Effect of Al Content on the Hot Corrosion of High Entropy Alloys

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1. Background

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$$

High entropy alloys (HEAs) have recently re-emerged as a new class of alloys with the potential to be utilized in advanced engineering applications. They exhibit an attractive combination of wear resistance, hardness and high temperature strength coupled with relatively low densities.[1] Unlike traditional alloys, HEAs contain five or more elements with equal or near-equal atomic percent.[2] The result of this unconventional alloying gives high entropy alloys extraordinary properties. Turbine blades are one of many potential applications that are being explored for HEAs.[3] Gas turbines operating in the 650-900°C range in marine environments, can be subjected to accelerated corrosion beneath a thin molten eutectic salt film consisting of NaCl and Na_2SO_4 (Type II hot corrosion).

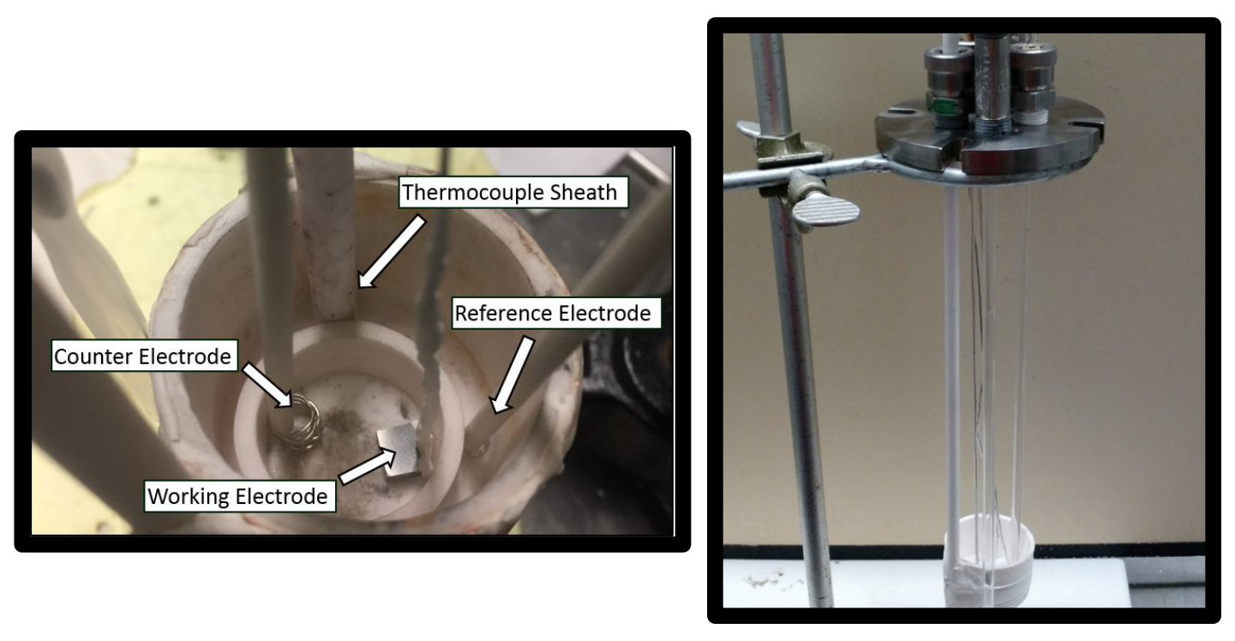
The behavior of HEAs under these corrosive conditions is virtually unknown. This study builds on our earlier studies of the hot corrosion behavior of an equimolar AlCoCrFeNi high entropy alloy with relatively high aluminum content. The questions raised by our earlier work led to the current study in which the aluminum content of this alloy was varied.

2. Objective

To evaluate the corrosion behavior of an AlxCoCrFeNi HEA at various aluminum contents (x=0, 0.3, 0.6)

3. Materials and Methods

The AlxCoCrFeNi high entropy alloy was produced at various aluminum contents (abbreviated as Al_0, $Al0_{.3}$, $Al0_{.6}$) and electrochemically tested at 700°C under a molten NaCl-Na_2SO_4 eutectic salt mixture. The electrochemical cell consisted of three electrodes positioned inside an alumina crucible as seen in Figure 1. Pure platinum wire was used for both the reference and counter electrodes. The working electrode was fabricated using rectangular coupons ground to a 600 grit surface finish. Electro-chemical tests were conducted using a commercially available potentiostat. The testing procedure involved recording the open circuit potential (OCP) for one hour and then a linear polarization (LP) and a cyclic potentiodynamic polarization (CPP) sweep. After exposure to the molten salt environment, the test specimens were Ni-plated to help retain the oxidation product and then epoxy mounted. The test coupons were metallographically prepared to a 1 µm surface finish and analyzed using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS).



(a) (b)

Figure 1. Electrochemical system (a) in the crucible (b) attached to the flange and gas lines

4. Results

Macrophotography

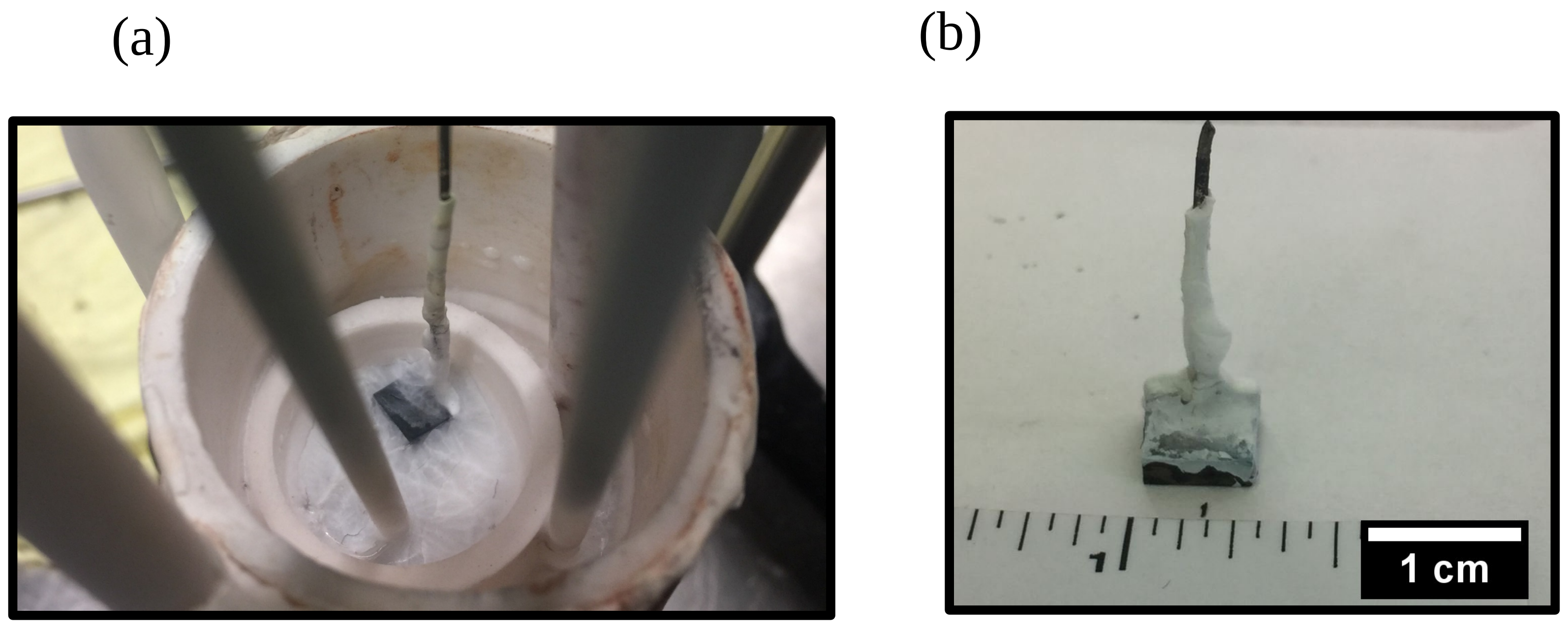


Figure 2. Macrographs of the high entropy alloy coupons (a) in the electrochemical cell (b) extracted for post-test analysis

Scanning Electron Microscopy

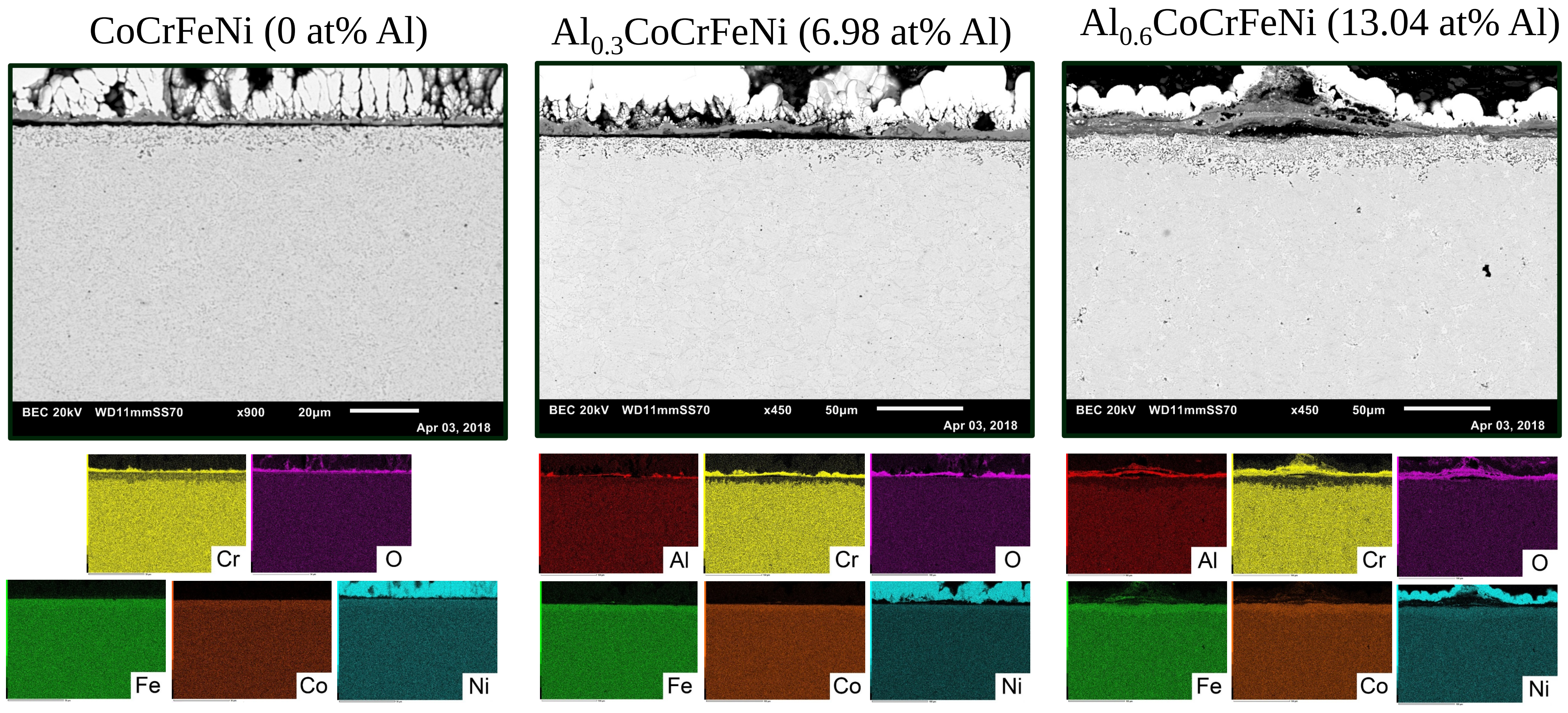


Figure 3: Backscattered electron images and EDS elemental maps of the Al_xCoCrFeNi HEAs sample cross section at the exposed surface.

X-ray Diffraction

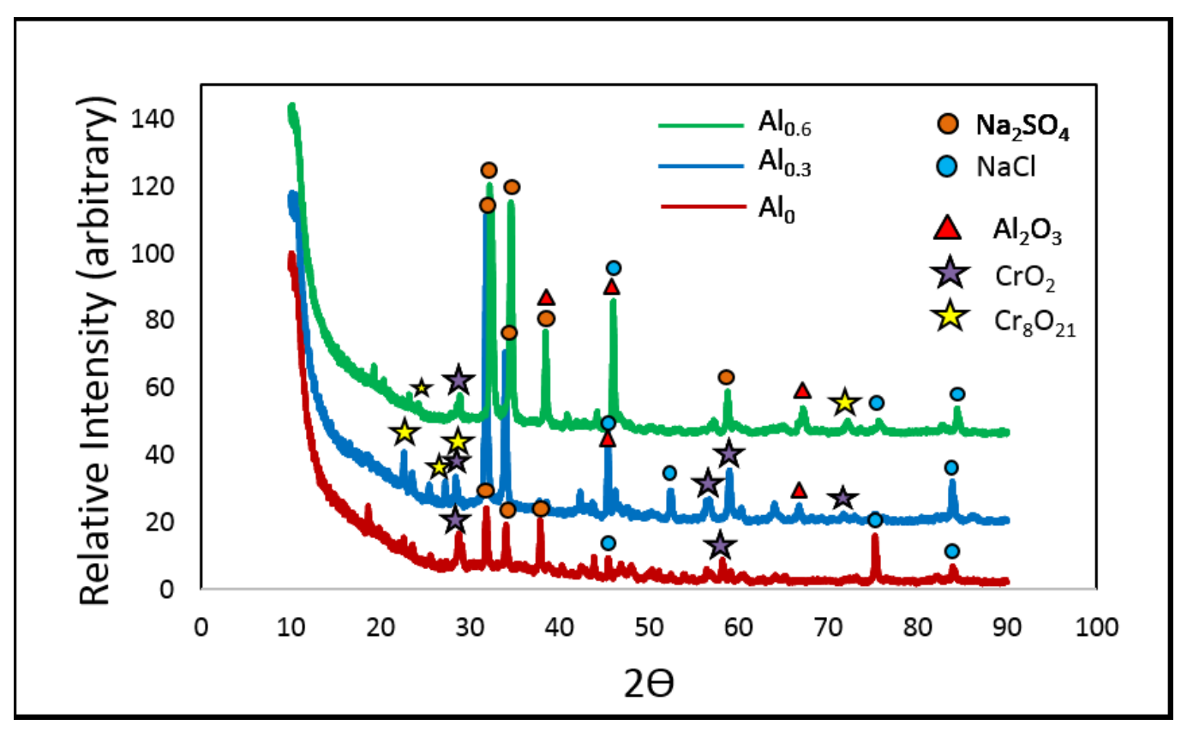


Figure 4. X-ray diffractogram for all HEAs tested

Cyclic Potentiodynamic Polarization

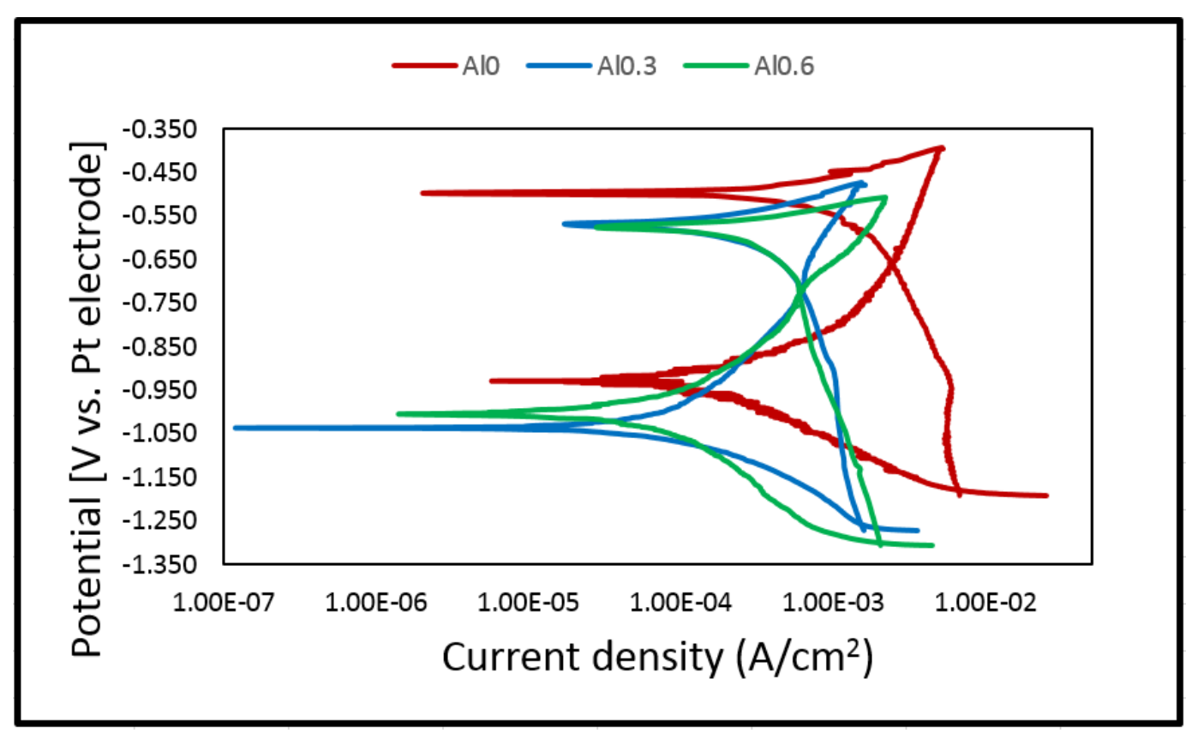


Figure 5. Cyclic Potentiodynamic Polarization (CPP) plot for all HEAs tested

Corrosion Rate

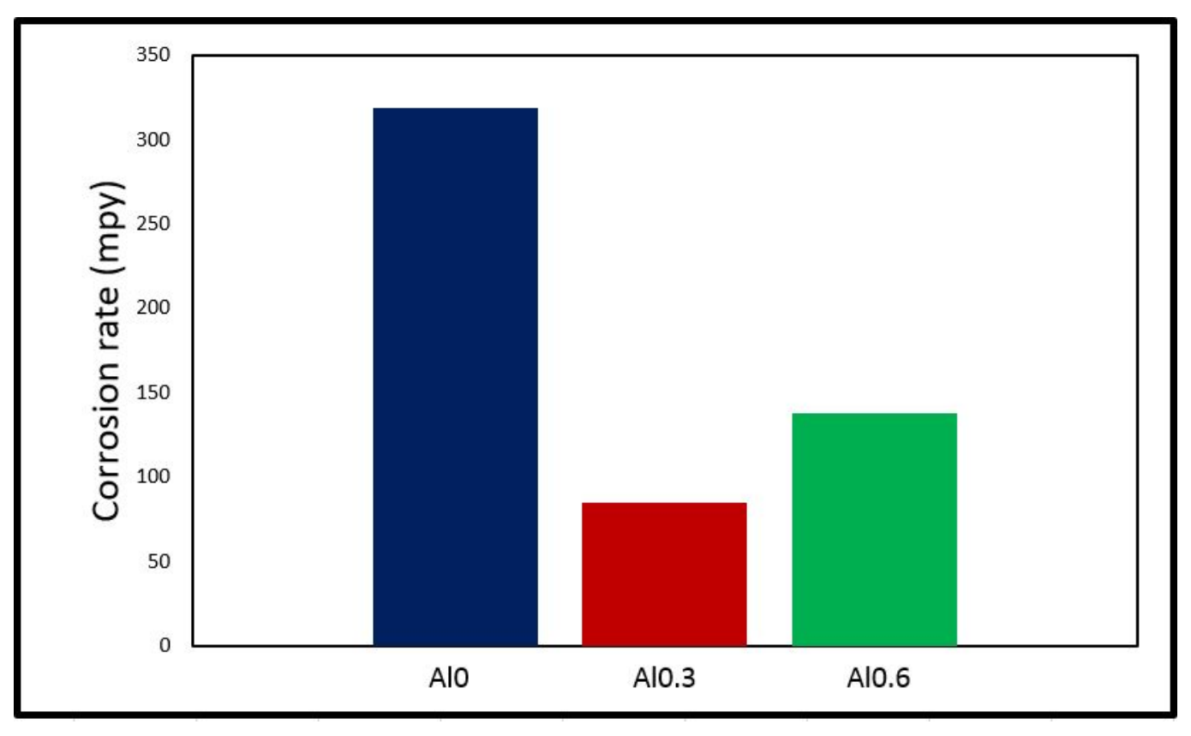


Figure 6. Corrosion rate values for all HEAs tested

5. Discussion

Figure 2 shows macrographs of the electrochemical cell and the coupon after testing. The white substance on the surface of the coupon is the remnant of the molten salt. This should not be confused with the white deposit on the wire. The latter is a ceramic cement used to prevent corrosion on the lead wire. Figure 3 shows a cross-sectional view of the post-tested coupons along with the elemental maps. The SEM/EDS results indicate the formation of an outer chromium oxide layer on all coupons and an internal aluminum oxide layer on the HEAs with the 0.3 and the 0.6 Al alloys along with a more continuous and uniform oxide layer formed on the $Al_{0.6}$ HEA, possibly attributed to the high Al content. These corrosion products were verified and analyzed using XRD (Figure 4). The electrochemical data (Figures 5 and 6) show that both Al-containing high entropy alloys have lower corrosion rates than the high entropy alloy with no aluminum (CoCrFeNi HEA or Al_0).

6. Summary and Conclusions

High Entropy Alloys (HEAs) with 3 different aluminum contents (CoCrFeNi, $Al_{0.3}$CoCrFeNi, $Al_{0.6}$CoCrFeNi) were electro-chemically tested in simulated gas turbine environments. The increased aluminum content results in increased stability of an internal aluminum oxide layer underneath an outer chromium oxide layer. The HEA with no aluminum exhibited the highest corrosion rate while the 0.3 and the 0.6 Al alloys indicated significantly lower corrosion rates. However, more tests need to be conducted to establish this comparative study.

7. Future Work

Future work of this study includes:

- Investigate trends at a variety of temperatures
- Conduct alternate testing methods (immersion, Dean's test) to verify electrochemical data
- Testing alternative HEAs for better suitability in these environments

8. References

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