Metallographic preparation and degradation of the τ-phase (FeAl$_2$S$_4$) formed after high-temperature oxidation–sulfidation of Fe–Al alloys

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Abstract

The stability of corrosion products formed after high-temperature exposure of an Fe–5 wt.% Al alloy in an oxidizing–sulfidizing environment was investigated both during metallographic preparation and subsequent exposure to the ambient environment. The primary phases formed were an outer layer of iron sulfide (Fe$_{1-x}$S) and an inner layer composed of τ-plates (FeAl$_2$S$_4$) and iron sulfide particles. No difficulties were found concerning the stability of the iron sulfide phases, but it is known that the τ-phase is easily hydrolyzed by water. Therefore, standard metallographic procedures where water is used as a lubricant and/or cleansing solution during preparation could not be exercised. Using scanning electron microscopy, energy dispersive spectroscopy, and electron probe microanalysis, the effect of the use of various lubricants and/or cleansing solutions was examined in order to produce good quality, polished cross-sections of the corrosion scales. The best results were obtained using 200-proof dehydrated ethyl alcohol as the lubricant and cleansing solution. It was also observed that post-exposure of polished samples to the ambient environment degraded the microstructure with time. It is believed that moisture from the air reacted with the τ-phase, resulting in the evolution of hydrogen sulfide gas. © 2000 Elsevier Science Inc. All rights reserved.

Keywords: Metallographic preparation; Degradation; FeAl$_2$S$_4$; High-temperature oxidation; Sulfidation; Fe–Al alloys

1. Introduction

An important aspect in determining the corrosion behavior of a material is the post-exposure characterization of the corrosion products that develop. Analysis typically requires observing the cross-sectional microstructure and determining the chemical composition in this orientation using electron probe micro-

analysis. This technique requires a flat, polished surface in order to gain quantitative chemical information. However, the corrosion products may not be stable with respect to the lubricants and/or cleansing solutions, usually water, used during standard metallographic procedures to prepare polished cross-sections. Many corrosion phases containing main and alloying elements standard in materials typically used for high-temperature applications are found to have some solubility in water. Sulfides and sulfates of aluminum (Al$_2$S$_3$, Al$_2$(SO$_4$)$_3$), iron (FeSO$_4$, Fe$_2$(SO$_4$)$_3$), and nickel (NiSO$_4$) are a few examples

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[1]. To substantiate this point, problems were encountered by Mrowec and Wedrychowska [2] during the preparation of corrosion scales after sulfidation of Fe−Cr−Al alloys at high temperature. They observed that the aluminum sulfide corrosion product degraded in a matter of hours when exposed to moisture from the air. A similar problem was also experienced during research conducted on Fe−Al alloys exposed to high-temperature oxidizing−sulfidizing atmospheres [3−5]. Surface reactions with the gaseous environments led to the development of a bi-layered scale composed of multiple sulfide phases. While the outer iron sulfide phase was stable with respect to the ambient environment and metallographic lubricants, the inner layer containing the τ-phase was not. This paper will briefly review the general characteristics of the τ-phase that was observed to develop in the corrosion product microstructure, followed by problems associated with preparing the samples using standard metallographic techniques and its degradation once exposed to ambient air. A procedure used to minimize degrada-

tion of the corrosion products during metallographic procedures will also be described.

2. Experimental procedure

Fe−Al alloys containing 5 wt.% Al were produced by arc melting high purity components under an argon atmosphere then drop casting into a water-cooled copper mold at Oak Ridge National Laboratory (Oak Ridge, TN). Sulfidation experiments were conducted using a Netzsch STA 409 high-temperature thermogravimetric balance. Before testing, specimens were cut to dimensions of $10 \times 10 \times 2$ mm, ground to 600 grit with silicon carbide papers, ultrasonically cleaned in methanol, and weighed to the nearest mg. Samples were heated at a rate of $50°C/min$ and isothermally held at $700°C$ for 50 h. An argon−base gas mixture of 0.1% H_2−1.0% H_2S−5 ppm O_2 (by volume percent) was used with the partial pressures of oxygen [pO_2] and sulfur [pS_2] set at 10^{-25} and 10^{-4} atm, respectively, at
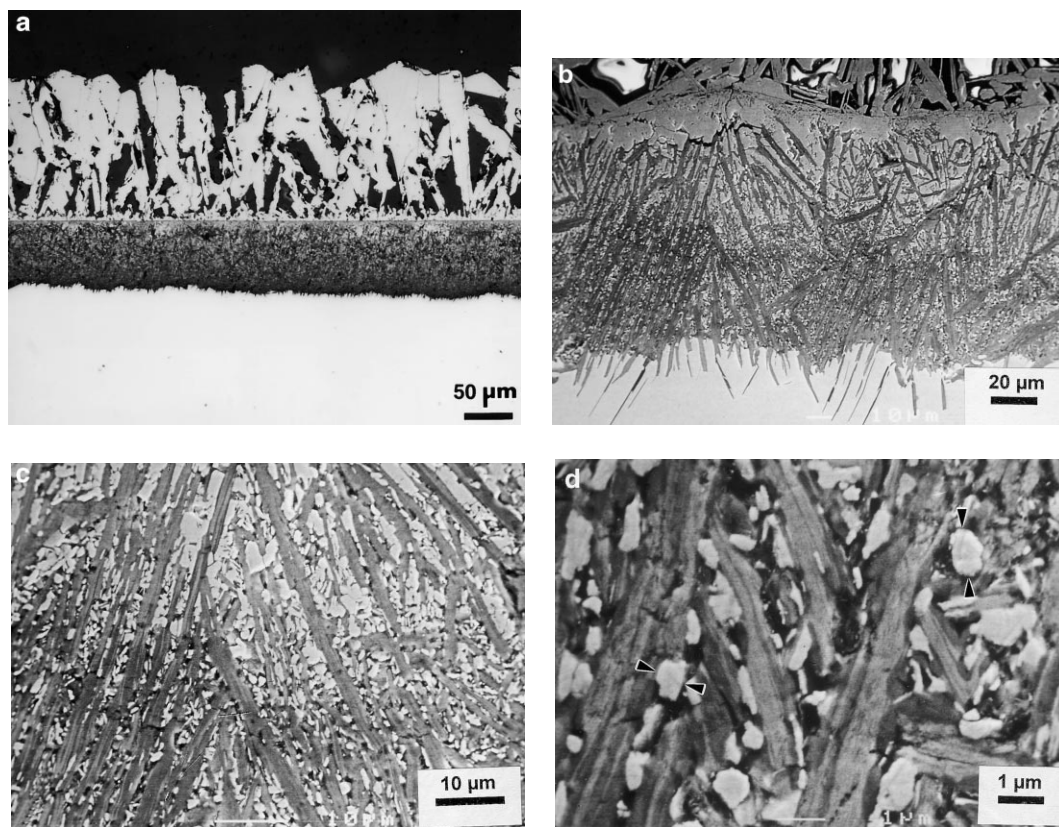

Fig. 1. Polished cross-sections of an Fe−5 wt.% Al alloy corroded at $700°C$ for 50 h in an oxidizing/sulfidizing atmosphere. (a) Light micrograph of the bi-layered scale. (b, c, and d) Secondary electron images of the inner scale. The τ-phase (dark plates with light-colored striations) can be seen, as well as light gray particles of iron sulfide (with arrow in (d)) and porosity (black).
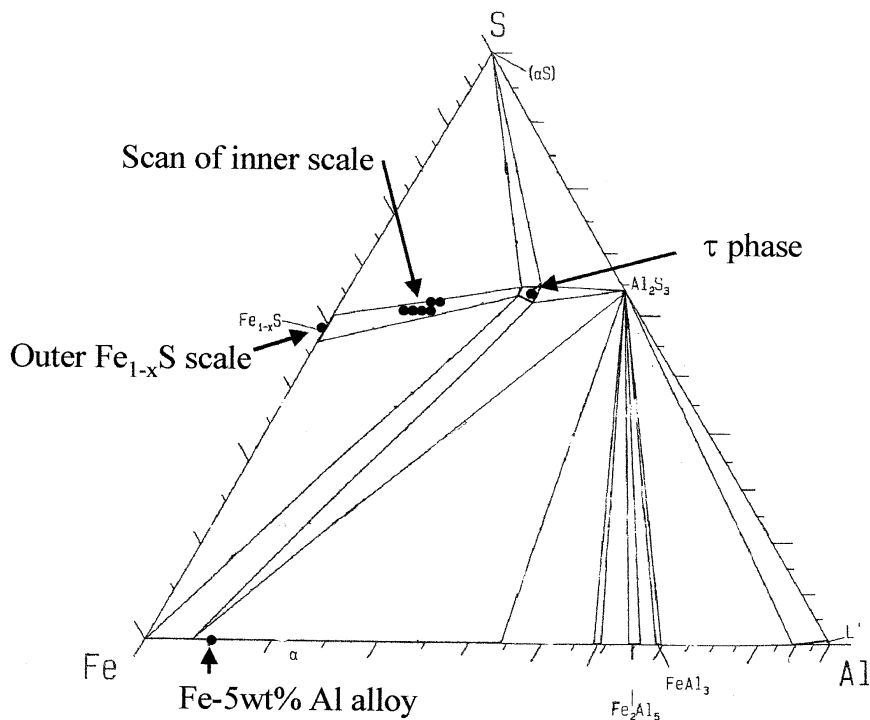
Fig. 2. EPMA data for the corrosion products and underlying substrate overlaid on the Fe−Al−S ternary phase diagram at 900°C from Ref. [8].

temperature. The oxygen partial pressure was measured by means of a solid state oxygen cell and the sulfur partial pressure was calculated using the SolGasMix program [6]. The corrosion samples were mounted in cold-setting epoxy and allowed to cure. Metallographic preparation consisted of grinding to 1200 grit with silicon carbide papers using various lubricants and cleansing solutions. Subsequent polishing with 1.0-μm diamond paste on a low-nap cloth was the only polishing step. Samples were dried using a cold air gun. Analysis of the cross-sectional morphology of the corrosion
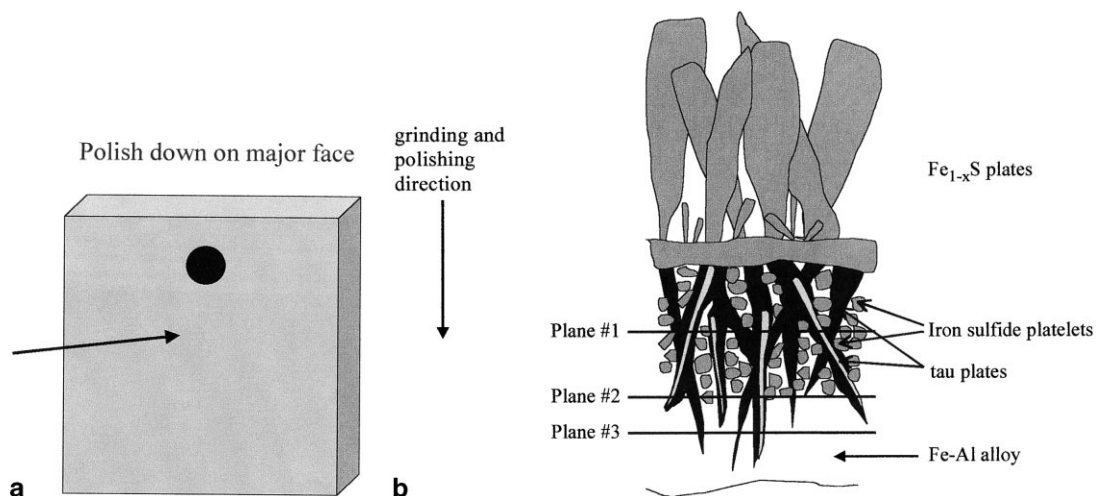

Fig. 3. Schematic diagrams showing (a) the direction of grinding and polishing of the major face and (b) the corrosion scale in cross-section, indicating the various planes that were analyzed.
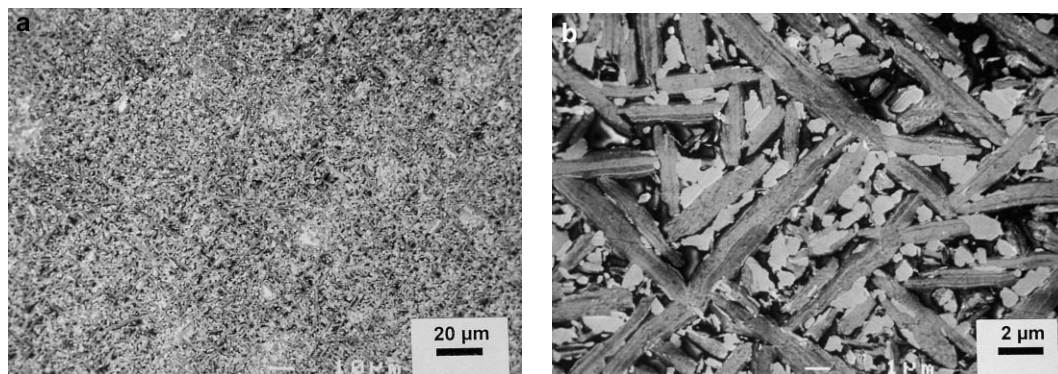
Fig. 4. Secondary electron images of a polished face on the Fe−5 wt.% Al alloy after 50-h exposure at 700°C, plane 1. The τ-phase (dark plates with light-colored striations) can be seen, as well as light gray particles of iron sulfide and porosity (black).

samples was conducted with light optical microscopy and scanning electron microscopy. Chemical analysis of the corrosion products was obtained with an energy dispersive spectrometer (EDS) and an electron probe microanalyzer (EPMA). For the latter, K_α X-ray lines were analyzed and counts converted to weight percentage using a $\phi(\rho z)$ correction scheme [7].

3. Results and discussion

3.1. General corrosion microstructure

Fig. 1 shows a typical cross-section of the bilayered corrosion scale that formed on the Fe−5 wt.% Al alloys after exposure to high-temperature oxidation/sulfidation environments. The porous outer layer consisted of irregularly shaped plates of iron sulfide ($Fe_{1-x}S$). The inner scale (Fig. 1b and c) was found to be composed of dark plates and light particles (shown by arrows in Fig. 1d). A fair amount of porosity (the

black regions in Fig. 1d) was observed due to the outward diffusion of iron to form the iron sulfide surface scale at the gas/scale interface, while the diffusion of sulfur inward along the phase boundaries occurred for further development at the scale/alloy interface. To obtain an overall average composition of the inner scale, microprobe scans of roughly 25 μm^2 were conducted. The results placed the composition for the inner scale in the two-phase region of $Fe_{1-x}S$ and τ-phase ($FeAl_2S_4$, a spinel-type compound) (Fig. 2). The dark plates were observed to have light-colored striations parallel to the lengths, Fig. 1d, and while the individual phases were too fine to analyze, the overall composition located the plates in the center of the τ-phase region, Fig. 2. The striations observed in the τ-phase plates may be due to a decomposition process that occurred upon cooling from high-temperature exposure. Mrowec et al. [2,9] surmised that this type of decomposition occurred during sulfidation experiments on Fe−Cr alloys, during which a complex $Fe(Fe_xCr_{2-x})S_4$ spinel was believed to have decomposed into sulfides
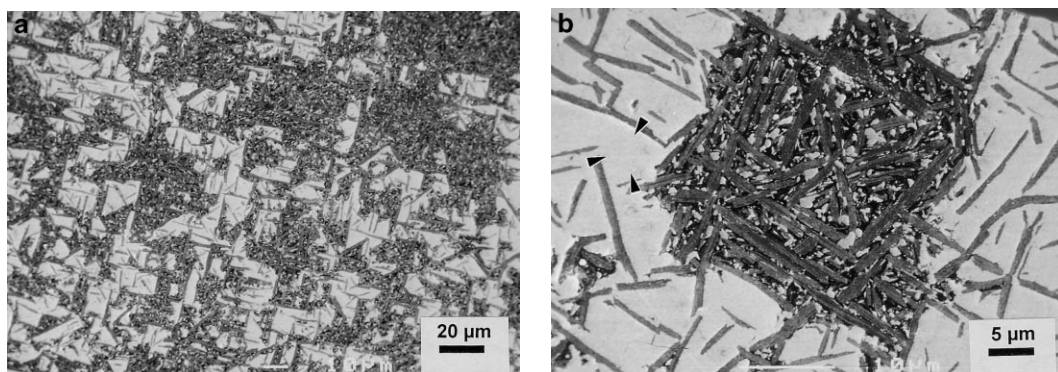

Fig. 5. Secondary electron images of a polished face on the Fe−5 wt.% Al alloy after 50-h exposure at 700°C, plane 2. Arrows indicate region of unattacked alloy surrounded by corrosion phases.

that were more stable at room temperature ($FeCr_2S_4$, FeS, and Cr_2S_3) after cooling down from the exposure temperature. The light-colored particles (with

arrow in Fig. 1d) were also too small to analyze quantitatively using the EPMA, but qualitative EDS analysis showed high counts of iron and sulfur with
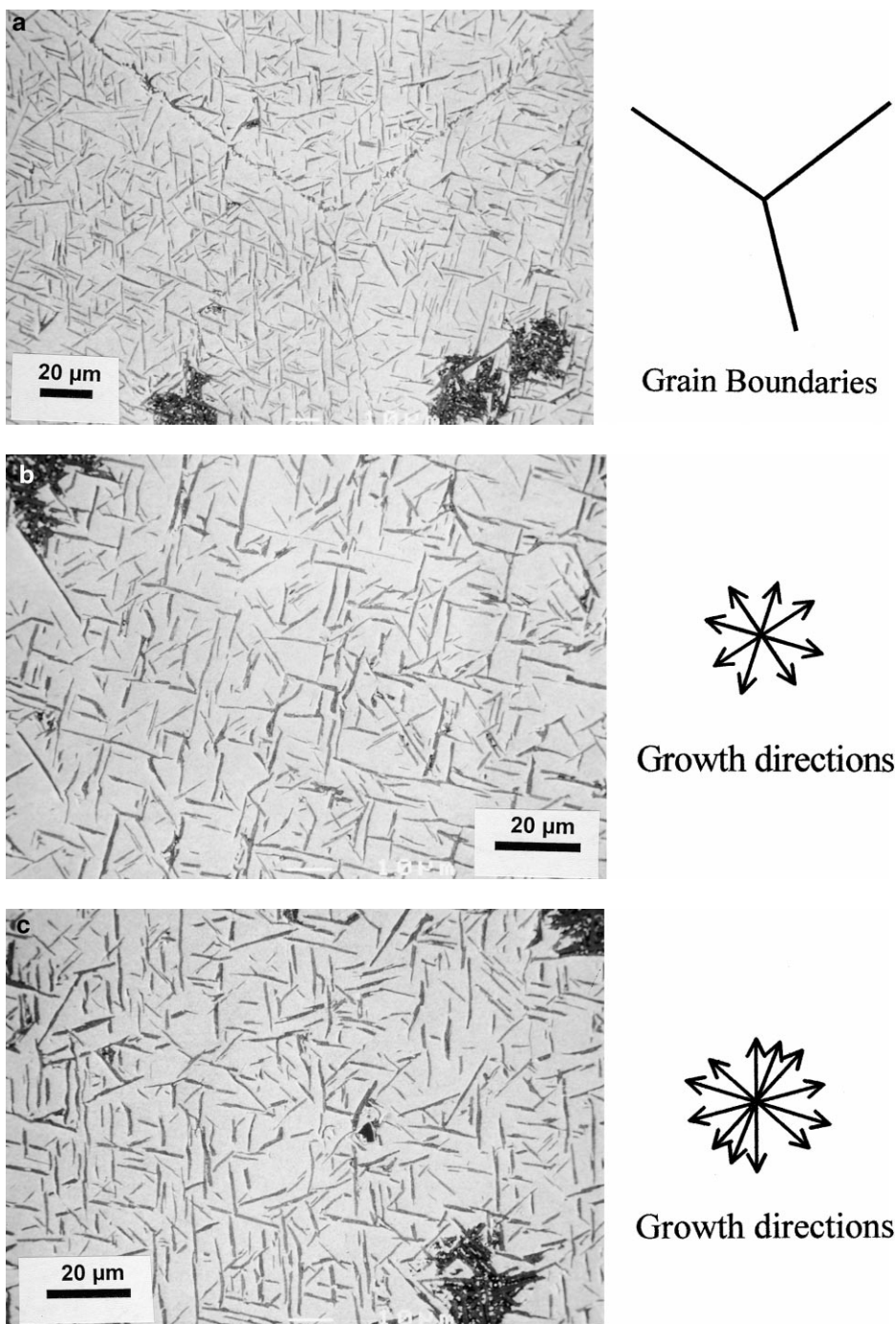

Fig. 6. Secondary electron images of a polished face on the Fe−5 wt.% Al alloy after 50-h exposure at 700°C, plane 3. (a) Attack within grains and grain boundaries; (b) four growth directions found in an individual grain; (c) six growth directions found in an individual grain.

very low counts of aluminum, suggesting that it was iron sulfide with some dissolved aluminum. EPMA data could not be obtained from the plate tips extending into the alloy due to their size (bottom of Fig. 1b), but high counts of iron, aluminum, and sulfur were found, indicating the possible continuation of the τ-phase.

In order to determine the exact shape of the two phases within the inner scale, a major face of the sample was polished as shown schematically in Fig. 3a, in addition to reviewing the results of the cross-sectional morphologies. Fig. 3b shows a schematic of the corrosion scale in cross-section indicating the various planes that were analyzed. The middle of the inner scale (plane 1) revealed the plate morphol-

ogy of the τ-phase and the particle nature of the iron sulfide, Fig. 4. Again, the porosity in the layer and the striations of the τ-phase can be seen. Closer to the alloy–scale interface (plane 2), the attack of the corrosion products into the substrate can be viewed, Fig. 5. EPMA data for the unattacked alloy (with arrow in Fig. 5b) near the plates showed no sulfur present and the EDS data for the light-colored particles showed high counts of iron and sulfur with low counts of aluminum. Further polishing led to the removal of the inner corrosion scale, with the substrate and plate protrusion left to be observed (plane 3), Fig. 6. The τ-phase can be seen to attack the substrate both in the grains and grain boundaries. Analysis of numerous grains revealed a crystallo-
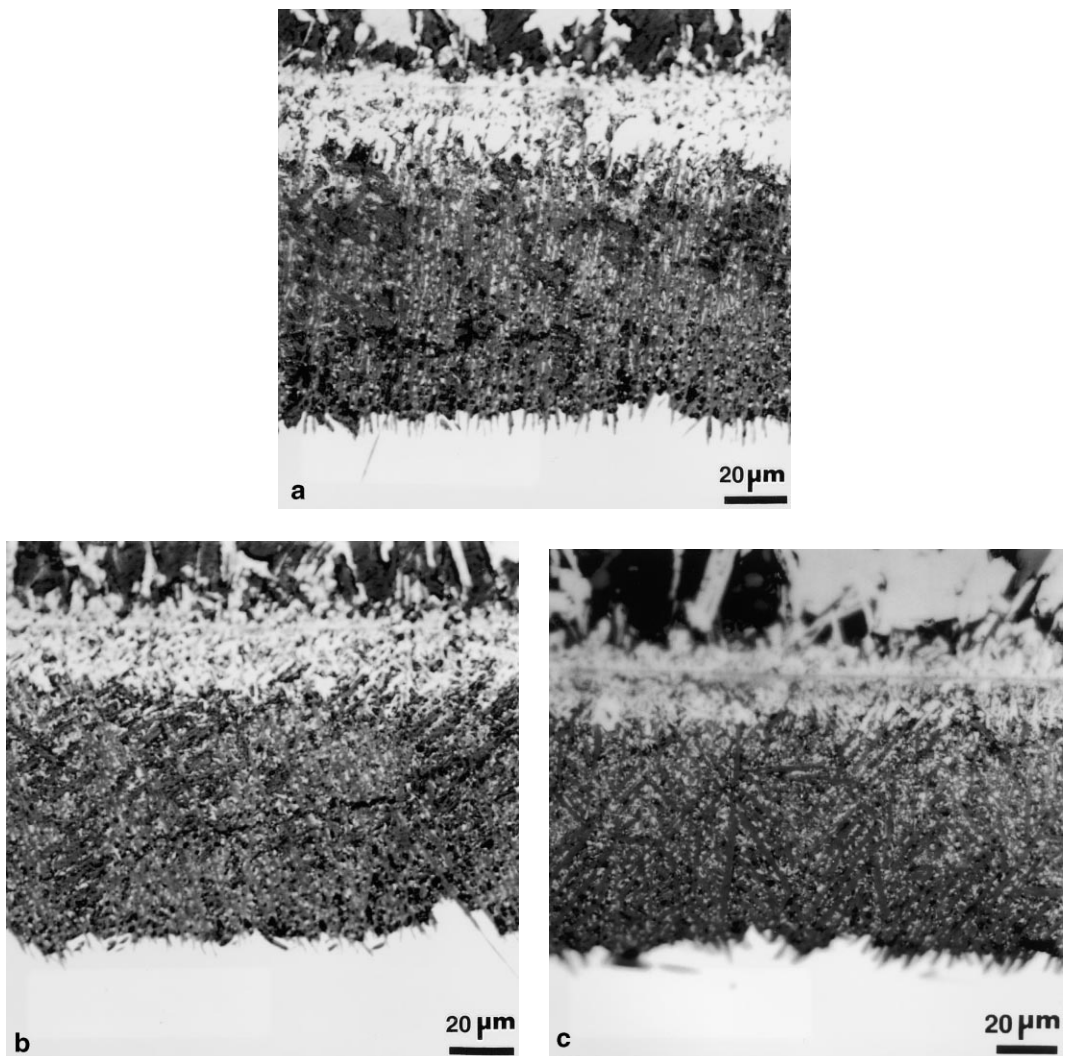

Fig. 7. Light optical micrographs of cross-sections polished by techniques using three different media: (a) methanol; (b) kerosene and methanol; and (c) 200-proof (dehydrated) alcohol.

graphic orientation of the plates with the substrate that may suggest easy growth directions for the corrosion product. Most grains displayed only four growth orientations (Fig. 6b), while some had six directions due to a few plates being oriented in a slightly different manner (Fig. 6c).

3.2. Sample preparation

Many different types of preparation techniques were tried in order to obtain good quality, polished cross-sections of the corrosion scales for quantitative chemical analysis. It is known that the τ-phase is easily hydrolyzed by water [10], and therefore, standard metallographic procedures in which water is used as a lubricant and/or cleansing solution during preparation could not be employed. Investigations were thus conducted to find a suitable preparation method.

Fig. 7 shows light optical micrographs of samples prepared using different media. All samples were prepared in the same manner, with the exception of lubricant or cleansing solution, and pictures taken immediately following preparation

(within 5 min). Fig. 7a shows the structure after preparation using methyl alcohol for the lubricant and cleansing solution. The structure of the inner scale appeared to be smudged and attempts to obtain photomicrographs with sharp definition were difficult. This was primarily due to loss of the τ-phase during the preparation procedure and the resulting difference in depth of field of the structure. Fig. 7b displays the structure after preparation with kerosene as the lubricant and methanol as cleansing solution. The structure appearance was slightly less smudged, but again, distinctive features could not be made out in the inner scale. Fig. 7c shows the microstructure after preparation with 200-proof (dehydrated) ethyl alcohol as the lubricant and cleansing solution. Features in the inner scale (in terms of the τ-plates and iron sulfide particles) can be clearly distinguished and the smudged appearance was not observed. However, these results were obtained only after using a fresh bottle of alcohol. Use of an aged bottle produced no better results than with the methanol. It was presumed that moisture became dissolved in the alcohol upon exposure to ambient air and
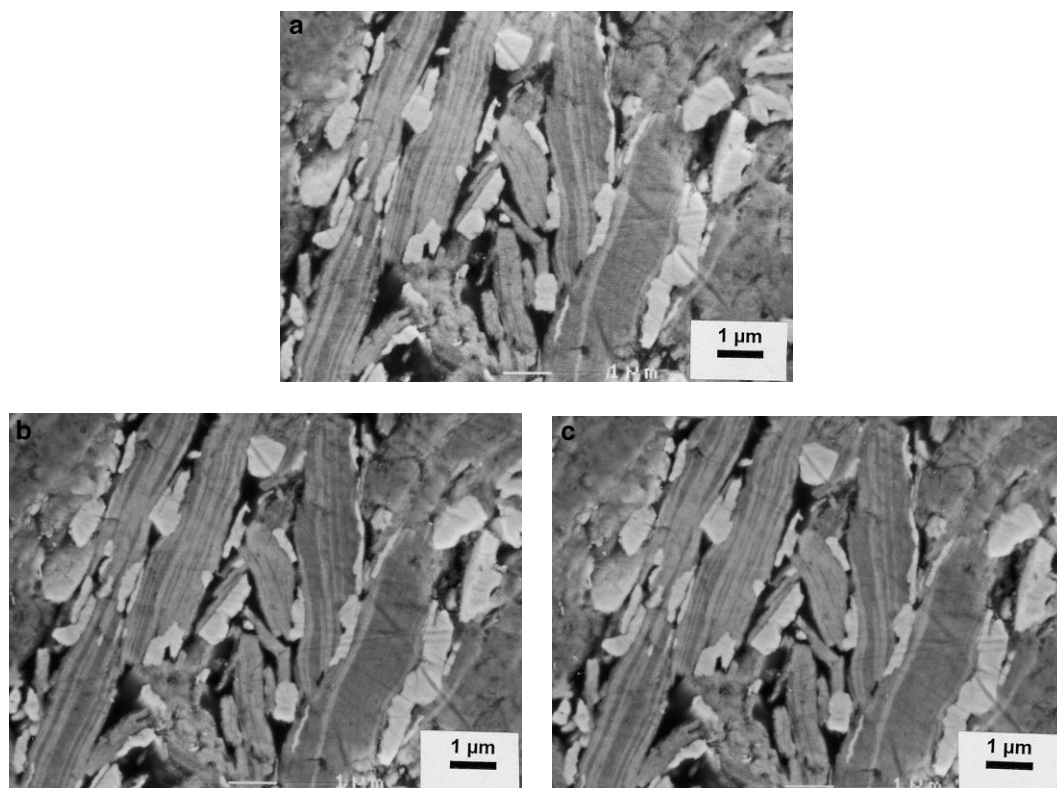

Fig. 8. Secondary electron images of the inner layer showing the τ-phase (a) after a fresh polish (day 1 in Table 1), (b) after 3 days of exposure to laboratory air, and (c) after 6 days of exposure to laboratory air.

Fig. 9. Secondary electron images showing the alloy–scale interface and protruding τ-phase (a) after a fresh polish (day 1 in Table 1), (b) after 3 days of exposure to laboratory air, and (c) after 6 days of exposure to laboratory air.
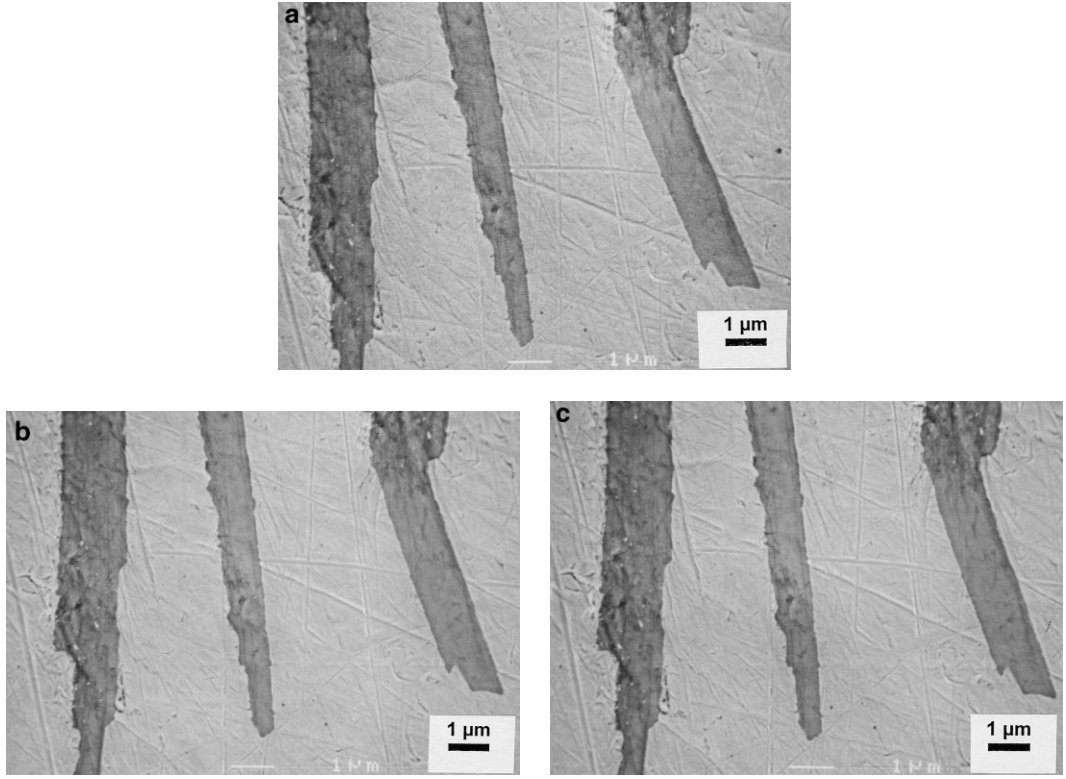
attacked the structure during the preparation procedure. Other lubricants or cleansing solutions used were water, general grade ethyl alcohol, isopropyl alcohol, and various dry techniques. However, those results were less satisfactory than the ones presented here.

3.3. Degradation in air

Upon re-examination of the polished samples after a few days, the observance of the "smudged" appearance was again found. It was also noted that upon opening the desiccator lid, a strong odor of hydrogen sulfide gas (rotten eggs) was released. In addition,

electron probe microanalysis of the same sample tested days apart detected a relatively large amount of oxygen in the structure at the later time. Thus, it was believed that the sample was degrading while exposed to ambient air, even with the use of fresh desiccant. Therefore, a study was conducted to determine the degradation of the τ-phase upon exposure to ambient air.

A freshly polished sample was characterized using scanning electron microscopy (Figs. 8a and 9a) and electron probe microanalysis (day 1 in Table 1) immediately after being prepared using the above technique. The areas of analysis were located in the middle of the inner scale and at the alloy–scale interface. After being exposed to la-

Table 1
EPMA data for the degradation of the τ-phase, Fe–5 Al at 700°C for 50 h

Time	Fe (wt.%)	Al (wt.%)	S (wt.%)	O (wt.%)
Stoichiometric composition	23.5	22.7	53.9	0.0
Day 1	24.5 ± 0.7	21.9 ± 0.7	53.3 ± 0.7	0.8 ± 0.4
Day 3	23.4 ± 0.8	21.6 ± 0.7	49.1 ± 0.5	4.8 ± 0.3
Day 6	24.8 ± 0.5	22.3 ± 0.4	46.6 ± 0.6	5.1 ± 0.4

boratory air for periods of 3 and 6 days, the sample was re-analyzed using the above mentioned techniques. These results can be found in Figs. 8 and 9, as well as the EPMA data in Table 1. It can be seen that the structure of the τ-phase did not appear to change significantly after 3 days of exposure but the oxygen content had increased to about 5 wt.%, concurrent with a decrease in the sulfur content. Similar results were obtained after an additional 3 days of exposure. From this analysis, it is believed that the τ-phase may be reacting with moisture from the atmosphere according to the reaction (Eq. (1)):

$$FeAl_2S_4 + 3H_2O(g) \rightarrow Al_2O_3 + FeS + 3H_2S(g). \tag{1}$$
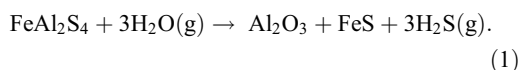
The release of hydrogen sulfide from the structure would account for the odor upon opening the desiccator. Mrowec and Wedrychowska [2] also observed the degradation of corrosion scales when sulfidizing Fe−Cr−Al alloys. They found that the Al_2S_3 reaction product that formed, which also reacts with moisture, degraded in a matter of hours.

4. Summary

The importance of obtaining good quality, polished cross-sections of the corrosion scale is an integral part of understanding the high-temperature corrosion behavior of Fe−Al alloys in an oxidizing/sulfidizing environment. The reaction of the corrosion products with both the environment and the materials used to prepare the cross-sections is of equal importance. This research has yielded a method for preparing metallographic cross-sections of corrosion scales that may react and/or dissolve when exposed to water, either from the ambient air or in the lubricant/cleansing solution. The use of 200-proof (dehydrated) ethyl alcohol was found to retain the τ-phase, while the stability of the iron sulfide phase was never a concern. In addition, this work has shown the importance of analyzing the structure in a timely manner as reactions with moisture from ambient air can degrade the corrosion products over time.

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