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Effect of Matrix Grain Size on the Oxidation and Carburization Resistance of Alloy 800HT in High Temperature CO_2 Environment

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1. Introduction

The generation IV sodium-cooled fast reactor (SFR) and high temperature gas-cooled reactor (HTGR) are conceptualized to utilize supercritical-CO_2 (S-CO_2) Brayton cycle for efficient power conversion [1]. The accelerated corrosion tests were performed at 650 °C and 20 MPa simulating S-CO_2 Brayton cycle in SFR [2, 3]. The preceding environment is both oxidizing and carburizing for the candidate Fe and Ni-based structural materials [4] which should withstand the demanding conditions for more than 20 years. The chromia forming heat resistant alloys, viz. Alloy 600, Alloy 690, and Alloy 800HT maintained better corrosion resistance due to stable and continuous chromia (Cr_2O_3) layer formation compared to stainless steels in S-CO_2 conditions [4, 5]. However, the existence of an amorphous carbon layer was identified beneath the chromia layer for those alloys, and additional Cr-rich $M_{23}C_6$ carbides in the matrix for Alloy 800HT.

On the other hand, the variation in matrix grain size has been known to either improve or deteriorate the oxidation resistance of several alloys depending upon their chemical compositions [6-9]. Meanwhile, the influence of grain size on the carburization resistance was not studied extensively in S-CO_2 environments. Thus, the objective of this study is to investigate the effect of matrix grain size on the oxidization and carburization behavior of Alloy 800HT in high temperature CO_2 environment. The tests were conducted at 650 °C and 0.1 MPa, since the effect of pressure on the carburization behavior was not significant [10].

2. Experimental Procedure

2.1 Specimen preparation

The chemical composition of Alloy 800HT is given in Table 1. Coupon type specimens with 12 mm diameter and 1 mm thickness were prepared. The specimens were solution annealed at 1120 and 1180 °C for 2 h in air followed by air cooling, in order to obtain variation in matrix grain size. The matrix grain size of solution annealed and as-received specimens were determined using Abrams three-circle intercept method described in ASTM E112-13 [11]. The specimen solution annealed at 1180 °C was found to be the coarsest (average grain size 180 μm) and the as-received specimen was the finest (average grain size 137 μm). The coupon type specimens were mechanically polished up to 1200 grit SiC paper and washed in ethanol before the oxidation test.

Table 1. Chemical composition of Alloy 800HT. (weight %)

Fe	Ni	Cr	C	Mo	Mn	Ti	Al	Si
42.3	33.9	21.0	0.06	0.2	0.9	0.55	0.48	0.4

2.2 Experimental methods

Oxidations tests are being carried out in high temperature CO_2 (99.999 % purity) at 650 °C and 0.1 MPa up to 500 h. A quartz vacuum furnace was used for the oxidation tests with a CO_2 flow rate of 150 cc/min. Simultaneously, oxidation tests are also conducted separately in air at 650 °C and 0.1 MPa to compare the oxidation rate in different oxygen partial pressures. The specimens oxidized for 24 h were characterized by XRD and SIMS. Additionally, the specimens will be characterized with weight gain measurement and cross-sectional SEM techniques.

3. Results

3.1 Oxide structure

Fig. 1 shows the XRD pattern of the as-received specimen exposed for 24 h in high temperature CO_2. The major diffraction peaks correspond to the austenite phase representing the base alloy while the minor peaks indicate presence of very thin chromia (Cr_2O_3) layer. In addition, weak peaks of $Mn_{1.5}Cr_{1.5}O_4$ and TiO_2 were also observed on the oxide layer formed in 24 h.

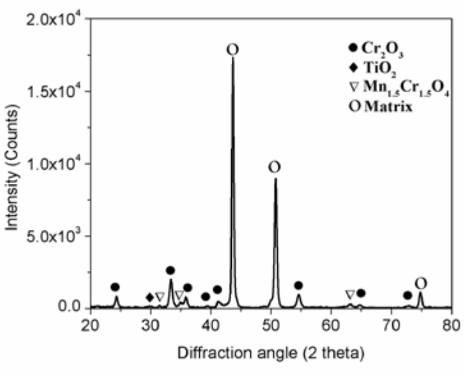

Fig. 1. XRD analysis of as-received Alloy 800HT exposed to CO_2 at 650 °C for 24 h.

3.2 SIMS analysis

Fig. 2 shows the SIMS depth profile for carbon diffusion into the matrix of the specimens exposed for 24 h. The presence of two carbon enriched regions corresponds to the amorphous carbon layer beneath the chromia layer and the Cr-rich $M_{23}C_6$ carbide developed deep into the matrix. The results were similar to that of Alloy 800HT exposed to S-CO_2 conditions, where the $M_{23}C_6$ carbides present was confirmed by the selected area diffraction (SAD) [4]. It is clear from Fig. 2 that thicker oxide and carburized layer was formed in as-received specimen. Also, the depth of oxidation and carburization was found to decrease with increase in matrix grain size, possibly due to decrease in short-circuit-diffusion paths in the matrix. This behavior is contradicting to the earlier reports for Cr-rich alloys in high temperature environments [6, 9]. However, current result is in agreement with the suggestion that the carbon penetrates the scale via oxide grain boundaries [12]. In our case, it is thought that the porous oxide structures formed from the fine grain specimens enhances the outward metal ion mobility (enhance oxidation) and carbon transportation through the oxide grain boundaries (enhance carburization).

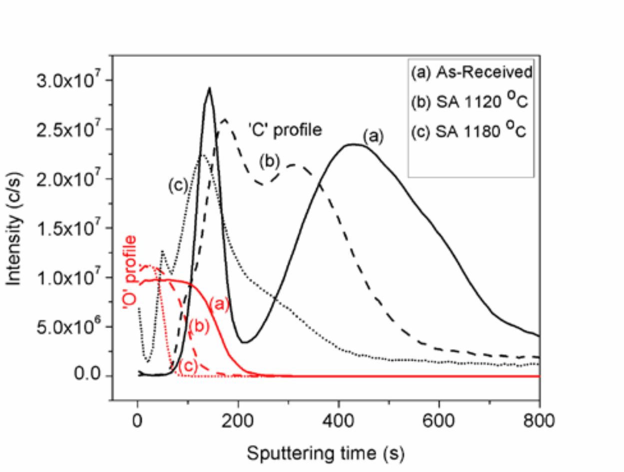

Fig. 2. SIMS depth profile of C and O for Alloy 800HT exposed to CO_2 at 650 °C for 24 h.

3.3 Cross-sectional SEM analysis

Fig. 3 shows the cross-sectional SEM images of the Alloy 800HT specimens exposed to CO_2 at 650 °C for 24 h. It is observed that the oxide thickness has been reduced on the solution annealed specimens. The average oxide thickness observed in as-received, solution annealed at 1120 and 1180 °C specimens are 188, 105 and 72 nm respectively.

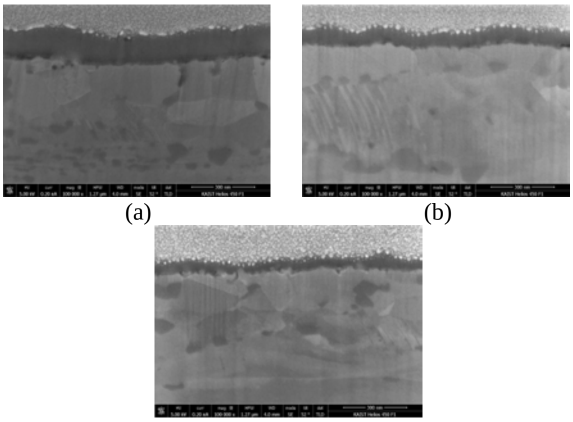
(a) (b)
(c)

Fig. 3. Cross-sectional SEM images of Alloy 800HT as-received (a), solution annealed at 1120 (b) and 1180 °C (c) specimens exposed to CO_2 at 650 °C for 24 h.

3.4 On-going test and analysis

The specimens are currently being exposed in high temperature CO_2 up to 500 h. Further, weight gain analysis is scheduled for determining the oxidation resistance along with SEM for the estimation of oxide thickness and Cr_2O_3 integrity. Both XRD and SIMS analysis will be performed for the long-term exposed specimens.

4. Conclusions

Alloy 800HT specimens with varying matrix grain size were obtained using solution annealing at 1120 and 1180 °C. When exposed to high temperature CO_2 environment, the oxidation and carburization rate was found to be decreasing with increasing the matrix grain size. The long term behavior on the influence of matrix grain size on the oxidation and carburization resistance is yet to be studied.

Acknowledgements

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