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Corrosion and carburization behavior of chromia-forming heat resistant alloys in a high-temperature supercritical-carbon dioxide environment

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Corrosion and carburization behavior of chromia-forming heat resistant alloys in high-temperature supercritical-CO_2 were investigated. For all alloys, a thin and continuous chromia (Cr_2O_3) layer was formed on the surface, while the existence of an amorphous carbon layer was identified at the chromia/matrix interface. Below the amorphous C layer, Cr-rich $M_{23}C_6$ carbides were extensively formed in Alloy 800HT but not in Alloy 600 or Alloy 690. The carburization resistance was dependent on whether the matrix is Fe-based or Ni-based. The existence of the carburized region with Cr-rich $M_{23}C_6$ carbides in Alloy 800HT contributed to additional loss of ductility.

1. Introduction

The supercritical-carbon dioxide (S-CO_2) Brayton cycle has been considered one of the promising alternatives to the conventional steam Rankine cycle for the sodium-cooled fast reactor (SFR) and other energy conversion applications [1–3]. By applying the S-CO_2 cycle to the SFR, the inherent safety could be improved by alleviating the concern of an explosive reaction between high-temperature steam and liquid sodium [4]. Moreover, compared to other Brayton cycles that use helium or nitrogen, an increase in thermal efficiency of the system could be achieved at the SFR operating temperature of 500–550 °C [2,5]. Meanwhile, from the structural material point of view, the compatibility of candidate materials in the S-CO_2 environment should be evaluated to assure the long-term integrity of the components in the power conversion system, including the compact-type intermediate heat exchanger (IHX). High-temperature corrosion of IHX materials is one of the important factors to be properly assessed because excessive corrosion may threaten the structural integrity and deteriorate the heat transfer capability of the IHX.

Corrosion behavior of several candidate materials in high-temperature S-CO_2 (or high-pressure CO_2) has been investigated at various temperatures (550–750 °C) and pressures (20–25 MPa) for up to 8000 h [6–16]. According to the previous results, for Fe-based austenitic alloys, the corrosion resistance was strongly dependent on Cr content, exposure temperature and time in S-CO_2 environments [7,9,13]. Also, the carburization of some Fe-based alloys was observed at the Fe-rich and Cr-rich oxide layers/matrix interface and underneath the oxide layers during S-CO_2 exposure at 550–650 °C [6,7,13]. Meanwhile, Ni-based alloys generally showed superior corrosion resistance with a small weight gain benefited from the formation of a stable and protective Cr-rich oxide layer [9,15]. However, it has been reported that Ni-based alloys are susceptible to carburization in high-temperature carbon-containing environments over 850 °C despite the existence of the Cr-rich oxide layer [17–19]. Nevertheless, the carburization behavior of chromia-forming heat resistant alloys and their effects on the mechanical properties have not yet been properly investigated.

In this study, for several chromia-forming heat resistant alloys such as Alloy 800HT, Alloy 600 and Alloy 690, the corrosion and carburization behavior in the SFR-relevant S-CO_2 environment were investigated by exposing the alloys at 550, 600, and 650 °C (20 MPa) for 1000 h. The weight gain was measured to compare the corrosion resistance of the alloys. The oxide layer was characterized using various analytical techniques. Carburization behavior were investigated based on the microstructure analysis, especially regarding the oxide/matrix interface and underlying matrix. Finally, the effects of exposure to the high-temperature S-CO_2 environment on tensile properties were measured, and the results were discussed in terms of the carburization behavior of the alloys.

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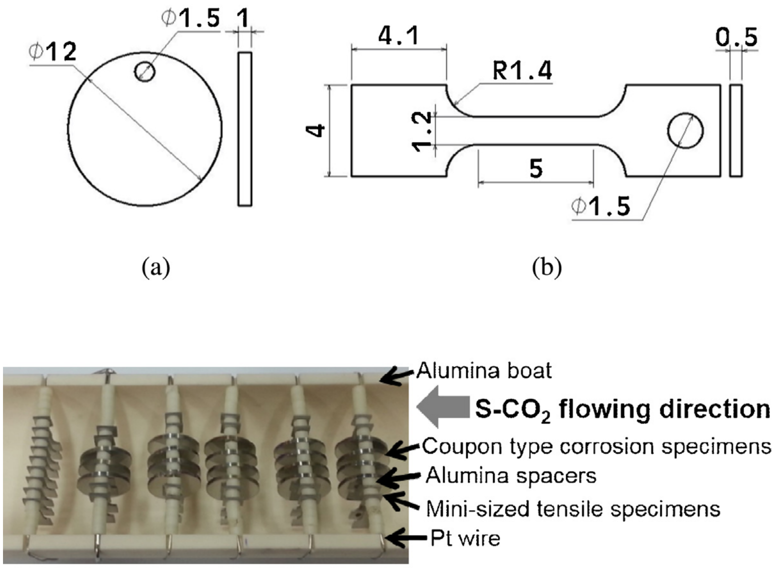
Table 1
Chemical compositions of test materials (in wt.%).

	Ni	Cr	Fe	C	Mo	Mn	Ti	Al	Si	Cu	Etc.
Alloy 600	Bal.	16.1	9.3	0.08	–	0.3	0.20	0.16	0.3	0.02	–
Alloy 690	Bal.	28.4	8.3	0.02	–	0.2	0.26	0.3	0.2	0.01	–
Alloy 800HT	33.9	21.0	42.3	0.06	0.2	0.9	0.55	0.48	0.4	0.1	0.05Co



(a) (b)

(c)

Fig. 1. Geometry and dimensions of (a) coupon and (b) mini-sized tensile specimen (in mm) and (c) photograph of installed both specimens on alumina boat.

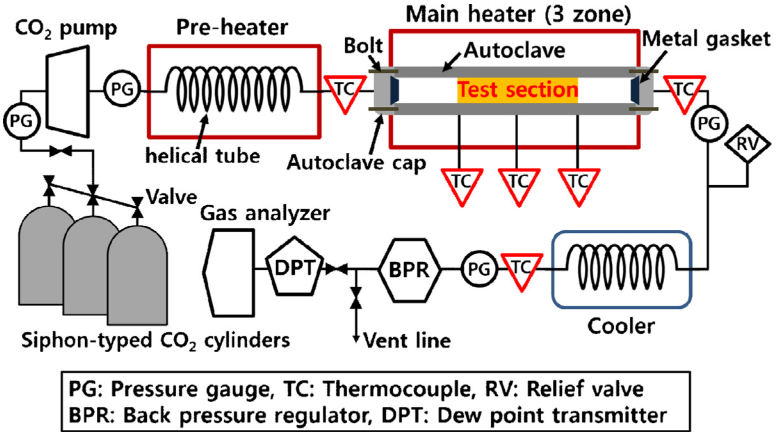


Fig. 2. Schematic of the S-CO_2 corrosion test facility.

2. Materials and experiment

2.1. Test materials and specimen preparation

Three commercial grade chromia-forming heat resistant alloys were used in this study. The selection of the test materials was based on the following industry experiences. Ni-based alloys, Alloy 600 and Alloy 690, are used for steam generator tubes in pressurized water reactors whereas Alloy 800HT is used for advanced high-temperature fossil power plants. These materials are generally known to have a high strength and good corrosion resistance at the anticipated operating temperature of the SFR (500–550 °C) and the IHX in the S-CO_2 power conversion cycle. The chemical compositions of the alloys were analyzed by the inductively coupled plasma (ICP) method, and the results are listed in Table 1.

For the S-CO_2 corrosion tests, the materials were electro-discharge machined to coupon-type specimens (12 mm in diameter and 1 mm in thickness) as shown in Fig. 1a. The specimens were ground with 1200 grit silicon carbide paper and ultra-sonically cleaned in ethanol prior to the tests. Also, mini-sized tensile specimens (16 mm in length and 0.5 mm in thickness) were machined (Fig. 1b). A hole of 1.5 mm in diameter was drilled at the upper part of both sample types to hang them on a Pt wire of 0.5 mm in diameter. Both samples were placed in parallel to S-CO_2 flow as shown in Fig. 1c. To prevent direct contact between the samples, alumina spacers of 2.5 mm in diameter were placed on the Pt wire between coupon samples. As the Pt wire is in contact with test coupons at the inner surface of the hole, there might be a concern of galvanic corrosion between Pt wire and test coupons. However, the test will be performed in high temperature S-CO_2 environment, which is