

## Characterization of oxide layers formed on FeCrSi alloy depending on oxygen partial pressure

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### 1. Introduction

After Fukushima accident, in order to prevent the severe accident of nuclear power plant, many ATF (Accident-tolerant fuel) cladding concepts have been researched in the world, such as coated Zr alloy, FeCrAl, SiC, Cr-Mo alloy etc [1]. Multi-metallic layered composite (MMLC) cladding is one of ATF cladding designs [2]. MMLC cladding is consisted inner Zr alloy, outer FeCrSi for for oxidation barrier and buffer layer for prevention to Fe-Zr intermetallic formation [2]. In the previous study, when the FeCrSi alloy has 20%Cr or more, protective Cr oxide was formed on the outmost layer, and it had excellent oxidation resistance in 1200 °C steam environment until 24 hours [2,3]. However, Cr oxide is known to be unstable in high temperature above 1000 °C because of high volatilization [4]. In order to evaluate why Cr oxide maintained the oxidation resistance until 24 hours, we conducted high temperature oxidation tests varying the oxygen partial pressure: in Ar-50% $H_2O$  and Ar-20% $O_2$  environments.

### 2. Experimental Methods

High-temperature oxidation testing was conducted using specimens of Fe-20Cr-2Si alloy. Before the oxidation test, the specimens of Fe-20Cr-2Si alloy were prepared as 30 × 20 × 2 mm coupons. These specimens polished using SiC paper up to P2400 (grit 800) and cleaned with acetone, ethanol, and pure water in series. The oxidation tests were conducted referring to NRC Reg. guide DG-1262 [5] in the resistance heating tube furnace. In order to increase the specimen heating speed, once a furnace was heated up to 1200 °C and stabilized, the specimen was inserted into the furnace. After the oxidation test, the specimen was taken out of the furnace and cooled down under air environment. It was oxidized at 1200 °C for up to 24 hours. During the Ar-50% $H_2O$  oxidation tests, steam and Ar gas were supplied into the furnace at 500 cc/hr, respectively. The mixture gas was heated up to 300 °C before injecting into the furnace in order to prevent the water condensation. In the Ar-20% $O_2$  tests, the mixture gas was supplied into the furnace at the rate of 1000 cc/hr

after heating to 300 °C. The chemical composition of the Fe-20Cr-2Si alloy is summarized in Table 1.

Table I: Compositions (wt. %) of Fe-20Cr-2Si alloys used in this study

	Fe	Cr	Si	Remarks
Fe20Cr2Si	Bal.	20.06	1.95	Measured by DCP-AES

### 3. Results and Discussion

After the high temperature oxidation tests, the oxide layers were observed using Optical Microscope (OM) and Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS).

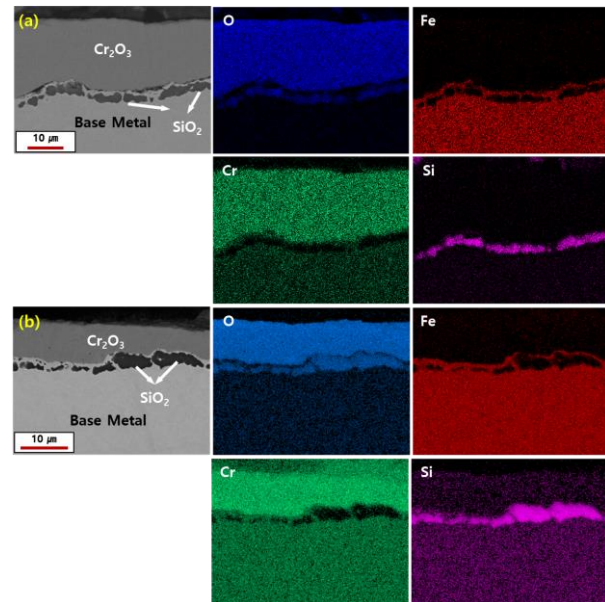


Fig. 1. Comparison of SEM-EDS mapping results on the cross-sectional images of Fe20Cr2Si at 1200 °C after 24 hours exposure: (a) Ar-50% $H_2O$ , (b) Ar-20% $O_2$

Fig. 1 shows that the oxide layers formed under lower oxygen partial pressure (Ar-50% $H_2O$ ) are similar to the oxide layers under higher oxygen partial pressure (Ar-20% $O_2$ ). It is thought that Fe-20Cr-2Si has oxidation resistance in 1200 °C Ar-20% $O_2$  environment

until 24 hours. However, it is shown that relatively thinner Cr oxide is formed in the Ar-20%O<sub>2</sub> environment. The 8 hours test results showed the same trend. The change in Cr oxide thickness over oxidation time is shown in Table II.

Table II: Comparison of Cr oxide thickness of Fe-20Cr-2Si after oxidation test over time in different environment

	10 min	1 hr	3 hr	8 hr	24 hr
Ar-50%H <sub>2</sub> O (μm)	2.34 ± 0.55	5.58 ± .33	9.10 ± 1.24	12.16 ± 1.46	14.23 ± 2.92
Ar-20%O <sub>2</sub> (μm)	-	-	-	7.15 ± 1.53	11.52 ± 1.28

A noticeable oxidation feature of the Ar-20%O<sub>2</sub> specimens is the formation of local degradation oxide areas as shown in Fig. 2.

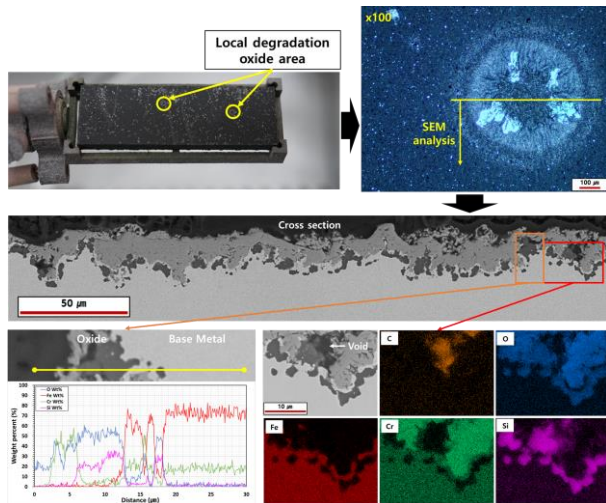
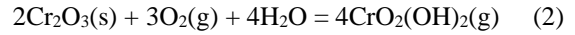
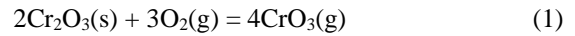


Fig. 2. OM and SEM-EDS mapping results on the degradation area of Fe20Cr2Si oxide layers formed in Ar-20%O<sub>2</sub> at 1200 °C after 24 hr exposure.

The concentric areas with a diameter of about 350 μm are observed on the oxide surface formed under Ar-20%O<sub>2</sub> environment. Cross-sectional analysis on the local degradation oxide area revealed the presence of some voids in the Cr oxide layer. However, Cr depletion is not observed at the base metal/oxide interface based on the line EDS result. It is thought that local degradation oxide area is not generated due to the Cr depletion.

Other than Cr depletion, the Cr oxide volatilization in high temperatures above 1000 °C may be one of the reasons for the onset of local degradation oxide areas in the Cr oxide layer on Fe-20Cr-2Si alloys under Ar-20%O<sub>2</sub> environment [4]. Chemical reactions of major volatile species in oxygen and steam environments are as follows.



From thermodynamic point of view, the driving force of the chemical reaction is thought to be proportional to the equilibrium partial pressure of each volatile species. Therefore, in order to evaluate the volatility of Cr oxide in each environment, the equilibrium partial pressure of major volatile species in the Ar-50%H<sub>2</sub>O, Ar-20%O<sub>2</sub> and pure H<sub>2</sub>O environments was calculated referring to the Gibbs free energy reported in earlier literatures [6-10].

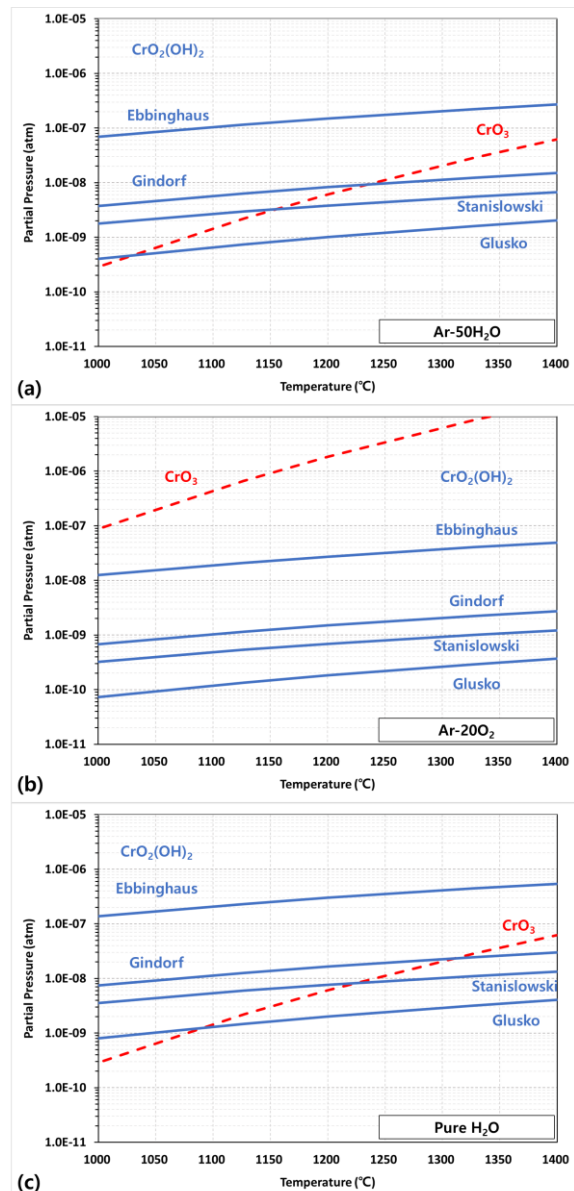


Fig. 3. Comparison of partial pressure of CrO<sub>3</sub> and CrO<sub>2</sub>(OH)<sub>2</sub> over Cr<sub>2</sub>O<sub>3</sub>: (a) Ar-50%H<sub>2</sub>O (b) Ar-20%O<sub>2</sub> (c) Pure H<sub>2</sub>O [6-10]

Fig. 3 shows the equilibrium partial pressure of volatile species in each environment. In the case of

$\text{CrO}_2(\text{OH})_2$ , it is shown that there is a difference in the partial pressure values up to 100 times depending on references. In 1200 °C Ar-20%O<sub>2</sub> result (Fig. 3(b)), although the equilibrium partial pressure of  $\text{CrO}_2(\text{OH})_2$  is relatively low, the equilibrium partial pressure of  $\text{CrO}_3$  is very high, so that the overall equilibrium partial pressure of volatile species is about 10 times or more compared to the overall partial pressure in the Ar-50%H<sub>2</sub>O environment. This is thought to be one of the reasons why the local degradation of the Cr oxide layer on Fe-20Cr-2Si alloy initiated in the Ar-20%O<sub>2</sub> environment. In pure H<sub>2</sub>O environment, the partial pressure value is slightly higher than that in Ar-50% H<sub>2</sub>O environment, but there is no significant difference. Therefore, in pure H<sub>2</sub>O environment similar to the loss of coolant accident (LOCA) environment, it is thought that the Fe-20Cr-2Si alloy can have oxidation resistance until 24 hours at least from the thermodynamic point of view.

#### 4. Conclusions and Future Works

In this study, the high temperature oxidation tests of Fe20Cr2Si alloy were conducted in 1200 °C Ar-50%H<sub>2</sub>O and Ar-20%O<sub>2</sub> until 24 hours. In both environments, it is observed that Cr oxide and Si oxide layers remain until 24 hours. However, Cr oxide is formed relatively thinner and local degradation oxidation areas is observed in the Ar-20%O<sub>2</sub> environment. The reason is thought to be that the volatilization driving force of Cr oxide is larger at Ar-20%O<sub>2</sub> environment due to the high equilibrium partial pressure of the volatile Cr species. On the other hand, in Ar-50%H<sub>2</sub>O and pure H<sub>2</sub>O environments, the equilibrium partial pressure of volatile species is relatively low, and thus it is thought that the oxidation resistance of Cr oxide is maintained relatively long. However, since the rate of chemical reaction cannot be confirmed by thermodynamic calculation, further research will be conducted from the viewpoint of oxidation kinetics.

#### ACKNOWLEDGEMENT

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