

THE INVESTIGATION OF ALLOY 800H DEGRADATION IN CONDITIONS SIMULATING HELIUM COOLANT IN HTGR SYSTEM

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Abstract

The corrosion coupons of 800H alloy with TIG weld filled with Nicrofer were exposed to impure helium in the High-Temperature Furnace (HTF) at 760 °C for 372, 1000 and 1500 hours. Impurities CH₄, CO, H₂ and H₂O were chosen to simulate conditions in a High-Temperature Gas Reactor system (HTGR). The specimen surface, corrosion layer thickness and composition were evaluated by Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS). Specimens were covered with a uniform protective oxide layer up to 3 μm thick, growing with exposure time. The layer contained mainly Cr, O₂ and a minor amount of Mn. Localized deep oxidation was found after 1500 hours in between the weld and base material. The output of these measurements is the evaluation of the properties of the tested materials and the assessment of their resistance to corrosion effects. 800H alloy and Nicrofer alloy were found to degrade similarly in an oxidizing environment. This combination of base material and weld metal appears to be suitable for use at high temperatures.

Keywords: Nuclear application, helium, corrosion layer, alloy 800H, alloy Nicrofer

1. INTRODUCTION

Gas-cooled reactors have been developed and constructed since the 1950s, the first type was developed in England and worked with natural uranium and used carbon dioxide as a cooling medium. The following types of gas-cooled reactors are known as high-temperature reactors (HTR and HTGR), and their coolant is helium. These reactors were designed and built in the US and Germany [1]. The Generation IV International Forum has selected six promising nuclear power technologies for continued research and development. Two candidates are Gas-Cooled Reactors (GCR), especially the Very High-Temperature Reactor (VHTR) and the Gas-cooled Fast Reactor (GFR), are two options. The fuel parts and core structures of these reactors are constructed of graphite in huge quantities. In contact with the heated graphite, the cooling helium warms up and transfers heat to a secondary fluid via tiny heat exchangers. The secondary coolant is then utilized to create power using large-scale gas turbines or to produce hydrogen with no carbon footprint [2].

Materials for application in gas-cooled reactors were researched in the 1970s and 1980s. The high temperature, pressure, and flow of the coolant raise the demands on building materials, which must be corrosion-resistant and mechanically robust for a long period under high-temperature coolant conditions. High-temperature steels and special alloys are used in the construction of thermally stressed components of gas-cooled reactors [2, 3]. Inconel 617, Alloy 230, Nimonic 86, and alloy 800 H are the most studied metallic alloys. Alloy 800H has been utilized on several occasions due of its high-temperature strength and resistance to high-temperature corrosion. This iron-based alloy, with a carbon content ranging from 0.05-0.10 wt% and aluminium and titanium contents ranging from 0.30 to 1.20 wt%, is suitable and certified for use in nuclear systems at temperature up to 760 °C [4-6]. The corrosion of alloys in helium coolant is dependent on the creation of a compact, non-spreading, and slow-growing oxide layer on the surface [2]. Corrosion resistance was tested in impure helium at 760 °C for up to 1500 hours.

This study sought to validate the corrosion resistance and degradation of alloy 800H in simulated conditions of high-temperature coolant of the HTGR reactor, measuring the thickness of the surface layer and determining changes in elemental composition on alloy 800H that had been exposed to the corrosive effects of high-temperature helium and noted changes in the alloy's surface layer as a result of exposure.

2. EXPERIMENTAL

2.1 Materials

Two kinds of materials – namely high temperature steel 800H (Ni30.5Cr20.5Fe, DIN 1,4958) and nickel alloy Nicrofer 3220H (NiCr20Nb, DIN 1,4876) were exposed to conditions simulating a HTGR system. The pressure of the primary helium coolant circuit was 3.0 MPa. The chemical composition of alloys is listed in **Table 1**.

Table 1 The chemical composition (in wt%) of 800H and Nicrofer

Elements	C	Mn	Si	Cu	Ni	Cr	Mo	V	Ti	W	Co	Nb	Al	Fe
800H	0.06	0.7	0.5	0.1	30.5	20.5	<0.001	<0.001	0.34	<0.001	0.1	0.01	0.28	46.7
Nicrofer	<0.01	3.2	0.11	0.01	72.9	20.4	<0.001	<0.001	0.32	<0.001	<0.001	2.7	<0.001	0.2

2.2 Specimens

Specimens of 800H alloy used for experiments were prepared with TIG welds filled with Nicrofer. Corrosion coupons contained both the weld joint and the heat-affected zone in the middle. Recrystallization annealing was performed on the samples. Specimens with grinded surfaces (using sandpaper with a grit size of 30 µm) of the weld metal (WM), the heat affected zone (HAZ), and the base metal (BM) were tested. The proportions of the tested specimens were 40 x10 x 2 mm. Before exposure, all specimens were ultrasonically cleaned with acetone and dried. The specimens were weighed before and after each exposure with an accuracy of 0.00001 g for post-exposure gravimetric evaluation of corrosion gains. Gravimetric measurements were performed on Radwag analytical balances XA 110.4Y PLUS series.

2.3 Corrosion testing in impure helium

The specimens were exposed for up to 1500 hours in a high-temperature furnace (HTF). Temperature during the experiment was 760 °C, and the pressure was 0.9 MPa. The desired experimental temperature was achieved gradually with a temperature ramp of 1 °C per minute, and a constant temperature was maintained inside the furnace. The cooling of the device was also gradual, with a temperature ramp of 1 °C per minute. The gas flow was approx. 0.1 l/min, and the composition of the gas mixture used as corrosion atmosphere for the exposure of the samples is listed in **Table 2**.

Table 2 The chemical composition of gaseous mixture

Component	Concentration (vol. ppm)	Partial pressure (Pa)
CH₄	100	10
CO	500	50
H₂	100	10
Helium	Bal.	Bal.

After exposure, the samples were metallographically cut, metallographically ground using sandpaper with a grain size of 1200, and polished using a diamond paste of 3 and 1 µm. This process was followed by the analysis and thickness measurements of the oxide layer via a Scanning Electron Microscope (SEM, LYRA3 TESCAN) equipped with detectors for the imaging of Backscatter Electrons (BSE) and Energy Dispersive Spectroscopy (EDS) for chemical analysis.

3. RESULTS AND DISCUSSION

SEM pictures of sample cross sections in the initial state and after exposure are showed in **Figures 1 to 4**. SEM examination of specimens after testing demonstrated localized deep oxidation between the weld and the base material, as well as Cr₂O₃ penetration into the material (see **Figure 2c**). The assessment of the cross-sections confirmed the presence of a protective Cr-rich passive layer (see **Figures 2a** and **2b**). According to EDS analysis, the oxide layer was largely made up of Cr, O₂, and a trace of Mn. To minimize degradation by severe corrosion processes in alloys used at high temperatures, the creation of a protective Cr₂O₃ scale is essential. It is known that a minimum Cr concentration of around 20 wt% is required to build a protective, continuous scale on Fe-Cr alloys and nickel alloys, which inhibits further assault [7].

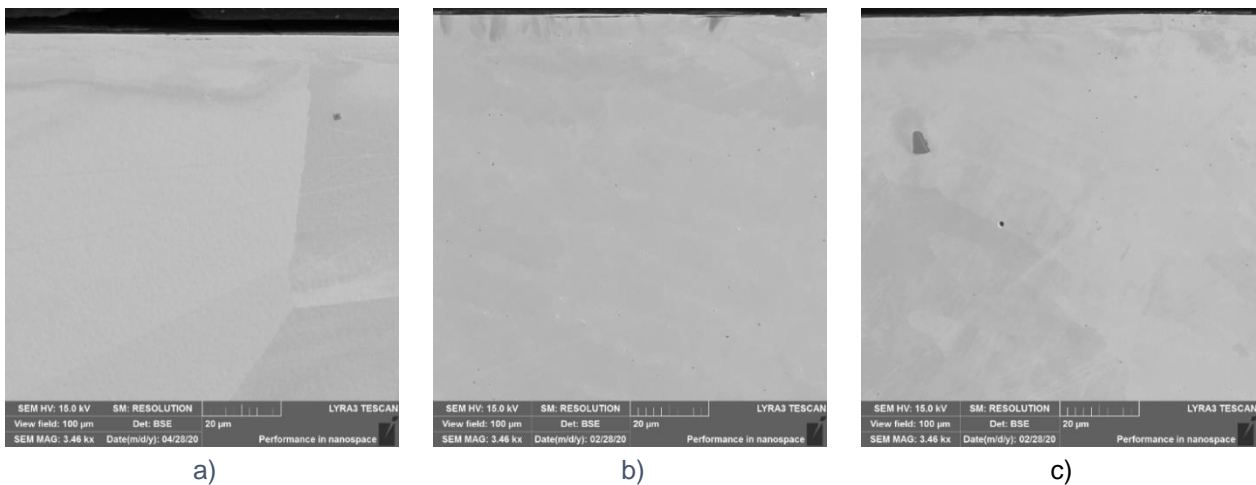


Figure 1 SEM BSE images of as-received specimen's surfaces of a) base metal 800H; b) weld metal Nicrofer; c) between the weld and the base material (HAZ)

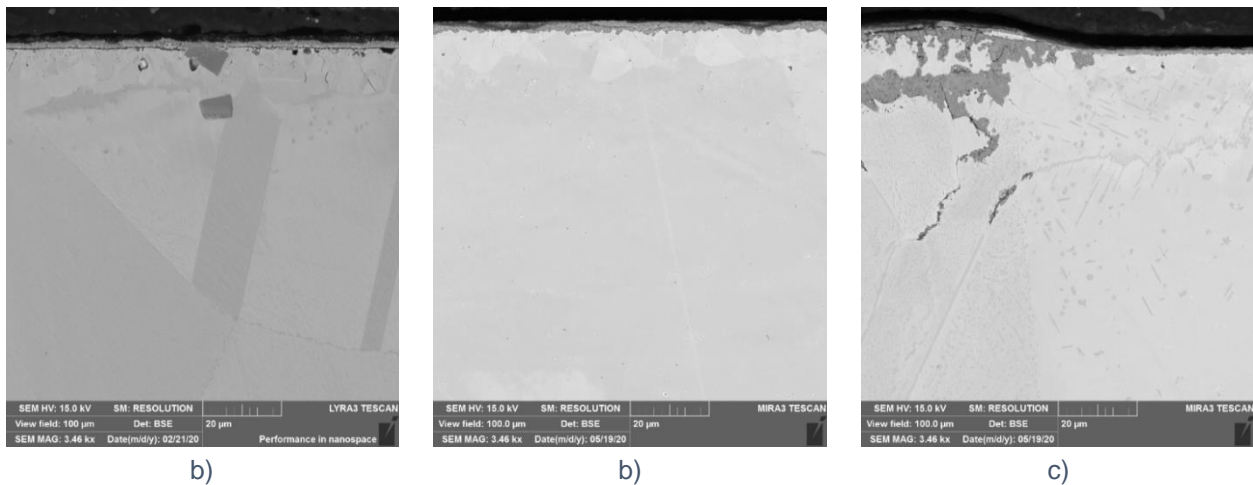


Figure 2 SEM BSE images of specimen's surfaces after exposure at 1500 h of a) base metal 800H; b) weld metal Nicrofer c) between the weld and the base material (HAZ).

Table 3 Oxide thickness of the corrosion layer

Exposure	Thickness of the corrosion layer (µm)		
	800H	Nicrofer	HAZ
x			
760 °C/372 h	1.95	1.80	2.42
760 °C/1000 h	2.23	2.20	2.97
760 °C/1500 h	2.51	2.45	3.10

Corrosive layer spallation was seen in some cases. Both the 800H alloy and the Nicrofer alloy degraded in the same way (see **Table 3**). On the surface of the specimens, a protective oxide layer up to 3 μm thick was discovered, which developed with exposure length. This measurement supported the findings of earlier Berka J. [8] research. The mass increase of the two alloys tested, 800H and 800H with weld at 760 °C, followed a parabolic behavior (see **Figure 5**).

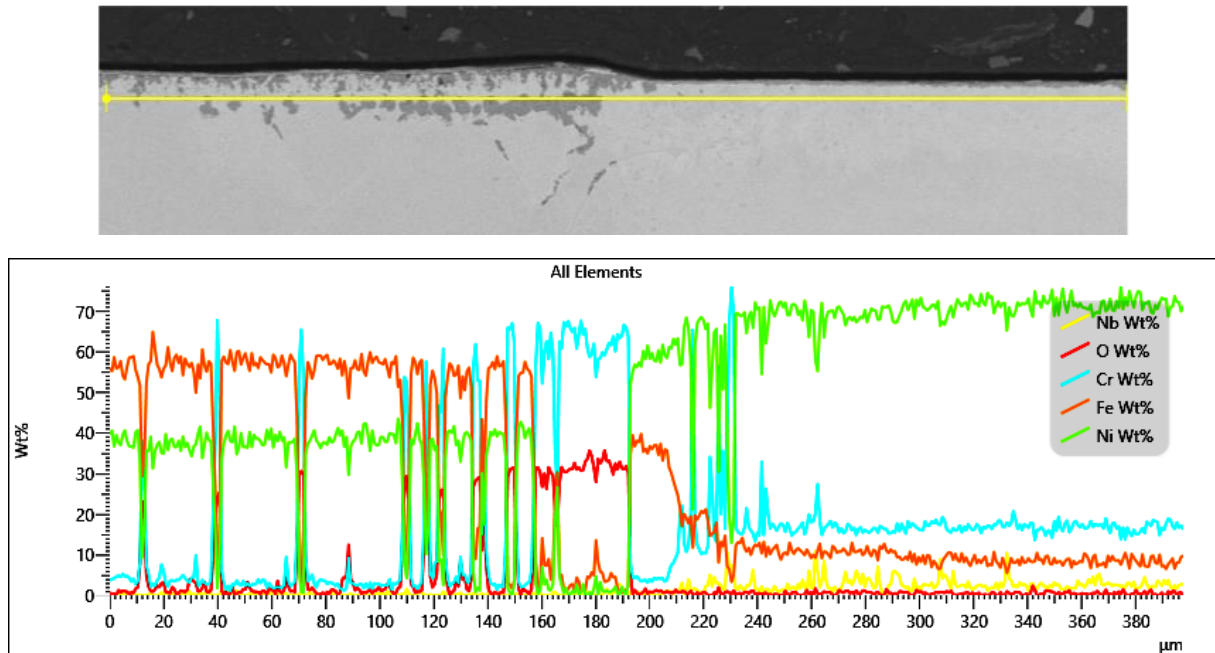


Figure 3 – EDS analysis between the weld and the base material after exposure at 1500 h

With time, the base metal grains and the heat-affected zone coarsened. Because the diffusivity of Cr at grain boundaries is substantially higher than in bulk, the grain size of the alloy plays an essential role in the delivery of Cr to the metal/oxide contact [9]. Internal corrosion occurred at grain boundaries in addition to the production of a passive oxide scale. Although the impure helium was passed through a molecular filter, the moisture content in the incoming gas was around 10 vol. ppm during the experiment, which can speed up internal corrosion because water vapour predominates over other processes such as carburization and decarburization. Deep interior oxidation can cause fatigue and creep fractures to form [2].

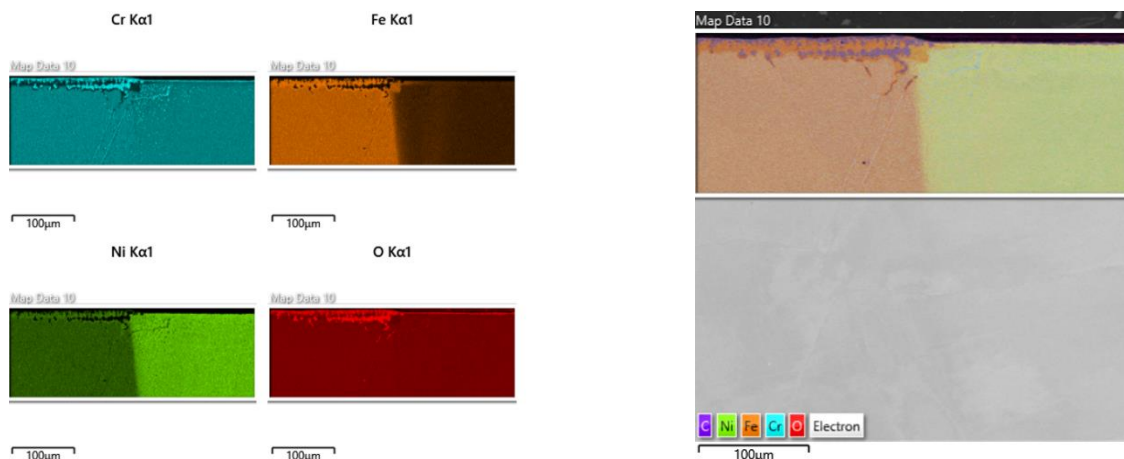


Figure 4 SEM image with EDS analysis of boundary of heat affected zone (HAZ) and weld metal (WM) of alloy 800 H after exposure at 1500 h

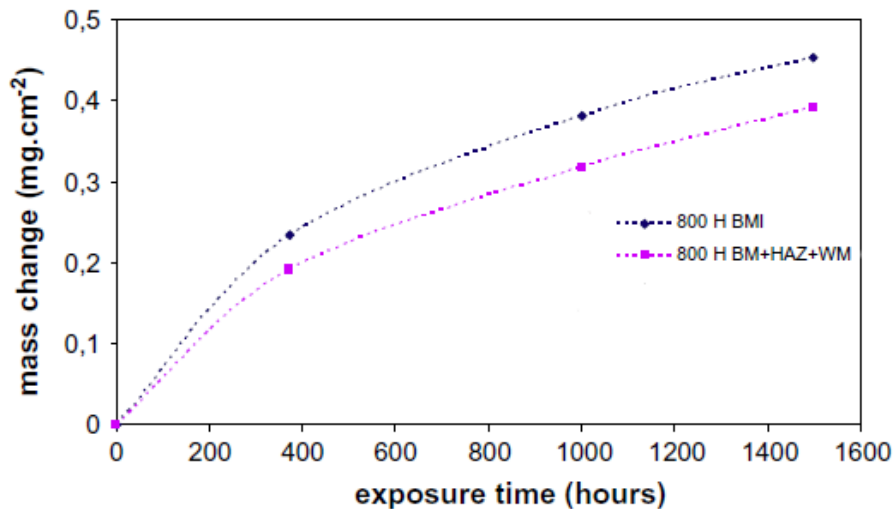


Figure 5 Mass changes of specimens of alloy 800H (blue colour) and alloy 800H with weld metal (purple colour) after exposure in impure helium at 760 °C [8].

CONCLUSION

Based on past scientific results, Alloy 800H was chosen as the best material for the HTGR system idea. Alloy 800H base metal, weld metal, and heat-affected zone specimens were subjected to an impure helium environment for up to 1500 hours at 760 °C.

- A protective oxide layer up to 3 µm thick was detected on the surface of specimens, which grew with exposure duration. The corrosion layer was mostly composed of Cr, O₂, and a trace of Mn. Spallation of corrosive layers was found in some situations.
- The base metal grains and the heat-affected zone coarsened with time and temperature.
- After 1500 hours, localized deep oxidation was discovered between the weld and the base material.
- Both 800H alloy and Nicrofer alloy degraded identically.

More tests on the exposed specimens using various techniques are planned to learn more about the material's degradation after exposure.

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