

Comparative Study of Corrosion Resistance of Hot Isostatically Pressed Ti6Al4V+10vol%TiB₂ Titanium Matrix Composite Vs. Wrought Ti6Al4V (UNS designation R56400) Alloy in Simulated High-Temperature Geothermal Environment

Danyil Kovalov
University of Iceland
VR-II, Hjarðarhagi 6
Reykjavík, 107
Iceland

Gifty Oppong Boakye
University of Iceland
VR-II, Hjarðarhagi 6
Reykjavík, 107
Iceland

Erlend Straume
University of Iceland
VR-II, Hjarðarhagi 6
Reykjavík, 107
Iceland

Sandeep Irukuvarghula
TWI Ltd
Granta Park
Cambridge, CB21 6AL
UK

Raja Khan
TWI Ltd
Granta Park
Cambridge, CB21 6AL
UK

Sigrun Nanna Karlsdottir
University of Iceland
VR-II, Hjarðarhagi 6
Reykjavík, 107
Iceland

ABSTRACT

A key factor successfully leading to long-term operation of the equipment in the aggressive environment at geothermal power plants is the proper selection of materials with high erosion-corrosion-resistant properties. One group of materials called to improve the erosion, corrosion, and wear resistance of pumps, turbines, and heat exchangers operated in the geothermal industry, is the titanium (Ti) alloys. In this paper, we report the comparative analysis of corrosion resistance for a newly developed hot isostatically pressed Ti6Al4V reinforced with a 10vol%-titanium diboride titanium matrix composite and a wrought Ti64 alloy (UNS designation R56400). Both the Ti64+10vol%TiB₂ and wrought Ti64 alloys were tested under simulated geothermal "steam/liquid" conditions at T=185 °C and P=10.2 barG for seven days. The liquid phase's controlled pH was 4, whereby concentrations of non-condensable gases of H₂S and CO₂ were 170 ppm and 1012 ppm, respectively. Using SEM/EDS and XRD analyzing techniques, the tested Ti64+10vol%TiB₂ and Ti64 samples were examined for localized corrosion and corrosion products penetration into the materials. The findings showed that the Ti64 alloy has a greater corrosion resistance than the Ti64+10vol%TiB₂ due to the titanium boride (TiB) phase being more susceptible to corrosion in the simulated geothermal environment.

Key words: Ti64; HIP; TMC; Geothermal Environment; CO₂/H₂S; High-Temperature Corrosion

INTRODUCTION

The aggressive nature of high-temperature geothermal environments, including the chemical composition of the steam and liquid, is one of the main factors leading to corrosion degradation of the metals that subsequently reduces the service life of the equipment geothermal power plants [1, 2]. The high-temperature two-phase flow from the geothermal wells is mixed with non-condensable gases that enhance the geothermal fluid's aggressiveness. The main gases are hydrogen sulfide (H_2S), carbon dioxide (CO_2), and in some cases, even hydrogen chloride (HCl) that primarily contribute to reducing the pH of the geothermal fluid as well as bring the aggressive ions (i.e., $[\text{HCO}_3^-]$, $[\text{S}^{2-}]$, $[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$, etc.) which accelerate corrosion processes in metals. Indeed, the proper selection of materials for geothermal applications can reduce the risk of corrosion and increase the service life of the power plant components [3, 4]. Materials that are feasible for geothermal power application are titanium (Ti) alloys. They have been used in pumps, turbines, and heat exchangers to improve the corrosion resistance and increases the lifetime of the equipment due to their high corrosion resistance.

Nevertheless, the materials' vulnerability remains the low wear properties that may still lead to premature failure of the equipment. The Geo-Coat project was aimed to develop new materials for improving the corrosion resistance and wear as an alternative for the existing materials used in the geothermal industry. One of the developed materials within the Geo-Coat project framework was HIPed titanium matrix composites (TMC). The new TMC composition named Ti64+10vol%TiB₂ was developed based on the Ti64 (UNS designation R56400) matrix reinforced by 10vol%TiB₂. The TiB₂ phase was added to improve the wear and erosion-corrosion resistance of the material by increasing the hardness. But for the TMC to be usable in the geothermal environment, it has to have comparable corrosion resistance to currently used Ti alloys.

Thus, in the present work, the high-temperature testing of HIPed Ti64+10vol%TiB₂ TMC and Ti64 alloy (UNS designation R56400) was conducted for a comparative investigation of their corrosion behavior under flow-through conditions of simulated geothermal steam/liquid phase at $T=185^\circ\text{C}$ and $P=10.2$ barG for seven days. The simulated geothermal liquid pH was 4 with H_2S - CO_2 gas concentrations of 170 ppm and 1012 ppm, respectively. The microstructural and chemical composition of the tested samples were examined using a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) techniques. Crystal structure and phase analysis were also performed by X-ray diffraction (XRD).

EXPERIMENTAL PROCEDURE

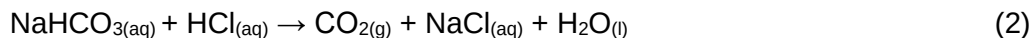
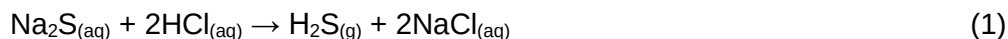
Simulated geothermal environment

Based on the chemical composition of utilized fluids in geothermal power plants in Iceland, i.e., Hellisheidi and Nesjavellir [7, 8], using PHREEQC (program version 3.4.0-12927) software for geochemical calculations, the chemical composition, temperature, pressure, and pH level for the simulated geothermal fluid for the corrosion testing in flow-through reactor (FTR) were chosen. The results of the calculations of the fluid composition and conditions for the corrosion tests are shown in Table 2.

Table 1. Chemical composition and parameters of simulated geothermal conditions in FTR.

Fluid pH	T, (°C)	P, (barG)	H ₂ S, (ppm)	CO ₂ , (ppm)	Cl, (ppm)	Medium	Experiment duration
4	185	10.5	170	1012	1202	Steam and liquid	7 days

As the inlet solution for high-temperature experiments in FTR, the aqueous solution of Na_2S (0.010 mol/kg) with NaHCO_3 (0.046 mol/kg) and HCl 0.066 mol/kg was prepared to obtain a reaction of forming H_2S - CO_2 gases and NaCl via the following reactions:



As shown in Figure 1a, the two aqueous-based solutions of #1 [$\text{Na}_2\text{S}+\text{NaHCO}_3$] and #2 [HCl] that flowed through the degassers of D1 and D2 were pumped by High-Performance Liquid Chromatography (HPLC) pumps into the Hastelloy C276 pipe of FTR where Reactions (1) and (2) occurred. In the FTR pipe, solutions #1 and #2 via reactions (1) and (2) were mixed to produce H_2S - CO_2 gases. To simulate the two-phase (i.e., steam/liquid) conditions, the reacted liquid with the gases in FTR was heated up to 185 °C by a heating element (HE) of the tubular oven (Carbolite) at a steam pressure of ~10.5 barG that was reached using booster pump (BPR) and back-pressure regulator (BPR).

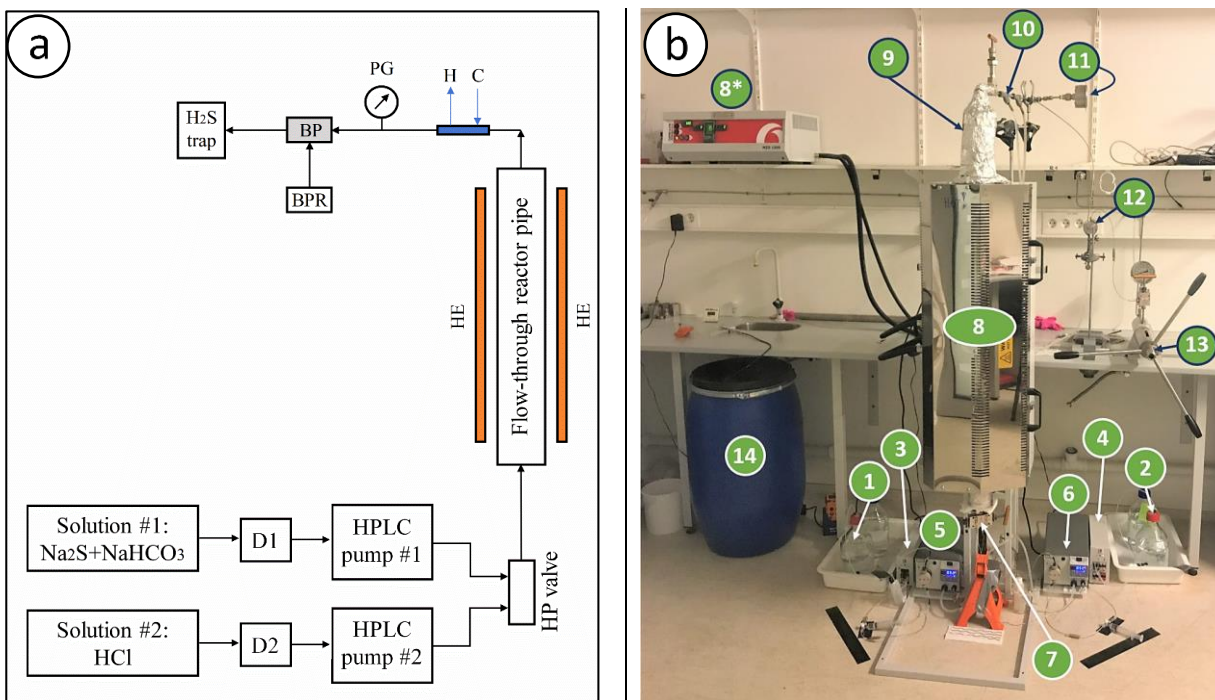


Figure 1: A scheme of low-flow-through reactor experimental setup (a) and the laboratory facility (b) for high-temperature corrosion test at the University of Iceland.

Where in Figure 1b: 1 – container with aqueous $\text{Na}_2\text{S}+\text{NaHCO}_3$ solution; 2 – container with aqueous HCl solution; 3 and 4 – HPLC solvent degassers for solutions "1" and "2", respectively; 5 and 6 – HPLC pumps for degassed solutions "1" and "2", respectively; 7 – high-pressure T-valve; 8 – tube furnace with 3-zone temperature control; 8* – temperature controller; 9 – reactor pipe placed in the tube furnace "8"; 10 – cooling loop; 11 – pressure-gauge; 12 - booster pump; 13 – back-pressure regulator; 14 – H_2S trap.

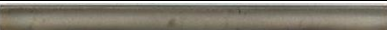
The simulated geothermal fluid was passed through the FTR pipe with a flow rate of 1.0 mL/min that allowed to adequately maintain the pH level of 4 and corrosive properties of the flowing fluid over the 7-day experiment. Passing the FTR outlet, the reacted fluid was cooled down in the cooling loop (H/C). Samples of the cooled fluid were regularly probed to control the pH level. The cooled fluid, containing unreacted H_2S gas, was utilized in the H_2S trap of highly alkaline zinc acetate dihydrate solution. The fluid outlet samples were periodically taken to control the fluid pH and $\text{H}_2\text{S}/\text{CO}_2$ gas concentration after reacting with tested materials in the FTR. For the detailed description of the titration procedure for $\text{H}_2\text{S}/\text{CO}_2$ gases, the reader refers to the previous work [5, 6]. The illustration of the FTR

experimental setup and photo of the testing facility for high-temperature corrosion tests conducted at University of Iceland are shown in Figure 1.

Materials

The down-selected TMC materials of HIPed Ti64+10vol%TiB₂ TMC and wrought Ti64 alloy were fabricated as rods and coupons (see photos in Table 2). The rod TMC samples had 7 mm diameter with 80 mm length. Ti64 samples were designed in a rectangular shape, coupons, with 4 mm thickness and 6 mm width with 50 mm length. The types of samples tested in FTR are shown in Table 2.

Table 2. HIPed Ti64+10vol%TiB₂ TMC and Ti64 samples for the corrosion testing in the simulated geothermal environment in FTR at University of Iceland.

	Conventional material	GeoCoat material	Industrial application
	Ti64	HIPed Ti64+10vol%TiB ₂ TMC	Pump impeller
Sample shape	#1 	#1 	
	#2 	#2 	
			

Due to the corrosiveness of the geothermal environment simulated in the FTR, the sample holder for the specimens shown above was manufactured from the inert (non-metal) material of Polyether Ether Ketone (PEEK) TECAPEEK®. The dimension of the sample holder was 15 mm diameter x 28 mm long. The illustration of the sample holders is shown in Figure 2.

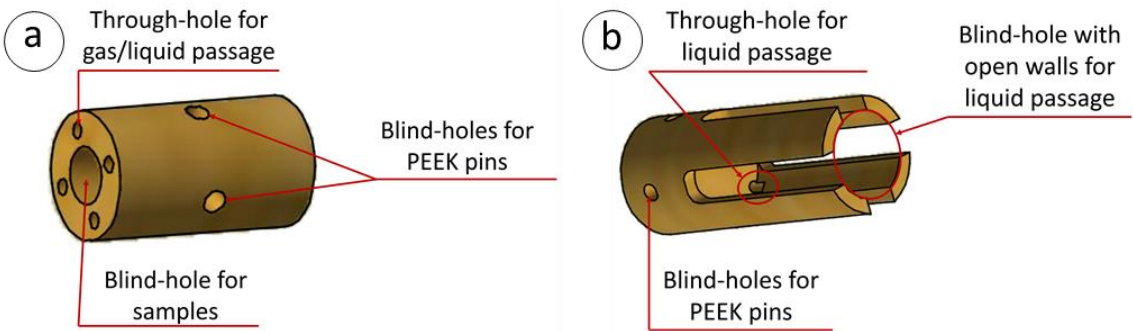


Figure 2: Illustration of the PEEK sample holder for an FTR pipe: (a) – sample holder component placing along (inside) the FTR pipe; (b) – sample holder component placing at the bottom inside the FTR pipe.

Experimental Design

The high-temperature corrosion tests were carried out separately for HIPed Ti64+10vol%TiB₂ TMC and wrought Ti64 samples, where the given samples were subject to the steam-liquid exposure in the FTR for seven days. Considering the fact that at the FTR bottom, the simulated two-phase conditions might have had the liquid-dominated geothermal flow, whereas the steam phase might have been dominating the flow at the FTR top, HIPed Ti64+10vol%TiB₂ TMC and wrought Ti64 samples were placed both at the bottom and top of the FTR. This allowed us to investigate the corrosive effects of fluid on the metals in mixed geothermal conditions simulated in the FTR pipe. The animation reproducing the simulated environmental conditions and samples placed in FTR is shown in Figure 3.