Formation condition of solid solution type high-entropy alloy

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Abstract: Formation condition of high-entropy alloys with solid solution structure was investigated. Seventeen kinds of the high-entropy alloys with different components were prepared, the influencing factors (the comprehensive atomic radius difference δ, the mixing enthalpy ΔH and the mixing entropy ΔS) of phase composition of the alloys were calculated, and the microstructure and phase compositions of alloys were analyzed by using SEM and XRD. The result shows that only the systems with $\delta \leq 2.77$ and $\Delta H \geq -8.8$ kJ/mol will form high entropy alloy with simple solid solution. Otherwise, intermetallic compounds will exist in the alloys. So, selection of the type of element has important effects on microstructure and properties of high entropy alloys.

Key words: high entropy alloy; solid solution; comprehensive atomic radius difference; mixing enthalpy; formation condition

1 Introduction

The design criterion of traditional alloys has been broken by high-entropy alloy developed by YEH et al in 2004 [1]. High-entropy alloys are defined as alloys that have at least five principal elements and the concentration of each element is between 5% and 35% (molar fraction). And high entropy alloys have higher mixing entropy than traditional alloys, $\Delta S_{cons} \geq 1.61R$ (R=8.314 J/(mol·K)). Early studies suggested that, due to the multi-component alloy with a high-entropy of mixing, formation of the intermetallic was inhibited [2,3]. The high-entropy alloys usually formed simple solid-solutions rather than many complex phases. These alloys show great potentials for engineering applications due to their multiple excellent properties, such as high strength, good ductility and outstanding resistances to wear, oxidation and corrosion [4−6]. However, with the deepening of research, other structural phases have been found in many high-entropy alloy systems. WANG et al [7,8] determined that the ordered BCC phase in the widely researched CoCrFeNiCuAl alloy was NiAl intermetallic phase. PI et al [9] found that Fe_2Ti intermetallic compound exists in the AlTiCrFeNiCu alloy. LIN and TSAI [10] discovered the existence of

Al−Ni rich phase in the Al0.5CoCrFeNi alloy. Thus, the conclusion that high-entropy alloys are prone to form simple solid- solutions needs to be revalued. ZHANG et al [11] studied the formation rules of solid-solutions for high-entropy alloys, but did not analyze the microstructure and phases of the selected alloys. However, as previously mentioned, the microstructure and phases of part of the alloy have been redefined. Therefore, the obtained conclusion is incomplete.

In this work, 17 kinds of high-entropy alloys were prepared by vacuum arc-melt casting, and the microstructure and phase composition were observed and analyzed. The conditions for the formation of simple solid solution of high-entropy alloys were investigated, and a theoretical basis for the organization of the high-entropy alloys was provided.

2 Experimental

The purity of all raw elemental metals (Al, Co, Cr, Cu, Fe, Ni, Ti, Mn, V) are above 99.9%. All high-entropy alloys (the nominal composition is equal for each element) were prepared using a vacuum arc melting furnace in a high-purity argon atmosphere. The ingots were remelted four times to improve homogeneity. Alloy rods were cast from the ingots into a copper molds

with 10 mm in diameter.

The structural features of the alloy samples were examined by a D/MAX-rB X-ray diffractometer (XRD) with Cu K_α radiation (λ=0.154 nm). The microstructure was characterized by a Hitachi S−4700 scanning electron microscope (SEM).

3 Results and discussion

Hume-Rothery Rules [12] elaborated the effect of atomic size, crystal structure, valence electron concentration and electronegativity on the formation of solid solution between elements in physical metallurgy. It is hard to form substitutional solid solution between two elements with atom-size difference larger than 15% and electron negativity difference higher than 0.4. However, Table 1 indicates that systems of Co−Cr, Ni−Cr, Ni−Fe do not conform to the Hume-Rothery rules, which shows that the Hume-Rothery rules summed up from two component systems does not fit to multi-component alloy system. For example, CrFeNiCoCu alloy system can form Cr, Fe, Ni, Co multi-component solid solution [8]. Therefore, the formation rules of simple solid solutions for high-entropy alloys should be extended over traditional alloys.

Table 1 Atom-size difference of element pairs [13]

Element	Fe	Cr	Ni	Co	Cu	Al
Fe	−	1.5%	18.25%	7.1%	13.1%	0.63%
Cr	−	−	16.4%	18.7%	13.2%	7.8%
Ni	−	−	−	10.37%	2.7%	12.5%
Co	−	−	−	−	12.5%	12.6%
Cu	−	−	−	−	−	13.7%
Al	−	−	−	−	−	−

According to the classical theory of the phase formation, the atomic radius and mixing enthalpy are selected to study the phase formation law of multi-component alloy. Mixing enthalpy, macroscopic comprehensive reflection of the atomic intrinsic characteristic, reflects atomic binding energy. It is related to the electronegativity, electron density etc, so it is an important factor that affects phase composition of alloys. So does the atomic radius.

Here, the parameter δ (comprehensive atomic radius difference) is adopted to describe the effect of the atom-size difference in multi-component alloys as follows [14]:

$$\delta = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i/\overline{r})^2} \tag{1}$$

where n is the number of the components in an alloy

system, c_i is the molar fraction of the i-th component, r_i is the atomic radius of the i-th component, and

$$\overline{r} = \sum_{i=1}^{n} c_i r_i \quad \text{is the average atomic radius.}$$

Generally speaking, mixing enthalpy of a solid solution includes chemical mixing enthalpy, structure mixing enthalpy and elastic mixing enthalpy. The structure mixing enthalpy can be ignored because of its small value [15], and the elastic mixing enthalpy refers to enthalpy changes caused by the difference of atomic radius. In order to solve problems qualitatively, the elastic mixing enthalpy is ignored.

Here, the chemical mixing enthalpy ΔH_{mix} is determined as [15,16]

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} c_i c_j \tag{2}$$

where Ω_{ij} is the regular melt-interaction parameter between the i-th and the j-th elements, and c_j is the molar fraction of the j-th component.

Ω_{ij} is determined as

$$\Omega_{ij} = 4 \times \Delta H_{AB}^{mix} \tag{3}$$

where ΔH_{AB}^{mix} is the mixing enthalpy of binary liquid alloys based on Miedema model [16].

The corresponding values of δ, ΔH and ΔS of alloy systems are listed in Table 2. It is shown that only systems of CrFeCoNi, CrFeCoNiCu, CrFeCoNiMn have

Table 2 Comprehensive atomic radius and mixing enthalpy

Alloy	δ	$\Delta H_{mix}/$ (kJ·mol^{-1})	$\Delta S_{mix}/$ (J·mol^{-1}·K^{-1})
AlCrFeNi	5.47	−13.25	11.53
TiFeNiAl	6.90	−29.25	11.53
CrFeCoNi	1.03	−3.75	11.53
CrFeCoNiCu	1.09	3.2	13.38
AlCrFeCoNi	5.25	−12.32	13.38
CrFeCoNiMn	0.924	−4.8	13.38
CrFeCoNiTi	6.42	−16.16	13.38
CrFeCoNiV	2.77	−8.8	13.38
AlCrFeNiCu	5.98	−4.64	13.38
AlCrFeCoNiCu	4.82	−4.78	14.90
AlCrFeCoNiMn	4.92	−11.89	14.90
AlCrFeCoNiTi	6.57	−20.44	14.90
AlCrFeCoNiV	5.11	−14.89	14.90
AlCrFeCoNiCuMn	4.32	−5.55	16.18
AlCrFeCoNiCuTi	6.23	−13.80	16.18
AlCrFeCoNiCuV	4.69	−7.76	16.18
AlCrFeCoNiCuMnTiV	5.75	−12.59	18.27

small atomic radius difference and mixing enthalpy, followed by CrFeCoNiV system. Previous work showed that CrFeCoNiCu system can be classified as FCC solid solution alloy and AlCrFeCoNiCu system can be classified as multi-phase alloys with intermetallic compounds [7]. In order to determine the region of the solid solution, the microstructures of CrFeCoNi, CrFeCoNiMn, CrFeCoNiV alloy systems were studied.

Figure 1 shows the XRD pattern and microstructure of CrFeCoNi alloy. It can be seen that only one FCC structured phase exists. Only microsegregation is observed in microstructure, so the alloy forms FCC solid

solution. Figure 2 shows XRD pattern and microstructure of CrFeCoNiMn alloy which is composed of FCC solid solution with dendritic microstructure. Figure 3 shows XRD pattern and microstructure of CrFeCoNiV alloy. It is shown that CrFeCoNiV alloy has very complex phase composition, and there is complex crystal structure phase. The alloy contains coarse gray phase, light-colored matrix phase, and similar eutectic structure. Therefore, CrFeCoNiV alloy does not have a simple phase composition.

To be specified, the quantitative criterion for the formation of simple solid-solutions is $\delta \leq 2.77$ and
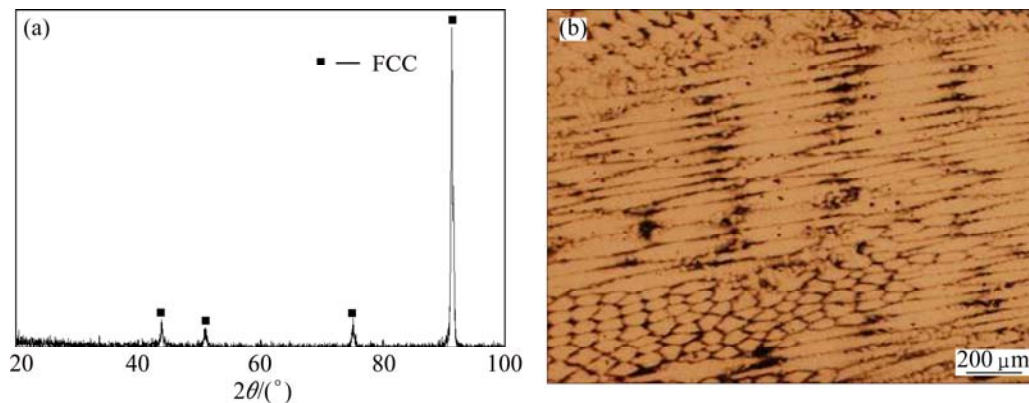

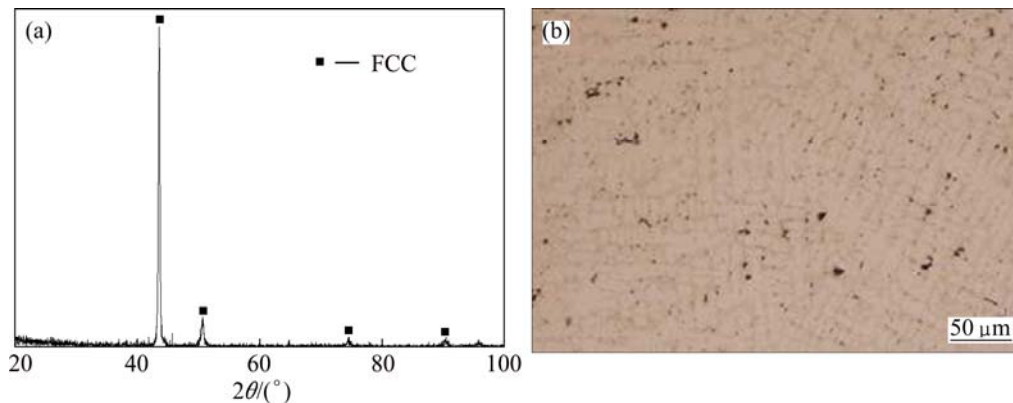**Fig. 1** XRD pattern (a) and SEM microstructure (b) of CrFeCoNi alloy

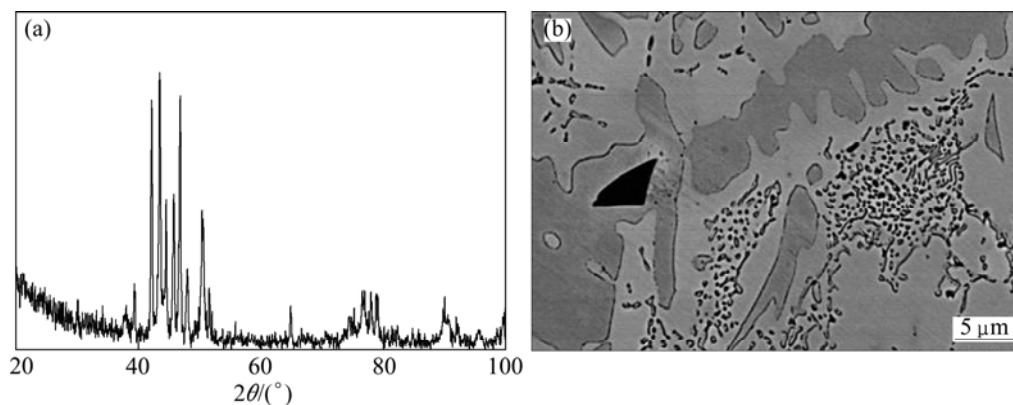**Fig. 2** XRD pattern (a) and SEM microstructure (b) of CrFeCoNiMn alloy

Fig. 3 XRD pattern (a) and SEM microstructure (b) of CrFeCoNiV alloy

$\Delta H \geq -8.8$ kJ/mol. Then we can draw the solid solution forming area, as shown in S zone of Fig. 4. In order to validate forming area of solid solution alloys, the microstructures of AlCrFeCoNiCuMn, AlCrFeCoNiCuV, AlCrFeCoNiCuTi, AlCrFeCoNiCuMnTiV, AlCrFeNi and AlCrFeCoNi alloys are further researched.

For the former four alloys [8], the AlCrFeCoNiCuMn alloy shows the same microstructure as the AlCrFeCoNiCu alloy except for a long-strip Cr-rich phase. Element V does not cause the change of the AlCrFeCoNiCu alloy. Ti added to the AlCrFeCoNiCu alloy changes its microstructure from the
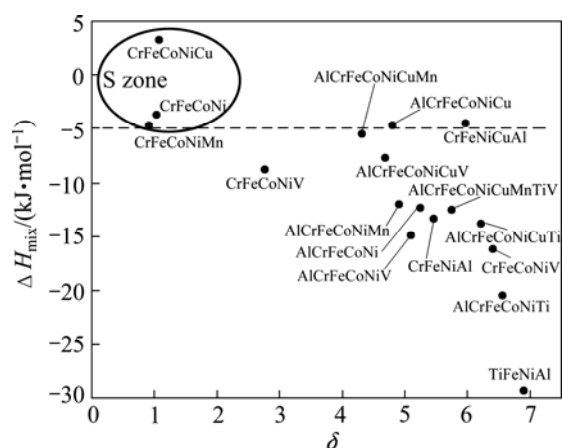

Fig. 4 Location of alloy by comprehensive atomic radius and mixing enthalpy

dendrite to the cellular eutectic. Inside the grains of AlCrFeCoNiCuMnTiV, nanoscale ordered phase and disordered phase are observed. The microstructures of AlCrFeCoNi and AlCrFeNi alloys show ordered NiAl intermetallic compounds, as shown in Figs. 5 and 6.

This shows that additions of equal-molar Mn, Ti and V cannot form solid solution type high entropy alloy, which is consistent with Fig. 4.

Theoretically, congeners (all late transition elements or all first transition elements) can make continuous solution between the elements in liquid, and the mixing enthalpy is close to zero, so change of mixing enthalpy is considered to be very small. In this situation, alloys with high mixing entropy tend to form a disordered solid solution, but not ordered intermetallic compounds. However, when the system contains both the first and late transition elements, the mixing enthalpy of multi-component alloy will become very negative, the effect of mixing entropy is very small, and phase composition will be more complex. The experimental results also confirm that CrFeCoNiMn, containing the late transition element combination of alloy, is easy to gain solid solution alloy. The addition of first transition element V into the CrFeCoNi alloy will make the microstructure complicated. The above analysis shows that in order to form a solid solution alloy, the type of selected elements is limited, and an arbitrary selection of five kinds of elements cannot form simple solid solution alloy.
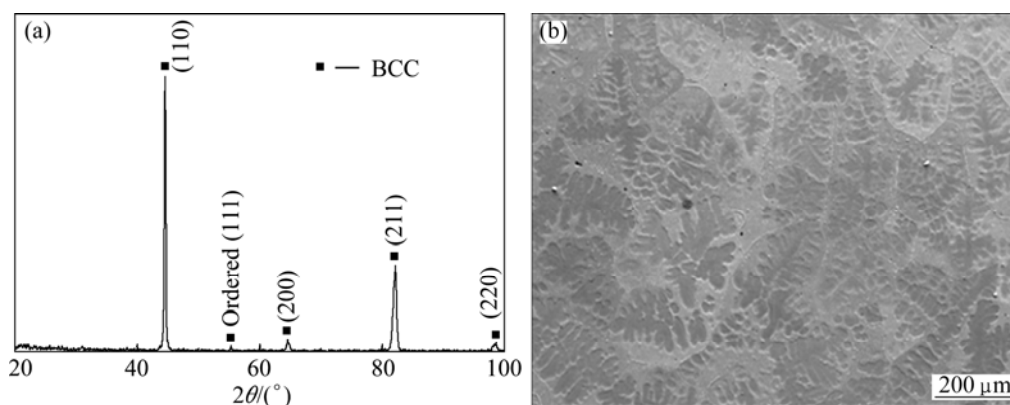

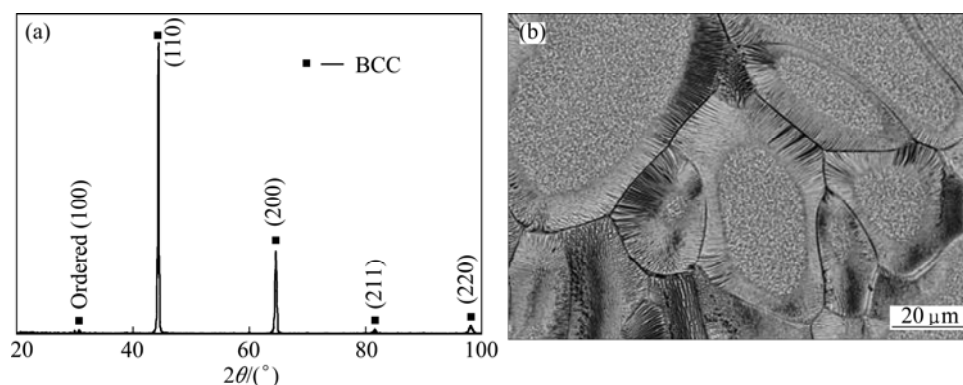**Fig. 5** XRD pattern (a) and SEM microstructure (b) of AlCrFeCoNi alloy

Fig. 6 XRD pattern (a) and SEM microstructure (b) of AlCrFeNi alloy

For the traditional alloy systems, microstructure and property are mainly determined by enthalpy change, because enthalpy change contributes far more than entropy change to free energy. In order to achieve order−disorder transition, it must be requested that the decrease of enthalpy change compensates for the loss of entropy in the system. In the multi-component alloy system, microstructure and property are determined by entropy, when the contribution to the free energy of entropy is much more than that to enthalpy. In fact, this is another form of phase transformation, namely entropy induced phase transition. To form disordered solid solution, the only way to decrease free energy is to increase entropy, because enthalpy contributes little in the phase change processes. However, based on the above research, microstructure and performance of multi-component alloy are mainly determined by the competition between enthalpy and entropy. The microstructure and property of alloy are determined by the entropy, only when the effect of enthalpy change is small in alloy system.

4 Conclusions

1) The formation conditions of solid solution type high entropy alloy are $\delta \leq 2.77$ and $\Delta H \geq -8.8$ kJ/mol in the investigated alloy systems.

2) The microstructure and property are mainly determined by the competition between enthalpy and entropy in multi-component high entropy alloys. Accordingly, selection of elements is of important significance to the structure of high entropy alloys.

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固溶体型高熵合金的形成条件

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摘　要：研究高熵合金形成固溶体型组织的条件。制备 17 种不同成分的高熵合金，计算合金相组成影响因素(综合原子半径差 δ、混合焓ΔH 和混合熵ΔS)，利用 SEM 和 XRD 分析合金的显微组织及相组成。结果表明：只有满足 $\delta \leq 2.77$ 和$\Delta H \geq -8.8$ kJ/mol 的体系，才会形成固溶体型高熵合金，否则合金中出现金属间化合物。选择元素类型对高熵合金的组织结构和性能具有重要影响。

关键词：高熵合金；固溶体；综合原子半径差；混合焓；形成条件

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