Microstructure and Properties of Coating of FeAlCuCrCoMn High Entropy Alloy Deposited by Direct Current Magnetron Sputtering

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Received: September 8, 2015; Revised: December 22, 2015; Accepted: May 10, 2016

The coatings of FeAlCuCrCoMn high entropy alloy were deposited by direct current magnetron sputtering. The microstructure and the mechanical and corrosion properties of the coatings are investigated. A perfect dense and smooth coating could be obtained. The coatings exhibit single FCC solid solution as increasing deposited time. The thickness of the coatings increases with the increasing deposited time, the biggest thicknesses is 1.788 µm. The hardness and Young’s modulus of the coatings are 17.5 and 186 GPa, respectively. All coatings exhibit better corrosion resistance than the 201 stainless steel in acidic alkali and salt corrosion mediums.

Keywords: High entropy alloy, coating, microstructure, properties, magnetron sputtering

1. Introduction

The conventional alloys generally consist of one principal element associated with a substantial amount of other elements to enhance the properties and processing¹, which differ from the high-entropy alloy (HEA) recently proposed by Yeh et al.²⁻³. HEA is a novel concept for the alloy system that has multiple principal elements with equimolar or near-equimolar ratios in the range of 5-35 at.% When all elements in the alloys have an equal atomic percentage, the configurational entropy of the liquid alloy \( S^L \) will reach its maximum of, \( S^L = -R \sum_{i=1}^{N} x_i \ln x_i \) where \( x_i \) is the concentration of component \( i \), and \( N \) denotes the number of principal components, \( R \) the ideal gas constant, and superscript \( L \) denotes the liquid. At \( N = 5 \), \( S^L = 1.61 R \); which is larger than the corresponding melting entropy \( S^m \) of metallic elements with usual values of 1.1-1.3 \( R \). Due to the high entropy characteristics, this kind of alloys is named as the high-entropy alloys (HEA). If the value of the formation enthalpy for an intermetallic compound \( H^F \) is comparable with the size of \( T S^L \), where \( T \) is the absolute temperature, and the cooling rate is big enough, a disordered solid solution could be present. During the formation of the solid solution, the atoms in the liquid need only minor movement being smaller than atomic radius \( r \). Thus, the formation barrier is small ⁴. In addition, a large value of the configurational entropy of the solid solution \( S^S \approx S^L \) exists, which stabilizes the solid solution, where the superscript \( S \) denotes the solid solution. Note that the solid solution here means that its structure is the same of the structure of a marginal component and all components are located freely at any site in the lattice. Due to the solution hardening effect, the HEA with high hardness offer potential industrial applications, such as tools, molds, dies, high temperature parts where high strength, good wear and oxidation resistances are required. HEA could be obtained by rapid solidification, mechanical alloying, chemical vapor deposition (CVD), physical vapor deposition (PVD) or direct current magnetron sputtering (DCMS) methods.

In recent years, HEA films have been widely studied, such as TiVCrZrHf film⁵, AlCrMoTaTiZr film⁶⁻⁷, etc. Moreover, HEA coatings have been proposed for the potential applications as protective films⁸⁻¹⁰, wear-resistant materials¹¹, corrosion-resistant materials¹², and coatings in communication devices¹³. That is due to their interesting properties, such as high hardness¹⁴, strength¹⁵⁻¹⁶, wear resistance¹⁷⁻¹⁸, and microstructure stability against heat treatment¹⁹⁻²¹.

In previous work²²⁻²³, we have developed the novel HEA alloys (i.e. FeCoNiCu system) with a single FCC crystalline structure, which exhibits good plastic properties with the tensile strain up to 18%. Musil et al. reported the hard and super-hard Zr-Ni-N nanocomposite films with the hardness of 40 GPa²⁴. The similar strengthening effect was also revealed in VN²⁵. Moreover, the addition of other element, such as Al, was found to further improve the thermal stability of the film²⁶⁻²⁷. Based on the above observations, the multicomponent FeAlCuCrCoMn film is expected to possess excellent mechanical properties.

In this contribution, the coatings of FeAlCuCrCoMn HEA are prepared by using direct current magnetron sputtering system at a low depositing temperature. In addition, the microstructure, hardness and Young’ modulus and electrochemical corrosion of the coatings were systematically investigated and discussed.

2. Experimental methods

The FeAlCuCrCoMn HEA was melted for at least 5 times by the arc melting-method under a purified argon gas atmosphere. Then, it was shaped into a disk of 60 mm in diameter and 5 mm in thickness as a target. Table 1 lists the composition of the target and the atomic ratios of each element measured by energy dispersive spectrometry (EDS). Quartz glass wafers were cleaned sequentially in de-ionized (DI)

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water, acetone and DI water, for the following deposition of the coatings of FeAlCuCrCoMn by DC magnetron sputtering in a mixture atmosphere of Ar, the coatings were deposited under a plasma power of 80-150 W, a constant working pressure of 0.9 Pa, the distance between the substrate and the target was set as 75 mm.

The phase structure analysis of the target and the coatings was performed on Rigaku D/max 2500 X-ray diffractometer at 50 KV and 250 mA (XRD, D/Max 2500pc) with the scanning angles ranging from 20 to 90 degree at a scanning rate of 2 degree/min. Both the surface morphology and thickness of the deposited coatings were observed by field-emission scanning electron microscopy (FESEM, JEOLJSM 6700F). The chemical compositions of the coatings were analyzed by EDS. The hardness and Young’s modulus of the coatings were measured by a nanoindenter (XP nanomechanical testing system, MTS Corporation), during which the penetration depths of the indenter was controlled at about 1/10 of the film thickness to avoid substrate effect.

The electrochemical measurement was performed on a V3 Microcomputer-based Electrochemical System, which was controlled by a computer and supported by self-designed software. Electrochemical tests were carried out in 3.5 % NaCl solution, 5% NaOH solution and 10% H2SO4 solution respectively using a classic three-electrode cell with a platinum plate (Pt) as counterelectrode and a Ag/AgCl electrode (+207 mV vs. SHE) as reference. Before testing, the working electrode was cleaned in acetone agitated ultrasonically for 10 min. The exposed area for testing was obtained by doubly coating with epoxy resin (EP 651), leaving an uncovered area of approximately 1 cm2. During the potentiodynamic sweep experiments, the samples were first immersed into the solution for about 20 min to stabilize the open circuit potential. The potentiodynamic curves were measured after the above electrochemical measurements. The corrosion potential $E_{corr}$ and corrosion current density $i_{corr}$ were deduced from these $\log(i)$–$E$ curves by using the CorrView software.

## 3. Results and discussion

Figure 1 shows the X-ray diffraction curve of the target of FeAlCuCrCoMn high-entropy alloy. As indicated, the crystalline structures are composed of a (cubic) phase with the space group of Fm3m (225). Figure 2 illustrates X-ray diffraction curves of the coatings of FeAlCuCrCoMn alloy at different deposited times under 100W plasma power. It can be clearly seen that the coatings exhibit amorphous structure at short deposited time, dramatically different from that of the as-melted HEA target shown in Figure 1. This phenomenon was also observed in the preparation of the coatings of the AlCrSiTiV28, AlCoCrCuNiFe29 and AlCoCrCuNiFe30, the films of AlCoCrCuNiFe31 and AlCrTaTiZr HEA32. The reason that the deposited HEA films were in amorphous state can be explained by the rules proposed by Inoue24, in which the glass-forming ability can be strengthened for multicomponent systems. When deposited time increase further, the structure of the coatings of FeAlCuCrCoMn alloy is single FCC solid solution. When the film is very thin after a short time of deposition, the structure of film is controlled by the substrate, so that film is amorphous similar to the substrate (quartz glass wafers), while the thickness of the film increases to a certain extent, the influence of substrate on film becomes less, hence the film transforms into FCC solid solution structure like the bulk alloy. Figure 3 is XRD patterns of the coatings of FeAlCuCrCoMn alloy under different deposited power at 60 minutes. The results show that the coatings all exhibit single FCC structure.

Figure 4 - Figure 6 show the top-view FESEM images of the FeAlCuCrCoMn HEA. As indicated, the crystalline structures are composed of a (cubic) phase with the space group of Fm3m (225). Figure 2 illustrates X-ray diffraction curves of the coatings of FeAlCuCrCoMn alloy at different deposited times under 100W plasma power. It can be clearly seen that the coatings exhibit amorphous structure at short deposited time, dramatically different from that of the as-melted HEA target shown in Figure 1. This phenomenon was also observed in the preparation of the coatings of the AlCrSiTiV28, AlFeCoNiCuZrV29,30 and AlMoNbSiTaTiVZr HEA31, the films of AlCoCrCuNiFe29 and AlCrTaTiZr HEA32. The reason that the deposited HEA films were in amorphous state can be explained by the rules proposed by Inoue24, in which the glass-forming ability can be strengthened for multicomponent systems. When deposited time increase further, the structure of the coatings of FeAlCuCrCoMn alloy is single FCC solid solution. When the film is very thin after a short time of deposition, the structure of film is controlled by the substrate, so that film is amorphous similar to the substrate (quartz glass wafers), while the thickness of the film increases to a certain extent, the influence of substrate on film becomes less, hence the film transforms into FCC solid solution structure like the bulk alloy. Figure 3 is XRD patterns of the coatings of FeAlCuCrCoMn alloy under different deposited power at 60 minutes. The results show that the coatings all exhibit single FCC structure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>V</th>
<th>Zr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition by EDS</td>
<td>13.96</td>
<td>13.95</td>
<td>13.20</td>
<td>13.83</td>
<td>14.57</td>
<td>15.19</td>
<td>15.31</td>
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Figure 1: X-Ray diffraction curve of the FeAlCuCrCoMn target.

Figure 2: X-Ray diffraction curves of the coatings at different time under 100W plasma power.
Figure 3: X-Ray diffraction curves of the coatings under different plasma power at 60 minutes.

Figure 4: FESEM morphology of the coatings at different times under 80W plasma power. (a) 10 minutes, (b) 20 minutes, (c) 40 minutes, (d) 60 minutes.

Figure 5: FESEM morphology of the coatings at different times under 100W plasma power. (a) 10 minutes, (b) 20 minutes, (c) 40 minutes, (d) 60 minutes.

Figure 6: FESEM morphology of the coatings at different times under 150W plasma power. (a) 10 minutes, (b) 20 minutes, (c) 40 minutes, (d) 60 minutes.

and the size of the particles increases with increasing time, a perfect dense coating can be obtained. However, when the power is 150 W, the particles coarsening obviously, and the dense coating seems to be destructed, the coating surfaces become looser and have more micro-holes. Figure 7 show that the thicknesses of the coatings increase with the increasing time, but the increasing of thickness is slowdown with further increasing of time. It is reason that a spot of oxide film easily formed on the target surface during sputtering due to the good affinity of all the target elements with oxygen, hindering the atoms from sputtering, which is a typical result of target poisoning. The largest thicknesses can reach 1.788 µm.

Figure 7: Thickness of the coatings at different time under 100 W plasma power. (a) 10 min, (b) 20 min, (c) 40 min, (d) 60 min.

Figure 8 plots the hardness and Young’s modulus of the FeAlCuCrCoMn coatings. The results show that the hardness and Young’s modulus of the coatings increase with increasing deposited time, and reach maximum values of 17.5 and 186 GPa, respectively. They are relatively superior to typical coatings of pure metals and alloys, which is mainly caused by the great solid-solution strengthening effect from the addition of a large amount of different-size atoms, and might be due to the perfect dense and smooth.

Figure 9 is the potentiodynamic polarization behaviour of the coatings and 201 stainless steel in sodium chloride, sodium hydroxide solution and sulfuric acid solution respectively. Table 2 is the electrochemical parameters associated with
Figure 8: Hardness and Young’s Modulus of the coatings at different time under 100 W plasma power.

Figure 9: The potentiodynamic polarization curves of the coatings in different corrosion mediums. (a) 3.5 NaCl, (b) 5% NaOH, (c) 10% H$_2$SO$_4$.

Table 2: The electrochemical parameters of the coatings in different corrosion mediums respectively

<table>
<thead>
<tr>
<th></th>
<th>3.5% NaCl</th>
<th></th>
<th>5% NaOH</th>
<th></th>
<th>10% H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{cro}$</td>
<td>$i_{cro}$</td>
<td>$E_{cro}$</td>
<td>$i_{cro}$</td>
<td>$E_{cro}$</td>
</tr>
<tr>
<td>201SS</td>
<td>-948.62</td>
<td>86.627</td>
<td>-1092.4</td>
<td>355.11</td>
<td>-348.25</td>
</tr>
<tr>
<td>100W-10 minutes</td>
<td>-934.43</td>
<td>17.425</td>
<td>-1050.1</td>
<td>15.123</td>
<td>-312.34</td>
</tr>
<tr>
<td>100W-20 minutes</td>
<td>-821.05</td>
<td>14.839</td>
<td>-1071.7</td>
<td>7.7652</td>
<td>-319.99</td>
</tr>
<tr>
<td>100W-40 minutes</td>
<td>-838.93</td>
<td>12.912</td>
<td>-1054.6</td>
<td>34.594</td>
<td>-336.41</td>
</tr>
<tr>
<td>100W-60 minutes</td>
<td>-702.33</td>
<td>2.6651</td>
<td>-1169.7</td>
<td>149.97</td>
<td>-333.93</td>
</tr>
</tbody>
</table>

the general corrosion behaviour of the coatings in different corrosion mediums respectively. The results show that the FeAlCuCrCoMn coatings have a wider passive region in these corrosion mediums, which indicates a tendency of the coatings to passivate. This superior corrosion resistance of the coatings of HEA may be attributed to the fact that there are fine grain and no segregation.

4. Conclusion

The coatings of FeAlCuCrCoMn high-entropy alloy have been deposited successfully using direct current magnetron sputtering. The coatings exhibit amorphous structure for short deposited time, dramatically different from the as-melted HEA target. The coatings exhibit single FCC solid solution as increasing deposited time. The thickness of the coatings increases with the increasing deposited time, the biggest thicknesses is 1.788 μm. a perfect dense and smooth FCC solid solution coating is obtained with the hardness and Young’s modulus up to the maximum values of 17.5 and 186 GPa, respectively. All coatings exhibit better corrosion resistance than the 201 stainless steel in acidic alkali and salt corrosion mediums.

5. Acknowledgements

The authors gratefully acknowledge the financial supports from NNSFC (Grant No. 50571040), National Key Basic Research and Development Program (Grant No.2014CB643306) and National Foundation of Doctoral Station (Grant No. 20100061110019).

6. References


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