The use of Thermodynamics and Phase Equilibria for Prediction of the Behavior of High Temperature Corrosion of Alloy 617 in Impure Helium Environment

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Thermodynamic consideration was performed for Alloy 617 exposed to an impure helium (H_2 20pa, H_2O 0.5pa, CH_4 2pa and CO 5pa) at 950 ℃. Oxidation power was decreased in the order Al > Ti > Si > Cr > Mn. Decarburization and carburization reactions were available leading to carbon activity decrease and increase, respectively, depending on carbon and Cr activities. The thermodynamic prediction was compared with the experimental results obtained in similar conditions ((H_2 20pa, H_2O 0.05pa, CH_4 5pa and CO 2pa) and 950 ℃) by others for Alloy 617. The driving force for oxidation of Al, Ti and Si is very large to be oxidized at a given impure helium and the environment is actually carburizing towards the structural alloy, which is consistent with this work.

Keywords : *impure helium, high temperature corrosion, thermodynamics, alloy 617*

1. Introduction

Helium is considered as a coolant in a very high temperature reactor (VHTR) among generation IV nuclear power plants due to its advantages of inert gas, high thermal conductivity, low neutron absorption and etc. Impurities such as hydrogen, water, methane and carbon monoxide are inevitably introduced in the helium coolant, which is related to the reactions with graphite in the core.[1] Compositional changes of these impurities change the surface reactions available on the material exposed to impure helium environment. Very high temperature above 850 ℃ for VHTR facilitates the surface reaction rate. In particular, surface reaction on the materials for intermediate heat exchanger (IHX) and reactor core which are exposed to very high temperature helium 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.[2] 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 occurrence of another reaction in the restricted area, kinetic irreversibility and long term material instability leading to material degradation.

Therefore a finding of an impurity range where material is stable will give a very important information for long term coolant chemistry guide line through a combination of thermodynamics and kinetics. In this work, surface reactions for Alloy 617 as a candidate for IHX exposed to an impure helium at 950 ℃ were investigated in view of thermodynamics. The thermodynamic prediction was compared with the experimental results which were obtained in similar gas composition (H_2 20pa, H_2O 0.05pa, CH_4 5pa and CO 2pa) and at 950 ℃ for Alloy 617.

2. Method

Table 1 shows chemical composition for Alloy 617. Alloy 617 strengthened by Mo and Co as the alloying elements of substitutional solid solution and by C and B as the alloying elements of interstitial solid solution is known as the most promising IHX material due to the high creep resistance.[1] Gas composition of H_2 20Pa, H_2O 0.5Pa, CH_4 2Pa and CO 5Pa was considered, based on

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Table 1. Chemical compositions of Alloy 617, wt.%.

	Chemical Analysis													
	C	Mn	Fe	S	Si	Cu	Ni	Cr	Al	Ti	Co	Mo	P	B
Alloy 617	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

previous reports.[1)-5)]

Thermodynamic considerations for the reactions were performed by using HSC Chemistry 6.0 as software for thermodynamic database.[6)]

3. Results and discussion

Gas/gas reaction is not considered because of very dilute and flowing condition where there is an extremely low collision probability. From this, steady state rather than thermodynamic equilibrium is assumed.[3)]

Regarding the impurities in helium coolant of VHTR, water and hydrogen are introduced inevitably due to out-gassing, air ingress and in-leakage. Consequently methane and carbon monoxide are formed by reactions (1) and (2), respectively, with graphite in the core.

$$C + 2H_2 = CH_4 \tag{1}$$

$$C + H_2O = CO + H_2 \tag{2}$$

Moreover oxygen can react with graphite to form CO. The equilibrium partial pressure of oxygen for this reaction at 950 ℃ is very low to be about 10^{-23} atm indicating that any introduction of oxygen can cause CO formation. Driving force for CO formation is larger than CO_2 formation and reduction of CO_2 to CO is available indicating that the presence of CO_2 as an impurity in the helium is much less probable.
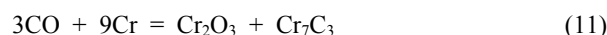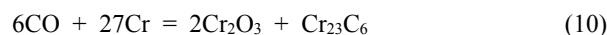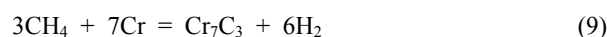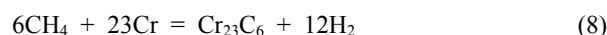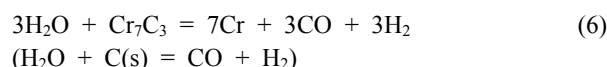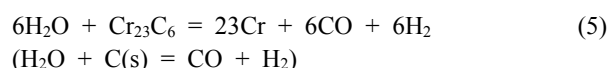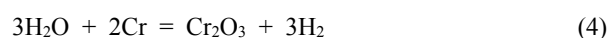
At a given gas composition, the equilibrium partial pressure of oxygen for the reaction (3) at 950 ℃ is about 10^{-19} atm which is very low value but higher than the equilibrium partial pressure of oxygen for CO formation reaction.

$$H_2 + 1/2O_2 = H_2O \tag{3}$$

Surface reactions on material used for IHX depend on material composition, helium impurity ratio, impurity concentration, temperature, time, kinetics and etc, which affect material corrosion and material degradation. This is why surface reaction should be predicted and a sample surface after high temperature experiment should be analyzed.

Reactions (4) ~ (13) can be considered for chromium. Reaction (4) represents oxidation of Cr. Reactions (5) and

(6) imply carbide decomposition following decarburization, respectively. By reactions with methane, oxide reduction and carburization, followed by carbide formation can be considered as shown for reactions (7) ~ (9). CO can react with Cr to form oxide and carbide like reactions (10) and (11). Reactions (12) and (13) show carbide formation reactions.

$$3H_2O + 2Cr = Cr_2O_3 + 3H_2 \tag{4}$$

$$6H_2O + Cr_{23}C_6 = 23Cr + 6CO + 6H_2 \tag{5}$$
$$(H_2O + C(s) = CO + H_2)$$

$$3H_2O + Cr_7C_3 = 7Cr + 3CO + 3H_2 \tag{6}$$
$$(H_2O + C(s) = CO + H_2)$$

$$3CH_4 + Cr_2O_3 = 3CO + 2Cr + 6H_2 \tag{7}$$

$$6CH_4 + 23Cr = Cr_{23}C_6 + 12H_2 \tag{8}$$

$$3CH_4 + 7Cr = Cr_7C_3 + 6H_2 \tag{9}$$

$$6CO + 27Cr = 2Cr_2O_3 + Cr_{23}C_6 \tag{10}$$

$$3CO + 9Cr = Cr_2O_3 + Cr_7C_3 \tag{11}$$

$$3C + 7Cr = Cr_7C_3 \tag{12}$$

$$6C + 23Cr = Cr_{23}C_6 \tag{13}$$

Moreover minor elements should be considered for surface reactions. It should be noted that the water tends to oxidize and decarburize the material, the methane tends to reduce and carburize the material and the carbon monoxide tends to oxidize and carburize the material. As mentioned above, a stable oxidation prevents material degradation under well balanced environment while an internal oxidation and/or non adherent oxide leads to mechanical weakening and spallation, carburization embrittles material and decarburization lessens high temperature creep strength.[2)] Therefore the well balanced environment should be determined and confirmed experimentally.

In particular, direction of reaction by CO (reactions (10) and (11), more generally reaction (14)) depends on CO

gas composition and activities of carbon and metallic element in the solid. Direction of this reaction called as microclimate reaction[2] is deeply related with the stability of metal under impure He. The physical size of the zone within which the processes occur is extremely small and probably at least an order of magnitude less than the thickness of the oxide - hence the term "microclimate".[4]

$$MO + C = CO + M \qquad (14)$$

As CO content is lower than a critical concentration, oxide and carbon in the alloy cannot coexist but forward reaction occurs to form CO until one of oxide or carbon disappears without a help of any gaseous species.[1] At this time, oxide is reduced and carbon is dissolved into material to be embrittled if CH_4 content is relatively higher than H_2O content. However metal is oxidized and decarburized to be less creep resistant if H_2O content is relatively higher than CH_4 content. Oxide is reduced again to form CO which makes surface layer porous. Therefore the CH_4/H_2O ratio is also important to prevent material degradation.

According to reaction (14), equilibrium constant K = $a_M \cdot p_{CO} / a_C$, where a_M, p_{CO} and a_C represent the activity of metal, the partial pressure of CO and the carbon activity, respectively.

Let us consider the surface reaction (14) during oxidation, decarburization and carburization. First, during the oxidation, Cr activity will decrease at oxide/metal interface causing an increase of CO partial pressure. Secondly, carbon activity will decrease leading to CO partial pressure decrease and carbide decomposition during decarburization. Finally, carburization induces carbon activity increase with the time causing the p_{CO} increase and carbide formation. Activity and partial pressure change with the time according to surface reaction (14) indicating that a determination of a protective range of p_{CO} rather than a finding of deterministic p_{CO} is a key to prevent a material from degradation.

Moreover carbide stabilizing element Mo and Mo_6C formation will also decrease carbon activity leading to pCO decrease.[3] Carbide formation and oxidation of minor elements will affect p_{CO}, p_{O2} and a_C. According to the previous reports,[3-5] carbon and Cr activities are not a unique value but 0.0015~0.004 and 0.35~0.77, respectively. Uncertainty of the carbon activity and Cr activity will change CO partial pressure. Consequently, an optimum range of gas composition in the operating temperature range should be found, based on thermodynamic prediction and experimental results.

Fig. 1 shows the standard free energy, ΔG^o for oxidation (oxidation 1) of various metals composing Alloy 617 by
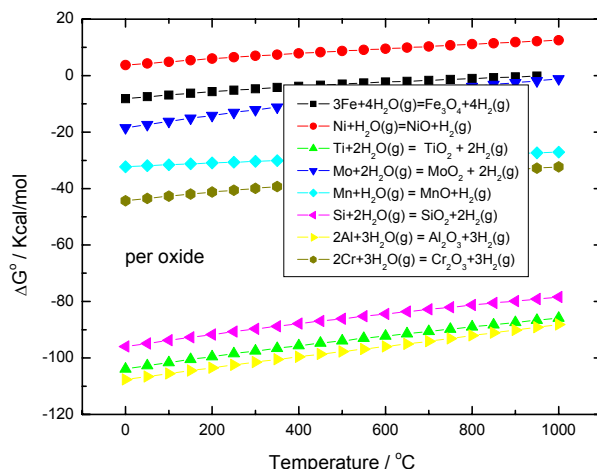

Fig. 1. Standard free energy, ΔG^o for oxidation (oxidation 1) of various metals composing Alloy 617 by the reaction with H_2O as a function of the temperature.
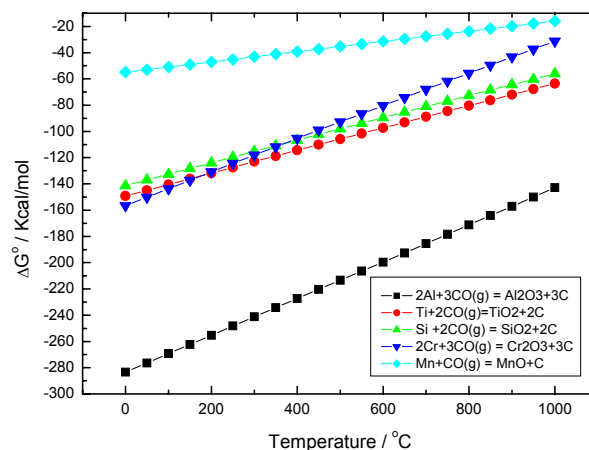

Fig. 2. Standard free energy, ΔG^o for oxidation (oxidation 2) of various metals composing Alloy 617 by the reaction with CO as a function of the temperature.

the reaction with H_2O as a function of the temperature. Positive slope and negative value at 0 ^oK represent the entropy decrease, caused by decrease of number of moles and exothermic reaction of oxidation, respectively. Oxidation power was Al > Ti > Si > Cr > Mn. Ni and Fe do not react with H_2O to be oxidized spontaneously.

Fig. 2 shows the standard free energy, ΔG^o for oxidation (oxidation 2) of various metals composing Alloy 617 by the reaction with CO as a function of the temperature. ΔG^o for oxidation 2 was larger than ΔG^o for oxidation 1 at the standard state. The slope was more positive, which is caused by removal of gaseous CO. Oxidation power was also Al > Ti > Si > Cr > Mn.

Table 2 represents the driving force for oxide formation through oxidation 1 and oxidation 2 at a given gas compo-

Table 2. Represents the driving force for oxide formation through oxidation 1 and oxidation 2 at a given gas composition and 950 ℃.

Oxide	Oxidation 1(cal/mol)	Oxidation 2(cal/mol)	Metal activity	Remark
Cr_2O_3	-37,132	-3,732	0.72	ΔG for rxn 2 +, -
Al_2O_3	-133,298	-49,949	0.024	
SiO_2	-47,793	-25,526	0.004	
TiO_2	-55,301	-33,035	0.004	
MnO	-18,380 -1,593	-7,247 +9,540	1 0.001	ΔG for rxn 2 +, -as a_{Mn}~0.1

Fig. 3. Standard free energy, ΔG^o for decarburization of carbide forming metals among metals composing Alloy 617 as a function of the temperature.

sition and 950 ℃. Driving force for oxidation 1 was larger than that for oxidation 2 unlike the results of the standard free energy. Oxidation power was Al > Ti > Si > Cr > Mn. Cr can be oxidized or reduced depending on p_{CO}, which is consistent with microclimate reaction at critical CO concentration (critical temperature, T_A, the critical concentration increases with the temperature). Moreover Mn can be also oxidized or reduced depending on p_{CO}.
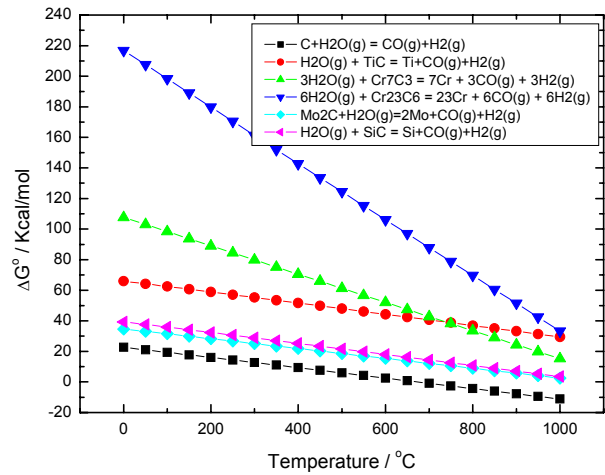
Fig. 3 shows the standard free energy, ΔG^o for decarburization of carbide forming metals among metals composing Alloy 617 as a function of the temperature. Standard free energy, ΔG^o for the combined reaction of the decarburization reaction, $C + H_2O = CO + H_2$ and the carbide decomposition reaction, M-C = M + C was plotted together. Negative slope and positive value at 0 ^{o}K represent the entropy increase, caused by increase of number of moles and endothermic reaction of decarburization, respectively. This decarburization reaction does not occur spontaneously at standard state. For this reaction, carbide formation tendency should be also considered.

Table 3 represents the driving force for the decarburization reaction, the combined reaction (reaction 1, M-C + H_2O = M + CO + H_2) of the decarburization reaction (C + H_2O = CO + H_2) and the carbide decomposition reaction

(M-C = M + C) and the carbide decomposition reaction (reaction 2, M-C = M + C) at a given gas composition and 950 ℃. Decarburization reaction is available leading to carbon activity decrease. Cr carbide can be decomposed depending on carbon and Cr activities. However driving force for TiC formation is too strong to be decomposed. Driving force for Mo_2C and SiC formation was very weak to form carbides. Power for the combined reaction of the decarburization reaction and the carbide decomposition reaction was $Cr_{23}C_6$ > Cr_7C_3.

Fig. 4 shows the standard free energy, ΔG^o for the carburization and the carbide formation of carbide forming metals among metals composing Alloy 617 as a function of the temperature. Negative slope and positive value at 0°K for the carburization reaction CH_4 = C + $2H_2$ represent the entropy increase, caused by increase of number of moles and endothermic reaction of carburization, respectively. At standard state, carbide formation power was $Cr_{23}C_6$ > Cr_7C_3 > TiC > SiC > Mo_2C.

Table 3. Driving force for the decarburization reaction, the combined reaction (reaction 1, M-C + H_2O = M + CO + H_2) of the decarburization reaction (C + H_2O = CO + H_2) and the carbide decomposition reaction (reaction 2, M-C = M + C) and the carbide decomposition reaction (M-C = M + C) at a given gas composition and 950 ℃.

| Formula	Reaction 1 (cal/mol)	Reaction 2 (cal/mol)	Activity	Remark
Decarburization	-11,133	-11,133	0.004	Decarburization from matrix is available
TiC	+2,805	+13,614	0.0035	Strong carbide bonding E
Cr_7C_3	-31,080	+2,319	0.72	Depending on carbon activity
$Cr_{23}C_6$	-66,611	+188	0.72	Depending on carbon activity
Mo_2C	-22,158	-11,024	0.1	Not easy carbide formation
SiC	-23,153	-12,020	0.004	Not easy carbide formation
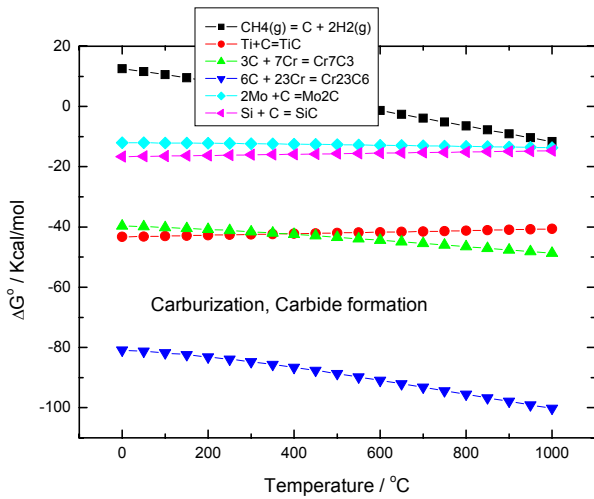
Fig. 4. Standard free energy, ΔG^o for the carburization and the carbide formation of carbide forming metals among metals composing Alloy 617 as a function of the temperature.
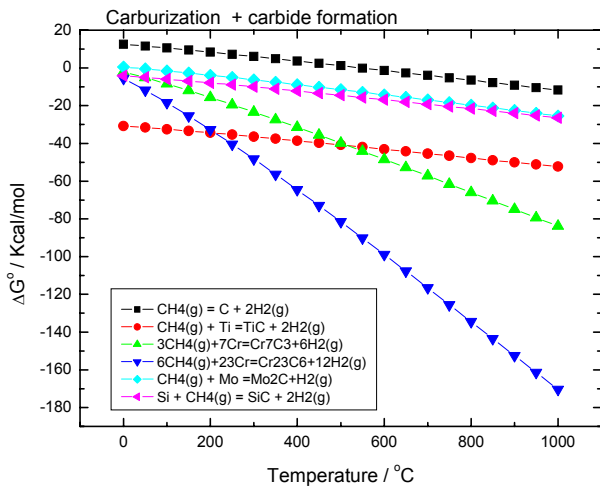

Fig. 5. Standard free energy, ΔG^o for the carburization and the combined reaction (reaction 1, $CH_4 + M = M\text{-}C + 2H_2$) of the carburization reaction ($CH_4 = C + 2H_2$) and the carbide formation (reaction 2, $M + C = M\text{-}C$) of carbide forming metals among metals composing Alloy 617 as a function of the temperature.

Fig. 5 shows the standard free energy, ΔG^o for the carburization ($CH_4 = C + 2H_2$) and the combined reaction (reaction 1, $CH_4 + M = M\text{-}C + 2H_2$) of the carburization reaction ($CH_4 = C + 2H_2$) and the carbide formation (reaction 2, $M + C = M\text{-}C$) of carbide forming metals among metals composing Alloy 617 as a function of the temperature. Power for the combined reaction of the carburization reaction and the carbide formation reaction was $Cr_{23}C_6 > Cr_7C_3 > TiC > SiC > Mo_2C$.

Table 4 represents the driving force for the carburization reaction, the combined reaction of the carburization reaction and the carbide formation reaction and the carbide formation reaction at a given gas composition and 950 ℃.

Carburization reaction is available leading to carbon activity increase. Cr carbide can be formed depending on carbon and Cr activities. However driving force for TiC formation is very strong. Mo_2C and SiC formation is not available even though the combined reaction seems to be available. Power for the combined reaction of the carburization reaction and the carbide formation reaction was $Cr_{23}C_6 > Cr_7C_3 > TiC$.

According to the previous report,[1] Alloy 617 was tested under gas composition of H_2 20pa, H_2O 0.05pa, CH_4 5pa and CO 2pa at 950 ℃. Long duration test in this impure helium showed that specimens still exhibit a surface oxide after 5000 h. This means that oxidation is a sustainable behavior for at least 5000 h. The surface chromia also contains titanium and some internal oxides containing Al, Ti or Si are also evident close to the oxide/alloy interface. $Cr_{23}C_6$ following the carburization was mainly observed. Mo rich M_6C was also observed. Beneath the growing oxide scale, a carbide free zone develops. However surface scale was changed with the change of gas composition. These results were compared with the results predicted in this work.

According to this work, driving force for oxidation of Al, Ti and Si is very large to be oxidized at a given impure helium, consistent with the results of the previous report.

Table 4. Driving force for the carburization reaction, the combined reaction (reaction 1) of the carburization reaction (reaction 2) and the carbide formation reaction and the carbide formation reaction at a given gas composition and 950 ℃.

Formula	Reaction 1 (cal/mol)	Reaction 2 (cal/mol)	Activity	Remark
Derburization	-38,914	-38,914	0.004	Carburization to matrix is available
TiC	-52,528	-13,614	0.0035	Carbide formation
Cr_7C_3	-119,061	-2,319	0.72	Carbide formation
$Cr_{23}C_6$	-233,672	-188	0.72	Carbide formation
Mo_2C	-27,890	+11,024	0.1	Difficult to form carbide
SiC	-26,894	+12,020	0.004	Difficult to form carbide

The environment is actually carburizing towards the structural alloy according to the prediction of this work but the formation of the surface oxide effectively can minimize the carburization by forming a barrier between the gas and the metal.

Regarding carbide, driving force for the combined reaction of carbide formation and the carburization is larger for $Cr_{23}C_6$ than Cr_7C_3 while the driving force for carbide formation is larger for Cr_7C_3 than $Cr_{23}C_6$ from the table 4 indicating that the main carbide would be $Cr_{23}C_6$, which is consistent with the experimental result. However thermodynamic data for Mo rich M_6C was not available unfortunately from the HSC Chemistry 6.0 database, based on numerous thermodynamic data.

There is a review article for Alloy 617.[7] With the annealing condition, two carbides are developed and observed along the grain boundary of Alloy 617. During the solution treatment at a minimum of 1150 ℃, M_6C carbide is stable and at an ageing temperature below 1000 ℃ following the solution treatment, $M_{23}C_6$ starts to form at the expense of the M_6C, based on THERMOCALC® calculation. This calculation predicts which carbides at the as solution annealed state and the aged state are stable, respectively.

$M_{23}C_6$ and M_6C are thought to be the most and the second abundant carbide forms in Alloy 617, respectively, according to many experimental results. $M_{23}C_6$ is observed in the ageing temperature range of 400~1000 ℃, irrespective of ageing time while M_6C is not observed after long time ageing at temperatures below 900 ℃, which is different from the result by THERMOCALC® calculation which predicts a presence of M_6C below 900 ℃ even though the amount of M_6C is decreased with the temperature. In spite of discrepancy between the calculation and the experimental results, the main carbide developed with the high temperature ageing in the report[7] is $Cr_{23}C_6$, which is well agreement with this work.

From this, it is expected that the carbide can be formed and developed variously during the alloy manufacturing and the ageing with the time and environment implying that the kinetics as well as thermodynamics should be considered together in order to understand accurately the material degradation behavior under a high temperature helium environment.

According to phase equilibrium diagram,[6] Cr oxide is more stable in relatively high oxygen partial pressure and Cr carbide is more stable in relatively high carbon partial pressure, as shown in Fig. 6. It should be noted that Cr_7C_3 rather than $Cr_{23}C_6$ is the most stable form considering only the carbide stability. At a given gas composition (equilibrium oxygen and carbon partial pressures), Cr is oxidized and
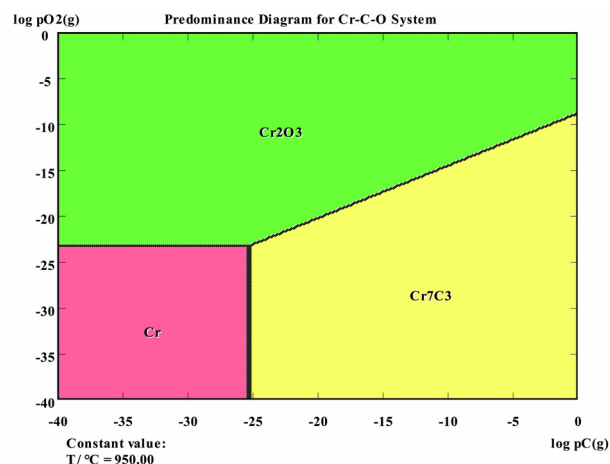

Fig. 6. Phase equilibrium diagram for Cr-C-O at 950 ℃.

carbon as the forms of methane and carbon monoxide is moved into material through the oxide leading to carbide formation. This carburization, followed by carbide formation can embrittle the materials. When the oxide is very protective and (or) carbon activity is not high, the carburization, followed by carbide formation can be retarded and the carbide developed internally during the alloy manufacturing itself can affect the surface reactions such as the oxidation behavior under an impure helium environment. This indicates that the selection of an optimum gas composition is important for a given system.

Development of a carbide free zone is caused by chromium activity decrease due to the oxidation as mentioned above.

From this, it was confirmed that the experimental results were fairly well agreed with the thermodynamic prediction of this work. However, a further study on long term stability and kinetic preference through the combination of kinetic and thermodynamic results is still needed under various gas compositions and variable gas composition.

4. Summary

Driving forces for many surface reactions available on Alloy 617 were investigated for gas composition of H_2 20Pa, H_2O 0.5Pa, CH_4 2Pa and CO 5Pa at 950 ℃. Oxidation power was decreased in the order Al > Ti > Si > Cr > Mn. Decarburization and carburization reactions were available leading to carbon activity decrease and increase, respectively, depending on carbon and Cr activities. Both powers for the combined reaction of the decarburization reaction and the carbide decomposition reaction and the combined reaction of the carburization reaction and the carbide formation reaction were $Cr_{23}C_6 > Cr_7C_3$.

The thermodynamic prediction was consistent with the

experimental results obtained in similar conditions ((H_2 20pa, H_2O 0.05pa, CH_4 5pa and CO 2pa) and 950 ℃) by others for Alloy 617.

An optimum impurity range as well as impurity ratio needs to be found, based on thermodynamics and kinetics in the future.

Acknowledgement

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