Corrosion and Mechanical Property at High Temperature of Nickel-Based Alloy for VHTR

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1. Introduction

Using a very high temperature reactor (VHTR), it is conceptually and practically possible to generate highly efficient electricity and produce massive hydrogen among generation IV nuclear power plants. The structural material for an intermediate heat exchanger (IHX) is exposed to high temperature of up to 950°C. In this harsh environment, nickel-based alloys such as Alloy 617 and Haynes 230 are considered as promising candidate materials for IHX material owing to their excellent creep resistances at high temperature. However, high-temperature degradation cannot be avoided even for nickel-based alloy.

Helium which inevitably includes impurities such as H_2, CH_4, H_2O and CO is used as a coolant in a VHTR. Material degradation is aggravated by corrosion under an impure helium environment, which is one of the main obstacles to overcome for the application and successful long-term operation of a VHTR.

A review of the thermodynamics indicates which reactions are available on the surface of the materials among oxidation, carburization and decarburization, but it does not give us the kinetic preference. This kinetic preference can induce localized corrosion, kinetic irreversibility and long-term material instability leading to material degradation.

In addition to a long-term corrosion test under a VHTR coolant environment, the development of new alloys superior to commercial nickel-based alloy also give way to the successful establishment of a VHTR.

Commercial nickel-based wrought alloy is strengthened by a solid solution and precipitation hardening mechanism in a wide temperature range of 500 to 900°C. The γ’ significantly contributes to the strengthening by locking dislocation motion by an anti-phase boundary at an intermediate temperature range of 700 to 800°C, but is no longer stable above this temperature range [1]. However, the material for an IHX needs to fulfill the mechanical property requirements in a narrow and very high temperature range of 850 to 950°C rather than in a wide temperature range.

Therefore, it is valuable to make an effort to find an optimum combination of alloying elements and processing parameters showing the best performance.

In this work, the surface reactions of Alloy 617 as a candidate for an IHX exposed to controlled impure helium at 950ºC were investigated based on thermodynamics. A corrosion test was carried out under a controlled impure helium environment at a temperature range of 850 to 950°C during 10-250 hr. Moreover, the mechanical property and microstructure for nickel-based alloys fabricated at a laboratory were evaluated as a function of processing parameters such as hot rolling and heat treatment condition.

2. Experimental

The material tested was a commercial grade Alloy 617 plate from Special Metals (Huntington, West Virginia, US). A schematic diagram of the experimental system is shown in Fig. 1. The input gas is controlled by a mass flow controller (MFC), which is monitored using gas chromatography (GC, HP 7890A, Agilent Technologies, USA), and moisture is monitored using a dew point meter (Shaw Moisture Meters, England). The outlet gas through the reaction furnace is monitored by GC continually. The furnace consists of a pre-heater and a reaction furnace. The pre-heater contains a graphite rod to reduce the partial pressure of oxygen in impure helium gas.

The concentration of impure helium gas was controlled by changing the mixing ratio of impurity/helium mixture gases (H_2-He, CO-He, CH_4-He) using MFC. The amount of impure gases H_2, CO, CO_2, CH_4, and N_2 were measured by GC. Prior to the test, GC was calibrated using a reference gas including hydrogen, methane and carbon mono oxide.

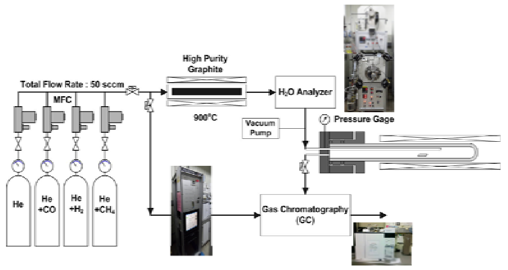

Fig. 1. Schematic drawing of system design.

The test temperatures were 850, 900, and 950°C, and the temperature of the pre-heater was fixed at 900°C. The duration of the holding period at the test temperature was up to 250 h. The impure helium composition was fixed as 200 ppm H_2, 50 ppm CO, 20 ppm CH_4, and H_2O < 2 ppm, and the flow rate of the gas was 50 cm^3/min.

Ni-Cr-Co-Mo alloy was melted by VIM (vacuum induction melting), followed by hot rolling at a temperature in a range of 1050 to 1200°C. The hot rolling pass and thickness reduction ratio are 3-7 and 50%, respectively. Subsequent heat treatment was conducted after hot rolling in the range of 1020 to 1175°C as a function of time duration, followed by water quenching.

An SEM (JEOL JSM-6300, Japan) with EDS (Energy-dispersive X-ray spectroscopy) was used to observe the microstructures and analyze the composition of the specimens. An electron back-scatter diffraction (EBSD, Oxford, INCA crystal) analysis was performed on the JEOL JSM-7000F.

3. Results and discussion

The reaction rate constant can be determined from the experimental results, as shown in table 1. It is predicted that the outer oxide layer thickness, internal oxide depth, and carbide-depleted zone depth may increase to ~116 μm, ~600 μm and ~1000 μm, respectively, if Alloy 617 is exposed to an impure helium environment at 950°C for 20 years. The removal of carbides at the grain boundaries may cause a critical decrease in the structural integrity including the creep properties because the grain boundary carbides act as obstacles for grain boundary sliding. Internal oxide can also lessen the material ductility. From these results, corrosion occurring during long-term operation at 950°C can induce significant material degradation.

Table 1. Surface reaction rate constants from the microstructure observation of Alloy 617 corroded in a controlled helium environment.

Condition	850°C	900°C	950°C
Outer oxide thickness ($\mu m^2 \cdot s^{-1}$)	1.9×10^{-6}	3.7×10^{-6}	1.1×10^{-5}
Internal oxide depth ($\mu m^2 \cdot s^{-1}$)	4.6×10^{-5}	1.2×10^{-4}	2.9×10^{-4}
Decarburized zone depth ($\mu m^2 \cdot s^{-1}$)	8.4×10^{-5}	2.3×10^{-4}	8.6×10^{-4}

Compared to the results obtained in air and pure helium, as shown in table 2, the reaction rate constants decreased in the order of reaction rate constant in controlled impure helium, that in air and that in pure helium. In view of the coolant guide line, the impurity concentration in impure helium should be controlled to be comparable with the surface reaction rate of air or pure helium. It should be noted that the reaction rate constant is determined assuming that a surface reaction occurs uniformly on the surface. However, a microclimate reaction can occur locally in air and pure helium environments at 950°C, which can cause an abrupt loss in the structural integrity. Therefore, it is not guaranteed that the lower reaction rate constant for corrosion determined from the apparent observation predicts a longer life of Alloy 617 under air and pure helium. This is why a long-term experiment is needed.

Table 2. Reaction rate constant as a function of ambient for Alloy 617 at 950°C.

Reaction rate constant	**Controlled He**	**Air**	**Pure He**
k_p [$mg^2 \cdot cm^{-4} \cdot s^{-1}$]	**110×10^{-8}**	**83×10^{-8}**	**1.9×10^{-8}**

In addition to an effort to find the optimum impurity concentration in helium through a long-term experiment under a VHTR coolant environment, the fabrication and assessment of a new nickel-based alloy was carried out.

Table 3 shows hot rolling and subsequent heat treatment conditions after Ni-Cr-Co-Mo alloy melting. After hot rolling and solution annealing, a tensile test was performed, as presented in Fig. 2.

There was no significant difference in the mechanical property among specimens except for that of the hot rolled specimen. The hot rolled specimen showed a smaller grain size than specimens with subsequent solution annealing leading to a higher tensile strength. There were no cracks or macro defects during the hot rolling. From these results, the hot rolling conditions of this work do not affect mechanical property significantly and were reproducibly controllable.

Table 3. Hot rolling and subsequent heat treatment conditions for nickel-based alloy.

Specimen ID	**HR temperature**	**Pass**	**Number of reheat**	**Cooling**	**Thickness reduction (%)**	**SA**
1	1100~1200	7	1	Water	90	O
2		7	1	Air	90	O
3		3	6	Water	90	O
4	1050~1150	7	1	Water	90	O
5		7	1	Water	90	O
6		7	1	Water	90	X
7		7	1	Water	90	X
8		7	1	Water	90	X
9		7	1	Air	90	O
10		3	6	Water	90	O

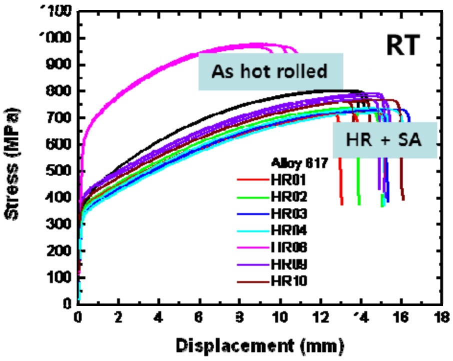

Fig. 1. Results for tensile tests as a function of hot rolling and heat treatment process.

4. Summary

The outer oxide layer thickness, internal oxide depth, and carbide-depleted zone depth were observed after a corrosion test at high temperature. It is predicted that high-temperature corrosion significantly affects the structural integrity for a long operation time.

For Ni-Cr-Co-Mo alloy fabricated by VIM and hot rolling, a combination of cold working and subsequent annealing enhanced the mechanical property at 950°C, changing the grain boundary carbide distribution and angular distribution of the grain boundary.

REFERENCES

[1] Roger C. Reed, The Superalloys Fundamentals and Applications, Cambridge University Press, 2006.