Phase structure of multiprincipal component AlCoCuFeMnNi alloy prepared by melting casting

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Abstract. AlCoCuFeMnNi high-entropy alloy was fabricated by noon-consumable arc remelter. The phase structure was investigated by x-ray diffraction, and thermodynamic parameters were discussed through calculation in detail. The results show that AlCoCuFeMnNi alloy has two BCC phase structure. The mixing entropy is 13.38J·mol⁻¹·K⁻¹, the mixing enthalpy is -2.56kJ·mol⁻¹, the atomic radius difference is 0.15, and the Gibbs free energy is -35.73kJ·mol⁻¹. The diffraction broad peaks were mainly due to the lattice distortion owing to the atomic radius of each element difference and inhomogeneous diffusion, the increment of residual stress because of cooling rapidly, the small grain size and wide distribution.

Keywords: high entropy; phase structure; microstructure; mechanical alloying

1. INTRODUCTION
High entropy alloys (HEAs) has broken through the design idea of traditional alloy with one or two main elements, and has been formed by various of alloying elements (≥5) with the nearly equal mole ratio (the mole ratio of each component is in the range of 5at%-35at%) [1]. Because of the high entropy effect, the phase number of this system has far below that the predicted phase number by equilibrium phase, which also has a simple solid solution structure (such as BCC, FCC). At the same time, multi-component high entropy alloys have many excellent performance, such as wear resistance and corrosion resistance such as high strength, high hardness, good resistance to high temperature oxidation [2-4], which may open the door of traditional metal materials limit and meet higher demand for materials in the development of industrial technology.

Yeh[1] reported AlxCrCuFeNi solid solution alloy had a simple solid solution structure and some excellent properties, and for the first time put forward the concept of high-entropy alloy. And then high-entropy alloy was quickly research focus [5-14], such as alloy microstructure, mechanical properties, corrosion resistance, thermal stability and magnetic properties, and the effect of changes in the proportion of elements and doping and aging on structure and properties. There are relatively few reports on AlCoCuFeMnNi high entropy alloys. In recent years, the mechanical properties of high entropy alloys were studied widely and deeply, and the components of high entropy alloys were focused on Fe, Co, Cr, Ni, Ti, V, Cu and Al. But there were so few of papers reporting to the other components, such as Mn. In this paper, multiprincipal component AlCoCuFeMnNi high entropy alloy was prepared by melting casting method. The phase structure and thermodynamic parameters were discussed in detail. These results will help to provide theoretical guidance of subsequent research for high entropy alloy.

2. EXPERIMENTAL
AlCoCuFeMnNi high-entropy alloy was fabricated by noon-consumable arc remelter. The pure metals of Al, Co, Cu, Fe, Ni and Mn with 200 mesh size and higher purity than 99.5wt% were used as raw materials. The above metal powders having equal molar ratio were mixed by ball milling, compacted, and prepared using WK type non-consumable arc melting furnace under argon environment. The alloy ingot was smelted five times in order to obtain uniform composition. The cast ingot was cut into 10mm*10mm*5mm block samples by DK7716
electrical discharge machining (EDM). The crystal structure and phase purity of the synthesized samples were identified by x-ray diffraction (XRD) analysis using an Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation operated at 40kV and 30mA. Diffraction data were recorded range from 30° to 80°.

Results and discussion

Fig.1 XRD pattern of AlCoCuFeMnNi high-entropy alloy

Fig.1 was XRD pattern of AlCoCuFeMnNi high-entropy alloy. Because AlCoCuFeMnNi alloy was no standard powder diffraction card, and the alloy phase was verified by derivation method. According to the Bragg equation [4,15]:

\[ 2d \sin \theta = \lambda \]  

Where \( d \) is the interplanar distance, \( \theta \) is the diffraction angle, and \( \lambda \) is the wavelength of diffraction target. The relationship between \( d \) and interference index was as following:

\[ \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \]  

Where \( a \) is the lattice constant, \( h, k \) and \( l \) are the crystal face indexes. Based on lattice extinction rule:

\[ \sin^2 \theta_1 : \sin^2 \theta_2 : \sin^2 \theta_3 : \sin^2 \theta_4 : \sin^2 \theta_5 : \sin^2 \theta_6 = 3.00 : 4.04 : 8.53 : 11.02 : \]  

Table 1 was the XRD peak data of AlCoCuFeMnNi high-entropy alloy. These peak data were brought into Eq. 4:

\[ 2 \sin \theta = \frac{\lambda}{d} \]  

\[ \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \]  

Compared with the lattice extinction rule, the phase structure was composed by two kinds of BCC phases for AlCoCuFeMnNi high-entropy alloy. The diffraction peaks of BCC1 were belonged to (111), (200), (220) and (311) crystal planes. The diffraction peaks of BCC2 were corresponded to (111), (200), (220), (311) and (222) crystal planes. According to the Gibbs phase law [4,16]:

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \]  

Where \( \Delta G_{\text{mix}} \) is the mixing enthalpy, \( \Delta H_{\text{mix}} \) is the thermodynamic temperature, and \( \Delta S_{\text{mix}} \) is the mixed entropy. From the Eq. 8, the mixing enthalpy and the mixed entropy were two competition factors for the change of the system free energy. There was beneficial to the reduce of system free energy, alloy ordering and segregation trend with the increment of the mixed entropy especially at high temperature, which made the disordered solid solution formed easily compared with the intermetallic compounds during solidification. Based on the Boltzmann hypothesis of the relationship between entropy and system confusion, the alloy mixed entropy \( \Delta S_{\text{mix}} \) can be expressed as [16]:

\[ \Delta S_{\text{mix}} = \frac{1}{N} \sum_{i=1}^{N} S_i \]
\[ \Delta S_{\text{mix}} = -R \sum_{i=1}^{n} c_i \ln c_i \]  
\[ \Delta S_{\text{mix}}^\text{max} = R \ln n \]  
Where \( c_i \) is the mole percent of the \( i \)-th component in the alloy system \( \sum_{i=1}^{n} c_i = 1 \), and \( R \) is the gas constant. When \( c_1 = c_2 = \ldots = c_i \), the mixed entropy can reach the maximum value. The mixing enthalpy \( \Delta H_{\text{mix}} \) can be expressed as [4,16]:

\[ \Delta H_{\text{mix}} = \sum_{i=1}^{n} \Omega_{ij} c_i c_j \]  

\[ \Omega_{ij} = 4 \Delta H_{\text{mix}}^{AB} \]  

Where \( \Omega_{ij} \) is the interaction parameter of component between the \( i \)-th and the \( j \)-th elements, \( \Delta H_{\text{mix}}^{AB} \) is the enthalpy of mixing for the binary equal atomic A-B alloy calculated by the Miedema model[17].

Table 2 Mixed enthalpy between the various elements[17] (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-</td>
<td>-19</td>
<td>-1</td>
<td>-11</td>
<td>-19</td>
<td>-22</td>
</tr>
<tr>
<td>Co</td>
<td>-19</td>
<td>-</td>
<td>6</td>
<td>-5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-1</td>
<td>6</td>
<td>-</td>
<td>13</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Fe</td>
<td>-11</td>
<td>-1</td>
<td>13</td>
<td>-</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Mn</td>
<td>-19</td>
<td>-5</td>
<td>4</td>
<td>0</td>
<td>-</td>
<td>-8</td>
</tr>
<tr>
<td>Ni</td>
<td>-22</td>
<td>0</td>
<td>4</td>
<td>-2</td>
<td>-8</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ \delta = \sqrt{\sum_{i=1}^{n} c_i (1 - \frac{r_i}{\bar{r}})^2} \]  

\[ \bar{r} = \sum_{i=1}^{n} c_i r_i \]  

Where \( r_i \) is the atomic radius of \( i \)-th component, \( \bar{r} \) is the average atomic radius of the alloy components. Table 3 was the element characteristic parameters of AlCoCuFeMnNi alloy. From Eq. 8-14, the mixing entropy is 13.38J·mol⁻¹·K⁻¹, the mixing enthalpy is -2.56kJ·mol⁻¹, the atomic radius difference is 0.15, and the Gibbs free energy is -35.73kJ·mol⁻¹ for AlCoCuFeMnNi high-entropy alloy.

Table 3 Element characteristic parameters of AlCoCrCuFeFe alloy

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting point (°C)</th>
<th>Electronegativity</th>
<th>Atomic radius (nm)</th>
<th>Lattice structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>660</td>
<td>1.61</td>
<td>0.143</td>
<td>FCC</td>
</tr>
<tr>
<td>Co</td>
<td>1495</td>
<td>1.88</td>
<td>0.125</td>
<td>HCP/BCC</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>1.90</td>
<td>0.128</td>
<td>FCC</td>
</tr>
<tr>
<td>Fe</td>
<td>1535</td>
<td>1.83</td>
<td>0.127</td>
<td>BCC/FCC</td>
</tr>
<tr>
<td>Mn</td>
<td>1244</td>
<td>1.55</td>
<td>0.126</td>
<td>BCC</td>
</tr>
<tr>
<td>Ni</td>
<td>1453</td>
<td>1.92</td>
<td>0.125</td>
<td>FCC</td>
</tr>
</tbody>
</table>

In addition, the diffraction peaks of AlCoCuFeMnNi high-entropy alloy were broad peaks. This was mainly due to: (1) the lattice distortion owing to the atomic radius of each element difference; (2) the lattice distortion as a result of inhomogeneous diffusion. The peak intensity decreased and the peak width increased because the degree of crystallinity was reduced with increasing of lattice distortion; (3) the increment of residual stress because of cooling rapidly [18,19]; (4) the small grain size and wide distribution.

CONCLUSION

The phase structure of AlCoCuFeMnNi high-entropy alloy was composed by two kinds of BCC phases. The diffraction peaks of BCC1 were belonged to (111), (200), (220) and (311) crystal planes. The diffraction peaks of BCC2 were corresponded to (111), (200), (220), (311) and (222) crystal planes. The mixing entropy is 13.38J·mol⁻¹·K⁻¹, the mixing enthalpy is -2.56kJ·mol⁻¹, the atomic radius difference is 0.15, and the Gibbs free energy is -35.73kJ·mol⁻¹ for AlCoCuFeMnNi high-entropy alloy. The diffraction broad peaks were mainly due to the lattice distortion owing to the atomic radius of each element difference and inhomogeneous diffusion, the increment of residual stress because of cooling rapidly, the small grain size and wide distribution.

REFERENCES


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