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Effect of Pt Addition on the Oxidation and Corrosion Resistance of Al_{0.25}CoCrFeNi High-Entropy Alloy

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Abstract: The effect of minor platinum alloying on the microstructure, phase composition, oxidation and corrosion resistance of Al_{0.25}CoCrFeNi high-entropy alloy (HEA) has been studied. It was observed that Pt does not segregate as a separate phase, but it is incorporated into the fcc solid solution. High-temperature oxidation of the as-cast Al_{0.25}CoCrFeNi and Al_{0.25}CoCrFeNiPt_{0.1} high-entropy alloys was carried out in a muffle furnace under isothermal conditions at 900 °C for 0–50 h (weighing was carried out every 10 h) in air atmosphere. The specific weight gain decreased from 0.58 mg/cm² for Al_{0.25}CoCrFeNi to 0.31 mg/cm² for the platinum-doped Al_{0.25}CoCrFeNiPt_{0.1} sample. It was determined that Pt triggers the formation of an interlayer Al-rich oxide phase between the outer Cr-rich oxide layer and the interior of the alloy, significantly reducing the oxidation rate of Al_{0.25}CoCrFeNiPt_{0.1} HEA. Electrochemical tests in 0.5 M H₂SO₄ solution demonstrated passive behavior with anodic control of the process.

Keywords: high-entropy alloys; microstructure; alloying; platinum; high-temperature oxidation; electrochemical corrosion



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1. Introduction

During the last two decades, the so-called “high-entropy alloys (HEAs)” have been one of the new promising areas in materials science. HEAs consist of five or more elements with an equiatomic or near-equiatomic ratio and are characterized by a high value of the configurational entropy of mixing [1,2]. Among different classes of HEAs, the Al_xCoCrFeNi type exhibited an optimal combination of various characteristics such as strength and ductility [3,4], hardness and wear resistance [5,6] and low-temperature resistance [7,8]. Moreover, due to the increased concentrations of aluminum, chromium and nickel compared to those of the conventional industrial alloys, these HEAs demonstrate superior resistance to high-temperature oxidation [9,10] and high resistance against corrosion in various solutions [11,12]. Evaluating the corrosion behavior of Al_xCoCrFeNi HEA is a rather urgent task since these alloys are potentially promising protective coatings for repairing machine parts operating under aggressive conditions [13–15].

Currently, alloying different amounts of various elements is the main route to improve the oxidation and corrosion resistance of HEAs. There are data in the literature on the negative effect of alloying Si [16,17], Mn [17], Ti [18] and V [18] and the positive effect of introducing Ti/Nb [19], Y/Hf [20] and Cu [18,21] on the oxidation resistance of Al_xCoCrFeNi base HEA. In particular, alloying by Nb the Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3} HEA allowed the specific weight gain to be decreased from 1.4 mg/cm² to 0.7 mg/cm² after

50 h of exposure at 900 °C; the isothermal oxidation resistance was enhanced owing to the presence of the Nb-rich layer [19]. Lu et al. [20] showed that the introduction of Y/Hf in the AlCoCrFeNi HEA practically did not affect the phase composition of the oxide film (consisting mainly of Al_2O_3) but significantly reduced the possibility of cracking it and, thus, increased the protective properties of the formed layer. Dabrowa et al. [21] determined that AlCoCrCuFeNi HEA after 50 h of exposure at 1000 °C had a specific weight gain of only 0.21 mg/cm² versus 0.72 mg/cm² for the HEA without copper addition.

Several works considered the effect of alloying Ti [22–24], Cu [22,25,26], Si [22,27], V [22] and Mn [22] on the behavior of $\text{Al}_x\text{CoCrFeNi}$ base HEA in various solutions, including sulfuric acid, simulating the conditions of natural resources extraction when the medium is a mixture of SO_2/SO_3 vapors and water. At the same time, with some exceptions, data were mainly obtained on the negative effect of additionally introduced elements on the electrochemical corrosion of HEAs due to the microstructural features since this leads to the creation of a number of galvanic couples and acceleration of the corrosion processes. For example, Jiang et al. in [23] demonstrated that titanium addition had a negative effect on the corrosion resistance of the base alloy in NaCl and NaOH solutions but had a positive effect on resistance in sulfuric acid solution (provided that the amount of added titanium equaled or exceeded the aluminum concentration). Pratskova et al. in [22] showed the selective dissolution of copper (when alloying the base alloy with it) in an acidic environment; on the contrary, Li et al. in study [25] indicated a positive effect of introducing copper into the composition on the corrosion behavior of HEAs in the same environment. According to Xiang et al. [27], the doping of silicon allowed pseudo-passive behavior of $\text{AlCoCrFeNiSi}_{0.1}$ alloy in 3.5 wt.% NaCl solution to be obtained, but, in the 0.5 mol/L H_2SO_4 solution, this HEA showed active–passive behavior. Pitting occurred in the chromium-depleted phase.

By analyzing the literature data, it can be noted that currently there are no optimal HEA compositions which can be distinguished by high resistance against high-temperature oxidation and corrosion in aggressive environments. Thus, works in this direction are ongoing.

Platinum belongs to the group of noble metals (Ag, Pt, Au), which ensures its chemical inertness upon heating. In addition, platinum is located after hydrogen in the electrochemical series of metals, which initially implies its high corrosion resistance in the acidic environments. Thus, Pt is a promising metal for alloying into $\text{Al}_x\text{CoCrFeNi}$ base alloys. In our previous study [28], we observed the positive effect of silver alloying into $\text{Al}_x\text{CoCrFeNi}$ base HEA on its passivation interval in a sulfuric acid solution.

Therefore, the aim of this work is to study the microstructure, high-temperature (at 900 °C) oxidation resistance and corrosion resistance (in a 0.5 M H_2SO_4 solution) of $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ high-entropy alloy.

2. Materials and Methods

Ingots of $\text{Al}_{0.25}\text{CoCrFeNi}$ (sample for comparison) and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEAs were melted according to the procedure proposed elsewhere [18]. The ingots were produced by induction melting in a reducing atmosphere using metals (granules and powders manufactured by JSC “POLEMA”, Tula, Russia) of high purity (>99.9 wt.%).

For oxidation tests, specimens with dimensions of 10 mm × 6 mm × 6 mm were cut from the ingots and then polished. Oxidation tests were carried out in a Plavka.Pro PM-1 SmartKiln muffle furnace (Plavka.Pro, Korolev, Russia) at 900 °C with an exposure time of 0–50 h in air. The samples were weighed every 10 h on a laboratory analytical balance, model Sartorius MSE225S-000-DU (Sartorius Group, Göttingen, Germany), with an accuracy of 0.00001 g. High-temperature oxidation tests were carried out using three parallel measurements. Standard deviation of the average values amounted to no more than 3%.

The working electrodes for the electrochemical corrosion test and recording of polarization curves were used according to the method outlined elsewhere [22]. 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 mercury sulfate reference electrode at room temperature (25 °C) with a sweep rate of 5 mV/s. The use of a lower scan rate (for example, 1 mV/s) led to the effect of “leveling” a number of ongoing processes; instead of a sharp peak on the anodic branch of the polarization curve, the peak became flatter. In addition, small peaks became less noticeable. The low sweep rate simply did not allow time to record the ongoing electrochemical processes on the potentiostat, stretching them out over time. Thus, in this investigation, a sweep rate of 5 mV/s was chosen. It should also be noted that, according to the results of preliminary measurements, the mercury sulfate reference electrode is most suitable for the sulfuric acid solution in which the measurements took place. The use of a silver chloride reference electrode could lead to contamination of the working solution with chlorine ions which could, in turn, affect the measurement results.

The open circuit potential E_{OCP} was measured for 3600–4400 s in a cell filled with 0.5 M H_2SO_4 electrolyte solution without applying current. The recorded open circuit potentials were $E_{OCP} = -0.005$ (V) for the reference sample and $E_{OCP} = +0.350$ (V) for the sample doped with platinum. Corrosion parameters such as corrosion potential (E_{corr}) and current density (I_{corr}) were determined by the Tafel extrapolation method using both the cathode and anodic branches of the polarization curves. The polarization resistance (R_p) was calculated using the formula:

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

where β_a and β_c are the slope of the anodic and cathodic straight lines of the Tafel equation, respectively, obtained by extrapolation.

The microstructure and surface morphology of the samples before and after corrosion tests were 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 diffraction (XRD) was carried out on an Ultima IV diffractometer (Rigaku, Tokyo, Japan) using $Cu K\alpha$. The scanning speed was 5 degrees per minute, and the scanning step was set to 0.02 degrees.

3. Results and Discussion

3.1. Microstructure and Phase Composition

Figure 1 shows the microstructure of the as-cast HEA samples and the corresponding elemental EDS mapping. According to the results, both samples demonstrated an almost homogeneous microstructure with a uniform distribution of the constituent elements. However, a slight unevenness, apparently along the grain boundaries, could be noted.

The average chemical composition of the as-cast samples is given in Table 1. For alloys, the change in the configurational entropy of mixing can be determined by the formula [29]:

$$\Delta S_{mix} = -R \sum_{i=1}^n X_i \ln X_i \quad (2)$$

where R is the universal gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and X is the atomic fraction of the elements in the alloy. When $\Delta S_{mix} \geq 1.5R$, the alloy can be considered a HEA. Using EDS data on the average composition, the changes in the configurational entropy of mixing were calculated for both alloys. According to the results (see Table 1), both samples can be categorized as HEA.

XRD patterns of the samples are shown in Figure 2. In the as-cast state, both samples exhibited a single-phase face-centered cubic (fcc) solid solution. According to the literature [30,31], $Al_xCoCrFeNi$ base HEAs with an aluminum content of $x < 0.3$ crystallize into

an fcc structure, which corresponds to our results. It seems that platinum is completely dissolved in the fcc solid solution phase and does not segregate as a separate phase.

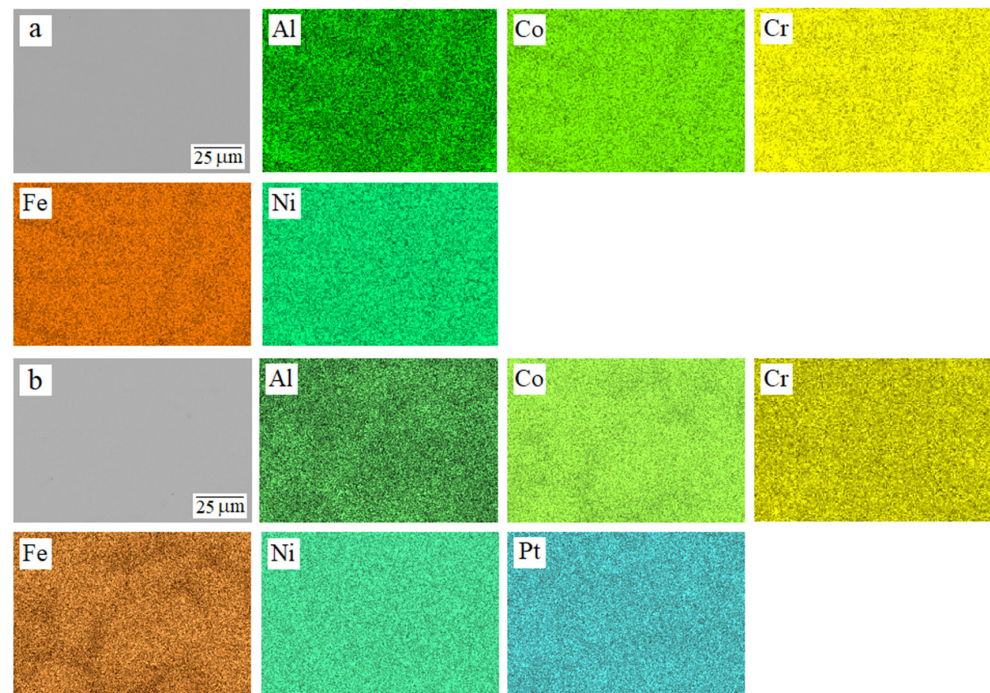


Figure 1. SEM images (in backscattered electrons mode) and the corresponding EDS maps of the as-cast $\text{Al}_{0.25}\text{CoCrFeNi}$ (a) and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ (b) HEAs.

Table 1. EDS-determined average chemical composition (at. %) and the configurational entropy of mixing for as-cast HEAs.

Alloy	Al	Co	Cr	Fe	Ni	Pt	$\Delta S_{\text{mix}}, \text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$
$\text{Al}_{0.25}\text{CoCrFeNi}$	5.86	23.47	23.88	23.21	23.58	–	1.53R
$\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$	5.64	22.93	23.10	22.96	23.05	2.32	1.60R

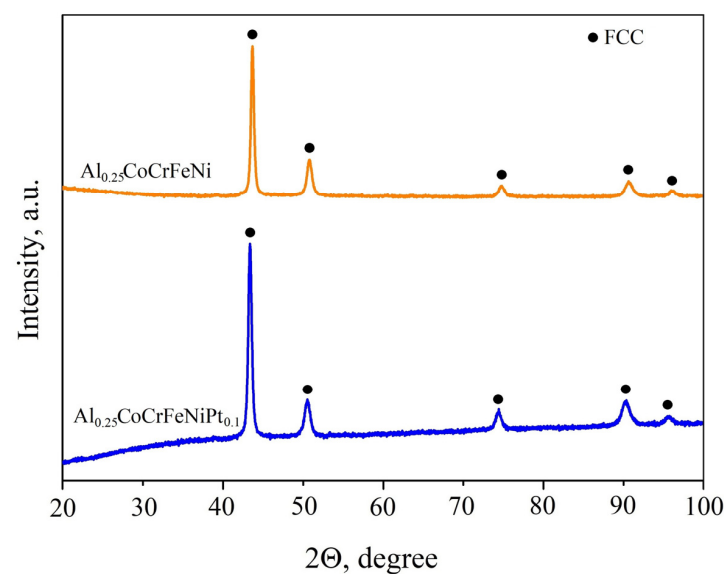


Figure 2. XRD patterns of the as-cast $\text{Al}_{0.25}\text{CoCrFeNi}$ and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEA samples.

3.2. High-Temperature Oxidation

Figure 3 shows the specific weight gains of the samples during the high-temperature oxidation test. Pt had a positive effect on the oxidation resistance of $\text{Al}_{0.25}\text{CoCrFeNi}$ HEA. The specific weight gain (after 50 h of oxidation duration) for the alloy doped with platinum was 0.31 mg/cm^2 , while it was 0.58 mg/cm^2 for the reference sample without platinum alloying. These results can be compared, for example, with the data reported by Zhu et al. [32], where a specific weight gain of 1.25 mg/cm^2 after 50 h of isothermal holding at 900°C was observed for AlCoCrFeNi HEA. Moreover, Abbaszadeh et al. [33] determined a specific weight gain of 0.42 mg/cm^2 after 72 h of exposure at 900°C for $\text{Al}_{0.5}\text{CoCrFeNi}$. Liu et al. [34] demonstrated a specific weight gain of 0.6 mg/cm^2 after 100 h holding at 1000°C for $\text{Al}_{0.5}\text{CoCrCuFeNi}$ HEA. For $\text{Al}_{0.3}\text{CoCrFeNi}$, Mohanty et al. [35] also obtained a value of 0.6 mg/cm^2 after 50 h of exposure at 1100°C . Thus, $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEA shows a rather high resistance to high-temperature oxidation.

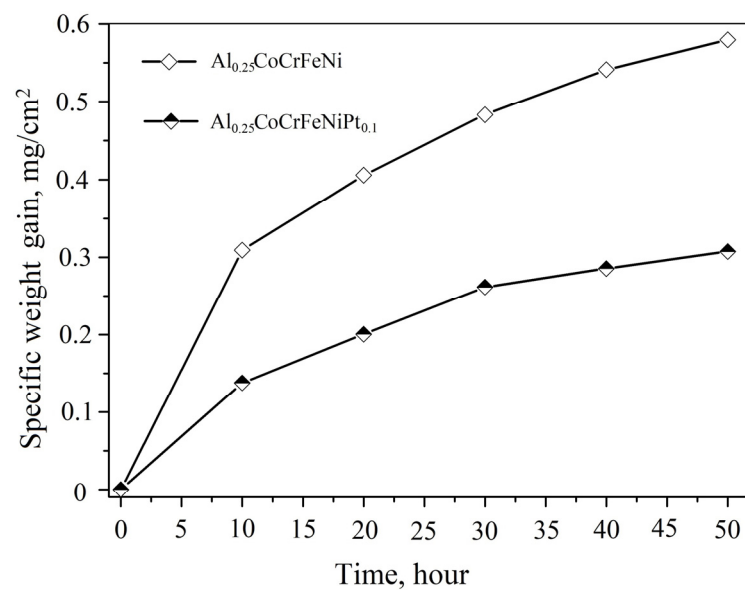


Figure 3. Specific weight gain for as-cast $\text{Al}_{0.25}\text{CoCrFeNi}$ and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEAs during oxidation at 900°C for 0–50 h.

The kinetic curves in Figure 3 suggest that the oxidation process follows the parabolic law, for which the specific weight gain (W) can be related to time by the formula:

$$W = k\sqrt{\tau}; \quad (3)$$

or

$$\left(\frac{\Delta m}{A}\right)^2 = k_p \tau, \quad (4)$$

where Δm is weight gain (g), A is surface area (cm^2), k_p is the parabolic oxidation rate constant ($\text{g}^2/\text{cm}^4 \text{ s}$) and τ is holding time (s). The determined parabolic oxidation rate constant in comparison with the literature data is given in Table 2. It can be noted that the oxidation rate of $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ alloy is comparable with the available literature data on other HEAs, and it is much lower than the oxidation rate of AISI 304L steel.

Table 2. Oxidation rate parabolic constant (k_p , $\text{g}^2/\text{cm}^4\text{s}$) of $\text{Al}_{0.25}\text{CoCrFeNi}$ and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEAs at 900 °C compared with the literature data.

Alloy	k_p	Alloy	k_p
$\text{Al}_{0.25}\text{CoCrFeNi}$	22×10^{-13}	$\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}\text{Nb}_{0.05}$ [19]	78.5×10^{-13}
$\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$	5.62×10^{-13}	$\text{Al}_{0.5}\text{CoCrFeNi}$ [33]	8.91×10^{-13}
$\text{Al}_{0.6}\text{CrFeCoNi}$ [16]	11.8×10^{-13}	FeCoNiCrAl [36]	4.9×10^{-13}
$\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$ [19]	280×10^{-13}	AISI 304L [37]	23×10^{-13}

The morphology of the oxide layers was studied by SEM, and the results are shown in Figure 4. It can be noted that the resulting oxide layers were quite even, without chips, cracks or pores and consist of two types of crystals; the compositions of these are given in Table 3. Lamellar crystals (Figure 4, on the left), in addition to oxygen, have an increased content of aluminum and chromium, and rhombohedral crystals (see Figure 4, on the right) are characterized by the presence (in addition to oxygen) of chromium, nickel, cobalt and iron. If we compare the distribution of crystals over the area of the oxide film (see Figure 4, center), it can be noted that rhombohedral crystals dominated in the sample without platinum, while the proportion of lamellar and rhombohedral crystals was almost same in the sample doped with platinum. This fact is also confirmed by chemical analysis (see Table 3), since the concentration of chromium in the average composition of the oxide film in the $\text{Al}_{0.25}\text{CoCrFeNi}$ sample was noticeably higher than that in $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEA. Additionally, the concentration of platinum in the composition of the oxide film formed on the surface of $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ alloy did not exceed 0.3 at. %.

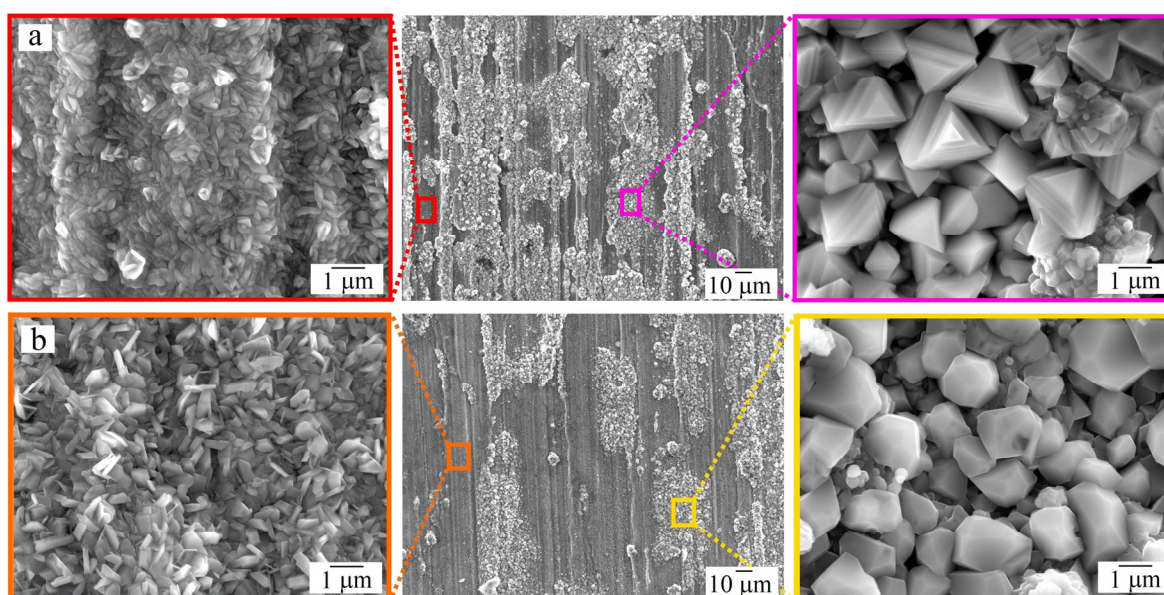


Figure 4. SEM images (in secondary electrons mode) indicating the morphology of oxide film formed after 50 h of high-temperature oxidation on the surface of $\text{Al}_{0.25}\text{CoCrFeNi}$ (a) and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ (b) HEAs.

Figure 5 shows XRD patterns recorded from the surface of the samples after high-temperature oxidation. In addition to the fcc solid solution, diffraction patterns showed peaks from the $(\text{Al,Cr})_2\text{O}_3$ solid solution based on aluminum oxide, $(\text{Cr,Al})_2\text{O}_3$ solid solution based on chromium oxide, NiCr_2O_4 , CoCr_2O_4 and FeCr_2O_4 oxide phases. If we compare XRD data with the data from Table 3 and Figure 4, it can be assumed that lamellar crystals belong to a solid solution based on aluminum oxide, while rhombohedral crystals

belong to a solid solution based on chromium oxide and spinels. No oxide compounds with platinum were found according to the results of X-ray diffraction.

Table 3. Chemical composition (determined by EDS, at. %) of the oxide film formed on the surface of HEAs samples after 50 h of high-temperature oxidation. Av—average composition; LC—lamellar crystals; RC—rhombohedral crystals.

Alloy		Al	Co	Cr	Fe	Ni	Pt	O
Al _{0.25} CoCrFeNi	Av	8.99	4.54	23.92	4.30	4.75	–	53.50
	LC	23.86	3.20	13.88	3.15	3.11	–	52.80
	RC	0.06	5.18	31.36	4.37	5.52	–	53.51
Al _{0.25} CoCrFeNiPt _{0.1}	Av	14.11	4.21	19.19	4.17	3.37	0.21	54.74
	LC	22.71	4.17	11.25	4.30	3.38	0.27	53.92
	RC	1.02	3.83	33.03	3.37	2.93	0.08	55.74

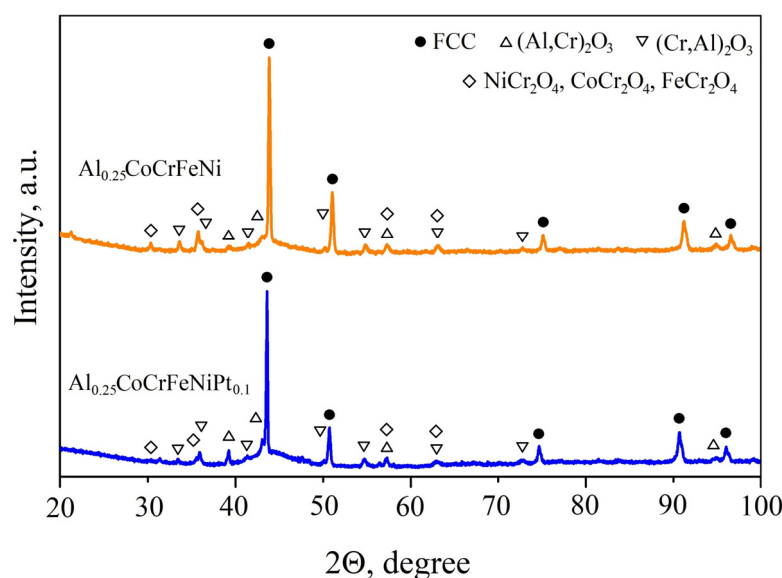


Figure 5. XRD patterns of Al_{0.25}CoCrFeNi and Al_{0.25}CoCrFeNiPt_{0.1} HEA samples after 50 h of high-temperature oxidation.

The transverse section of the samples after the oxidation test was further investigated. It can be seen that the thickness of the formed oxide film for both samples was almost same, and it was about 5–7 μm , but there were differences in the thickness of the internal oxidation layer (Figure 6). Moreover, while Cr-rich oxide phase formed on the outer layer of both samples, Al_{0.25}CoCrFeNiPt_{0.1} was characterized by the formation of an interlayer Al-rich oxide phase between the outer Cr-rich oxide layer and the interior of the alloy. For platinum-doped Al_{0.25}CoCrFeNiPt_{0.1} HEA, the thickness of internal oxidation did not exceed 10 μm , while it was about 20–25 μm for Al_{0.25}CoCrFeNi, which is 2–2.5 times higher than that of Al_{0.25}CoCrFeNiPt_{0.1}.

The Al content of HEAs affects their resistance against high-temperature oxidation. The higher the Al concentration, the higher the oxidation resistance of the alloy [9]. Therefore, for Al_{0.25}CoCrFeNi HEA with an aluminum content of 0.25, rather low resistance to high-temperature oxidation can be expected, since a film consisting mainly of Cr₂O₃ is formed (see Figure 6a). Such a film does not have the necessary protective properties. Introducing platinum into Al_{0.25}CoCrFeNi does not trigger the formation of other oxide phases on the surface, but it triggers the formation of continuous aluminum oxide beneath the Cr-rich outer oxide layer (see Figure 6b). Apparently, platinum in the composition of the

solid solution affects the diffusion characteristics of the elements and slows down diffusion processes that occur in the surface layers of the metal when interacting with oxygen atoms. Furthermore, the noble nature of Pt inherently improves the oxidation resistance of the alloy and prevents in-depth oxidation. As a result, there is enough time for Al to form a continuous oxide layer beneath the outer scale layer. This, in turn, significantly decreases the internal oxidation layer (see Figure 6b).

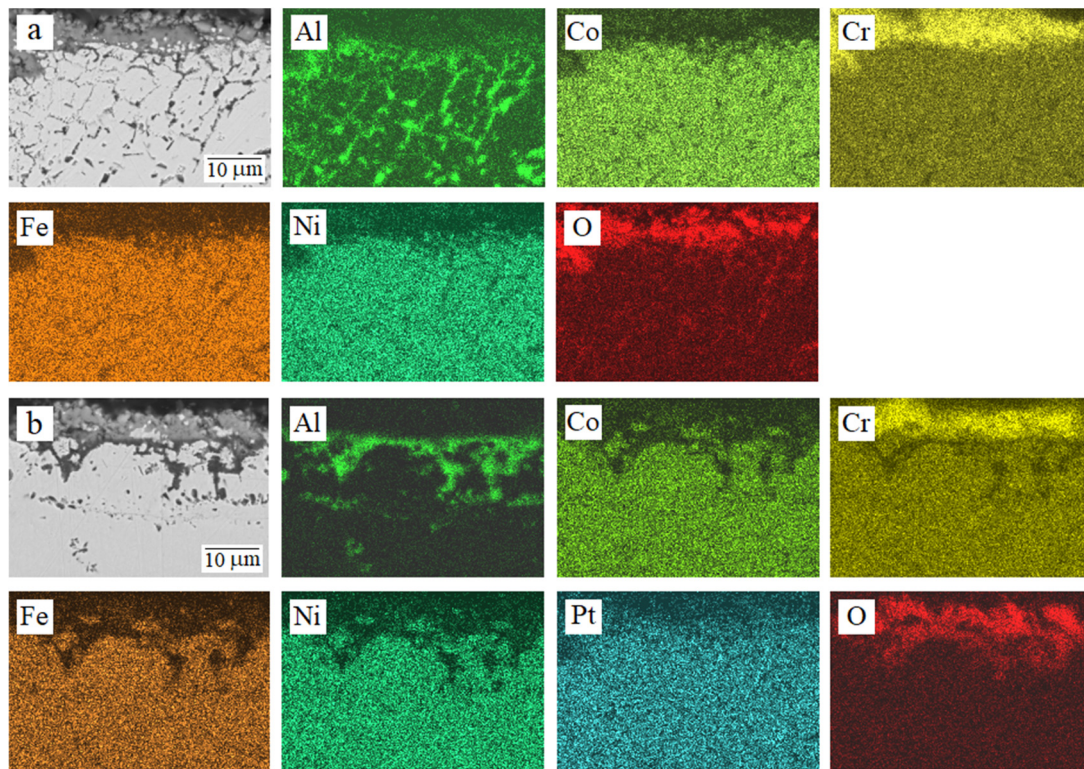


Figure 6. SEM micrographs (in backscattered electrons mode) and the corresponding EDS maps of the transverse section of $\text{Al}_{0.25}\text{CoCrFeNi}$ (a) and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ (b) HEAs after 50 h of high-temperature oxidation.

A similar effect of introducing platinum on the formation of a denser β -NiAl coating with good adhesion to the substrate material and improved high-temperature oxidation resistance was discovered in [38–41]. It has been shown that platinum in the β -(Ni,Pt)Al coating promotes the formation of a single α - Al_2O_3 scale during oxidation and improves the self-healing ability of the Al_2O_3 film. Moreover, Baskaran et al. in [39] showed the best effect of introducing platinum on the formation of the interdiffusion zone since platinum is an element that directly affects the diffusion characteristics in relation to alloys. In addition, the oxide film obtained on the surface of the Ni40Pt10Al50 bond coat (after oxidation of the sample at 1100 °C) did not show cracking or spallation and had the best protective properties. The effect of platinum on the diffusion between the (Ni,Pt)Al coating and the superalloy matrix material was also discussed in detail in a study by Bai et al. [40].

3.3. Corrosion Resistance Test

Figure 7 shows the polarization curves of the HEAs in a 0.5 M H_2SO_4 solution. Samples in sulfuric acid solution demonstrated passive behavior with anodic process control. However, according to the results of calculating E_{corr} and I_{corr} , as well as the polarization resistance (Table 4), $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEA with platinum showed a slightly higher resistance to electrochemical corrosion. In comparison with the available literature data (see Table 4), it can be noted that both investigated HEAs had high corrosion resistance

in 0.5 M H₂SO₄ solution. Table 4 also shows data on the passive current density (I_{pas}), passivation interval (ΔE) and breakdown potential (E_b).

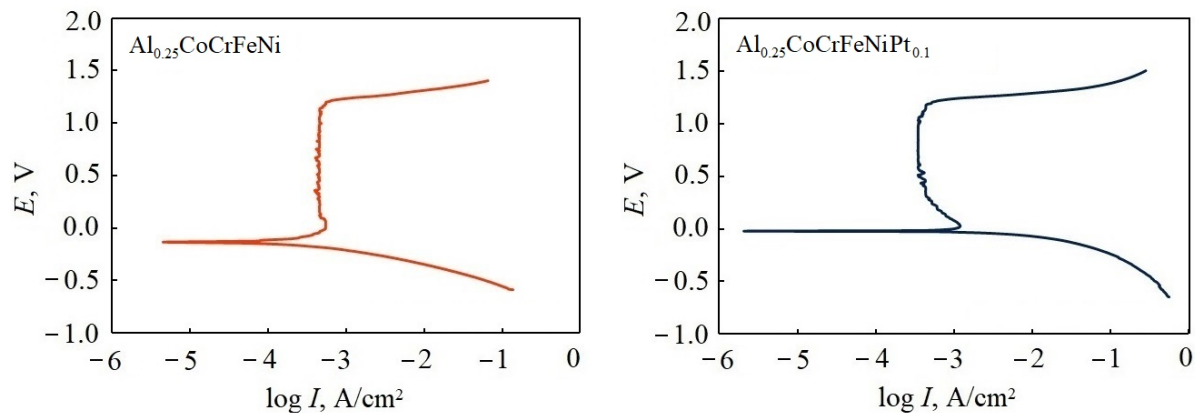


Figure 7. Polarization curves in 0.5 M H₂SO₄ solution for Al_{0.25}CoCrFeNi and Al_{0.25}CoCrFeNiPt_{0.1} HEAs.

Table 4. Potentials and current densities of Al_{0.25}CoCrFeNi and Al_{0.25}CoCrFeNiPt_{0.1} HEAs in 0.5 M H₂SO₄ solution compared with different alloys reported in the literature.

Alloy	E_{corr} , V	I_{corr} , $\mu\text{A}/\text{cm}^2$	R_p , $\text{k}\Omega\text{cm}^2$	I_{pas} , $\mu\text{A}/\text{cm}^2$	ΔE	E_b , V
Al _{0.25} CoCrFeNi	-0.132 ± 0.003	6.67 ± 0.05	1.12 ± 0.03	417	1.262	1.195
Al _{0.25} CoCrFeNiPt _{0.1}	-0.018 ± 0.002	3.93 ± 0.02	6.79 ± 0.05	356	1.222	1.218
Al _{0.25} CoCrFeNiCu [22]	-0.164 ± 0.002	607 ± 3	0.088 ± 0.001	271	0.077	–
Al _{0.5} CoCrFeNiTi _{0.5} [23]	-0.400	320	–	24.8	0.650	0.980
FeCoNiCrCu _{0.5} Al _{0.5} [25]	-0.112	4.190	–	3000	0.550	–
AlCoCrFeNiSi _{0.1} [27]	-0.453	304.20	–	19.35	1.350	0.925
SS 304 [27]	-0.438	105.12	–	4.47	1.261	0.925
Al _{0.5} CoCrFeNiCu _{0.25} [28]	-0.112 ± 0.002	3.52 ± 0.02	7.81 ± 0.05	21.5	0.967	–
Al _{0.5} CoCrFeNiCu _{0.25} Ag _{0.1} [28]	-0.143 ± 0.002	5.21 ± 0.05	8.47 ± 0.05	28.8	1.282	–
Al _{0.25} CoCrFeNi [42]	-0.095	16.7	–	7.1	1.080	–
SS 304 [42]	-0.185	45.3	–	19.1	0.750	–
Co _{1.5} CrFeNi _{1.5} Ti _{0.5} [43]	-0.092	30	–	9	1.130	1.089
Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.1} [43]	-0.071	78	–	9	1.112	1.089
AlCoCuFeNiCr [44]	-0.075	5.09	14.450	–	0.650	–
AlCoCuFeNiCrTi [44]	-0.256	39.59	1.558	–	0.940	–
Al _{0.3} CrFe _{1.5} MnNi _{0.5} [45]	-0.194	2390	–	73.9	1.176	–

It should be noted that passivation of the alloys under study occurred at higher passive current density than for some compositions presented in the literature (see Table 4). Thus, the passivation process did not begin immediately, which may indicate the initial appearance of microgalvanic cells. However, the obtained values for the studied samples showed their high corrosion resistance to general corrosion.

Breakdown potential is defined as the surface potential at which the surface's passive film breaks down. The more positively its value is shifted, the more corrosion-resistant the sample is. The obtained data for both HEAs showed better values compared to alloys, data for which are given in the literature (see Table 4).

The surface of $\text{Al}_{0.25}\text{CoCrFeNi}$ and $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEAs practically indicated no corrosion pits, pores or pitting after electrochemical corrosion (Figure 8). However, it can be clearly seen that the $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ sample was subjected to a stronger effect of sulfuric acid, possibly due to a somewhat uneven distribution of platinum in the solid solution (see Figure 1). Areas with a higher concentration of platinum (see point B in Figure 8b and Table 5) hardly corroded, while areas with a lower content of platinum (see point A in Figure 8b and Table 5) underwent partial dissolution. If we compare the average compositions of the sample doped with platinum before and after electrochemical tests (see Tables 1 and 5), it can be noted that all elements, except platinum, passed into the sulfuric acid solution; therefore, platinum concentration in the sample after testing was almost two times higher than that of the as-cast sample.

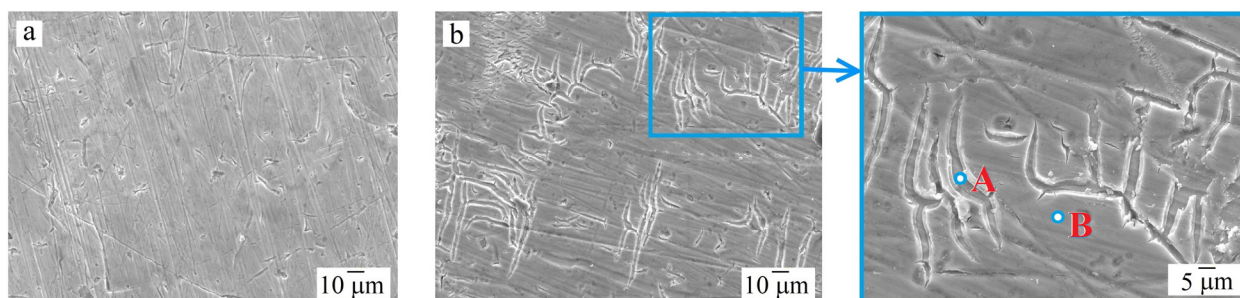


Figure 8. SEM micrographs (in secondary electrons mode) indicating morphology of the corroded surfaces for (a) $\text{Al}_{0.25}\text{CoCrFeNi}$ and (b) $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEAs. Points A and B are the locations of EDS analysis (see Table 5).

Table 5. EDS chemical composition (at. %) recorded from the surface of the samples after testing in 0.5 M H_2SO_4 solution. Av—average composition; points A and B—see Figure 8b.

Alloy		Al	Co	Cr	Fe	Ni	Pt	O	S
$\text{Al}_{0.25}\text{CoCrFeNi}$	Av	5.66	21.88	23.17	21.54	22.03	–	5.64	0.08
	Av	4.10	19.91	21.45	19.56	19.50	5.60	8.94	0.94
$\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$	A	2.40	19.68	24.64	18.11	19.36	2.62	12.08	1.11
	B	4.53	20.45	20.72	20.56	20.64	6.91	5.77	0.42

It is possible that the manifested negative effect of the uneven platinum distribution in the as-cast microstructure can be avoided by subjecting the sample to homogenizing annealing, which will be studied in our future work. However, due to the fact that platinum is highly incorporated into the solid solution of $\text{Al}_{0.25}\text{CoCrFeNi}$ and does not segregate as second phases, it is a promising element for doping $\text{Al}_{0.25}\text{CoCrFeNi}$ HEA.

4. Conclusions

The effect of alloying Pt on the microstructure, high-temperature oxidation resistance (at 900 °C) and corrosion resistance (in a 0.5 M H_2SO_4 solution) of $\text{Al}_{0.25}\text{CoCrFeNi}$ high-entropy alloy was investigated. It was found out that Pt can be incorporated into the fcc solid solution phase of $\text{Al}_{0.25}\text{CoCrFeNi}$ up to 2.3 at. % without segregation and phase separation. At the same time, it affects diffusion processes during high-temperature oxidation owing to its chemical inertness and consequently decreases the oxidation rate of $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ alloy at 900 °C compared to that of $\text{Al}_{0.25}\text{CoCrFeNi}$ HEA. Apparently, the noble nature of Pt inherently improves the oxidation resistance of the alloy and prevents in-depth oxidation so that it provides enough time for Al to form a continuous oxide layer beneath the outer scale layer and protect $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ HEA from further oxidation. On the other hand, $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ also exhibited higher corrosion resistance compared to $\text{Al}_{0.25}\text{CoCrFeNi}$, which may be attributed to the synergistic effects of chromium and the

chemically inert platinum in the alloy composition. In particular, the corrosion current density of $\text{Al}_{0.25}\text{CoCrFeNiPt}_{0.1}$ was $3.93 \pm 0.02 \mu\text{A}/\text{cm}^2$ versus the obtained value of $6.67 \pm 0.05 \mu\text{A}/\text{cm}^2$ for $\text{Al}_{0.25}\text{CoCrFeNi}$ HEA.

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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. 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. [\[CrossRef\]](#) [\[PubMed\]](#)
4. 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. [\[CrossRef\]](#)
5. Kasar, A.K.; Scalero, K.; Menezes, P.L. Tribological properties of high-entropy alloys under dry conditions for a wide temperature range—A review. *Materials* **2021**, *14*, 5814. [\[CrossRef\]](#)
6. Feng, C.; Wang, X.; Yang, L.; Guo, Y.; Wang, Y. High hardness and wear resistance in AlCrFeNiV high-entropy alloy induced by dual-phase body-centered cubic coupling effects. *Materials* **2022**, *15*, 6896. [\[CrossRef\]](#)
7. 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. [\[CrossRef\]](#)
8. 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. [\[CrossRef\]](#)
9. Cho, F.Y.; Tung, S.W.; Ouyang, F.Y. High temperature oxidation behavior of high entropy alloy $\text{Al}_4\text{Co}_3\text{Cr}_{25}\text{Cu}_{10}\text{Fe}_{25}\text{Ni}_{33}$ in oxygen-containing atmospheres. *Mater. Chem. Phys.* **2022**, *278*, 125678. [\[CrossRef\]](#)
10. Kumar, P.; Lam, T.-N.; Tripathi, P.K.; Singh, S.S.; Liaw, P.K.; Huang, E.-W. Recent progress in oxidation behavior of high-entropy alloys: A review. *APL Mater.* **2022**, *10*, 120701. [\[CrossRef\]](#)
11. Shi, Y.; Yang, B.; Liaw, P.K. Corrosion-resistant high-entropy alloys: A review. *Metals* **2017**, *7*, 43. [\[CrossRef\]](#)
12. Qiu, Y.; Thomas, S.; Gibson, M.A.; Fraser, H.L.; Birbilis, N. Corrosion of high entropy alloys. *NPJ Mater. Degrad.* **2017**, *1*, 15. [\[CrossRef\]](#)
13. Meghwal, A.; Anupam, A.; Murty, B.S.; Berndt, C.C.; Kottada, R.S.; Ang, A.S.M. Thermal spray high-entropy alloy coatings: A review. *J. Therm. Spray Technol.* **2020**, *29*, 857–893. [\[CrossRef\]](#)
14. Liu, J.; Liu, H.; Chen, P.; Hao, J. Microstructural characterization and corrosion behaviour of AlCoCrFeNiTi_x high-entropy alloy coatings fabricated by laser cladding. *Surf. Coat. Technol.* **2019**, *361*, 63–74. [\[CrossRef\]](#)
15. Samoilova, O.; Shaburova, N.; Samodurova, M.; Pashkev, K.; Ostovari Moghaddam, A.; Trofimov, E. Microstructure and wear behavior of $\text{Al}_{0.25}\text{CoCrFeNiSi}_{0.6}$ high-entropy alloy coating deposited on stainless steel by detonation spraying. *J. Therm. Spray Technol.* **2023**, *32*, 1220–1229. [\[CrossRef\]](#)
16. Chen, L.; Zhou, Z.; Tan, Z.; He, D.; Bobzin, K.; Zhao, L.; Öte, M.; Königstein, T. High temperature oxidation behavior of $\text{Al}_{0.6}\text{CrFeCoNi}$ and $\text{Al}_{0.6}\text{CrFeCoNiSi}_{0.3}$ high entropy alloys. *J. Alloys Compd.* **2018**, *764*, 845–852. [\[CrossRef\]](#)
17. Ostovari Moghaddam, A.; Shaburova, N.A.; Sudarikov, M.V.; Veselkov, S.N.; Samoilova, O.V.; Trofimov, E.A. High temperature oxidation resistance of $\text{Al}_{0.25}\text{CoCrFeNiMn}$ and $\text{Al}_{0.45}\text{CoCrFeNiSi}_{0.45}$ high entropy alloys. *Vacuum* **2021**, *192*, 110412. [\[CrossRef\]](#)
18. Shaburova, N.A.; Ostovari Moghaddam, A.; Veselkov, S.N.; Sudarikov, M.V.; Samoilova, O.V.; Trofimov, E.A. High-temperature oxidation behavior of $\text{Al}_x\text{CoCrFeNiM}$ ($M = \text{Cu}, \text{Ti}, \text{V}$) high-entropy alloys. *Phys. Mesomech.* **2021**, *24*, 653–662. [\[CrossRef\]](#)
19. Yang, J.-J.; Kuo, C.-M.; Lin, P.-T.; Liu, H.-C.; Huang, C.-Y.; Yen, H.-W.; Tsai, C.-W. Improvement in oxidation behavior of $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$ high-entropy superalloys by minor Nb addition. *J. Alloys Compd.* **2020**, *825*, 153983. [\[CrossRef\]](#)

20. Lu, J.; Chen, Y.; Zhang, H.; Ni, N.; Li, L.; He, L.; Mu, R.; Zhao, X.; Guo, F. Y/Hf-doped AlCoCrFeNi high-entropy alloy with ultra oxidation and spallation resistance. *Corros. Sci.* **2020**, *166*, 108426. [\[CrossRef\]](#)
21. 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_xFeNi high entropy alloys ($x = 0; 0.5; 1$). *Intermetallics* **2017**, *84*, 52–61. [\[CrossRef\]](#)
22. Pratskova, S.; Samoilova, O.; Ageenko, E.; Shaburova, N.; Ostovari Moghaddam, A.; Trofimov, E. Corrosion resistance of Al_xCoCrFeNiM (M = Ti, V, Si, Mn, Cu) high entropy alloys in NaCl and H₂SO₄ solutions. *Metals* **2022**, *12*, 352. [\[CrossRef\]](#)
23. Jiang, S.; Lin, Z.; Xu, H.; Sun, Y. Studies on the microstructure and properties of Al_xCoCrFeNiTi_{1-x} high entropy alloys. *J. Alloys Compd.* **2018**, *741*, 826–833. [\[CrossRef\]](#)
24. Qiu, Y.; Thomas, S.; Fabijanic, D.; Barlow, A.J.; Fraser, H.L.; Birbilis, N. Microstructural evolution, electrochemical and corrosion properties of Al_xCoCrFeNiTi_y high entropy alloys. *Mater. Des.* **2019**, *170*, 107698. [\[CrossRef\]](#)
25. Li, B.Y.; Peng, K.; Hu, A.P.; Zhou, L.P.; Zhu, J.J.; Li, D.Y. Structure and properties of FeCoNiCrCu_{0.5}Al_x high-entropy alloy. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 735–741. [\[CrossRef\]](#)
26. Qiu, X.W. Microstructure and properties of AlCrFeNiCoCu high entropy alloy prepared by powder metallurgy. *J. Alloys Compd.* **2013**, *555*, 246–249. [\[CrossRef\]](#)
27. Xiang, C.; Zhang, Z.M.; Fu, H.M.; Han, E.-H.; Zhang, H.F.; Wang, J.Q. Microstructure and corrosion behavior of AlCoCrFeNiSi_{0.1} high-entropy alloy. *Intermetallics* **2019**, *114*, 106599. [\[CrossRef\]](#)
28. Samoilova, O.; Pratskova, S.; Shaburova, N.; Ostovari Moghaddam, A.; Trofimov, E. Corrosion resistance of Al_{0.5}CoCrFeNiCu_xAg_y ($x = 0.25, 0.5; y = 0, 0.1$) high-entropy alloys in 0.5M H₂SO₄ solution. *Materials* **2023**, *16*, 3585. [\[CrossRef\]](#)
29. Swalin, R.A. *Thermodynamics of Solids*, 2nd ed.; Wiley: New York, NY, USA, 1972; 400p.
30. Wang, W.-R.; Wang, W.-L.; Yeh, J.-W. Phases, microstructure and mechanical properties of Al_xCoCrFeNi high-entropy alloys at elevated temperatures. *J. Alloys Compd.* **2014**, *589*, 143–152. [\[CrossRef\]](#)
31. Ogura, M.; Fukushima, T.; Zeller, R.; Dederichs, P.H. Structure of the high-entropy alloy Al_xCrFeCoNi: Fcc versus bcc. *J. Alloys Compd.* **2017**, *715*, 454–459. [\[CrossRef\]](#)
32. Zhu, J.; Lu, S.; Jin, Y.; Xu, L.; Xu, X.; Yin, C.; Jia, Y. High-temperature oxidation behaviours of AlCoCrFeNi high-entropy alloy at 1073–1273 K. *Oxid. Met.* **2020**, *94*, 265–281. [\[CrossRef\]](#)
33. Abbaszadeh, S.; Pakseresht, A.; Omidvar, H.; Shafiei, A. Investigation of the high-temperature oxidation behavior of the Al_{0.5}CoCrFeNi high entropy alloy. *Surf. Interf.* **2020**, *21*, 100724. [\[CrossRef\]](#)
34. Liu, Y.Y.; Chen, Z.; Chen, Y.Z.; Shi, J.C.; Wang, Z.Y.; Wang, S.; Liu, F. Effect of Al content on high temperature oxidation resistance of Al_xCoCrCuFeNi high entropy alloys ($x = 0, 0.5, 1, 1.5, 2$). *Vacuum* **2019**, *169*, 108837. [\[CrossRef\]](#)
35. Mohanty, A.; Sampreeth, J.K.; Bembalge, O.; Hascoet, J.Y.; Marya, S.; Immanuel, R.J.; Panigrahi, S.K. High temperature oxidation study of direct laser deposited Al_xCoCrFeNi ($x=0.3, 0.7$) high entropy alloys. *Surf. Coat. Technol.* **2019**, *380*, 125028. [\[CrossRef\]](#)
36. Kai, W.; Li, C.C.; Cheng, F.P.; Chu, K.P.; Huang, R.T.; Tsay, L.W.; Kai, J.J. Air-oxidation of FeCoNiCr-based quinary high-entropy alloys at 700–900 °C. *Corros. Sci.* **2017**, *121*, 116–125. [\[CrossRef\]](#)
37. Lussana, D.; Baldissin, D.; Massazza, M.; Baricco, M. Thermodynamic and kinetics aspects of high temperature oxidation on a 304L stainless steel. *Oxid. Met.* **2014**, *81*, 515–528. [\[CrossRef\]](#)
38. Li, W.; Fu, L.B.; Liu, Y.D.; Zhang, W.L.; Wang, T.G.; Jiang, S.M.; Gong, J.; Sun, C. The role of Re in effecting isothermal oxidation behavior of β -(Ni,Pt)Al coating on a Ni-based single crystal superalloy. *Corros. Sci.* **2020**, *176*, 108892. [\[CrossRef\]](#)
39. Baskaran, T.; Esakkiraja, N.; Samartha, C.; Kumar, P.; Jayaram, V.; Paul, A. Effect of addition of Pt, Pd and Ir to β -NiAl-bond coat on oxidation resistance and growth of interdiffusion zone. *Surf. Coat. Technol.* **2021**, *426*, 127766. [\[CrossRef\]](#)
40. Bai, M.; Chen, Y.; Xiao, P. Investigations on the diffusion of platinum between CMSX-4 superalloy and platinum-enriched bond coat. *Coatings* **2021**, *11*, 441. [\[CrossRef\]](#)
41. Zhou, Z.M.; Peng, H.; Zheng, L.; Guo, H.B.; Gong, S.K. Thermal cycling performance of La₂Ce₂O₇/YSZ TBCs with Pt/Dy co-doped NiAl bond coat on single crystal superalloy. *Rare Met.* **2021**, *40*, 2568–2578. [\[CrossRef\]](#)
42. Kao, Y.F.; Lee, T.D.; Chen, S.K.; Chang, Y.S. Electrochemical passive properties of Al_xCoCrFeNi ($x = 0, 0.25, 0.50, 1.00$) alloys in sulfuric acids. *Corros. Sci.* **2010**, *52*, 1026–1034. [\[CrossRef\]](#)
43. Chou, Y.L.; Yeh, J.W.; Shih, H.C. The effect of molybdenum on the corrosion behaviour of the high-entropy alloys Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_x in aqueous environments. *Corros. Sci.* **2010**, *52*, 2571–2581. [\[CrossRef\]](#)
44. Xiao, D.H.; Zhou, P.F.; Wu, W.Q.; Diao, H.Y.; Gao, M.C.; Song, M.; Liaw, P.K. Microstructure, mechanical and corrosion behaviors of AlCoCuFeNi-(Cr,Ti) high entropy alloys. *Mater. Des.* **2017**, *116*, 438–447. [\[CrossRef\]](#)
45. Lee, C.P.; Chang, C.C.; Chen, Y.Y.; Yeh, J.W.; Shih, H.C. Effect of aluminium content of Al_xCrFe_{1.5}MnNi_{0.5} high-entropy alloys on the corrosion behaviour in aqueous environments. *Corros. Sci.* **2008**, *50*, 2053–2060. [\[CrossRef\]](#)

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