



Oxidation and carburizing of FBR structural materials in carbon dioxide



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ABSTRACT

A key problem in the application of a supercritical CO₂ turbine cycle to a fast breeder reactor is the corrosion of structural materials brought about by supercritical CO₂ at high temperatures. In this study, metallurgical analysis of the ferritic–martensitic steels (12Cr-steel and T91) exposed at 400–600 °C for up to 8000 h in supercritical CO₂ pressurized at 20 MPa and at 550 °C for up to 5000 h in CO₂ gas at atmospheric pressure has been carried out.

Two successive oxide layers formed on the steels were kept under the maximum testing conditions (at 600 °C for 8000 h at 20 MPa), and no breakaway corrosion was observed. Each oxide layer thickness increased with exposure time, due to parabolic oxide growth. By using the electron backscattering diffraction technique, the outer oxide layer could be separable into thin Fe₂O₃ and thick Fe₃O₄, and the formation behavior was clarified. Carburizing was observed in the base metal just under the oxide layer, and the crystal structure was mainly M₂₃C₆.

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1. Introduction

A disadvantage of conventional fast breeder reactors (FBRs) is the chemical reaction between sodium and water in the tube failure incident at the steam generator. The application of a supercritical carbon dioxide (SC-CO₂) turbine cycle to FBRs has the potential to enhance reliability from the viewpoint of plant safety because the compact SC-CO₂ turbine system is capable of replacing the steam generator turbine system used in conventional liquid-metal-cooled FBRs.

In the past, a large number of corrosion tests in high temperature carbon dioxide gas (CO₂ [gas phase]) have been performed for the development of gas cooled reactors. The results of such tests have made it clear that the most important issue for materials in high temperature CO₂ is breakaway corrosion caused by the reiteration of exfoliation of the oxide scale and the nucleation of oxides (Pritchard and Truswell, 1974; Taylor and Trotsenberg, 1974; Nakanishi, 1975, 1974; Jones, 1985; Newcob and Stobbs, 1986).

Based on such knowledge, the corrosion research of steels in SC-CO₂ has been recently performed in U.S., Europe and Japan in order to obtain the corrosion behavior in supercritical phase. Allen (Firouzdor et al., 2013; Cao et al., 2012; Tan et al., 2011) performed corrosion experiments on various structural materials such as austenitic stainless steels, ferritic–martensitic steels, and nickel-based alloys at 650 °C and 20 MPa for up to 3000 h, and then compared the corrosion performance with that evaluated by weight change measurements and microstructure examination. We performed corrosion tests on Japanese candidate structural materials for sodium cooled FBRs, i.e., high-chromium martensitic and austenitic stainless steels, in supercritical CO₂ pressurized at 10 MPa and 20 MPa for up to 8000 h, and then proposed corrosion allowances of the steels for the preliminary design of a compact SC-CO₂ turbine system for FBRs based on the weight change measurement (Furukawa et al., 2007, 2010, 2011). We also performed a test on T91 steel, which is one of the candidate materials in Europe, in CO₂ at atmospheric pressure [gas phase] and 25 MPa [supercritical phase] for up to 5000 h, and proposed the modeling and simulation of duplex oxide growth (Rouillard et al., 2012; Rouillard and Martinelli, 2012). However, no experimental knowledge on the breakaway corrosion, which is observed under gas phase conditions, has been obtained from these tests; hence, more detailed studies are needed to estimate the long-term compatibility of the steels from the viewpoint of the structural integrity of FBR plants.

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Table 1
Chemical compositions of as-received steels.

	Fe	C	Si	Mn	Cu	Ni	Cr	Mo	V	Unit: mass%	
										N	W
12Cr-steel	Bal.	0.11	0.26	0.64	1.03	0.39	10.87	0.31	0.20	0.064	1.86
T91	Bal.	0.10	0.31	0.43	0.05	0.23	8.63	0.95	0.21	0.03	–

In this study, detailed microstructural analyses of the corroded materials (two ferritic–martensitic steels, 12Cr-steel and T91) in SC-CO₂ at 20 MPa and in CO₂ at atmospheric pressure, as obtained in [Furukawa et al. \(2011\)](#) and [Rouillard and Martinelli \(2012\)](#), were performed; then, the progress of oxidation and carburizing was investigated to understand the mechanism of breakaway corrosion of the steels.

2. Experiments

In this research, corroded samples of two ferritic–martensitic steels (12Cr-steel and T91) exposed in SC-CO₂ and CO₂ were analyzed metallographically. The chemical composition and the experimental conditions are shown in [Tables 1 and 2](#), respectively.

The microstructure was observed using an optical microscope, a scanning electron microscope (SEM), and an electron probe microanalyzer (EPMA). The crystal structure was analyzed by using a field-emission transmission electron microscope (TEM), a Raman microscope whose laser wavelength was 532 nm, and an electron backscatter diffraction (EBSD) system, which was combined with the SEM. Glow discharge optical emission spectroscopy (GDOES) was used to determine the distribution of elements near the specimen surface.

3. Results and discussion

3.1. Oxidation behavior

Backscattered electron images of the cross section of the 12Cr-specimens exposed to SC-CO₂ at 20 MPa for 6019 h and 8010 h are shown in [Fig. 1](#). All specimens were covered by two successive layers, and the internal oxidation zone (IOZ) was intermittently observed between the inner successive layer and the base metal. A similar observation was described for up to 5000 h of exposure in a previous report ([Furukawa et al., 2011](#)), and no traces of breakaway corrosion were observed. The thickness of the successive layers increased with temperature. On the other hand, the increases accompanying the exposure time were slight as compared with 6019 h and 8010 h in all temperatures. This result was in agreement with the results of weight change measurements ([Furukawa et al., 2011](#)).

In a previous study ([Furukawa et al., 2011](#)), we found that the weight gain caused by the oxidation of 12Cr-steel in SC-CO₂ can be estimated from following equations.

Table 2
Experimental conditions for the samples subjected to metallurgical examination.

Materials	Pressure/MPa	CO ₂ phase	Temp/°C	Exposure time/h	Ref.
12Cr-steel	20	Supercritical	400	~8010	Furukawa et al., 2010, 2011
			500		
			550		
			600		
T91	Atmospheric pressure	Gas	550	~5000	Rouillard et al., 2012

$$\Delta W = K_p \sqrt{t} \quad (1)$$

$$K_p = K_0 \exp(-Q/RT) \quad (2)$$

where ΔW : weight gain (g/m²); K_p : oxidation coefficient (g/m² s^{-1/2}); t : time (s); K_0 : constant (–); Q : apparent activation energy (J/mol); R : gas constant (J/K mol); T : temperature (K).

Then, the relationship between the weight gain and the oxide thickness was investigated. The result is shown in [Fig. 2](#). In this investigation, each layer of oxide formed on the specimen was separated, and those thicknesses were measured. The data for T91 steel tested at atmospheric pressure are also over-plotted in this figure for comparison.

It was confirmed that each oxide thickness except for the IOZ increased in the direct proportion with the weight gain. The slope, which was the ratio of the total thickness to the weight gain, was 0.763, and it was equivalent to that in the 10 MPa test ([Furukawa et al., 2007](#)). On the other hand, the thickness of the IOZ randomly changed to 15 μ m or lesser. Although it was reported that the IOZ formation was related to the chromium concentration in the boundary, on the basis of oxide formation in lead bismuth eutectic at 650 °C ([Aoto et al., 2003](#)), such a behavior was not observed in the tested specimens in CO₂. The data for T91 were within the data band for 12Cr-steel, and the effects of minor elements and CO₂ pressure were not observed.

We have investigated the crystal structure of each oxide layer formed on high-chromium martensitic steels by using X-ray diffraction and Raman techniques. [Fig. 3](#) shows an example of the Raman spectra of T91 steel after 150 h in CO₂ at 550 °C in atmospheric pressure. The outer successive oxide layer (zones 1 and 2 in the figure) consists of Fe₂O₃ and Fe₃O₄, and both the inner layer (zone 3) and IOZ (zone 4) consist of spinel Fe(Fe_{1-x}Cr_x)₂O₄. However, the structures in the outer successive oxide layer were not clearly separated in the Raman microscopy images. Hence, the progress of oxide growth of the outer oxide layer was investigated by using EBSD. The EBSD result of the specimens tested at 600 °C for 1000 h and 2000 h in CO₂ at the pressure of 20 MPa is shown in [Fig. 4](#). Many black holes, which are observed in the SEM images, are vacancies, and they are formed by the diffusion of iron from the metal. By using the EBSD technique, it could be found that the outer oxide layer consists of hematite (Fe₂O₃) and magnetite (Fe₃O₄), as shown in the phase map. In the 1000 h specimen, hematite was intermittently formed on the rough surface; it was also partly observed inside magnetite, although the portion was mainly under the hollow of rough surface. On the other hand, layered hematite was formed on the magnetite layer of the 2000 h specimen, and it was hardly observed inside magnetite. This means that the equilibrium of oxygen partial pressure in the outer successive layer was stably formed by 2000 h of exposure. The thickness of hematite on the 2000 h specimen was 2 μ m, and it was in single crystallographic orientation in the thickness direction. The grain size in the magnetite differed in the thickness direction. Near the inner oxide layer, the grain size was less than 1 μ m, and it exceeded 25 μ m on the surface. This means that the formation of oxide grains occurred with the progress of oxide growth.

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