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Effects of surface-applied ceria on the stability of thermally growing chromia scale of FeCr alloys and 310 steel

J. SHEN[*,†], L. ZHOU[†], T. LI[†]
[*]*Institute of Materials, Shanghai University, 149 Yanchang Road, 200072 Shanghai, China*
[†]*State Key Lab. of Corrosion and Protection, 62 Wencui Road, 110015 Shengyang, China*
E-mail: jianianb@online.sh.cn

The influence of surface-applied ceria on the oxidation behavior of FeCr alloys and 310 stainless steel at 1000 °C and 1100 °C has been studied. The surface-applied ceria were beneficial in reducing the growth rate of chromia scale, and were particularly effective in inhibiting the accelerated breakaway oxidation of Fe20Cr alloy in wet oxygen and spalling and cracking of the scale under cyclic oxidation. The beneficial effects of the ceria have been attributed to the improvement in the stability of the thermally growing chromia scale.

1. Introduction

Many high temperature alloys rely on the development of thermally growing chromia scale on their surface to resist the attack of high temperature oxidation. In some specific environments, the protective chromia scale may lost its stability and accelerated oxidation of the alloys occur. The protective chromia scale, which develops in dry oxygen, fails to maintain in an oxidizing atmosphere containing sufficiently large amounts of water vapor for Fe-Cr alloys [1]. Under thermal cyclic oxidation condition, the chromia scale may crack and spall because of the effect of thermal stress [2–3]. The surface-applied ceria can produce the reactive element effects (REE) to increase the oxidation resistance of the Cr_2O_3-forming alloys [4–6]. The present paper reports the studies of the effects of surface-applied ceria on the stability of chromia scale that is thermally growing on Fe-Cr and 310 stainless steel in wet oxygen and cyclic oxidation conditions.

2. Experimental procedure

The FeCr binary alloys were prepared from high purity Fe and Cr by nonconsumable arc melting and casting in an argon atmosphere. The ingots were vacuum annealed at 1100 °C for 50 h for homogeneity. The 310 stainless steel was prepared by melting and casting in a vacuum induction furnace. The compositions of the alloys determined by chemical analysis are listed in Table I. The samples (about $20 \times 10 \times 2$ mm in size) were cut, abraded and polished to 1 μm diamond surface finish.

The surface application of ceria were prepared by dipping the samples into a mixture of fine CeO_2 Powder(1 μm) with methanol, placing them in a supersonic water bath, and then drying them at room temperature. The average amount of the applied CeO_2 was 3–4 mg/cm^2, corresponding to $\sim$2% surface coverage.

The oxidation tests in wet oxygen were carried out in a thermobalance. The detailed procedure was described in the previous paper [1]. The thermal cyclic oxidation tests were conducted in an electric heating furnace. Each cycle consisted of keeping the specimens at temperature for 20 h, then cooling them down to room temperature. The total number of cycles is 20, corresponding to 400 h oxidation. The cumulative events of acoustic emission were used to monitor the cracking and spall of the oxide scale during cooling down. The assessment and procedure of the acoustic emission measurement was described in [7].

Surface analysis of the oxidized specimens involved phase identification using X-ray diffraction, scale morphology, and composition studies using SEM with an energy-dispersive X-ray analysis. The cross-sections of the oxidized specimens were examined and analyzed using optical microscopy and EPMA.

3. Results

3.1. Oxidation kinetics

The accelerated breakaway oxidation of Fe20Cr in wet oxygen (10 vol.% H_2O) at 1000 °C has been inhibited effectively by the surface-applied ceria prior-oxidation (Fig. 1). It is also shown that the chromia scale which developed in dry oxygen (pre-oxidized for 5.5 h) is not stable when water vapor is introduced. There is a more than 10 times reduction of the oxidation kinetics of Fe25Cr at 1100 °C in 1 atm oxygen by the surface-applied ceria (Fig. 2). This is equivalent to the effect of surface-applied ceria by ion sputtering [6]. The surface-applied ceria shows even more beneficial effects for the cyclic oxidation of 310 steel (Fig. 3). The 310 steel without ceria addition shows mass loss behavior after about 2 cycles of oxidation. By contrast, the steel with surface-applied ceria shows steady mass gain behavior during the whole 20 cycles exposure.

TABLE I Chemical composition (wt %) of FeCr alloys 310 steel

	Cr	Mn	Si	C	S	P	Ni	Fe
Fe-20Cr	19.65	<0.01	<0.005	0.009	0.008	<0.005		bal.
Fe-25Cr	24.74	<0.01	<0.005	0.010	0.008	<0.005		bal.
310 S.S.	24.82	1.50	0.60	0.06	0.009	<0.005	19.85	bal.

TABLE II The cumulative acoustic emission (AE) counts of Fe25Cr and Fe25Cr-CeO_2 alloys during cooling down after oxidation at 1100 °C for 20h

	Cooling temperature (°C)						
	500	450	400	350	300	250	200
Fe25Cr	1×10^2	6×10^2	5×10^3	2×10^4	1×10^5		
Fe25Cr-CeO_2	0	0	0	57	340	470	650

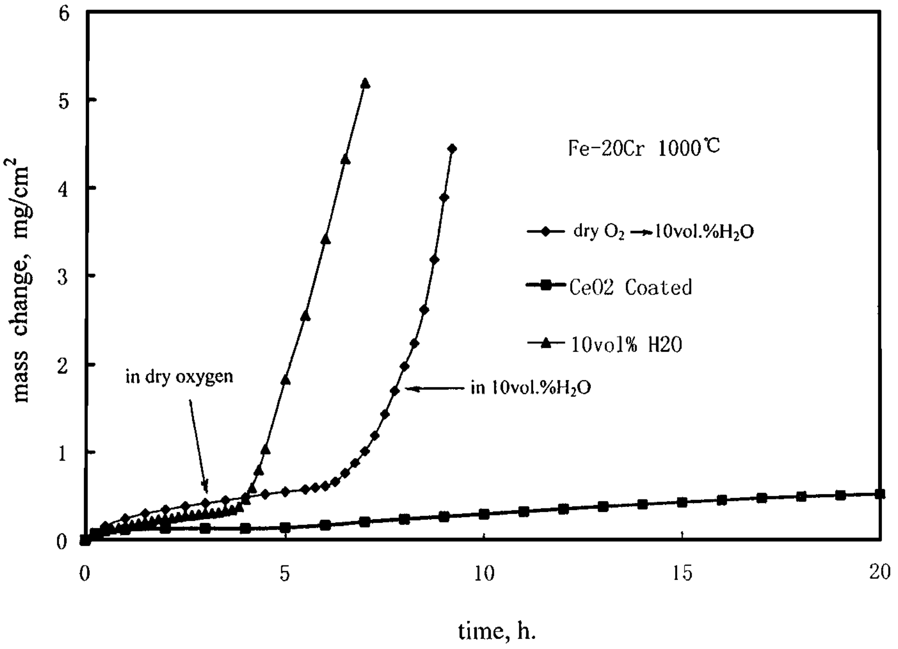


Figure 1 Oxidation kinetics of Fe20Cr and Fe20Cr-CeO_2 in wet oxygen (10 vol.% H_2O) at 1000 °C.

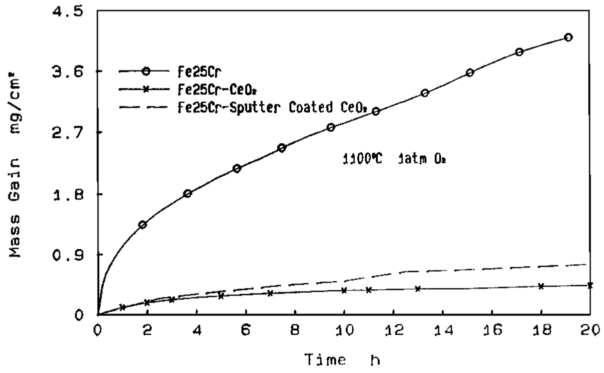


Figure 2 Oxidation kinetics of Fe25Cr and Fe25Cr-CeO_2 in 1 atm O_2 at 1100 °C.

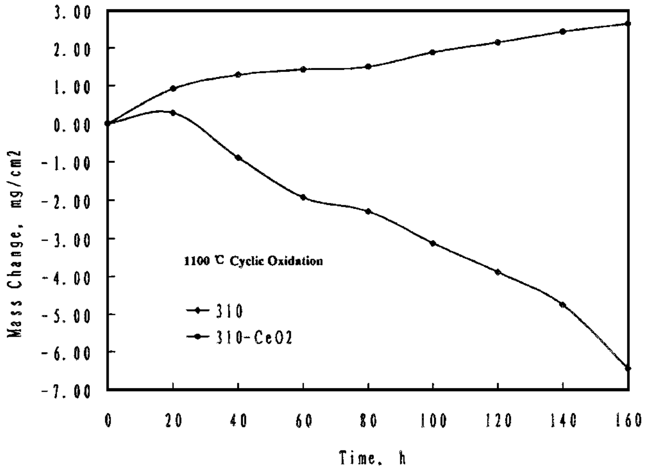


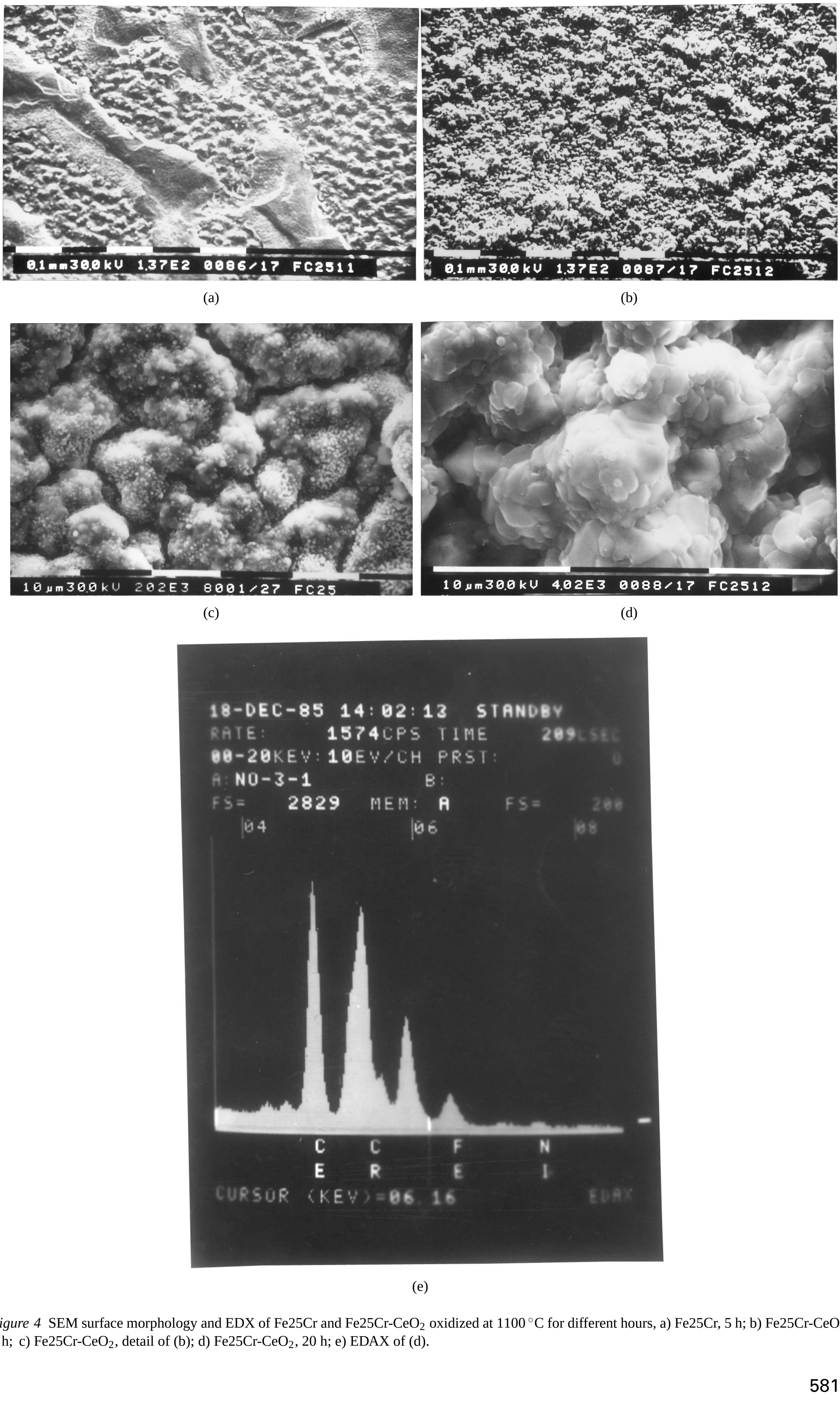
Figure 3 Cyclic oxidation kinetics of 310 s.s. and 310 s.s.-CeO_2 in air at 1100 °C.

3.2. Acoustic emission measurement

The cumulative acoustic emission counts of Fe25Cr during cooling down after oxidation at 1100 °C for 20 h is decreased by about 3 order of magnitude by the surface-applied ceria (Table II). Moreover, the cooling temperature which initiates the acoustic emission events is decreased greatly by the surface-applied ceria.

3.3. Scale morphology and composition

The surface morphology and composition of Fe25Cr and Fe25Cr-CeO_2 oxidized at 1100 °C for different times are shown in Fig. 4. The oxide scale on Fe25Cr



(a)

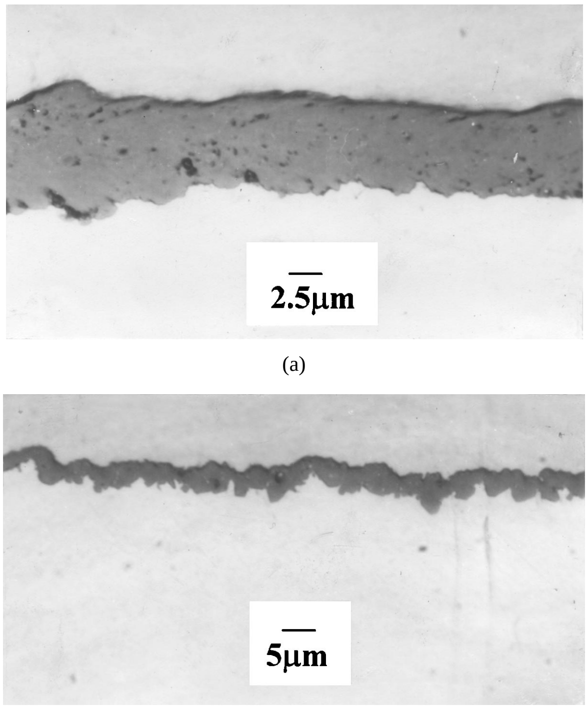
(b)

(c)

(d)

(e)

Figure 4 SEM surface morphology and EDX of Fe25Cr and Fe25Cr-CeO$_2$ oxidized at 1100 °C for different hours, a) Fe25Cr, 5 h; b) Fe25Cr-CeO$_2$, 5 h; c) Fe25Cr-CeO$_2$, detail of (b); d) Fe25Cr-CeO$_2$, 20 h; e) EDAX of (d).



(a)

(b)

Figure 5 Optical metallurgraph of cross section of Fe25Cr and Fe25Cr-CeO_2 oxidized at 1100 °C for 20 h, a) Fe25Cr; b) Fe25Cr-CeO_2.

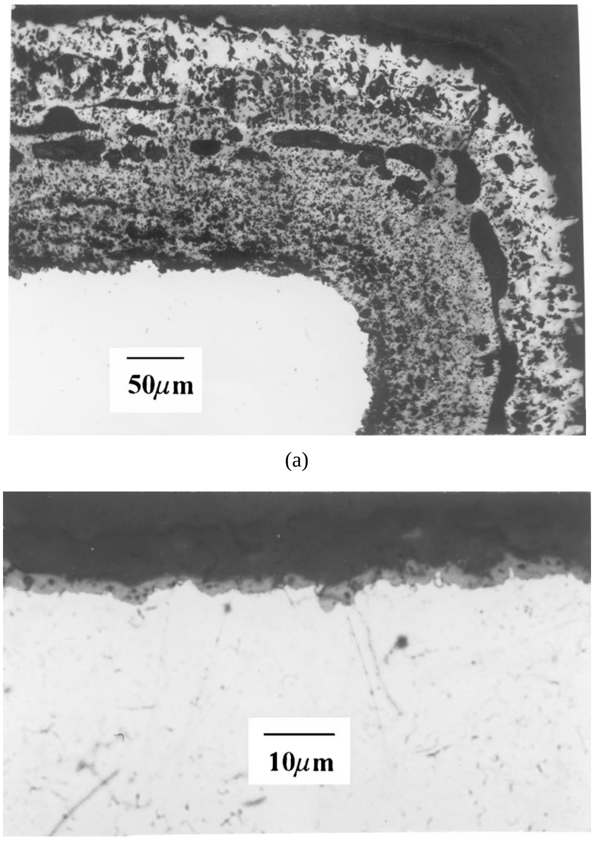
alloy shows swelling and non-uniform morphology after being oxidized for 20 h. By contrast, the oxide scale on the Fe25Cr-CeO_2 alloy shows smooth and uniform "dumbbell" morphology. The applied ceria particle has been embedded in the "dumbbell" growing scale after oxidation. The granular of the scale has become rich in cerium, though the particle morphology of applied ceria has not been shown. This implies that a kind of solid-solid reaction between the growing chromia scale and the applied ceria has taken place during the exposure.

The optical metallurgraph observation and EPMA analysis of the cross section of the oxide scale on Fe25Cr-CeO_2 reveal that a continuous thin (about 2.5 μm) chromia scale is formed after oxidation at 1100 °C for 20 h (Fig. 5). For comparison, the oxide scale on Fe25Cr is much thicker (about 30 μm) and with iron oxide is rich in the outer surface of the chromia scale.

A thick (300 μm) porous iron-rich oxide scale with wustite outer layer and FeCr spinal ($FeCr_2O_4$) inner layer is formed on Fe20Cr alloy, while a thin (3 μm) chromia scale is formed on Fe20Cr-CeO_2 after oxidation at 1000 °C in wet oxygen (10 vol.% H_2O) for 20 h (Fig. 6).

4. Discussion

Numerous studies have shown that the high temperature oxidation resistance of chromia forming alloys can be improved greatly by the addition of oxygen active elements or their oxides, either as alloying addition or as surface coating. These are so-called reactive element effects (REE) [4–5]. One of the main REE is that the scale adherence is greatly enhanced by the addition of small amounts of cerium or yttrium or their oxides. Many suggestions have been presented to explain the REE. Nicholls and Hancock [2] have suggested that the reactive element reduces the proportion of voids and flaws in the scale cross-section and so inhibits the initiation of through-scale cracking. Our recent study of the measurement of the defects (voids, flaws) at the interface of chromia/Co40Cr alloy by acoustic emission analysis confirmed that the proportion and size of the defects at the interface are decreased by ion implantation of yttrium before oxidation [8]. However, there is still no sound understanding of the mechanism of improvement of compactness of the growing chromia scale by the addition of reactive elements.



(a)

(b)

Figure 6 Optical metallurgraph of cross section of Fe20Cr and Fe20Cr-CeO_2 oxidized at 1000 °C for 20 h, a) Fe20Cr; b) Fe20Cr-CeO_2.

The results of this study clearly shows that the oxidation kinetics of FeCr alloys and 310 steel are decreased greatly by the surface-applied ceria. The beneficial effects of the surface-added ceria are more obvious in the cyclic oxidation of 310 steel and in wet oxygen oxidation of Fe20Cr. The improvement of the oxidation behavior of the tested alloys can be regarded as the increase in stability of the chromia scale thermally growing on the alloys during oxidation. the observation and analysis of the morphology and composition of the oxide scale have further revealed that the added ceria has been embedded in the growing chromia scale during oxidation.

The dissolution of ceria into the chromia scale can act as a promoter for the sintering of the chromia granular. The "dumbbell" morphology of the chromia scale with some cerium dissolved in provide some evidence for this suggestion. The voids and flaws can be reduced and the growing stress of the scale can be released during the sintering process. The chromia scale after sintering becomes more compact and coherent and has fewer defects, resulting in enhanced stability under the effects of thermal stresses. The penetration of water vapor molecules through the defects of chromia scale has been contributed to the initiation of accelerated breakaway oxidation of FeCr alloys in wet oxygen [1]. The increase of compactness of the scale by the sintering process can retard the penetration of water vapor molecules and result in inhibition of the breakaway oxidation of FeCr alloys in wet oxygen.

5. Conclusions

1. The high temperature oxidation resistance of FeCr and 310 steel have been improved significantly by surface-applied ceria before oxidation.

2. The stability of the chromia scale thermally growing on FeCr alloys is increased greatly by the surface-applied ceria under cyclic oxidation and in wet oxygen exposure.

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References

1. J. SHEN, L. ZHOU and T. LI, *Oxid. Met.* **48** 3/4, (1997) 355.
2. J. R. NICHOLLS and P. HANCOCK, in "The Reactive-Element Effects on Oxidation of Alloys," E. Lang, ed. (Amsterdam, Elsevier, 1989), p. 195.
3. J. SHEN, *Corrosion Sci. Prot. Tech.* **4** (1992) 289.
4. P. Y. HOU and J. STRINGER, *J. Electrochem. Soc.* **134** (1987) 1836.
5. E. LANG, "The Role of Reactive Elements in Oxidation Behavior of High Temperature Metals and Alloys," Elsevier Applied Sic., London/New York, 1989.
6. R. HUSSEY, P. PAPAIACOVOU, J. SHEN and M. GRAHAM, *Mat. Sci. Eng.* **A120** (1989) 147.
7. M. LI, J. SHEN and T. LI, *Acta Univ. of Beijing Sci. and Tech.* **13** (1991) 619.
8. H. JING, M. LI and J. SHEN, to be published in *The Chin. J. Corr. Prot. Met.*

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