Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Titanium Alloy Casing for High Temperature Geothermal Field Application

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Keywords: Titanium alloy, casing material, high temperature corrosion, HCl, CO_2, H_2S

ABSTRACT

A new titanium alloy, with nominal composition of Ti-0.4Ni-3.6Mo-0.75Zr has been developed for application in high temperature, high salinity and low pH geothermal wells. To select the alloy composition, hot rolled and heat-treated alloy-samples were corrosion tested in a simulated geothermal brine. The final alloy composition was then extruded into casing pipe and corrosion tested in a laboratory flow through system at temperature range 180-350°C and 10 barg in a testing fluid containing H_2S, CO_2 and HCl as the corrosive species. The aim of testing setup was to simulate conditions in deep geothermal systems previously experienced in deep drilling well in Krafla, IDDP-1. The testing were conducted in three testing units connected in series; *in the first reactor* where the rapid heating and boiling of the aqueous testing solution from RT to boiling and superheating of the fluid occurred, *in the second reactor* where superheated conditions are maintained at 350°C and lastly, *in the third reactor* where the temperature was set to 180°C or below the saturation temperature of the fluid to provoke condensation in the test chamber. This paper discusses the corrosion effects of the three conditions applied and how it compares to in-situ analysis performed previously at the IDDP-1 well. Microstructural and chemical composition analysis with SEM and EDS equipment were used for evaluating the corrosion resistance of the titanium alloy. The corrosion rate was also measured and compared to other corrosion resistant alloys (CRAs). The results observed in the various testing conditions in the three flow-through reactors and the potential future application of the alloy for high temperature geothermal field application is also discussed.

1. INTRODUCTION

The Iceland Deep Drilling Project (IDDP) was established in the beginning of the 21st century with the aim to drill deep geothermal wells up to 5 km depth to utilize high enthalpy fluid for economic power production (Fridleifsson, et al., 2005). The first deep geothermal well was drilled in Iceland in 2008 where the geothermal fluid was superheated at 450°C and 140 bars gauge at the wellhead. The geothermal fluid contained CO_2, H_2S, HCl, HF and H_2 gases but with superheated steam as the bulk chemical. Corrosion testing was done in almost 3-month period for several metallic samples and alloys at a testing chamber at the wellhead 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, including titanium alloys, were prone to localized corrosion damage but the general corrosion rate was however measured as being extremely low for all the testing samples because of scaling (Karlsdottir, et al., 2015).

The physical condition and state of the geothermal fluid in the production of geothermal energy depends on the design of the process and equipment used at each location in the energy production system. A superheated geothermal fluid from the wellhead can be expected to partly or completely condense or even boil in the power production equipment. Hence, a different corrosion behavior for construction materials in power production system can also be expected depending on the physical conditions of the geothermal fluid.

Application of titanium alloys in geothermal casing material is not common and the main reason is lower mechanical strength at high temperatures in comparison with more commonly used iron and nickel-based alloys.

A new titanium alloy, Ti-0.4Ni-3.6Mo-0.75Zr has been recently developed showing good mechanical strength and excellent corrosion resistance in high temperature geothermal environment. The scope of this paper is a corrosion testing of this alloy in asset of three flow-through reactors connected in series. Simulated geothermal fluid was heated from room temperature to 350°C in the first reactor where boiling occurs. In the second reactor, the geothermal fluid was maintained superheated at 350°C but in the third reactor, the temperature was lowered below saturation temperature to provoke condensation. Corrosion samples were placed throughout the volume in all the units to observe possible corrosion gradients within the testing volume. The purpose of this paper is to investigate the corrosion behavior of Ti-0.4Ni-3.6Mo-0.75Zr in simulated geothermal environment at boiling, superheated and condensing environment at 180-350°C and 10 bar gauge.

2. EXERIMENTAL

2.1 Testing Material and Samples

Titanium alloys have generally continuous, adherent protective oxide film, TiO_2, which forms in a wide pH range. TiO_2 is known to be protective in both alkaline and acidic environment (Jones, 1996). However, under high temperature reducing acid conditions, the oxide film on titanium can be subject to breakdown, leading to corrosion of the metal. When conditions such as this are encountered, alloying of the titanium is done in order to strengthen and enobilize the oxide film. The most potent of these alloying agents are the platinum metal group elements, such as palladium or ruthenium. These additions have proven themselves to be very resistant to even the most aggressive of geothermal brines, however, the cost of adding these precious metals dramatically limits the utilization of titanium in these applications (Grauman & MacDonald, 2014). Other, less expensive alloying elements, such as nickel and molybdenum, have also been used to enhance the resistance of the titanium oxide film, without the associated high costs (Schutz, et al., 1982). These alloying agents also have the benefit of increasing the mechanical strength of titanium alloys, which is important for high temperature geothermal applications. Thus, a titanium alloy with the appropriate balance of nickel and molybdenum satisfies both the corrosion and strength requirements and can be cost effective for applications such as geothermal casing material. The mechanical properties and chemical composition of the test samples are shown in Tables 1 and 2, respectively:

Table 1: Mechanical properties of Ti-0.4Ni-3.6Mo-0.75Zr Test Material.

Mechanical properties	Value	Unit
Yield Strength (YS)	786	MPa
Ultimate Tensile Strength (UTS)	965	MPa
Ductility EL(%)	21	%
Ductility RA(%)	55	%

Table 2: Actual Chemical Composition of Ti-0.4Ni-3.6Mo-0.75Zr Test Material.

Element	wt%
Ni	0.44
Mo	3.43
O	0.16
Fe	0.18
Zr	0.74
Ti	Res.

All the testing samples were electrically insulated from the walls of the reactors. The samples were fastened with UNS N06625 fastener, but samples were decoupled from the fasteners with alumina washers. Three samples placed in each testing unit, two 100 mm x 7 mm x 2 mm coupons and one 50 mm x 7 mm x 2 mm coupon. The total number of samples was nine in the three reactors. The testing sample units used for each reactor are illustrated in Figure 1:

Figure 1: Illustration of three testing samples as used in each reactor for corrosion testing.

2.2 Testing fluid

The simulated geothermal fluid was prepared by making two separate solutions and mixing them 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 prior to the inlet of the first reactor to make the simulated geothermal testing fluid. The concentration of the dissolved species in the two mixing solutions can be seen in Table 3:

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 was dissolved in a solution of NaOH, acetone and dithizone. The total solution was then titrated with mercury acetate. To find the equivalent concentration of CO_2 in the mixing solution, a known volume of mixing solution 2 was titrated with a standard solution of HCl and back titrated with a standard solution of NaOH. The mixed solution was also titrated during test run to verify chemical composition of the test fluid. The detailed titration procedures can be viewed in (Arnorsson, 2000), (Arnorsson, et al., 2006). After mixing of the two mixing solutions the HCl 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 and concentrations of CO_2 = 250 ppm and H_2S = 150 ppm. A summary of the testing conditions is shown in Table 4:

Table 3: Concentration of the dissolved species in the mixing solutions.

Parameter	Value	Unit
Mixing solution 1:		
HCl	31	mM
Total volume of mixing solution 1	1.0	L
Mixing solution 2:		
Na_2S	8.8	mM
$NaHCO_3$	11.4	mM
Total volume of mixing solution 2	1.0	L
		mM = mmol/L

Table 4: Physical condition, chemical composition of testing fluid and duration of testing.

Parameter	Value	Unit
pH	3	
Temperature	350	°C
Fluid pressure	10	bar gauge
Testing period	10	Days
CO_2	250	ppm
H_2S	150	ppm*

** ppm = mg/kg*

2.3 Testing Equipment

In total, nine samples were tested for 10 days in three separate testing reactors connected in series. The setup of the testing equipment was as follows (in the flow direction order): 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 solution, withdrawing the mixing solutions to a mixing chamber prior to the inlet of the first testing unit. Three reactors were used in the testing and three samples were accommodated in each reactor, total of 9 samples, and aligned along the whole testing volume in the direction of flow. This was done to see if any corrosion gradient was apparent on the testing samples within the testing volumes. The first reactor was thermally insulated and set to 350°C temperature. As the testing fluid was almost pure water it can be expected that the boiling point of the fluid is approximately 184°C. As a result, when the testing fluid enters the preheater, the liquid fluid heats up to approximately 184°C at the inlet of the preheater, the liquid boils and then the temperature of the gas will be superheated when the temperature increases from 184°C up to 350°C. The second reactor was set to 350°C and connected in series with the first reactor. The second reactor was thermally insulated to maintain the testing fluid superheated at 350°C. The third reactor was set to 180°C and connected in series with the second reactor. The third reactor was not thermally insulated. This was done to provoke condensation in the third reactor. The fluid was cooled after the second reactor in a condenser. Inline pressure transducer and pressure gauge were connected to the process to monitor the pressure during the testing. A back-pressure regulator, controlled by a 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 a data logging system. The main equipment used for the testing is shown in Figure 2 and a process flow diagram is given in Figure 3:

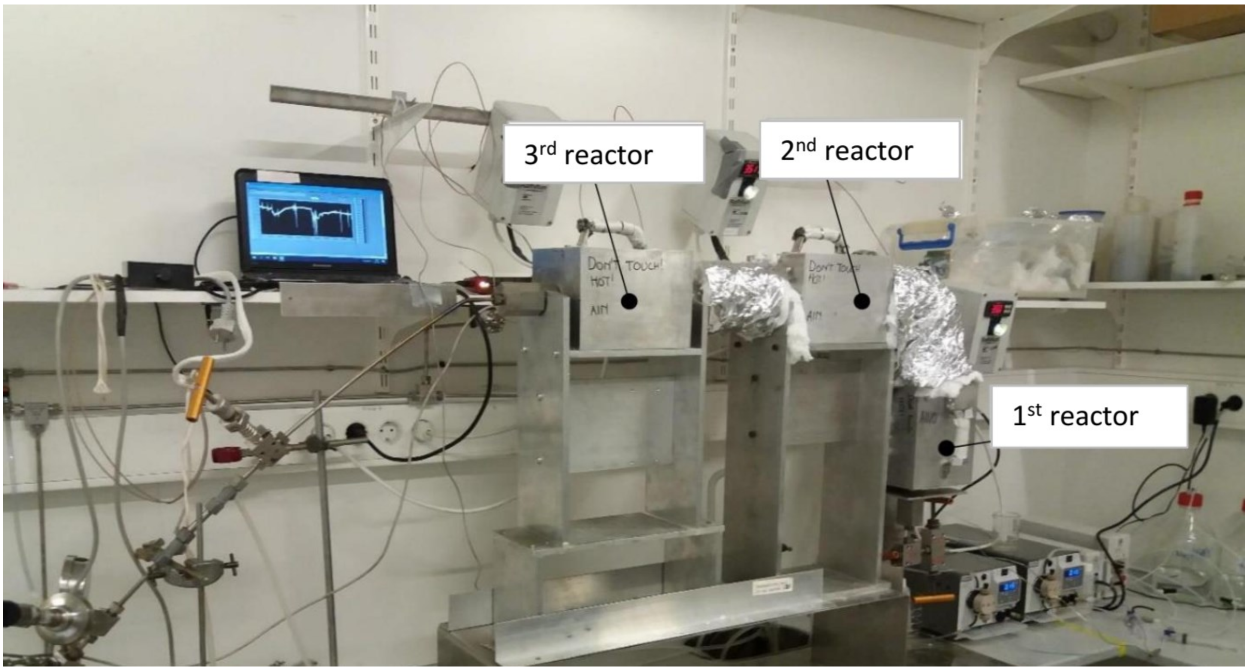

Figure 2: Main equipment used in corrosion testing setup.

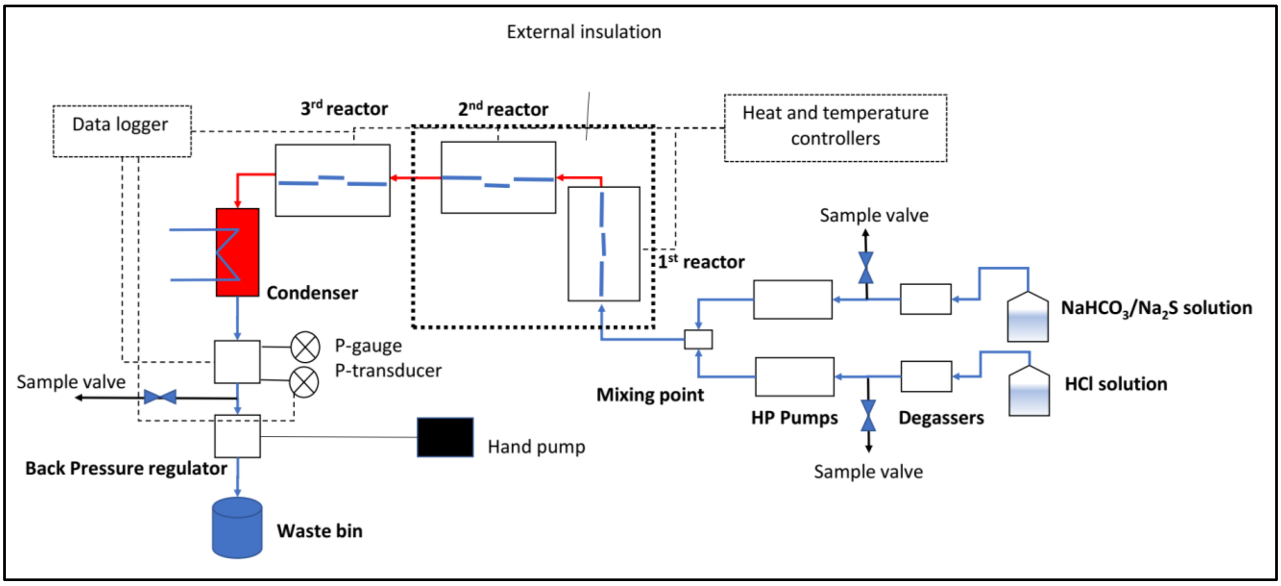

Figure 3: Corrosion testing flow diagram.

Corrosion testing of carbon steel in previous work with the same testing setup indicated that boiling occurs in the first few cm of the first sample at the inlet of the first reactor. Furthermore, condensation apparently occurs in the last few cm of last sample at the outlet of the third reactor. This was concluded from severe corrosion observed at the inlet sample in the first reactor and the outlet sample of the third reactor, but corrosion was less severe in all other samples. This is illustrated in Figure 4.

2.4 Post exposure measurements and analysis

Weight loss method was used to determine the corrosion rate of the Ti-alloy coupons. For weight loss analysis, the samples were cleaned before corrosion testing and weighed with a 0.1 mg precision. After the corrosion testing the samples were cleaned again in ethanol in an ultrasonic bath to remove corrosion products and weighed again. No standard procedure is available for Ti-alloys due to extreme adhering titanium oxide film. For SEM/XEDS and grain boundary analysis, the samples were sectioned with diamond wafering blade, mounted in thermosetting phenol formaldehyde resin (bakelite) under pressure. The samples were ground to 1000 grit 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. Samples were analyzed in SEM and XEDS prior to and after the corrosion testing. The SEM equipment used was a Zeiss Supra 25. The XEDS instrument used was from Oxford Instruments with Si(Li) X-ray detector and INCA Energy 300 software. XRD analysis was done with a X´Pert Pro XRD meter from PANalytical with Data Collector software but results are not published in this paper.

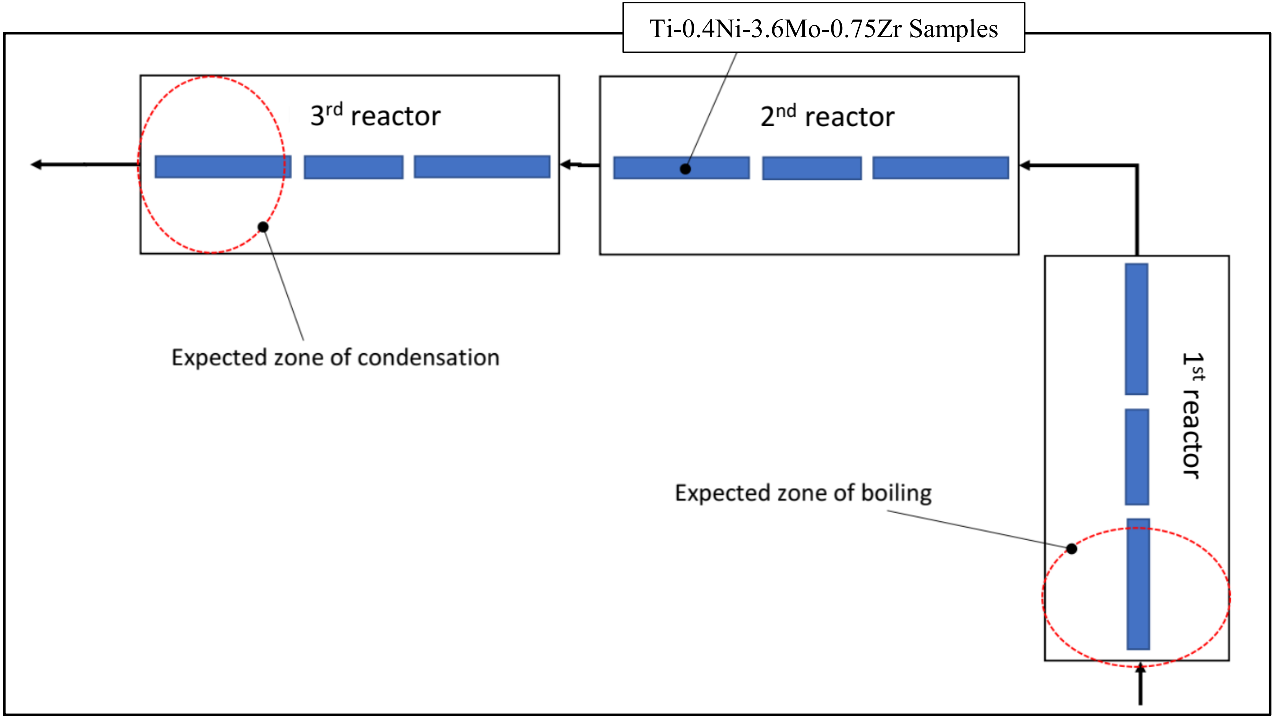

Figure 4: Expected zone where boiling occurs in first reactor and expected zone where condensation of testing fluid occurs in third reactor. Three samples were accommodated in each of the testing units.

3. RESULTS

Prior to weight loss determination and sectioning of samples, surface analysis was done on all the samples in SEM and XEDS, see Figure 5. Cross sectional analysis was done for two locations on the first sample in the first reactor (boiling and superheated), for one location in the middle sample in reactor 1 (superheated) and for two locations on the last sample in reactor 3 (superheated and condensation), see Figure 6. Weight loss analysis was done for all other samples. Microstructural and chemical analysis were done by SEM and XEDS. Some S and Cl rich deposits were observed on the surface of the sample examined form the inlet of preheater, but no corrosion products were detected.

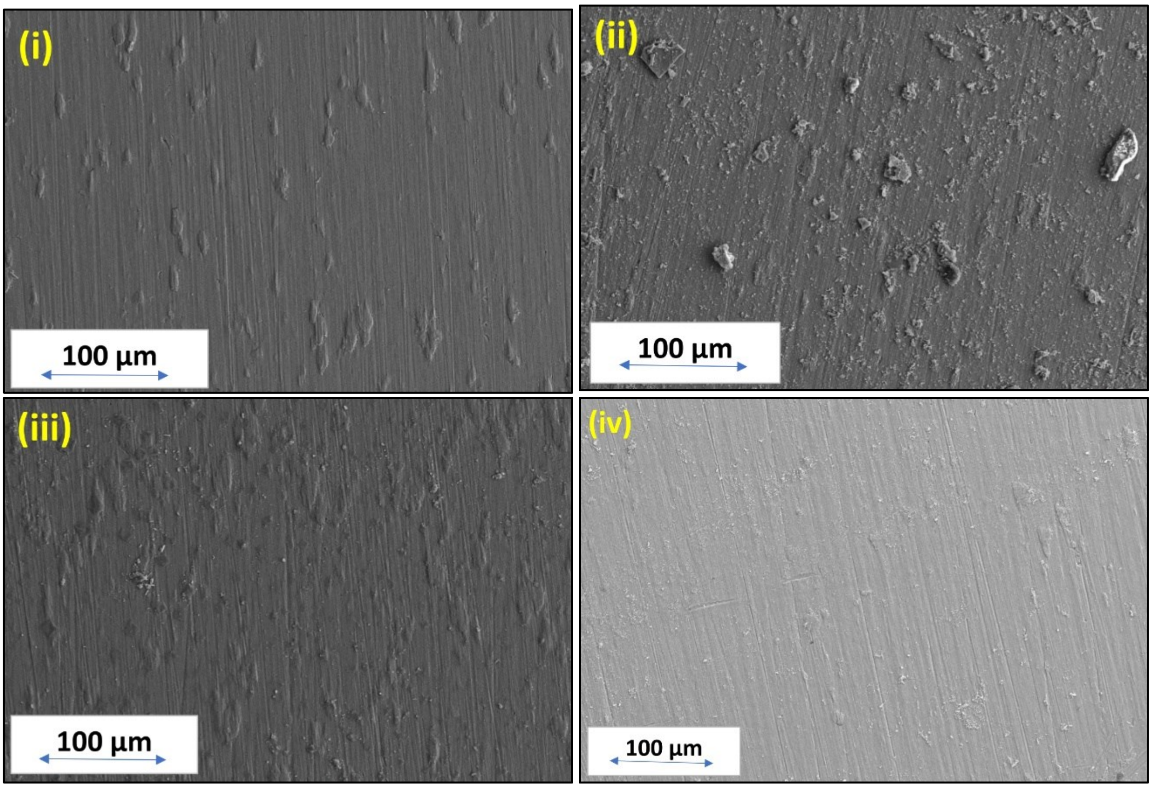

Figure 5: Surface analysis of (i) blank Ti sample, (ii) Corroded sample from inlet of the first reactor with Cl and S richdeposits on surface, (iii) Sample from the middle of the second reactor and (iv) sample from outlet of the third reactor.

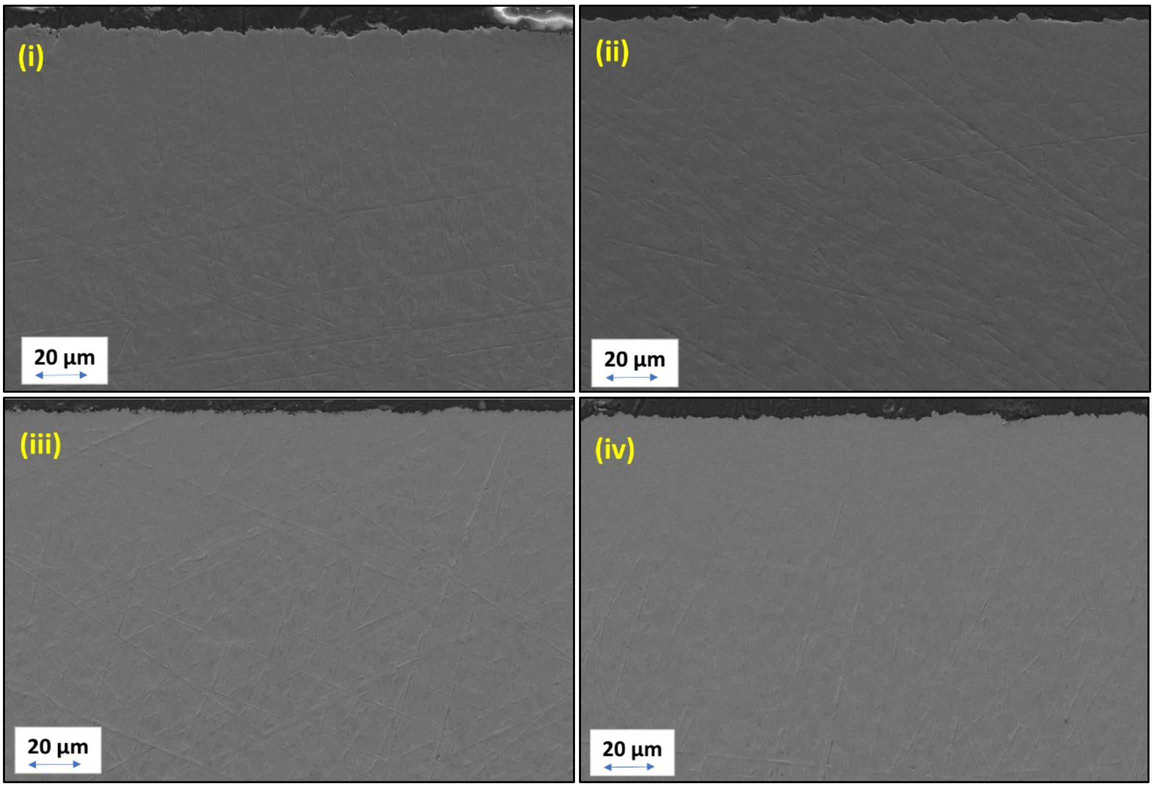

Figure 6: (i) Cross section of first sample at inlet of first reactor, (ii) cross section of first sample in first reactorfurther away from inlet, (iii) cross section of sample from the middle of the second reactor and (iv) cross section from the last sample at the outlet of the third reactor.

Furthermore, weight difference before and after corrosion testing was within order of 0.1 mg precision or 0 for all the samples analyzed indicating immunity to corrosion. Negligible weight gain was observed in all samples except for middle sample in third reactor which had negligible weight loss.

4. DISCUSSION

The extremely low corrosion rate of the Ti-0.4Ni-3.6Mo-0.75Zr is in an agreement with corrosion rate experienced for other corrosion resistant alloys in corrosion testing done in simulated superheated geothermal environment (Thorhallsson, et al., 2019), (Thorhallsson, et al., 2018) and other testing not currently published by the authors. The low corrosion rate in gaseous fluid is believed due to the strong passive oxide film protecting the bulk alloy and due to the low conductivity and low-density superheated fluid which make ionic dissociation and electrochemical reactions in the gaseous superheated fluid negligible as summarized in (Kritzer, 2004). Ti-0.4Ni-3.6Mo-0.75Zr alloy apparently shows excellent corrosion resistance in two phase system and better corrosion resistance than some nickel-based alloys tested in similar conditions where boiling or condensation might occur (Thorhallsson, et al., 2019) Some Ti alloys in the in-situ testing in Iceland Deep Drilling Well no. 1 (IDDP-1) 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 is interesting for future work to see the effect of H_2 and HF on the corrosion behavior of Ti-0.4Ni-3.6Mo-0.75Zr when these corrosive species are added to the simulated geothermal fluid.

CONCLUSION

The Ti alloy tested here has shown excellent corrosion resistance in a simulated high temperature geothermal environment where HCl, CO_2 and H_2S are the corrosive species. From the result of this study it can be concluded that the Ti alloy, Ti-0.4Ni-3.6Mo-0.75Zr has an excellent corrosion resistance in liquid geothermal environment below the saturation temperature at 10 bar gauge but also at boiling and superheated conditions at this same pressure at temperature up to 350°C. As the mechanical strength of this Ti-based alloy is greater at high temperature in comparison with other commercial Ti-based alloys, the alloy Ti-0.4Ni-3.6Mo-0.75Zr can be considered as a feasible material for geothermal surface equipment but also feasible as a casing material where mechanical strength and corrosion resistance at high temperature are critical properties.

ACKNOWLEDGEMENTS

The authors would like to thank the Icelandic Research Fund (RANNÍS) and Geothermal Research Group (GEORG) for funding this project and TIMET for providing samples. We would also like to thank employees at Innovation Center of Iceland (ICI) and employees at Grein Research for their technical assistance.

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