

Assessment of Material Degradation under High Temperature Impure Helium

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1. Introduction

Helium is used as a coolant in a very high temperature reactor (VHTR) among generation IV nuclear power plants. Helium inevitably includes impurities. Reactions of water and hydrogen with graphite in a reactor core form mainly carbon mono oxide and methane [1]. Compositional changes of these impurities change the surface reactions available on the material exposed to impure helium environment. Very high temperature above 900°C facilitates the surface reaction rate. In particular, surface reaction on the materials for intermediate heat exchanger and reactor core which are exposed to very high temperature should be paid great attention.

A stable oxidation prevents material degradation, an internal oxidation lessens mechanical resistance, carburization embrittles material and decarburization makes material weak. Moreover long term integrity of protective oxide should be achieved without a significant spallation of oxide for a long term operation of nuclear power plants.

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

Therefore it is very important to investigate the effect of impurity concentration on surface reaction on the material. A finding of an impurity range where material is stable will give a very important information for long term coolant chemistry guide line.

In this work, an impure helium control system for a material evaluation was set up and equipped with gas chromatography. Individual gas content is controlled by using mass flow controller. A mixed gas is flowed into the chamber and gas composition is changed with the time in the isothermal condition. Outlet gas composition and corroded materials were analyzed based on thermodynamics and kinetics.

2. Experimental

Schematic diagram of experimental system is shown in Fig. 1. Input gas is controlled by mass flow controller, which is monitored by gas chromatography (GC) and moisture is monitored by dew point meter. Outlet gas through furnace where a specimen (Alloy 617) prepared for surface reaction test is positioned is monitored by GC continually.

GC is calibrated by reference gas including hydrogen, methane and carbon mono-oxide. Furnace is designed to apply stress by using load.

Chemical composition of Alloy 617 is shown in Table 1.

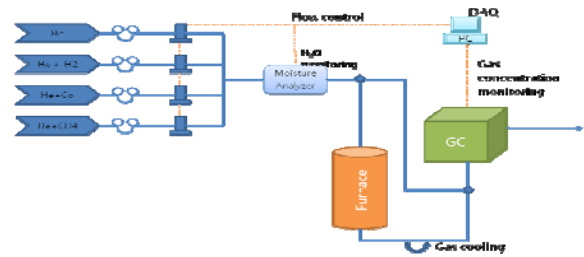


Fig. 1. Schematic drawing of system design.

Table 1. Chemical composition of Alloy 617(wt%).

C	Mn	Fe	S	Si	Cu	Ni	Cr	Al	Ti	Co	Mo	P	B
0.08	0.11	1.49	0.001	0.06	0.08	53.16	22.16	1.12	0.35	11.58	9.80	0.003	0.002

3. Results and discussion

Table 2 shows surface reactions available on Alloy 617 exposed to high temperature impure helium environment including several hundreds ppm H₂, several tens ppm CO, CH₄ and several ppm H₂O. One gas species reaction with the other gas species is not considered because of very dilute and flowing condition which a gas hardly meet the gas. A H₂O tends to oxidize and decarburize the metal while a CH₄ tends to reduce and carburize the metal strongly. CO facilitates oxidation and carburization. Direction of reaction by CO depends on CO gas composition and activities of carbon and metallic element in the solid. Direction of this reaction called as microclimate reaction [2] are deeply related with the stability of metal under impure He.

Table 2. Surface reactions available on Alloy 617.

$3\text{CH}_4 + \text{Cr}_2\text{O}_3 = 3\text{CO} + 2\text{Cr} + 6\text{H}_2 \rightarrow$ oxide reduction
$6\text{CH}_4 + 23\text{Cr} = \text{Cr}_{23}\text{C}_6 + 12\text{H}_2 \rightarrow$ carburization($\text{CH}_4 = \text{C(s)} + 2\text{H}_2$)
$3\text{CH}_4 + 7\text{Cr} = \text{Cr}_7\text{C}_3 + 6\text{H}_2 \rightarrow$ carburization($\text{CH}_4 = \text{C(s)} + 2\text{H}_2$)
$3\text{H}_2\text{O} + 2\text{Cr} = \text{Cr}_2\text{O}_3 + 3\text{H}_2 \rightarrow$ oxidation
$6\text{H}_2\text{O} + \text{Cr}_{23}\text{C}_6 = 23\text{Cr} + 6\text{CO} + 6\text{H}_2 \rightarrow$ decarburization
$(\text{H}_2\text{O} + \text{C(s)} = \text{CO} + \text{H}_2)$
$3\text{H}_2\text{O} + \text{Cr}_7\text{C}_3 = 7\text{Cr} + 3\text{CO} + 3\text{H}_2 \rightarrow$ decarburization
$6\text{CO} + 27\text{Cr} = 2\text{Cr}_2\text{O}_3 + \text{Cr}_{23}\text{C}_6 \rightarrow$ oxidation & carburization
$3\text{CO} + 9\text{Cr} = \text{Cr}_2\text{O}_3 + \text{Cr}_7\text{C}_3 \rightarrow$ oxidation & carburization
$3\text{C} + 7\text{Cr} = \text{Cr}_7\text{C}_3 \rightarrow$ carbide formation
$6\text{C} + 23\text{Cr} = \text{Cr}_{23}\text{C}_6 \rightarrow$ carbide formation

As CO content is lower than a critical concentration, oxide and carbon in the alloy can not coexist but backward reaction occurs to form CO until one of oxide or carbon disappears. At this time, oxide is reduced and carbon is dissolved into material to be embrittled if CH₄ content is relatively higher than H₂O content. However metal is oxidized and decarburized to be less creep resistant if H₂O content is relatively higher than CH₄ content. Oxide is reduced again to form CO which makes surface layer porous. Moreover it is questionable that mechanical property of alloy is stable irrespective of CO, CH₄, H₂ and H₂O contents if CO above a critical concentration is satisfied. Mechanical property of metallic alloys is affected by minor alloying elements such as Al, Ti, Si, W, Mo, Mn and etc so that reactions of these minor elements should be investigated.

4. Summary

An impure helium control system for a material evaluation was set up, which was equipped with gas chromatography.

Surface reactions available on Alloy 617 showing the best creep resistance was investigated. Driving forces for many surface reactions were compared.

A finding of an optimum impurity range as well as impurity ratio, based on thermodynamics and kinetics will be very important for the prevention of material degradation.

REFERENCES

- [1] C. Cabet and F. Rouillard: J. Nuclear Materials, Vol. 392 (2009), p. 235-242.
- [2] K.G.E. Brenner and L.W. Graham, Nucl. Technol. Vol. 66 (1984) 404.