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$Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$ high entropy alloys behavior in superheated geothermal steam

Andri Isak Thorhallsson[1], Ioana Csaki[2], Sigrun Nanna Karlsdottir[1], Laura Elena Geambazu[2]

[1]University of Iceland, Hjardarhagi 2-6, 107 Reykjavik, Iceland

[2]University “Politehnica” Bucharest, Splaiul Independentei 313, 060042 Bucharest, Romania

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ABSTRACT

Equiatomic high entropy alloys (EHEA) are a class of materials exhibiting tremendous properties due to the four characteristics effect: high entropy, sluggish diffusion, lattice distortion and cocktail effect. $Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$ composition was tested in situ, at Reykjanes power plant and the results revealed a very low corrosion rate for the bulk material (Csaki, et al., 2018). The most effective way to protect components interacting directly to geothermal steam would be coating the parts with HEA (High-Entropy-Alloy), $Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$. This paper presents the behavior in simulated superheated geothermal steam of bulk samples of $Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$ and copper added $Co_{16.67}Cr_{16.67}Fe_{16.67}Ni_{16.67}Mo_{16.67}Cu_{16.67}$. The samples were prepared using vacuum arc melting (VAM) technique. The exposure was produced in the reactor present in University of Iceland, in simulated superheated geothermal environment at 350°C and 10 bar gauge. The corrosion was investigated using optical and scanning electron microscope and X rays diffractometer. The investigation of the samples revealed promising results for the $Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$ in superheated geothermal steam.

1. INTRODUCTION

Corrosion of materials in geothermal power production equipment is quite common, mainly due to corrosive environment and application of low corrosion resistant materials. Application of bulk, corrosion resistant alloys can be extremely expensive and economic methods to coat low corrosion resistant materials to enhance the corrosion resistance and increase the lifetime of the equipment could be very beneficial for the geothermal power production industry. New emerging method to make a corrosion resistance coating is the application of high entropy alloys (HEA), alloy of five or more elements in or close to equiatomic order. HEA coated carbon steel in geothermal environment has given promising results (Karlsdottir, et al., 2019). High entropy alloys can have many feasible properties including high corrosion resistance.

At high temperature it is well known that the corrosion rate can be extremely high for the materials if the geothermal fluid is concentrated with corrosive species and if the geothermal fluid is totally or partly in liquid state. In the Iceland Deep Drilling Project, the aim is to drill deep geothermal wells up to 5 km depth to utilize high enthalpy fluid at high temperatures (Fridleifsson, et al., 2005). Corrosion testing was done in the first Iceland Deep Drilling well at 350°C and 12-13 bars gauge to gain a better understanding on the corrosion behavior in superheated geothermal environment. The results from the in-situ testing showed that all the samples, were prone to localized corrosion damage but the general corrosion rate was however measured extremely low (Karlsdottir, et al., 2015). Furthermore, severe corrosion rate was experienced in downhole and surface equipment were probable condensation of the geothermal fluid had occurred. The physical condition and state of the geothermal fluid in the production of geothermal energy can be various depending on the design of the process part equipment and on the location in the energy production system. A superheated geothermal fluid from wellhead can expected to partly or completely condense or boil again in the power production equipment. As a result, rapid corrosion can occur where geothermal equipment is made of low corrosion material. Application of corrosion resistance, high entropy alloys, could therefore be beneficial to mitigate corrosion of geothermal equipment. The HEA alloy $Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$ has been previously tested as an electro-spark-deposited (ESD) coating on a steel substrate with promising results (Arnorsson, 2000).

In this paper, results for the high entropy bulk alloys HEA1 ($Co_{20}Cr_{20}Fe_{20}Ni_{20}Mo_{20}$) and HEA1-Cu ($Co_{16.67}Cr_{16.67}Fe_{16.67}Ni_{16.67}Mo_{16.67}Cu_{16.67}$) tested in superheated geothermal fluid will be discussed. The HEA were prepared with vacuum arc melting (VAM). The testing was done in 8 days at 350°C and 10 bar gauge in a facility with a laboratory prepared corrosive fluid containing HCl, CO_2 and H_2S with a pH = 3 at liquid state at 20°C. The aim was to test the bulk high entropy alloys in superheated geothermal environment.

2. EXERIMENTAL

2.1 Testing fluid

The simulated geothermal fluid was prepared by making two separate mixing solutions and mixing them together in the testing volume. One solution contained diluted $HCl_{(aq)}$ solution but the other solution contained dissolved anhydrous $Na_2S_{(aq)}$ and $NaHCO_{3(aq)}$. The two mixing solutions were mixed together prior to the first unit, preheater, to make the simulated geothermal testing fluid. The concentration of the dissolved species in the both mixing solutions can be seen in Table 1:

Table 1: Concentration of the dissolved species in the mixing solutions.

Parameter	Value	Unit
Mixing solution 1:		
HCl	31	mmole
Total volume of mixing solution 1	1.0	litre
Mixing solution 2:		
Na_2S	8.8	mmole
$NaHCO_3$	11.4	mmole
Total volume of mixing solution 2	1.0	litre

The equivalent concentrations of S^{2-} and CO_2 in mixing solutions were verified with titration. In order to titrate S^{2-} a known volume of mixing solution 2 were dissolved in solution of NaOH, acetone and dithizone. The total solution was then titrated with mercury acetate in microburette. To find the equivalent concentration of CO_2 in the mixing solution, a known volume of mixing solution 2 was titrated with standard solution of HCl and back titrated with standard solution of NaOH using Metrohm Dosimeter. The detailed titration procedure can be viewed in (Arnorsson, et al., 2006), (Arnorsson, 2000). After the mixing of the two mixing solutions the HCl had reacted with Na_2S and $NaHCO_3$ to make final testing fluid containing HCl, CO_2 and H_2S. The resulting testing fluid had pH = 3 in liquid state at room temperature and concentrations of CO_2 = 250 ppm and H_2S = 150 ppm.

Table 2: Physical condition, chemical composition of testing fluid and duration of testing.

Parameter	Value	Unit
$pH_{@20°C}$	3.0	
Temperature	350	°C
Fluid pressure	10	bar gauge
Testing period	10	Days
CO_2	250	ppm
H_2S	150	ppm

2.2 Testing facility for HEA1 and HEA1-Cu in simulated superheated geothermal environment

The HEA samples were tested for 8 days in two reactors connected in series. The simulated geothermal fluid was made by mixing two solutions together in the testing process. The two mixing solutions were stored in storage flasks connected to Labhut degassers to remove volatiles and dissolved gasses from the testing fluid. Two high pressure ChromTech pumps were then connected to each inlet mixing solutions, withdrawing the mixing solutions to a mixing chamber prior to the inlet of the preheater were the simulated geothermal fluid was superheated. Three HEA testing samples were accommodated in each reactor unit, total of 6 samples with the approximate dimensions 50 mm x 7 mm x 2 mm. All the testing samples were electrically insulated from reactor walls by using alumina washers as a foundation for the samples. The testing fluid was cooled after the second reactor in a condenser. Inline pressure transducer and gauge were connected to the process to monitor the pressure during the testing. Back pressure regulator, controlled by SITEC hand pump, was connected the testing equipment after the pressure transducer to set and control the testing pressure. The temperature and pressure were monitored with data logging system. The main equipment in the testing can be seen in Figure 1 and flow diagram in Figure 2.

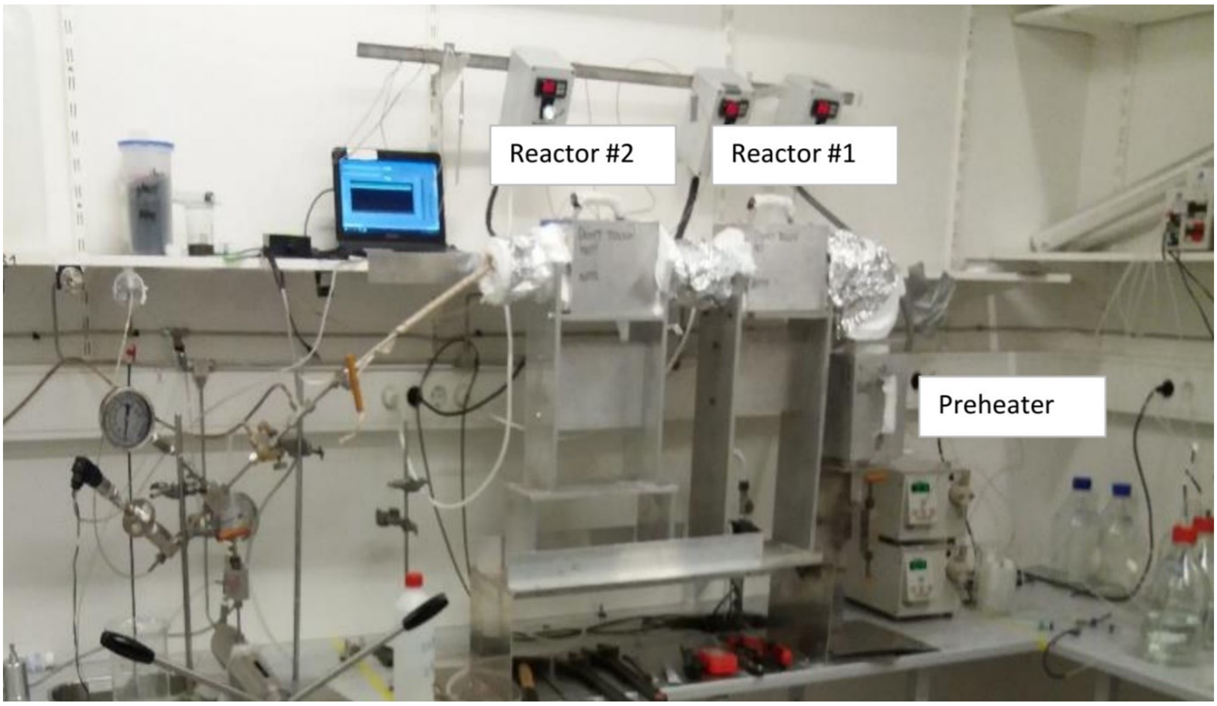

Figure 1: Testing facility

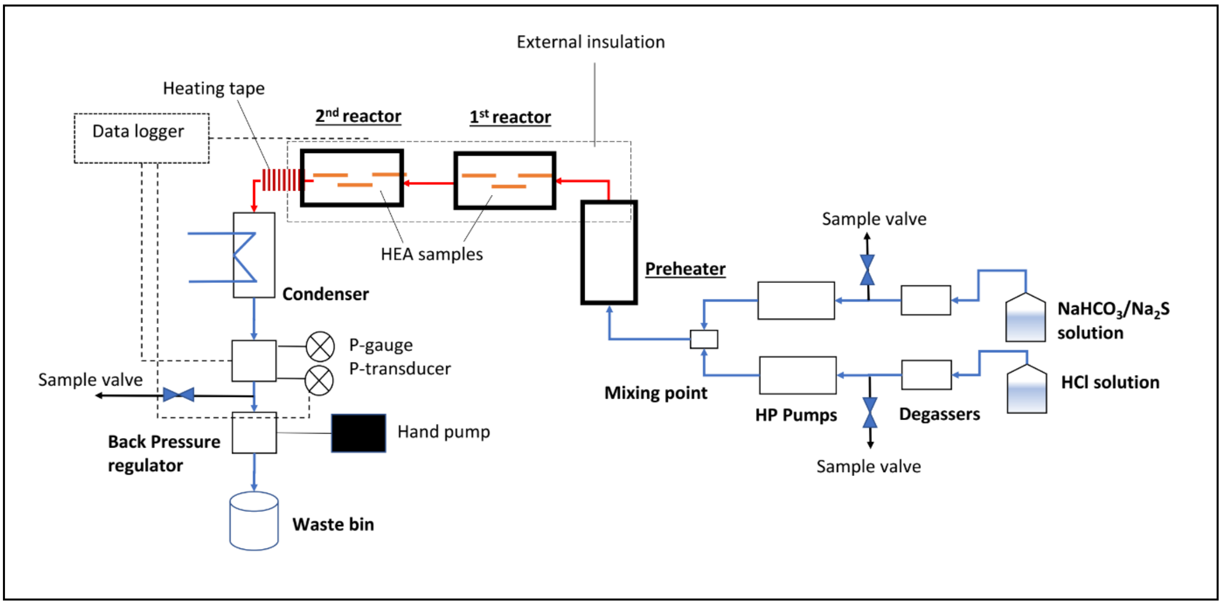

Figure 2: Corrosion testing flow diagram. High entropy alloy samples were in reactor 1 and 2. The HEA1 alloy was the first sample in reactor 1 and HEA1-Cu was the middle sample in reactor 2.

The HEA testing samples were placed inside along reactor pipes 1 and 2 and alumina washers were used to insulate the samples from the reactor wall.

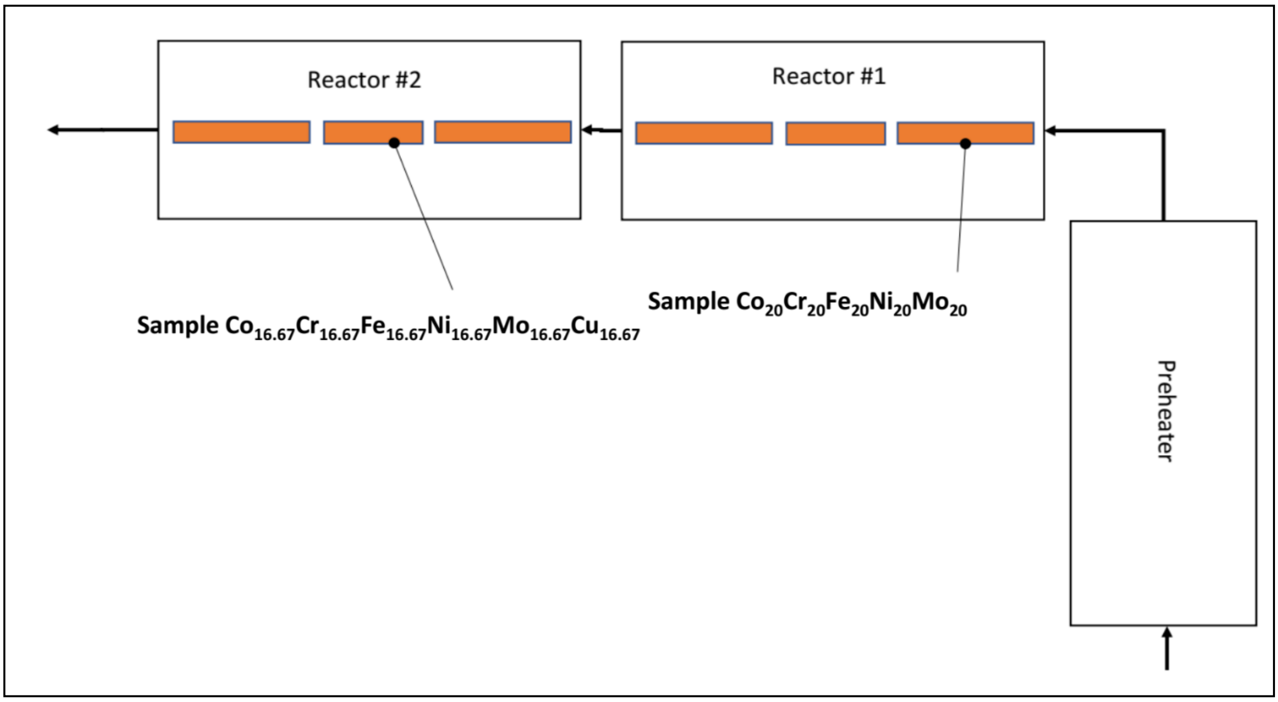

Figure 3: Three HEA samples were accommodated in each reactor in superheated fluid.

2.3 Preparation of the high entropy alloys with vacuum arc melting (VAM)

The HEA samples were prepared by vacuum arc melting (VAM) from melting of a mixture of high purity metals of Co, Cr, Fe, Ni and Mo and additionally Cu for alloy HEA1-Cu. The mixture was melted under high-purity Argon-gas with water cooled Cu hearth from Material Research Furnaces. The alloys were re-melted and turned around about five times to induce homogeneity of the composition and distribution of phases in samples.

2.4 Chemical composition of the bulk high entropy alloys

The chemical composition for the two alloys was selected in a such way that the HEA1, was in equiatomic proportions (of Co, Cr, Fe, Ni and Mo) and HEA1-Cu in equiatomic proportions (of Co, Cr, Fe, Ni, Mo and Cu) The atomic proportions of sample alloys HEA1 and HEA1-Cu can be viewed in Table 3.

Table 3: Atomic proportions (at%) of elements in the HEA alloys.

Atomic composition:	HEA1 [at%]	HEA1-Cu [at%]
Co	20	16.67
Cr	20	16.67
Cu		16.67
Fe	20	16.67
Ni	20	16.67
Mo	20	16.67

2.5 SEM and XEDS analysis

The samples were analyzed prior and after the corrosion testing in SEM and XEDS. The samples were sectioned with diamond wafering blade, mounted in thermosetting phenol formaldehyde resin (bakelite) and cast under pressure. The samples were ground down to 1000 grit in the cross section with SiC abrasive paper and polished with 3 µm and 1 µm diamond paste slurry and 0.02-0.06 µm particle size colloidal silica. The SEM equipment applied was a Zeiss Supra 25. The XEDS instrument used is from Oxford Instruments with Si(Li) X-ray detector and INCA Energy 300 software. XRD analysis was done with X´Pert Pro XRD meter from PANalytical with Data Collector software but XRD results are not published in this paper.

3. RESULTS

3.1 Corrosion testing of HEA1 and HEA1-Cu

Prior to cross sectional cut of samples, surface analysis was done on all the samples in SEM and XEDS. Microstructural and chemical analysis were done in SEM and XEDS. No corrosion was observed for the equiatomic HEA1 but the Cu added HEA1-Cu alloy was prone to general corrosion. Surface analysis can be viewed in Figure 4 and cross-sectional analysis in Figure 5. Oxide and palladium inclusions were observed in some of the HEA samples and multiphases were apparent in the cross section. Negligible corrosion film was observed in HEA1 but S rich corrosion film was observed in HEA1-Cu.

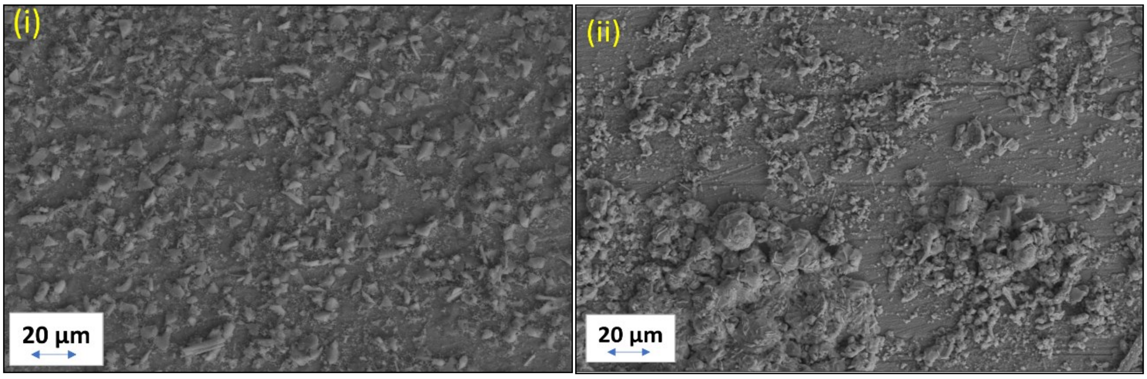

Figure 4: SEM and XEDS surface analysis from corroded (i) HEA1 and (ii) HEA1-Cu, sulfur deposits are evident on HEA1 but both sulfur deposits and corrosion products are apparent on HEA1-Cu.

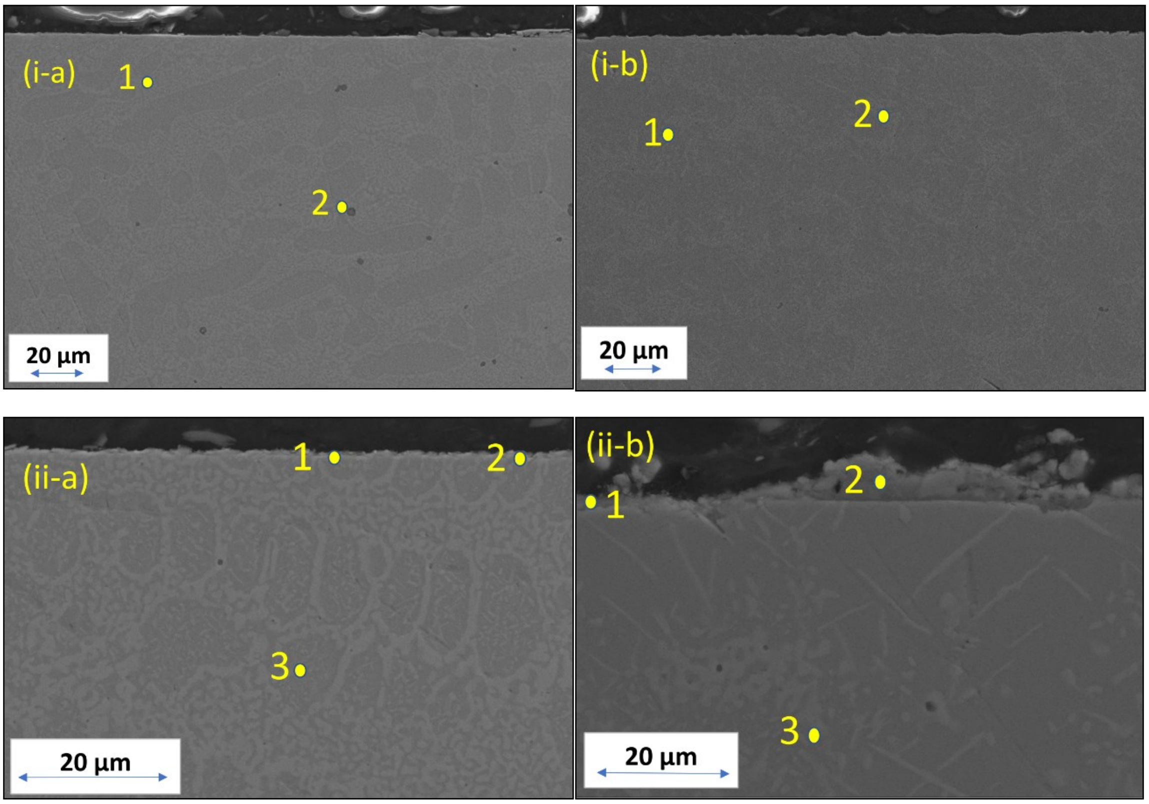

Figure 5: SEM and XEDS analysis from cross section of blank (i-a) HEA1 and (i-b) HEA1-Cu and cross-sectional analysis of corroded (ii-a) HEA1 and (ii-b) HEA1-Cu.

Table 4: XEDS elemental analysis from locations in blank HEA1 from Figure 5 (i-a).

			Element (wt%)			
Location	**Cr**	**Fe**	**Co**	**Ni**	**Mo**	**Pd**
1	17.6	22.4	20.5	21.7	17.8	
2	17.3	20.6	19.1	19.8	22.9	0.4

Table 5: XEDS elemental analysis from locations in blank HEA1-Cu from Figure 5 (i-b)

	Element (wt%)					
Location	**Cr**	**Fe**	**Co**	**Ni**	**Cu**	**Mo**
1	16.4	22.3	21.3	19.5	9.6	11.0
2	15.2	14.2	15.5	10.0	12.0	33.2

Table 6: XEDS elemental analysis from locations in corroded HEA1 from Figure 5 (ii-a)

	Element (wt%)				
Location	**Cr**	**Fe**	**Co**	**Ni**	**Mo**
1	17.0	22.3	20.7	23.0	17.0
2	17.4	22.6	20.2	23.1	16.8
3	18.2	23.5	21.5	24.1	12.7

Table 7: XEDS elemental analysis from locations in corroded HEA1-Cu from Figure 5 (ii-b)

	Element (wt%)							
Location	**O**	**S**	**Cr**	**Fe**	**Co**	**Ni**	**Cu**	**Mo**
1	26.1	8.7	13.6	12.7	9.8	6.0	3.7	19.5
2		21.1	2.1	5.3	1.8	1.0	65.7	3.2
3			16.7	22.4	21.7	21.9	8.9	8.4

4. DISCUSSION

The apparent low corrosion rate and immunity towards localized corrosion of HEA1 is compliant with experience of good corrosion resistance of same alloy tested as ESD coating on carbon steel substrate (Arnorsson,et al., 2000). The result is also compliant with other testing with corrosion resistant alloys (Thorhallsson, et al., 2018), (Thorhallsson, et al., 2019) tested at similar conditions. The negligible corrosion effect observed in superheated fluid is probably due to low conductivity and low-density property of the electrolyte which makes the ionic dissociation and electrochemical reactions in the superheated fluid negligible as mentioned in (Kritzer, 2004). This was though not the case with the Cu added HEA alloy, HEA1-Cu. Corrosion film in HEA1-Cu was concentrated with S and Cu indicating that gaseous reactions could be taking place between the H_2S and Cu. In in-situ testing in Iceland Deep Drilling Well no. 1 (IDDP-1) all alloys tested were prone to localized damage at 350°C and 12-13 bar in a geothermal fluid containing HCl, CO_2, H_2S but also HF and H_2 (Karlsdottir, et al., 2015). It could be interesting for future work to see the effect of H_2 and HF on the corrosion behavior of HEA alloys when these corrosive species are added to the simulated geothermal fluid.

5. CONCLUSIONS

The HEA1 alloy showed very good corrosion resistance in the simulated high temperature geothermal environment. Furthermore, HEA1 showed no indication of general corrosion or localized damage which is compliant with other similar testings with corrosion resistant alloys. The HEA1-Cu was though prone to some general corrosion and analysis of surface film indicated reaction between H_2S and Cu at the surface. These results imply that the HEA, CoCrFeNiMo alloy could be a promising candidates as a bulk material or as a protective coatings for carbon steel and low alloy steel in the geothermal industry.

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