

Effect of Creep on the Oxidation Characteristics of Fe-Si Alloys at 973–1073 K

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Studies of the simultaneous creep and oxidation of Fe-1Si and Fe-4Si alloys at a constant tensile stress of $16 \text{ N} \cdot \text{mm}^{-2}$ at 973–1073 K have shown that scales formed at oxygen partial pressures of 20–1013 mbar were thicker by a factor of 2 than those formed on uncrept specimens. Scales on uncrept alloys comprised alternate layers of wustite and fayalite, whereas scales on crept alloys exhibited an additional external layer of magnetite. Only intergranular oxidation (fayalite) was observed in uncrept alloys, but crept alloys showed both intra- and intergranular oxidation (silica). Uniquely nodular scales were formed only on the Fe-4Si alloy on crept and uncrept specimens. Oxidized, uncrept Fe-1Si showed a fine-grained ferrite substrate which was absent in the crept alloy. It is believed that oxide growth stresses stimulated a recrystallization process.

KEY WORDS: Iron-silicon; oxidation; creep; scale morphology.

INTRODUCTION

Many studies¹⁻⁶ of the mechanical aspects of the high-temperature oxidation of metals have been concerned primarily with the generation and relief of stress during the growth or spalling of oxide scales. Where volume changes in a strongly adherent, growing oxide produce a compressive stress, there is usually a matching tensile stress in the underlying metal substrate for strain compatibility across the interface. Stress relief or relaxation may

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be achieved through either fracture or deformation of the oxide or by recovery, recrystallization, or deformation of the substrate.

It has become increasingly important to regard the mechanical and chemical aspects of oxidation as *interdependent*. In this respect the present work has been chiefly concerned with simultaneous oxidation and creep of Fe-Si alloys at 973–1073 K in environments of different oxygen potential. In earlier work,⁷⁻¹¹ we have shown that oxidation strengthening or weakening can arise from oxidation products or mechanisms, respectively. For example, strongly adherent scales and internal oxides oppose deformation of the substrate in dislocation creep. However, an oxidation-induced vacancy flux will facilitate dislocation climb, thereby producing an increased creep rate. Each of these effects was found to be strongly dependent on the oxygen partial pressure of the test environment.

A further objective of this work was to examine the effects of an externally applied tensile stress, and the consequent substrate creep deformation, on the oxidation characteristics of Fe-1Si and Fe-4Si alloys, which we now describe.

EXPERIMENTAL PROCEDURE

A detailed account of the creep testing facility for ultrahigh vacuum (UHV) and controlled atmosphere conditions used in the present studies has been given elsewhere¹² and therefore only an outline of the procedure is now presented.

Creep test specimens of nominal composition Fe-1Si and Fe-4Si (Table I) were machined to 25-mm gauge length \times 5-mm gauge diameter from a rolled rod, then vacuum annealed, electropolished, and finally cleaned in the test rig by adapting the UHV system to permit hydrogen reduction of the air-formed surface oxide film before commencing a test. The partial pressure of oxygen in the test chamber was then adjusted to be within the range 10^{-9} – 10^{-4} mbar to produce thin surface oxide films of \sim 2–4 μ thick; thicker scales up to 40- μ thickness were produced in a second rig with higher oxygen pressures in the range 20–1013 mbar. Initial oxidation took place under zero applied stress conditions.

Table I. Composition of Experimental Alloys

Alloy	Elements (wt.%)						
	C	Mn	Si	S	P	Cr	Al
Fe-1Si	0.002	0.009	1.07	0.006	0.006	0.015	0.004
Fe-4Si	0.006	0.013	4.22	0.007	0.017	0.015	0.007

Separate constant stress and constant load tests were conducted in the applied stress range of $13\text{--}26\text{ N}\cdot\text{mm}^{-2}$ at temperatures of 973 K, 998 K, 1023 K and 1073 K with constant oxygen partial pressures. The minimum detectable creep strain was $5\times 10^{-3}\%$.

Additional unloaded cylindrical specimens, 2 mm length \times 5 mm diameter, were supported alongside the creep specimens in order to obtain a comparison of the uncrept and crept alloy and scale microstructures on examination by conventional optical and electron metallographic techniques. X-ray powder samples, replicas, and thin foils were also prepared to identify the nature of the scales and internal oxide particles, and to observe the form of particle-dislocation interactions.

RESULTS AND DISCUSSION

Effect of Creep on Scale Morphology

At 998 K with a $p_{\text{O}_2} = 10^{-3}$ mbar and an applied tensile stress of $16\text{ N}\cdot\text{mm}^{-2}$, where higher creep rates were found $\sim 10^{-4}\text{ min}^{-1}$, the scale formed on the Fe-1Si alloy was $\sim 4\text{-}\mu$ thick comprising a porous region of wustite and magnetite with a $6\text{-}\mu$ thick subscale of mainly fayalite (Fig. 1). The corresponding scale formed on the Fe-4Si alloy showed a thicker subscale with internal oxidation and cracks in the outer scale region. A fine grain size was evident in the subscale of the Fe-1Si alloy which had been crept at 1073 K at a higher rate, $\sim 10^{-3}\text{ min}^{-1}$.

At higher p_{O_2} (> 20 mbar), where lower creep rates were observed, $\sim 10^{-5}\text{ min}^{-1}$, thicker scales were formed ($\sim 40\text{-}\mu$ thick) with subscales in which intergranular oxidation had occurred (Fig. 2). The alloys, however, showed some significant differences between their respective scale morphologies.

Uncrept alloys of Fe-1Si and Fe-4Si oxidized at 998 K for 330 min at oxygen pressures of 20–152 mbar and 59–1013 mbar, respectively, showed surface scales comprising alternate layers of wustite and fayalite. The number of discontinuous fayalite layers increased with increasing p_{O_2} as the inner fayalite layer became separated from the alloy surface. In contrast, the *crept* alloys, similarly oxidized, were found to have an outer layer of magnetite below which wustite and fayalite formed the remainder of the scale. The incidence of scale cracking was less evident when compared with that observed for the *uncrept* alloys.

Internal oxidation in the *uncrept* alloys was mostly confined to the grain boundaries (intergranular oxidation) whereas in *crept* alloys, internal oxidation within the grains in addition to intergranular oxidation was most apparent (Fig. 3). Microanalysis confirmed that the internal oxide particles

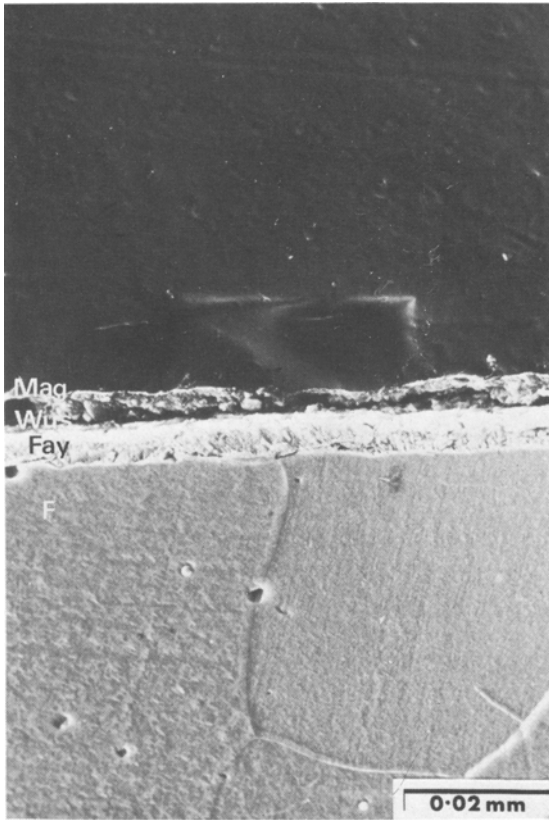


Fig. 1. Transverse section of Fe-1Si crept at $16 \text{ N} \cdot \text{mm}^{-2}$ at 998 K in argon ($p_{\text{O}_2} = 10^{-3}$ mbar); $\epsilon = 9\%$ in 330 min; showing subscale and porous outer scale. Etched 3% Nital. Mag = Fe_3O_4 ; Wus = FeO; Fay = Fe_2SiO_4 ; F = ferrite (Fe).

were silica (SiO_2) in the *crept* alloys but primarily fayalite ($2\text{FeO} \cdot \text{SiO}_2$) in the *uncrept* material. This latter feature was also found by Logani and Smeltzer.¹³ Undoubtedly, grain boundaries are effective paths for oxygen migration and convenient sites for the nucleation and growth of internal oxides. The applied tensile stress, augmented by tensile stresses in the substrate through scale growth, may additionally increase the likelihood of oxygen diffusion favoring the formation of internal oxides within substrate grains. Fayalite forms from a reaction involving silica, wustite, iron, and oxygen which for the *uncrept* material would be less disrupted than in the *crept* condition, in which it is possible that recrystallization processes might change more markedly the chemical activity of each reactant in the

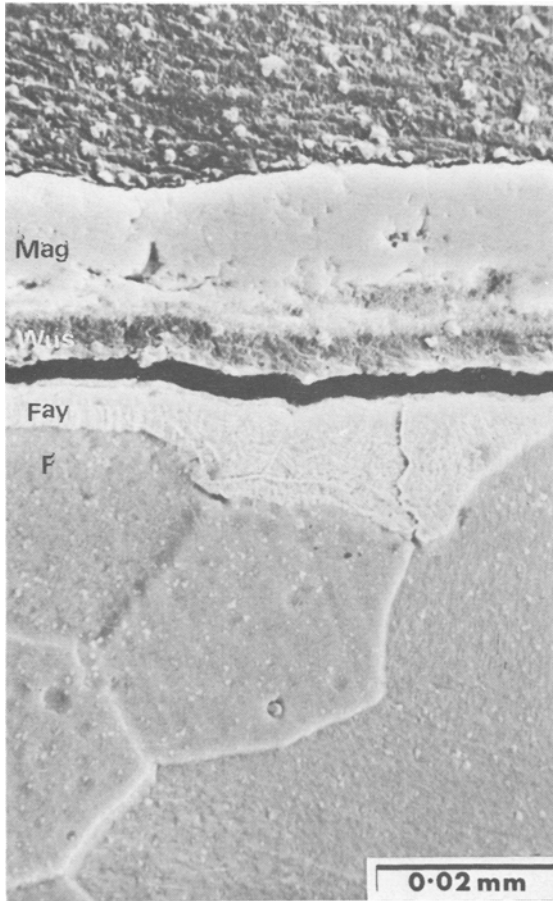


Fig. 2. Transverse section of Fe-1Si crept at $16 \text{ N} \cdot \text{mm}^{-2}$ at 998 K with $p_{\text{O}_2} = 160 \text{ mbar}$ showing subscale with intergranular oxidation. Etched 3% Nital. Mag = Fe_3O_4 ; Wus = FeO ; Fay = Fe_2SiO_4 ; F = Fe.

substrate. It is also conceivable that the local compressive stress generated in the substrate when silica particles are formed may be more readily accommodated in *crept* material. It is interesting to note that a stress between 34 and $123 \text{ N} \cdot \text{mm}^{-2}$ was produced by SiO_2 formation in the substrate of an Fe-0.27%Si alloy internally oxidized at 1523 K for 4 hr.¹⁴

A unique feature of the Fe-4Si alloy crept at the higher p_{O_2} of 1013 mbar was the occurrence of oxide nodules (Figs. 4 and 5). These were randomly sited in the outer scale together with a well-developed subscale,

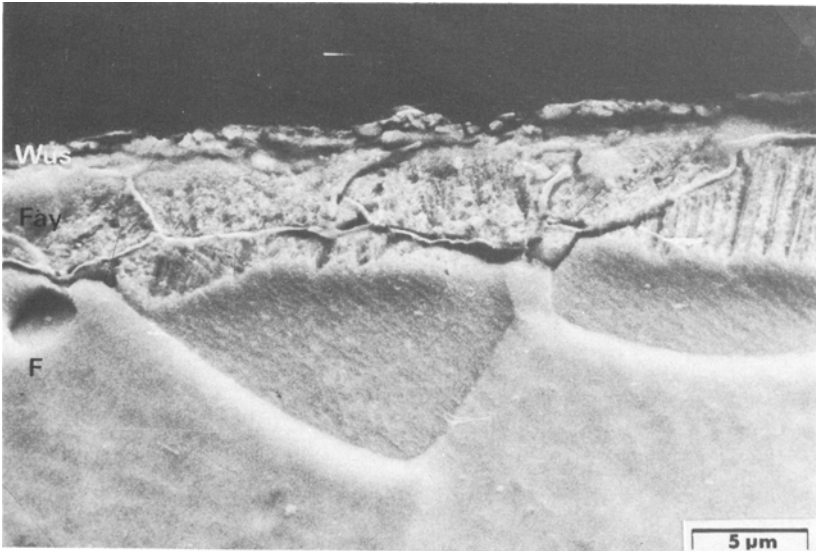


Fig. 3. Transverse section of Fe-1Si crept at $16 \text{ N} \cdot \text{mm}^{-2}$ at 1073 K in argon; $\epsilon = 16\%$ in 25 min; showing fine grains in subscale and fragmented outer scale. Etched 3% Nital. Wus = FeO; Fay = Fe_2SiO_4 ; F = Fe.

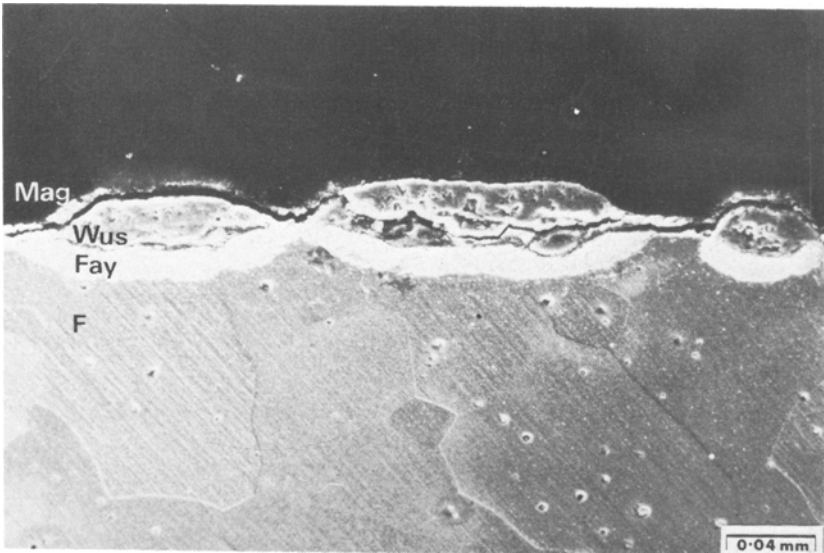


Fig. 4. Transverse section of Fe-4Si crept at $16 \text{ N} \cdot \text{mm}^{-2}$ at 998 K with $p_{\text{O}_2} = 1013 \text{ mbar}$ for 330 min, showing internal oxides, subscale and nodular outer scale. Etched 3% Nital. Mag = Fe_3O_4 ; Wus = FeO; Fay = Fe_2SiO_4 ; F = Fe.

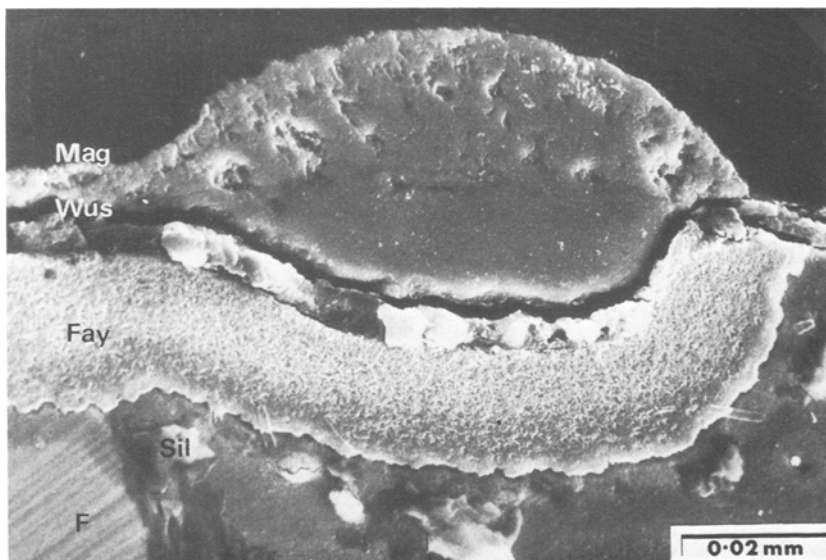


Fig. 5. Higher magnification of a single oxide nodule shown in Fig. 4. Mag = Fe_3O_4 ; Wus = FeO ; Fay = Fe_2SiO_4 ; Sil = SiO_2 ; F = Fe.

internal oxides, and some recrystallized grains. No nodular scale features were observed for the lower p_{O_2} tests whereas in the higher p_{O_2} tests the number of nodules increased with increasing oxygen pressure. For example, the number of nodules per unit length of oxide scale for $p_{\text{O}_2} = 1013$ mbar was almost twice that for the $p_{\text{O}_2} = 162$ mbar environment. It was also noted that cracking had occurred in the nodules and in the areas of scale adjacent to the nodules. It would not be appropriate to discuss nodular scale formation at length in this paper; it is a well-known phenomenon which has been repeatedly documented for many years.¹³ Suffice it to say that the upper domes of the nodules on Fe-Si alloys comprise wustite and magnetite which is anchored to the substrate through a subscale of fayalite and silica particles. It is believed that intergranular regions may serve as effective sites for oxide nodules growth. Nodular scale, intergranular oxidation, and internal oxides, separately or combined, could provide strengthening effects. In this respect, the experimental results bear out the experiences of many other workers.^{2,3}

Effect of Creep on Scale Thickness and Growth Rate

A necessary adjunct of our work was to compare *uncrept* oxidized surface structures with those of *crept* specimens, which had been oxidized

together in the same environment, in order to establish the nature and possible cause of changes due to oxidation alone or from simultaneous processes of creep and oxidation. There is supporting evidence^{2,9} for the claim that the rate and extent of growth of an oxide scale are enhanced by an applied tensile stress in creep conditions.

We found that the thickness of scale formed on *crept* Fe-1Si at 998 K in 330 min with $p_{O_2} = 152$ mbar was 35 μ , whereas for an *uncrept* specimen, the scale was only 16- μ thick. Likewise for the Fe-4Si alloy, also at 998 K but with $p_{O_2} = 1013$ mbar, the *crept* specimen had a scale 40- μ thick and for the *uncrept* specimen a scale only 20- μ thick had formed. The reason why a scale grown on a stressed specimen should be approximately twice as thick as one produced on an unstressed specimen may be linked with the possibility of there being a greater vacancy flux injected into the substrate of the crept alloy. In dislocation creep, the climb process would tend to reduce the vacancy concentration, V_{Fe} near the substrate-scale interface region, which would promote a continuation of the reaction:



thereby relieving growth stresses in the oxide and increasing the oxidation rate. Gibbs and Hales¹⁵ proposed the following equation for the rate of thickening of an oxide scale (dx/dt):

$$dx/dt = B\Omega(p_{O_2})^{-1/n}[(V_L)_e/(V_L)]^{2/n}(D_L/x) \quad (2)$$

where Ω is the atomic volume; $(V_L)_e$ is the equilibrium vacancy concentration of metal; (V_L) is the vacancy supersaturation at the scale-metal interface; D_L is the self-diffusion coefficient of the diffusing ion across the scale; x is the thickness of the scale; and n , B are constants. According to Eq. (2) a decrease in the vacancy supersaturation at the scale-metal interface would favor an increase in the rate of thickening of the scale.

Effect of Creep on Scale Adhesion

It was observed that as the oxidation temperature increased there was a greater tendency for the scales to become less adherent (Figs. 1, 3). Weak scale adhesion might arise when growth-stress effects contribute to interfacial cracks and when the creep ductility of a scale is more limited than that of the underlying substrate. However, there have been instances⁷ when scales comprised mainly of wustite on iron have shown strong adhesion at temperatures of 923–1123 K in tensile creep conditions albeit at a lower applied stress of $4 \text{ N} \cdot \text{mm}^{-2}$ than for the present results. Ilschner *et al.*¹⁶ experimentally determined creep rates for wustite and suggested that it was creep by dislocation climb that relieved growth stresses thereby pre-

venting spalling during isothermal oxidation. A similar explanation for CoO was offered by Strafford and Gartside.¹⁷

We found some evidence for the Fe-1Si alloy to support the view that where substrate deformation had occurred as a consequence of oxide stress generation the resultant stress relaxation in the oxide might have led to fewer cracks forming, thereby enabling stronger adhesion to be maintained.

Effect of Simultaneous Creep and Oxidation on Cavitation

Cavitation and small cracks (Fig. 6) observed in the grain boundaries of the Fe-1Si alloy after creep at the higher $p_{O_2} = 101$ mbar were not observed after creep at lower p_{O_2} , nor were they found in uncrept Fe-1Si specimens which had been oxidized at either low or high p_{O_2} . This suggests, therefore, that cavitation and void linking to give small cracks are perhaps dependent on the *joint* processes of creep and oxidation acting simultaneously.

The origins of cavitation and internal cracks in creep processes are associated with the combined effects of vacancy condensation and grain-boundary sliding which may have been augmented in the present work by oxidation-induced vacancies and further influenced by oxidation stresses. Harris,¹⁸ however, has argued that the growth of intergranular voids in metal substrates during oxidation is not due to vacancy injection from the

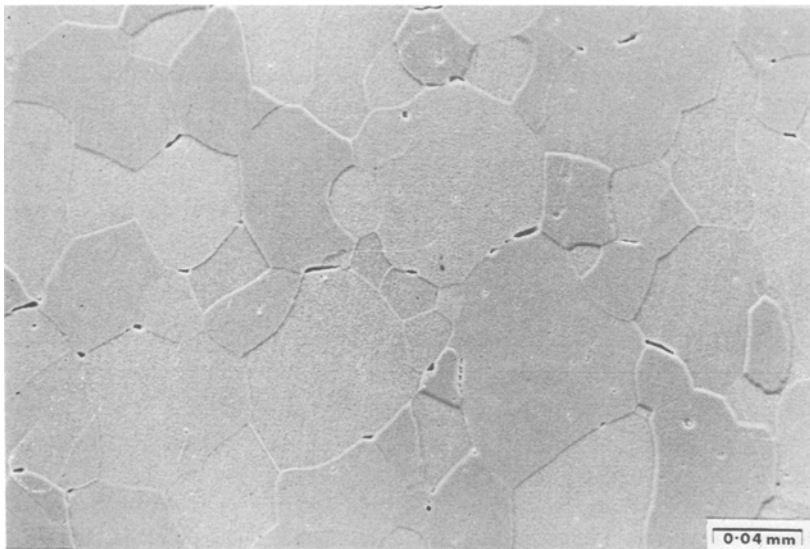


Fig. 6. Transverse section of Fe-1Si crept at $16 \text{ N} \cdot \text{mm}^{-2}$ at 998 K with $p_{O_2} = 101$ mbar; $\epsilon = 7.5\%$ in 330 min; showing central cavitation and small cracks. Etched 3% Nital.

scale–metal interface but is a consequence of the oxidation-induced tensile stress causing void growth by the Hull–Rimmer creep mechanism.¹⁹ But the substantial evidence for oxidation-induced void formation in the oxidation of nickel^{20–22} is suggested to be due to vacancy precipitation from the reaction:



A more recent study by Caplan *et al.*²³ has further challenged the earlier work on nickel concluding that it is probably traces of carbon segregated in grain boundaries which promote void nucleation during grain-boundary sliding. No cavitation was observed when the nickel was decarburized before oxidation.

In spite of these contrasting explanations for cavitation in nickel, we believe that in the present work the source of the vacancy flux and its contribution to cavitation in the Fe–Si alloys is described in Eq. (1).

Creep tests at the higher p_{O_2} revealed a strengthening effect which we ascribed to internal oxidation. This response would favor the development of a supersaturation of vacancies in the substrate when absorption through dislocation climb became less effective than at lower p_{O_2} . On the one hand, it is quite conceivable that some of the internal oxide particles, as well as grain boundaries, could act as favorable sites for vacancy condensation leading to cavitation. On the other hand, the incidence of cavitation and wedge cracking through grain-boundary sliding in the substrate would be considerably lessened by the intergranular oxides. It seems reasonable to conclude, therefore, that the cavitation observed in the Fe–Si alloys has arisen primarily from the oxidation process and that vacancy injection and subsequent condensation has contributed a greater part than that due to either the oxidation stress effects described by Harris¹⁸ or grain-boundary sliding. Even so this is clearly an area for further study which requires a far more discriminating experiment than has been possible in the current work.

Effect of Simultaneous Creep and Oxidation on Substrate Recrystallization

One of the most striking differences observed between the structures of the uncrept and crept oxidized Fe–1Si alloy was the appearance of fine, apparently recrystallized, grains in the substrate of the *uncrept* material. After 330 min oxidation at 998 K with $p_{\text{O}_2} = 60$ mbar, the near-surface substrate ferrite grain size was $\sim 5 \mu$ in a band of depth 10–15 μ , whereas the remainder of the substrate and the bulk structure grain size was 39 μ . No such difference in grain size was observed in the crept specimens, nor

when uncrept specimens were oxidized for similar periods at a much lower $p_{\text{O}_2} = 10^{-9}$ mbar.

There is a wealth of evidence²⁴ for the claim that oxide growth stresses may be large enough to cause the underlying metal substrate to deform locally. The ensuing dislocation network refinement may later be altered, during oxidation, by partial recovery and sub-grain formation which would contribute to some stress relaxation as oxidation continued. In the present work, there is the distinct possibility that the final sub-grain or recrystallized grain size may have been governed by the subscale internal oxides, which have pinned some of the grain boundaries thereby preserving a relatively fine grain size in the oxidized material. The absence of such a fine grain size in the uncrept Fe-1Si alloy oxidized at the lowest p_{O_2} is thought to be due to the relatively lower growth stress produced by the considerably thinner oxide film, which would grow at a much slower rate and be much less effective in stimulating substrate deformation.

The absence of a fine grain substrate in the *crept* Fe-1Si alloy is believed to be because the steady-state deformation of the bulk material, which would yield a final grain size based upon characteristic recovery creep events, would override the oxidation-induced grain refinement previously mentioned. We have no evidence to the contrary. Similarly in the *crept* Fe-4Si alloy, no difference in grain size was observed between the near-surface and bulk structures, nor was any difference found between the grain sizes of uncrept and crept specimens. It would seem therefore, that the solute strengthening by silicon in the Fe-4Si alloy has been responsible for the greater resistance to oxidation stress effects and hence the apparent uniformity of grain size throughout the specimen section.

CONCLUSIONS

1. Scales formed at $p_{\text{O}_2} = 20$ –1013 mbar at 973–1073 K on Fe-1Si and Fe-4Si alloys crept under an applied tensile stress of $16 \text{ N} \cdot \text{mm}^{-2}$ were thicker by a factor of 2 than for uncrept alloys.

2. Alternate layers of wustite and fayalite were formed on uncrept alloys, but an additional outside layer of magnetite was formed on crept alloys.

3. Only intergranular oxidation (fayalite) was observed in uncrept alloys, whereas, inter- and intragranular oxidation (silica) occurred in crept alloys.

4. Nodular scales were produced only on the Fe-4Si alloy for both crept and uncrept alloys.

5. Oxidized, uncrept Fe-1Si showed a fine-grained ferrite substrate, which was probably induced by oxide growth stresses.

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