The formation of sigma phase in the CoCrFeNi high-entropy alloys

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Abstract

The as-cast CoCrFeNi high-entropy alloys show simple FCC structure and outstanding deformation ability at room temperature. Respectively, after 50% of deforming at room temperature and annealing at intermediate temperature range of 600 °C–800 °C for 2 h, CoCrFeNi alloys still show simple-phase FCC structure. It is noteworthy that CoCrFeNi high-entropy alloys can’t be strengthened by means of annealing, while deformation is an effective way to strengthen the alloys. It is investigated that the formation of sigma (σ) phase in high-entropy alloys is closely related to the difference of atomic radius (δ), the concentration of valence electron (VEC) and paired sigma-forming element (PSFE) content, and PSFE plays an crucial role. When PSFE > 40 at.%, 6.75 ≤ VEC ≤ 7.86, 4.0 ≤ δ ≤ 7.2, σ phase is prone to form in high-entropy alloys. In addition, alloying and processing route are two important factors that affect the sigma-formation in CoCrFeNi high-entropy alloys.

Known as a new branch of metal materials, high entropy alloys (HEAs) have attracted extended attention because of their excellent performances [1, 2]. Originally, HEAs are defined as equiatomic or near-equatomic alloys containing five or more elements, each multi-principal components has a content of 5%–35%, and simple solid-solution structures are preferred to form. During the past ten years, HEAs have been greatly developed and the definition of HEAs have been improved. Currently, the quantity of component elements in HEAs is not limited to five any more, the ternary or quaternary HEAs have been derived; moreover, the restriction on the content of each elements (in the range of 5%–35%) has been broken. Meanwhile, single-phase solid-solution structures, two-phase eutectic and even multi-phase structures including intermetallic compounds or amorphous have been obtained in HEAs [3–8].

It is investigated that the phase selection of HEAs is determined by the following thermodynamics parameters, such as mixing entropy (ΔSmix), mixing enthalpy (ΔHmix), atomic radius difference (δ), and valence electron concentration (VEC) [9–13]. When −19 ≤ ΔHmix ≤ 5 kJ·mol⁻¹, δ ≤ 6.5, 12 ≤ ΔSmix ≤ 17.5 JK⁻¹·mol⁻¹, simple solid solution phases, i.e., FCC, BCC, and mixtures thereof-including both ordered and disordered solid solution phases will form in MPCAs [12, 13]. Later, Guo et al [10] proposed VEC value to predict the types of simple solid solution phases, the formation of FCC is favorable when VEC > 8, the BCC phase is stable when VEC < 6.87.

Sigma phase is an intermetallic compound, and is frequently observed in aged HEAs with VEC values ranging from 6.88 to 7.84. Later, Tsai et al [21] put forward a new parameter called the paired sigma-phase forming elements (PSFE) as the second criterion to predict the formation of σ-phase, if two composing elements in a multi-component alloy are known to form binary σ phase, they are called the sigma-forming elements (SFEs) in that alloy. For example, binary σ phases are formed between so-called A and B elements, in the CoCrFeNi alloys, Cr is the only A element, and the corresponding B elements available in the alloy are Co and Fe. Therefore, Cr, Co, and Fe are the SFEs in CoCrFeNi alloys. As is known, the structure prototype of the σ phase is Cr₅₀Fe₅₀, therefore, A₅₀B₅₀ is considered as the representative formula of the σ phase. If an alloy contains 30 at% of A element, 50 at% of B element, and 20 at% of other elements that do not form the σ phase with any other components, then the content of PSFE is 60 at%, i.e. 30 at% A and 30 at% of B [15]. When PSFE ≤ 20 at %,
σ phase will not form even if the VEC value of the alloy is between 6.88 and 7.84; when PSFE ≥ 40 at.%, σ phase will appear in some of the HEAs after heat treatment, even they are σ-free in as-cast state, however, it is still not clear what is the main factors that affect the formation of σ phase when the PSFE value is in the range of 20 at.% − 40 at.% [21].

Phase evolution and thermal stability of HEAs were studied based on equilibrium and non-equilibrium routes [22–32]. The CoCrFeNi HEA was founded as a thermally stable solid-solution HEA with FCC structure [25–32]. However, according to a recent research by He et al [33] composition decomposition occurred in the CoCrFeNi HEAs and two FCC structural phases with different lattice constants were found, and Cr-rich σ phase was not observed in the pure CoCrFeNi HEA, but only appeared in the CoCrFeNiAl0.1 alloy after long-term (800 h) annealing at 750 °C. Also, Dahlborg et al [34] reported that the structure of the CoCrFeNi(y = 0.8 and 1.2) alloys is not affected by 3 h heat treatment up to 1100°C, and changing the amount of Fe has no drastic effect on alloy structure.

Accordingly, in the current work, the contents of σ-PSFE (Co, Cr, and Fe) elements were changed to research the formation of σ phase in Co0.5CrFeNi, CoCr0.5FeNi, CoCrFe0.5Ni, and CoCrFeNi (The subscript is the molar ratio of the element, where 1 is omitted.) HEAs. In addition, the structural stability and mechanical properties of the alloys were studied after heat treatment and deformation, in order to explore the feasible strengthening method of CoCrFeNi HEAs, and provide a theoretical basis for the phase selection of HEAs.

1. Experimental procedure and phase selection

Alloy ingots with nominal compositions of Co0.5CrFeNi, CoCrFeNi, CoCr0.5FeNi, CoCrFe0.5Ni were synthesized by melting appropriate mixtures of high-purity (>99.95%) constituent elements at least 4 times in Ar at high temperature in an electric arc furnace to ensure chemical homogeneity. To study the effects of heat treatment, annealing temperature was varied from 600 °C to 800 °C, 2 h annealing duration was chosen, followed by water quenching. HF + HNO3 was used to etch CoCrFeNi, while other CoCrFeNi series HEAs etched with HCl + HNO3 (3:1) or FeCl3 + HCl + H2O (5 g + 50 ml + 100 ml). The as-cast and heat-treated microstructures are characterized by using XRD-6000 x-ray diffractometer (XRD, Rigaku ME510-FM2, Cu Kα radiation) and scanning electron microscope (SEM, JEM-2100F). For the deformation CoCrFeNi sample, the microstructure is also characterized by using transmission electron microscopy (TEM, JEM-2100F). Micro-hardness was measured using a Vickers hardness tester with loads of 200 g, with a duration of 15 s. Room-temperature compressive properties were tested on samples of Φ5 mm × 10 mm by an UTM5205X testing machine with a loading speed of 0.02 mm s⁻¹. To study the stability of phase structures and properties of the deformed alloys, when the deformation rate reached 50%, compression was stopped.

The calculated parameters of the CoCrFeNi HEAs are listed in table 1, and the small atomic radius difference δ(0.76 1.31) and suitable mixing enthalpy ΔHmix (−4.25 ~ −2.94 kJ·mol⁻¹) indicate the formation a simple solid solution structure. According to Guo’s criterion of VEC, the CoCrFeNi series HEAs are FCC structure. Based on the criterion proposed by Tsai et al [21], after heat treatment σ phase may form in Co0.5CrFeNi, CoCrFeNi and CoCrFe0.5Ni, however, it is still uncertain whether σ phase will form in CoCr0.5FeNi alloy.

### 2. Result and discussion

#### 2.1. Experimental results

As presented in figure 1, the as-solidified structures of CoCrFeNi HEAs are typical dendrites. The XRD patterns of the as-cast Co0.5CrFeNi, CoCrFeNi, CoCr0.5FeNi, and CoCrFe0.5Ni (figure 1(f)) HEAs only show a set of peaks attributable to the FCC solid solution phase, and no σ phase was formed. The stress-strain curves of CoCrFeNi HEAs (figure 1(e)) exhibit that the alloys do not break even when the compression deformation reaches 50%, but the compressive yield strength is only 180 MPa. Moreover, the alloys show obvious work hardening.
After 50% of deformation, the CoCrFeNi HEAs are strengthened significantly, and XRD patterns show that no new phase is formed after deformation (figure 2). Clearly, the intensity of the first reflection is decreased prominently after 50% of deformation. As shown in figure 3a, where CoCr0.5FeNi alloy was taken as an example to study the influence of compression deformation on the microstructure of the alloy, the directional microstructures can be obtained after deformation, which results in the weakness of the (111) peak. After 50% of deformation, deformation bands, fibrous and feathery structures can be seen in the CoCr0.5FeNi alloy. According to TEM analysis, after 50% of deformation a large number of dislocation tangles appear, which hinder the further slip of the dislocations, so the alloys are greatly strengthened. In addition, selected area electron diffraction (SAED) conforms that the CoCr0.5FeNi alloy is single-phase FCC solid solution structure after deformation.

After heat treatment at 600 °C, 700 °C, and 800 °C for 2 h, the CoCrFeNi HEAs maintain typical dendrites and FCC structure (figure 4), indicating that CoCrFeNi HEAs are stable after a short-term annealing at 600–800 °C. Figure 5 shows that little variety of hardness can be found after heat treatment at different temperatures. It means that CoCrFeNi HEAs can’t be strengthened by the way of heat treatment.

2.2. Phase selection analysis

Based on [12, 13, 20], the δ, VEC and PSFE values of nearly 100 HEAs were calculated and presented in appendix table to explore the relationship between the formation of σ phase and the above parameter values. As shown in figure 6, the capability of forming σ phase is plotted as functions of PSFE, VEC, and δ values. Although the statistical data is limited, it does support the existence of σ–prone zone boundary conditions. It is found that σ phase forms when PSFE values exceed 40 at.%, δ and VEC in the range of 6.75 ≤ VEC ≤ 7.86, 4.0 ≤ δ ≤ 7.2.
According to the $\delta$-VEC-PSFE criterion, $\sigma$ phase would not form in the CoCrFeNi HEAs designed in this paper, it is consistent with the experimental results in this work. However, a few $\sigma$-free HEAs are found in the $\sigma$-prone area in figure 6. For L1 and L6 alloys, although all the $\delta$, VEC and PSFE values fit well with the criterion for forming $\sigma$ phase, but no $\sigma$ phase is found in Al0.3CrFe1.5MnNi0.5 alloy prepared by surfacing welding (L1) and AlCoCrFeNi alloy prepared by arc furnace melting (L6). According to the references [19, 35], $\sigma$ phase precipitates after heat treatment, which means that L1 and L6 alloys are $\sigma$-prone alloys, but the formation of $\sigma$ phase are affected not only by the component element and composition of the alloys but also by the processing method. In addition, the $\sigma$ phase will not form when the PSFE, VEC, and $\delta$ values fail to simultaneously reach the criterion for forming $\sigma$ phase, such as the L2, L52, L60, L65, L70, and L95-98 HEAs. The parameter calculation results show that $\sigma$ phase might form in L3-L5 (AlTiCr$_2$FeNiCu) alloys, but actually they are $\sigma$-free. Careful inspection of microstructures demonstrates that with the change of Cr content, the Cu content of the Cu-rich phase between dendrites varies from 76.6 to 77.9 at% in L3-L5 [36]. Taking the AlTiCr$_2$FeNiCu HEAs (L5) as an example, the theoretical copper content of the
alloy is 14.3at%, for the positive \( \Delta H \) values between Cu and other elements, a small amount of Cu exists in primary dendrites with solid solution structure, and substantial Cu elements segregate in the interdendritic region. This fact of serious segregation is not taken into account during the calculation of the VEC value, because of the higher VEC value of copper element (\( \text{VEC}_{\text{Cu}} = 11 \)), the theoretically calculated VEC values are higher than the actual values, it affects the judgment of the phase structure as a result.

Moreover, it is noteworthy that most of the CoCrFeNi based HEAs containing Al and Mo are prone to form \( \sigma \) phase, it indicates that the alloying of Al and Mo elements can improve the formation of \( \sigma \) phase.

Figure 5. Micro-hardness of CoCrFeNi HEAs after heat treatment.

Figure 6. Relationship between \( \sigma \) phase and \( \delta \), VEC, PSFE values in multi-component alloys. (a) \( \delta - \text{VEC} - \text{PSFE} \), (b) VEC - PSFE, (c) \( \delta - \text{PSFE} \), (d) \( \delta - \text{VEC} \).
Therefore, when the PSFE-VEC-δ criterion is used, the following factors should be comprehensively considered: (1) the synergy of the three parameters; (2) the serious segregation and phase separation occurred during the solidification process, which will cause the difference between the actually VEC and PSFE values and the theoretically calculated values, and result in the invalid of the σ-forming criterion; (3) Some alloys are σ-free in the as-cast state, but σ-prone after heat treatment, so the preparation processing method and state of the alloy should be considered. (4) Alloying is another noticeable factor that affects the formation of σ phase.

3. Conclusions

(1) Changing the amount of Co, Cr, and Fe has no obvious effect on the FCC solid solution structure of the as-cast CoCrFeNi HEAs and no σ phase was formed. Moreover, CoCrFeNi HEAs show excellent structure stability after short-term annealing at intermediate temperatures of 600 °C—800 °C or 50% of compression deformation at room temperature.

(2) The as-cast CoCrFeNi HEAs can’t be strengthened by the way of heat-treatment, while the as-deformed CoCrFeNi HEAs were strengthened dramatically. It shows that deformation is an effective way to strengthen the CoCrFeNi HEAs.

(3) The formation of σ phase in HEAs can be predicted by using the parameters of δ, VEC and PSFE, among which the PSFE plays a crucial role. When the PSFE value is higher than 40 at.%, 6.75 ≤ VEC ≤ 7.86, and 4.0 ≤ δ ≤ 7.2, σ phase is favored in HEAs.

(4) It is noteworthy that alloying and processing route are noticeable factors that affects the formation of σ phase in the CoCrFeNi based HEAs.

Appendix table: the calculated parameters of high-entropy alloys

| NO. | High entropy alloys | PSFE (at.%%) | VEC | δ | Phase structure | Preparation |
|-----|---------------------|-------------|-----|---|----------------|------------|
| L1  | Al0.5CrFe1.5MnNi1.5 | 47          | 7.19 | 6.18 | BCC + B2 | TIG overlay |
| L2  | Al0.4CoCrFeNi      | 50          | 6.75 | 6.63 | BCC + FCC | Arc melting |
| L3  | AlCrFeNiCuTi       | 54          | 6.92 | 6.97 | BCC + FCC | Arc melting |
| L4  | AlCrFeNiCuTi       | 57          | 6.86 | 6.86 | BCC + FCC | Arc melting |
| L5  | AlCrFeNiCuTi       | 57          | 7.25 | 6.69 | BCC + FCC | Arc melting |
| L6  | AlCoCrFeNi         | 33          | 7.3  | 3.82 | BCC + FCC | Arc melting |
| L7  | AlCoCrFeMoNi       | 46          | 6.46 | 6.39 | BCC+1+BCC+2+σ | Arc melting |
| L8  | AlCoCrFeMoNi       | 75          | 7.53 | 3.35 | FCC+σ+BCC | Arc melting+700 °C 20 h ageing |
| L9  | AlCoCrFeMoNi       | 63          | 7.2  | 5.9  | BCC+1+BCC+2+σ | Arc melting+700 °C 20 h ageing |
| L10 | AlCoCrFeMoNi       | 62          | 7.77 | 4.02 | BCC+1+BCC+2+σ | Arc melting |
| L11 | AlCoCrFeMoNi       | 53          | 7.95 | 4.06 | BCC+1+BCC+2+σ | Arc melting |
| L12 | AlCoCrFeMoNi       | 57          | 8.76 | 4.03 | BCC+1+BCC+2+σ | Arc melting |
| L13 | AlCoCrFeMoNi       | 60          | 7.5  | 4.79 | FCC+σ | Arc melting |
| L14 | AlCoCrFeMoNi       | 40          | 7.13 | 6.71 | BCC+1+BCC+2+σ | Arc melting |
| L15 | AlCoCrFeMoNi       | 44          | 7.7  | 6.87 | BCC+σ | Arc melting+700 °C 12 h ageing |
| L16 | AlCoCrFeMoNi       | 60          | 6.9  | 5.82 | BCC+σ | Arc melting |
| L17 | AlCoCrFeMoNi       | 60          | 6.95 | 6.76 | σ | Arc melting+700 °C 20 h ageing |
| L18 | AlCoCrFeMoNi       | 50          | 7.25 | 5.5  | BCC+1+BCC+2+σ | Arc melting |
| L19 | AlCoCrFeMoNi       | 46          | 7.38 | 5.35 | BCC+1+BCC+2+σ | Arc melting |
| L20 | AlCoCrFeMoNi       | 62          | 6.92 | 5.35 | BCC+1+BCC+2+σ | Arc melting |
| L21 | AlCoCrFeMoNi       | 59          | 7.02 | 5.74 | BCC+1+BCC+2+σ | Arc melting |
| L22 | AlCoCrFeMoNi       | 46          | 7.23 | 5.43 | BCC+1+BCC+2+σ | Arc melting |
| L23 | AlCoCrFeMoNi       | 54          | 7.09 | 5.66 | BCC+1+BCC+2+σ | Arc melting |
| L24 | AlCoCrFeMoNi       | 60          | 6.8  | 5.82 | BCC+1+BCC+2+σ | Arc melting |
| L25 | AlCoCrFeMoNi       | 64          | 7.02 | 5.61 | BCC+1+BCC+2+σ | Arc melting |
| L26 | AlCoCrFeMoNi       | 67          | 7.59 | 5.59 | BCC+1+BCC+2+σ | Arc melting |
| L27 | AlCoCrFeMoNi       | 62          | 7.23 | 5.47 | BCC+1+BCC+2+σ | Arc melting |
| L28 | AlCoCrFeMoNi       | 57          | 7.43 | 5.35 | BCC+1+BCC+2+σ | Arc melting |
| L29 | AlCoCrFeMoNi       | 40          | 7.16 | 7.2  | BCC+1+BCC+2+σ | Arc melting+1400K500 h ageing |
| L30 | AlCoCrFeMoNi       | 42          | 6.63 | 5.89 | B2+1+FCC+σ | Arc melting |
| L31 | AlCoCrFeMoNi       | 40          | 6.6  | 5.82 | B2+1+FCC+σ | Arc melting |
| L32 | AlCoCrFeMoNi       | 50          | 6.75 | 6.13 | BCC+1+FCC+σ | Arc melting |
| L33 | AlCoCrFeMoNi       | 40          | 7.8  | 4.83 | FCC+σ | Arc melting+700 °C 20 h ageing |
| NO. | High entropy alloys | PSFE (at.%.) | VEC | δ | Phase structure | Preparation |
|-----|---------------------|--------------|-----|---|----------------|-------------|
| 35  | Co,AlCrFeNi3,5  | 50            | 7.92 | 5.19 | FCC + σ | Induction melting |
| 36  | Co,CoCrFeNi        | 80            | 7.8  | 0.32 | FCC + σ | Arc melting +700 ℃ 20 h ageing |
| 37  | CoCrCuFeMn         | 40            | 8.2  | 4.53 | FCC1 + FCC2 + σ | Injection melting |
| 38  | CoCrCuFeMNiTiV      | 50            | 7.5  | 7.2  | BCC + FCC + σ | Arc melting |
| 39  | CoCrFeNiMnMo0.5    | 67            | 8    | 2.82 | FCC + σ | Arc melting |
| 40  | CoCrFeNiMo0.5      | 76            | 7.86 | 3.39 | FCC + σ | Arc melting |
| 41  | CoFeMnNiTi         | 44            | 7.78 | 5.51 | FCC + Laves + σ | Induction melting |
| 42  | CoFeMnNiV          | 40            | 7.8  | 5.23 | FCC + σ | Injection melting |
| 43  | CrFe3.5MnNi0.5     | 50            | 7.5  | 4.47 | FCC + σ | Arc melting |
| 44  | CrFeMnNiTi         | 40            | 7    | 8.94 | FCC + σ + laves | Injection melting |
| 45  | CrFeMnTiW          | 40            | 6    | 6.36 | BCC + σ | Laser cladding |
| 46  | Co3CrFeNi3,5Mo0.5  | 50            | 7.92 | 5.19 | FCC + σ | Arc melting |
| 47  | Co3CrFeNi3,5Mo0.5  | 57            | 7.82 | 5.24 | FCC + σ | Arc melting |
| 48  | Al0.5CoCrCuFeNiTi  | 33            | 7.92 | 5.79 | BCC + B2 + FCC | Arc melting |
| 49  | Al0.5CoCrFeNiTi    | 36            | 7    | 7.19 | BCC + B2 + FCC + Laves | Arc melting |
| 50  | Al0.5CoCrFeNiTi    | 39            | 7.22 | 6.44 | BCC + FCC + Laves | Arc melting |
| 51  | Al0.5CoCrFeNiTi    | 38            | 7.06 | 6.62 | BCC + FCC + Laves | Arc melting |
| 52  | Al0.5CoCrFeNi      | 42            | 6.76 | 7.57 | BCC | Arc melting |
| 53  | Al0.5CoCrFeNi      | 38            | 6.46 | 8.13 | BCC | Arc melting |
| 54  | Al0.5CoCrCuFeNi    | 27            | 6.87 | 6.37 | BCC + B2 + FCC | Sputtering |
| 55  | Al0.5CoCrCuFeNi    | 29            | 7.14 | 6.16 | B2 | Arc melting |
| 56  | Al0.5CoCrFeNi      | 33            | 6.5  | 6.58 | B2 | Arc melting |
| 57  | Al0.5CoCrFeNi      | 29            | 6.14 | 7.23 | B2 + BCC | Laser RSP |
| 58  | Al0.5CoCrFeNi      | 29            | 7.29 | 6.16 | BCC + B2 | Arc melting |
| 59  | Al0.5CoCrFeNi      | 29            | 6    | 6.81 | B2 + FCC | Laser cladding |
| 60  | AlCr0.5CoFeNi0.5V  | 36            | 6.64 | 7.64 | BCC | Arc melting +700 ℃ 20 h ageing |
| 61  | AlCr0.5CoFeNi0.5V  | 40            | 6.8  | 7.94 | BCC | Arc melting +700 ℃ 20 h ageing |
| 62  | AlCoCrCuFeNi      | 33            | 7.83 | 5.2  | B2 + FCC | Arc melting |
| 63  | AlCoCrCuFeNiTi    | 29            | 7.29 | 6.86 | BCC1 + BCC2 + FCC | Arc melting |
| 64  | AlCoCrCuFeNiTi    | 31            | 7.54 | 6.25 | BCC1 + BCC2 + FCC | Arc melting |
| 65  | AlCoCrFeMnNi0.5Ti | 40            | 6.27 | 7.73 | B2 + FCC1 + FCC2 | Arc melting |
| 66  | AlCoCrFeTi        | 33            | 6.67 | 7.32 | BCC1 + BCC2 | Arc melting |
| 67  | AlCoCrFeTi        | 36            | 6.91 | 6.75 | FCC + BCC + Laves | Laser cladding |
| 68  | AlCoCrFeTi        | 25            | 6    | 7.9  | BCC1 + FCC2 + BCC2 | Arc melting |
| 69  | AlCuFeNiTi        | 33            | 7    | 7.08 | BCC1 + FCC2 + BCC2 | Arc melting |
| 70  | AlCuFeNiTi        | 46            | 5.85 | 8.11 | B2 + FCC1 + FCC2 | Arc melting |
| 71  | AlCuFeNiTi        | 33            | 7    | 7.08 | BCC1 + BCC2 + FCC | Arc melting |
| 72  | AlFeNiCuTi0.5      | 36            | 7.27 | 6.54 | BCC1 + BCC2 + FCC | Arc melting |
| 73  | AlCoCrFeNiCu      | 36            | 7.73 | 5.36 | BCC + FCC | Arc melting |
| 74  | AlCoCrFeNiCu      | 18            | 8    | 5.36 | BCC + FCC | Arc melting |
| 75  | AlCoCrFeNiCu      | 36            | 7.82 | 5.31 | BCC + FCC | Arc melting |
| 76  | AlCoCrFeNiCu      | 36            | 7.64 | 5.36 | BCC + FCC | Arc melting |
| 77  | AlCoCrFeNiCu0.5   | 36            | 7.55 | 5.43 | BCC + FCC | Magnetron sputtering |
| 78  | AlCoCrFeNiCu      | 36            | 8.27 | 4.11 | FCC | Arc melting |
| 79  | AlCoCrFeNiCu      | 34            | 8    | 4.85 | BCC + FCC | Arc melting |
| 80  | AlCoCrFeNiCu      | 32            | 7.6  | 5.6  | BCC + FCC | Arc melting |
| 81  | AlCoCrFeNiCu      | 31            | 7.46 | 5.8  | BCC + FCC | Arc melting |
| 82  | AlCoCrFeNiCu      | 29            | 7.26 | 6.03 | BCC + FCC | Arc melting |
| 83  | AlCoCrFeNiCu      | 28            | 7.14 | 6.16 | BCC + FCC | Arc melting |
| 84  | AlCoCrFeNiCu      | 27            | 6.97 | 6.3  | FCC | Arc melting |
| 85  | AlCoCrFeNiCu      | 27            | 6.87 | 6.37 | BCC | Arc melting |
| 86  | AlCoCrFeNiCu      | 26            | 6.71 | 6.46 | BCC | Arc melting |
| 87  | AlCoCrFeNiCu      | 25            | 6.63 | 6.5  | BCC | Arc melting |
| 88  | AlCoCrFeNiCuSi    | 28            | 7.29 | 5.97 | BCC + FCC | Arc melting |
| 89  | AlMnCrFeNiCu      | 33            | 7.5  | 7.2  | FCC | Electrodeposition |
| 90  | AlCoCrFeNTi0.5    | 36            | 6.9  | 6.75 | BCC1 + BCC2 | Injection melting |
| 91  | AlCoCrFeNTi0.5    | 33            | 7.17 | 6.97 | BCC + Cu+Cr | Arc melting |
| 92  | AlCoFeNiCuTi      | 18            | 7.09 | 7.17 | FCC + FCC | Arc melting |
| 93  | Co1,5CrFeMn0.5Ni  | 22            | 8.44 | 3.26 | FCC | Arc melting +700 ℃ 20 h ageing |
| 94  | CoCr4,5FeMn0.5Ni  | 33            | 8.19 | 3.88 | FCC | Arc melting +700 ℃ 20 h ageing |
| 95  | CoCr4,5FeMn0.5Ni  | 55            | 8.06 | 2.38 | FCC | Arc melting +700 ℃ 20 h ageing |
| 96  | CoCrFe3,5Mn0.5Ni  | 44            | 8.33 | 3.29 | FCC | Arc melting +700 ℃ 20 h ageing |
| 97  | CoCrFeNiCu        | 40            | 8.8  | 1.08 | FCC | Arc melting |
(Continued.)

| NO. | High entropy alloys | PSF (at.%) | VEC | δ | Phase structure | Preparation |
|-----|----------------------|------------|-----|---|----------------|-------------|
| 98  | CoCrFeNiMn          | 40         | 8   | 4.18 | FCC            | Arc melting |
| 99  | CoCrFeNiCuTi_{0.5}  | 36         | 8.36 | 4.98 | FCC            | Arc melting |

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