WRINKLING OF \( \alpha \)-ALUMINA FILMS GROWN BY OXIDATION—II. OXIDE SEPARATION AND FAILURE

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Abstract—Two types of localized separation of the \( \alpha \)-Al\(_2\)O\(_3\) scale, grown on a Fe–Cr–Al alloy at 1000°C, occur after isothermal oxidation and cooling to room temperature. One type is a form of buckling where the size of the detached region is much larger than the thickness of the oxide and is usually accompanied by substantial stress relaxation and cracking of the scale. It is observed within a narrow range of oxide thickness of about 0.2–0.5 \( \mu \)m. The second type is intimately related to the wrinkling morphology of the scale and takes place primarily along the ridges of the longer wavelength wrinkles. No significant stress relaxation in the oxide appears to accompany this form of separation unless cracking of the scale occurs as well. The consequences of thermal cycling on these modes of separation and how they may lead to oxide spalling are discussed. © 1998 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

High-temperature oxidation of Fe–22% Cr–5% Al alloy results in the formation of a continuous surface layer of \( \alpha \)-Al\(_2\)O\(_3\) with a typical wrinkled or convoluted morphology. In the first part of this work, the evolution of the wrinkling morphology during oxidation was quantified in terms of the amplitude and wavelength of the undulations and these geometric parameters were related to the residual stress in the oxide [1]. In this second part, a similar Fe–Cr–Al alloy but in polycrystalline form is examined with the emphasis placed on observations of the separation of the oxide from the underlying alloy and its relation to the wrinkling morphology. Two distinct forms of localized separation are observed. These are believed to be precursors to the spalling failure of the oxide under cyclic oxidation conditions.

2. EXPERIMENTAL

The chemical composition of the alloy studied was similar to that used in the first part, namely (wt%): Fe (bal.)–22.0% Cr–5.28% Al. The content of impurities was determined to be: 82 p.p.m. C; 49 p.p.m. S; 23 p.p.m. P; 120 p.p.m. Si. The alloy was vacuum-induction melted, annealed at 1100°C and cut into rectangular specimens. The specimens were mechanically polished to a 1 \( \mu \)m surface finish and oxidized in air at 1000°C. The oxide scale was studied using optical and scanning electron microscopy (SEM) and the residual stress in the oxide measured using photostimulated chromium luminescence piezospectroscopy [2]. All the relevant experimental details are given in the first part [1].

3. RESULTS

3.1. Observations of scale separation

The wrinkled scale generally exhibits good spalling resistance after isothermal oxidation at 1000°C. However, the oxide does not remain in contact with the metal after cooling to room temperature everywhere over the surface. Observations using a conventional optical microscope in the back-reflection mode reveal localized oxide separation or debonding but no visible spalling. Any debonded (but not spalled) areas of the scale larger than a few micrometers are clearly observed through an optical microscope as brighter regions [Figs 1(a) and 2]. The origin of this optical contrast is believed to be as follows. The oxide is transparent in the visible spectrum and so most of the reflection of incident light comes from the metal surface. Since the difference in index of refraction of the metal–gas interface is higher than that of the metal–oxide interface [3], the metal surface under debonded oxide appears brighter than the same surface in contact with the oxide. An additional observation made was that the debonded regions of the scale form during cooling within a few minutes after removing a specimen from the furnace. This indicates that the debonded regions “pop-in” on cooling rather than steadily grow as the temperature decreases.

Similar optical contrast is observed when large interfacial cavities form during oxidation. In this case, a higher reflectivity of these regions is also

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due to the smooth metal surface at the bottom of the cavity. Generally, it is not possible to distinguish the localized separation induced by cooling and the cavities formed during oxide growth, unless the scale is separated and the oxide–metal interface is exposed for direct observation. In the present case, as indicated earlier [1], almost no cavities formed during isothermal oxidation, so nearly all the debonded areas arise on cooling. (Cyclic oxidation, however, may result in cavity formation at high temperature as will be discussed later.) Spallation of the scale, exposing a bare metal surface, produces even more distinct optical contrast and can easily be detected and distinguished from the oxide–metal separation described below.

Two types of oxide separation and debonding were observed. One is in the form of large blisters such as shown in Fig. 1. These are dome-shaped regions of the scale, 20–40 \( \mu \)m in diameter, elevated up to a few micrometers above the metal surface. Another distinguishing feature is that the area of a single blister covers a number of oxide wrinkles. Since the metal surface under the blisters is seen to replicate the wrinkles and grain structure of the scale, it is concluded that the debonding must have occurred on cooling, not during the scale growth.

![Fig. 1](image1.png)

Fig. 1. Local buckling of the alumina scale on the Fe–Cr–Al alloy after oxidation for 10 h at 1000 °C: (a) optical micrograph showing the detached regions of the scale apparent from their higher reflectivity; (b) scanning electron micrograph showing the pronounced oxide up-lift associated with the buckling (“blistering”).

Usually, the perimeter of the blisters is fringed by cracks which most probably inhibit lateral propagation of the blisters. However, in cyclic oxidation experiments, the cracks often lead to spalling of the buckled regions of the scale. This type of separation was observed after oxidation for 3–20 h when the oxide is still relatively thin, typically only about 0.2–0.5 \( \mu \)m thick. Interestingly, for thinner scales, no separation was observed and the oxide remained perfectly adherent after isothermal oxidation.

The second type of debonding is shown in the sequence of optical micrographs in Fig. 2. These smaller regions are also visible through an optical microscope but, importantly, cannot be revealed in SEM images. They appear after oxidation for 20–25 h and both their size and number increase after longer oxidation times. Comparing the size of

![Fig. 2](image2.png)

Fig. 2. The second type of oxide detachment discernible by its higher optical reflectivity. The detached regions increase in size with increasing oxidation time: (a) 30 h; (b) 100 h; (c) 400 h (optical micrographs).
debonded regions with the wrinkling wavelength measured in the first part [1], it is concluded that each corresponds to the crest of the wrinkles in the scale. This becomes clear after prolonged oxidation when individual wrinkles can be resolved by optical microscopy. For instance, after 400 h oxidation the scale at almost every crest or ridge is debonded after cooling to room temperature [Fig. 2(c)].

A closer examination of relatively thick scales after 200–400 h oxidation reveals small cracks (Fig. 3). These cracks can be found near the most pronounced ridges (but never at the valleys) of the scale. Both the debonded regions and the cracks do not propagate over larger areas, at least after isothermal oxidation and air cooling, therefore no spalling occurs. In cyclic tests, however, a gradual accumulation of the debonded regions results in oxide spalling.

It was found that both types of oxide debonding are greatly affected by cooling rate. The separations presented in Figs 1–3 were observed after fast air cooling (about 500°C/min). With decreasing cooling rate, the number of debonded areas is smaller, for example after furnace cooling at 5–10°C/min. Conversely, quenching from the oxidation temperature significantly enhances the scale debonding and invariably leads to local spalling.

The observations of oxide debonding presented so far clearly show that it occurs after cooling to room temperature whereas, during isothermal exposure, the scale remains in contact with the metal. Cyclic oxidation, however, leads to localized debonding at high temperature. This process causes the formation of interfacial cavities which appear as smooth craters on the metal surface. A typical structure of the metal surface exposed by spalling of the scale after five 50 h oxidation cycles (250 h total exposure at 1000°C) is shown in Fig. 4(a). No such cavities were observed after isothermal oxidation. For instance, the SEM micrograph showing the absence of cavities on the metal surface after isothermal oxidation for 20 h at 1200°C is presented in Fig. 4(b). The oxide adherence after isothermal oxidation at 1000°C was strong enough, so that only small areas of the oxide could be removed to reveal the underlying metal surface. Therefore, for illustrative purposes, the interfacial structure is shown after oxidation at 1200°C, when the scale spalled almost completely.

3.2. Residual stress in the oxide

Measurements of the residual stress in the oxide scale at room temperature after isothermal oxidation at 1000°C were made using photostimulated

![Fig. 3. SEM micrographs showing the presence of microcracks in thick scales after oxidation for 400 h at 1000°C. The crack is indicated by arrows in (a) and shown at higher magnification at the crest of oxide wrinkle in (b).](image)

![Fig. 4. The microstructure of the metal surface exposed by spalling of the scale: (a) after five 50 h oxidation cycles at 1000°C showing interfacial cavities (smooth craters) and imprinted contact interface; (b) after 20 h isothermal oxidation at 1200°C showing the absence of cavities.](image)
luminescence spectroscopy [2]. Two types of measurement were made: one with a probe size comparable to the oxide wrinkling wavelength so as to obtain the spatial average of the residual stress, and the other with a much smaller probe so that the local residual stress could be determined. No systematic difference between the average residual stress was detected after isothermal and cyclic oxidation (for times $t \leq 100$ h) of the same cumulative exposure. This suggests that cooling from the oxidation temperature does not lead to irreversible plastic relaxation in the scale. With increasing time of cyclic oxidation, however, local spalling and cracking of the scale occurred, therefore the results presented in the following paragraphs refer only to isothermal oxidation.

Apart from significant variations at short oxidation times due to differences in crystallographic orientation of the underlying metal grains [1], the value of the spatial average of the residual stress became almost constant after about 60 h oxidation at 1000°C [Fig. 5(a)]. By this time, the wrinkling wavelength was sufficiently large, so that the residual stress in the vicinity of the ridges and the valleys between them could be measured with a small (<3 µm) optical probe. The results are shown in Fig. 5(a) together with the spatial average values. Here, the piezospectroscopic frequency shift is presented as a function of oxidation time, and the second $y$-axis indicates the stress calculated from the frequency shift assuming that the oxide is under biaxial compression. Note that these stress values are not directly applicable for the wrinkled oxide, as discussed previously [1, 4], and can only be used for a flat oxide layer. For comparison, the residual stress in the flat scale formed on the yttrium-containing alloy is included [5]. Two luminescence spectra in Fig. 5(b) illustrate a marked difference between the ridge and valley regions of the scale after oxidation for 400 h. Clearly, the frequency shift is much smaller on the oxide ridges and larger at the valleys. The implications of these results with respect to the local stress state of the scale will be discussed below.

As shown in Fig. 2(c) (400 h oxidation), a large proportion of the scale, namely the majority of ridge regions, is debonded from the metal surface after cooling to room temperature. It is, therefore, natural to suppose that the stress in the oxide near the ridges can, at least partially, be relieved as a result of scale separation during cooling. After shorter oxidation time [Fig. 2(b), 100 h], some oxide ridges are debonded, however there are many others where the scale apparently remains in contact with the metal. These two regions were analyzed using a small probe size in order to compare the frequency shifts between the debonded and intact ridges. Surprisingly, no systematic difference between these two has been detected (Fig. 6). In other words,
alumina scales. One is a form of buckling in which a large area, of dimensions much larger than the oxide thickness, of the scale separates from the underlying metal (Fig. 1). This form of failure is accompanied by distinct cracks through the oxide at the periphery of the buckle, a displacement away from the metal surface and a relaxation of the residual stress in the oxide in the buckled region. The observations show that it occurs occasionally and at random locations on the metal surface after short isothermal oxidation times, when the scale is relatively thin. The reason for this buckling is not known but it is assumed to be due to the presence of localized patches of (unidentified) impurities that significantly decrease the local interfacial fracture resistance. The size of these blistered regions is consistent with that calculated from the usual mechanics criteria \[a_c \approx g h^2 \frac{E}{\sigma_c}\] for buckling of a compressively stressed thin film, namely that the buckle diameter, \(a_c\), is given by

\begin{equation}
    a_c = gh \sqrt{\frac{E}{\sigma_c}}
\end{equation}

and the elastic strain energy relieved exceeds the interface fracture resistance. In this equation, \(g\) is a geometric parameter (\(g \approx 2.2\) for an axisymmetric buckle), \(h\) the scale thickness, \(E\) the oxide elastic modulus, and \(\sigma_c\) the biaxial compressive stress. Substituting in appropriate values (\(h \approx 0.5\ \mu m\), \(\sigma_c \approx 3\ \text{GPa}\) and \(E \approx 400\ \text{GPa}\)), the predicted buckle size is about \(12\ \mu m\), a value similar to that seen in Fig. 1.

The second type of separation is directly related to the wrinkling morphology, occurring primarily along the crests of the wrinkles with equal probability all over the metal surface (Fig. 2). It is the most common form of oxide separation after isothermal oxidation at 1000°C for 25–400 h in the experiments but, importantly, it does not cause spalling of the scale. There appears to be almost no accompanying stress relaxation in the oxide unless cracking of the scale also occurs.

Debonding of the scale at the crests and ridges is attributed to the existence of local tensile stresses across the oxide–metal interface created from the thermal mismatch stress in the scale as a result of the wrinkling geometry. Both analytical solutions \([4, 9]\) and finite element calculations \([4, 10]\) show that cooling of the wrinkled scale produces regions of tensile stress across the interface at the ridges and corresponding compressive stress in the valley regions. (For all but the most convoluted scales, the finite element results for the tensile stress across the interface can be represented with considerable accuracy by using a soap-film analogy in which the normal stress is given by the Laplace equation, namely the biaxial stress divided by the local curvature \([4]\).) The results (Figs 5 and 6) confirm this conclusion since the piezospectroscopic frequency shift is much higher at the valleys than at the ridges. A schematic illustration of the oxide wrinkling morphology is shown in Fig. 7(a). The stress component normal to the interface varies...
from a maximum tensile value to zero in the ridge region and from a maximum compressive value to zero in the valley region [4,9,10]. For the small volumes of the oxide analyzed by the optical probe, these normal stresses contribute with opposite sign to the piezospectroscopic shift, therefore causing the frequency shift from the ridge to be smaller than the spatial average and that from the valley to be larger. The maximum magnitude of the normal stress at the interface is in the range (0.1–0.4)$\sigma_{\text{flat}}$ [4], where $\sigma_{\text{flat}}$ is the residual biaxial compression of the flat oxide layer. A typical value for $\sigma_{\text{flat}}$ caused by thermal expansion mismatch is about 3.0–3.2 GPa. Thus, the magnitude of the maximum tensile stress is expected to be 0.3–1.3 GPa depending on the geometry of the oxide wrinkles. It is argued in the following paragraphs that the existence of spatially varying tensile and compressive stresses across the oxide–metal interface has two consequences that are consistent with observations associated with the second type of detachment: the interface separation along the ridges with no stress relaxation and the observed size of the detached regions.

The piezospectroscopic measurements of the scale around the wrinkling ridges demonstrate that no systematic difference exists between the areas where oxide is detached (without cracking) and the areas where it apparently remains in contact with the metal (Fig. 6). This means that separation during cooling does not lead to significant stress relaxation in the oxide and raises the question of why the observed separation occurs. To answer the question, the stresses need to be considered not only in the oxide layer, but also in the underlying metal. In contrast to the stress distribution at the planar interface, where a biaxial uniform tension in the metal can usually be ignored (the stress in the metal is very small if the oxide is much thinner than the metal), the stresses in the metal beneath the wrinkled interface are inhomogeneous and may be sufficiently large in some locations, as discussed above, so as to cause metal deformation. If the oxide does not deform, the most probable result of metal deformation is debonding at the interface. This process will create isolated crescent-shaped separations at the concave regions of the interface during cooling [Fig. 7(b)]. So, unlike buckling (Fig. 1) where the oxide layer bends away from the metal surface, these smaller debonded regions are believed to be due to the deformation (plastic, elastic, or both) of the underlying metal.

The existence of a tensile stress acting normal to the oxide–metal interface is commonly considered to be an essential pre-requisite for oxide separation and spalling. However, the separation observed in the ridge areas does not lead to spalling of the scale, at least within the oxidation times studied (400 h at 1000°C). The reason is, probably, that each crest or ridge of the scale is surrounded by regions where the stress across the interface is compressive. Thus, the size of the detached regions is expected to be related to the size of the regions over which tensile stresses are created, i.e. about half of the wrinkling wavelength. In fact, consideration of the energy associated with the separation suggests that, as with other fracture phenomena, there will be a critical size below which separation cannot occur whereas above which it will occur. The existence of a critical size is consistent with two of the observations mentioned above. Firstly, that separations at the ridges only occur after some intermediate oxidation time, 20–25 h at 1000°C, and the secondly, that the separations “pop-in” on cooling. As shown in the quantitative morphological investigations described in part I [1], both the wavelength and amplitude of the wrinkles increase with oxidation time, so the critical size of separation corresponds to approximately half of the wrinkling wavelength after 20–25 h, i.e. about 3.5 μm. The observation of separation “pop-in”—the sudden growth to a stable size—is characteristic of crack-like growth in a spatially varying stress field and then arrest when the strain energy release rate falls below the interfacial fracture resistance.

Provided that the size of separated regions is less than the critical buckling size, the scale cannot buckle. Following these arguments, the extensive spalling of the scale after oxidation at 1200°C may simply be related to a substantially larger wrinkling wavelength, as shown in Fig. 4(b). Certainly, with increasing oxidation temperature, the thermal mismatch strain increases, and so the elastic strain energy, available for decohesion, is greater in the thicker scales formed at the higher temperatures. Both factors lead to propagation of the detached regions beyond a single ridge of the interface and cause spalling of large areas of the scale. The progressive increase in size of the separated regions along the ridges with time of isothermal oxidation at 1000°C is associated with the coarsening of the wrinkling morphology, specifically the growth of the larger wavelength undulations at the expense of the shorter wavelength undulations [11]. The observation that not all the interfaces along the ridges are separated [for example, after 100 h in Fig. 2(b)] further suggests that it is primarily the larger sized ridges that separate. Furthermore, the scale after oxidation at higher temperatures [Fig. 4(b)] is probably best described in terms of percolation of separated regions. It is expected that once the connected regions of separation reach the critical buckle size, buckling and spalling spontaneously occur.

Cracking of the oxide takes place at, or near, the ridges in the wrinkling scale after prolonged isothermal oxidation, for instance 200–400 h at 1000°C (Fig. 3). It is believed to be associated with the development of tangential tensile stresses at the outer surface of debonded oxide once a critical thickness of the scale is reached. Cracking leads to
stress relaxation in the adjacent area of the oxide (as confirmed by piezospectroscopic measurements), including the normal tensile component. No cracking was observed in the adjoining valleys where the oxide remains under compression. Cracking is also observed at the periphery of the buckled regions in thin scales (Fig. 1), presumably in response to the large deformations associated with the buckling event.

The existence of debonded regions of the scale after cooling to room temperature raises the question as to what happens with such regions during cyclic oxidation. Obviously, if oxide detachment is accompanied by cracking, then oxygen can penetrate into the gap between the scale and the metal and form a secondary oxide layer during subsequent oxidation cycles. This process was, in fact, observed in the case of the large blisters shown in Fig. 1 in the course of 5 or 10 h oxidation cycles. However, the smaller debonded regions (Fig. 2) are usually not cracked. It can be expected, therefore, that the separation between the scale and the metal will close during subsequent heating and the oxide–metal contact will be restored at temperature until the next cooling. The major requirement for such a repeated debonding–bonding process, besides the absence of cracks, is a purely elastic behavior of both the metal and oxide during temperature change. If decohesion occurs without plastic deformation in both phases, the oxide inner surface and metal surface should perfectly match each other after next heating to oxidation temperature. This possibility is schematically shown in Fig. 8 (route 1).

Although it is difficult to prove experimentally, it is supposed that repeated debonding–bonding may indeed occur in some cases, i.e. the changes of the oxide and metal surface configuration within the debonded region can be completely reversible. There are, however, at least two factors which complicate this simple conclusion. First, as mentioned previously, metal plastic deformation may in fact occur during cooling, especially, at the perimeter of the debonded region, where the shear stresses are

Fig. 8. Schematic diagram illustrating three different routes of oxide debonding and failure during cyclic oxidation.
highest and where significant stress gradients develop between separated and contact areas. This is illustrated in Fig. 8 (route II). Any plastic deformation of the metal surface would lead to a geometrical mismatch with the oxide inner surface during subsequent heating. Second is a complex morphology of the oxide–metal interface itself. The interface is formed by facets of alumina grains of various orientations and their replicas on the metal surface. Simple geometric considerations imply that it is unlikely to restore intimate contact after separation over the whole interface. For both reasons, many debonded regions remain after next heating. During subsequent oxidation exposure, these regions transform into normal interfacial cavities with smooth surface at the metal side in order to minimize surface energy [Fig. 4(a)]. That is probably the reason why cavities can be observed after cyclic oxidation but not after isothermal oxidation of the same total exposure. Certainly, if separation after cooling is followed by oxide cracking, a similar geometrical mismatch at the interface would prevent contact from being restored (route III in Fig. 8).

In these examples of oxide detachment, spalling was not specifically considered since it did not occur after isothermal oxidation at 1000°C. However, spontaneous spalling with a loss of a significant portion of the scale was observed in the experiments under cyclic conditions. During cyclic oxidation, accumulation of local damage in the scale (through-cracks, debonded regions around ridges) and formation of interfacial cavities (as described above) result in the development of large debonded areas which eventually separate from the metal after a number of cycles.

5. CONCLUSIONS

Two distinct forms of detachment of the alumina scale from the underlying Fe–Cr–Al alloy occur after isothermal oxidation at 1000°C and cooling to room temperature. One is a conventional form of buckling which is observed in the case of relatively thin scales (0.2–0.5 μm) and may be attributed to the presence of localized patches of impurities at the interface that form a critical flaw size for the onset of buckling. The other, and more general, is associated with the ridges in the wrinkling morphology and resulting local tensile stresses across the oxide–metal interface. The size and the number of separated regions increase with oxidation time as the wavelength of oxide wrinkles increases. No significant stress relaxation in the oxide is associated with this form of oxide–metal separation and so it is believed to be attributed to the underlying metal contracting away from the oxide on cooling. Localized separation of the scale after isothermal oxidation does not lead to spalling. During cyclic oxidation, the separated regions can propagate over larger areas of the interface and lead to failure of the scale by complete detachment from the metal surface.

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