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High-throughput synthesis and corrosion behavior of sputter-deposited nanocrystalline $Al_x(CoCrFeNi)_{100-x}$ combinatorial high-entropy alloys



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- High-throughput synthesis of Al_x (CoCrFeNi)_{100-x} high-entropy alloys is achieved.
- The influences of Al on the microstructure and corrosion behavior are evaluated.
- Al_x(CoCrFeNi)_{100-x} thin films possess outstanding corrosion-resistant properties.

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ABSTRACT

High-entropy alloys (HEAs) are inherently complex and potentially span a vast composition space, making their research and discovery challenging. In the present study, high-throughput synthesis of an $Al_x(CoCrFeNi)_{100-x}$ combinatorial material library covering x = 4.5-40 atomic percent Al is achieved, using magnetron cosputtering. The effects of Al on the microstructure and corrosion behavior are investigated. With the increased amount of Al, crystal-structures of thin films transform from face-centered cubic (FCC) to body-centered cubic (BCC). Both the FCC and BCC thin films demonstrate a uniform elemental distribution. Corrosion characteristics of combinatorial samples immersed in the 3.5 wt% (wt%) NaCl solution are evaluated via electrochemical tests. Complementary X-ray photoelectron spectroscopy analysis reveals the compositional variation of passivated films formed on the sample surface after immersion. The results show that the $Al_x(CoCrFeNi)_{100-x}$ HEA thin films possess outstanding corrosion resistance is revealed to be directly related to the constituents of passivated films.

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1. Introduction

High-entropy alloys (HEAs) are novel alloys that combine multiprincipal elements with an equal or near-equal atomic ratio [1,2]. Yeh et al. reported that the inherent high mixing entropy in a multi-

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component metallic system promoted the formation of random solid solutions [face-centered-cubic (FCC)/body-centered-cubic (BCC)/hex-agonal-close-packed (HCP)] rather than intermetallic phases [3,4]. Nonetheless, several studies revealed that the configurational entropy is not the only criterion determining the phase formation, multiphases instead of a single solid solution phase also has been observed [5,6]. Besides unique microstructures, the excellent properties of HEAs including high corrosion resistance [7,8], good mechanical properties [9–12], and thermal stability [13,14] have been extensively investigated.

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The unique composition of HEAs lead to the cocktail effect, as first mentioned by Ranganathan [15], implying that the properties of the alloy can be adjusted by changing the composition or by alloying additional elements. For example, adding Al to the equal atomic FeCoNiCrMn alloy makes the structure transit from FCC to BCC phases. At the same time, the strength increases sharply with the reduced ductility [16].

Many researchers are exploring the impact of alloying elements on the mechanical behavior and corrosion performance of HEAs [3,17–19], which are highly dependent on the phase structure and composition. However, as multi-component systems with near equi-molar elemental rations, HEAs are positioned at the center of the multicomponent phase diagram. Limited prediction is available about the phase formation of HEAs, thus hindering the optimization and development of HEAs by alloy design [20]. The screening of HEAs combinations by standard bulk metallurgical preparation methods is expensive and time consuming. Alternatively, the high-throughput methods for developing material libraries has received great attention. The highthroughput methods provide an efficient way for searching and screening new materials, and more importantly, for optimizing material properties [21,22].

The high-throughput physical vapor deposition (PVD) methodology allows the controllable deposition of compositional gradients of a large range of thin-film materials [23,24]. In the present study, a combinatorial thin-film sputtering technique, which can reduce the alloyprocessing times, is explored for screening the structures and to investigate the corrosion properties of a library of $Al_x(CoCrFeNi)_{100-x}$ HEAs. The $Al_x(CoCrFeNi)_{100-x}$ combinatorial HEAs have been synthesized by magnetron sputtering from pure Al and equiatomic CoCrFeNi targets without substrate rotation. Co-sputtering from two opposite targets creates a one-dimensional gradient in the compositional ratio of Al/ CoCrFeNi along the axis. The composition, structure, and morphology are characterized, using the energy-dispersive X-ray spectroscopy (EDX), grazing-incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The corrosion resistances of the thin films with various Al contents are evaluated using electrochemical measurements. Complementary X-ray photoelectron spectroscopy (XPS) analysis reveals the compositions of the passivated film formed on the thin film after immersion in the 3.5 wt% NaCl solution. Based on the present study, the alloving effect of Al on the structure and corrosion behavior of HEAs can be effectively investigated by applying the high-throughput thin film synthesis methodology.

2. Materials and methods

2.1. Combinatorial deposition

A radio frequency (RF) magnetron sputtering system was used to fabricate the Al-CoCrFeNi combinatorial HEA thin films on Si substrates. The equal-atomic CoCrFeNi target was 50 mm in diameter and 3.5 mm in thickness and was synthesized by vacuum arc melting with high purity (99.99%) raw materials of cobalt, chromium, iron, and nickel. The Al target (with 99.99% purity) was 50 mm in diameter and procured from ACI Alloys Inc. Standard microscope silicon slides with dimensions 3 in \times 1 in (76.2 mm \times 25.4 mm) and with a thickness of about 1 mm were used as substrates. A one-dimensional map revealing various compositions of Al was generated by co-sputtering pure Al and CoCrFeNi targets without substrate rotation. A schematic diagram of the deposition setup is shown in Fig. 1. The pure Al and CoCrFeNi targets were placed 180° apart, with the substrate centered. Target centers were 16.5 cm from the substrate center and were titled at 32° relative to the substrate normal. Co-sputtering from two opposite targets creates one-dimensional gradient in the compositional ratio of Al/CoCrFeNi along that axis. The substrates were divided equally into 10 parts along the compositional gradient, and noted as #1 (Al-depleted) to #10 (Al-rich) HEA thin films, as shown in Fig. 1. The analysis point for each sample was chosen



Fig. 1. Schematic representation of a combinatorial high-throughput high entropy alloy synthesis setup using two individual magnetron sputtering sources, and the top-surface view of the substrate containing the high-entropy alloy library with a constant concentration gradient.

and marked as close to the sample center as possible. Prior to the deposition, the substrate surfaces were cleaned in-situ using an Ar⁺ ion bombardment for 2 min., and the targets were also pre-sputtered for 2 min. to remove any oxidized surface layers. The Al-CoCrFeNi combinatorial films were grown by co-sputtering Al and CoCrFeNi targets at room temperature with an original base pressure of ~4 × 10⁻⁷ Torr and then backfilled with argon atmosphere at a working pressure of 4 mTorr. Based on the sputter yields and predetermined rate data, the RF powers for Al and CoCrFeNi targets were set to 150 W and 200 W, respectively. The film thickness was controlled to be ~ 240 nm based on the sputtering rate of about 4 nm/min.

2.2. Characterization of thin films

The surface morphology of the HEA thin films are examined under the SEM equipped with EDX. The SEM observations are performed in both planar and cross-section views to investigate the microstructure and thickness of the film. EDX was used to perform mapping the element concentrations of high-entropy alloy films across the sample surface. The crystal structure of HEA thin films were examined by GIXRD. The measurements were carried out in a conventional Bragg-Brentano $(\theta - 2\theta)$ geometry with the Cu K α radiation. An offset angle of 2° between the X-ray source and detector was set to minimize the contribution of the substrate. The samples were scanned from 20° to 100° with a resolution of 0.01° per step and a step time of 2 s. For TEM observation, the cross-sectional thin-foil specimen was prepared by focused ion beam (FIB). TEM analysis (bright-field imaging and selected area electron diffraction) for the HEA thin films were conducted with a field-emission transmission electron microscope (JEOL, model JEM-2100F FE-TEM) equipped with the Gatan GIF Quantum®system.

2.3. Electrochemical experiments

The electrochemical measurements were performed using the Potentiostat Workstation (Reference 600^{TM} , Gamry Instruments, Inc., USA) in a conventional three-electrode cell, with a saturated calomel electrode (SCE) as the reference electrode, a platinum sheet as the auxiliary electrode, and specimen as the working electrode. The 3.5 wt% NaCl in H₂O served as electrolytes. Prior to all electrochemical measurements, the specimens were initially reduced potentiostatically at -800 mV vs. SCE for 3 min to remove air-formed oxides on the surface. Then, the working electrode was allowed to corrode freely in the 3.5 wt% NaCl solution at 25 °C for 30 min to reach a quasistatic value of the open circuit potential (OCP). The potentiodynamic-polarization tests were performed at a scan rate of 1 mV/s from an initial potential of - 0.25 V vs. OCP until the current density increased to 1 mA/cm².

2.4. XPS measurements

An X-ray photoelectron spectrometer (XPS, Specs Phoibos 150) with a monochromatic Al anode source was employed to analyze the compositions as a function of depth of the HEA thin films after the immersion of 24 h in the 3.5 wt% NaCl solution. Ar^+ etching is performed at 3 kV acceleration voltages and the sputtering rate was estimated to be about 0.12 nm/s for a SiO₂ standard sample. The obtained spectra were analyzed using the XPS peak 4.1 software, and the peaks were fitted by the mixed Gaussian-Lorentzian functions after the Shirley background subtraction. The identifications of peaks are based on NIST XPS database, and the binding energy (BE) scale was calibrated by shifting the C 1 s peak to 284.5 eV.

3. Results and discussion

3.1. Structure and morphology

The EDX analysis of sample #1 (Al-depleted) to #10 (Al-rich) HEA thin films are shown in Fig. 2(a). It reveals a compositional spread of Al-CoCrFeNi combinatorial library ranging from 4.5 to 40 atomic percent (at.%) of Al as a function of position on a silicon substrate. Fig. 2(a) suggests the presence of a uniform and systematic composition gradient for Al and Co-Cr-Fe-Ni. Since the atomic percents of Co, Cr, Fe, and Ni elements are approximately the same at the same position, the HEA thin films would appropriately be described as $Al_x(CoCrFeNi)_{100-x}$ (x = -4.5-40). The GIXRD patterns of #1 to #10 HEA thin films are presented in Fig. 2(b), which reveals a structure transition from FCC to BCC phases due to the increase of the Al content. Samples #1 to #6 Al_x $(\text{CoCrFeNi})_{100-x}$ (x = ~4.5-16) thin films are single FCC-phase solid solutions with the broad diffraction peaks located at about 43.68°, which represent the (111) peak of the FCC structure. The broad peak is associated with the nano-scale grain size and distortion in the crystal lattice, which is caused by the random occupation of variously-sized atoms on lattice sites. Sample #7 to #10 Al_x(CoCrFeNi)_{100-x} ($x = \sim 23-40$) thin films are single BCC-phase solid solutions with a (110) characteristic peak located at about 44.44°. As can be seen in Fig. 2(b), the diffraction peaks of FCC and BCC structures both shift to low diffraction angles with increasing Al contents. The shift of diffraction peaks to low angels implies the lattice parameter increases with increasing Al addition. This phenomenon might be attributed to the fact that the Al content has a ~ 15% larger atomic radius than the average radius of the other alloy constituents [25]. Therefore, the increase of the Al content leads to a lattice expansion. Meanwhile, the peak intensity decreases with the increase of the Al concentration. The substantially enhanced atomic radius of Al leads to lattice distortion as well as the decrease of crystallinity, thus presenting the decreased peak intensity [26]. The structure transition from FCC to BCC phases with increasing the Al content is reported to be associated with the atom radius as well [14]. The incorporation of Al atoms into the Co-Cr-Fe-Ni FCC lattice increases the lattice distortion whereas the BCC lattice has a lower packing fraction and is more open to accommodate the larger Al atoms. Therefore, the enhancement of the Al content results in the phase transformation of HEA thin films from FCC to BCC structures.

The surface morphologies of the $Al_x(CoCrFeNi)_{100-x}$ thin films were investigated by SEM, and representative images are shown in Fig. 3. The #1 HEA thin film, which possesses an FCC structure, has a relatively-compact column structure with column diameters of about 20 nm. The surface morphology starts to be slowly modified with the increase of the Al content. The number of columns of smaller sizes (less than 10 nm) increases from #1 to #6 HEA thin film. The decrease of the column size with the increase of the Al content in FCC thin films might be related to the latticed distortion induced by the Al addition. The increased lattice distortion results in a large amount of defects including the distorted non-equilibrium boundaries and vacancies [27]. The exceeded volume is favorable to diffusion. Therefore, in the case of #1 to #6 HEA thin films, the higher Al content leads to greater surface diffusivities. Starting at the #7 HEA thin film, which has a BCC crystalstructure, the smaller elongated columns form on the surface. As Al content increases continuously from #7 to #10 HEA thin films, the elongated small columns grow to accumulate to form elliptic columns of larger sizes, as can be seen in #9 and #10 HEA thin films. The SEM results indicate that the column morphology changes are associated with composition of the thin films. However, the elongated columns are typically while thin films grow under shallow angles, so the position of the thin film during sputtering also has an influence on the morphology.

To further provide insight into the morphologies, crystalline structures, and growth modes, cross-sectional morphologies of #2, #6, and #9 HEA thin films were examined by TEM and exhibited in Fig. 4 (a-c). Nano-scaled columnar structures along the growth direction are clearly observed in the TEM bright-field images, which are typical of the deposition by the magnetron-sputtering process. The grain growths begin with thin columns, and the columns remain relatively-cylindrical and slightly broaden out as the film grows. It can be seen that the column width of #2 HEA thin film is about 20–30 nm. With the increase of Al, the column width decreases to 10–20 nm in the #6 HEA thin film, which is consistent with the SEM observation in Fig. 3. Extensive stacking faults can be observed inside the column grains of #2 and #6 samples. With the Al content further increases, the column width



Fig. 2. Chemical compositions and crystal structures of HEA thin films along the Al concentration gradient (Spots #1 to #10): (a) EDX atomic percent versus sample number analysis; (b) GIXRD patterns of diffraction intensity versus diffraction angle 20.



Fig. 3. SEM images of Al_x(CoCrFeNi)_{100-x} thin films along the Al concentration gradient.

increases to 30-40 nm in the #9 HEA thin film, and the columns morphologies change to the oblique cylinders. The alteration of morphology could be influenced by the position, since the #9 thin film with the higher Al content growing under the shallow angle of the incoming flux of Al. The corresponding selected area diffraction (SAD) patterns for the #2, #6, and #9 HEA thin films are shown in Fig. 4(d-f). The SAD patterns in Figs. 4(d) and (e) reveal that the #2 and #6 HEA thin films are consistent with FCC phase with lattice constants of about 0.34 nm and 0.35 nm, respectively. Fig. 4(f) indicates that the #9 HEA thin film is consistent with a BCC structure with lattice constant of about 0.27 nm. The SAD patterns are in good agreement with the results obtained from XRD in Fig. 2(b). Fig. 5 shows the SEM-EDX mappings [Fig. 5(a, b)] from the planar-view and TEM-EDX mappings [Fig. 5(c, d)] from the cross-sectional of the #1 and #10 thin films. As can be seen from Fig. 5(a, b), both the FCC and BCC thin film samples demonstrate a uniform elemental distribution on the surface. The TEM-EDX mapping is conducted to reveal the local composition on a finer scale. As shown in Fig. 5(c, d), all the elements are uniformly distributed. It should be noted that the mixtures of FCC and BCC phases are often reported in bulk HEA materials with an increase of Al content [28,29], whereas mixed structures and elemental separation are not obtained in the present study, combining the XRD, TEM, and EDX results. The mixed structures observed in bulk Al_x(CoCrFeNi)_{100-x} HEAs are accompanied by strong elemental separations. In contrast, the HEA thin films exhibit a relatively-uniform distribution of all elements (Fig. 5). Because of the magnetron arrangement, the fluxes of the five elements closely overlap onto the substrate surface. The energetic atoms quench and condense rapidly $(\sim 10^9 \text{ K/s})$ [30,31], thus, leading to the limited elemental migration during thin film formation. Therefore, in the composition region which FCC and BCC co-exist in the bulk HEAs, the HEA thin films are consist of single solid solution with slightly different lattice parameters and tiny chemical composition variation, indicated by the shifted and asymmetric XRD peaks. Magnetron co-sputtering deposition is thus found to promote the compositional uniformity and hinder the atomic diffusion.

3.2. Corrosion behavior

The potentiodynamic-polarization test is used to characterize the corrosion properties of the HEA thin films. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are calculated by using the Tafel extrapolation method on anodic polarization curves. The corrosion current density can be used to calculate the corrosion rate of metals. The passivation area is a potential domain where a protective oxide film forms to prevent the continual metal dissolution, while the critical pitting potential (E_p) indicates the breakdown of the passivated film. The *I*_{pass} represents the current density in the passivation region, and its value is taken from the potentiodynamic polarization curve in the middle of the passive region. The potentiodynamic polarization curves of the #3 HEA thin film (~ 7 at. % Al) and a bulk Al_{0.3}CoCrFeNi HEA [atom ratios of Al/(CoCrFeNi) is 0.3/(1 + 1 + 1 + 1), ~7 at.% Al], which possess similar compositions, are displayed in Fig. 6(a). Both the bulk Al_{0.3}CoCrFeNi HEA and the thin-film sample exhibit excellent passivation abilities. However, the #3 HEA thin film presents a 0.45 V higher $E_{\rm corr}$, 1.5 V higher $E_{\rm p}$, and smaller $I_{\rm corr}$, implying the better corrosion resistant ability of the HEA thin film.

Fig. 6(b) presents the polarization curves of the #1 to #10 HEA thin films. All the thin-film samples change directly from the Tafel region



Fig. 4. Bright-field TEM images of (a) #2, (b) #6, and (c) #9 HEA thin films, showing columnar grains along the growth direction. Selected area diffraction (SAD) patterns of (d) #2, (e) #6, and (f) #9 HEA thin films.

into the stable passive region. This feature indicates that the protective oxide film is formed spontaneously at the corrosion potential. The electrochemical parameters are given in Table 1. With the increase of Al content, the $E_{\rm corr}$ decreases, whereas the $I_{\rm corr}$ increases, indicating that the general corrosion resistance is weakened. Moreover, at a higher Al

content, the I_{pass} increases and the E_p decreases, revealing that the protection of the oxide layer on the Al rich thin film is inferior to those at lower Al concentration. Fig. 6(c) shows the comparison of the I_{corr} and E_p among HEA thin films, Bulk-HEAs, and other conventional corrosion resistant materials [7]. The HEA thin films in the present study present



Fig. 5. SEM-EDX mappings of #2 (a) and #9 (b) HEA thin films of the planar-view surfaces. Cross-sectional TEM-EDX mappings of #2 (c) and #9 (d) HEA thin films.



Fig. 6. (a) Comparison of the potentiodynamic-polarization curves between the #3 HEA thin film and the Al_{0.3}CoCrFeNi bulk HEA; (b) Polarization curves of the #1 to #10 HEA thin films; (c) Comparison of the corrosion current density (*I*_{corr}) and pitting potential (*E*_p) among HEA thin films, Bulk-HEAs, and other materials in the 3.5 wt% NaCl solution.

 Table 1

 Eletrochemical parameters obtained from the polarization curves of #1 to #10 HEA thin films

| HEA thin films | $E_{\rm corr}({\rm mV}_{\rm SCE})$ | $I_{\rm corr}(\mu A/cm^2)$ | $E_{\rm p}({\rm V}_{\rm SCE})$ | $I_{\rm pass}(\mu {\rm A/cm^2})$ |
|----------------|------------------------------------|----------------------------|--------------------------------|----------------------------------|
| #1 | 306 | 1.01×10^{-3} | 2.12 | $3.76 	imes 10^{-2}$ |
| #2 | 226 | 2.35×10^{-3} | 2.04 | 4.52×10^{-2} |
| #3 | 181 | 2.91×10^{-3} | 1.99 | 5.26×10^{-2} |
| #4 | 164 | 3.36×10^{-3} | 1.93 | 5.47×10^{-2} |
| #5 | 122 | 4.11×10^{-3} | 1.77 | 5.89×10^{-2} |
| #6 | 89 | 5.12×10^{-3} | 1.51 | 7.71×10^{-2} |
| #7 | 33 | 6.27×10^{-3} | 1.31 | 8.95×10^{-2} |
| #8 | 3 | 7.22×10^{-3} | 1.04 | 9.32×10^{-2} |
| #9 | -52 | 9.97×10^{-3} | 0.77 | 1.01×10^{-1} |
| #10 | -171 | 1.05×10^{-2} | 0.61 | 1.25×10^{-1} |

much better performance than the bulk materials do. This novel improvement of corrosion resistant properties for current thin films could be attributed to the nano-crystalline grain size and homogeneous elemental distribution, which can enhance the corrosion resistance by inhibiting the transition of metastable pits to stable pits and retarding the growth process of stable pits [32–35].

In order to investigate further the corrosion resistance of the HEA thin films, the polarization resistance (R_p) of the thin films has been extracted from the voltammetry by the linear polarization resistance (LPR) methodology. The slope of the linear current-potential dependence at the zero current limit is expressed as:

$$R_{\rm p} = \left(\frac{\Delta E}{\Delta i}\right)_{i=0} (\Omega \ {\rm cm}^2) \tag{1}$$

Fig. 7(a) shows an example of the linear current-potential dependence at the zero current limit as expressed in Eq. (1) for anodic and cathodic over-potentials of ± 20 mV: R_p in the LPR method is extracted from the slope of a linear fit to the data. The R_p of #1 to #10 HEA thin films determined by the LPR method is calculated and presented in Fig. 7(b). It revealed that in spite of the crystal-structure of the thin film (FCC or BCC), the polarization resistance decreases continuously with increasing the Al content from #1 to #10 HEA thin films, suggesting that the corrosion resistance is weakened. Since the thin film samples fabricated by magnetron sputtering have relatively smooth surfaces with the surface roughness usually less than 10 nm. The surface roughness differences among the #1 to #10 HEA thin films are not significant enough to influence the corrosion behavior [36]. Therefore, the corrosion properties of the HEA thin films are mainly influenced by the compositions.

3.3. XPS analysis

As indicated in the polarization curves [Fig. 6(b)] of the Al_x (CoCrFeNi)_{100⁻x} HEA thin films, the protective passive film is formed on the surface, and its characteristic is closely related to the corrosion behavior. XPS is used to provide chemical information of the oxide



Fig. 7. (a) Example of linear polarization resistance (LPR) plot from which the polarization resistance (R_p) could be obtained as the fitted slope. The results are presented for the #1 HEA thin film; (b) The R_p of #1 to #10 HEA thin films determined by the LPR method.

film. Among the 5-alloying elements in the HEA films, Co and Ni remain in the metallic state. The chemical information of other elements in the oxide films is illustrated in Fig. 8. It shows the Al 2p, Cr 2p3/2, Fe 2p3/2, and O 1 s spectra of the #2, #4, #6, and #8 HEA thin films. The Al 2p spectra are composed of the metallic-state Al and Al oxide/hydroxide $(Al_{ox,hy}^{3+})$ [37]. Similarly, the Cr 2p3/2 spectra contain the metallic-state Cr and Cr oxide/hydroxide $(Cr_{ox/hy}^{3+})$ [38], and the Fe 2p3/2 spectra exhibit the metallic-state Fe and the ionic-state Fe $^{3+}$ $_{ox/hy}$ [38]. The O 1 s spectra are composed of the O^{2-} , OH^{-} , and bound water (H₂O) peaks [39]. The peak-area ratios of the Al³⁺/Al, Cr³⁺/Cr, Fe³⁺/Fe, and OH⁻/ O^{2-} in the passive films of the #1 to #10 HEA thin films are summarized in Table 2.



Fig. 8. High-resolution XPS Al 2p, Cr 2p3/2, Fe 2p3/2, and O 1 s spectra of the #2, #4, #6, and #8 HEA thin films after the immersion in the 3.5 wt% NaCl solution for 24 h.

Table 2

Peak-area ratios of Al³⁺/Al, Cr³⁺/Cr, Fe³⁺/Fe, and OH⁻/O²⁻ acquired from the passive film of #1 to #10 HEA thin films.

| HEA thin films | Al^{3+}/Al | Cr ³⁺ /Cr | Fe ³⁺ /Fe | $0 H^{-} / 0^{2-}$ |
|----------------|--------------|----------------------|----------------------|--------------------|
| #1 | 3.72 | 8.91 | 10.5 | 0.58 |
| #2 | 3.93 | 8.21 | 7.39 | 1.07 |
| #3 | 4.57 | 8.07 | 7.31 | 1.27 |
| #4 | 4.66 | 6.69 | 5.82 | 1.40 |
| #5 | 5.33 | 6.05 | 4.57 | 3.05 |
| #6 | 5.58 | 4.12 | 3.35 | 4.12 |
| #7 | 6.13 | 3.46 | 2.92 | 5.01 |
| #8 | 7.43 | 3.12 | 2.21 | 6.32 |
| #9 | 7.82 | 2.15 | 1.95 | 8.25 |
| #10 | 7.91 | 1.95 | 1.60 | 10.5 |
| | | | | |

Table 3

Percentage (%) of Al³⁺, Cr^{3+} , and Fe³⁺ with respect to the total metal cations (Al³⁺, Cr^{3+} , and Fe³⁺) in the passive film of #1 to #10 HEA thin films.

| HEA thin films | Al ³⁺ /metal cations | Cr ³⁺ /metal cations | Fe ³⁺ /metal cations |
|----------------|---------------------------------|---------------------------------|---------------------------------|
| #1 | 22.3 | 37.3 | 40.4 |
| #2 | 25.1 | 36.7 | 38.2 |
| #3 | 29.2 | 35.8 | 35.0 |
| #4 | 34.5 | 34.7 | 30.8 |
| #5 | 40.3 | 33.6 | 26.1 |
| #6 | 46.1 | 32.5 | 21.4 |
| #7 | 60.5 | 23.7 | 15.8 |
| #8 | 71.4 | 14.2 | 14.4 |
| #9 | 72.3 | 13.9 | 13.8 |
| #10 | 81.7 | 12.5 | 5.79 |

Fig. 8(a) shows that with increasing the Al content, there is a concomitant increase in the Al^{3+} peak area. It can be seen from Table 1 that as the Al concentration increases from #1 to #10, the peak-area ratio of Al^{3+}/Al increases from 3.72 to 7.91. However, the peak-area ratios of Cr^{3+}/Cr and Fe^{3+}/Fe decrease from 8.91 to 1.95 and 10.5 to 1.60, respectively. The results indicate that increasing the Al content in the HEA thin films leads to more Al oxides/hydroxides and less Cr and Fe oxides/hydroxides in the passivated films. To quantitatively reveal the compositions of the oxide film, Al^{3+} , Cr^{3+} , and Fe^{3+} contents were computed according to the intensity/area of the corresponding peak by

$$X_i = 100 \frac{A_i}{\sum_{i=1}^n A_i}$$
 (2)

where *i* represents each cation, X_i is the percentage of each cation, *n* is the number of cations, and A_i is the adjusted intensities, which is given by

$$A_i = \frac{J_i}{R_i K} \tag{3}$$

where J_i is the measured intensity for each cation, R_i is the relative sensitivity factor, which could be obtained from the SPECSLab2 software, and K is the kinetic energy. The calculated contents of Al³⁺, Cr³⁺, and Fe³⁺ with respect to the total metal cations (Al³⁺, Cr³⁺, and Fe³⁺) in the passive film are given in Table 3. The results show that from #1 to #10 thin films, the contents of Al³⁺ increases continually from 22.3% to 81.7%. Conversely, the contents of Cr³⁺ and Fe³⁺ decrease from 37.3% to 12.5% and 40.4% to 5.79%, respectively. It is reported that the compact



Fig. 9. XPS depth profiles of Al, Co, Cr, Fe, Ni, and O acquired from the (a) #3, (b) #7, and (c) #9 HEA thin films after the immersion in the 3.5 wt% NaCl solution for 24 h.

Cr₂O₃ is favorable to maintain the passivity of the oxide film, while the Al oxides/hydroxides easily form a porous surface film [40]. The increased Al^{3+} and decreased Cr^{3+} contents in the oxide films indicating that the passive films contain more Al oxides/hydroxides and less Cr oxides, therefore, the compactness and protection of the passive films decrease. Moreover, the peak-area ratio of OH^{-}/O^{2-} also increases from 0.58 to 10.5 with the increased Al content from #1 to #10 HEA thin films, as can be seen in Fig. 8(d) and Table 2. Previous studies have demonstrated that the presence of hydroxide in the passive film has a negative effect on the compactness of the passive film [41]. The hydroxides in the passive film are of a lower density than the oxides. The ratio change of OH^{-}/O^{2-} demonstrates possible reasons for the decreased critical pitting potential of the thin-film with a higher Al content. Fig. 8(d) presents that the peak area of the bound water (H₂O) is diminished from #1 to #10 HEA thin films. Okamoto has proposed that a passive film with a large amount of bound water has a higher buffering capacity against the breakdown of the passive film [42]. The bound water within the passive film mainly has two functions. Firstly, the bound water can capture the dissolved metal ions and form a new passive film. Additionally, the bound water can be replaced by chloride ions from the surrounding environment. If the passive film transforms to a less hydrated structure due to the replacement of chloride ions, the corrosion resistance of the passive film subsequently decreases. In the present work, the decreased amount of bound water in the passivated films reflects an additional reason for the decreased corrosion resistance from #1 to #10 HEA thin films.

Fig. 9 shows the XPS depth profiles of Al, Co, Cr, Fe, Ni, and O in the passive film corresponding to the #3, #7, and #9 HEA thin films after immersion in the 3.5 wt% NaCl solution for 24 h. All of the HEA thin films show that the concentrations of O, Cr, and Al decrease and the concentrations of Ni, Co, and Fe increase with the increased sputtering depth. The concentrations of Cr and Al are higher than those in the base HEA thin film. On the contrary, the concentrations of Ni, Co, and Fe in the passivated film are lower than in the thin film matrix. The alternation of elemental concentrations along the depth suggests that the Cr and Al elements accumulate in the top surface to form the Cr oxide/hydroxide and Al oxide/hydroxide, providing the corrosion protection of the passive film. When comparing the effect of the Al content on the passivated film formed on the HEA thin films, it is noted that increasing Al content results in more Al oxide/hydroxide and less Cr oxide/hydroxide formation in the passive film. From #3 to #7 HEA thin films, the Cr content on the surface decreases from 27.8 at.% to 16.4 at.%, at the same time, the Al content increases from 5.15 at.% to 24.0 at.%. It is notable that the O content decreases with increasing sputtering depth for all three thin films. However, at the same etching depth, the O content in the passive film increases from #3 to #9 HEA thin films, indicating that the passive film of the HEA thin films with the higher Al content is thicker.

4. Conclusions

In the present study, high-throughput synthesis of the Al_x (CoCrFeNi) _{100-x} combinatorial material library is achieved using magnetron cosputtering. The influence of the Al content on the structure and corrosion behavior is revealed. Based on the investigation in the current study, the following conclusions can be drawn.

(1) The crystal structures of the thin films transit from FCC to BCC with the increase of the Al content. Both the FCC and BCC structure thin films show typical morphologies of deposition by the magnetron-sputtering process, which are dense cylindrical-columns growth along the deposition direction. The uniform elemental distribution indicates that the magnetron co-sputtering could minimize the concentration fluctuations due to fast quenching in the sputter procedure.

- (2) The HEA thin film shows better corrosion resistance than bulk HEAs. However, with the increase of the Al content, the resistance of the HEA thin films to both the general and localized corrosion is weakened.
- (3) The passivated films contain more Al oxides/hydroxides and less Cr oxides/hydroxides with the increase of the Al content, thus weakening the compactness and protection of the oxide films, which leads to the weakened corrosion resistance of the HEA thin films.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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