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Oxidation characteristics of the electron beam surface-treated Alloy 617 in high temperature helium environments

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ABSTRACT

The oxidation characteristics of the electron beam surface-treated Alloy 617, which has an Al-rich surface layer, were evaluated in high temperature helium environments. Isothermal oxidation tests were performed in helium (99.999% purity) and VHTR-helium (helium of prototypical VHTR chemistry containing impurities like CO, CO_2, CH_4, and H_2) environments at 900 °C for up to 1000 h. The surface-treated Alloy 617 showed an initial transient oxidation stage followed by the steady-state oxidation in all test environments. In addition, the steady-state oxidation kinetics of the surface-treated Alloy 617 was 2-order of magnitude lower than that of the as-received Alloy 617 in both helium environments as well as in air. The improvement in oxidation resistance was primarily due to the formation of the protective Al_2O_3 layer on the surface. The weight gain was larger in the order of air, helium, and VHTR-helium, while the parabolic rate constants (k_p) at steady-state were similar for all test environments. In both helium environments, the oxide structure consisted of the outer transition Al_2O_3 with a small amount of Cr_2O_3 and inner columnar structured Al_2O_3 without an internal oxide. In the VHTR-helium environment, where the impurities were added to helium, the initial transient oxidation increased but the steady state kinetics was not affected.

1. Introduction

One of the generation-IV reactors, a very high temperature gas-cooled reactor (VHTR), is expected to be operated at about 900 °C with a pressurized helium coolant to achieve high efficiency [1]. It was reported that during normal operation, the coolant helium would be contaminated with impurities such as CO, CO_2, CH_4, H_2, and H_2O ranging from a few to hundreds of microbar because of: (1) the reaction of hot graphite core and in-leaked air and (2) the degassing of components at high temperatures [2,3]. To survive the harsh operating conditions of the VHTR Ni-base superalloy, a solid solution hardened Alloy 617, is considered the most promising structural material because of its high temperature strength and oxidation resistance. Several studies have been conducted for Alloy 617 to investigate the high temperature oxidation behaviors in air [4,5], helium [4,5], and various impure helium environments [2,3,6–9]. In those studies, the external Cr_2O_3 layer and the internal Al_2O_3 oxides were developed in all testing conditions due primarily to the high Cr (22 wt.%) and low Al (~1 wt.%) contents of Alloy 617. However, the external Cr_2O_3 layer could be susceptible to volatility and spallation in helium environments at high temperatures [4,6,8] while the internal Al_2O_3 oxide could act as preferential sites for crack propagation under the tensile loading [4,9,10]. Therefore, the external Cr_2O_3 layer would not be sufficient to assure the long-term integrity of the components made of Alloy 617 and operated in the high temperature helium environments of the VHTR.

When Al_2O_3 is formed as an external layer, it is known to be more protective than Cr_2O_3 due to its highly stoichiometric structure and low oxide growth rate at high temperatures [11,12]. Previously, it has been reported that at least 4–5 wt.% Al is required to develop an external Al_2O_3 layer while lower amounts of Al would cause internal oxidation in the Ni–Cr–Al and Fe–Cr–Ni systems [12–14]. Consequently, various surface-treatment processes have been applied to promote the formation of an external Al_2O_3 layer by increasing the Al content in the surface region [15–17]. For example, authors have applied the electron beam (EB) surface-treatment process for Alloy 617 to make an Al-rich micro-alloying zone. The benefit of surface micro-alloying zone was demonstrated by an isothermal oxidation test in air at 900 °C [17]. However, in order to be assured of the benefit of using the surface-treated Alloy 617 for high temperature components like intermediate heat exchangers and hot gas ducts in VHTR, oxidation behaviors in an impurity-containing helium environment should be evaluated. Therefore, in this study, isothermal oxidation tests of the EB surface-treated Alloy 617 have been carried out in helium (99.999%

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purity) and impure helium of prototypical VHTR chemistry at 900 °C for up to 1000 h. The oxidation kinetics and characteristics of oxides in helium environments have been evaluated together with the effects of EB surface treatment on the oxidation behaviors.

2. Experimental

2.1. Materials and surface treatment

A previously developed EB surface-treatment technique [17] was applied to prepare the Al-rich micro-alloying region in the surface of Alloy 617. However, in this study, the Al content in the micro-alloying zone was increased from 4 to 5 wt.% to fully suppress the formation of Al_2O_3 islands below the outer oxide layer during the isothermal oxidation tests [17]. To prepare the EB surface treated specimens about 7 μm of high purity Al (99.999%) was pre-deposited on Alloy 617 plates (14 × 33 mm in length and width with 1 mm in thickness) by using a direct current Physical Vapor Deposition (PVD) for 2 h, and then a high energy electron beam was applied to the Al deposited substrates. As a result, Al was enriched to 4.4–5.6 wt.% within a depth of 50 μm of micro-alloying zone as shown in Fig. 1. The surface-treated Alloy 617 plates were cut to coupons of 12 mm in diameter, which were used for the high temperature oxidation test. A hole of 1.5 mm in diameter was drilled through the upper part of the specimen to hang it on an alumina rod.

2.2. Oxidation test and analysis

Table 1 shows the compositions of the helium (99.999% purity) and impure helium of prototypical VHTR chemistry (henceforth, designated as VHTR-helium). In the latter case, the impurity contents were similar to those used in the previous study [7] to simulate the helium coolant of the experimental gas-cooled reactors [2]. Also the oxygen partial pressures (P_{o_2}) of the test environments are shown in Table 1. In both helium environments, a trace amount of O_2 (0.62 ppm) and H_2O (0.68 ppm) were present. For the isothermal oxidation test in helium environments, a quartz vacuum furnace was used. Alumina spacers were placed between the test specimens on an alumina boat to prevent direct contact between the specimens as illustrated in Fig. 2. Before the test, the furnace was purged with the test gas three times to reduce the remaining impurities in the quartz tube. Then test gas was supplied by a mass flow controller (MFC) for 3 h at a constant gas flow rate of 200 cc/min while the furnace was heated up at 5 °C/min to the test temperature. The isothermal oxidation test was performed at 900 °C for up to 1000 h. After a certain exposure period the furnace was cooled to room temperature and a set of two specimens was removed from the alumina boat for analysis. The alumina boat

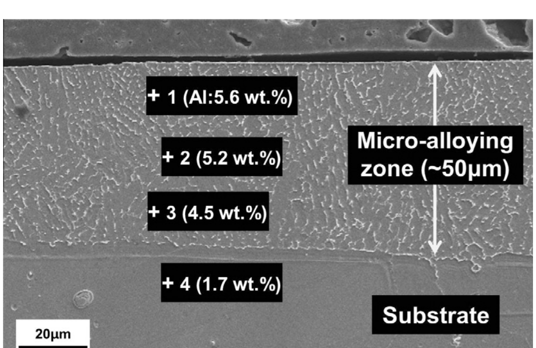

Fig. 1. Cross-sectional microstructure and Al content within micro-alloying zone after electron beam surface-treatment of Alloy 617.

Table 1
Chemical compositions (in μbar) and oxygen partial pressures (in atm) of the test environments.

	He	O_2	CO	CO_2	CH_4	H_2	H_2O	P_{o_2}
Air		2.0×10^5						$\sim 10^{-1}$ [a]
Helium	Bal.	0.62	–	–	–	–	0.68	$\sim 10^{-7}$
VHTR-helium	Bal.	0.62	50	10	20	500	0.68	$\sim 10^{-7}$

[a] Oxygen partial pressure in air was approximately 20 vol.% of O_2 in air.

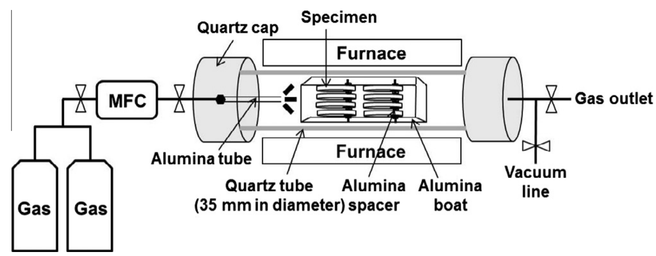

Fig. 2. A schematic diagram of a quartz vacuum furnace system.

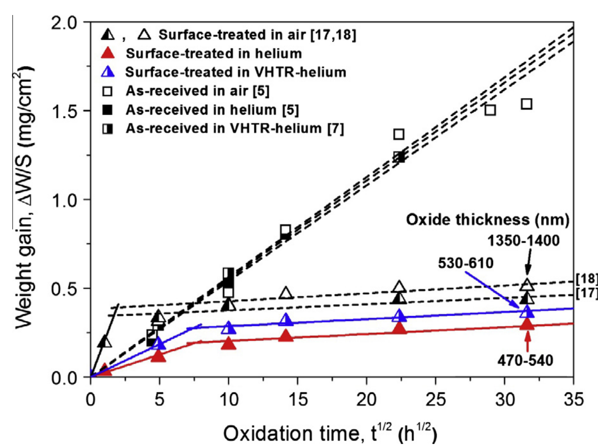

Fig. 3. Weight gain curve versus oxidation time for the surface-treated and as-received Alloy 617 oxidized in air, helium and VHTR-helium at 900 °C up to 1000 h.

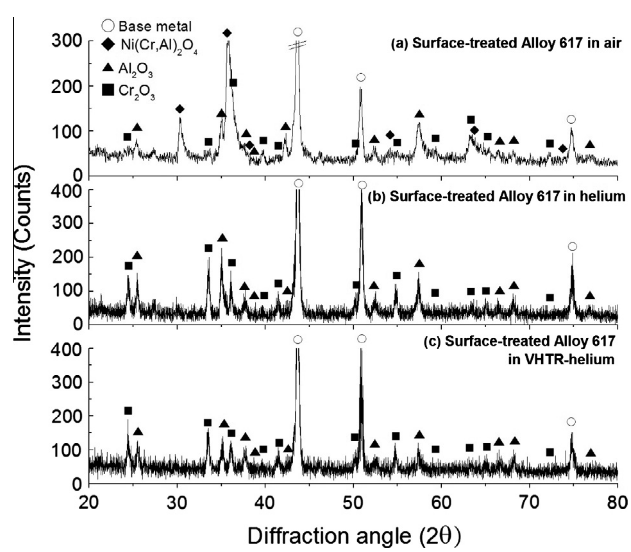

Fig. 4. XRD peaks of the surface-treated Alloy 617 oxidized in air, helium and VHTR-helium environments at 900 °C for 1000 h.