**Microstructural evolution and corrosion behavior of directionally solidified FeCoNiCrAl high entropy alloy**

*Cui Hongbao*, Wang Ying¹, Wang Jinyong¹, Guo Xuefeng¹ and Fu Hengzhi ¹,²

(1. School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China; 2. State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an 710072, China)

**Abstract:** The FeCoNiCrAl alloys have many potential applications in the fields of structural materials, but few attempts were made to characterize the directional solidification of high entropy alloys. In the present research, the microstructure and corrosion behavior of FeCoNiCrAl high entropy alloy have been investigated under directional solidification. The results show that with increasing solidification rate, the interface morphology of the alloy evolves from planar to cellular and dendritic. The electrochemical experiment results demonstrate that the corrosion products of both non-directionally and directionally solidified FeCoNiCrAl alloys appear as rectangular blocks in phases which Cr and Fe are enriched, while Al and Ni are depleted, suggesting that Al and Ni are dissolved into the NaCl solution. Comparison of the potentiodynamic polarization behaviors between the two differently solidified FeCoNiCrAl high entropy alloys in a 3.5%NaCl solution shows that the corrosion resistance of directionally solidified FeCoNiCrAl alloy is superior to that of the non-directionally solidified FeCoNiCrAl alloy.

**Key words:** microstructure; corrosion behavior; directional solidification; FeCoNiCrAl high entropy alloy

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Extensive and rapid development in high entropy alloys has been conducted since the recent years by Yeh and his coworkers[1]. These alloys are defined to have five or more principal metallic elements, with the concentration of each element varying between 5% and 35%. It is generally found that high entropy alloys form simple solid solution structures (rather than many complex phases) at elevated temperatures because of large mixing entropies. The simple crystal structures possess many excellent properties[2], such as easy of nanoprecipitation, high hardness and superior resistance to temper softening, wear, oxidation and corrosion. Among the high-entropy alloys investigated, FeCoNiCrAl is an attractive system that has many potential applications in the fields of structural materials.

Most of previous works [3-5] on FeCoNiCrAl alloys focused on bulk solidification. Few attempts were made to characterize the directional solidification of high entropy alloys. Directional solidification (DS) is a technology used for crystal growth, which allows precise control of the temperature gradient and growth rate to keep the solidification interface macroscopically planar and eliminate lateral grain boundaries. Moreover, the decrease in grain boundaries could be advantageous in improving corrosion resistance. In this paper, the influence of directional solidification on microstructure evolution of FeCoNiCrAl high entropy alloys has been studied at a constant temperature gradient over a wide range of growth rates. The corrosion behavior of directionally solidified FeCoNiCrAl high entropy alloys has also been investigated.

1 Materials and experimental procedure

1.1 Alloy preparation

The high purity (99.99%) Fe, Co, Ni, Al, and Fe-60wt.%Cr intermediate alloy were melted in an arc induction melting furnace under an atmosphere of argon to prepare the FeCoNiCrAl high entropy alloys. The nominal composition (at.%) is listed in Table 1. The as-cast rods were machined into the size of 100 mm in length and 3.8 mm in diameter, and each rod was put into a high purity alumina crucible which is 150 mm in length and 4 mm in inner diameter. Directional solidification experiments were carried out using a Bridgman vertical vacuum induction furnace. A watercooled cylinder containing liquid Ga–In–Sn metal was used to cool down
the specimen. Each specimen was directionally solidified to a constant length using a constant growth rate \( V \) and a constant temperature gradient of \( G = 160 \text{ K} \cdot \text{cm}^{-1} \) at the solid-liquid interface. The temperature gradient \( G \) was measured using two thermocouples placed along the axis of the crucible. The samples were heated and melted by a graphite heater and pulled downwards at different constant growth velocities including 1, 5, 100 and 200 \( \mu \text{m} \cdot \text{s}^{-1} \). After the sample was moved to the pre-set value (position), it was then quenched into the liquid Ga-In-Sn alloy to obtain the interface growth morphology.

### 1.2 Metallography

The alloy specimens were polished both in longitudinal and transverse sections. The polished specimens were etched with aqua regia reagent for microstructures observation under an optical microscope and a scanning electron microscope. The compositions of various phases and microstructural features were determined by microprobe techniques using Oxford Instruments Inca-Energy 250 operated at 15 kV.

### 1.3 Electrochemical measurements

Potentiodynamic polarization measurements were performed in a typical three-electrode cell setup with the specimen as a working electrode, and the other two are a saturated calomel reference electrode (SCE) and a platinum counter electrode. The measurements were conducted in a 3.5% NaCl solution at 25\(^\circ\)C under atmospheric conditions.

### 2 Results and discussion

#### 2.1 Interface morphologies and dendrite structure

In the present work, the morphology variations in the solidification interface of directionally solidified FeCoNiCrAl high entropy alloy were studied after quenching. Microstructures of the longitudinal sections at the various growth rates \( (V) \) are presented in Fig.1. The quenched liquid is ahead of the solid-liquid interface. Two types of interface morphologies have been identified based on the growth pattern of the primary phase. Planar interfaces are observed at the growth rate of 1 \( \mu \text{m} \cdot \text{s}^{-1} \), as shown in Fig.1(a). When the growth rate is increased to 5 \( \mu \text{m} \cdot \text{s}^{-1} \), the planar interface transforms to cellular, where the axes are parallel to each other along the solidification direction. Figure 1(b) shows a longitudinal section through the cellular interface in the vicinity of the grain boundary. A significant shape change in the cell tip region can be found at a growth rate of 5 \( \mu \text{m} \cdot \text{s}^{-1} \), while the dendrite interface morphology appears at growth rate of 100 \( \mu \text{m} \cdot \text{s}^{-1} \) and 200 \( \mu \text{m} \cdot \text{s}^{-1} \), as can be seen in Figs. 1(c) and (d), respectively. It is clear that, at higher growth rates, the developed dendrite grows along the main branch direction smoothly and the growth of side branches of dendrites is suppressed during the directional solidification.

![Fig.1: Longitudinal sections of directionally solidified FeCoNiCrAl high entropy alloy with different growth rates (Growth direction from bottom to top)](image)
Figure 2 shows the optical metallographs of transverse microstructures of directionally solidified FeCoNiCrAl high entropy alloy at growth rates of 1 μm·s⁻¹, 5 μm·s⁻¹, 100 μm·s⁻¹ and 200 μm·s⁻¹, respectively. It should be noted that the transverse section morphology shows a steady-state flat interface structure, and lateral grain boundaries can not be found, which is in agreement with the observation of the planar microstructure in the longitudinal optical photomicrograph at 1 μm·s⁻¹, as shown in Fig. 2(a). Figure 2(b) shows cellular transverse microstructure which slightly transitioned into the dendrite microstructure at the growth rate of 5 μm·s⁻¹. When the growth rate is increased to 100 μm·s⁻¹, a dendritic structure with coarse trunks and side-branches can be observed, with a majority of cells preserving regular dendritic morphology. The secondary dendrite arms tend to form around some cells, as shown in the transverse section in Fig.2(c). As the growth rate reaches 200 μm·s⁻¹, the primary phase is in the morphology with thinner trunks and finer secondary arms, typical of well-developed dendrites, as shown in Fig. 2(d).

Figure 2 demonstrates that the microstructure can be in the typical dendritic pattern at different growth rates. The dendrite arm spacing decreases with increasing solidification rate, and the primary dendrite arm spacing (PDAS) becomes smaller. Dynamical studies were carried out to investigate the mechanism of primary arm spacing selection. Figure 3 shows the microstructure evolution in the case of a sudden increase in the growth rate from 1 μm·s⁻¹ to 500 μm·s⁻¹. The unsteady planar interface (region P) first forms a transient cellular structure (region C) which then transforms to a dendritic structure (region D). The primary arm spacing of the transient cells is significantly smaller than the final dendritic spacing. These results indicate that an unstable planar interface first forms a transient cellular structure even in the case of relatively high growth rates at which only dendritic structure is stable. Some cells are required to vanished so that the primary dendrite arm spacing can increase at the given growth rate. But, if a regular array of cells is formed with a cellular spacing close to the primary dendritic arm spacing, then this cellular structure is retained.

2.2 Electrochemical behaviors

Figure 4 presents the microstructures of non-directionally and directionally solidified FeCoNiCrAl alloys. It is clear that no lateral grain boundaries appear in the microstructure of the directionally solidified FeCoNiCrAl alloys between
Fig. 4: Microstructures of non-directionally and directionally solidified FeCoNiCrAl high entropy alloys: (a) non-directionally solidified FeCoNiCrAl alloy; (b) directionally solidified FeCoNiCrAl alloy.

The initial growth interface and quenched interface, while the non-directionally solidified FeCoNiCrAl alloy consists of polygonal grains with intragranular dendritic segregation.

The potentiodynamic polarization curves of the directionally solidified FeCoNiCrAl alloys in a 3.5% NaCl solution are given in Fig. 5 along with the curves of the non-directionally solidified FeCoNiCrAl alloys for comparison. Table 2 summarizes the electrochemical parameters associated with the general corrosion behaviors of the non-directionally and directionally solidified FeCoNiCrAl alloys in the 3.5% NaCl solution. The passivation regions can be clearly observed in both curves. The directionally solidified FeCoNiCrAl alloys have a wider passive region, which signifies higher corrosion and pitting potentials in comparison with those of the non-directionally solidified FeCoNiCrAl alloys. Pitting is a localized attack that causes relatively rapid penetration at small discrete areas. Higher value of $E_{\text{pit}}$ (pitting potential) is associated with an increased resistance to pitting. In the present work, the $E_{\text{pit}}$ value of the directionally solidified FeCoNiCrAl alloy is significantly higher than that of the non-directionally solidified FeCoNiCrAl alloy. These results indicate that directionally solidified FeCoNiCrAl alloy is easier to passivate, leading to better corrosion resistance than the non-directionally solidified FeCoNiCrAl alloy in the 3.5% NaCl solution. Aluminum forms an adsorptive layer of Al(OH)$_3$ on the metal in the NaCl solution by the following mechanism:\(^6\):

$$\text{Al} + 2\text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Al}^{3+} + 2\text{H}_2\text{O} + 3\text{e}^- \quad (1)$$

$$\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \quad (2)$$

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \quad (3)$$

The corrosion produces an Al(OH)$_3$ cover on the metal surface and prevents the invasion of Cl$^-$ in the NaCl solution. Therefore, aluminum can form a more stable passive film with lower passivation current density, broadening the passivation region. The curves and parameters in Fig. 5 and Table 2 demonstrate that the directionally solidified FeCoNiCrAl alloys have a relatively stable passive film with low passivation current density. It is also well known that more lateral grain boundaries exist in the microstructure of non-directionally solidified FeCoNiCrAl alloys, in which the corrosion attacks take place preferentially. Therefore, the FeCoNiCrAl alloys prepared by directional solidification can enhance the stability of passive films.

Figures 6 and 7 present the SEM micrographs of the non-directionally and directionally solidified FeCoNiCrAl alloys in a 3.5% NaCl solution at 25°C.

Table 2: Electrochemical corrosion parameters of non-directionally and directionally solidified FeCoNiCrAl alloys in a 3.5% NaCl solution at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ ($10^{-6}$A·cm$^{-2}$)</th>
<th>$E_{\text{pit}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-directionally solidified FeCoNiCrAl alloy</td>
<td>$-0.52198$</td>
<td>$34.053$</td>
<td>$0.0814$</td>
</tr>
<tr>
<td>Directionally solidified FeCoNiCrAl alloy</td>
<td>$-0.41795$</td>
<td>$4.7769$</td>
<td>$0.1287$</td>
</tr>
</tbody>
</table>

$E_{\text{corr}}$: Corrosion potential; $i_{\text{corr}}$: Corrosion current density; $E_{\text{pit}}$: Pitting potential.
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