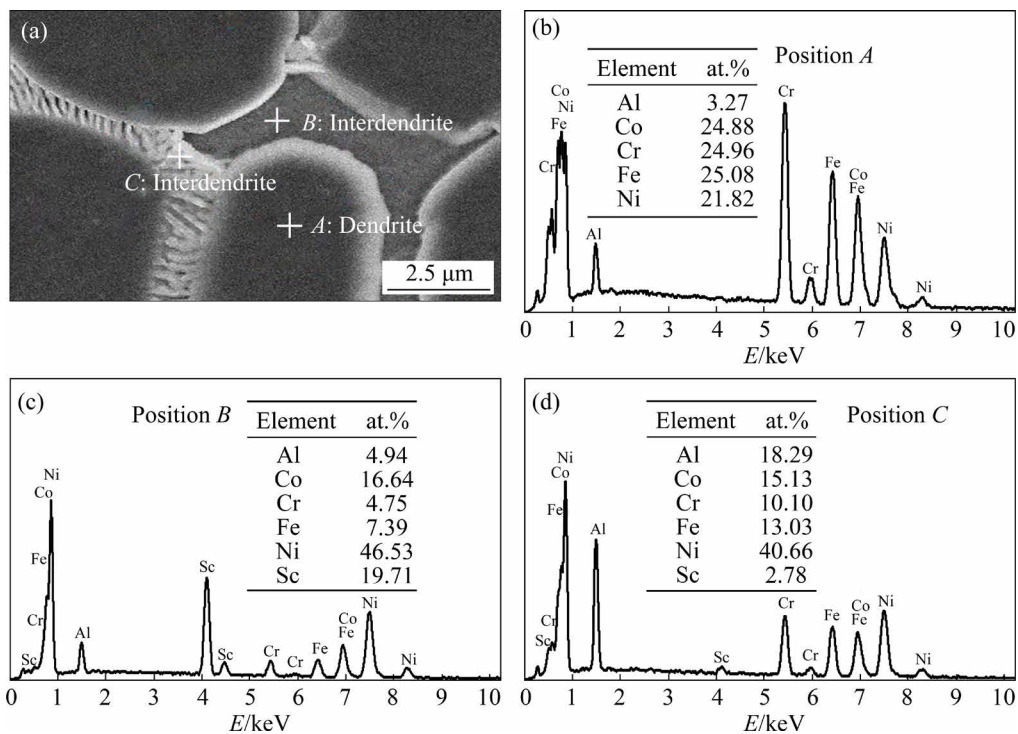
**Fig. 2** Metallographic structures of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys: (a)  $x=0$ ; (b)  $x=0.1$ ; (c)  $x=0.2$ ; (d)  $x=0.3$

**Table 2** Grain sizes of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys

Alloy	$\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$	$\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$	$\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$
Grain size/ $\mu\text{m}$	17.2	10.2	8.5



**Fig. 3** SEM images of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys: (a)  $x=0$ ; (b)  $x=0.1$ ; (c)  $x=0.2$ ; (d)  $x=0.3$

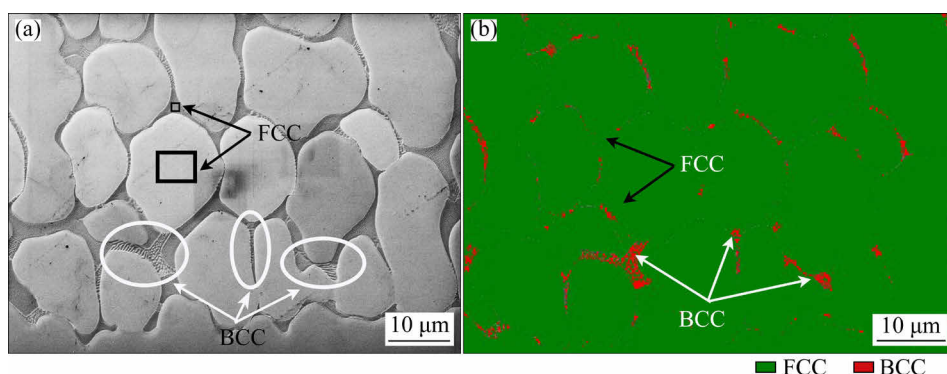


**Fig. 4** EDS data of different regions in Fig. 3(b)

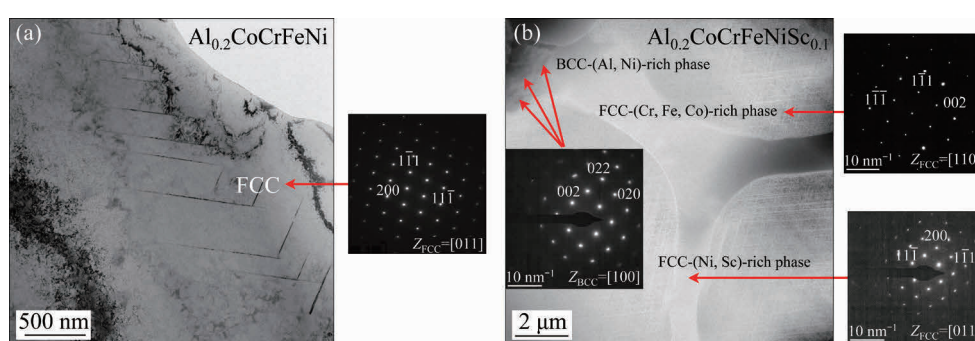
Figure 5 shows the EBSD phase map of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy. The columnar dendritic structure mainly consisted of FCC and BCC phases. The FCC phase appeared in the regions of (Co, Cr, Fe)-rich dendrites and (Ni, Sc)-rich interdendrites.

The BCC phase was primarily located in the (Al, Ni)-rich interdendritic region with stripe shape.

Figure 6 shows the TEM images and the corresponding diffraction patterns (DPs) of the  $\text{Al}_{0.2}\text{CoCrFeNi}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloys. For



**Fig. 5** EBSD images showing distribution of FCC and BCC phases for  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy: (a) EBSD band contrast; (b) Phase distribution image



**Fig. 6** TEM images and corresponding diffraction patterns of  $\text{Al}_{0.2}\text{CoCrFeNi}$  (a) and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  (b) alloys

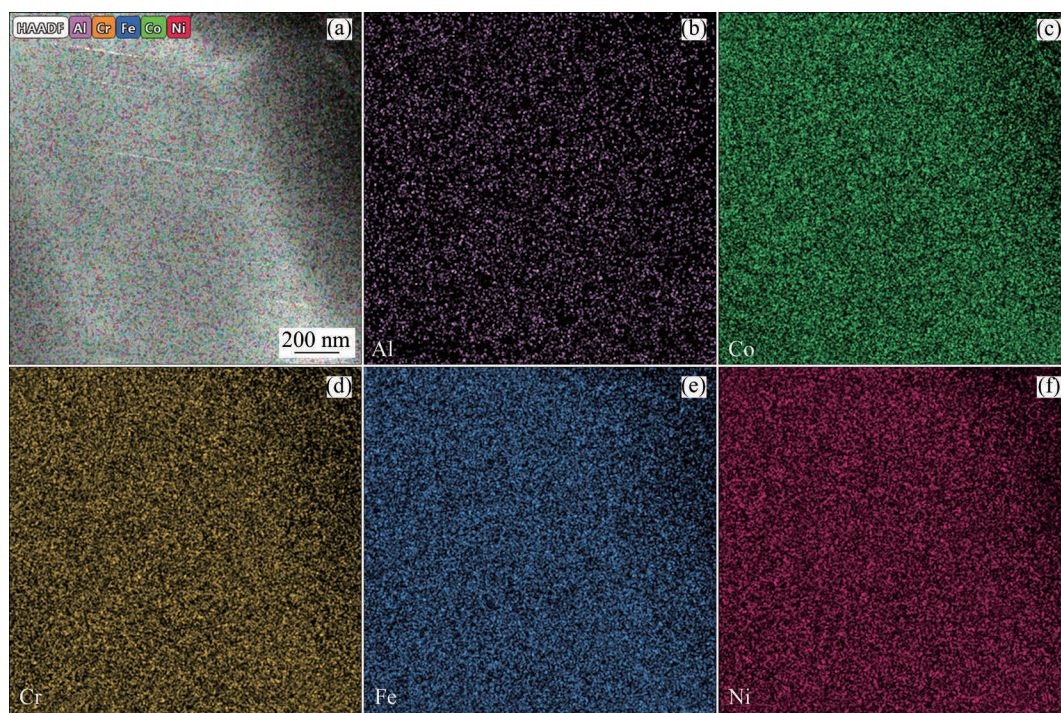
the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy, the DP in Fig. 6(a) demonstrated that only FCC phase existed in the alloy, which is in accordance with the XRD results shown in Fig. 1(a). For the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy, as shown in Fig. 6(b), the (Co, Cr, Fe)-rich dendritic phase and (Ni, Sc)-rich interdendritic phase were confirmed to be FCC structure, while the (Al, Ni)-rich interdendritic phase was confirmed to be BCC structure. This result was in good agreement with the EBSD result shown in Fig. 5. It was reported that  $\text{Ni}_2\text{Sc}$  has a  $\text{MgCu}_2$ -type FCC structure and can be formed by the following reactions:  $\text{Liquid} \rightleftharpoons \text{Ni}_7\text{Sc}_2 + \text{Ni}_2\text{Sc}$  at 1270 °C,  $\text{Liquid} \rightleftharpoons \text{Ni}_2\text{Sc}$  at 1330 °C and  $\text{Liquid} \rightleftharpoons \text{Ni}_2\text{Sc} + \text{NiSc}$  at 1100 °C [45]. In addition,  $\text{Ni}_2\text{Sc}$  formed a homogeneous solid solution in the range of 27–35 at.% Sc [46]. As shown in Fig. 4(c), the molar fraction of Ni and Sc was 46.53% and 19.71%, respectively, which was close to that of  $\text{Ni}_2\text{Sc}$ . Besides, the (Ni, Sc)-rich phase was confirmed to be FCC structure by EBSD and TEM, which was the same as the  $\text{Ni}_2\text{Sc}$  phase structure. In summary, the chemical formula of (Ni, Sc)-rich phase was possibly  $\text{Ni}_2\text{Sc}$ .

STEM mapping was performed to further analyze the element distributions of  $\text{Al}_{0.2}\text{CoCrFeNi}$

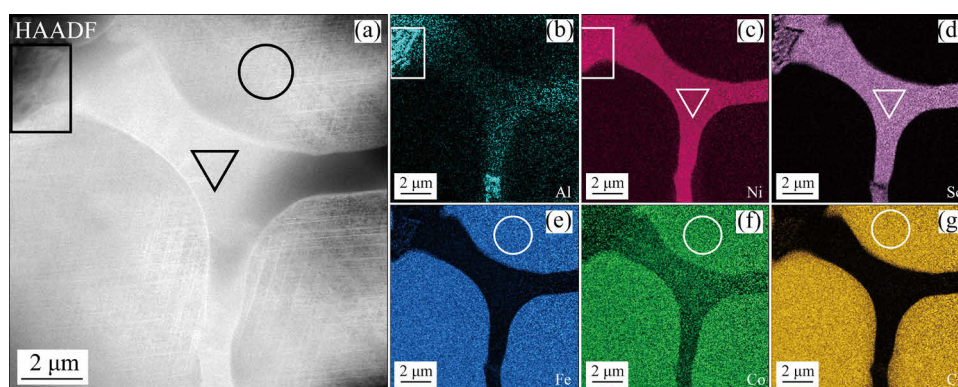
and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloys, and the results are shown in Fig. 7 and Fig. 8, respectively. Figure 7 indicated that element segregation did not occur in the entire tested region for the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy. However, when Sc was added to the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy, an apparent segregation phenomenon appeared, as shown in Fig. 8. Co, Cr and Fe were more concentrated in the dendritic region, marked by the circle in Fig. 8. Ni and Sc were primarily segregated into the interdendritic region with an FCC structure, marked by the triangle in Fig. 8. Al and Ni were mainly segregated into the interdendritic region with a BCC structure, marked by the rectangle in Fig. 8. This result agreed with that reported by WANG et al [15]. For the  $\text{Al}_x\text{CoCrFeNi}$  alloy with  $x \geq 0.7$ , the FCC structure was an (Fe, Cr)-rich phase, and the BCC structure was an (Al, Ni)-rich phase. Figure 8 also shows that a small amount of Sc remained segregated in the interdendritic region with a BCC structure, although the majority segregated into the interdendritic region with an FCC structure.

### 3.2 Hardness and compressive property

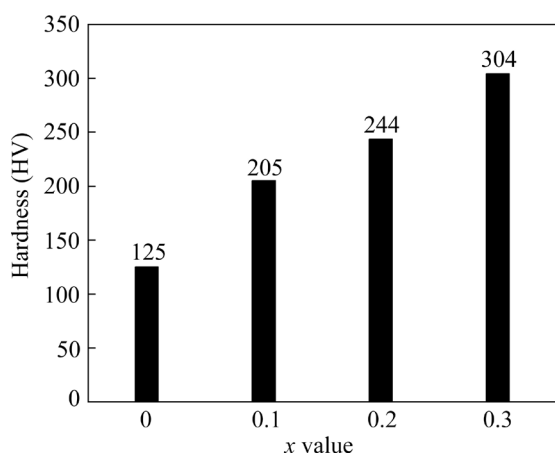
Figure 9 shows the hardness of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys. For the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy with a single



**Fig. 7** STEM image of  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy with corresponding element distribution mappings: (a) TEM image; (b) Al; (c) Co; (d) Cr; (e) Fe; (f) Ni



**Fig. 8** STEM image of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy with corresponding element distribution mappings: (a) TEM image; (b) Al; (c) Ni; (d) Sc; (e) Fe; (f) Co; (g) Cr

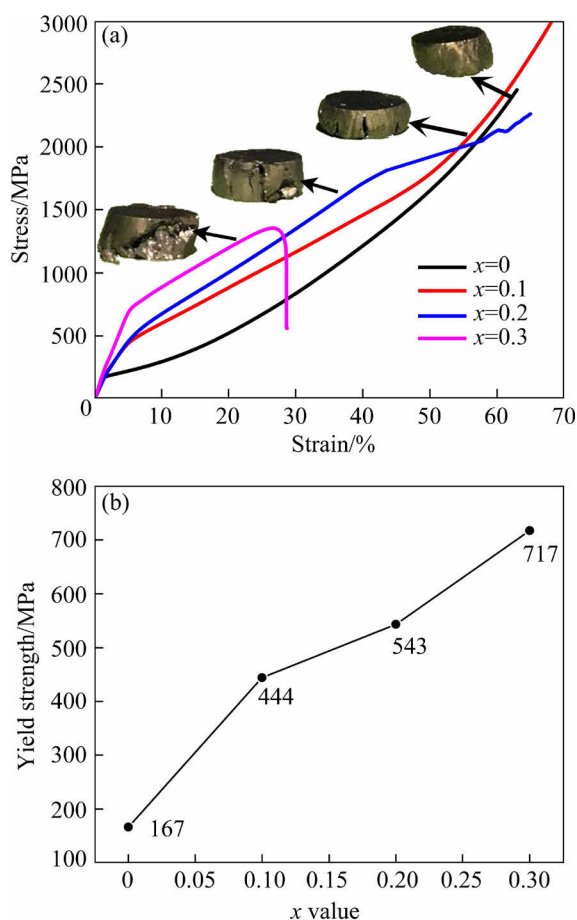


**Fig. 9** Hardness of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys

FCC structure, the hardness was only HV 125. However, the hardness dramatically increased after the addition of Sc. For the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloy, the hardness reached HV 304, an improvement of 143.2% compared to that of  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy.

The mechanical properties of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys were evaluated by compression tests, and the results are shown in Fig. 10. Notably, the yield strength and ductility strongly depended on the Sc content. The  $\text{Al}_{0.2}\text{CoCrFeNi}$ ,  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$  alloys externally appeared intact. The side surfaces appeared to be cracked but not crushed after the compression test (see the

insert in Fig. 10(a)). This morphology corresponded to a high strain value, indicating excellent ductility. However, the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloy was crushed after the compression test, corresponding to a lower strain value of only 28.6%. In contrast to the ductility, the yield strength increased as the Sc content increased. The yield strength increased almost linearly from 167 to 717 MPa as  $x$  increased from 0 to 0.3, as shown in Fig. 10(b), which indicated that adding Sc to the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy improved its strength.



**Fig. 10** Compressive stress–strain curves of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys (a) and yield strength as function of  $x$  value (b)

## 4 Discussion

### 4.1 Effect of Sc on microstructure and phase evolution

As the Sc content increased from 0.1 to 0.3, the grain size of the alloy decreased from 17.2 to 8.5  $\mu\text{m}$ , as shown in Table 2, which implied that Sc had the grain-refining effect. The element segregation in the front of the solid–liquid interface

decreased as the Sc content increased and the constitutional supercooling decreased, thereby inhibiting the extension of the primary dendrite and the growth of the secondary dendrite. As a result, the grain size decreased. Sc is generally believed to act as a powerful grain refiner in aluminium alloys, which effectively refines the structure. MOUSAVI et al [47] reported that the grain size of casting 7108 aluminium alloy decreased from 380 to 50  $\mu\text{m}$  after adding 0.3 wt.% Sc to the alloy. In addition, a powerful grain-refining effect occurred in the casting 7050 aluminium alloy: when the Sc content reached 0.28 wt.%, the grain size decreased from 250 to 60  $\mu\text{m}$  [48]. In the present study, adding Sc to the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy also had a grain-refining effect, which will greatly influence the mechanical properties of the alloy.

Previous studies have reported that  $\text{Al}_x\text{CoCrFeNi}$  alloys had a single FCC structure for  $x < 0.4$  [16,49,50], while they evolved into a mixed FCC and BCC structure for  $0.4 < x < 0.9$  [15,51]. When Sc was added to the alloy, the structure changed from a single FCC phase ( $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy) to a mixed phase ( $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$ ,  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.2}$  and  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloys), including two types of FCC phases and one type of BCC phase based on the analysis of XRD patterns (Fig. 1), SEM images (Fig. 3), EBSD images (Fig. 5) and TEM images (Fig. 6). Table 3 lists the mixing enthalpies of atom pairs between each element. The mixing enthalpy between Sc and Ni was the most negative,  $-39$  kJ/mol, which could be the reason for the formation of the (Ni, Sc)-rich phase with an FCC structure. The mixing enthalpy between Al and Ni was also relatively negative,  $-22$  kJ/mol. This finding indicated that Al and the remaining Ni were segregated again after Ni element was excluded by the (Ni, Sc)-rich phase with an FCC structure and ultimately formed a new phase with a BCC structure. However, the mixing enthalpy between Al and Sc ( $-38$  kJ/mol) was slightly higher than that between Ni and Sc ( $-39$  kJ/mol), which implied that a small amount of Sc segregation formed the BCC phase in addition to forming the FCC phase with Ni. The TEM analysis and the calculated mixing enthalpy indicated that during solidification, the (Co, Cr, Fe)-rich dendrite region with an FCC structure nucleated first from the liquid, and Al, Ni and Sc atoms were repelled from the dendritic region as the dendrite grew and



finally formed a (Ni, Sc)-rich interdendritic region with an FCC structure and an (Al, Ni)-rich interdendritic region with a BCC structure.

**Table 3** Mixing enthalpies of atom-pairs between elements of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys [52] (kJ/mol)

Element	Element					
	Al	Co	Cr	Fe	Ni	Sc
Al	0	-19	-10	-11	-22	-38
Co	-19	0	-4	-1	0	-30
Cr	-10	-4	0	-1	-7	1
Fe	-11	-1	-1	0	-2	-11
Ni	-22	0	-7	-2	0	-39
Sc	-38	-30	1	-11	-39	0

**4.2 Effect of Sc on hardness and mechanical properties**

There are multiple contributions from solid solution strengthening, dislocation strengthening, precipitation strengthening, and grain size strengthening, etc, which increase the hardness and strength of HEA alloys. SRIHARITHA et al [53] reported that the hardness of Al<sub>x</sub>CoCrFeNi alloys increased with increasing the Al content, which was attributed to the grain size strengthening, solid solution strengthening, order strengthening and particles strengthening. The grain size strengthening and precipitation strengthening were the main strengthening mechanisms for Al<sub>0.3</sub>CoCrFeNi alloy [54]. The solid solution strengthening together with precipitation strengthening resulted in the increase of hardness for Al<sub>x</sub>CoCrFeNi alloys [3]. The improvement of strength for AlCoCrFeNiSi<sub>x</sub> alloys was attributed to the solid solution of Si element and precipitation strengthening of nanoscale cellular structure [22]. In the present study, solid solution strengthening, grain size strengthening and other strengthening factors from phase evolution are considered as the main strengthening mechanisms. The overall hardness of the alloy can be expressed as

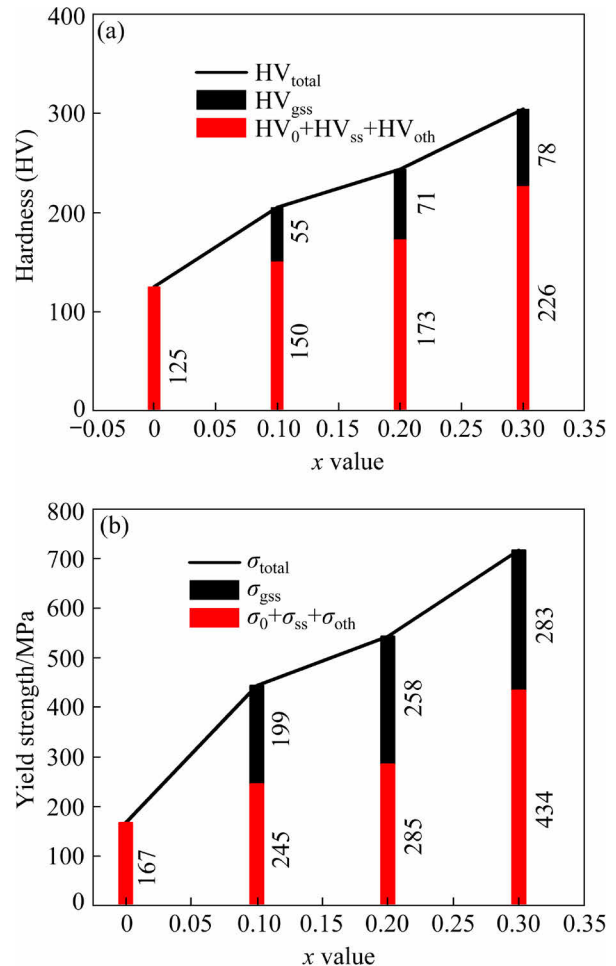
$$HV_{total} = HV_{gss} + HV_{ss} + HV_0 + HV_{oth} \tag{1}$$

where HV<sub>gss</sub>, HV<sub>ss</sub>, HV<sub>0</sub> and HV<sub>oth</sub> represent the grain size hardening, solid solution hardening, lattice friction hardening and other hardening caused by phase evolution, respectively.

Since, HV<sub>gss</sub> can be expressed as

$$HV_{gss} = K_{HV} d^{-1/2} \tag{2}$$

where K<sub>HV</sub> is the Hall–Petch coefficient (HV·μm<sup>1/2</sup>) and d is the average grain size (μm). WU et al [55] reported that the CoCrFeNi alloy had a K<sub>HV</sub> of 165.5 HV·μm<sup>1/2</sup>, while GWALANI et al [54] obtained a K<sub>HV</sub> of 227.4 HV·μm<sup>1/2</sup> for the Al<sub>0.3</sub>CoCrFeNi alloy. The addition of Al to CoCrFeNi alloy increased the value of Hall–Petch coefficient. Therefore, the value of K<sub>HV</sub>=227.4 HV·μm<sup>1/2</sup> was used in the present study. The value of d is taken from Table 2. Taking the values of K<sub>HV</sub> and d into Eq. (2), and the HV<sub>gss</sub> was obtained. Since the HV<sub>gss</sub> was calculated, the rest of contributions to hardness can be due to solid solution, lattice friction and other factor caused by the phase evolution. Different contributions are illustrated in Fig. 11(a).



**Fig. 11** Hardness (a) and yield strength (b) of Al<sub>0.2</sub>CoCrFeNiSc<sub>x</sub> alloys as function of x value

Additionally, the effect of grain size on the yield strength was investigated. According to the Hall–Petch relationship, the yield strength caused by grain size strengthening (σ<sub>gss</sub>) is given below:

$$\sigma_{\text{gss}} = K_{\sigma} d^{-1/2} \quad (3)$$

where  $K_{\sigma}$  ( $=824 \text{ MPa} \cdot \mu\text{m}^{1/2}$ ) is a coefficient and taken from the literature [54].

The yield strength caused by solid solution, lattice friction and phase evolution can be expressed as

$$\sigma_{\text{ss}} + \sigma_0 + \sigma_{\text{oth}} = \sigma_{\text{total}} - \sigma_{\text{gss}} \quad (4)$$

where  $\sigma_{\text{ss}}$ ,  $\sigma_0$  and  $\sigma_{\text{oth}}$  represent the solid solution strengthening, lattice friction strengthening and other strengthening caused by phase evolution, respectively.

Taking the values of  $K_{\sigma}$  and  $d$  into Eq. (3), the  $\sigma_{\text{gss}}$  was obtained. Similar to the contributions to hardness, different contributions to strength are illustrated in Fig. 11(b).

As seen from Fig. 11, the hardness increased from HV 55 to HV 78 and the yield strength increased from 199 to 283 MPa by Hall–Petch strengthening due to the decrease of grain size. It indicated that the grain refinement induced by the addition of Sc element played an important role in the improvement of mechanical properties for  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy. Additionally, the hardness and yield strength caused by solid solution, lattice friction and phase evolution increased with increasing the Sc content. The lattice friction was originated from the multicomponent characteristics of HEA alloys [56]. The values of  $\text{HV}_0$  and  $\sigma_0$  were determined as HV 125 and 167 MPa in accordance with the experimental hardness and yield strength in the  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy.

Solid solution strengthening is another main cause for improving the mechanical properties of HEA alloys [57]. TONG et al [3] believed that the increasing hardness with the increase of Al content in as-cast  $\text{Al}_x\text{CoCrFeNi}$  alloy was attributed to the solid solution hardening. SRIHARITHA et al [53] had drawn the same conclusion that the solid solution strengthening considerably increased with increasing Al content in sintered  $\text{Al}_x\text{CoCrCuFeNi}$  alloy. In recent years, some researcher have proposed physical models to describe solid solution strengthening of HEA alloys, such as Senkov model [58], Toda–Caraballo model [59] and Varvenne model [60], among which the Varvenne model successfully predicted the yield strength of  $\text{Al}_x\text{CoCrFeNi}$  and  $\text{Al}_x\text{CoCrFeNiMn}$  alloys [61]. According to the Varvenne model, the solid solution strengthening can be expressed as

$$\sigma_{\text{ss}} = 0.01785 M \alpha^{-1/3} G \left( \frac{1+\nu}{1-\nu} \right)^{4/3} \left[ \frac{\sum_n (c_n \cdot \Delta V_n^2)}{b^6} \right]^{2/3} \quad (5)$$

where  $M$  is Taylor factor,  $\alpha$  is dislocation line tensor parameter,  $G$  is shear modulus,  $\nu$  is Poisson ratio,  $b$  is the amplitude of Burgers vector,  $c_n$  is molar content of element  $n$ , and  $\Delta V_n$  is misfit volume.

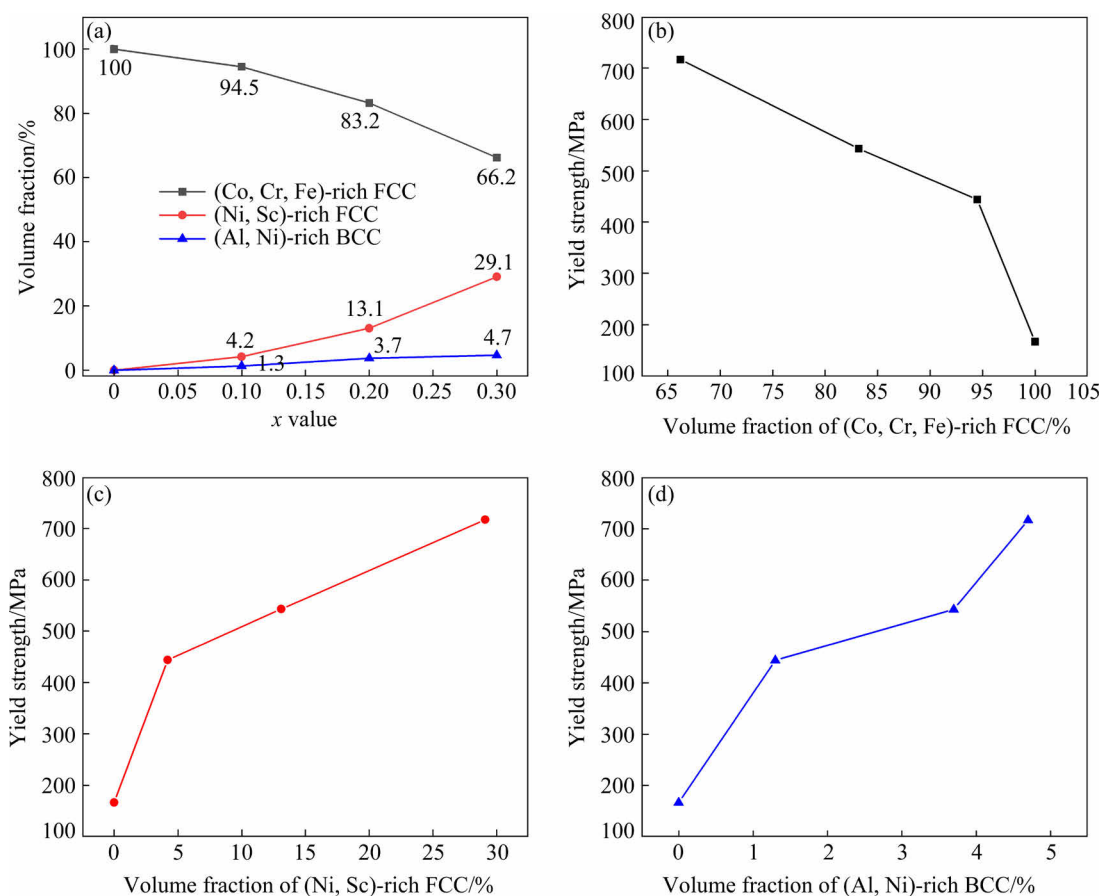
$\sum_n (c_n \cdot \Delta V_n^2)$  can be expressed by the following equation [62]:

$$\sum_n (c_n \cdot \Delta V_n^2) = 9V^2 \left[ \frac{\sum_n (c_n \cdot r_n^2)}{r^2} - 1 \right] \quad (6)$$

where  $V$  is the average atomic volume,  $r_n$  is the atomic radius of the element  $n$ , and  $r$  is the average atomic radius.

According to Eqs. (5) and (6), it can be inferred that the elements with large atomic radius added to HEA alloys could result in large misfit volume and thus enhance the strength of the alloy. The atomic radius of Sc is 2.09 Å, which is larger than that of Al (1.82 Å), Co (1.67 Å), Cr (1.88 Å), Fe (1.72 Å) and Ni (1.62 Å). Therefore, Sc element could cause solid solution strengthening. And with the increase of Sc content, the solid solution strengthening effect was improved. YIN et al [60] reported that V element with large atomic radius of 1.92 Å could induce large misfit volume and thus lead to high solid solution strengthening effect in Co–Cr–Fe–Mn–Ni–V and Cr–Mo–Nb–Ta–V–W–Hf–Ti–Zr alloy families.

In addition to grain size strengthening and solid solution strengthening, the phase evolution can also improve mechanical properties of the alloy. The hardness of  $\text{Al}_x\text{CoCrFeNi}$  alloys increased as the crystal structure changed from a single FCC phase to a mixed FCC+BCC phase [16,51]. In the present study,  $\text{Al}_{0.2}\text{CoCrFeNi}$  alloy was a single FCC phase, but it evolved into two types of FCC phases and one type of BCC phase after adding Sc. The volume fractions of (Co, Cr, Fe)-rich FCC phase, (Ni, Sc)-rich FCC phase and (Al, Ni)-rich BCC phase were calculated based on SEM images in order to better clarify the effects of different phases on the strength of the alloy, and the results are shown in Fig. 12. As seen from Fig. 12(a), the volume fraction of (Co, Cr, Fe)-rich FCC phase



**Fig. 12** Volume fractions of different phases with different Sc contents (a) and yield strength with volume fraction of different phases (b–d)

dramatically decreased, while the volume fractions of (Ni, Sc)-rich FCC phase and (Al, Ni)-rich BCC phase increased as the Sc content increased. The yield strength decreased with increasing the volume fraction of (Co, Cr, Fe)-rich FCC phase, but increased with increasing the volume fraction of (Ni, Sc)-rich FCC phase and (Al, Ni)-rich BCC phase, as shown in Figs. 12(b–d). Therefore, it can be concluded that the formation of (Ni, Sc)-rich FCC phase and (Al, Ni)-rich BCC phase played an important role in improving the yield strength of the alloy.

## 5 Conclusions

(1) Sc had an apparent grain-refining effect on the  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys. As the Sc content increased, the grain size decreased. The grain size of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.3}$  alloy ( $8.5 \mu\text{m}$ ) was reduced by approximately 50.6% compared to that of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_{0.1}$  alloy ( $17.2 \mu\text{m}$ ).

(2) The phase evolved from a single FCC

phase to a mixed phase, including two types of FCC phases and one type of BCC phase. The FCC phase appeared in the regions of (Co, Cr, Fe)-rich dendrites and (Ni, Sc)-rich interdendrites, while the BCC phase was mainly located in the region of (Al, Ni)-rich interdendrites. Sc tended to segregate at the interdendrite and formed FCC structure.

(3) Sc effectively improved the mechanical properties of  $\text{Al}_{0.2}\text{CoCrFeNiSc}_x$  alloys. The hardness increased from HV 125 to HV 304 and the yield strength increased from 167 to 717 MPa as the Sc content increased from 0 to 0.3. The hardness was improved by 143.2% and the yield strength was improved by 329.3%.

(4) Grain size strengthening, solid solution strengthening and phase evolution were responsible for the improvement of yield strength. The addition of Sc reduced the grain size and increased the misfit volume, thereby inducing grain size strengthening and solid solution strengthening. The formation of (Ni, Sc)-rich FCC phase and (Al, Ni)-rich BCC phase also improved the yield strength.

## Acknowledgments

The work was supported by the Natural Science Foundation of Shandong Province, China (No. ZR2021QE136).

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## Sc 添加对 $Al_{0.2}CoCrFeNi$ 高熵合金显微组织、相演变及力学性能的影响

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**摘要:** 采用电弧熔炼法制备  $Al_{0.2}CoCrFeNiSc_x$  ( $x=0, 0.1, 0.2, 0.3$ , 摩尔分数)合金, 研究 Sc 添加对合金显微组织、相演变和力学性能的影响。结果表明, Sc 能细化晶粒、改变相类型以及提高合金的力学性能。相较于  $Al_{0.2}CoCrFeNiSc_{0.1}$  合金的晶粒尺寸(17.2  $\mu\text{m}$ ),  $Al_{0.2}CoCrFeNiSc_{0.3}$  合金的晶粒尺寸仅为 8.5  $\mu\text{m}$ , 减小了约 50.6%。合金的晶体结构由 FCC 相演变为包括两种 FCC 相和一种 BCC 相的混合相。FCC 相主要出现在富 Co、Cr 和 Fe 枝晶区域和富 Ni 和 Sc 枝晶间区域, 而 BCC 相主要出现在富 Al 和 Ni 枝晶间区域。当  $Al_{0.2}CoCrFeNiSc_x$  合金中  $x$  值由 0 增加到 0.3 时, 合金的屈服强度由 167 MPa 增加至 717 MPa, 提高了 329.3%, 这主要归因于晶粒强化、固溶强化和相演变。

**关键词:** 高熵合金; 相演变; 显微组织; 晶粒细化; 屈服强度

(Edited by Wei-ping CHEN)