

Analysis of Oxide Layers in FeCrSi Alloys at High Temperature Steam Environment

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***Keywords** : Fe-Cr-Si alloy, high temperature oxidation test, SiO₂, metal-oxide interface

1. Introduction

The FeCrSi alloy is being developed as the outermost oxidation protection layer of multi-metallic layered composite (MMLC) fuel cladding, which is a candidate material for accident tolerant fuel (ATF) cladding [1]. Previous studies have investigated the high temperature oxidation resistance and behavior of FeCrSi alloys in a steam environment [1,2]. Especially, it was confirmed that the addition of Si to the FeCr alloy improved oxidation resistance by preventing the formation of cavities at the metal-oxide interface in high temperature steam [2,3]. However, little study has been conducted on the cause of the cavity formation and the role of Si in preventing the formation of cavities. In this study, additional analyses were conducted to determine the cause of the cavity formation at the metal-oxide interface in the FeCr alloy and the mechanism by which Si prevents the cavity formation in the high temperature steam.

2. Background and Analysis Methods

In the previous study [2,3], high temperature oxidation tests were conducted on three types of specimens: Fe20Cr, Fe20Cr1Si, and Fe20Cr2Si. The chemical composition of FeCrSi specimens is shown in Table I.

Table I: Chemical composition of FeCrSi specimens

	Fe	Cr	Si	Method
Fe20Cr	Bal.	20.42	0.00	LIBS
Fe20Cr1Si	Bal.	20.39	1.14	LIBS
Fe20Cr2Si	Bal.	20.06	1.95	DCP-AES

When the oxidation tests were conducted for 10 min at 1200 °C, Cr₂O₃ was formed as the outermost oxide layer in all specimens, and amorphous SiO₂ was formed between Cr₂O₃ and metal matrix in Fe20Cr1Si and Fe20Cr2Si specimens [2,3]. In addition, cavities were observed at the metal-oxide interface only in Fe20Cr [3]. It is known that Cr₂O₃ formed on the outermost surface during high temperature oxidation of FeCrSi alloys tends to buckle as the oxide layer grows, and oxide

layers can be locally cracked by accumulation of compressive stress [4]. However, this does not explain the formation of cavities at the metal-oxide interface only in the Fe20Cr alloy. In the previous study [5], it showed that if the p(H₂O)/p(O₂) ratio is high enough, migration of oxygen and hydrogen containing species from water vapor to the metal-oxide interface seems to be possible. Furthermore, previous studies have shown that hydrogen can combine with existing vacancies to form more stable voids [6]. Since the oxidation testing was conducted in Ar-50%H₂O and the ratio of p(H₂O)/p(O₂) is high, hydrogen originated from water vapor may be able to penetrate into the metal-oxide interface. Therefore, it was assumed that hydrogen could form cavities at the metal-oxide interface by stabilizing the vacancies. In Fe20Cr1Si and Fe20Cr2Si, it was assumed that cavities could not form because amorphous SiO₂ formed under Cr₂O₃ prevents hydrogen from accumulating at metal-oxide interface. To verify this assumption, hydrogen analysis on the oxide layers including the metal-oxide interface was conducted using FT-IR (Fourier Transform Infrared Spectroscopy), XPS (X-ray photoelectron spectroscopy), and GDS (Glow Discharge Spectrometer).

3. Results and Discussion

FT-IR and XPS analysis methods, which can analyze hydrogen bonds, are difficult to analyze the entire thick oxide layer. Therefore, as shown in Fig. 1, after lifting off the oxide layers with the carbon tape and securing the tape on a base plate, direct analysis on the SiO₂ oxide layer became possible. FT-IR was used for surface analysis, but XPS was used for obtaining the depth-profile, which was made at intervals of 20 s up to max. etching time of 100 s. The results of the FT-IR and XPS analysis are shown in Figs. 2 and 3, respectively.

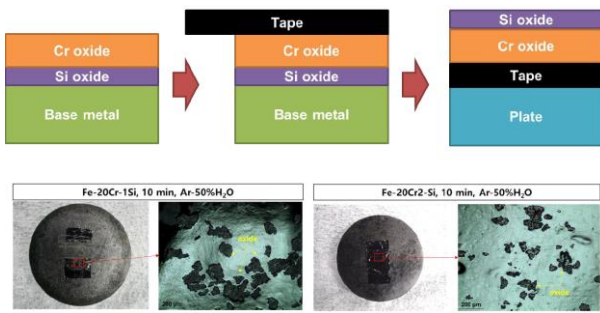


Fig. 1. Specimen preparation for SiO₂ layer analysis

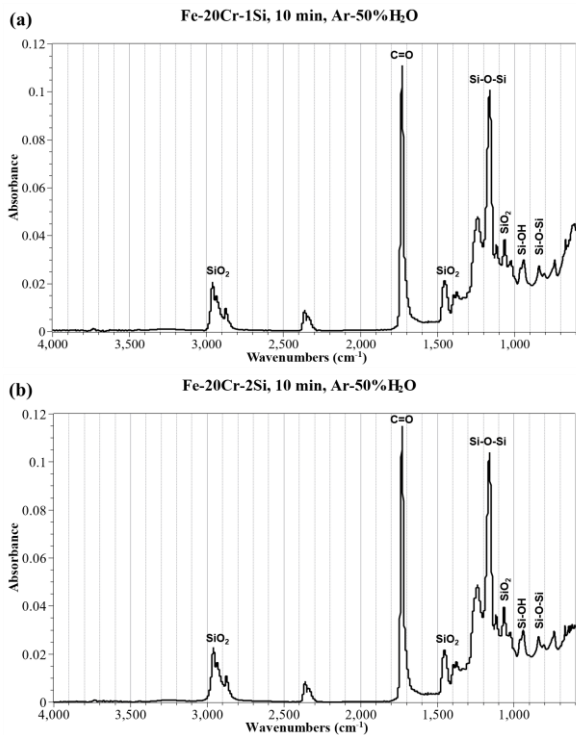


Fig. 2. FT-IR results of SiO₂ layer in (a) Fe20Cr1Si and (b) Fe20Cr2Si exposed to Ar-50% H₂O at 1200 °C for 10 min.

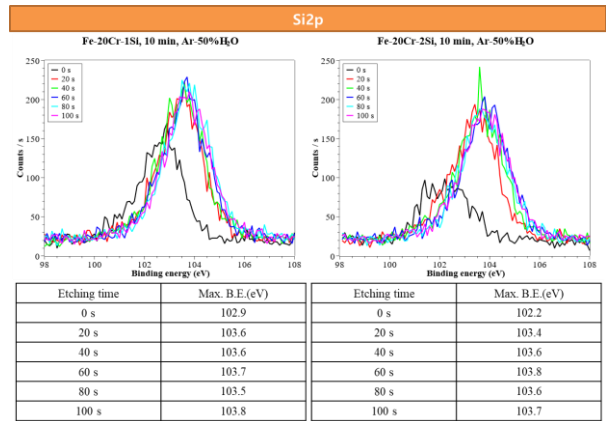
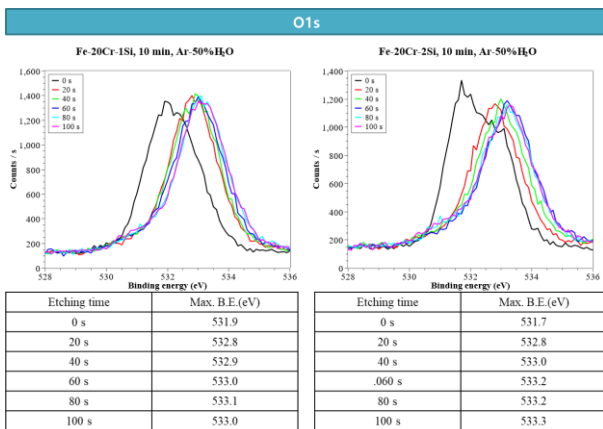
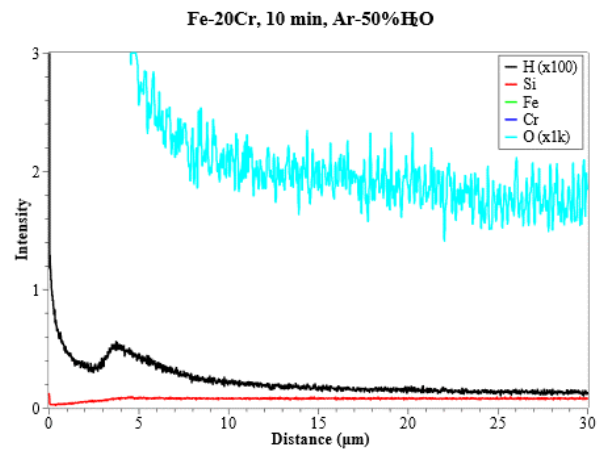


Fig. 3. XPS depth-profile results of SiO₂ layer in Fe20Cr1Si and Fe20Cr2Si exposed to Ar-50% H₂O at 1200 °C for 10 min.

From the FT-IR analysis results in Fig. 2, it can be seen that the spectra of Fe20Cr1Si and Fe20Cr2Si specimens are almost identical. The results reveal the existence of SiO₂, Si-O-Si, and Si-OH bonds and the C=O peak due to the influence of the carbon tape. In the XPS depth profile results in Fig. 3, it can be seen that there is no significant difference between the peaks of the two specimens. However, it is interesting to note that all O1s and Si2p peaks have about 1 eV lower binding energy on the surface (i.e., when the etching time is 0 s) than inside the oxide layer. The cause may be a peak shift due to the formation of other substances from contamination when SiO₂ is exposed to the atmosphere. Peak deconvolution was conducted to determine the exact cause of the peak shift, but the range of the SiO₂ binding energy in O1s and Si2p was greater than 1 eV [7]. Therefore, it was difficult to determine the exact cause of the peak shift.

GDS analysis can detect hydrogen and etch down to a few tens of micrometer. Therefore, the depth profile analysis was conducted directly starting from the specimen surface without the oxide lift-off process.



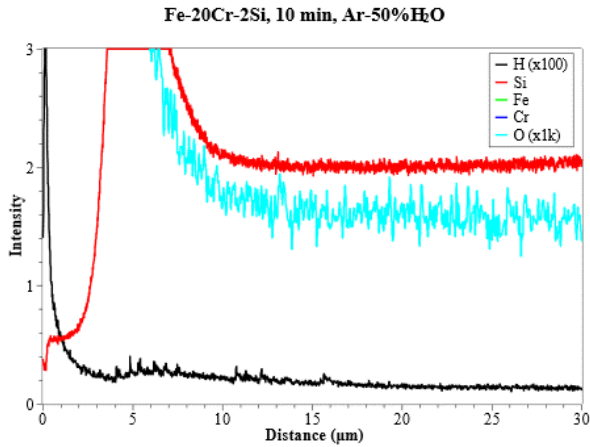


Fig. 4. GDS depth-profile results of Fe20Cr (top) and Fe20Cr2Si (down) exposed to Ar-50% H_2O at 1200 °C for 10 min.

Two important points can be made from the GDS analysis results in Fig. 4. First, high concentrations of hydrogen are observed on the surfaces of the two specimens. When the oxide layer of the specimen is exposed to the atmosphere, it is suspected that water vapor in the atmosphere adsorbs and makes the hydrogen bonding. Therefore, it is very likely that the Si-OH peak observed in the FT-IR results of Fig. 2 was generated during the exposure to air, not during the oxidation experiments. Similarly, the surface peak shift in the XPS results of Fig. 3 may also be caused by exposure of the specimen to the atmosphere and formation of other substances. Second, no hydrogen enrichment was observed at the metal-oxide interface in Fe20Cr2Si, but hydrogen enrichment was observed at the interface in the Fe20Cr specimen. Although GDS analysis for Fe20Cr1Si was not conducted, the previous FIB cross-sectional analysis results showed similar results to Fe20Cr2Si [3], so it is expected that hydrogen was not enriched at metal-oxide interface. This supports the assumption that the cavity formed in the absence of Si is caused by hydrogen. When Si is present in the alloys and SiO_2 is formed, it is thought that SiO_2 layer can prevent hydrogen from penetrating into the oxide layer. Further analysis will be conducted on other specimens to confirm this.

4. Conclusions and Future Work

In the MMLC cladding, the FeCrSi alloy plays a role in improving the accident tolerance of zirconium nuclear fuel cladding. Therefore, it has been designed to use commercial zirconium alloys, Zircaloy-4 or ZIRLO, as the base metal. In addition, it may be considered to use HANA-6, a domestically developed nuclear fuel cladding. Analyses were conducted to determine why cavities were observed only in the FeCr alloy at the metal-oxide interface when FeCr and FeCrSi alloys were oxidized for 10 min in 1200 °C steam. Based on previous studies [4,5], it was assumed that this cavity could be caused by hydrogen. FT-IR, XPS and GDS

analyses were conducted to confirm hydrogen or hydrogen bonding. As a result, the GDS analysis confirmed that hydrogen was enriched at the metal-oxide interface only in the Fe20Cr alloy without Si, and supported the possibility that Si in alloys can prevent hydrogen accumulation while forming SiO_2 . However, in order to have more concrete conclusions, it is necessary to conduct additional testing and confirm that cavities are not formed during the oxidation of the Fe20Cr alloy in a steam-free environment.

ACKNOWLEDGEMENT

This study was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20168540000030). This work was also supported by KETEP and MOTIE of the Republic of Korea (No. 20214000000410).

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