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Effects of Ni-P amorphous films on mechanical and corrosion properties of $Al_{0.3}CoCrFeNi$ high-entropy alloys

Z.H. Xia[a], M. Zhang[a,b], Y. Zhang[c], Y. Zhao[d], P.K. Liaw[e], J.W. Qiao[a,b,*]

[a] Research Center for High-entropy Alloys, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China
[b] Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, China
[c] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China
[d] National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing, 100072, China
[e] Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996-2200, USA

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ABSTRACT

Through electroless plating, the $Al_{0.3}CoCrFeNi$ high-entropy alloys were successfully coated with the Ni-P amorphous film with a thickness of 1.2 μm. For studying the surface change of samples after chemical plating, the surface morphologies of the as-cast HEA substrate and HEA with the Ni-P film were contrasted by atomic-force microscopy. The tensile properties of the samples with and without the Ni-P film, and the deformational behavior of thin Ni-P film were researched, respectively. In addition, the effect of the Ni-P amorphous film on corrosion resistance of the coated HEAs was also investigated. The experimental results show that in contrast to the uncoated samples with a yielding strength of 275 MPa, the yielding strength of the coated samples exhibits 400 MPa, with a 45% improvement, which can be attributed to the very high yield strength of the Ni-P amorphous film. A tensile strain up to 10% was achieved in the Ni-P film since the propagation of one primary shear band was inhibited, and the stress/strain concentration was retarded by the plastic substrate. The corrosion resistance of the HEA with the Ni-P film is superior to that of the bare HEA in the 3.5 wt percent NaCl solutions due to the chemical homogeneity and the absence of microscopic defects in the Ni-P amorphous film. The current results indicate that the surface coating is an effective means for optimizing the properties of HEAs, and the thin Ni-P coating can remarkably improve the strength of the present HEAs.

1. Introduction

High-entropy alloys (HEAs), originally based on the novel alloy-design philosophy of mixing five or more elements in equiatomic or near-equiatomic proportions, have proven to be a promising class of materials [1–3]. Massive research has been carried out to study HEAs, and many alloy systems have been developed for their excellent properties [4–6], such as high strength and hardness [7], exceptional ductility and fracture toughness as well as superparamagnetism that provide great potential for various industrial applications [8,9]. According to traditional existing knowledge of physical metallurgy and phase diagrams, multicomponent alloys may be more inclined to develop a great variety of complex and brittle intermetallic phases that are not conductive to analyze and design. However, what is surprising is that the high mixing entropy in these alloys promotes the formation of single body-centered cubic (bcc), face-centered cubic (fcc), or hexagonal close-packed (hcp) solid-solution phases with simple structures and thereby decreases the number of phases, which provide them with many unusual performance [9].

From the mechanical-properties perspective, it is already known that in general, the single-phased bcc-structured HEAs have limited ductility [4,10], while single-phased fcc structured HEAs could have high ductility but their strength is low [11–13]. Therefore, how to fabricate the HEAs with both high strength and high ductility is a challenging topic during its research and development. In recent years, numerous efforts have been devoted to improving the strength of HEAs, and many significant progresses have been made. For instance, after the annealing heat treatment at 750 °C, the yield stress of the $CoCrFeNiNb_{0.25}$ HEAs with good ductility is almost doubled due to the strengthening of a lath-shaped fcc precipitates with nano basket-weaves microstructures [14]. The eutectic $CoCrFeNiNb_{0.5}$ HEAs, composed of a ductile fcc phase and a hard Laves phase and prepared by He et al. [15] on the basis of the computer-aided thermodynamic calculations, display an unprecedented combination of the compressive fracture strength and strain up to 2300 MPa and 23.6%, respectively. Meanwhile, by decreasing the Mo and W contents to 0.8 in the $Co_2Mo_xNi_2VW_x$ alloy,

* Corresponding author. Research Center for High-entropy Alloys, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China.
E-mail address: qiaojunwei@tyut.edu.cn (J.W. Qiao).

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Jiang et al. [16] obtained a fully-eutectic HEA that exhibited a high compression strength of 2364 MPa. In addition, Wang et al. [17] employed the cold rolling to break down the as-cast dendrite microstructure of the $Al_{0.25}CoCrFe_{1.25}Ni_{1.25}$ HEAs, and with increasing the thickness reduction from cold rolling, the hardness, yielding strength, and fracture strength increased at the cost of reducing ductility. He et al. [18] also demonstrated that the properties of the fcc-HEA systems could be manipulated using integrated strengthening approaches.

Furthermore, some unique approaches have been utilized to treat as-prepared alloys for optimizing their mechanical properties through surface modification [19,20]. Surface coating, one of surface modifications, is recently considered to be a valid technique to enhance the ductility of metallic glass, owing to the important role of coating in confining the propagation of shear bands [21]. Hence, thin coatings and the corresponding preparation methods should receive enough attention. In the present study, the Ni-P amorphous coating is successfully deposited on the $Al_{0.3}CoCrFeNi$ HEA substrate by electroless plating, and the effects of the Ni-P coating on the mechanical and corrosion properties of substrates have been researched.

2. Experimental

The HEAs, with the nominal composition of $Al_{0.3}CoCrFeNi$, were prepared by arc-melting a mixture of Al, Co, Cr, Fe, and Ni elementary substances with purities greater than 99.9 wt% in a Ti-gettered high purity-argon atmosphere, and re-melting at least four times to ensure homogeneity. The master ingots were, then, drop-casted into a copper mold with a dimension of $85 \times 10 \times 2\,mm^3$. Dog bone-shaped platy tensile samples, with a gauge length of 10 mm and a width of 2 mm, were cut from the as-cast sample using a wire-cut electric-discharge machine. The as-cast HEA samples, used as the substrate, were firstly grinded by fine sandpapers and mechanically-polished to make a relatively-smooth surface, which might contribute to improving the binding strength between the Ni-P coating and HEA substrate. Then, these polished specimens with a final thickness of 1.80 mm were separately washed by ultrasonic cleaning with ethanol and acetone for the purpose of removing the surface grease of the substrate. Prior to chemical plating, the cleaned samples were activated by chemistry.

After the pretreatment, the samples were immersed into the electroless plating solution which consists of the 25 g/l nickel sulfate, 25 g/l sodium hypophosphite, 10 g/l ammonium bifluoride, 4 g/l sodium hydroxide, 20 g/l citric acid, 10 ml/l hydrofluoric acid, and 1 mg/l thiourea. The pH value of the plating solution, which was measured by a PH-100 model pH meter with an accuracy of ± 0.02, was adjusted to 6.0–6.5 with a moderate-aqueous ammonia solution. The temperature of the plating solution was maintained at 80–90 °C during plating. The plating process lasted for 30 min.

Uniaxial tensile tests were carried out on an Instron 5969 material machine at room temperature and with a strain rate of $1 \times 10^{-3}\ s^{-1}$. The coated samples, subjected to different strain, were examined by the scanning-electron microscope (SEM) after tensile tests. In order to measure the thin-film thickness, the cross-sectional microstructure of the coated sample before tensile deformation was also examined by SEM. The phase structures of the HEA substrates and Ni-P films were examined by X-ray diffraction (XRD). Chemical compositions of the coating were determined, using an energy-dispersive spectrometer (EDS). A nano-indentation test was performed to measure the elasticity modulus of the HEA substrate. Atomic force microscopy (AFM) was employed to obtain the surface morphology and average roughness of specimens before and after coating, respectively. The corrosion resistance of the samples with or without the Ni-P film was studied by a CS350 electrochemical-measurement system in a 3.5 wt% NaCl solution at room temperature. The rod samples with a diameter of 3 mm were cut into 5 mm in length and then mechanically polished carefully. For electrochemical testing, the samples were electrically connected to an isolated copper wire and embedded in the epoxy resin so that only the polished surface of the cross-sectional area was exposed in the aqueous solution. The electrochemical measurements were conducted in a three-electrode cell, a saturated calomel electrode was used as the reference electrode and platinum as the counter electrode. Potentiodynamic-polarization curves were obtained with a potential sweep rate of 1 mV/s, when the open-circuit potential became almost steady.

3. Results

During the electroless plating, there are some reactions maintaining the Ni-P codeposition, which is considered as autocatalytic oxidation process. According to the hydrogen free radical theory, the surface nickel atoms coming from HEA substrate act as the reaction catalyst. The first step is that $H_2PO_2^-$ ions are reacted with H_2O molecule to produce hydrogen free-radical in the presence of catalyst and water-bath heating, as shown in Eq. (1). Due to their high energy and chemical activity, then, these free radicals are unstable and liable to have reaction with Ni^{2+} ions in the solution, producing Ni atoms adsorbed on the surface of substrate, as shown in Eq. (2). Meanwhile, as shown in Eq. (3), the $H_2PO_2^-$ ions can also react with hydrogen free radicals to produce the P atoms. It is worth noting that the Ni atoms, provided by Ni-P film rather than HEA substrate, act as the catalyst triggering oxidation reaction of sodium hypophosphite after the substrate was plated with a thin layer of Ni-P alloy, thus promoting the chemical nickel-plating. The main chemical equation during the electroless deposition are as follows:

$$H_2PO_2^- + H_2O \xrightarrow[\text{Heating}]{\text{Ni}} HPO_3^{2-} + 2H\cdot + H^+ \quad (1)$$

$$Ni^{2+} + 2H\cdot \rightarrow Ni + 2H^+ \quad (2)$$

$$H_2PO_2^- + H\cdot \rightarrow H_2O + OH^- + P \quad (3)$$

By Eqs. (2) and (3), which can be well described by a parallel reaction, the codeposition of Ni and P occurs sustainably, and eventually forms a Ni-P coating on the surface of HEA substrate.

3.1. Microstructure of the samples

Fig. 1a shows the sandwich structure consisting of the protecting coating, 1.2-μm-thick Ni-P amorphous film, and $Al_{0.3}CoCrFeNi$ HEA substrate. It can be seen that there is a clear and straight interface between the Ni-P coating and HEA substrate, basically suggesting that the

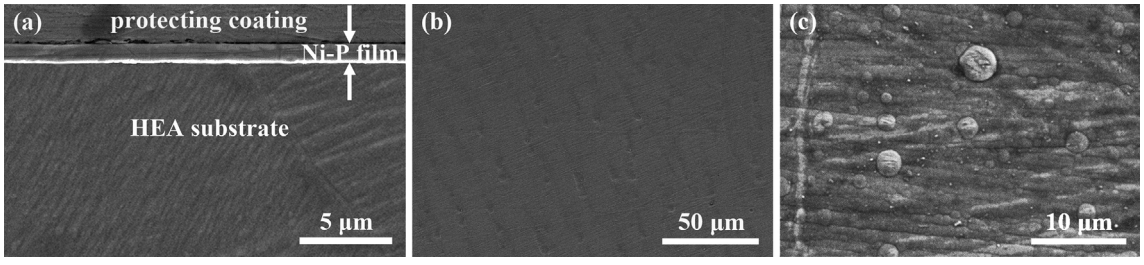

Fig. 1. (a) Cross-sectional SEM images of the HEA substrate with the Ni-P amorphous film. SEM images of the HEA substrate (b) and Ni-P film (c).