Microstructure and Anticorrosion Property of High-Entropy Alloy AlFeNiCrCoTi0.5Vx
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The influence of vanadium element on the microstructure, microhardness, and electrochemical corrosion resistance properties of as-cast AlFeNiCrCoTi0.5Vx (x = 0, 0.5, 1, 1.5, 2) was studied. The microstructures of the alloys with V contents lower than 1.0 are mainly comprised of the simple body-centered cubic (BCC) and face-centered cubic (FCC) composite structures. With V mole ratio increased to 1.5, the FCC structure plays the leading role in the alloys, which enhances the plasticity and toughness of the alloys. The microhardness of the alloys increased with the increasing of V content in the alloys. Cr, Ni, Ti, and Al elements in the alloys facilitate passivation in 3.5 M NaCl solution. V element mainly enriched in interdendritic region of the alloys, which alters the distribution of Cr and Ti. Cr and Ti is benefit to the passivation, which enlarges the corrosion potential of the alloys and lowers the passive current. Consequently, the alloys present a protective effect in 3.5 M NaCl solution.

Keywords: high-entropy alloy, microstructure, hardness, anti-corrosion

1. Introduction

Multi-element high-entropy alloys are composed of at least five major elements. Each constituent element can be considered as a solute atom with high hybrid entropy. Under the as-cast condition, a simple FCC (face-centered cubic) or BCC (body-centered cubic) solid solution, nanocrystalline structure, and even amorphism can be formed. These structures contribute to high strength, wear and corrosion resistance, excellent thermodynamic stability, and other outstanding performances of the alloys. Typical high-entropy alloy systems and compositions, such as CuTiVFeNiZr, AlTiVFeNiZr, MoTiVFeNiZr, CuTiVFeNiZrCoCr, AlTiVFeNiZrCoCr, TiVCrAlSi, AlFeNiCrCo, and AlTiVFeNiZrCoCr, were studied in many works. Notably, the constituent elements of these high-entropy alloys principally derive from transition metals, along with Al and Si. The phase constitution of high-entropy alloys can be preliminarily understood with the aid of existing phase diagrams. For example, in the Cr–Ti–V system, V and Cr form a continuous BCC solid solution at high temperatures. In addition, the binary Al–V, Al–Cr and Al–Ti phase diagrams show the considerably high solubility of Al in V, Cr, and Ti. According to literature, the additions of V and Mo in the TiZr0.5NbCr0.5V and TiZr0.5NbCr0.5Mo alloys refine dendrites. V and Mo can also significantly decrease the grain size in Fe-based steel. Ti, Cr, Al, V, and other similar elements exhibit strong passivation abilities that facilitate the formation of oxide films with densely packed structures. Consequently, the chloridion cannot easily penetrate through. Thus, high-entropy alloys containing Ti, Cr, Al, and V possess the potential to resist pitting corrosion in an environment containing chloride ions. Moreover, V plays an important role in the microstructure and corrosion-resistant property of such high-entropy alloys. In this study, high-entropy alloys AlFeNiCrCoTi0.5Vx (x = 0, 0.5, 1, 1.5, 2) were prepared by the vacuum arc melting method. Then, the influence of V on the as-cast microstructure, phase composition, composition segregation, and anti-corrosion property of the alloys was explored systematically.

2. Experimental Processes

High-purity (99.9%) Al, Co, Cr, Fe, Ni, Ti, and V (China Material Technology Co., Ltd.) were selected as raw materials for the fabrication of the experimental alloy. The average particle size of the materials used was 200 to 325 mesh. After Moore proportional weighing and performing, the alloy samples AlFeNiCrCoTi0.5Vx (x = 0, 0.5, 1, 1.5, 2) were prepared by adopting a vacuum arc melting method under a high-purity argon shield. Metallographic observation was performed under optical microscopy (OM; XJL-02A), whereas the micromorphology was studied through scanning electron microscopy (SEM; KYKY-2800B). The compositions of the alloy samples were tested by energy-dispersive X-ray spectroscopy (EDS; Quantax). Phase analysis was carried out through X-ray diffraction (D/MAX2500PC, 2θ –100°, 8’/min). The microhardness of the samples was measured by an FM-700/SVDM4R microhardness tester under 100 g of load. The corrosion resistance of the samples was tested by an LFK2005 electrochemical workstation in 3.5 M NaCl solution (scanning speed: 0.002 V/s; potential scan range: –2.0 V to +1.5 V).

3. Results and Discussions

3.1 Influence of increasing V content on metallographic morphology

Figure 1 shows the microstructures of the as-cast AlFeNiCrCoTi0.5Vx alloys with five different V contents observed by OM. All of the alloys exhibited a dendritic microstructure, with dendrite size and morphology varying from one alloy to another with increased V content. The dendritic region mainly presents an irregular block morphology and aggregation (Fig. 1(a)). The interdendritic region distributes at the border of the dendrite phase continuously. With the increasing of V content, the morphology of the dendritic region...
changes from discontinuous columnar crystal ($x = 0$) to chrysanthemum shape ($x = 0.5, 1.0, 1.5$), then to fish-bone structure ($x = 2.0$). When the V content is increased to 1.5, the dendritic region presents a chrysanthemum shape. The area of the interdendritic region decreases, and its morphology changes from continuous to discontinuous. When the V content is increased to 2.0, the dendritic region assumes a fish-bone structure (Fig. 1(e)).

### 3.2 Influence of different V contents on the phase structure of AlFeNiCrCoTi$_{0.5}$V$_x$

The XRD diffraction spectra of as-cast AlFeNiCrCoTi$_{0.5}$V$_x$ with different V contents are shown in Fig. 2. The V$_0$ alloy is mainly composed of FCC and BCC structure phases. A minor $\sigma$ phase can also be found in V$_0$ alloy. Upon the addition of Al, a BCC structure is produced. According to reference 19), FCC structure has higher atomic packing efficiency than BCC structure, the solid solution of Al will lead to larger lattice strain and higher lattice distortion energy in FCC structure, which promoted the transformation from FCC structure to BCC structure. The V$_{0.5}$ and V$_{1.0}$ alloys shows similar XRD pattern with the V$_0$ alloy, but the diffraction peak intensity of $\sigma$ phase is higher than that of V$_0$ alloy. With increased V content to 1.5, the BCC structure disappeared in the alloy. So the FCC structure becomes the main phase of V$_{1.5}$ alloy. The high hybrid entropy of the alloys is conducive to the reduction of the free energy of the system. In the process of the alloys melting and cooling, the hybrid entropy played a leading role at high temperature, which effectively facilitates the miscibility of alloy elements and promotes the formation of multi-component solution with simple structure.20–23). The V$_{2.0}$ alloys show similar XRD pattern with the V$_{1.5}$ alloy, but its reflections shift to the leftwards slightly. The reflection shift can be attributed to the increment of lattice constant caused by the solid solution of V. As V has similar atomic radius with that of Co, Fe, Cr and other transition metal elements. So the solid solubility of V in the alloy is large. According to Co-V and Fe-V alloy phase diagrams, $\sigma$ phase can exist in a wide composition range of V. So The $\sigma$ phase forms easily with the addition of V element in the alloy. It can be identified as NiCoCr type in V$_0$ and V$_{0.5}$ alloys, Co$_{4.35}$Fe$_{13.47}$V$_{12.2}$ type in V$_{1.0}$, V$_{1.5}$ and V$_{2.0}$ alloys.

### 3.3 Influence of different V contents on the microstructure and micro-area composition of AlFeNiCrCoTi$_{0.5}$V$_x$

Figure 3 shows the SEM backscattered electron images of the as-cast AlFeNiCrCoTi$_{0.5}$V$_x$ alloys. The chemical compositions of the different regions and phases are obtained by EDS and listed in Table 1. The composition is evaluated by EDS. The analyzing spot size is about $2 \times 2 \mu m$ and the measurement regions are marked by arrows in Figs. 3(a)–(e). Fig
Figure 3(a) displays the microstructure of the AlFeNiCrCoTi0.5 alloy, which presents a typical dendrite and interdendrite structure. Through microanalysis, as shown in the micro-area compositions of the alloy series in Table 1, we note that the Al, Ni, Co, and Ti contents in the dendritic region are higher than those in the interdendritic region. By contrast, the Fe content is lower in the dendritic region than in the interdendritic region. The XRD analysis results in Fig. 2 reveal that the main phases in the alloy are FCC and BCC structures, accompanied with minor amounts of $\sigma$ phase. FCC structure has the strongest diffraction peak. It can be identified as AlCo2Ti type and AlFe3 type in the alloys. So the composition of the alloys is quite different from dendritic region to interdendritic region. According to the binary Al–Ni, Al–Co, and Al–Ti phase diagrams, the solubility of Al in Ni, Co, and Ti is substantially high. Moreover, when the Al and Ni or Al and Co contents are approximately equal, the Al-rich B2-BCC phase forms first at high temperature. Therefore, two kinds of BCC structure are found in the AlFeNiCrCoTi0.5 alloy.

With increased V content, Al and Ni segregates among the dendrite crystals. The distribution of Co and Ni are comparatively stable within and among dendrite crystals because the hybrid enthalpy of Co–Ni is relatively lower\(^{24}\). The segregation of V also occurs mainly within dendrite crystals, and the amount of dendrite decreases correspondingly with increased V content. However, after the increase in V content to 2, the dendrite number obviously increases. The content of Al is relatively higher in the presence of V than when no V is added. The Al atom is large and hence exerts a solution strengthening effect on the crystal structures of the other elements. Such phenomenon promotes considerable lattice distortion in the alloy. With the rising V content, the segregation is mainly confined within the dendrite crystal. The V atoms become balanced inside and outside of the dendrite crystal, thereby shrinking the dendrite crystal. After the increase in V content to 2, the additional V atoms will again cause the lattice to generate a larger distortion and consequently, a larger dendrite crystal.

### 3.4 Influence of different V contents on the hardness of AlFeNiCrCoTi0.5V\(_x\)

Figure 4 shows the average microhardness of the alloys with different V contents after 12 repeat measurements. With the increase in V content to 1, the average hardness of the alloy reaches the maximum value. Because of the difference of the atomic radius of V and alloy elements, the increase of V in the alloys leads to lattice distortion. The resistance against dislocation movement also rises. The increase in V content improves alloy hardness. The forming of $\sigma$ phase also increased the microhardness of the alloys. On the other hand, after V content reaches to 1.5, the BCC phase disappeared. Only FCC structure phase plays the leading role in the alloys. So the microhardness of the V1.5 alloy decreased. The large grain size generated also reduces the alloy hardness.

### 3.5 Influence of different V contents on the electrochemical corrosion property of AlFeNiCrCoTi0.5V\(_x\)

Figure 5 shows the Tafel curves of the different V contents of AlFeNiCrCoTi0.5V\(_x\). The Tafel curves of the different V contents of AlFeNiCrCoTi0.5V\(_x\) are shown in Fig. 5. With the increase in V content to 1, the average hardness of the alloy series in Table 1, we note that the Al, Ni, Co, and Ti contents in the dendritic region are higher than those in the interdendritic region. By contrast, the Fe content is lower in the dendritic region than in the interdendritic region. The XRD analysis results in Fig. 2 reveal that the main phases in the alloy are FCC and BCC structures, accompanied with minor amounts of $\sigma$ phase. FCC structure has the strongest diffraction peak. It can be identified as AlCo2Ti type and AlFe3 type in the alloys. So the composition of the alloys is quite different from dendritic region to interdendritic region. According to the binary Al–Ni, Al–Co, and Al–Ti phase diagrams, the solubility of Al in Ni, Co, and Ti is substantially high. Moreover, when the Al and Ni or Al and Co contents are approximately equal, the Al-rich B2-BCC phase forms first at high temperature. Therefore, two kinds of BCC structure are found in the AlFeNiCrCoTi0.5 alloy.

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### Table 1: Micro-area compositions of the AlFeNiCrCoTi0.5V\(_x\) alloy series.

<table>
<thead>
<tr>
<th>Alloy Zone</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Ti0.5</th>
<th>V</th>
</tr>
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<tbody>
<tr>
<td>Nominal</td>
<td>18.18</td>
<td>18.18</td>
<td>18.18</td>
<td>18.18</td>
<td>9.09</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Dendrite</td>
<td>19.95</td>
<td>16.38</td>
<td>22.41</td>
<td>11.28</td>
<td>19.31</td>
<td>10.67</td>
<td>0</td>
</tr>
<tr>
<td>Interdendrite</td>
<td>17.62</td>
<td>20.11</td>
<td>15.68</td>
<td>20.06</td>
<td>15.59</td>
<td>7.10</td>
<td>9.63</td>
</tr>
<tr>
<td>Dendrite</td>
<td>9.37</td>
<td>20.95</td>
<td>13.26</td>
<td>24.10</td>
<td>15.59</td>
<td>7.10</td>
<td>9.63</td>
</tr>
<tr>
<td>Interdendrite</td>
<td>16.65</td>
<td>24.18</td>
<td>15.75</td>
<td>15.66</td>
<td>7.10</td>
<td>9.63</td>
<td></td>
</tr>
<tr>
<td>Nominal</td>
<td>15.38</td>
<td>15.38</td>
<td>15.38</td>
<td>15.38</td>
<td>7.69</td>
<td>15.38</td>
<td></td>
</tr>
<tr>
<td>Dendrite</td>
<td>12.68</td>
<td>16.12</td>
<td>14.69</td>
<td>17.30</td>
<td>13.50</td>
<td>7.89</td>
<td>17.83</td>
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<td>11.13</td>
<td>15.64</td>
<td>17.07</td>
<td>16.22</td>
<td>13.57</td>
<td>9.81</td>
<td>14.76</td>
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<tr>
<td>Interdendrite</td>
<td>11.58</td>
<td>13.81</td>
<td>11.13</td>
<td>29.73</td>
<td>12.22</td>
<td>5.46</td>
<td>20.07</td>
</tr>
<tr>
<td>Dendrite</td>
<td>9.23</td>
<td>16.46</td>
<td>11.14</td>
<td>12.70</td>
<td>12.85</td>
<td>3.98</td>
<td>33.64</td>
</tr>
<tr>
<td>Interdendrite</td>
<td>12.04</td>
<td>10.82</td>
<td>14.40</td>
<td>14.60</td>
<td>12.95</td>
<td>9.10</td>
<td>24.09</td>
</tr>
</tbody>
</table>

The Tafel curves of the different V contents of AlFeNiCrCoTi0.5V\(_x\) are shown in Fig. 5. With the increase in V content to 1, the average hardness of the alloy series in Table 1, we note that the Al, Ni, Co, and Ti contents in the dendritic region are higher than those in the interdendritic region. By contrast, the Fe content is lower in the dendritic region than in the interdendritic region. The XRD analysis results in Fig. 2 reveal that the main phases in the alloy are FCC and BCC structures, accompanied with minor amounts of $\sigma$ phase. FCC structure has the strongest diffraction peak. It can be identified as AlCo2Ti type and AlFe3 type in the alloys. So the composition of the alloys is quite different from dendritic region to interdendritic region. According to the binary Al–Ni, Al–Co, and Al–Ti phase diagrams, the solubility of Al in Ni, Co, and Ti is substantially high. Moreover, when the Al and Ni or Al and Co contents are approximately equal, the Al-rich B2-BCC phase forms first at high temperature. Therefore, two kinds of BCC structure are found in the AlFeNiCrCoTi0.5 alloy.

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3.4 Influence of different V contents on the hardness of AlFeNiCrCoTi0.5V\(_x\)

Figure 4 shows the average microhardness of the alloys with different V contents after 12 repeat measurements. With the increase in V content to 1, the average hardness of the alloy reaches the maximum value. Because of the difference of the atomic radius of V and alloy elements, the increase of V in the alloys leads to lattice distortion. The resistance against dislocation movement also rises. The increase in V content improves alloy hardness. The forming of $\sigma$ phase also increased the microhardness of the alloys. On the other hand, after V content reaches to 1.5, the BCC phase disappeared. Only FCC structure phase plays the leading role in the alloys. So the microhardness of the V1.5 alloy decreased. The large grain size generated also reduces the alloy hardness.

3.5 Influence of different V contents on the electrochemical corrosion property of AlFeNiCrCoTi0.5V\(_x\)

The Tafel curves of the different V contents of the AlFeNiCrCoTi0.5V\(_x\) alloys at 3.5 M NaCl are shown in Fig. 5. With the increase in V content to 1, the passive current relatively decreases, and the corrosion rate becomes slower. The passivation potential range expands with the rise in V, and alloy passivation is generated. As V content further increases, the
passivation range and passivation potential area also augment. The passivation is related to the distribution of Cr, Ni, Ti, and Al elements in the alloys. For AlFeNiCrCoTi0.5Vx alloys, as the V element is added, the relative content of V in the dendritic region is high, which changes the distribution of Cr and Ti dramatically. More Cr and Ti elements were motivated into the interdendritic region. The corrosion resistance of this region was enhanced. So the alloys gain a protective effect. The corrosion potential of the alloys rises and the passive current becomes left shift. The passivation potential effect. The corrosion potential of the alloys rises and the passive current becomes left shift. The passivation potential area also increases. All of these effects lower the corrosion rate of the alloys. In the case of \( x/uni00A0=/uni00A01.5 \), the as-cast alloy sample exhibits many pores, which can accelerate material corrosion. In the case of \( x/uni00A01.5 \), the as-cast alloy sample exhibits many pores, which can accelerate material corrosion. The microstructure of the as-cast sample becomes dense again after the V content increased to 2.

### 4. Conclusion

As-cast AlFeNiCrCoTi0.5V \( x \) high-entropy alloys (\( x=0, 0.5, 1, 1.5, 2 \)) were obtained through vacuum arc melting. Preliminary investigations were performed on the microstructures and structures of the alloys through OM, SEM, and XRD. Studies on the microhardness and corrosion resistance of the alloy were carried out. The investigation found that:

1. The AlFeNiCrCoTi0.5V \( x \) alloy possesses a dendritic microstructure. The alloy microstructure can be refined by adding appropriate amounts of V. Meanwhile, the alloy series exhibits simple BCC and FCC composite structures when the V content is lower than 1.0. After the V content increased to 1.5, BCC structure disappeared. FCC structure became the main phase of the alloys, accompanied with some minor \( \sigma \) phase.

2. The increase of V content in the alloys causes lattice distortion, which increases the resistance against dislocation movement and thereby improves alloy hardness. The formation of \( \sigma \) phase also increased the microhardness of the alloys when the V content is under 1.0 or lower level. After V content reaches to 1.5, only FCC structure phase plays the leading role in the alloys, thereby decreasing the alloy hardness.

3. The distribution of V in the AlFeNiCrCoTi0.5Vx alloys is ununiformed. The relative content of V in the dendritic region is high, which motivated more Cr and Ti diffusing into the interdendritic region. So the interdendritic region contains more Cr and Ti elements than that in V0 alloy. The alloys containing V element gain a protective effect in corrosion environment.

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### Reference