Oxidation Behavior of Surface-modified Stainless Steel 316LN in Supercritical-CO₂ Environment

Sung Hwan Kim*, Jin Woo Heo, Hyunmyung Kim, Changheui Jang
Dept. of Nuclear and Quantum Engineering, KAIST, Daejeon, Rep. of Korea
Corresponding Author: sciencetom@kaist.ac.kr

1. Introduction

The sodium-cooled fast reactor (SFR) is one of the Generation IV nuclear reactor designs under active research. Recently, in place of the conventional steam Rankine cycle, the supercritical-carbon dioxide (S-CO₂) Brayton cycle is being considered as the advanced energy conversion system for the SFR.

Application of the S-CO₂ Brayton cycle can improve the safety of the system, as the possibility of the explosive steam-liquid sodium reaction is eliminated. In addition, compared to other working fluids such as helium or nitrogen, S-CO₂ offers a higher efficiency at operating temperatures of advanced reactors above 550 °C. Moreover, the S-CO₂ cycle is expected to have a significantly smaller footprint compared to other power conversion cycles, resulting in a broader range of applications with lower capital costs [1].

Currently, stainless steel 316 is considered as the candidate structural material for the SFR. However, it has been previously reported that, in S-CO₂ environment, SS 316 displays poor oxidation behavior characterized with the high weight gain caused by spallation of Cr-rich oxide layer and subsequent formation of thick and porous Fe-rich oxide layer [2].

In comparison, it is well known that alumina (Al_2O_3) have superior oxidation and carburization resistance specifically at higher temperatures where α-Al_2O_3 may form. Thus, various surface modification techniques have been applied to mostly Ni-base alloys so that a protective and continuous Al-rich oxide layer forms on the surface, conferring superior oxidation and carburization resistance [3, 4].

In this study, SS 316LN was deposited with Al via physical vapor deposition (PVD) method followed by heat treatment processes to develop an Al-rich layer at the surface. The specimens are to be exposed to high temperature S-CO₂ environment to evaluate the oxidation and carburization resistance.

2. Experimental Procedure and Results

2.1 Materials and Analysis Methods

SS 316LN, a low carbon, nitrogen-enhanced version of SS 316 was used in this study. The chemical composition is as listed in Table 1. The material was fabricated into coupon-type specimens with 10 mm diameter and 1 mm thickness. The coupon specimens were mechanically polished on both sides with 1200 grit SiC paper and ultrasonically cleaned in ethanol prior to either surface modification processes or oxidation test.

Various analysis techniques such as weight change measurement, X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with energy dispersive spectroscope (EDS) will be utilized to analyze both the surface-modified and oxidized specimens.

Table I: Chemical composition of SS 316LN used in this study (in wt.%)

Fe	Cr	Ni	C	N	Mo	Mn	Si
Bal.	18.9	13.9	.03	0.2	2.8	1.9	0.6

2.2 Surface Modification Process

The specimens were loaded into a physical vapor deposition (PVD) equipment and coated with high purity Al (99.999 %) resulting in Al deposition of around 8 µm thickness on the surface. Then, for diffusion of the deposited Al into the substrate to develop an Al-rich layer at the surface, the Al-coated specimens were placed into a high-vacuum ($< 2.0 \times 10^{-6}$ torr) furnace and heat-treated at 600 °C for 0.5 h followed by 1000 °C for 0.5 h. The specimens were cooled in vacuum after the heat treatment process.

The resulting microstructure is expected to be similar to that of Al surface-modified SS 316L, which was conducted in the laboratory previously (shown in Fig. 1) [5]. It was found that as a result of the surface modification process, an Al-rich layer was formed at the surface of SS 316L substrate as shown in Fig. 2. The Al content in the Al-rich layer was found to be generally above 5 wt.%, which is considered sufficient for the formation of a continuous alumina (Al_2O_3) layer [5].

Meanwhile, during the exposure to S-CO₂ at the temperature range of 550–650 °C, α-Al_2O_3 is not expected to form. Rather, a transitional Al_2O_3 phase such as γ or θ phases may form. Thus, prior to exposure to S-CO₂ environment, some of the surface-modified specimens were pre-oxidized in pure He at 900 °C to form a continuous α-Al_2O_3 layer.
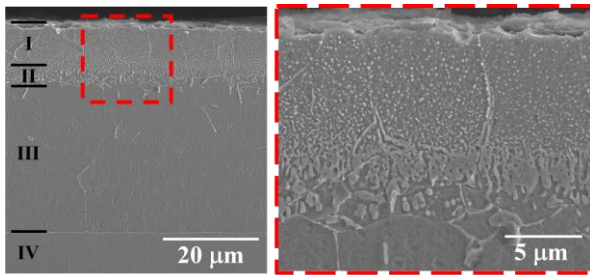
Fig. 1. Cross-sectional scanning electron microscope (SEM) micrograph of surface-modified SS 316L [5].
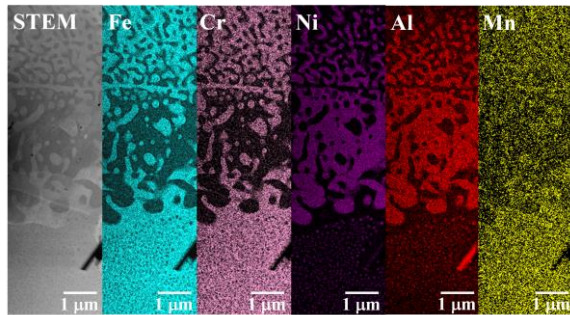

Fig. 2. Scanning transmission electron microscopy (STEM) and element mapping images of previously surface-modified SS 316L [5].

2.3 Exposure to S-CO₂ Environment

In this study, the specimens are being exposed to S-CO_2 (99.999 % purity) at 600 ºC and 20 MPa for 500 h. Comparisons among the as-received, surface-modified, and surface-modified+pre-oxidized specimens will be made in terms of oxidation behavior.

Previously, oxidation tests in He and CO_2 environments (1000 ºC 50 h) were conducted with surface-modified 316L specimens [5]. As can be seen in Fig. 3, surface-modified 316L specimens exhibited superior oxidation resistance compared to the as-received state, indicated by low weight gains. The result implies that the surface-modification process may confer superior oxidation resistance at a high temperature of 1000 ºC. However, the effect of surface-modification on oxidation behavior at a comparatively low temperature of 600 ºC in S-CO_2 environment is unclear, and will be analyzed in this study.
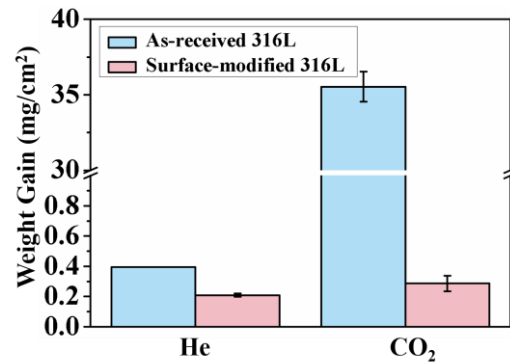

Fig. 3. Weight gains of as-received and surface-modified SS 316L after oxidation tests in CO_2 and He (1000 ºC 50 h).

3. Conclusions

Stainless steel 316LN was surface-modified to develop an Al-rich layer for improvement of oxidation behavior in S-CO_2 environment. As the test temperature of 600 ºC is not sufficiently high for the formation of protective α-Al_2O_3 formation, pre-oxidation of surface-modified SS 316LN was conducted. The oxidation behavior in S-CO_2 at 600 ºC and 20 MPa for 500 h of the specimens in the three states (as-received, surface-modified, and pre-oxidized) will be discussed.

Acknowledgements

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