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Effect of surface-applied reactive elements on the early stage oxidation of Fe-18Cr-5Al and Fe-18Cr-5Al-1Hf alloys (*)

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Abstract. — The effect of lanthanum implantation on the early stage oxidation of Fe-18wt%Cr-5wt%Al and Fe-18wt%Cr-5wt%Al-1wt%Hf alloys at 1100 °C has been investigated. It was found that the reactive element enriched surfaces oxidized almost two times faster initially, and the scale that formed had a higher iron content. An extremely wavy scale/alloy interface developed in the early stage due to the accelerated growth and the change in scale composition. More scale separation was observed on the implanted surface of the Fe-Cr-Al alloy. Once separated, the alumina scale was free to grow laterally, and large growth buckles developed with oxidation time. The Hf-containing alloy did not show any scale separation regardless of the accelerated initial growth from lanthanum implantation. Sulfur was found everywhere at the scale/alloy interface on the Fe-Cr-Al alloy, but not on the Hf-containing alloy. These results suggest that for this alloy system, scale adhesion was dominated by a strong scale/alloy interface, and weakening of the interface may be caused by interfacial sulfur segregation.

1. Introduction.

The protection of high temperature alloys and coatings against oxidation is provided by the formation of slow-growing oxide films, which often consist of Al_2O_3 and/or Cr_2O_3 . One major limiting factor in the protection is extensive oxide loss from the surface, or oxide spalling, under thermal cycling conditions. It has been known for many years that minor additions of oxygen active elements, such as Hf, La, Y and Ce, could significantly improve the spallation resistance of these oxide scales [1]. Although numerous mechanisms have been proposed [2-5] to explain the role of the reactive elements in reducing scale spallation or in enhancing scale adhesion, the cause of the beneficial effect is still under much debate.

While most studies concentrated on the effect of reactive element additions within the alloys, it was found with chromia-formers that the application of reactive metals or metal oxides on alloy surfaces could equally be beneficial. These results have recently been reviewed by Moon and Bennet [6]. For Al_2O_3 -formers, however, the effect of reactive elements applied using such surface techniques has not been under much investigation. Bennet *et al.* [7] and Smeggil and Shuskus [8] did some early work and reported limited benefits with ion-implantation of yttrium. Jedlinski and co-workers [9, 10] have carried out studies using ion-implanted yttrium and found that unlike alloying additions, the implanted yttrium did not cause a significant improvement in alumina scale adhesion. On the contrary, a higher degree

(*) Invited paper.

of scale convolution developed with higher dosages of yttrium implant. Similar results have been found by Hou [11] with ion-implanted Ce, La, Th, Gd, Hf and Zr.

Hou *et al.* [12] also showed that when the reactive element was deposited as a thin oxide coating on the surface of an Fe-18Cr-5Al alloy, the effects were the same as that of ion-implantation. It was found that the primary influence of the surface coatings was to increase the number of buckles in the alumina scale at the early stage of oxidation. Growth of the buckled scale into large ridges took place by way of aluminum vapor phase transport and oxide lateral growth. The reason for the increased initial scale convolution was however unclear. The focus of this paper is to study the early stages of alumina scale formation on reactive element implanted surfaces using the Fe-18Cr-5Al alloy and a Hf-containing alloy with the same base composition. The aim is to gain better understanding of the effect of reactive elements on alumina scale adhesion.

2. Experimental methods.

Two alloy ingots, with the nominal composition of Fe-18Cr-5Al and Fe-18Cr-5Al-1Hf (all wt%) were made by induction melting and casting under an argon atmosphere, followed by a homogenization anneal at 1200 °C for 24 hours in vacuum. Actual composition of the alloys was very close to that of the intended, except that the Hf concentration was only 0.5wt%. Both alloys contained approximately 15 ppm sulfur as an impurity. Specimens 15 mm × 10 mm × 1 mm were cut from the center of the ingots. All specimen surfaces were ground to a 1200-grit finish on SiC paper, followed by ultrasonic cleaning in alcohol prior to ion-implantation or oxidation procedures.

Ion implantation was carried out using a metal vapor vacuum arc (MEVVA) high current metal ion source with a mean ion energy of approximately 80 keV. The actual dosage, obtained by RBS analysis, was $2\text{-}3 \times 10^{16}$ ions/cm², which has a peak concentration of 5 at% at 18-19 nm. The total penetration depth was about 48 nm, and the average concentration within this layer was 3.6 at%.

Isothermal oxidations were carried out in a horizontal tube furnace with flowing dry oxygen at a total pressure of 1 atm. Specimens were placed in an alumina boat and the oxidation test was considered to begin when the boat was pushed into the hot zone of the furnace. Most tests were carried out at 1100 °C for 15 minutes, followed by fast cooling in room air.

Characterization of the thin scale which formed on these specimens involved using techniques such as scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and Rutherford backscattering (RBS) with particle induced X-ray emission (PIXE). The RBS and PIXE were performed using 2 MeV ⁴He⁺ particles with an approximate penetration depth of 3 μm. An *in-situ* scratch device [13] attached to the high vacuum chamber of the Auger microprobe was used to study the chemistry at the scale/alloy interface.

3. Results.

The surface morphology of La-implanted Fe-18Cr-5Al and Fe-18Cr-5Al-1Hf after 15 minutes oxidation at 1100 °C is shown in figure 1. Except for the unimplanted Hf-containing alloy, whose surface oxide was very smooth with few randomly spaced small nodules, all other surfaces developed convoluted scales. The degree of such convolution was higher on the implanted surfaces than on the untreated one. This enhanced scale convolution however, is

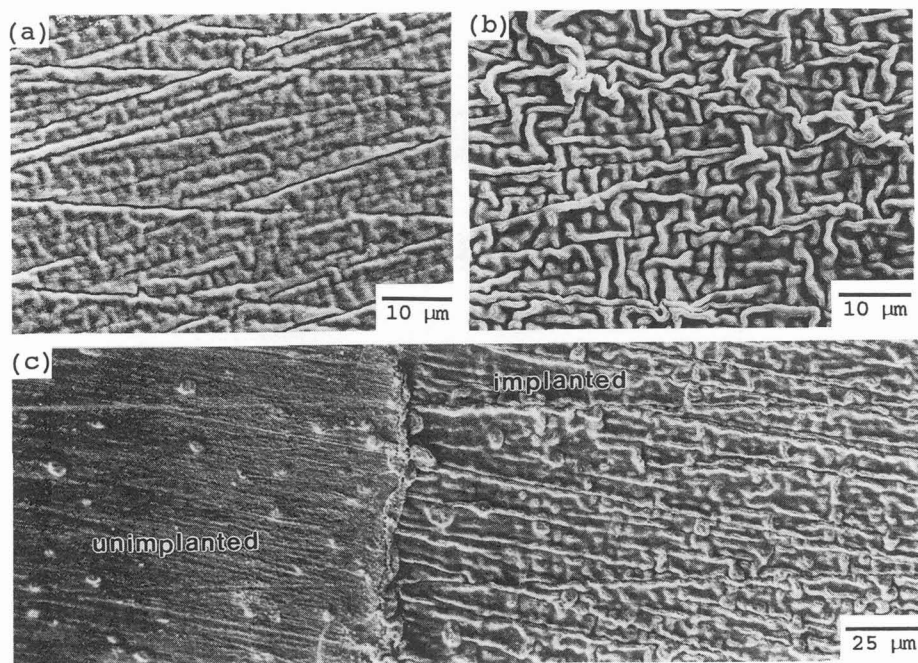


Fig. 1. — Morphology of Al_2O_3 scales formed after 15 minutes at 1100°C on: a) untreated Fe-18Cr-5Al; b) La-implanted Fe-18Cr-5Al; c) La-implanted Fe-18Cr-5Al-1Hf near the implanted/unimplanted interface region.

not caused by radiation damage, because there were other implants, such as Pt, Ti and W, that did not affect the oxidation behavior in any way.

Polished cross-sections of these thin scales are presented in figure 2. Other than the unimplanted FeCrAlHf alloy, all alloy substrates became rather wavy after oxidation. For the FeCrAl alloy, implantation decreased the mean wavelength of the waviness only slightly, but increased the amplitude by nearly a factor of two compared to the unimplanted alloy (Figs. 2a, b). For the Hf-containing alloy, implantation changed a nearly flat interface to a wavy one, as seen from figures 2d, c. No oxide pegs were observed in the Hf-containing alloy at this early stage. Randomly distributed Hf-rich particles, revealed under back-scattered electron imaging mode, were seen within the bulk of the alloy. The distribution of these particles corresponds well with the surface oxide nodules found on the unimplanted surface of this alloy (see Fig. 1c).

After longer oxidation times, oxide pegs began to develop in the Hf-containing alloy, usually along Hf-rich particles (Fig. 3c). Although the surface oxide of the implanted FeCrAlHf surface still appeared convoluted at this time, the scale remained very adherent. In contrast, the scales formed on the implanted surface of the FeCrAl alloy developed into large growth buckles, as seen in figure 3b. Compared to the untreated FeCrAl (Fig. 3a), the interface on the implanted one was now smoother, and there was a much greater degree of scale-alloy separation.

All of the alumina scales were identified by X-ray diffraction to be $\alpha\text{-Al}_2\text{O}_3$. RBS analyses were performed on the early stage scales (15 min oxidation), and figure 4 shows the results for the FeCrAl alloy with or without the La-implant. From this it is seen that the La-implanted

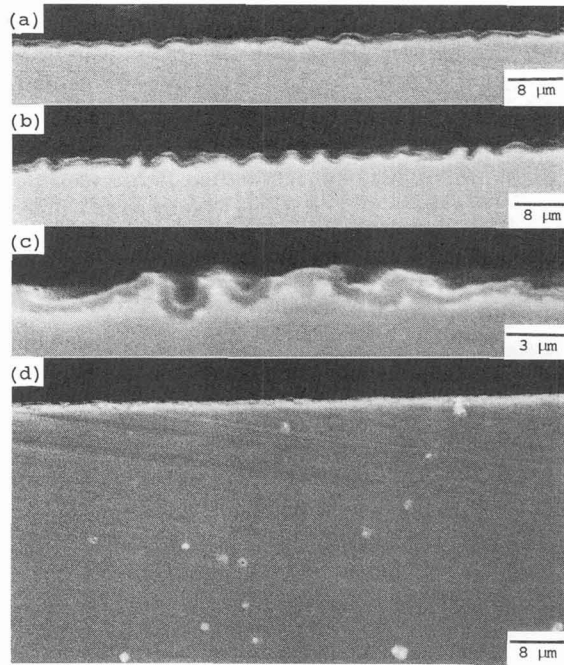


Fig. 2. — SEM image using backscattered electrons of scale cross-sections after oxidation at 1100 °C for 15 minutes. a) untreated Fe-18Cr-5Al; b) La-implanted Fe-18Cr-5Al; c) La-implanted Fe-18Cr-5Al-1Hf; d) untreated Fe-18Cr-5Al-1Hf.

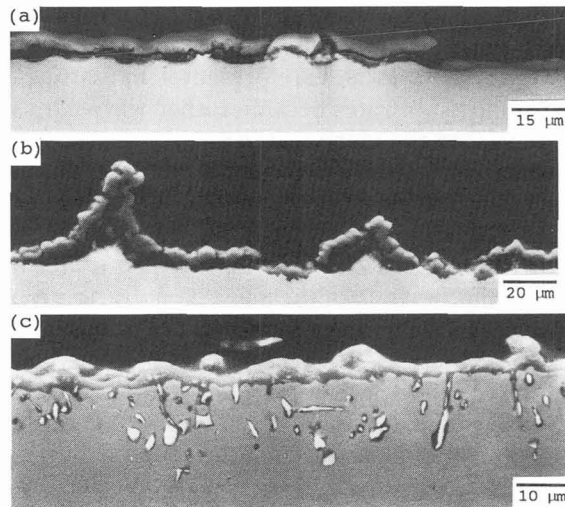


Fig. 3. — Polished cross-sections of Al₂O₃ formed at 1100 °C for 50 hours on: a) untreated Fe-18Cr-5Al; b) La-implanted Fe-18Cr-5Al; c) La-implanted Fe-18Cr-5Al-1Hf.

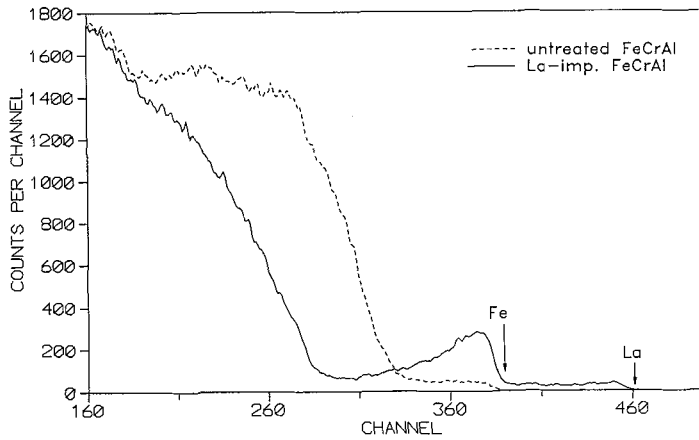


Fig. 4. — RBS spectra of implanted and unimplanted Fe-18Cr-5Al surfaces after 15 minutes oxidation at 1100 °C.

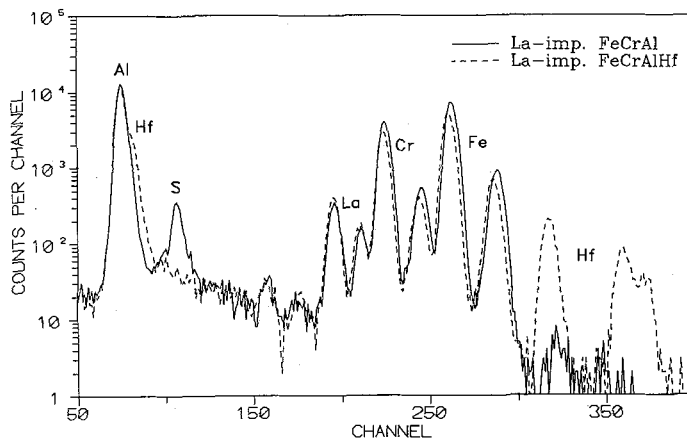


Fig. 5. — PIXE analyses of implanted Fe-Cr-Al and implanted Fe-Cr-Al-Hf alloys after oxidation at 1100 °C for 15 minutes.

surface had a thicker oxide which was enriched with iron. The oxide thickness was calculated to be 0.28 μm on the implanted surface and 0.16 μm on the unimplanted. The increase in the scale's iron content was ten-fold, and the iron concentrated at the outer surface of the scale. Lanthanum could be detected within the entire scale, with a slight enrichment at the outer surface. PIXE analysis of both the implanted and the unimplanted region of this alloy showed a clear sulfur peak as shown in figure 5. The detectability of PIXE for sulfur in this case was approximately 30 ppm. With the alloy having a sulfur content of only 15 ppm, the detected sulfur seen in figure 5 must be due to an enrichment within the surface region.

For the Hf-containing alloy, whether implanted or not, no sulfur was detected with PIXE (Fig. 5), but the implantation again increased the alumina scale thickness, as measured by RBS, from about 0.16 μm to 0.3 μm after a 15 minutes oxidation. Auger analysis showed that

the small oxide nodules on the unimplanted surface (see Fig. 1c) were richer in Fe and Hf than the smooth oxide underneath, which was mainly aluminum oxide. On the implanted side of the same specimen however, a surface enrichment of Fe was detected everywhere.

The scale on the untreated FeCrAl alloy delaminated easily under indentation loading, and the substrate surface was seen to convolute with the oxide above it (Fig. 6a). A very large portion of this alloy surface was covered with "oxide-imprinted" area, where the scale was believed to be in contact with the alloy at temperature. Only a few smooth areas corresponding to interface voids could occasionally be seen along surface polishing marks. On the implanted surface, indentation loading only caused small areas of scale decohesion. However, in this case, a large number of voids were found at the scale/alloy interface beneath the convoluted scale (Fig. 6b). The scales formed on the Hf-containing alloy, whether implanted or unimplanted, was very resistant to delamination. With a thicker scale, i.e. 50 hours at 1100 °C, some small areas of oxide from the implanted side could occasionally be removed, but the fractures occurred within the oxide layer, not at the scale/alloy interface.

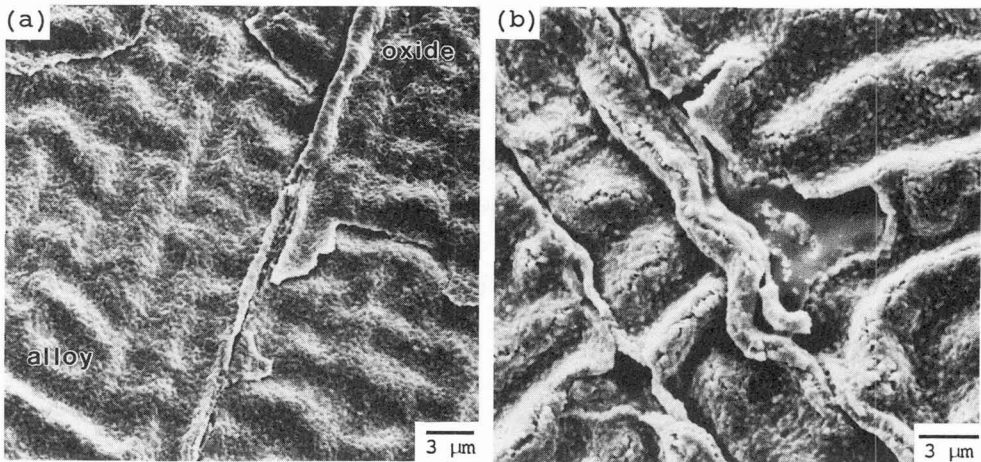


Fig. 6. — SEM image of the scale/alloy interface of: a) untreated Fe-Cr-Al b) La-implanted Fe-Cr-Al, after 15 min oxidation at 1100 °C. More voids were found beneath the convoluted scales of the implanted surface.

The chemistry of alloy surfaces exposed under high vacuum was studied using Auger electrons. Figure 7a shows a typical AES spectrum of the FeCrAl alloy surface underneath its 15 min oxide. The surface was slightly enriched in chromium. Both the sulfur and the carbon were believed to be impurities in the alloy which segregated to the growing interface [14]. The amount of interfacial sulfur and carbon was found to be the same on oxide-imprinted areas as on voids. Similar amounts of sulfur were found for the La-implanted sample, as seen in figure 7b. In this case, there was more carbon and oxygen due to a poorer vacuum condition.

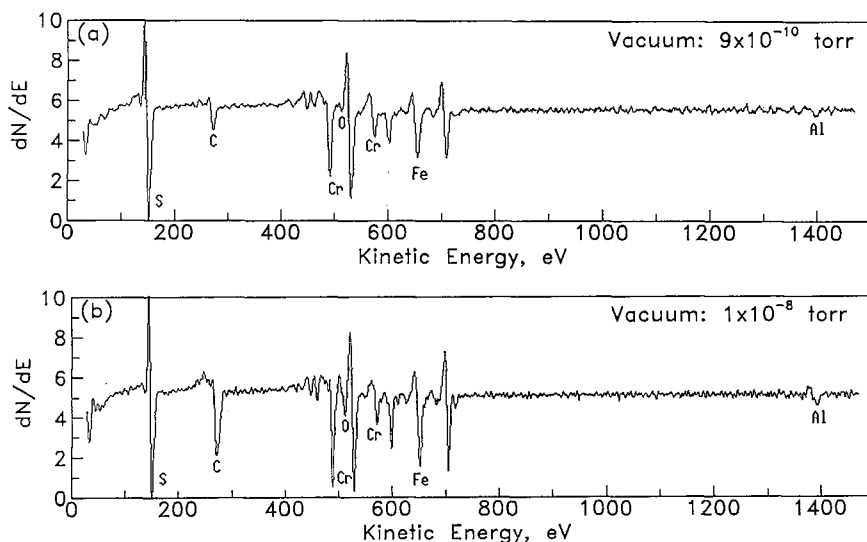


Fig. 7. — Typical Auger analyses of the substrate surface on: a) untreated Fe-Cr-Al alloy; b) La-implanted Fe-Cr-Al, after removal of the surface scales under ultra high vacuum. The surface scales were formed at 1100 °C for 15 minutes in oxygen.

4. Discussion.

With or without reactive metal implantation, the Fe-18Cr-5Al developed a continuous external α -Al₂O₃ scale upon oxidation at 1100 °C. The implanted reactive metal affected the early stage oxidation behavior of this alloy by: i) increasing the scale growth rate; ii) incorporating more iron in the first-formed oxide, with a higher concentration being at the scale surface; iii) developing a more convoluted oxide scale; iv) causing an increased scale separation from the underlying alloy and v) forming a very wavy scale/alloy interface. The implanted La was incorporated within the entire scale, with only a slight enrichment at the scale surface. However, the surface applied reactive element did not prevent impurity segregation, particularly sulfur, to the scale/alloy interface.

From the distribution of implanted La in the first formed Al₂O₃, and some recent transport studies conducted on growing alumina scales [15], the early stage scale growth must involve both cation outward transport and anion inward transport, resulting in a compressive stress, σ_{ox} , in the plane of the interface [16]. This σ_{ox} apparently deformed the underlying substrate in order for the thin scale to remain adherent to the alloy. Significantly more substrate deformation occurred on the implanted surface. The plasticity of the alloy should not be affected much by the implantation due to its shallow depth. Even if there were deep radiation damage, the effect would be to harden the alloy, making it more difficult to deform. Therefore, the wavier interface found on the implanted alloy must be caused by a higher σ_{ox} . Oxide growth which involved more transport of Fe into the scale on the La-implanted surface is believed to have produced the higher σ_{ox} . The Fe enrichment in the scale should have resulted from the high surface La concentration (3-4 at%), since stable La-Fe intermetallic compounds are thermodynamically favored [17].

A schematic of the wavy interface on the implanted alloy is presented in figure 8a. After 15 minutes oxidation, r was on the average of 1.2 μm , while the scale thickness was only

about $0.3 \mu\text{m}$. Due to the presence of σ_{ox} , there will be a tensile component, σ_n^i , normal to the interface at the asperity tips. The magnitude of σ_n^i increases with increasing curvature, r [18]. Since r was two times greater on the implanted alloy than on the untreated one, the interfacial tensile stress at asperity tips will be higher on the implanted alloy. The higher tensile stress could either by itself cause scale decohesion, or stabilize vacancy condensation to initiate scale separation [19]. Once there is an initial detachment, cracking could take place. According to Evans *et al.* [18], figure 8b, an initial decohesion of size $2a$ on a flat interface will not extend until the compressive stress in the oxide exceeds a critical value for oxide buckling. Once buckling starts, both normal and shear displacements occur at the interface, resulting in a stress concentration at the crack tip hence, a crack driving force. In the case of a wavy interface on the other hand, (Fig. 8c), once there is a small decohesion at the interface, there will automatically be a stress concentration at the edge of the separation, and crack extension half way down the asperity would be very easy. As soon as the scale has buckled away from the alloy, lateral growth within the scale would be no longer constrained by adhesion; consequently, large oxide growth buckles in the form of ridges could be expected.

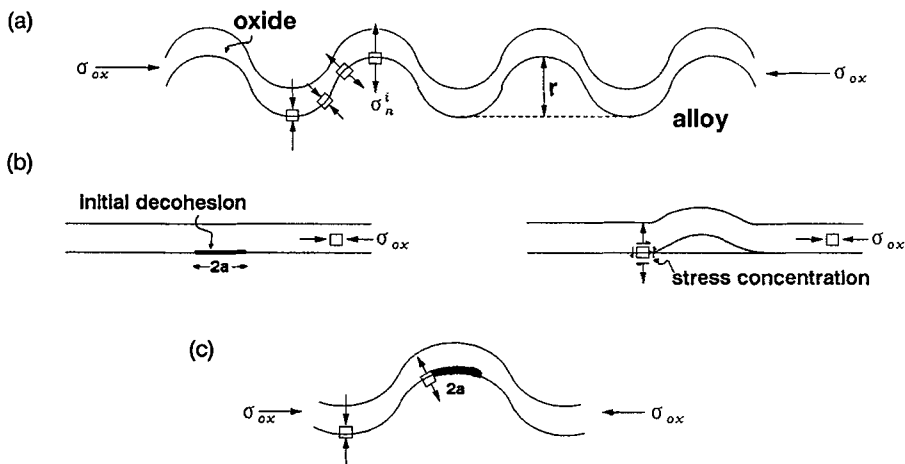


Fig. 8. — Schematic illustrations of a) the wavy interface developed on the La-implanted Fe-Cr-Al alloy and the local stress concentration at asperities; and the effect of scale decohesion on crack extension on: b) a flat interface; c) a wavy interface.

For the Hf-containing alloy, surface implantation of La also increased the initial oxide growth rate and caused the development of a more convoluted surface oxide with a wavier scale/alloy interface. Without the implantation, nodules of oxides rich in Hf and Fe grew from Hf-rich precipitates in the starting material. After implantation of La, a surface layer of Fe-rich oxide formed uniformly over the entire implanted surface. This implies that the high concentration of implanted La must have reacted with Fe in the alloy to form some intermetallic phases which would have given rise to an accelerated oxide growth with an enriched Fe content in the oxide. Again, this is expected to generate a higher stress within the alloy, which then caused the substrate to deform more severely.

From the above discussion, it appears that La-implantation affected the initial scale development on the Hf-containing alloy in the same way it affected the FeCrAl alloy. Nevertheless,

the scale which formed on the former was much more adherent, and this must be attributed to the presence of Hf in the alloy. In this study, sulfur was detected on all the non-adherent scales, but not on the adherent scales. These results together with recent publication on the strong adhesion of alumina scale on clean alloys [20] suggest that for the Al_2O_3 -forming MCrAl alloy systems, where M = Fe, Ni or Co, a strong interface seems to dominate over growth stresses, and interfacial strength may be enhanced by preventing impurities from segregating to the interface.

5. Conclusions.

Lanthanum implantation in Fe-18Cr-5Al, with or without alloying Hf addition, affected the early stage scale development on the two alloys in similar ways. The high concentration of implanted La immediately below the alloy surface reacted preferentially with Fe and formed a scale richer in Fe with an accelerated initial growth rate. A higher growth stress must have been generated which caused more substrate deformation, and a very wavy scale/alloy interface formed. Scale separation was then made easier at the asperities of the wavy interface, and a higher degree of oxide buckling resulted on the implanted FeCrAl alloy. The Hf-containing alloy however, never showed scale/alloy separation even though the substrate was equally deformed and the interface equally wavy. Sulfur was detected on scales formed on the FeCrAl alloy, but not on scales formed on the Hf-containing alloy. This was true with or without the implantation. Although growth stress played an important role in scale development, a stronger interface dominated the adhesion behavior in this alloy system.

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