

INFLUENCE OF THE COLD WORK ON THE SUPERCRITICAL WATER OXIDATION OF Fe14Cr1.5Si MODEL ALLOY.

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Abstract

Ferritic/martensitic model alloy Fe14Cr1.5Si was exposed to the supercritical water (SCW) for 250 h. Oxidation was monitored through mass gain. Oxidation products of selected samples were imaged in planar and cross-sectional views. The oxidation mode depended on the surface finish of the coupons that ranged from the highly deformed surface created by sectioning with a band saw to the fine polished one. Highly deformed surface was covered by a uniform layer of protective oxide roughly 200 nm thick. Decrease in surface cold work resulted in gradual transition from thin protective to thick un-protective oxidation product.

1. Introduction

It is well known that addition of small amounts of Si to Fe-Cr alloys significantly improves oxidation resistance and scale adhesion during high temperature oxidation [1]. It has also been reported that the formation of the protective scale is affected by the surface cold work [2]. As oxidation of steels in SCW shows features of both gaseous and aqueous oxidation it can be expected that corrosion products formed in SCW are sensitive to the same variables.

A model alloy Fe14Cr1.5Si was chosen for this study as Fe14Cr is a base composition for ODS steels which are considered candidate materials for SCW applications.

2. Experimental procedure

Model alloy Fe14Cr1.5Si was supplied by CMAT in the form of a hot rolled sheet 13 mm thick. Oxidation coupons 10x20x2 mm were cut from the rolled sheet. The sectioning was performed with a band saw. Before exposure to SCW, coupon surfaces were subjected to different surface treatments. These ranged from leaving the surface unchanged after the band saw sectioning to polishing with 0.05 μm Al_2O_3 suspension. After surface preparation, coupons were ultrasonically cleaned in DI water followed by rinsing in ethanol.

Exposure was conducted in a SCW loop at the University of New Brunswick [3]. The exposure parameters were 25 MPa, 500 °C and 5 ppb of dissolved oxygen (DO). The total exposure was 250 h with one interruption after 100 h. Mass gain was recorded at the 100 h interruption and at the completion of exposure.

Oxidized surfaces were imaged after the exposure completion. Selected specimens were cross sectioned in order to analyse the oxide structure. Depending on the oxide thickness conventional SEM/EDX or STEM/ATEM were used for imaging and analysis.

3. Results and discussion

The microstructure of the hot rolled model alloys consisted of a mixture of ferrite and martensite as shown in Figure 1. Planar and cross sectional views (Figure 2) of the oxidized surfaces revealed two coexisting oxidation products – a thick porous oxide (A) and a thin compact one (B). The surface coverage with the later decreased with the decrease of surface cold work as shown in Table 1. The coverage with oxide A correlated with mass gain.

The type A oxide is a dual oxidation product typical for ferritic/martensitic Fe-Cr alloys with a Cr content too low for the formation of a protective Cr_2O_3 layer. It consists of Fe_3O_4 growing outwards from the initial sample surface and mixed $(\text{FeCr})_3\text{O}_4$ growing inwards from the original surface. A thin layer of internal oxide is also visible at the interface between the mixed oxide and the matrix.

The TEM micrograph through the oxide B is shown in Figure 3. Elemental analysis across the oxide/metal interface is shown in Figure 4. The oxide consists of an external layer of chromia, roughly 200 nm thick. At the interface between the chromia and the matrix there is a thin (less than 50 nm) layer enriched in Si, in which the Si content reaches 14 atomic percent. Formation of a pure chromia layer as well as Si enrichment at the chromia/metal interface can only be achieved through substantial outward diffusion of the two elements. For the case of Cr the extent of this diffusion is reflected by the Cr depletion zone, located immediately under the oxide/metal interface and extending 3 μm towards the bulk. Diffusion of Cr is facilitated by the high density of lattice defects present in the sub-surface deformation zone. As sample surface finish changes from untreated band saw surface to fine polishing the density of the lattice defects as well as the thickness of the deformation zone decreases. Eventually the zone of enhanced diffusion is too small to provide enough Cr for formation of a continuous Cr_2O_3 layer and the oxidation mode degrades. The degradation manifests itself through an increasing surface coverage with oxide of type A.

4. Conclusions

- Fe14Cr1.5Si alloy can form a mixture of protective and un-protective oxides in SCW.
- The un-protective oxide has a dual $\text{Fe}_3\text{O}_4/(\text{FeCr})_3\text{O}_4$ structure.

- The protective oxide is an external Cr_2O_3 scale. The fraction of the surface covered by the chromia scale increases with the increased degree of surface cold work.
- Formation of the Cr_2O_3 layer is associated with formation of a Cr depletion zone.

5. Acknowledgements

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6. References

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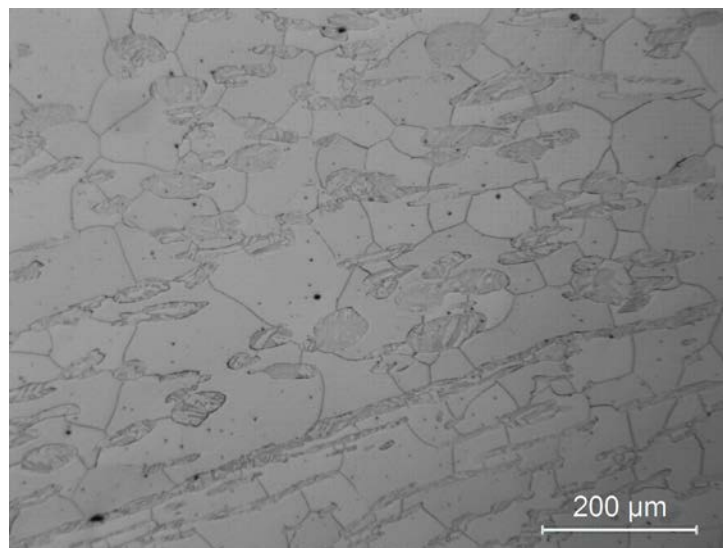


Figure 1 Optical micrograph of the hot rolled Fe-14Cr-1.5Si model alloy.

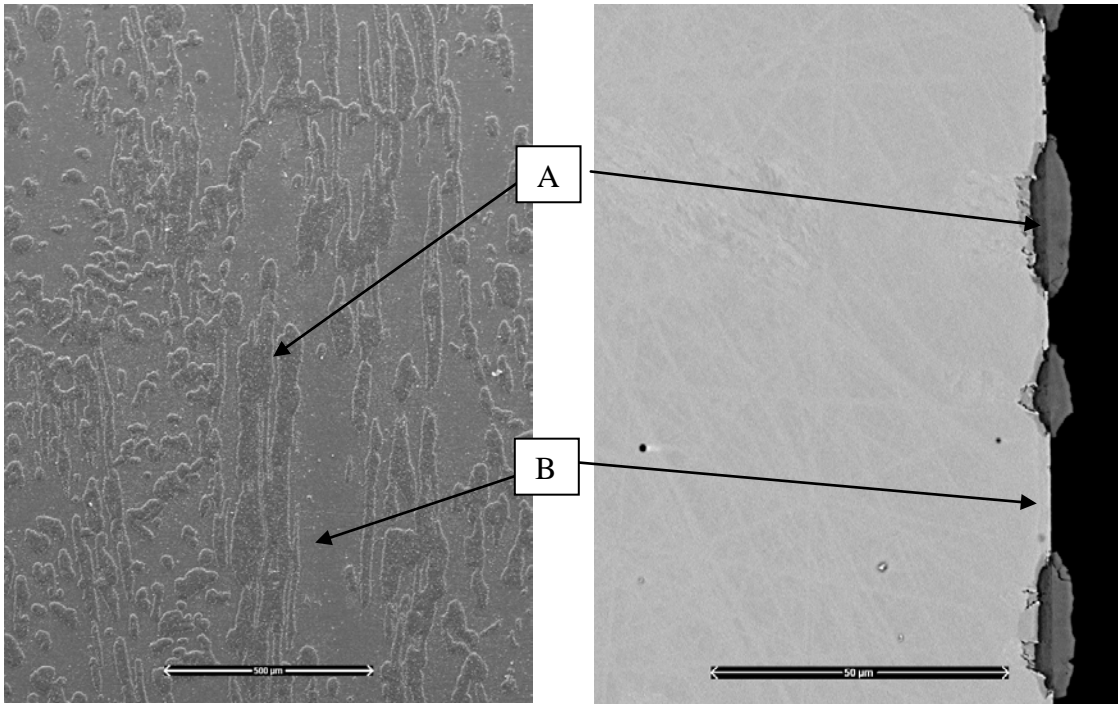


Figure 2 Planar (left) and cross sectional (right) SEM micrographs of the Fe14Cr1.5Si sample with 800 grit surface finish after 250h exposure in SCW.

Table 1 Fraction of surface covered by thick porous oxide (oxide A) for different surface finishes

surface finish	coverage by oxide A [%]	mass gain [mg/dm ³]	
		after 100h	after 250h
band saw	0	9.4	11
180 grit	30	13	17
800 grit	45	17	29
1µm diamond	100	39	66
0.05 µm Al ₂ O ₃	100	41	71

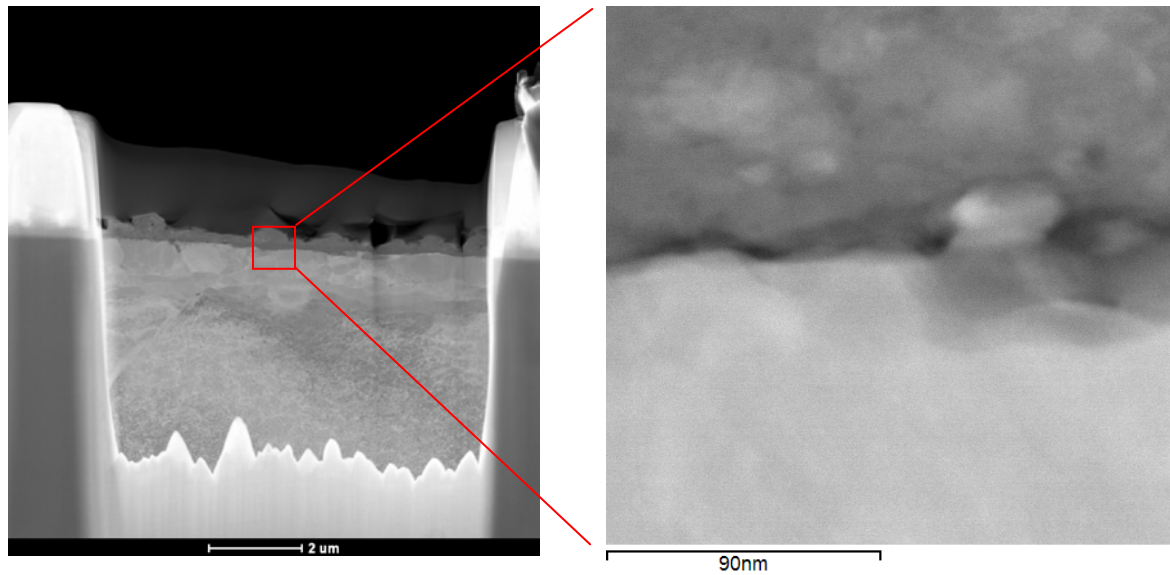


Figure 3 TEM of the cross section of the B type oxide. The cross section was prepared by the Focused Ion Beam (FIB) technique.

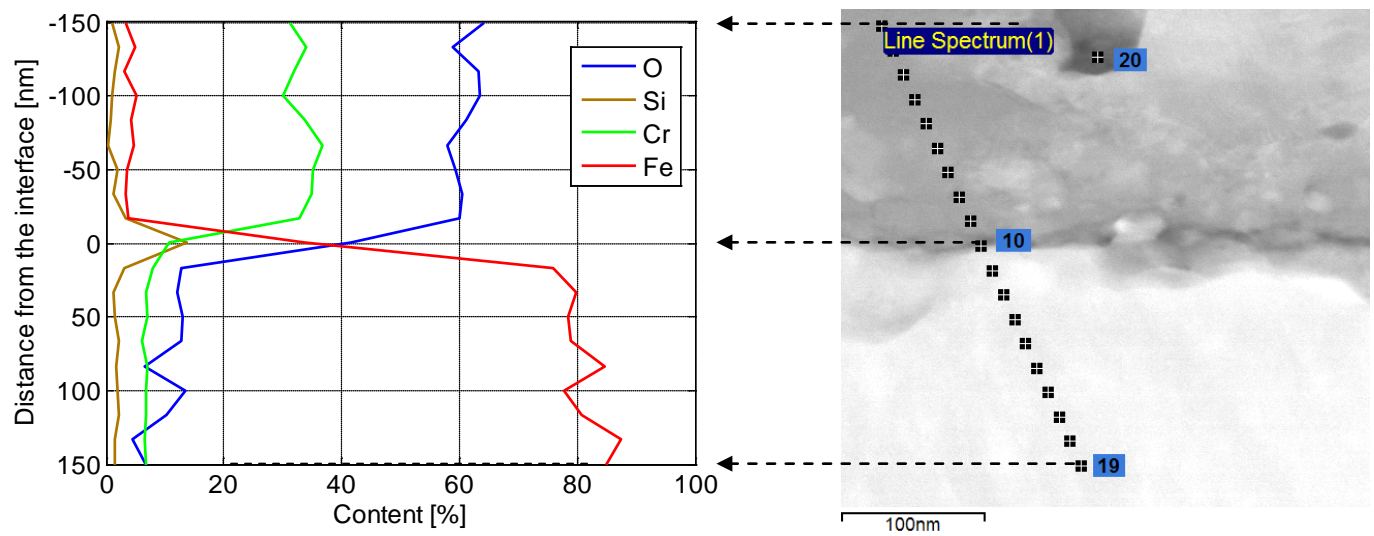


Figure 4 Elemental analysis across the oxide B/ metal interface. Positive distances are from the interface towards the bulk.