**Surface oxidation of Alloy 617 in low oxygen partial pressure He - CO - CO₂ environments
at 750 - 850 °C**

G. Gulsoy^{1,*}, G.S. Was¹

¹Department of Materials Science and Engineering, University of Michigan

2355 Bonisteel Boulevard, Ann Arbor, MI, 48109, gulsoy@umich.edu

Abstract

Surface Cr oxidation mechanism of Alloy 617 was investigated in He - CO - CO₂ environments with $P_{\text{CO}} / P_{\text{CO}_2}$ of either 9 or 1320 at temperatures 750 - 850 °C. The activation energy for surface oxidation was 169.0 ± 13.2 kJ/mol in He - $P_{\text{CO}} / P_{\text{CO}_2} = 9$ and 234.4 ± 8.9 kJ/mol in He - $P_{\text{CO}} / P_{\text{CO}_2} = 1320$. The ambient oxygen partial pressure dependence of the measured oxidation rates was consistent with n-type behavior of Cr₂O₃, in which Cr interstitials are the primary mobile species. The oxidation rates measured were greater than that can be sustained only by lattice diffusion of Cr in Cr₂O₃, indicating that grain boundary diffusion of Cr plays a role in the Cr₂O₃ growth kinetics.

Keywords: oxidation; superalloy; activation energy; diffusion coefficient

* Corresponding author. Tel: +1 734 846 1125; fax: +1 734 763 4540
E-mail address: gulsoy@umich.edu (G. Gulsoy)

1. Introduction

High temperature gas-cooled reactors (HTGR) are mid-sized, graphite moderated, helium cooled, thermal neutron spectrum reactors with a pebble bed or prismatic core using tristructural-isotopic (TRISO) fuel particles [1,2]. The reactor size and core configuration facilitate very high reactor core outlet helium temperatures resulting in high electrical generation efficiency (~50%), thermal power output (600 - 800 MWt) and fuel burn-up rates. Given these features, HTGRs are suitable for the generation of electricity, hydrogen and process heat for both residential and commercial uses. The latest HTGR design requires an intermediate heat exchanger (IHX) to transfer the coolant helium to power a gas turbine for electricity generation, and to provide heat for hydrogen processing.

The IHX is expected to operate at temperatures of up to 850 °C and under cyclic stresses of 7 - 9 MPa in helium containing CO, CO₂, H₂, H₂O and CH₄ in ppm levels due to leaks in the seals and welds, or outgassing of the reactor core internals and thermal insulators [3–5]. At the designated operating temperatures, these impurities in helium are known to result in surface chromium and internal aluminium oxidation, carburization or decarburization of the IHX alloys [2–13]. The combination of these corrosion modes with cyclic stresses at high temperatures can have severe negative impact on the microstructure stability and mechanical properties of the IHX alloys. Therefore, IHX materials must exhibit good oxidation resistance, carburization / decarburization resistance, and creep-rupture properties at temperatures up to 850 °C. Based on these requirements, Ni-Cr based Alloy 617 has been identified as the primary candidate IHX alloy [2–8].

The oxidation resistance of Alloy 617 is mainly attributable to the formation of a continuous surface Cr₂O₃ film. Therefore, the defect and transport properties that govern the

growth rate of Cr_2O_3 in IHX helium environments are of particular interest. The objective of this work is to examine the mechanism by which Cr_2O_3 scale grows on Alloy 617 in low oxygen partial pressure He - CO - CO_2 environments at 750 - 850 °C.

2. Experimental Methods

Alloy 617 (heat number: XXX2323UK) used in this study was in the form of a 12 mm thick plate that was solution annealed at 1175 °C followed by air cooling. The chemical composition of the alloy obtained from the manufacturer is given in Table 1. The average grain size of the alloy was 65 μm and the as-received microstructure contained globular intergranular and transgranular M_{23}C_6 and M_6C type carbides aligned along the rolling direction. Detailed microstructure characterization of the as-received alloy has been reported elsewhere [12].

Alloy 617 corrosion coupons of dimensions 4.5 mm x 10 mm x 1.5 mm and 10.5 mm x 6.5 mm x 1.5 mm were ground and polished down to 1 μm diamond finish to ensure that the surfaces were free of scratches under optical microscopy. The samples were then cleaned and degreased ultrasonically in an ethanol-acetone mixture followed by cleaning in distilled water.

Two He - CO - CO_2 environments that represent the simplified IHX helium coolant chemistry were selected for the exposures. Environments are designated according to their $P_{\text{CO}}/P_{\text{CO}_2}$ ratios, as shown in Table 2, and henceforth will be referred as Env. 9 and Env. 1320. Three major criteria were considered in selecting the compositions of the He-CO- CO_2 environments. First, the gas composition should reproduce the degradation modes predicted for the real IHX helium coolant chemistry. Second, the gas composition should be kept simple to understand the mechanism of oxidation without introducing the complex kinetic competition between different oxidizing molecules. Third, the environment should lend itself to systematic variation to understand the effect of gas composition on the oxidation kinetics.

Exposures in Env. 9 and Env. 1320 at 750 - 850 °C were conducted in the controlled-impurity helium flow system (CIHFS) [14]. The main components of the CIHFS are a helium purification system, gas mixing section composed of a series of mass-flow controllers, a multi-quartz tube furnace, and a discharge ionization detector gas chromatograph (DIDGC), which is capable of analysing H₂, Ar, O₂, N₂, CH₄, CO and CO₂ molecules in a helium stream with a resolution of 0.1 mol ppm. Before starting the exposures, temperatures corresponding to the sample locations in each quartz tube were measured using an external K-type thermocouple under flowing helium. The gas flow rates in each test tube were set at 200 ± 5 ml/min and coupons were exposed to Env.9 and Env. 1320 for various times between 25 h to 500 h.

Alloy 617 samples oxidized in He - CO - CO₂ environments were weighed before and after the exposures to determine the weight gain kinetics. Three measurements were taken each time the samples were weighed. Cross-sections of the samples oxidized in He - CO - CO₂ environments were prepared for SEM analysis by sectioning the samples with a diamond blade, followed by nickel plating to preserve the surface features. Surface and sub-surface oxidation features were characterized by SEM using JEOL™ JSM-6480 SEM.

3. Defect structure and growth mechanism of Cr₂O₃

The rate and mechanism by which Cr₂O₃ grows are governed by two major factors: the defect structure of Cr₂O₃, and nature of the charge carriers that are predominantly mobile in Cr₂O₃. The majority of the research published in the literature indicated that Cr₂O₃ grows predominantly at the oxide - gas interface by outward migration of Cr cations [15–25]. However, there has been a lack of consensus whether Cr cations migrate via interstitial or vacancy diffusion mechanisms, which depends on the defect structure of Cr₂O₃. Hindam and Whittle [23,24] showed that the Cr oxidation rate constant is independent of the oxygen partial pressure

in the range of 10^{-8} - 10^{-14} atm at 1000°C and that Cr_2O_3 exhibited n-type semiconductor behavior in which Cr interstitials were the predominant mobile species. Based on four-point conductivity measurements, Park and Natesan [26] reported that Cr_2O_3 exhibited p-type semiconductor behavior, indicating Cr vacancies were the primary charge carriers in the temperature range of 577 - 1088°C . On the other hand, Atkinson and Taylor [27] proposed that at low ambient oxygen partial pressures ($P_{\text{O}_2}^{\text{ext}} < 10^{-15}$ atm at 1100°C) Cr_2O_3 exhibited n-type semiconductor behavior and that Cr cations diffused interstitially; whereas at relatively higher ambient oxygen partial pressures ($P_{\text{O}_2}^{\text{ext}} > 10^{-10}$ atm at 1100°C) Cr vacancies were the dominant defects in Cr_2O_3 , which exhibited p-type semiconductor behavior.

The oxygen partial pressure dependence of the rate by which Cr_2O_3 grows is the key to determine the mechanism by which Cr_2O_3 grows. For this purpose, here, we provide a summary of Wagner's treatment of surface oxidation [28], which relates the oxidation rate constant to the oxygen partial pressure and the diffusion coefficient of the dominant charge carriers in Cr_2O_3 .

Deriving the oxidation rate constant of p-type Cr_2O_3 requires knowledge of the point defect balance equation for triple charged Cr vacancies in Cr_2O_3 :

$$\text{O}_2(\text{g}) = \frac{4}{3}V_{\text{Cr}}''' + 4h' + \frac{2}{3}\text{O}_0^{\text{X}}, \quad (1)$$

where O_0^{X} designates the normal lattice positions of O in the Cr_2O_3 lattice, h' is electron holes and V_{Cr}''' represents the triple charged Cr vacancies. The rate at which Cr_2O_3 grows is:

$$k_S^{\text{Cr}_2\text{O}_3} = -\frac{3}{4} \int_{P_{\text{O}_2}^{\text{ext}}}^{P_{\text{O}_2}^{\text{int}}} D_{V_{\text{Cr}}'''}^{\circ, \text{Cr}_2\text{O}_3} C_{V_{\text{Cr}}'''} d \ln P_{\text{O}_2} [\text{cm}^2/\text{s}], \quad (2)$$

where $k_S^{\text{Cr}_2\text{O}_3}$ is the oxidation rate constant, $D_{V_{\text{Cr}}'''}^{\circ, \text{Cr}_2\text{O}_3}$ is the diffusion coefficient of Cr vacancies at $P_{\text{O}_2} = 1$ atm, $C_{V_{\text{Cr}}'''}$ is the concentration of triply charged Cr vacancies, and $P_{\text{O}_2}^{\text{int}}$ and $P_{\text{O}_2}^{\text{ext}}$ represent the oxygen partial pressures at the metal - oxide and oxide - gas interfaces,

respectively. Based on the equilibrium reaction constant of Eq. (1) and assuming charge neutrality across the Cr_2O_3 scale ($C_{h\cdot} = 3 \times C_{V_{\text{Cr}}}'''$, where $C_{h\cdot}$ is the concentration of electron holes), $C_{V_{\text{Cr}}}'''$ is proportional to $P_{\text{O}_2}^{3/16}$. Integrating Eq. (2) yields the oxygen partial pressure dependence of the oxidation rate constant:

$$k_S^{\text{Cr}_2\text{O}_3} = 4 \times D_{V_{\text{Cr}}}^{\circ, \text{Cr}_2\text{O}_3} \times \left[(P_{\text{O}_2}^{\text{ext}})^{\frac{3}{16}} - (P_{\text{O}_2}^{\text{int}})^{\frac{3}{16}} \right]. \quad (3)$$

On the other hand, the oxidation rate constant of n-type Cr_2O_3 can be derived by writing the point defect balance equation for triply charged Cr interstitials in Cr_2O_3 :

$$\frac{3}{2} \text{O}_0^{\text{X}} + \text{Cr}_{\text{Cr}}^{\text{X}} = \text{Cr}_i''' + 3e' + \frac{3}{4} \text{O}_2(\text{g}), \quad (4)$$

where $\text{Cr}_{\text{Cr}}^{\text{X}}$ designate the normal lattice positions of Cr in the Cr_2O_3 lattice, e' represents electrons and Cr_i''' represents the triply charged Cr interstitials. In this case, the oxygen partial pressure dependence of the oxidation rate constant is:

$$k_S^{\text{Cr}_2\text{O}_3} = 4 \times D_{\text{Cr}_i}^{\circ, \text{Cr}_2\text{O}_3} \times \left[(P_{\text{O}_2}^{\text{int}})^{-\frac{3}{16}} - (P_{\text{O}_2}^{\text{ext}})^{-\frac{3}{16}} \right], \quad (5)$$

where $D_{\text{Cr}_i}^{\circ, \text{Cr}_2\text{O}_3}$ is the diffusion coefficient of Cr interstitials at $P_{\text{O}_2} = 1$ atm.

Note that Eqs. (3) and (5) also enable prediction of the oxidation rate constants using the independently measured lattice diffusion coefficients of Cr in Cr_2O_3 . However, recent Secondary ion mass spectroscopy (SIMS) measurements indicated that the measured lattice diffusion coefficients of Cr in Cr_2O_3 appear to be too slow to sustain the experimentally measured oxidation rate constants [25,29,30]. This suggests that grain boundary diffusion of Cr cations controls the growth of polycrystalline Cr_2O_3 .

To determine the mechanism by which Cr_2O_3 scale grows on Alloy 617, first, the growth of Cr_2O_3 is characterized to verify that Cr cations are the primary charge carriers in Cr_2O_3 . Next, the defect structure of Cr_2O_3 growing on Alloy 617 in He - CO - CO_2 environments is identified

by examining the oxygen partial pressure dependence of the Cr oxidation rate constants determined in this study in comparison with those reported for similar alloys in a wide oxygen partial pressure range. If the vacancy diffusion of Cr is the dominant mechanism for Cr_2O_3 growth, then the oxidation rate constant should increase with increasing ambient oxygen partial pressure according to Eq. (3). However, if the oxidation rate constant shows a slightly negative dependence on the ambient oxygen partial pressure, then the interstitial diffusion of Cr cations is the dominant mechanism for Cr_2O_3 growth, as given by Eq. (5). Finally, the diffusion coefficients of Cr in Cr_2O_3 are calculated based on the measured oxidation rate constants in Env. 9 and Env. 1320 using either Eq. (3) or Eq. (5). If the calculated diffusion coefficients are significantly greater than those reported in the literature based on independent SIMS measurements, then it can be deduced that the grain boundary diffusion of Cr plays a role in the Cr_2O_3 growth kinetics.

4. Results and Discussion

Fig. 1 shows that the surface Cr oxidation rate constants, $k_s^{\text{Cr}_2\text{O}_3}$, of Alloy 617 in Env. 9 and Env. 1320 at 750 - 850 °C (reported previously in [31]) agreed reasonably well with those reported for similar Ni-Cr based superalloys in low oxygen partial pressure H_2 - H_2O [32] and impure helium [33–35] environments. The slopes of the linear fit to the data presented in Fig.1 yielded the activation energy values for surface Cr oxidation of Alloy 617 to be 169.0 ± 13.2 kJ/mol in Env. 9 and 234.4 ± 8.9 kJ/mol in Env. 1320. These values were in close agreement with the range of activation energies reported for the alloys exposed to the H_2 - H_2O environment at 700 - 1100 °C (148 - 240 kJ/mol [32]).

Note that, at temperatures below 900 °C, the same Ni - Cr based alloys exhibited noticeably lower rate constants in air ($P_{\text{O}_2} = 0.21$ atm) [36] than those in low oxygen partial

pressure environments. As such, the activation energy values for surface Cr oxidation of these alloys were much higher in air (314 - 340 kJ/mol [32,36]). This suggests that a different mechanism controls the surface Cr oxidation of Alloy 617 and similar Ni - Cr based superalloys in low oxygen partial pressure environments than that in high oxygen partial pressure environments.

The first step to determine the surface Cr oxidation mechanism of Alloy 617 in He - CO - CO₂ environments, was to identify the direction of growth of Cr₂O₃ by microstructure characterization. Fig. 2 shows a representative microstructure of an Alloy 617 sample exposed to Env. 9 at 800 °C for 225h. The bright phase in the sub-surface region of the microstructure is an M₆C type carbide, which presumably remained stable throughout the exposure. Smooth top surface of the carbide precipitate indicated that it was present at the surface of the as-polished sample. Considering that the carbide precipitate marks the original alloy surface, the growth direction of the surface Cr₂O₃ film is mainly outward. No significant cracking or blistering of the Cr₂O₃ film was observed; therefore nucleation of new oxide particles within the existing oxide film due to possible inward oxygen diffusion, as suggested by Caplan and Sproule [15], can be ruled out. Similar observations were made by Guillou et al. [35] for surface Cr oxidation of Alloy 230, confirming that Cr₂O₃ grows on the surface of Alloy 617 by outward diffusion of chromium cations.

Next, the ambient oxygen partial pressure dependence of the surface Cr oxidation rate constants of Alloy 617 in Env. 9 and Env. 1320 was investigated in comparison with those reported for similar Ni - Cr based alloys in H₂ - H₂O, impure helium and air at 850 °C, because the data presented in Fig. 1 for a given environment exhibited the least scatter at this temperature. Fig. 3 shows that the oxidation rate constants of Alloy 617 and the rest of the Ni -

Cr based superalloys exhibited slightly negative ambient oxygen partial pressure dependence over a wide partial pressure range of 3.6×10^{-24} - 0.21 atm. This trend is in disagreement with that predicted by Eq. (3) indicating that Cr_2O_3 did not exhibit p-type behavior.

Chapovaloff et al. [33,34] took a different approach and investigated the dependence of the surface Cr oxidation rate constants of Alloy 617 on the partial pressure of water vapor, the main oxidizing species in their complex impure helium composition. They reported that the long-term surface oxidation rate of Alloy 617 was also independent of the ambient water vapor pressure. Therefore, Cr_2O_3 growth on the Ni-based superalloys in low oxygen partial pressure environments by vacancy diffusion of Cr can be ruled out. This leaves Cr interstitials as the primary mobile species in Cr_2O_3 growing on Alloy 617 in He - CO - CO_2 environments.

The self-diffusion coefficients of Cr interstitials in Cr_2O_3 growing on Alloy 617 ($D_{\text{Cr,i}}^{\text{Cr}_2\text{O}_3, \text{Alloy 617}}$) in Env. 9 and in Env. 1320, which were related to $D_{\text{Cr,i}}^{\circ, \text{Cr}_2\text{O}_3}$ in Eq. (5) as follows:

$$D_{\text{Cr,i}}^{\text{Cr}_2\text{O}_3, \text{Alloy 617}} = D_{\text{Cr,i}}^{\circ, \text{Cr}_2\text{O}_3} \times \left[(P_{\text{O}_2}^{\text{int}})^{-\frac{3}{16}} - (P_{\text{O}_2}^{\text{ext}})^{-\frac{3}{16}} \right]. \quad (6)$$

$P_{\text{O}_2}^{\text{ext}}$ values for Env. 9 and Env. 1320 were calculated according to the following reaction:

where $P_{\text{O}_2}^{\text{ext}}$ is equal to:

$$P_{\text{O}_2}^{\text{ext}} = (P_{\text{CO}_2} \times K_{(7)} / P_{\text{CO}})^2. \quad (8)$$

$K_{(7)}$ is the equilibrium constant of the reaction given in Eq. (7) and can be calculated as follows:

$$K_{(7)} = \exp(-\Delta G_{(7)}^{\circ} / RT), \quad (9)$$

where $\Delta G_{(7)}^{\circ f}$ is the standard Gibbs free energy of the reaction given in Eq. (7) and equal to $-282400-86.8 T$ [J/mole O_2] [37]. Table 3 summarizes the $P_{O_2}^{ext}$ values calculated for Env. 9 and Env. 1320 in the temperature range of 750 - 850 °C using Eq. (8).

We previously reported that the oxygen partial pressures attained at the alloy - oxide interfaces ($P_{O_2}^{int}$) of Alloy 617 oxidized in Env. 9 and Env. 1320 were greater than the dissociation oxygen partial pressure of Cr_2O_3 due to the gas permeability of the surface Cr_2O_3 film [14]. To determine the exact values of $P_{O_2}^{int}$ in the temperature range of 750 - 850 °C, Sievert's constants ($S_O^{Alloy\ 617}$) relating the oxygen concentration in Alloy 617 to the oxygen partial pressure at the alloy surface or at the alloy - Cr_2O_3 interfaces ($N_O^{Alloy\ 617}$) were determined using the following equation:

$$N_O^{Alloy\ 617} [at. fr.] = S_O^{Alloy\ 617} \times \sqrt{P_{O_2}^{int} [atm]}. \quad (10)$$

Sievert's constant at 850 °C was calculated to be 39.0 at.fr./ $\sqrt{atm}$ by inserting the values of dissolved oxygen concentration at the surface of Alloy 617 (5.57×10^{-12} at. fr.) and the dissociation oxygen partial pressure of Cr_2O_3 (2.0×10^{-26} atm, $\Delta G_{Cr/Cr_2O_3}^{\circ f} = -740635-163.5 T$ [J/mole O_2] [37]) maintained in a Cr - Cr_2O_3 Rhines pack exposure [14] in Eq. (10). The values of $S_O^{Alloy\ 617}$ at 800 and 750 °C were calculated as 96.6 at. fr./ $\sqrt{atm}$ and 261.6 at. fr./ $\sqrt{atm}$, respectively, by extrapolating the dissolved oxygen concentration values maintained in the Rhines pack exposure at 850 °C to 800 and 750 °C using the activation energy of 94.4 kJ/mol for oxygen dissolution in Alloy 617 [31]. After determining Sievert's constants in the temperature range of 750 - 850 °C, the values of the oxygen concentrations maintained at the alloy - Cr_2O_3

interfaces of Alloy 617 in Env. 9 and Env. 1320 [31] were inserted in Eq. (10) to obtain the $P_{O_2}^{int}$ values reported in Table 3.

Fig. 4 shows the values of $D_{Cr,i}^{Cr_2O_3, Alloy\ 617}$ determined based on the measured surface oxidation rates of Alloy 617 in Env. 9 and Env. 1320 in comparison with the lattice, grain boundary and effective diffusion coefficients of Cr in Cr_2O_3 reported in the literature using SIMS and radiotracer techniques. Note that the $D_{Cr,i}^{Cr_2O_3, Alloy\ 617}$ values are greater than the lattice diffusion coefficients of Cr in polycrystalline Cr_2O_3 measured by Tsai et al. [25] (5.9×10^{-18} cm²/s at 800 °C and 2×10^{-17} at 900 °C) and by Lobnig et al. [30] (4×10^{-16} - 1×10^{-14} at 900 °C). On the other hand, the $D_{Cr,i}^{Cr_2O_3, Alloy\ 617}$ values appear to be in very good agreement with the effective diffusion coefficients of Cr in Cr_2O_3 reported by Tsai et al. [25] both at 800 and 900 °C. This indicates that the growth kinetics of Cr_2O_3 on Alloy 617 is facilitated by the grain boundary diffusion of Cr cations in addition to the lattice diffusion of Cr interstitials in Cr_2O_3 . This can further be supported by considering that the activation energy values for surface Cr oxidation of Alloy 617 in Env. 9 (169.0 ± 13.2 kJ/mol) and in Env. 1320 (234.4 ± 8.9 kJ/mol) are lower than those reported by Kofstad and Lillerud [16–20] for the interstitial diffusion of Cr in Cr_2O_3 lattice (230 - 245 kJ/mol).

5. Conclusions

This work established that surface Cr oxidation of Alloy 617 in He - CO - CO₂ environments is primarily controlled by the outward diffusion of Cr cations. The oxygen partial pressure dependence of the Cr oxidation rates of Alloy 617 in Env. 9 and Env.1320 and that of similar Ni - Cr alloys in low oxygen partial pressure environments are consistent with the n-type behavior of Cr_2O_3 scale in which Cr interstitials are the predominant mobile species. The diffusion coefficients of Cr in Cr_2O_3 calculated based on the surface oxidation rate constants of

Alloy 617 in Env. 9 and Env.1320 are at least an order of magnitude faster than those reported in the literature, indicating that grain boundary diffusion of Cr cations plays a role in the surface Cr oxidation kinetics of Alloy 617.

Acknowledgements

This research was supported by the DOE Office of Nuclear Energy's Nuclear Energy University Programs under award 00087993. The authors would like to thank Special Metals Corporation, Inc. (Huntington, WV) for providing Alloy 617 plate used in this study.

Table 1. Chemical composition of Alloy 617 (heat number: XXX2323UK) as reported by Special Metals Inc. in wt.%.

element	Ni	Cr	Co	Mo	Al	Ti	Fe	Si	C	Mn, Cu
Wt. %	54.6	21.8	11.5	9.7	1.1	0.3	0.8	0.1	0.1	Trace

Table 2. Compositions of the selected He - CO - CO₂ environments for exposures conducted at 750 - 850 °C.

	Env. 9	Env. 1320
P_{CO} (mol ppm)	13.5	1980
P_{CO_2} (mol ppm)	1.5	1.5
P_{CO}/P_{CO_2} ratio (designation)	9	1320

Table 3. Oxygen partial pressures attained at the alloy - oxide and oxide - gas interfaces in Env. 9 and Env. 1320 at 750 - 850 °C.

Temperature (°C)	Env. 9		Env. 1320	
	$P_{O_2}^{ext}$ (atm)	$P_{O_2}^{int}$ (atm)	$P_{O_2}^{ext}$ (atm)	$P_{O_2}^{int}$ (atm)
850	7.75×10^{-20}	2.02×10^{-25}	3.60×10^{-24}	1.63×10^{-25}
800	4.62×10^{-21}	1.28×10^{-26}	2.15×10^{-25}	1.04×10^{-26}
750	2.09×10^{-22}	6.21×10^{-28}	9.73×10^{-27}	5.04×10^{-28}

Fig. 1. Surface Cr oxidation rate constants of Alloy 617 in Env. 9 and Env.1320 at 750 - 850 °C in comparison with those reported for Alloy 617 in He - CO - H₂ - H₂O [33,34] at 850 °C; for Haynes 230 in He - H₂ - H₂O at 850 °C (the error bar in green represents the standard deviation of the multiple oxidation rate constants reported) [35]; for IN625, IN718, Hastelloy X and Haynes 230 in H₂ - H₂O ($P_{O_2} \cong 10^{-23} - 10^{-17}$ atm) [32] and in air ($P_{O_2} = 0.21$ atm) [36] in the temperature range of 700 - 1100 °C².

² The reference data used in Fig.1 were originally reported as weight gain rate constants (k'_W) similar to the following relationship: $[\Delta W/A]^2 = k'_W \times t$, where $\Delta W/A$ is the specific weight gain. For direct comparison with the surface oxidation rate constants determined in this study, the reference weight gain rate constants are divided by 2 and then converted into surface Cr oxidation rate constants using the following equation: $k_s^{Cr_2O_3} = (V_{Cr_2O_3}/482 \times k_W)$, where $V_{Cr_2O_3}$ is the molar volume of Cr₂O₃ and $k_W = k'_W/2$.

Fig. 2. A representative backscattered electron image of an Alloy 617 sample exposed to Env. 9 and at 800 °C for 225h. The flat top surface of the M_6C type carbide (bright phase) designate the original alloy surface marked with red dashed lines in the micrograph.

Fig. 3. The ambient oxygen partial pressure dependence of the surface Cr oxidation rate constants of Alloy 617 in Env. 9 and Env. 1320; Haynes 230 in He - H_2 - H_2O [35]; IN625, IN718, Hastelloy X and Haynes 230 in H_2 - H_2O [32] and in air [36] at 850 °C.

Fig. 4. Comparison of the $D_{Cr,i}^{Cr_2O_3, Alloy 617}$ values determined based on the measured surface oxidation rates of Alloy 617 in Env. 9 and Env. 1320 with the lattice, grain boundary and effective diffusion coefficients of Cr in Cr_2O_3 reported in the literature using SIMS and radiotracer techniques. The legend has the following format: [parameter] - [environment] - [the substrate material that Cr_2O_3 is growing on] - [Citation]. Open and closed symbols designate the lattice and grain boundary diffusion coefficients of Cr in Cr_2O_3 , respectively.

References

- [1] R.E. Mizia, Next Generation Nuclear Plant Intermediate Heat Exchanger Acquisition Strategy; INL/EXT-08-14054, 2008.
- [2] J.K. Wright, Next Generation Nuclear Plant Steam Generator and Intermediate Heat Exchanger Materials Research and Development Plan; INL/EXT-08-14107, 2010.
- [3] C. Cabet, A. Terlain, P. Lett, L. Guétaz, J.-M. Gentzbittel, High temperature corrosion of structural materials under gas-cooled reactor helium, *Mater. Corros.* 57 (2006) 147–153.
- [4] C. Cabet, J. Chapovaloff, F. Rouillard, G. Girardin, D. Kaczorowski, K. Wolski, M. Pijolat, High temperature reactivity of two chromium-containing alloys in impure helium, *J. Nucl. Mater.* 375 (2008) 173–184.
- [5] R. Wright, J. Wright, C. Cabet, Material Performance in Helium-Cooled Systems, in: *Compr. Nucl. Mater.*, Elsevier Inc., 2012: pp. 251–277.
- [6] K. Natesan, A. Purohit, S.W. Tam, Materials Behavior in HTGR Environments; NUREG/CR-6824, ANL-02/37, Argonne, IL, 2003.
- [7] J.K. Wright, L.J. Carroll, C. Cabet, T.M. Lillo, J.K. Benz, J.A. Simpson, W.R. Lloyd, J.A. Chapman, R.N. Wright, Characterization of elevated temperature properties of heat exchanger and steam generator alloys, *Nucl. Eng. Des.* 251 (2012) 252–260.
- [8] R.N. Wright, Summary of Studies of Aging and Environmental Effects on Inconel 617 and Haynes 230; INL/EXT-06-11750, 2006.
- [9] H. Christ, D. Schwanke, T. Uihlein, Mechanisms of high-temperature corrosion in helium containing small amounts of impurities. I. Theoretical and experimental characterization of the gas phase, *Oxid. Met.* 30 (1988) 1–26.
- [10] H. Christ, U. Künecke, K. Meyer, H. Sockel, Mechanisms of high-temperature corrosion in helium containing small amounts of impurities. II. Corrosion of the nickel-base alloy inconel 617, *Oxid. Met.* 30 (1988) 27–51.
- [11] W. Quadackers, H. Schuster, Thermodynamic and kinetic aspects of the corrosion of high-temperature alloys in high-temperature gas-cooled reactor helium, *Nucl. Technol.* 66 (1984) 383–391.
- [12] D. Kumar, R.R. Adharapurapu, T.M. Pollock, G.S. Was, High-temperature oxidation of Alloy 617 in helium containing part-per-million levels of CO and CO₂ as impurities, *Metall. Mater. Trans. A.* 42 (2011) 1245–1265.
- [13] R.R. Adharapurapu, D. Kumar, J. Zhu, T.M. Pollock, Carburization of W- and Re-rich Ni-based alloys in impure helium at 1000°C, *Corros. Sci.* 53 (2011) 388–398.

- [14] G. Gulsoy, G.S. Was, Mechanism of internal oxidation of Alloy 617 in He-CO-CO₂ environments at 850 °C, Metall. Mater. Trans. A. in press.
- [15] D. Caplan, G.I. Sproule, Effect of oxide grain structure on the high-temperature oxidation of Cr, Oxid. Met. 9 (1975) 459–472.
- [16] P. Kofstad, K.P. Lillerud, On high temperature oxidation of chromium: II. Properties of formula and the oxidation mechanism of chromium, J. Electrochem. Soc. 127 (1980) 2410–2419.
- [17] K.P. Lillerud, P. Kofstad, On high temperature oxidation of chromium I. Oxidation of annealed, thermally etched chromium at 800°–1100° C, J. Electrochem. Soc. 127 (1980) 2397–2410.
- [18] P. Kofstad, K. Lillerud, Chromium transport through Cr₂O₃ scales I. On lattice diffusion of chromium, Oxid. Met. 17 (1982) 177–194.
- [19] K. Lillerud, P. Kofstad, Reoxidation of chromium with densified Cr₂O₃ Scales, Oxid. Met. 17 (1982) 127–139.
- [20] P. Kofstad, High Temperature Corrosion, Elsevier Applied Science, 1988.
- [21] C. Giggins, F. Pettit, The oxidation of TD NiC (Ni-20Cr-2 vol pct ThO₂) between 900° and 1200° C, Metall. Trans. 2 (1971) 1071–1078.
- [22] C.M. Cotell, G.J. Yurek, R.J. Hussey, D.F. Mitchell, M.J. Graham, The influence of grain-boundary segregation of Y in Cr₂O₃ on the oxidation of Cr metal, Oxid. Met. 34 (1990) 173–200.
- [23] H. Hindam, D. Whittle, Microstructure, adhesion and growth kinetics of protective scales on metals and alloys, Oxid. Met. 18 (1982) 245–284.
- [24] H. Hindam, D.P. Whittle, Evidence for the Growth Mechanism of Cr₂O₃ at Low Oxygen Potentials, J. Electrochem. Soc. 130 (1983) 1519–1523.
- [25] S. Tsai, A. Huntz, C. Dolin, Growth mechanism of Cr₂O₃ scales: oxygen and chromium diffusion, oxidation kinetics and effect of yttrium, Mater. Sci. Eng. A. 212 (1996) 6–13.
- [26] J. Park, K. Natesan, Electronic transport in thermally grown Cr₂O₃, Oxid. Met. 33 (1990) 31–54.
- [27] A. Atkinson, T. R., Transport in Nonstoichiometric Oxides, in: G. Simkovich, V.S. Stubican (Eds.), NATO ASI Ser. B, 1984: p. 285.
- [28] C. Wagner, Beitrag zur theorie des anlaufvorgangs, Zeitschrift Für Phys. Chemie. 21 (1933) 25–41.

- [29] A. Sabioni, A. Huntz, F. Millot, C. Monty, Self-diffusion in Cr_2O_3 III. Chromium and oxygen grain-boundary diffusion in polycrystals, *Philos. Mag. A.* 66 (1992) 361–374.
- [30] R. Lobnig, H. Schmidt, K. Hennesen, H. Grabke, Diffusion of cations in chromia layers grown on iron-base alloys, *Oxid. Met.* 37 (1992) 81–93.
- [31] G. Gulsoy, G.S. Was, Enhanced oxygen diffusion within the internal oxidation zone of Alloy 617 in controlled impurity helium environments at 750 - 850 °C, *Metall. Mater. Trans. A.* submitted.
- [32] D.M. England, A. V. Virkar, Oxidation kinetics of some Nickel-based superalloy foils in humidified hydrogen and electronic resistance of the oxide scale formed Part II, *J. Electrochem. Soc.* 148 (2001) A330–338.
- [33] J. Chapovaloff, F. Rouillard, P. Combrade, M. Pijolat, K. Wolski, Assessing the kinetics of high temperature oxidation of Inconel 617 in a dedicated HTR impure helium facility coupling thermogravimetry and gas phase chromatography, *J. Nucl. Mater.* 441 (2013) 293–300.
- [34] J. Chapovaloff, F. Rouillard, K. Wolski, M. Pijolat, Kinetics and mechanism of reaction between water vapor, carbon monoxide and a chromia-forming nickel base alloy, *Corros. Sci.* 69 (2013) 31–42.
- [35] S. Guillou, C. Cabet, C. Desgranges, L. Marchetti, Y. Wouters, Influence of hydrogen and water vapour on the kinetics of chromium oxide growth at high temperature, *Oxid. Met.* 76 (2011) 193–214.
- [36] D. England, A. Virkar, Oxidation kinetics of some Nickel-based superalloy foils and electronic resistance of the oxide scale formed in air Part I, *J. Electrochem. Soc.* 146 (1999) 3196–3202.
- [37] O. Kubaschewski, C.B. Alcock, *Materials thermochemistry*, 6th ed., Oxford: Pergamon Press, 1993.