Rare Metal Materials and Engineering
Volume 46, Issue 12, December 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(12): 3621-3625.

ARTICLE

Microstructure and Corrosion Properties of Al_xFeCoCrNiCu (x=0.25, 0.5, 1.0) Thin Coatings on Steel Substrates Deposited by Electron Beam Evaporation

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Abstract: High entropy alloy (HEA) thin coatings have been deposited on steel substrate of a mixed alloy power made of high purity elemental aluminium, cobalt, chromium, copper, iron and nickel by electron beam evaporation and effects of the Al content of the coating on its structure, surface morphology and electrical properties were investigated. The results of X-ray diffraction (XRD) show that coatings are typical dendrite and interdendrite structures with different aluminum contents. The coatings' surface chemical components are basically similar to originally designed alloys by electron probe micro-analyzer (EPMA). Atomic force microscopy (AFM) results indicate that the modified surface of all coatings are very smooth and uniform. HEA coatings exhibit wide passive regions$>$700 mV in aqueous solutions of H_2SO_4 and NaCl. A large corrosion potential ($-$129 mV) and a small corrosion current density ($\approx 2.2\times10^{-6}$ A/cm^2) clearly reveals that the corrosion resistance of the $Al_{0.5}$FeCoCrNiCu coating is superior to that of the coatings.

Key words: high-entropy alloy; coating; steel; corrosion resistance

In the last two decades, the design concept of new alloy systems has been conventionally based on an element as major constituent, including Fe-, Mg-, Zr-, Ln-, and FeAl-based alloys [1-3]. In this case, multi-principal elements alloys have been restricted by the traditional metallurgical understanding and engineering practice. Multicomponent high entropy alloys were a new concept in alloy design in which an alloy was defined to have five or more principal metallic elements with the concentration for each one ranges between 5 and 35 at% by Yeh et al. in 1995 [4]. High entropy alloys (HEA) had better stability of the solution due to the contribution of the mixing entropy complexity. To estimate the entropy of metallic alloy formation, Boltzaman's hypothesis can be made and may be calculated from the following equation [5]:

$$\Delta S = -R\ln(\frac{1}{n}) = R\ln(n) \tag{1}$$

where R is the ideal gas constant and n is the number of mixed elements. The multiple element system has been called the HEA because its mixing entropy exceeds that of an ordinary alloy. When n =6, ΔS = 1.79R, which approaches the size of the melting entropy of most intermetallic compounds with structure of a single fcc, a single bcc or fcc and bcc [6,7]. Thus, compared with conventional alloy, literatures have shown that the HEA has novel properties, including good thermal stability, high hardness and strength, wear resistance, oxidation resistance, and corrosion resistance [8-11]. Although a large number of studies have been done about microstructure, there were few studies regarding the coating applications of the HEA. The surface coating technology was an alternative to corrosion protection of steel due to the formation of barrier over the metal surface to block the interaction between metal substrate and electrochemical environment. To overcome the limitations on design and application, therefore HEA coatings Al_xFeCoCrNiCu (x = 0.25, 0.5, 1.0)

Received date: December 14, 2016
Foundation item: National Key Technology Research and Development Program of the Ministry of Science and Technology of China (2013BAC05B03); China Scholarship Council ([2012]3013)

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deposition on steel substrates were investigated using the electron beam evaporation technology. The effects of corrosion resistance of the coatings with different Al contents were also discussed in this study. Meanwhile, taking into account the poor corrosion resistance of steel, so we have taken advantage of excellent corrosion resistance of the HEA to improve corrosion resistance of steel, and this method can increase the life of steel in industrial use.

The present study was focused on the investigation of microstructure and corrosion properties of HEA coatings. Chemical composition, surface roughness, morphology and other electrical properties of the resulting coatings were analyzed using various characterization techniques. The purpose of this investigation was to develop a new method and verify the effect on corrosion properties of HEA coatings.

1 Experiment

The HEA thin coatings were deposited on a steel substrate in a vacuum chamber with a base pressure of 1.2×10^{-3} Pa, using e-beam evaporation method. Al, Fe, Co, Cr, Ni, and Cu with purity larger than 99.99% were used as raw materials for producing the HEA. The Al_xFeCoCrNiCu (x=0.25, 0.5, 1.0) alloys were remelted at least four times to insure that the alloys were well mixed by vacuum arc-smelter. These ingots were used as the precursor in evaporation. Table 1 listed the theoretical compositions of the alloys. All steel substrates were mechanically polished using a series of 240#~1200# SiC grit papers and cleaned in ultrasonic bath containing acetone and deionized water. The source material was evaporated e-beam and steel substrates were maintained at 300 ℃. The accelerating voltage of the e-beam was kept 6 kV and emission current was in the range of 200~250 mA. The chamber was evacuated up to 1×10^{-4} Pa. The substrate was rotated at 20 r/min for uniform deposition of the coating.

The phase structure analysis of the coatings was made by D/max 2500 X-ray diffractometer (XRD) at 50 kV and 250 mA. Scanning ranged from 20° to 80° with a scanning rate of 5°/min. The morphology and chemical composition of alloys were examined with scanning electron microscope (SEM) equipped with electron probe micro-analyzer (EPMA). The surface morphology of the coatings was investigated by atomic force microscopy (AFM). AFM topography images were measured in dry nitrogen atmosphere.

Table 1 Chemical composition of the designed Al_xFeCoCrNiCu (x=0.25, 0.5, 1.0) alloys (wt%)

x	0.25	0.5	1.0
Al	2.28	4.46	8.54
Fe	19.93	18.46	17.67
Co	17.57	19.49	18.65
Cr	21.49	17.18	16.46
Ni	18.88	19.41	16.46
Cu	19.85	21.00	20.11

Potentiodynamic polarization measurements were used in a typical three-electrode cell setup with coated steel as a working electrode, exposed area of 0.6 cm^2, an Ag/AgCl electrode (3 mol/L KCl) as the reference electrode and a platinum sheet as the counter electrode. All electrochemical experiments were carried out in H_2SO_4 and NaCl solutions. The specimens were cathodically polarized at a potential of -0.3 V_{SHE} for 300 s before the test for the purpose of removing surface oxides. The linear polarization measurements were conducted at ±20 mV around its open circuit potential (OCP) by a direct current signal around its open circuit potential at a scan rate of 0.2 mV/s. For comparison, stainless steel (SS 304) was also used in this study.

2 Results and Discussion

2.1 Microstructure of the HEA coating

From XRD analysis, shown in Fig.1, it is found that two main structures have been evidenced fcc solid solution, fcc and bcc solid solution phases with different Al contents which are abbreviated as Al-0.25, Al-0.5 and Al-1.0 coatings. HEA coatings are found to be more or less ordered depending on the samples, which have already been observed for bulk alloys [12,13]. With low contents of aluminum (x=0.25, 0.5), the coatings mainly present only one simple fcc solid-solution structure. As the x value reaches 1.0, an ordered bcc phase (similar to a NiAl structure) appears. The intensity of the diffraction peak decreases with increasing of Al content because the addition of Al induces aberrance of the crystal lattice [14, 15]. Although Al has a fcc structure, it does not help the formation of a fcc solid solution. In addition, the diffusive scattering effect is explained due to larger lattice distortion

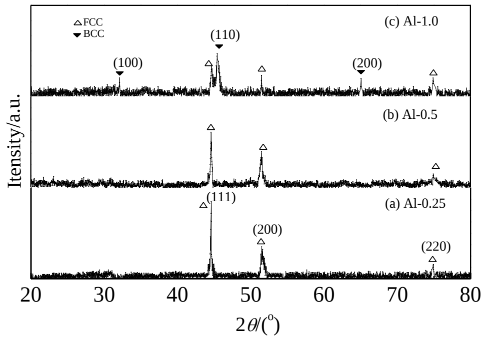


Fig.1 XRD patterns of HEA coatings (Al_xFeCoCrNiCu)

caused by larger amount of larger atomic size of Al into the lattice of small atoms, leading to the formation of one or another crystalline structure.

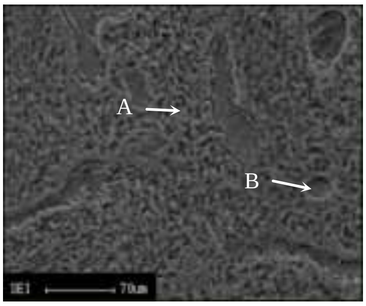
The chemical composition of the $Al_{0.5}$FeCoCrNiCu coating in the dendrite area (labelled A in Fig. 2) and interdendrite area (labelled B in Fig.2) characterized by EPMA are summarized in Fig.2. Typical dendrite and interdendrite structure are observed in the deposited coatings, which are noted to have a similar composition originally designed to the alloy. It is shown that the area A is rich in Fe, Co, Cr and B area is rich in Cu. The relative atomic percentages of Al and Ni elements are slightly rich in area B. However, the segregation of Cu is caused by different Gibbs free energy between every two elements[16]. According to Gibbs free energy described as follows:

$$G_{\rm mix} = H_{\rm mi} - TS_{\rm mi} \qquad (2)$$

a phase with high negative entropy of mixing has a lower Gibbs free energy. Therefore, the positive mixing entropies between Cu-Cr, Cu-Fe are more higher than that between Cu-Al, Cu-Co and Cu-Ni [17].

2.2 Morphology of the HEA coating

Fig. 3 show the AFM micromorphology of HEA coatings. We can observe two different kinds of surface roughness of substrate. Compared Fig. 3a with 3b, it can be obviously found that deposited at a good condition substrate has smooth surface, while the other is poor. The thickness of coatings is more than 100 μm. The other coatings has the same situation as the $Al_{0.5}$FeCoCrNiCu coating, so we do not show the picture here. However, there are still other factors to influence the properties of the coating/substrate system. Furthermore, morphology of the HEA coating would be affected by several factors among which different substrate temperatures are the leading factor in the course of atoms' transportation. And the loose bottom of the coating also decreases the adhesion between coating and substrate.



Region	Al	Co	Cr	Fe	Ni	Cu
A	4.14	19.97	18.76	21.04	17.22	18.87
B	6.61	8.22	7.30	10.00	18.84	49.03

Fig.2 EPMA analysis regions (labelled A, labelled B) and results of the $Al_{0.5}$FeCoCrNiCu coating (wt%)

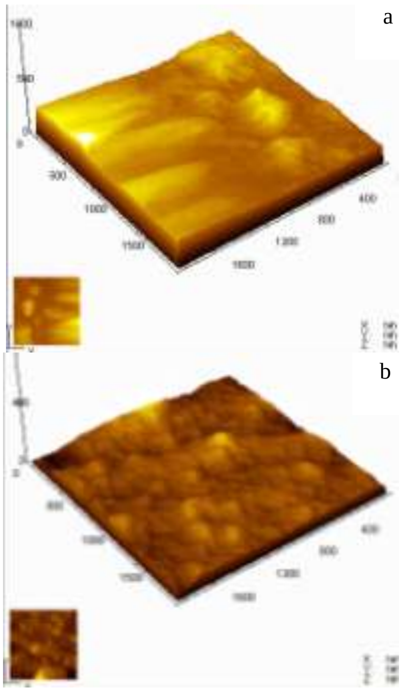


Fig.3 AFM images of the $Al_{0.5}$FeCoCrNiCu coating with different roughness of substrate

2.3 Corrosion-resistance of the HEA coating

Fig. 4 plots the polarization curves for HEA coatings and SS 304 in 0.5 mol/L H_2SO_4 solution at 25 ℃. Meanwhile, Table 2 summarizes relevant data. The curve for SS 304 is also plotted for comparison. The passivation regions can be clearly observed in all curves. HEA coatings have better overall general corrosion behaviour, with a larger E_{corr} and smaller i_{corr} than SS 304. HEA coatings have a wider passive region for the $Al_{0.5}$FeCoCrNiCu coating (750 mV),

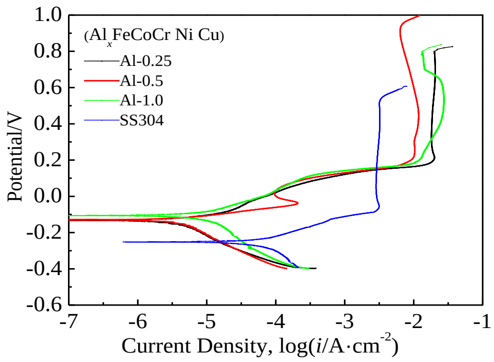


Fig.4 Polarization curves for HEA coatings and SS 304 stainless steel in 0.5 mol/L H_2SO_4 solution

Table 2 Polarization parameters of HEA coatings and SS 304 in 0.5 mol/L H_2SO_4 solution

Parameter	Al-0.25	Al-0.5	Al-1.0	SS304
E_{corr} /mV	-131	-129	-106	-253
i_{corr}/×10^{-6}A·cm^{-2}	2.182	2.185	4.291	0.214
E_{pit} /mV	798	921	796	533

which signifies higher corrosion and pitting potentials in comparison with SS 304. Pitting corrosion is a localized attack that causes relatively rapid penetration at a small discrete area. Higher value of pitting potential was associated with a good ability of resistance to pitting. In the present work, the E_{pit} values of HEA coatings are significantly higher than that of SS 304. Moreover, as the concentration of aluminum increases from 0.25 to 1.0, E_{corr} varied from −131 to −106 mV, while it has a value of −253 mV for SS 304 that is in good agreement with the previous experiment study [18]. Meanwhile, i_{corr} increases to values that are one order of magnitude higher than that observed in SS 304. However, Table 2 indicates that the variation of Al affects the active region of the polarization curves only slightly. These results verify that HEA coatings show better corrosion resistance than SS 304 in the 0.5 mol/L H_2SO_4 solution at 25 ℃.

A cyclic polarization technique was used to determine whether HEA coatings suffered from pitting corrosion in 1 mol/L NaCl solution. Fig.5 plots the cyclic polarization curves of HEA coatings and electrochemical parameters shown in Table 3. The red and blue arrows next to the forward and reverse anodic branches indicate the potential scan directions. The negative hysteresis loop in the reverse scan of the cyclic polarization curve is not susceptible to localized corrosion, and a positive hysteresis loop is related to the amount of pit propagation that occurred during the cycle, according to Wilde [19]. Fig. 5 does not show a classical passive region with the current density totally independent of applied potential. The $Al_{0.25}$FeCoCrNiCu and $Al_{0.5}$FeCoCrNiCu coatings show big area of the positive hysteresis loop in the cyclic polarization curve, indicating that the coatings are resistant to pitting corrosion in 1 mol/L NaCl solution, as can be seen in Fig. 5a and Fig. 5b. However, the small area of the negative hysteresis loop of the cyclic polarization curve demonstrates that pitting of the $Al_{1.0}$FeCoCrNiCu coating could be induced in 1 mol/L NaCl solution, as in Fig. 5c. Table 3 presents the electrochemical parameters of HEA coatings. As the Al content in the coating increases from 0.25 to 1.0, the corrosion potential E_{corr} varies from −262 to −157 mV, the corrosion current densities (i_{corr}) of the $Al_{0.25}$FeCoCrNiCu, $Al_{0.5}$FeCoCrNiCu and $Al_{1.0}$FeCoCrNiCu coatings are 1.672×10^{-7}, 1.716×10^{-7}, and 2.910×10^{-7} A/cm^2, respectively. The repassivation potential of SS 304 is 533 mV more positive than HEA coatings. In this paper, the X-ray diffraction results show that alloy grain boundaries become less and less, which is helpful to decrease intercrystalline corrosion, but the passivation ability has nothing to do with Al content [20]. By comparison with the scan results, it indicates that the $Al_{0.5}$FeCoCrNiCu coating has the most positive effect on the pitting corrosion with a large corrosion potential and a small corrosion current density.

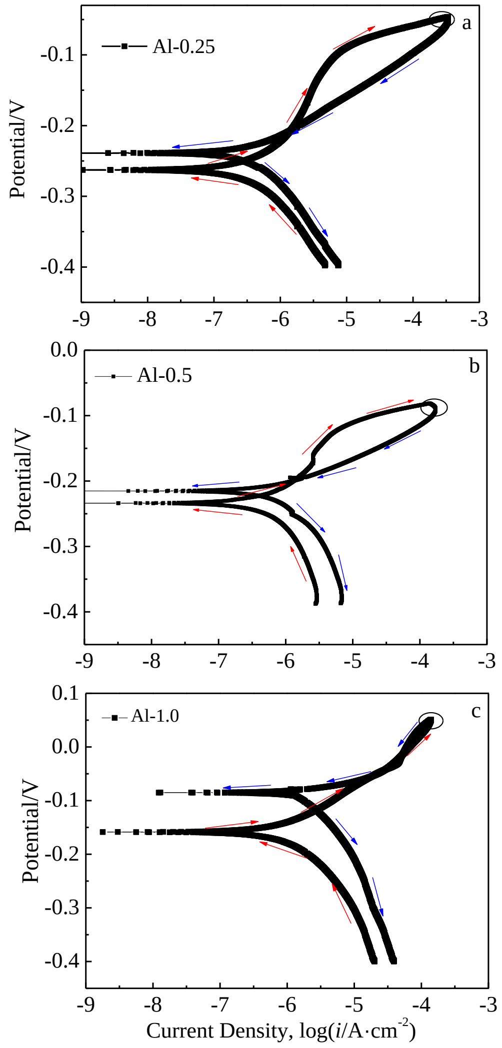


Fig.5 Cyclic polarization curves for $Al_{0.25}$FeCoCrNiCu (a) $Al_{0.5}$FeCoCrNiCu (b), and $Al_{1.0}$FeCoCrNiCu (c) in 1 mol/L NaCl solution

Table 3 Polarization parameters of HEA coatings in 1 mol/L NaCl solution

Parameter	Al-0.25	Al-0.5	Al-1.0
E_{corr}/mV	-262	-234	-157
i_{corr}/×10^{-7}A·cm^{-2}	1.672	1.716	2.910
E_{rp}/mV	-239	-215	-85

3 Conclusions

1) HEA coating consists of typical dendrite and interdendrite structure, which is noted to have a similar composition originally designed to the alloy. HEA coatings exhibit a rather smooth surface composed of uniform and dense grains with increasing roughness of substrate surface.

2) HEA coatings show better corrosion resistance than SS 304 in the 1 mol/L H_2SO_4 solution. The $Al_{0.5}$FeCoCrNiCu alloy coating has the most positive effect on the pitting corrosion with a large corrosion potential and a small corrosion current density in 1 mol/L NaCl solution.

3) The coatings also greatly reduce the risk of pitting corrosion and enhance the corrosion resistance of the steel substrate in the basic and salty environment. This study laid the groundwork for developing a cost-effective method to protect steel for concrete applications.

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电子束蒸发制备高熵合金涂层 Al_xFeCoCrNiCu (x = 0.25, 0.5, 1.0)的微观结构和耐腐蚀性能研究

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摘 要：实验采用电子束蒸发法在钢基体表面制备高熵合金(HEA)涂层，探究不同 Al 元素对微观结构、表面形貌和电化学性能的影响。涂层表面的 X 射线衍射、电子探针和原子力显微镜实验结果表明，不同成分的合金涂层均呈典型的树枝晶结构，组织中仍保持原有的化学组成。涂层表面平整分布均匀，膜层致密。在 0.5 mol/L H_2SO_4 溶液和 1 mol/L NaCl 溶液中，高熵合金的宽钝化区大于 700 mV，具有较大的腐蚀电势−129 mV 和较小的腐蚀电流密度约 2.2×10^{-6} A/cm^2，$Al_{0.5}$FeCoCrNiCu 涂层的耐蚀性最佳。

关键词：高熵合金；涂层；钢筋；耐蚀性

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