High-Temperature Oxidation Behavior of CrAl Alloys in Ar-Steam with Increasing Al Content

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1. Introduction

Globally, Accident Tolerant Fuel (ATF) claddings are being extensively studied to enhance the safety of nuclear power plants [1,2]. Among various candidates, coated zirconium (Zr) alloy claddings are under development for rapid commercial application [3]. While chromium (Cr)-coated Zr cladding remains a major focus, CrAl coated Zr cladding has gained significant attention due to its superior high-temperature oxidation resistance compared to pure Cr [4]. However, the oxidation mechanisms of such coated systems are inherently complex. Investigating coated cladding involves accounting for the simultaneous high-temperature behavior of the Zr substrate and the interdiffusion between the coating and the base metal. Consequently, the oxidation behavior of these systems under accident conditions exceeding 1000℃ is still being extensively explored. Despite their importance, the fundamental oxidation behavior of the CrAl alloys themselves—which form the basis of the coating—has not been sufficiently explored, particularly in 1200 ℃ steam environments. A fundamental understanding of the intrinsic oxidation properties of CrAl alloys is essential for optimizing coating compositions. Therefore, this study aims to evaluate the effect of Al content on the oxidation kinetics and oxide stability of CrAl alloys in an Ar-steam at 1200 ℃, providing the necessary groundwork for the development of high-performance ATF claddings.

2. Experimental Methods

CrAl alloys with compositions of Cr10Al, Cr15Al, and Cr20Al (in wt.%) alloys were prepared as experimental specimens. The specimens were fabricated into plate-shaped samples with dimensions of 10 x 10 x 2 mm and subsequently polished using SiC paper up to 1200 grit. The polished specimens were oxidized using a SHIMADZU TGA-51H thermogravimetric analyzer. The samples were heated to 1200 ℃ at a constant heating rate of 50 ℃/min and maintained for 4 hours in an Ar-steam atmosphere. Following the oxidation tests, the oxides and microstructures were characterized using Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and X-ray Diffraction (XRD).

3. Result and Discussion

During the oxidation tests, the weight changes of the specimens were measured, and their surface morphologies were subsequently observed. To identify the composition of the oxides, cross-sectional SEM-EDS analysis and XRD measurements were performed.

2.1 Surface Morphology and Weight Change

The surface morphologies of the specimens were first examined following the oxidation tests. As shown in Fig. 1, the Cr10Al and Cr15Al alloys developed greenish oxides. In contrast, the Cr20Al alloy exhibited oxides with brownish appearance. The oxidation kinetics, represented by the weight changes in Fig. 2, further highlighted these differences. The Cr10Al and Cr15Al alloys showed a typical weight gain following a parabolic oxidation rate. However, a significant weight loss was observed in the Cr20Al alloy during oxidation at 1200 ℃, confirming that extensive spallation of the oxide occurred. Based on the differences in both oxide coloration and oxidation behavior, it can be inferred that Cr10Al and Cr15Al exhibit similar oxidation mechanisms, whereas Cr20Al follows a distinct path. Furthermore, a comparison with literature data for pure Cr reveals that the Cr10Al and Cr15Al alloys possess superior oxidation resistance, demonstrated by their lower oxidation rates [4].

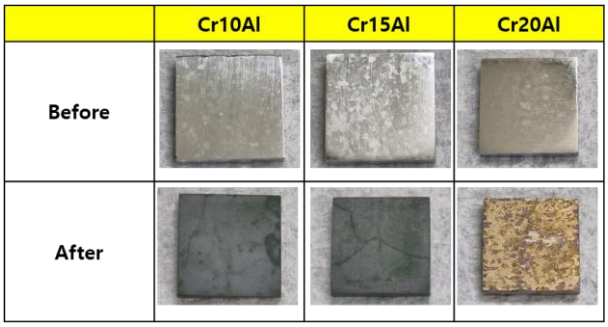

Fig. 1. Photographs of the specimens before and after the oxidation test.

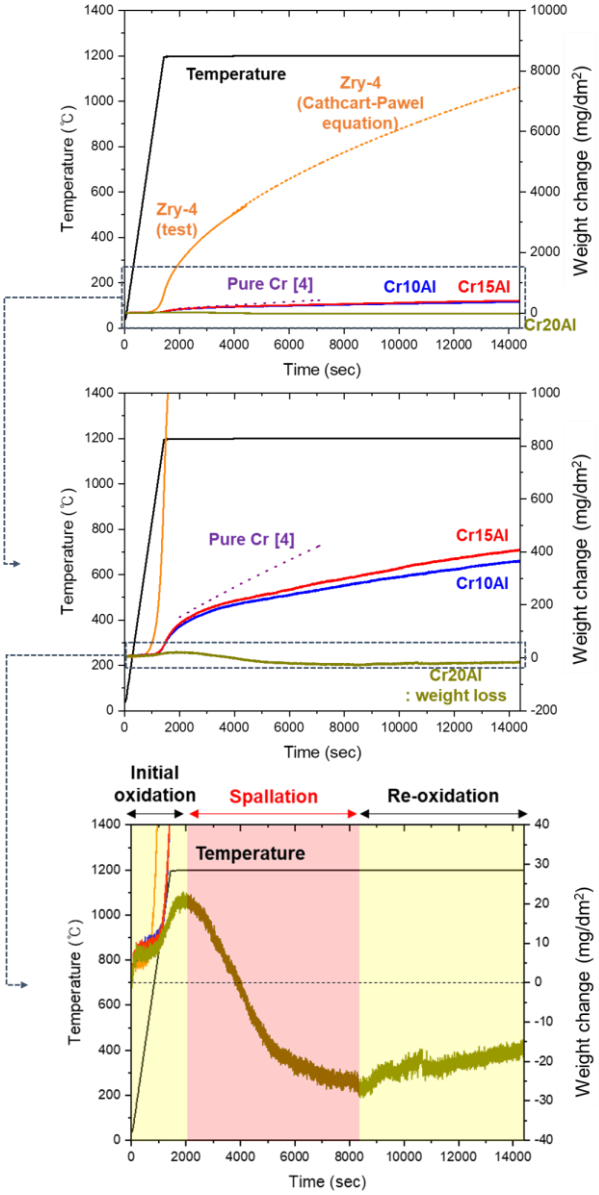

Fig. 2. Weight changes of CrAl alloys in Ar-steam at 1200 ℃ compared with Zry-4 and pure Cr [4].

2.2 Microstructure and Phase Analysis of Oxide

The cross-sectional SEM-EDS mapping results in Fig. 3 and Fig. 4 confirm that Cr10Al and Cr15Al exhibited similar oxidation behavior. In both specimens, a continuous Cr-oxide layer was formed at the outermost surface, followed by a continuous CrAl solid solution oxide layer beneath it. Within the base metal, regions considered to be Al-oxide were observed, and further inward, localized areas where Al and Cr were segregated were identified .In contrast, the Cr20Al alloy showed significant oxide spallation. Upon examining the remaining oxide (Fig. 4), it was confirmed that an Al-oxide layer had predominantly formed. Notably, a CrAl oxide phase was observed as an outer layer of the Al-oxide.

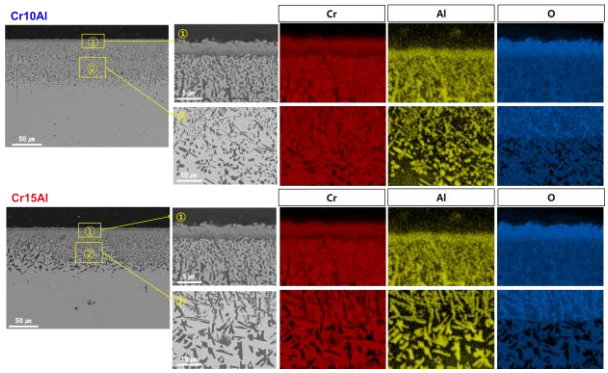

Fig. 3. Cross-sectional SEM-EDS mapping of Cr10Al and Cr15Al metal-oxide interfaces.

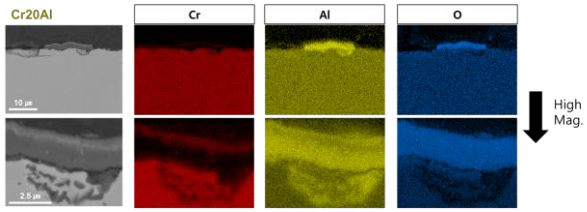

Fig. 4. Cross-sectional SEM-EDS mapping of Cr20Al metal-oxide interface.

The XRD patterns in Fig. 5 are consistent with the SEM-EDS results, showing identical peaks for Cr10Al and Cr15Al, while distinct peaks were observed for Cr20Al. Based on the EDS mappings, XRD peak matching was performed, confirming that Cr10Al and Cr15Al primarily consist of Cr and Cr_2O_3 phases. In contrast, for Cr20Al, the peaks were matched to metallic Cr and α-Al_2O_3, with the notable presence of the metastable θ-Al_2O_3 phase. According to literature, the presence of Cr can stabilize the metastable θ-Al_2O_3 phase, potentially preventing its complete transformation into the stable α-Al_2O_3 phase even at 1200 ℃ [5]. In Fig. 2, oxide spallation is observed approximately 500 s after reaching 1200 ℃. This phenomenon is suggested to have been accelerated by internal stresses, which were potentially induced during the phase transformation from the initially formed θ-Al_2O_3 to α-Al_2O_3. Therefore, it is highly probable that the CrAl oxide observed at the outermost surface of Cr20Al corresponds to θ-Al_2O_3 which remained partially untransformed. Consequently, despite the formation of α-Al_2O_3, which typically offers superior oxidation resistance, the overall oxidation performance of Cr20Al was significantly degraded due to this extensive spallation.

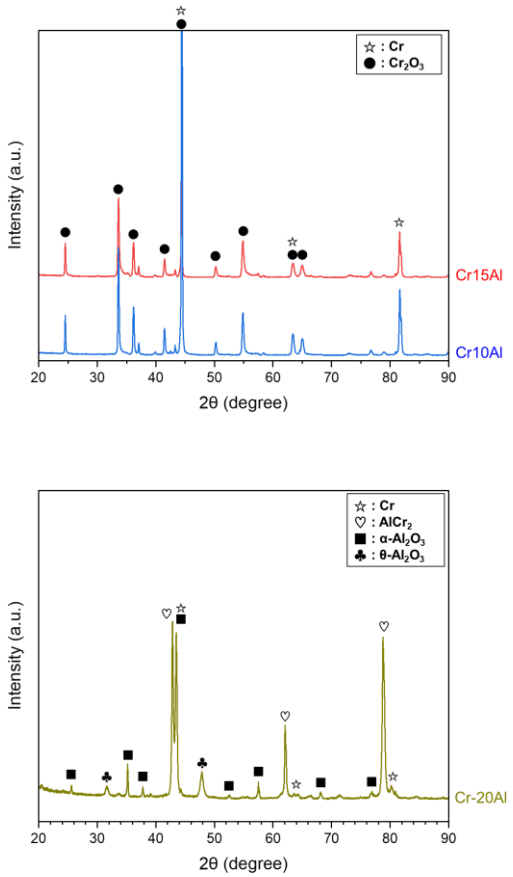

Fig. 5. XRD patterns of Cr10Al, Cr15Al, and Cr20Al alloys after oxidation..

4. Conclusions

The high-temperature oxidation behavior of CrAl alloys at 1200 ℃ was investigated, revealing distinct oxide formations depending on the Al content. It was observed that Cr10Al and Cr15Al alloys primarily developed Cr_2O_3-based oxides, whereas Cr20Al formed an Al_2O_3-based oxide. From the perspective of oxide growth, the Al_2O_3-forming Cr20Al initially appeared to offer superior oxidation resistance. However, after a certain period, the overall oxidation resistance was significantly degraded due to the extensive spallation of the oxide. In contrast, Cr10Al and Cr15Al exhibited enhanced oxidation resistance compared to pure Cr, which is thought to be due to the formation of a $(Cr,Al)_2O_3$ solid solution the primary beneath the Cr_2O_3 oxide. These results suggest that an Al content as high as 20 wt.% may adversely affect oxidation performance by inducing oxide spallation. Therefore, selecting the optimal Al concentration and ensuring precise local compositional control may be necessary for the successful development of CrAl coatings for nuclear fuel cladding

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