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Effect of surface roughness on the development of protective Al$_2$O$_3$ on Fe–10Al (at.%) alloys containing 0–10 at.% Cr

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Abstract

The effect of alloy surface roughness, achieved by different degrees of surface polishing, on the development of protective alumina layer on Fe–10 at.% Al alloys containing 0, 5, and 10 at.% Cr was investigated during oxidation at 1000 °C in 0.1 MPa oxygen. For alloys that are not strong Al$_2$O$_3$ formers (Fe–10Al and Fe–5Cr–10Al), the rougher surfaces increased Fe incorporation into the overall surface layer. On the Fe–10Al, more iron oxides were formed in a uniform layer of mixed aluminum- and iron-oxides since the layer was thicker. On the Fe–5Cr–10Al, more iron-rich nodules developed on an otherwise thin Al$_2$O$_3$ surface layer. These nodules nucleated preferentially along surface scratch marks but not on alloy grain boundaries. For the strong Al$_2$O$_3$-forming Fe–10Cr–10Al alloy, protective alumina surface layers were observed regardless of the surface roughness. These results indicate that the formation of a protective Al$_2$O$_3$ layer on Fe–Cr–Al surfaces is not dictated by Al diffusion to the surface. More cold-worked surfaces caused an enhanced Fe diffusion, hence produced more Fe-rich oxides during the early stage of oxidation.
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1. Introduction

Corrosion of an alloy, being a type of chemical reaction between the alloy and the environment, can be effectively retarded if a continuously compact and slow growing oxide layer forms on the surface. Al$_2$O$_3$ is one of the most commonly utilized oxides that offers corrosion protection to alloys or metallic coatings operated at high temperatures, >900 °C [1,2], and the oxidation behaviors of binary Fe–Al and ternary Fe–Cr–Al alloys have been investigated quite extensively in view of their strong oxidation resistance [3–8]. The addition of Cr in binary Fe–Al alloys has been shown to reduce the level of alloy Al content needed to form a protective Al$_2$O$_3$ layer [2,9]. Thus, Fe–Cr–Al alloys offer an example of the so-called third-element effect [2,9,10], where the addition of B to an A–B–C alloy can reduce the critical C concentration to establish an

external scale of the C oxide: A is the most noble and C the most reactive component, while B has an oxygen affinity intermediate between those of A and C. Some have suggested [1,2] that the effect of adding B is to enhance the diffusivity of C and/or retard the diffusivity of A, so as to promote the establishment of the C oxide to the surface.

It has been demonstrated by several studies that during high temperature oxidation, Cr$_2$O$_3$ layer forms more readily on a more cold-worked surface [11–16], which often resulted from a rougher surface polish. The reason is due to an enhanced Cr diffusion within the cold-worked alloy, which supplies more Cr to the alloy surface and allows for an easier establishment of a complete protective Cr$_2$O$_3$ layer. The enhanced diffusion could arise from a higher density of dislocations in the alloy or a fine-grained near surface layer that resulted from fast recrystallization upon heating. Both provide more short circuit paths for diffusion. Preferential Cr$_2$O$_3$ growth has also been clearly demonstrated along alloy grain boundaries [13,17,18] indicating the important role of these short circuit paths on chromia scale formation. Whether the same can be achieved for alumina

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has never been investigated. Moreover, in light of the third element effect exerted by Cr in Fe–Al, how a rough surface would affect the alloy's ability to establish the protective alumina layer is indeed an important question. The purpose of this work, therefore, is to study the influence of surface roughness on the formation of Al_2O_3 oxides. Fe-based alloys containing 10 at.% Al and 0–10 at.% Cr were used with different surface finishes.

2. Experimental

Three alloys with nominal compositions of Fe–10Al, Fe–5Cr–10Al, and Fe–10Cr–10Al (all in at.%) were used in this study. The actual compositions determined by energy dispersive X-ray spectroscopy (EDS) of the alloys are Fe–9.8Al, Fe–5.3Cr–9.6Al, and Fe–10.3Cr–9.6Al, respectively. The alloys were prepared by vacuum arc-melting using appropriate mixtures of high purity metals (99.999 wt.%), and were rod-shaped with diameters of 7–8 mm. After annealing at 1100 °C in vacuum (below 10^{-7} atm) for 12 h, specimens about 0.6 mm thick were cut from each ingot along its length. A 1 mm diameter hole was drilled on each specimen near its edge for suspension purpose during weight gain studies. All specimens were mechanically abraded on successively finer abrasive SiC papers down to 1000 polishing grit (14 μm). Some of these samples were further polished to a 1.5 μm finish using diamond polishing paste. Specimen dimensions were measured for surface area calculation; they were then cleaned with water, acetone and ethanol immediately before oxidation. For the remainder of this paper, any specimen with the 1000 grit SiC finish will be referred to as having a "rough surface", while that with the 1.5-μm diamond finish, a "smooth surface".

Oxidation tests were carried out in 1 atm flowing dry oxygen at 1000 °C. Each test specimen was suspended with a quartz filament in an alumina reaction tube. A vertical tube furnace below the reaction chamber was preheated to the oxidation temperature, and then elevated to locate the specimen in its hot zone. The start of the oxidation test was taken as the time the furnace was raised, and specimen weight changes were continuously recorded with a SETARAM thermobalance.

Compositions and morphologies of the oxides formed on these specimens were first examined from their surfaces using scanning electron microscopy (SEM) coupled with EDS, and then through cross-sections after the oxidized specimens were mounted in a cold-setting epoxy resin and polished. Auger electron spectroscopy (AES) was used on some specimens to determine the in-depth distribution of elements in the scales.

3. Results

Surface roughness did not affect the oxidation kinetics of the Fe–10Cr–10Al, but significant differences were observed on the other two alloys. Fig. 1 shows the specimen weight gain as a function of oxidation time at 1000 °C for the Fe–10Al and the Fe–5Cr–10Al. For both alloys, specimens with the rough surface oxidized faster. On the Fe–10Al, a continuous, steady weight increase was observed (Fig. 1a); similar behavior was
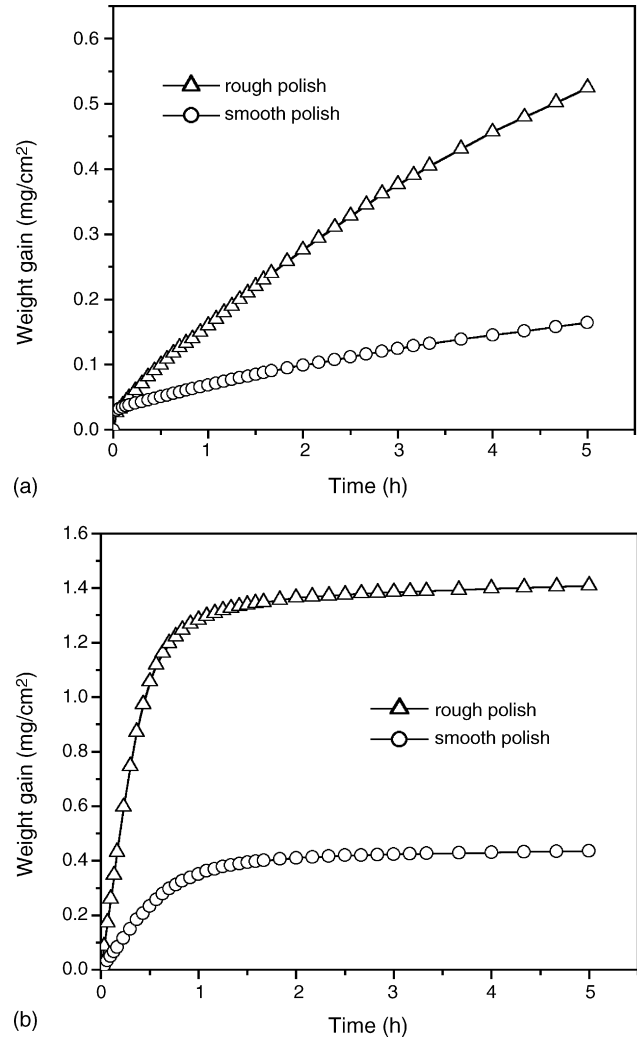

Fig. 1. Effect of specimen surface roughness on the oxidation kinetics of (a) Fe–10Al and (b) Fe–5Cr–10Al at 1000 °C in 1 atm O_2.

found on the Fe–10Cr–10Al but with much lower rates. The Fe–5Cr–10Al, on the other hand, had a pronounced fast initial stage, followed by a very slow steady stage after ∼1 h (Fig. 1b). Approximate parabolic rate constants, determined by the slope of weight gain versus time$^{1/2}$ plots, in $g^2\ cm^{-4}\ s^{-1}$, are presented in Table 1. The rate is seen to be nearly a factor of 10 higher on the rougher surface of Fe–10Al compared to that on

Table 1
Approximate parabolic rate constants, in $g^2\ cm^{-4}\ s^{-1}$, for the oxidation of Fe–10Al, Fe–5Cr–10Al and Fe10Cr10Al alloys at 1000 °C in 1 atm O_2 with different starting surface finish

Surface finish	Alloys		
	Fe–10Al	Fe–5Al–10Al	Fe–10Cr–10Al
1000 grit	2.5×10^{-11}	1.4×10^{-9}	1.7×10^{-13}
		8.5×10^{-13}	
1.5 μm	1.7×10^{-12}	7.2×10^{-11}	$1.7 \pm 0.9 \times 10^{-13}$
		2.2×10^{-13}	

The two numbers for the Fe–5Al–10Al alloy indicate initial and steady-state levels.