

## Article

# Corrosion Resistance of $\text{Al}_x\text{CoCrFeNiM}$ ( $\text{M} = \text{Ti}, \text{V}, \text{Si}, \text{Mn}, \text{Cu}$ ) High Entropy Alloys in $\text{NaCl}$ and $\text{H}_2\text{SO}_4$ Solutions

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**Abstract:** The electrochemical behavior of as-cast  $\text{Al}_x\text{CoCrFeNiM}$  ( $\text{M} = \text{Ti}, \text{V}, \text{Si}, \text{Mn}, \text{Cu}$ ) high entropy alloys (HEAs) in 1 M  $\text{NaCl}$  and 0.5 M  $\text{H}_2\text{SO}_4$  solutions is studied. Polarization measurements were carried out in a standard three-electrode electrochemical cell with a platinum auxiliary electrode using a P-30J potentiostat device. The potentials were measured relative to a saturated silver chloride reference electrode EVL-1M3 at room temperature (25 °C) with a sweep rate of 5 mV/s. It is shown that despite a wide passivation region,  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$  HEA undergoes significant corrosion in both sodium chloride and sulfuric acid solutions and exhibits low corrosion potential and current density. Energy-dispersive X-ray spectroscopy (EDS) analysis revealed that Ti-containing eutectic areas are the most susceptible regions to corrosion. Intergranular corrosion was found in  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  and  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  HEAs. Moreover,  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  possesses the smallest passivation interval  $\Delta E$  among all the investigated HEAs. For samples with Ti, Mn, and Cu, a protective film layer is not formed on the surface of the phases enriched in these elements, or it is brittle and crumbles. For samples with Si and V, a passivating film is formed. Thus,  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  and  $\text{Al}_{0.25}\text{CoCrFeNiV}$  HEAs exhibited the highest resistance in 1 M  $\text{NaCl}$  and 0.5 M  $\text{H}_2\text{SO}_4$  corrosive environments, respectively.

**Keywords:** high entropy alloys; corrosion resistance; polarization; electrochemical behavior



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## 1. Introduction

For about 20 years, high entropy alloys (HEAs) have been highly studied by specialists in the field of materials science. For the first time, the HEAs concept was proposed by Cantor and Yeh in 2004 [1,2], according to which, when alloying five or more elements in an equimolar ratio, the entropy of mixing of such compositions will be high enough to stabilize a single-phase solid solution phase, and likely achieve superior mechanical properties compared with conventional alloys. Further studies [3–7] showed that these types of alloys are potential candidates for a large number practical application. This, in turn, caused a surge in studies of the behavior of HEAs at ultralow [8–10] and high temperatures [11–14], as well as their behavior in aqueous solutions of alkalis, acids, and salts [15–19]. The latter is substantiated by the possibility of applying corrosion-resistant coatings of HEAs on the surface of materials operating in aggressive aqueous solutions [20].

According to a literature review by Shi et al. [19], one can note the great interest of researchers in Mo-containing HEAs as promising corrosion-resistant compositions. Based on the results of the analysis of the literature data, Shi et al. [19] pointed to the HEA of the composition  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.1}$ , which in a 1 M  $\text{NaCl}$  solution showed a corrosion current of the order of  $0.13 \times 10^{-6} \text{ A/cm}^2$ , and the corrosion potential turned out to be

−0.38 V; in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the corrosion current was  $78 \times 10^{-6}$  A/cm<sup>2</sup>, and the corrosion potential was −0.071 V.

In literature, there are a limited number of studies on the corrosion resistance Al<sub>x</sub>CoCrFeNi HEAs, and the effect of alloying elements such as Cu and Ti on its corrosion behavior [20–25]. For example, Li et al. in [20] reported that AlCoCrFeNi exhibits higher corrosion resistance compared to stainless steel AISI 1045 in 3.5 wt.% NaCl solution. According to the polarization curves obtained in [20], the corrosion current turned out to be three orders of magnitude lower for HEA ( $9.3 \times 10^{-8}$  A/cm<sup>2</sup>) compared to stainless steel ( $1.17 \times 10^{-5}$  A/cm<sup>2</sup>). Kao et al. [21] observed that Al<sub>x</sub>CoCrFeNi HEA also shows high corrosion resistance in sulfuric acid 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, moreover, with an increase in the aluminum concentration to  $x = 1.0$ , the resistance to the acid solution decreased due to the formation of a porous film that does not protect against the impact of an aggressive environment. Qiu [22] reported that Cu has a positive effect on the corrosion resistance of AlCrFeNiCoCu HEA in 1 M NaCl solution. Potentiodynamic polarization tests in 0.5 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions, in the work carried out by Li et al. [23], indicated a high corrosion resistance for a series of FeCoNiCrCu<sub>0.5</sub>Al<sub>x</sub> alloys. It was further determined that the samples with bcc crystal structure exhibit better corrosion resistance than those with fcc crystal structure. Qiu et al. [24] reported that Ti has an inferior influence on the corrosion resistant of Al<sub>0.9</sub>CoCrFeNi HEA, where Al<sub>0.9</sub>CoCrFeNiTi<sub>0.5</sub> exhibited less corrosion resistant than Al<sub>0.9</sub>CoCrFeNi alloy in a 0.6 M NaCl solution. This was attributed to the precipitation of a  $\sigma$ -FeCr phase when titanium is added to the Al<sub>0.9</sub>CoCrFeNi HEA. On the contrary, Liu et al. [25] showed a positive effect for Ti on the electrochemical behavior of AlCoCrFeNiTi<sub>x</sub> alloy.

The interest in addition of Cu and Ti for improving corrosion resistance is actually due to their significant positive effect on the corrosion resistance of steels [26,27], which also suggests a possible positive effect on the properties of HEAs. An increase in the corrosion resistance of steels is also provided by addition of vanadium [28] or increasing the content of silicon and manganese in steels [29,30], arousing a scientific interest in the effect of these elements on the properties of Al<sub>x</sub>CoCrFeNi HEAs.

Despite a certain amount of data available in literature, a systematic study on the effect of alloying elements on the corrosion resistance of Al<sub>x</sub>CoCrFeNiM (M = Ti, V, Si, Mn, Cu) HEAs in salt and acidic solutions is still missing, which requires further research to fill this scientific gap. Therefore, the aim of this work is to study the effect of Ti, V, Si, Mn and Cu on the corrosion resistance of Al<sub>x</sub>CoCrFeNi HEA in 1 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions to determine the feasibility of introducing these elements into its composition.

## 2. Materials and Methods

Samples of Al<sub>x</sub>CoCrFeNiM (M = Ti, V, Si, Mn, Cu) HEAs were prepared by induction melting in a reducing atmosphere using metals (granules and powders) of high purity (>99.9 wt.%) according to the procedure described in our previous works [31,32]. For preparing working electrodes, bar-shaped samples with dimensions of 8 mm × 2 mm × 3 mm were cut from the as-cast ingots, then placed in glass tubes and connected to current leads. To avoid the solution becoming inside the glass tubes, the space around the samples was insulated with epoxy resin. The composition of the samples and the exposed free surface areas of the working electrodes are presented in Table 1.

Polarization measurements were carried out in a standard three-electrode YaSE-2 electrochemical cell (OJSC “Gomel Plant of Measuring Instruments”, Gomel, Belarus) with a platinum auxiliary electrode using a P-30J potentiostat device (LLC “Elis”, Chernogolovka, Russia). The potentials were measured relative to a saturated silver chloride reference electrode EVL-1M3 (OJSC “Gomel Plant of Measuring Instruments”, Gomel, Belarus) at room temperature (25 °C) with a sweep rate of 5 mV/s. Thus, alloys were used as working electrodes, a silver chloride electrode served as a reference electrode, a platinum electrode was an auxiliary electrode. The corrosion tests were carried out in 1 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. Sulfuric acid was used as the acidic electrolyte because it provides high

rates for anodic dissolution processes, as well as it inhibits passivation processes on the sample surface and avoids the formation of poorly soluble compounds in the volume of the electrolyte. Before electrochemical tests, the surface of electrodes was mechanically polished with emery paper, degreased with isopropyl alcohol, and then washed with distilled water.

**Table 1.** The chemical formula (determined from Energy-dispersive X-ray spectroscopy (EDS) analysis), working surface area, and stationary potentials ( $E_{OCP}$ ) without current imposition for the studied high entropy alloys (HEA) samples.

| HEA                                                         | Working Surface Area, mm <sup>2</sup> | $E_{OCP}$ , V (in 1 M NaCl) | $E_{OCP}$ , V (in 0.5 M H <sub>2</sub> SO <sub>4</sub> ) |
|-------------------------------------------------------------|---------------------------------------|-----------------------------|----------------------------------------------------------|
| Al <sub>0.5</sub> CoCrFeNi <sub>1.6</sub> Ti <sub>0.7</sub> | 4.0                                   | −0.226 ± 0.002              | 0.084 ± 0.001                                            |
| Al <sub>0.25</sub> CoCrFeNiV                                | 5.0                                   | −0.195 ± 0.002              | −0.076 ± 0.001                                           |
| Al <sub>0.45</sub> CoCrFeNiSi <sub>0.45</sub>               | 5.0                                   | −0.183 ± 0.002              | −0.024 ± 0.001                                           |
| Al <sub>0.25</sub> CoCrFeNiMn                               | 7.5                                   | −0.131 ± 0.002              | −0.088 ± 0.001                                           |
| Al <sub>0.25</sub> CoCrFeNiCu                               | 4.5                                   | −0.228 ± 0.003              | 0.012 ± 0.001                                            |

The open circuit potential  $E_{OCP}$  was measured for 3600–4400 s in a cell filled with electrolyte solutions without applying current. This time was enough to stabilize each of the working electrodes. The potentials of the samples shifted to a more negative region over time, which indicates the activation of the electrode surface. The obtained  $E_{OCP}$  of the samples are presented in Table 1.

When polarization curves were taken with applying current, then the interval for investigation was set on the potentiostat from ( $E_{OCP} - 1$ ) V to ( $E_{OCP} + 1$ ) V. Corrosion parameters such as corrosion potential ( $E_{cor}$ ), current density ( $I_{cor}$ ) were determined by the Tafel extrapolation method using both the cathode and anodic branches of the polarization curves. A silver chloride electrode was used as the reference electrode, and then the potentials were recalculated to the scale of a normal hydrogen electrode.

The polarization resistance ( $R_p$ ) was calculated using the formula:

$$R_p = \frac{1}{2.303 \left( \frac{1}{\beta_a} + \frac{1}{\beta_c} \right) I_{cor}}$$

where  $\beta_a$  and  $\beta_c$  are the slope coefficients of the anode and cathode straight lines of the Tafel equation, respectively, obtained by extrapolation.

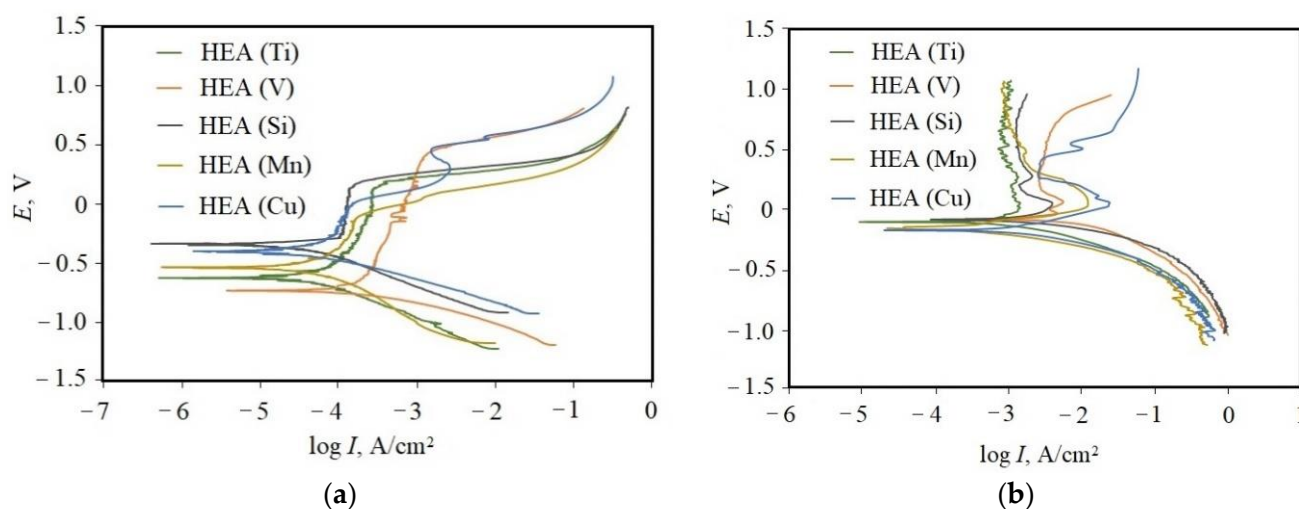
The surface morphology of the electrodes was examined using a JSM-7001F scanning electron microscope (SEM) (JEOL, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscopy detector (EDS) (Oxford Instruments, Abingdon, UK) for quantitative chemical analysis.

X-ray phase analysis (XRD) was carried out on the thin sections of the samples on an Ultima IV diffractometer (Rigaku, Tokyo, Japan) using Cu K $\alpha$ . The scanning speed was 5 degrees per min and the scanning step was set to 0.02 degrees.

### 3. Results

#### 3.1. Electrochemical Behavior

The polarization curves of the samples in 1 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions are shown in Figure 1a,b. The determined corrosion potentials ( $E_{cor}$ ), corrosion current density ( $I_{cor}$ ), polarization resistance ( $R_p$ ), range of passivation  $\Delta E$ , and passivation current ( $I_{pas}$ ) in both electrolytes are listed in Tables 2 and 3. The cathodic curves of the studied alloys exhibit a nearly same slope in both solutions.



**Figure 1.** Polarization curves of HEAs samples in solution: (a) 1 M NaCl; (b) 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Table 2.** Potentials and current densities of corrosion for alloys in 1 M NaCl solution.

| Alloy                                                       | $E_{cor}$ , V      | $I_{cor}$ , A/cm <sup>2</sup>   | $R_p$ , kΩcm <sup>2</sup> | $I_{pas}$ , A/cm <sup>2</sup> | $\Delta E$ |
|-------------------------------------------------------------|--------------------|---------------------------------|---------------------------|-------------------------------|------------|
| Al <sub>0.5</sub> CoCrFeNi <sub>1.6</sub> Ti <sub>0.7</sub> | $-0.626 \pm 0.003$ | $(16.2 \pm 0.2) \times 10^{-6}$ | $2.93 \pm 0.02$           | $132 \times 10^{-6}$          | 0.730      |
| Al <sub>0.25</sub> CoCrFeNiV                                | $-0.735 \pm 0.003$ | $(20.9 \pm 0.2) \times 10^{-6}$ | $3.96 \pm 0.03$           | $264 \times 10^{-6}$          | 0.933      |
| Al <sub>0.45</sub> CoCrFeNiSi <sub>0.45</sub>               | $-0.340 \pm 0.003$ | $(8.0 \pm 0.2) \times 10^{-6}$  | $1.86 \pm 0.02$           | $93 \times 10^{-6}$           | 0.570      |
| Al <sub>0.25</sub> CoCrFeNiMn                               | $-0.545 \pm 0.003$ | $(15.6 \pm 0.2) \times 10^{-6}$ | $1.20 \pm 0.02$           | $123 \times 10^{-6}$          | 0.248      |
| Al <sub>0.25</sub> CoCrFeNiCu                               | $-0.401 \pm 0.003$ | $(8.6 \pm 0.2) \times 10^{-6}$  | $3.89 \pm 0.03$           | $109 \times 10^{-6}$          | 0.278      |
| AlCrFeNiCoCu [22]                                           | -0.012             | $0.003 \times 10^{-6}$          | -                         | -                             | 0.525      |
| SS 304 [22]                                                 | -0.238             | $0.35 \times 10^{-6}$           | -                         | -                             | -          |

The corrosion potentials obtained from the polarization curves are more negative values compared to the stationary potentials measured under no-current conditions, which can be explained by the fact that the polarization curves were recorded in the potentiodynamic mode with a certain potential sweep rate.

The Ti-containing Al<sub>0.5</sub>CoCrFeNi<sub>1.6</sub>Ti<sub>0.7</sub> alloy exhibits the ability to become passive in aggressive environments. According to the Pourbaix diagram, titanium is in a passive state in a wide range of potentials, this is due to the formation of amorphous oxide TiO<sub>2</sub>. In addition to TiO<sub>2</sub>, the oxide layer also contains other oxides, Ti<sub>2</sub>O<sub>3</sub> and TiO. In an acidic environment, titanium can be oxidized to the Ti<sup>3+</sup> ion, however, in the presence of oxygen, further oxidation to the Ti<sup>4+</sup> ion is possible, which in turn is hydrolyzed to TiO<sub>2</sub>. This contributes to the spontaneous cessation of local corrosion of titanium. The polarization curve of this alloy is characterized by a rather wide range of passivation  $\Delta E = 0.730$  V in a 1 M NaCl solution. From the theory of passivity point of view [34], chloride ions penetrate into the oxide film through pores and defects more easily than other ions. On the other hand, according to the adsorption theory [34], competing with dissolved oxygen and OH<sup>-</sup> ions, Cl<sup>-</sup> anions are adsorbed on the surface of the metal matrix, significantly increase the passivation current and shift the full passivation potential towards positive values. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the process of active dissolution of metals from the electrode surface at a potential  $E_{pas} = +0.404$  V turns into the process of trans-passivation. From the standpoint of the phase theory, the trans-passive state is where the passive film of an insoluble oxide at a low oxidation state of the metal, dissolves with an increase in the potential. In the trans-passive state compounds of a higher degree of oxidation of the metal can be formed. According to the adsorption theory [34], with an increase in potential, the chemisorption of oxygen increases, the number of O-atoms coordinating with the metal ion increases, bonds

in the metal lattice are weakened, and well-soluble complexes with metals in a higher oxidation state (Cr, Ti) are formed.

**Table 3.** Potentials and current densities of corrosion for alloys in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

| Alloy                                                          | $E_{\text{cor}}$ , V | $I_{\text{cor}}$ , A/cm <sup>2</sup> | $R_p$ , kΩcm <sup>2</sup> | $I_{\text{pas}}$ , A/cm <sup>2</sup> | $\Delta E$ |
|----------------------------------------------------------------|----------------------|--------------------------------------|---------------------------|--------------------------------------|------------|
| Al <sub>0.5</sub> CoCrFeNi <sub>1.6</sub> Ti <sub>0.7</sub>    | −0.115 ± 0.002       | (354 ± 3) × 10 <sup>−6</sup>         | 0.161 ± 0.001             | 90.6 × 10 <sup>−6</sup>              | 0.606      |
| Al <sub>0.25</sub> CoCrFeNiV                                   | −0.072 ± 0.002       | (128 ± 2) × 10 <sup>−6</sup>         | 0.145 ± 0.001             | 30.4 × 10 <sup>−6</sup>              | 1.105      |
| Al <sub>0.45</sub> CoCrFeNiSi <sub>0.45</sub>                  | −0.087 ± 0.002       | (393 ± 3) × 10 <sup>−6</sup>         | 0.095 ± 0.001             | 150.3 × 10 <sup>−6</sup>             | 0.321      |
| Al <sub>0.25</sub> CoCrFeNiMn                                  | −0.124 ± 0.002       | (239 ± 3) × 10 <sup>−6</sup>         | 0.360 ± 0.002             | 168.7 × 10 <sup>−6</sup>             | 0.120      |
| Al <sub>0.25</sub> CoCrFeNiCu                                  | −0.164 ± 0.002       | (607 ± 3) × 10 <sup>−6</sup>         | 0.088 ± 0.001             | 271.1 × 10 <sup>−6</sup>             | 0.077      |
| Al <sub>0.25</sub> CoCrFeNi [21]                               | −0.095               | 16.7 × 10 <sup>−6</sup>              | -                         | 7.1 × 10 <sup>−6</sup>               | 1.200      |
| SS 304 [21]                                                    | −0.185               | 45.3 × 10 <sup>−6</sup>              | -                         | 19.1 × 10 <sup>−6</sup>              | 0.750      |
| FeCoNiCrCu <sub>0.5</sub> Al <sub>0.5</sub> [23]               | −0.112               | 4.190 × 10 <sup>−6</sup>             | -                         | -                                    | 0.550      |
| SS 321 [23]                                                    | −0.003               | 2.248 × 10 <sup>−6</sup>             | -                         | -                                    | 0.325      |
| Al <sub>0.3</sub> CrFe <sub>1.5</sub> MnNi <sub>0.5</sub> [33] | −0.194               | 2390 × 10 <sup>−6</sup>              | -                         | 73.9 × 10 <sup>−6</sup>              | 1.176      |
| SS 304 [33]                                                    | −0.186               | 74.5 × 10 <sup>−6</sup>              | -                         | 8.05 × 10 <sup>−6</sup>              | 1.178      |

Al<sub>0.25</sub>CoCrFeNiV HEA exhibits the lowest corrosion potential ( $E_{\text{cor}} = -0.735$  V) among all the studied samples in 1 M NaCl solution. The formation of a passive film starts from  $E_{\text{pas}} = -0.513$  V and continues up to +0.420 V. On the contrary, in acidic solution this HEA has the highest corrosion potential among all the studied samples  $E_{\text{cor}} = -0.072$  V. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, on the polarization curve after dissolution process an abrupt change in potential from −0.068 V to +0.023 V is observed, most likely due to the formation of a protective film of corrosion products. In a wide interval  $\Delta E = 1.105$  V, the passivation of the electrode surface occurs, which passes into the region of complete passivation due to the HSO<sub>4</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup> anions, which are adsorbed on the surface of the alloy and shift the potential to the region of positive values.

The Al<sub>0.45</sub>CoCrFeNiSi<sub>0.45</sub> alloy in 1 M NaCl solution has the highest potential of corrosion and the lowest corrosion current density, which characterizes this alloy as a corrosion-resistant material in this environment. At a potential  $E_{\text{pas}} = -0.260$  V the sample is covered with a passive film. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the Al<sub>0.45</sub>CoCrFeNiSi<sub>0.45</sub> alloy dissolves quite actively and has large positive passivation and trans-passivation potentials of +0.407 V and +0.728 V, respectively.

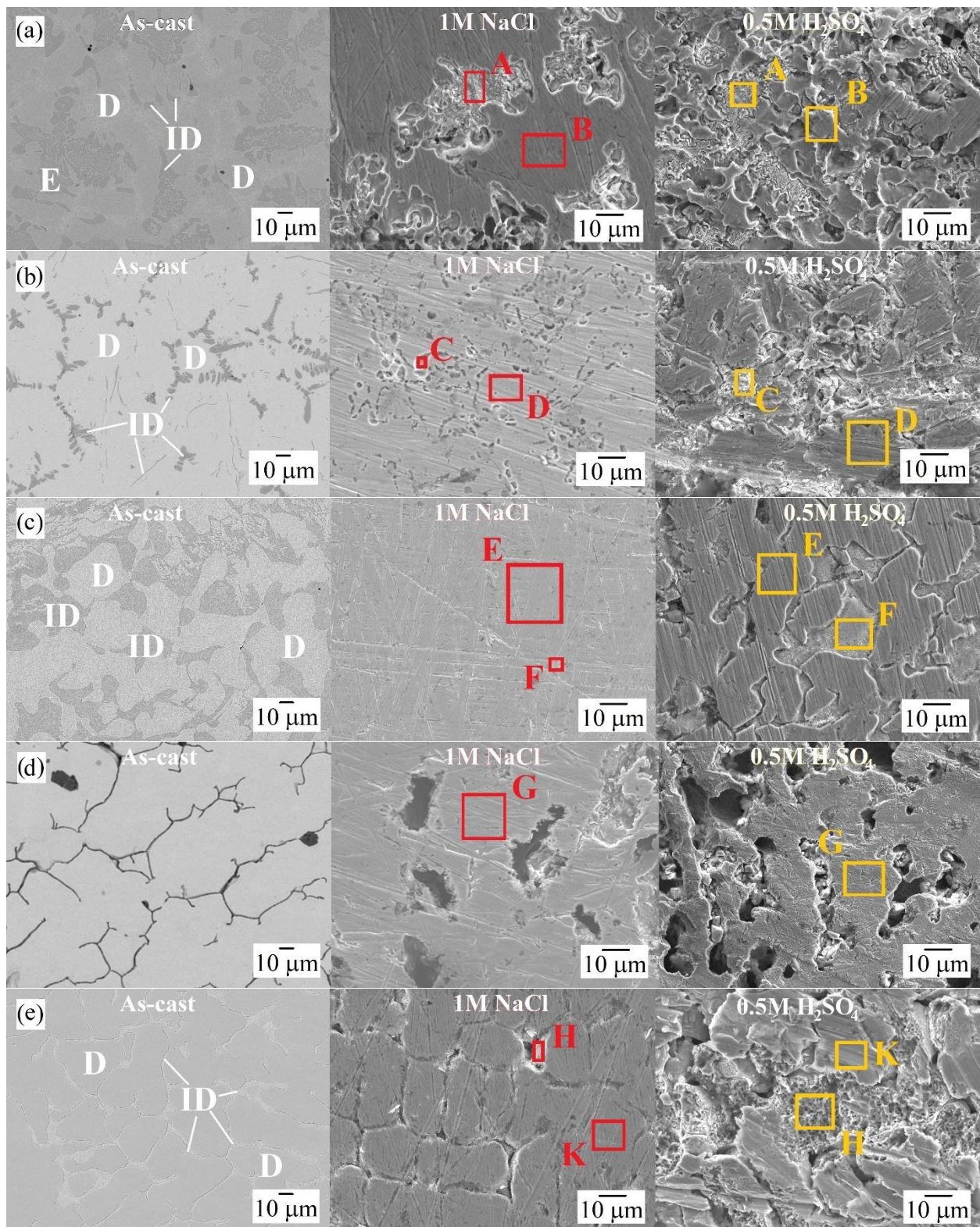
The corrosion behavior of Al<sub>0.25</sub>CoCrFeNiMn HEA in 1 M NaCl solution is characterized by a region from  $E_{\text{cor}} = -0.545$  V to  $E_{\text{pas}} = -0.345$  V, in which the corrosion rate increases, then the alloy actively begins to become passive and the corrosion rate rapidly decreases, which creates a characteristic loop. This alloy exhibits a similar behavior in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

For Al<sub>0.25</sub>CoCrFeNiCu HEA in 1 M NaCl, the passivation region is narrow ( $\Delta E = 0.278$  V), and the passivation potential reaches the value  $E_{\text{pas}} = -0.281$  V. At potential values −0.031 V and higher, we observed peaks in which the oxide film is re-formed. In 0.5 M sulfuric acid solution, the potential for the formation of a protective film is  $E_{\text{pas}} = +0.264$  V, and at a potential of +0.341 V trans-passivation occurs.

### 3.2. Microstructural Investigation

The as-cast microstructure of the samples prior to corrosion tests is shown in Figure 2, and their corresponding chemical compositions are given in Table 4. XRD spectra of the as-cast HEAs are shown in Figure 3. The microstructural and phase analysis are already discussed in our previous studies [31,32] and briefly reviewed here.

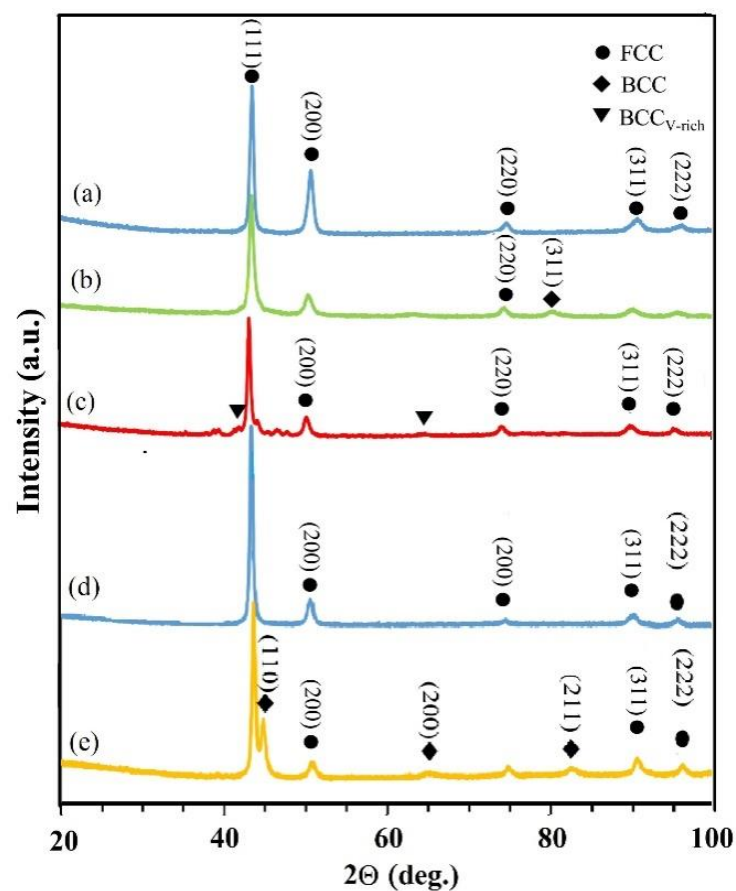




**Figure 2.** SEM micrographs of the as-cast samples before (white symbols) and after corrosion tests (for 1 M NaCl—red squares, for 0.5 M H<sub>2</sub>SO<sub>4</sub>—yellow squares), (a) Al<sub>0.5</sub>CoCrFeNi<sub>1.6</sub>Ti<sub>0.7</sub>, (b) Al<sub>0.25</sub>CoCrFeNiV, (c) Al<sub>0.45</sub>CoCrFeNiSi<sub>0.45</sub>, (d) Al<sub>0.25</sub>CoCrFeNiMn, (e) Al<sub>0.25</sub>CoCrFeNiCu HEAs. The microstructure of the as-cast samples was studied in backscattered electrons (BSE); the microstructure of the samples after corrosion tests was studied in secondary electrons (SE).

**Table 4.** EDS chemical composition of as-cast samples prior to corrosion tests (at. %), Av—average composition, D—dendritic region, ID—interdendritic region.

| Alloy                                                 |    | Al    | Cr    | Fe    | Co    | Ni    | Ti    | V     | Si    | Mn    | Cu    |
|-------------------------------------------------------|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$ | Av | 8.14  | 17.85 | 17.90 | 17.78 | 26.01 | 12.32 | -     | -     | -     | -     |
|                                                       | D  | 6.47  | 20.01 | 18.76 | 18.56 | 28.13 | 8.07  | -     | -     | -     | -     |
|                                                       | ID | 20.71 | 5.75  | 7.39  | 17.74 | 29.25 | 19.16 | -     | -     | -     | -     |
| $\text{Al}_{0.25}\text{CoCrFeNiV}$                    | Av | 4.68  | 19.47 | 18.20 | 19.34 | 19.17 | -     | 19.15 | -     | -     | -     |
|                                                       | D  | 4.85  | 20.35 | 19.10 | 20.09 | 19.33 | -     | 16.28 | -     | -     | -     |
|                                                       | ID | 0.87  | 8.75  | 0.80  | 0.90  | 0.96  | -     | 87.72 | -     | -     | -     |
| $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$            | Av | 9.13  | 20.45 | 19.27 | 20.61 | 20.91 | -     | -     | 9.63  | -     | -     |
|                                                       | D  | 5.43  | 21.62 | 21.49 | 23.64 | 19.89 | -     | -     | 7.93  | -     | -     |
|                                                       | ID | 12.57 | 17.34 | 17.72 | 17.03 | 20.51 | -     | -     | 14.83 | -     | -     |
| $\text{Al}_{0.25}\text{CoCrFeNiMn}$                   | Av | 3.50  | 19.82 | 19.87 | 19.92 | 18.92 | -     | -     | -     | 17.97 | -     |
| $\text{Al}_{0.25}\text{CoCrFeNiCu}$                   | Av | 5.75  | 19.87 | 18.62 | 18.65 | 18.87 | -     | -     | -     | -     | 18.24 |
|                                                       | D  | 3.28  | 21.22 | 21.91 | 22.01 | 19.80 | -     | -     | -     | -     | 11.78 |
|                                                       | ID | 8.43  | 5.27  | 4.75  | 5.93  | 15.09 | -     | -     | -     | -     | 60.53 |

**Figure 3.** XRD spectra of the as-cast HEAs: (a)  $\text{Al}_{0.25}\text{CoCrFeNiCu}$ , (b)  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$ , (c)  $\text{Al}_{0.25}\text{CoCrFeNiV}$ , (d)  $\text{Al}_{0.25}\text{CoCrFeNiMn}$ , (e)  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$ . FCC—face-centered cubic structure, BCC—body-centered cubic structure,  $\text{BCC}_{\text{V-rich}}$ —body-centered cubic phase based on vanadium.

$\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$  alloy has a rather complex structure consisted of light gray dendritic areas (D) with body-centered cubic (bcc) structure, dark gray interdendritic areas (ID) with face-centered cubic (fcc) structure, and a light eutectic-like phase (E) (see Figure 2a). EDS analysis indicated that Cr and Fe are segregated in the dendritic regions, Al and Ti are segregated mainly in the interdendritic regions, and Co and Ni are distributed almost evenly in the eutectic region (see Table 4). In the as-cast  $\text{Al}_{0.25}\text{CoCrFeNiV}$  HEA, a dendritic (D) fcc matrix (light gray phase in Figure 2b), and a vanadium-rich (ID) bcc phase is present in the form of coarse dendrites and acicular precipitates (dark gray phase in Figure 2b). In  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  alloy, the light gray dendritic (D) fcc phase is enriched in Cr, Fe and Co, while the dark gray interdendritic bcc regions (ID) are enriched in Al and Si (see Table 4).

The alloy of composition  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  in the as-cast state is characterized by a single-phase fcc structure, the average chemical composition (Av) of which is given in Table 4.  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  HEA with a single fcc structure consists of a dendritic microstructure (see Figure 2e), in which the dendrite arms (D) are enriched mainly in Co, Fe, and Cr, and the interdendritic (ID) regions are formed mainly by Cu, while Ni and Al exhibit a nearly homogenous distribution (see Table 4).

The surface morphology of the samples after corrosion tests are also shown in Figure 2. The EDS analysis of the different regions is given in Tables 5 and 6.

**Table 5.** EDS analysis after corrosion test in 1 M NaCl solution (at. %) measured from the different regions indicated in Figure 2 with red squares.

| № | Al   | Cr    | Fe    | Co    | Ni    | Ti   | V     | Si    | Mn    | Cu    | O     | Cl   |
|---|------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|------|
| A | 5.10 | 19.86 | 17.09 | 16.54 | 23.80 | 8.16 | -     | -     | -     | -     | 9.08  | 0.37 |
| B | 3.03 | 25.02 | 20.05 | 20.08 | 24.75 | 6.17 | -     | -     | -     | -     | 0.90  | -    |
| C | 3.88 | 21.89 | 17.50 | 18.52 | 16.07 | -    | 19.87 | -     | -     | -     | 2.27  | -    |
| D | 3.07 | 20.83 | 19.82 | 20.94 | 18.52 | -    | 16.02 | -     | -     | -     | 0.80  | -    |
| E | 7.87 | 21.62 | 20.23 | 21.15 | 21.07 | -    | -     | 7.40  | -     | -     | 0.66  | -    |
| F | 5.22 | 13.06 | 17.60 | 15.44 | 9.93  | -    | -     | 12.07 | -     | -     | 26.23 | 0.45 |
| G | 4.48 | 19.58 | 19.17 | 19.06 | 18.50 | -    | -     | -     | 18.09 | -     | 1.12  | -    |
| H | 1.18 | 8.89  | 7.77  | 8.38  | 10.25 | -    | -     | -     | -     | 60.80 | 2.38  | 0.35 |
| K | 4.81 | 23.16 | 21.70 | 22.01 | 18.24 | -    | -     | -     | -     | 9.10  | 0.98  | -    |

**Table 6.** EDS analysis after corrosion test in 0.5 M  $\text{H}_2\text{SO}_4$  solution (at. %) measured from the different regions indicated in Figure 2 with yellow squares.

| № | Al   | Cr    | Fe    | Co    | Ni    | Ti    | V     | Si   | Mn    | Cu   | O     |
|---|------|-------|-------|-------|-------|-------|-------|------|-------|------|-------|
| A | 9.91 | 17.00 | 15.88 | 17.87 | 26.70 | 10.92 | -     | -    | -     | -    | 1.72  |
| B | 2.14 | 25.66 | 21.20 | 19.36 | 24.71 | 6.22  | -     | -    | -     | -    | 0.71  |
| C | 2.16 | 30.05 | 20.36 | 18.38 | 10.10 | -     | 18.27 | -    | -     | -    | 0.68  |
| D | 5.48 | 18.63 | 19.43 | 20.50 | 21.23 | -     | 14.28 | -    | -     | -    | 0.44  |
| E | 7.22 | 22.33 | 21.64 | 22.35 | 20.39 | -     | -     | 4.82 | -     | -    | 1.25  |
| F | 1.72 | 28.76 | 14.98 | 14.48 | 10.55 | -     | -     | 6.13 | -     | -    | 23.37 |
| G | 4.97 | 18.85 | 19.64 | 18.83 | 18.10 | -     | -     | -    | 18.05 | -    | 1.56  |
| H | 2.24 | 23.39 | 22.71 | 23.24 | 17.27 | -     | -     | -    | -     | 9.13 | 2.02  |
| K | 4.09 | 23.61 | 22.19 | 22.34 | 17.58 | -     | -     | -    | -     | 9.33 | 0.86  |



According to the obtained data,  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  HEA showed the lowest resistance in 1 M NaCl solution, and its surface was covered with corrosive ulcers. In the uncorroded regions, an approximately equal concentration of Cr, Fe, Co, Ni, and Mn was measured by EDS analysis (see spectrum G in Table 5).  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$  and  $\text{Al}_{0.25}\text{CoCrFeNiV}$  samples also exhibit some traces of corrosion attacks on the surface, and the sample with Ti underwent corrosion to a greater extent than the sample with V. For  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$ , the Cr-rich and a Ti-poor regions turned out to be resistant to the chloride ions (see spectrum B in Table 5). For  $\text{Al}_{0.25}\text{CoCrFeNiV}$  sample, regions with approximately equal concentrations of Cr, Fe, Co, and Ni and a lower concentration of vanadium turned out to be more resistant to corrosion (see spectrum D in Table 5).  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  alloy has insignificant traces of corrosion attacks on the surface (see Figure 2e), and copper-rich areas interacted with the aggressive Cl-containing solution. After corrosion test in 1 M NaCl,  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  sample showed the highest corrosion resistance (see Figure 2c), and it exhibits a flat surface with rarely found corroded areas (see spectrum F in Table 5).

After corrosion test in 0.5 M  $\text{H}_2\text{SO}_4$  solution, the surface of  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  sample exhibits the most corrosion damages (see Figure 2d), which looks similar to intercrystalline corrosion. Areas with equal contents of Mn, Fe, Co, Ni, and Cr turned out to be resistant to sulfuric acid solution (see Table 6, spectrum G). Etching traces and corroded areas are clearly distinguishable on the  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$  sample. Quasi-eutectic areas enriched in Ti and depleted in Cr were exposed to the highest corrosion attacks by the acid solution. Areas depleted in Ti but enriched in Cr turned out to be resistant to sulfuric acid (see Table 6, spectrum B). Etching traces are also visible on the surface of  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  sample, while the high corrosion resistance was found in the areas enriched in Ni and depleted in Si. The selective dissolution of Cu in sulfuric acid was observed on the surface of  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  sample (see Figure 2e), where the Cu-rich areas were completely dissolved, and leaved characteristic etching patterns.  $\text{Al}_{0.25}\text{CoCrFeNiV}$  HEA showed the highest resistance to the corrosion action of 0.5 M  $\text{H}_2\text{SO}_4$  solution (see Figure 2b), and its surface exhibits comparatively lower corrosion damages.

#### 4. Discussion

The as-cast  $\text{Al}_x\text{CoCrFeNiM}$  ( $M = \text{Ti, V, Si, Mn, Cu}$ ) HEAs are characterized by the presence of several phases (with the exception of  $\text{Al}_{0.25}\text{CoCrFeNiMn}$ ). This is consistent with Wang et al. [35] and Chen et al. [36] that by increasing Al content in  $\text{Al}_x\text{CoCrFeNi}$  HEA, a two-phase fcc + bcc structure is stabilized. Moreover, in addition to the bcc dendrites and fcc interdendrite regions, the microstructure of the  $\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$  sample obtained in our study is characterized by the presence of a pseudo-eutectic phase. A similar structure for the  $\text{AlCrFeCoNiCuTi}$  alloy was observed by Li et al. [37] and also for  $\text{CoCrFeNiTiAl}_{0.5}$  alloy by Zhang et al. [38]. The presence of a two-phase fcc + bcc structure is also confirmed by Jin et al. [39] for  $\text{Al}_x\text{CoCrFeNiSi}$  HEAs. Copper tends to segregate as clusters, forming Cu-depleted dendritic arms and Cu-rich interdendrites during solidification owing to its high enthalpy of mixing with other Fe, Co, Ni and Cr elements. Similar dendritic structures with nearly same elemental segregation have been already observed for  $\text{Al}_{0.5}\text{CoCrCuFeNi}$  [40],  $\text{AlCoCrCu}_{0.5}\text{FeNi}$  [14],  $\text{AlCoCrCuFeNi}$  [14], and  $\text{AlCrFeCoNiCu}$  [37]. On the other hand, Dong et al. [41] indicated that vanadium is also prone to segregate and precipitate into a separated phase, a same finding as our study. Overall, the observed microstructures of the as-cast HEAs are consistent with the data available in literature.

Based on the data obtained on the electrochemical behavior of the investigated HEAs, it can be concluded that the addition of Ti, V and Cu to the base alloy  $\text{Al}_x\text{CoCrFeNi}$  does not have a positive effect on the resistance to  $\text{Cl}^-$  ions. Since areas with an increased concentration of these elements are prone to corrosion in 1 M NaCl solution at the first place (see Figure 2). The influence of Mn requires additional research, since, despite obvious corrosion pits, in the non-corroded areas, approximately equal concentrations of Cr, Fe, Co, Ni, and Mn were established. Si, at a minimum, does not degrade the corrosion

performance of the base alloy. This coincides with the data of the polarization curves (see Table 2), where  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  demonstrated the best corrosion resistance based to the calculated corrosion potential and current density.

The concentration of Cr not only in the composition of the sample, but also in the structural phases plays a significant role in the corrosion resistance of the samples in sulfuric acid solution. The higher the concentration of Cr in a segregated region, the higher is the corrosion resistant of that area to the effects of an aggressive environment. Among all the alloyed elements, V can be considered as the most effective candidate to improve the corrosion resistance of  $\text{Al}_x\text{CoCrFeNi}$  HEA against 0.5 M  $\text{H}_2\text{SO}_4$  solution. For all other samples, the areas enriched with the added elements (M in  $\text{Al}_x\text{CoCrFeNiM}$  compositions) turned out to be the most susceptible area to the corrosive attacks of sulfuric acid (see Figure 2). This is in agreement with the data from Table 3, where the best combination for  $E_{\text{cor}}$  and  $I_{\text{cor}}$  was obtained for  $\text{Al}_{0.25}\text{CoCrFeNiV}$  sample.

The addition of Ti to the composition of the base HEA did not increase its corrosion resistance; the areas with Ti-containing eutectic were subjected to the highest corrosion attacks, in consistent with the data reported by Qiu et al. [24]. The as-cast  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  alloy (see Figure 2d) has defects along the grain boundaries. After tests, both in salt and acidic environments, we observe intergranular corrosion for this HEA. The low corrosion resistance of the  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  sample in both solutions is due to the segregation of Cu in the interdendritic space. Due to this, local corrosion is possible along interdendrites with a high Cu content, which was also observed by other authors [40,42]. Removing Cu-segregated regions can improve corrosion resistance of the alloy [43,44]. Finally, it can be concluded that  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  and  $\text{Al}_{0.25}\text{CoCrFeNiV}$  demonstrate the highest corrosion resistance among all the investigated samples.

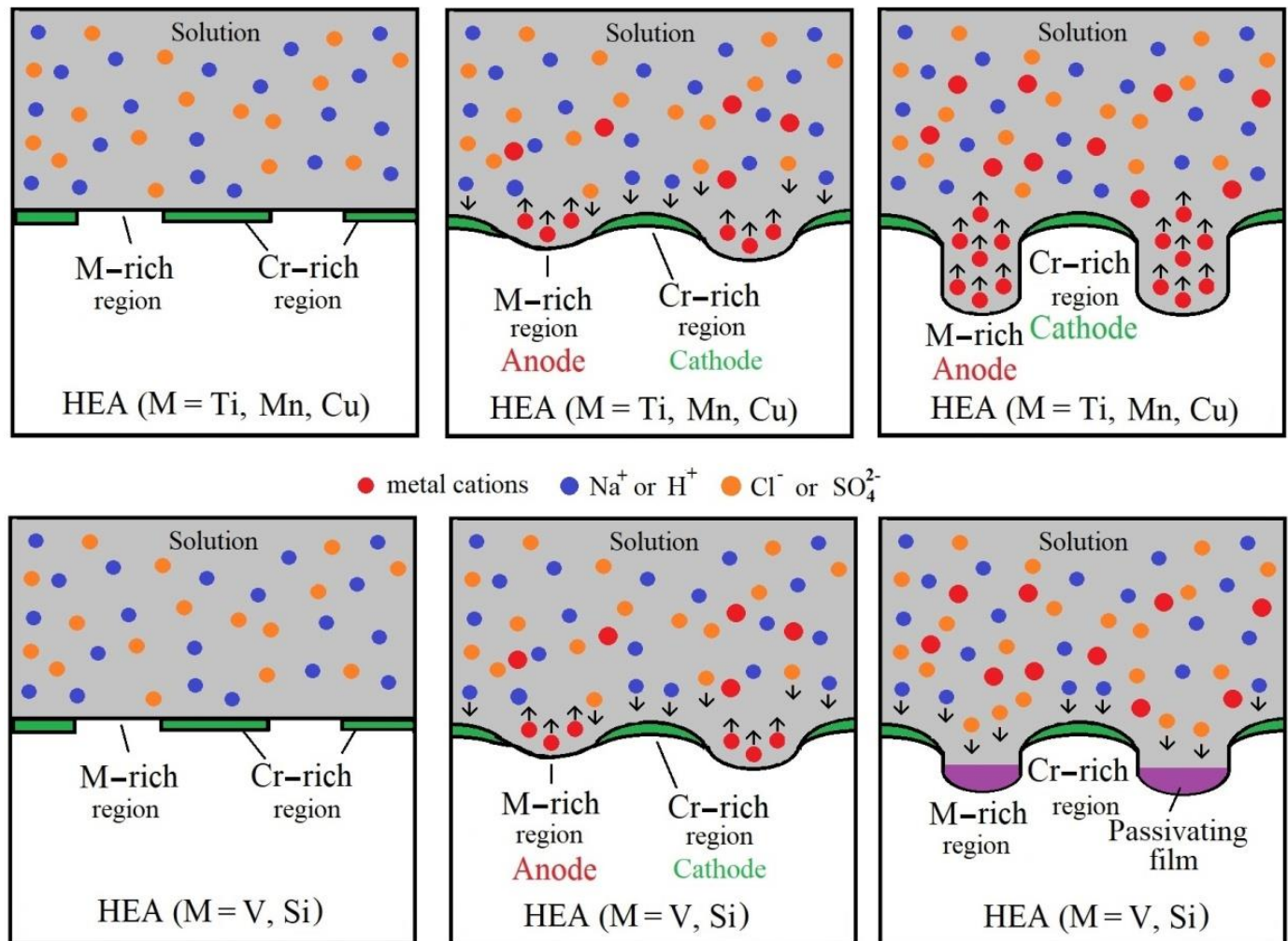
In general case, the corrosion mechanism is shown in Figure 4. When an aggressive solution-electrolyte interacts with alloy samples, a galvanic couple is most likely formed on the metal surface, while metal areas enriched in Cr will act as a cathode area, and areas enriched with additional elements—anode areas. A similar mechanism is described in the work Li et al. [20]. For samples with Ti, Mn, and Cu, a protective film layer is not formed on the surface of the anode sections, or it is brittle and crumbles. Thus, for these samples, there is a rather strong dissolution of phases enriched in additional elements (M-rich region). For samples with Si and V, a passivating film is formed. It should be noted that for a single-phase sample with Mn, the anode section will be likely the areas adjacent to the grain boundaries.

$\text{Al}_{0.5}\text{CoCrFeNi}_{1.6}\text{Ti}_{0.7}$ ,  $\text{Al}_{0.25}\text{CoCrFeNiMn}$ , and  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  HEAs are characterized by the presence of a trans-passivation process under the action of a strong 0.5 M  $\text{H}_2\text{SO}_4$  oxidizer solution. In a same solution,  $\text{Al}_{0.25}\text{CoCrFeNiV}$  alloy is in a passive state even at strong anodic polarization.  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  is passivated at a small range of potentials in a Cl-containing environment.

All the investigated samples in this study showed inferior corrosion behavior (in terms of corrosion potential and current density) than that of  $\text{Al}_x\text{CoCrFeNi}$  HEA [20,21] and SS 304 stainless steel [21,22,33] (see Tables 2 and 3). However, our samples indicated an order of magnitude better results than  $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$  HEA [33] when tested in 0.5 M  $\text{H}_2\text{SO}_4$  solution (see Table 3).

On the other hand,  $\text{Al}_{0.25}\text{CoCrFeNiV}$  HEA exhibits a wide range of passivation ( $\Delta E$ ), both in NaCl and  $\text{H}_2\text{SO}_4$  solutions (see Tables 2 and 3), comparable and even exceeding the available literature data on stainless steels and high-entropy alloys with good indicators of corrosion current density. The sample with the addition of Ti is also characterized by a rather wide range of passivation, which was not observed for  $\text{Al}_{0.25}\text{CoCrFeNiCu}$  and  $\text{Al}_{0.25}\text{CoCrFeNiMn}$  HEAs. This fact requires additional studies, since the narrow passivation interval may not be directly related to the influence of manganese. Thus, in the work Sun et al. [17] for  $\text{CrMnFeNi}$  and  $\text{CrMnFeNiLa}_{0.1}$  alloys, a passivation interval of the order of  $\Delta E = 1.203$  in 0.5 M  $\text{H}_2\text{SO}_4$  solution was determined.  $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$  occupies an intermediate position among the existing literature, since it exhibited a  $\Delta E$  in 1 M NaCl

solution ( $\Delta E = 0.570$ ) that exceeds the data reported by Qiu et al. [22] for AlCrFeNiCoCu HEA ( $\Delta E = 0.525$ ), and in 0.5 M  $H_2SO_4$  solution ( $\Delta E = 0.321$ ) that is comparable to the reported value by Li et al. [23] for stainless steel SS 321 ( $\Delta E = 0.325$ ).



**Figure 4.** A schematic of corrosion mechanisms of investigated HEAs.

## 5. Conclusions

In summary, the corrosion behavior of  $Al_xCoCrFeNiM$  ( $M = Ti, V, Si, Mn, Cu$ ) HEAs is studied in 1 M NaCl and 0.5 M  $H_2SO_4$  solutions. Among all the investigated alloys,  $Al_{0.25}CoCrFeNiV$  exhibited the best corrosion resistance in sulfuric acid, and  $Al_{0.45}CoCrFeNiSi_{0.45}$  demonstrated the best performance in sodium chloride solution. From the passivation point of view,  $Al_{0.25}CoCrFeNiMn$  HEA could be passivated in a narrow range of potential in both solutions.  $Al_{0.5}CoCrFeNi_{1.6}Ti_{0.7}$  HEA shows a rather wide range of passivation potentials ( $\Delta E = 0.6\text{--}0.7$  V) in both NaCl and  $H_2SO_4$  solutions, nevertheless, it is actively dissolved and corroded due to its low potential and high corrosion current.  $Al_{0.25}CoCrFeNiCu$  alloy is less active and can be passivated well in 1 M NaCl solution, however, it actively dissolved in sulfuric acid solution with the narrowest passivation region. All the investigated samples in this study showed inferior corrosion behavior (in terms of corrosion potential and current density) than that of  $Al_xCoCrFeNi$  HEA. Finally, to increase the resistance to electrochemical corrosion, it is necessary to obtain either single-phase alloys, or samples where each of the phases will contain a sufficiently high percentage of corrosion resistant elements.

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## References

1. Cantor, B.; Chang, I.T.H.; Knight, P.; Vincent, A.J.B. Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* **2004**, *375–377*, 213–218. [\[CrossRef\]](#)
2. Yeh, J.W.; Chen, S.K.; Lin, S.J.; Gan, J.Y.; Chin, T.S.; Shun, T.T.; Tsau, C.H.; Chang, S.Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303. [\[CrossRef\]](#)
3. Liu, Y.; Ma, S.; Gao, M.C.; Zhang, C.; Zhang, T.; Yang, H.; Wang, Z.; Qiao, J. Tribological properties of AlCrCuFeNi<sub>2</sub> high-entropy alloy in different conditions. *Metall. Mater. Trans. A* **2016**, *47*, 3312–3332. [\[CrossRef\]](#)
4. Guo, X.; Jin, X.; Shi, X.; Yang, H.; Zhang, M.; Qiao, J. Tribological behavior of boronized Fe<sub>40</sub>Mn<sub>20</sub>Cr<sub>20</sub>Ni<sub>20</sub> high-entropy alloys. *Metals* **2021**, *11*, 1561. [\[CrossRef\]](#)
5. Hemphill, M.A.; Yuan, T.; Wang, G.Y.; Yeh, J.W.; Tsai, C.W.; Chuang, A.; Liaw, P.K. Fatigue behavior of Al<sub>0.5</sub>CoCrCuFeNi high entropy alloys. *Acta Mater.* **2012**, *60*, 5723–5734. [\[CrossRef\]](#)
6. Li, Z.; Pradeep, K.G.; Deng, Y.; Raabe, D.; Tasan, C.C. Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off. *Nature* **2016**, *534*, 227–230. [\[CrossRef\]](#)
7. George, E.P.; Curtin, W.A.; Tasan, C.C. High entropy alloys: A focused review of mechanical properties and deformation mechanisms. *Acta Mater.* **2020**, *188*, 435–474. [\[CrossRef\]](#)
8. Gludovatz, B.; Hohenwarter, A.; Catoor, D.; Chang, E.H.; George, E.P.; Ritchie, R.O. A fracture-resistant high-entropy alloy for cryogenic applications. *Science* **2014**, *345*, 1153–1158. [\[CrossRef\]](#)
9. Yang, T.; Zhao, Y.L.; Luan, J.H.; Han, B.; Wei, J.; Kai, J.J.; Liu, C.T. Nanoparticles-strengthened high-entropy alloys for cryogenic applications showing an exceptional strength-ductility synergy. *Scr. Mater.* **2019**, *164*, 30–35. [\[CrossRef\]](#)
10. Qiu, Z.; Yao, C.; Feng, K.; Li, Z.; Chu, P.K. Cryogenic deformation mechanism of CrMnFeCoNi high-entropy alloy fabricated by laser additive manufacturing process. *Int. J. Lightweight Mater. Manuf.* **2018**, *1*, 33–39. [\[CrossRef\]](#)
11. Veselkov, S.; Samoilova, O.; Shaburova, N.; Trofimov, E. High-temperature oxidation of high-entropic alloys: A review. *Materials* **2021**, *14*, 2595. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Butler, T.M.; Weaver, M.L. Oxidation behavior of arc melted AlCoCrFeNi multi-component high-entropy alloys. *J. Alloys Compd.* **2016**, *674*, 229–244. [\[CrossRef\]](#)
13. Butler, T.M.; Alfano, J.P.; Martens, R.L.; Weaver, M.L. High-temperature oxidation behavior of Al-Co-Cr-Ni-(Fe or Si) multicomponent high-entropy alloys. *JOM* **2015**, *67*, 246–259. [\[CrossRef\]](#)
14. Dąbrowa, J.; Cieślak, G.; Stygar, M.; Mroczka, K.; Berent, K.; Kulik, T.; Danielewski, M. Influence of Cu content on high temperature oxidation behavior of AlCoCrCu<sub>x</sub>FeNi high entropy alloys (x = 0; 0.5; 1). *Intermetallics* **2017**, *84*, 52–61. [\[CrossRef\]](#)
15. Rodriguez, A.A.; Tylczak, J.H.; Gao, M.C.; Jablonski, P.D.; Detrois, M.; Ziomek-Moroz, M.; Hawk, J.A. Effect of molybdenum on the corrosion behavior of high-entropy alloys CoCrFeNi<sub>2</sub> and CoCrFeNi<sub>2</sub>Mo<sub>0.25</sub> under sodium chloride aqueous conditions. *Adv. Mater. Sci. Eng.* **2018**, *2018*, 3016304. [\[CrossRef\]](#)
16. Wei, L.; Wang, Z.; Wu, Q.; Shang, X.; Li, J.; Wang, J. Effect of Mo element and heat treatment on corrosion resistance of Ni<sub>2</sub>CrFeMo<sub>x</sub> high-entropy alloy in NaCl solution. *Acta Metall. Sin.* **2019**, *55*, 840–848. [\[CrossRef\]](#)
17. Sun, Y.; Lan, A.; Zhang, M.; Yang, H.; Qiao, J. Influence of lanthanum on passivity behavior of CrMnFeNi high entropy alloys. *Mater. Chem. Phys.* **2021**, *265*, 124509. [\[CrossRef\]](#)
18. Birbilis, N.; Choudhary, S.; Scully, J.R.; Taheri, M.L. A perspective on corrosion of multi-principal element alloys. *NPJ Mater. Degrad.* **2021**, *5*, 14. [\[CrossRef\]](#)
19. Shi, Y.; Yang, B.; Liaw, P.K. Corrosion-resistant high-entropy alloys: A review. *Metals* **2017**, *7*, 43. [\[CrossRef\]](#)
20. Li, Q.H.; Yue, T.M.; Guo, Z.N.; Lin, X. Microstructure and corrosion properties of AlCoCrFeNi high entropy alloy coatings deposited on AISI 1045 steel by the electrospark process. *Metall. Mater. Trans. A* **2013**, *44A*, 1767–1778. [\[CrossRef\]](#)
21. Kao, Y.F.; Lee, T.D.; Chen, S.K.; Chang, Y.S. Electrochemical passive properties of Al<sub>x</sub>CoCrFeNi (x = 0, 0.25, 0.50, 1.00) alloys in sulfuric acids. *Corros. Sci.* **2010**, *52*, 1026–1034. [\[CrossRef\]](#)



22. Qiu, X.W. Microstructure and properties of AlCrFeNiCoCu high entropy alloy prepared by powder metallurgy. *J. Alloys Compd.* **2013**, *555*, 246–249. [\[CrossRef\]](#)
23. Li, B.Y.; Peng, K.; Hu, A.P.; Zhou, L.P.; Zhu, J.J.; Li, D.Y. Structure and properties of FeCoNiCrCu<sub>0.5</sub>Al<sub>x</sub> high-entropy alloy. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 735–741. [\[CrossRef\]](#)
24. Qiu, Y.; Thomas, S.; Fabijanic, D.; Barlow, A.J.; Fraser, H.L.; Birbilis, N. Microstructural evolution, electrochemical and corrosion properties of Al<sub>x</sub>CoCrFeNiTi<sub>y</sub> high entropy alloys. *Mater. Des.* **2019**, *170*, 107698. [\[CrossRef\]](#)
25. Liu, J.; Liu, H.; Chen, P.; Hao, J. Microstructural characterization and corrosion behaviour of AlCoCrFeNiTi<sub>x</sub> high-entropy alloy coatings fabricated by laser cladding. *Surf. Coat. Technol.* **2019**, *361*, 63–74. [\[CrossRef\]](#)
26. Xi, T.; Babar Shahzad, M.; Xu, D.; Sun, Z.; Zhao, J.; Yang, C.; Qi, M.; Yang, K. Effect of copper addition on mechanical properties, corrosion resistance and antibacterial property of 316L stainless steel. *Mater. Sci. Eng. C* **2017**, *71*, 1079–1085. [\[CrossRef\]](#)
27. Mallaiah, G.; Ravinder Reddy, P.; Kumar, A. Influence of titanium addition on mechanical properties, residual stresses and corrosion behaviour of AISI 430 grade ferritic stainless steel GTA welds. *Proc. Mater. Sci.* **2014**, *6*, 1740–1751. [\[CrossRef\]](#)
28. Hu, W.; Zhu, H.; Hu, J.; Li, B.; Qiu, C. Influence of vanadium microalloying on microstructure and property of laser-cladded martensitic stainless steel coating. *Materials* **2020**, *13*, 826. [\[CrossRef\]](#)
29. Nishimura, T. Corrosion behavior of silicon-bearing steel in a wet/dry environment containing chloride ions. *Mater. Trans.* **2007**, *48*, 1438–1443. [\[CrossRef\]](#)
30. Kim, M.J.; Kim, J.G. Effect of manganese on the corrosion behavior of low carbon steel in 10 wt.% sulfuric acid. *Int. J. Electrochem. Sci.* **2015**, *10*, 6872–6885.
31. Ostovari Moghaddam, A.; Shaburova, N.A.; Sudarikov, M.V.; Veselkov, S.N.; Samoilova, O.V.; Trofimov, E.A. High temperature oxidation resistance of Al<sub>0.25</sub>CoCrFeNiMn and Al<sub>0.45</sub>CoCrFeNiSi<sub>0.45</sub> high entropy alloys. *Vacuum* **2021**, *192*, 110412. [\[CrossRef\]](#)
32. Shaburova, N.A.; Ostovari Moghaddam, A.; Veselkov, S.N.; Sudarikov, M.V.; Samoilova, O.V.; Trofimov, E.A. High-temperature oxidation behavior of Al<sub>x</sub>CoCrFeNiM (M = Cu, Ti, V) high-entropy alloys. *Phys. Mesomech.* **2021**, *24*, 653–662. [\[CrossRef\]](#)
33. Lee, C.P.; Chang, C.C.; Chen, Y.Y.; Yeh, J.W.; Shih, H.C. Effect of aluminium content of Al<sub>x</sub>CrFe<sub>1.5</sub>MnNi<sub>0.5</sub> high-entropy alloys on the corrosion behaviour in aqueous environments. *Corros. Sci.* **2008**, *50*, 2053–2060. [\[CrossRef\]](#)
34. Popov, Y.A. The main aspects of the modern theory of the passive state of metals. *Russ. Chem. Rev.* **2005**, *74*, 397–412. [\[CrossRef\]](#)
35. Wang, W.R.; Wang, W.L.; Wang, S.C.; Tsai, Y.C.; Lai, C.H.; Yeh, J.W. Effects of Al addition on the microstructure and mechanical property of Al<sub>x</sub>CoCrFeNi high-entropy alloys. *Intermetallics* **2012**, *26*, 44–51. [\[CrossRef\]](#)
36. Chen, M.; Shi, X.H.; Yang, H.; Liaw, P.K.; Gao, M.C.; Hawk, J.A.; Qiao, J. Wear behavior of Al<sub>0.6</sub>CoCrFeNi high-entropy alloys: Effect of environments. *J. Mater. Res.* **2018**, *33*, 3310–3320. [\[CrossRef\]](#)
37. Li, B.S.; Wang, Y.P.; Ren, M.X.; Yang, C.; Fu, H.Z. Effects of Mn, Ti and V on the microstructure and properties of AlCrFeCoNiCu high entropy alloy. *Mater. Sci. Eng. A* **2008**, *498*, 482–486. [\[CrossRef\]](#)
38. Zhang, K.; Fu, Z. Effects of annealing treatment on phase composition and microstructure of CoCrFeNiTiAl<sub>x</sub> high-entropy alloys. *Intermetallics* **2012**, *22*, 24–32. [\[CrossRef\]](#)
39. Jin, B.; Zhang, N.; Yu, H.; Hao, D.; Ma, Y. Al<sub>x</sub>CoCrFeNiSi high entropy alloy coatings with high microhardness and improved wear resistance. *Surf. Coat. Technol.* **2020**, *402*, 126328. [\[CrossRef\]](#)
40. Chen, Y.Y.; Hong, U.T.; Shih, H.C.; Yeh, J.W.; Duval, T. Electrochemical kinetics of the high entropy alloys in aqueous environments—A comparison with type 304 stainless steel. *Corros. Sci.* **2005**, *47*, 2679–2699. [\[CrossRef\]](#)
41. Dong, Y.; Zhou, K.; Lu, Y.; Gao, X.; Wang, T.; Li, T. Effect of vanadium addition on the microstructure and properties of AlCoCrFeNi high entropy alloy. *Mater. Des.* **2014**, *57*, 67–72. [\[CrossRef\]](#)
42. Lee, C.P.; Chen, Y.Y.; Hsu, C.Y.; Yeh, J.W.; Shih, H.C. The effect of boron on the corrosion resistance of the high entropy alloys Al<sub>0.5</sub>CoCrCuFeNiB<sub>x</sub>. *J. Electrochem. Soc.* **2007**, *154*, C424–C430. [\[CrossRef\]](#)
43. Hsu, Y.J.; Chiang, W.C.; Wu, J.K. Corrosion behavior of FeCoNiCrCu<sub>x</sub> high-entropy alloys in 3.5% sodium chloride solution. *Mater. Chem. Phys.* **2005**, *92*, 112–117. [\[CrossRef\]](#)
44. Doğan, Ö.N.; Nielsen, B.C.; Hawk, J.A. Elevated-temperature corrosion of CoCrCuFeNiAl<sub>0.5</sub>B<sub>x</sub> high-entropy alloys in simulated syngas containing H<sub>2</sub>S. *Oxid. Met.* **2013**, *80*, 177–190. [\[CrossRef\]](#)