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The effect of cerium on the oxidation resistance of Fe-20Cr-1.7C-1Si

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Co is the major contributor to the radiation build-up in nuclear power plants. Many studies have been done to develop Co-free hardfacing alloys to replace Co-based Stellite 6 which is used for valve hardfacing. The Co-free alloys should have equivalent wear resistance, cavitation erosion resistance, and oxidation resistance to Stellite 6. Recently, we developed Fe-20Cr-1.7C-1Si alloy to replace Stellite 6. The new alloy has equivalent sliding wear resistance, and cavitation erosion resistance to Stellite 6. However, the high temperature oxidation resistance of the Fe-based hardfacing alloy is not as good as much as that of Stellite 6 due to the Cr deficiency in the Fe-based hardfacing alloy matrix. Ce is known to improve oxidation resistance of Fe-based alloys at elevated temperatures due to the beneficial effects of Ce such as formation of fine oxide layers and reduction of oxide-growth stresses. Therefore, in present study, the effect of Ce on the oxidation resistance was investigated in pressurized-water at 300□ under 7 MPa for 200 days in an autoclave. The concentration range of Ce was up to 0.2 wt.%. The specimens containing 0.2 wt.% Ce showed lower weight loss compared to that of the Ce-free specimen. With increasing Ce concentration, high temperature oxidation resistance of new alloy increased. The increased high temperature oxidation resistance may be due to the formation of adhesive oxide layers.

KEYWORDS: Radiation build-up, Hardfacing alloy, Oxidation

I. Introduction

Co-base Stellite 6 alloys have generally been used as hardfacing materials for nuclear power plant valves due to their superior wear resistance, high cavitation erosion resistance and oxidation resistance 1). However, Co has been known to be the major contributor to the radiation build-up in nuclear power plants 2). Wear and cavitation erosion products of Co-containing alloys are released into the primary cooling water and transported to the reactor core where ^{59}Co is transmuted to ^{60}Co. A number of studies of nuclear power plants showed that Co-base hardfacing alloys are responsible for up to about 40% of the total Co released to the primary water circuit 3). Moreover, in nuclear power plants of recent construction, the amount of Co produced from the steam generator tube decreased from about 60% to 30% by replacing Inconel 690 which contains 0.015wt.% Co as an impurity with Inconel 600 which contains 0.045wt.% as an impurity. Therefore, the amount of Co, which is produced from Co-based hardfacing alloys, increased about from 40% to 70% 4).

Many new Co-free hardfacing alloys have been developed to replace Co-based Stellite 6 which is currently used for valve hardfacing. The new Co-free alloys should have equivalent wear resistance, cavitation erosion resistance, and oxidation resistance to Stellite 6 5).

We developed Fe-20Cr-1.7C-1Si alloy to replace Stellite 6. The new alloy has equivalent sliding wear resistance and cavitation erosion resistance to Stellite 6 6, 7). However, the new Fe-based hardfacing alloy showed somewhat lower high temperature oxidation resistance in the pressured water environment than Stellite 6. At this time, it is thought that this is due to Cr deficiency caused by the formation of Cr-carbide. Therefore, it is necessary to improve the high temperature oxidation resistance of the Fe-based hardfacing alloy.

Many studies for improving high temperature oxidation resistance of Fe-based alloys have been done and it has been found that Ce is one of the most effective adding elements. Ce is reported to improve oxidation resistance of Fe-based alloys at elevated temperatures due to the beneficial effects of Ce such as formation of fine oxide layers and reduction of oxide-growth stresses 8~10).

The objectives of this study are to investigate the effect of Ce on high temperature oxidation resistance of the new Fe-based hardfacing alloy and to evaluate the possibility for replacing Stellite 6 with the new Fe-based hardfacing alloy.

II. Experiment details

1. Specimens

The Fe-based hardfacing alloy specimens for the oxidation test were prepared by adding Ce to the Fe-20Cr-1.7C-1Si alloy. The concentration of Ce was increased from 0 wt.% up to 0.2 wt.%. The chemical composition of the specimens and Stellite 6 was analyzed with an inductively coupled plasma spectrophotometer (ICP). The results are presented in **Table 1**.

2. Oxidation test

The oxidation tests were conducted in an autoclave filled with distilled water at 300 °C under a pressure of 7 MPa for 200 days. Oxidation test specimens with the dimension of 15 X 25 X 1 mm^3 and with total area of 8.3 cm^2 were prepared from the sheet specimens which were

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Table. 1. Chemical composition of the Fe specimens and Stellite 6(wt.%).

	Fe	Cr	Si	C	Ce	Co	W
0Ce	Bal.	20.1	1.05	1.68	0	-	-
0.1Ce	Bal.	20	1.05	1.66	0.07	-	-
0.2Ce	Bal.	19.8	0.93	1.68	0.12	-	-
Stellite	-	28	-	1.1	-	Bal.	4

mechanically polished before testing. The weight losses were measured 10 times with a microbalance with an accuracy in the order of 0.1 mg. The test was conducted to the ASTM G-2 method [11]. The oxidation behavior was evaluated by the weight loss (ΔW) as a function of exposure time. The thickness loss in **Fig. 1** is measured by dividing the weight loss into a density of the 0Ce specimen (7.6 g/cm^2).

3. Examination of oxide layer

The morphologies of the oxide layers of the Ce added Fe-based hardfacing alloys were examined by scanning electron microscopy (SEM). The thickness and phase of oxide layers were investigated by Auger Electron Spectroscopy (AES) and X-ray Diffractometry (XRD), respectively.

III. Results

1. Oxidation behavior

The weight loss versus oxidation time curves for the Ce added Fe-based hardfacing alloys and Stellite 6 are shown in **Fig. 1**. It is clear that weight loss increases with increasing exposure time. The weight loss or oxidation behavior of the Ce added Fe-based alloys was similar to the Fe-based hardfacing alloys and Co-based hardfacing alloys [12, 13]. All the weight loss curves of the Ce added Fe-based hardfacing alloys are higher than that of Stellite 6. The weight loss of specimens containing Ce decreases with increasing Ce content. The weight loss of the Ce-free specimen was 0.42 mg/cm^2. The weight loss decreased 0.36 mg/cm^2 and 0.28 mg/cm^2 as the Ce content increased from 0 wt.% to 0.1 wt.% and 0.2 wt.%, respectively. In other words, the high temperature oxidation resistance of the Ce added Fe-based hardfacing alloys increased with increasing the Ce content. These differences in weight loss are significant since the measured whole weight loss of the present specimens was in the order of 0.1 mg and the accuracy of the microbalance was 0.1 mg.

The weight loss was converted to thickness loss to evaluate thickness loss due to oxidation (**Fig. 1**). Thickness loss of the Ce added Fe-based hardfacing alloys in the oxidation test for 200 days ranged from 0.35 ㎛ to 0.55 ㎛ and thickness loss of Stellite 6 was about 0.13 ㎛.

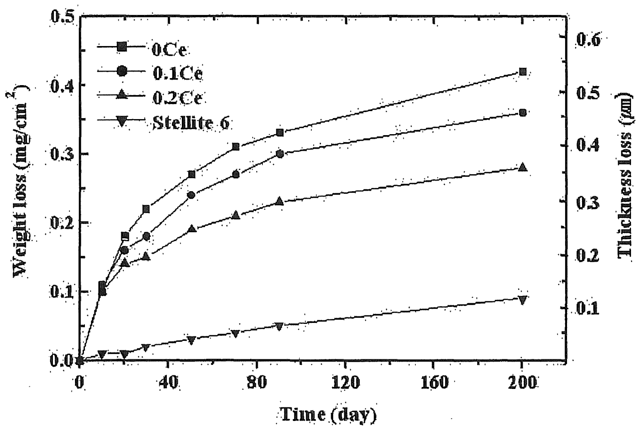


Fig. 1. Weight losses of the Ce added Fe-based hardfacing alloys and Stellite 6 as function of exposure time at 300 °C.

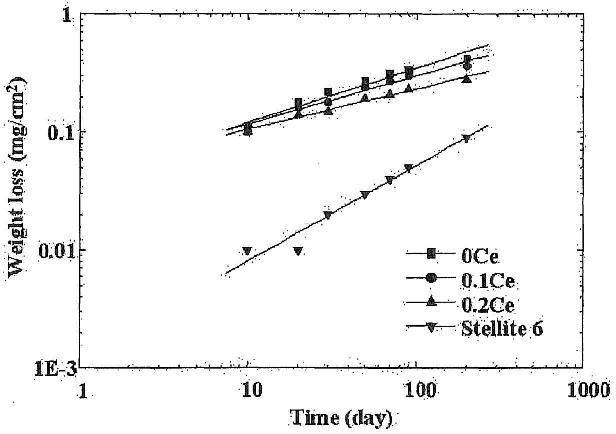


Fig. 2. Plot of logarithmic weight loss at 300 °C vs. logarithmic time for determining the rate constants

Fig. 2 is the log-log plots of $W^n=kt$ obtained from the oxidation test at 300℃, where W, k, t are weight loss, rate constant, and time, respectively. The values of n and k are summarized in Table 2. The value k, obtained from the intercepts in the log-log plots, decreased with increasing Ce content. The values of n obtained from the least square method ranged from 2.17 to 2.90. If it are operated for 30 years in nuclear power plants, it is expected that weight losses of the Ce added Fe-based hardfacing alloys and Stellite 6 would be 3.01 mg/cm^2, 1.99 mg/cm^2, 1.16 mg/cm^2, and 2.25 mg/cm^2, respectively using the predictive

Table 2. Rate constants for the oxidation of the the Ce added Fe-based hardfacing alloys and Stellite 6 at 300℃.

C	n	k, $(mg/cm^2)^n/day$	reliability
0Ce	2.17	$10*10^{-4}$	97.2%
0.1Ce	2.47	$5*10^{-4}$	98.9%
0.2Ce	2.90	$1.4*10^{-4}$	99.3%
Stellite 6	1.24	$2.5*10^{-4}$	97.9%

equations in Table 2. The predicted results for the 0.1Ce specimen and the 0.2Ce specimen are smaller than that for Stellite 6. Therefore, Ce added Fe-based hardfacing alloys are acceptable for use in nuclear power plant valves.

2. The effect of Ce on oxide layer

(1) AES analysis

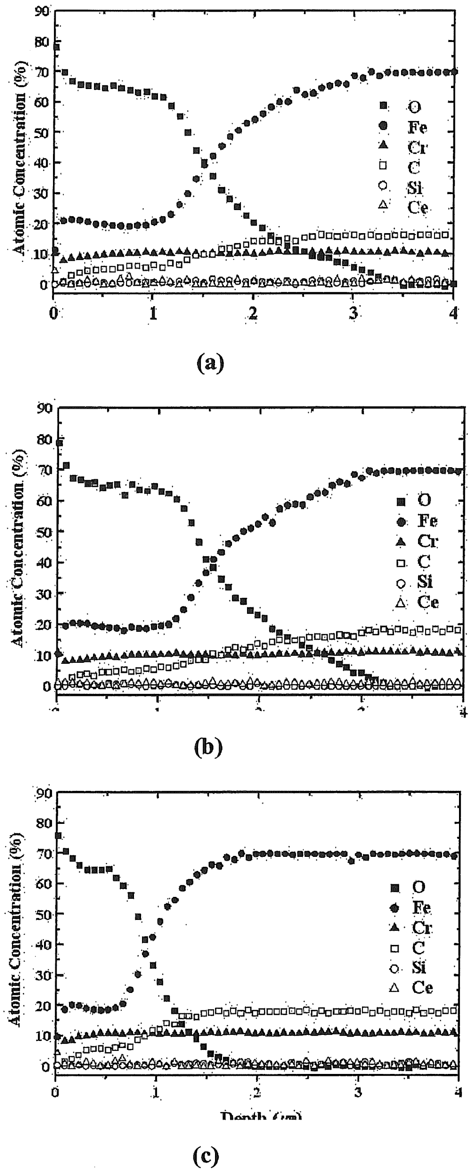
Figures. 3(a)-(c) indicate three AES spectra of the Ce added Fe-based hardfacing alloys with 0Ce, 0.1Ce and 0.2Ce, respectively. In the AES measurement, the sputter velocity was about 173Å/min. With a known velocity (V) and the sputter time (T), sputter depths (D) can be obtained by the equation, $D=VT$ [14]. The thickness of the oxide layer of the Ce-free specimen was 3.5±0.01㎛ and the oxide layer thickness of the 0.1 wt.% Ce specimen and the 0.2 wt.% Ce specimen decreased by 3.3±0.01㎛ and 1.8±0.005㎛ as the Ce content increased from 0 wt.% to 0.1 wt.% and 0.2 wt.%, respectively.

The reduction in oxide thickness is possibly due to the Ce addition. It was reported that Ce addition decreased the rate of isothermal scale growth and the maintained a fine grained oxide [15]. It also reduces the rate of oxide layer growth and the amount of compressive growth stress within the oxide layer, keeping the oxide layer from spalling. Another important Ce effect is the improvement of the adherence between the oxide layer and metal surface due to the formation of pegs of the stable oxide which extend from the metal into the oxide layer [9]. Consequently, it is thought that Ce prevents the oxide layer from spalling [10] and the weight loss of the Ce added Fe-based hardfacing alloys decreases with increasing Ce content.

(2) SEM and XRD analysis

In order to understand the effects of Ce on the new Fe-based hardfacing alloys, SEM and XRD analyses were carried out. However, no significant difference was found in SEM micrographs and XRD patterns between oxidized specimens. SEM micrographs of oxide layers of the Ce added Fe-based hardfacing alloys to 300 °C pressured-water for 200 days are shown in **Fig. 4**. It has been reported that the oxide layer of the Fe-based alloys is composed of a double layer [16]. The outer layer consists of Fe_2O_3 and is formed by the precipitation of metal ions released from the corroding surface [17]. The inner layer consists of a chromium-rich $(Fe, Cr)_3O_4$ formed by a solid state growth process [18]. These results were confirmed by XRD analyses (**Fig. 5**).

As shown in **Fig. 5**, XRD patterns of the Ce added Fe-

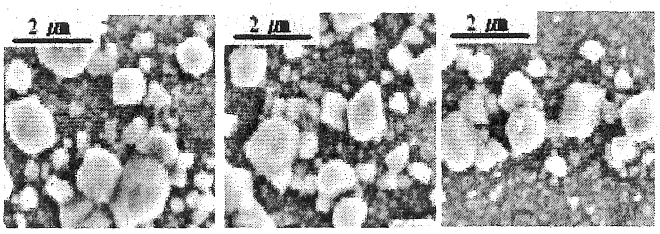


(a)

(b)

(c)

Fig. 3. AES depth profiles of the Ce added Fe-based hardfacing alloys after oxidation test for 200 days; (a) 0Ce (b) 0.1Ce (c) 0.2Ce.



(a) (b) (c)

Fig. 4. SEM micrographs of the Ce added Fe-based hardfacing alloys after oxidation test for 200 days; (a) 0 Ce (b) 0.1Ce (c) 0.2Ce.

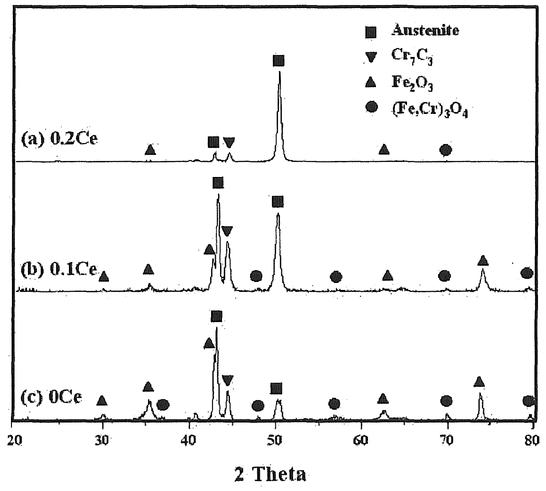


Fig. 5. XRD patterns of the Ce added Fe-based hardfacing alloys after oxidation test for 200 days; (a) 0.2Ce (b) 0.1Ce (c) 0Ce

based hardfacing alloys after oxidation test for 200 days have four phases; austenite, Cr-carbide, Fe_2O_3, and $(Fe, Cr)_3O_4$. The Ce added Fe-based hardfacing alloys had austenite and Cr-carbide phases before oxidation test. After the oxidation test, Fe_2O_3 and $(Fe, Cr)_3O_4$ were observed in these phases. XRD pattern of the Ce oxide phase on the Ce added Fe-based hardfacing alloys was not detected since Ce content was a small weight percentage.

IV. Discussion

The weight loss of the Ce added Fe-based hardfacing alloys decreased with increasing the Ce content (**Fig. 1**). It is considered that the Ce has beneficial effects on high temperature oxidation resistance of the new Fe-based hardfacing alloys. It was reported Ce improved oxide layer adherence as well as reduces the amount of compressive growth stress [13]. In this study, those two effects were thought to prevent oxide layer from spalling [10] and decrease weight loss.

As shown in **Fig. 2** and **Table 2**, the oxidation behavior of the Ce added Fe-based hardfacing alloys does not obey the simple diffusion controlled parabolic rate law, but follows the cubic rate law. Meier explained that grain boundaries were the important short-circuit paths for cations and that ions from Ce addition blocked these paths [13]. It seems that these results additionally have an effect on the improvement of the high temperature oxidation resistance in the new Fe-based hardfacing.

The high temperature oxidation resistance of the Ce added Fe-based hardfacing alloys is not better than that of Stellite 6. However, after considering all the results, it can be concluded that the results of the high temperature oxidation resistance of the Ce added Fe-based hardfacing alloys is acceptable for preventing valve water leakage. In addition, the weight loss of the oxidation test is much lower than that of cavitaton erosion test and sliding wear test in the previous studies [6, 7]. Consequently, the oxidation of the new Fe-based hardfacing alloy is not considered a contributor to radiation build-up in nuclear power plants as compared with cavitation erosion and sliding wear.

V. Summary

In order to investigate the effect of Ce on oxidation resistance of the Fe-based hardfacing alloy and to evaluate the possibility for replacing Stellite 6 with the Fe-based hardfacing alloy in term of high temperature oxidation resistance, an oxidation test was conducted with distilled water at 300 °C under 7 MPa for 200 days in an autoclave. It is thought that Ce improves high temperature oxidation resistance of the Fe-based alloy due to formation of a fine-grained oxide layer and a change from parabolic rate law to the cubic rate law. Based on the results of the oxidation test, it is expected that radiation build-up would decrease in the primary coolant water in nuclear power plants by adding Ce to the new Fe-based alloy.

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