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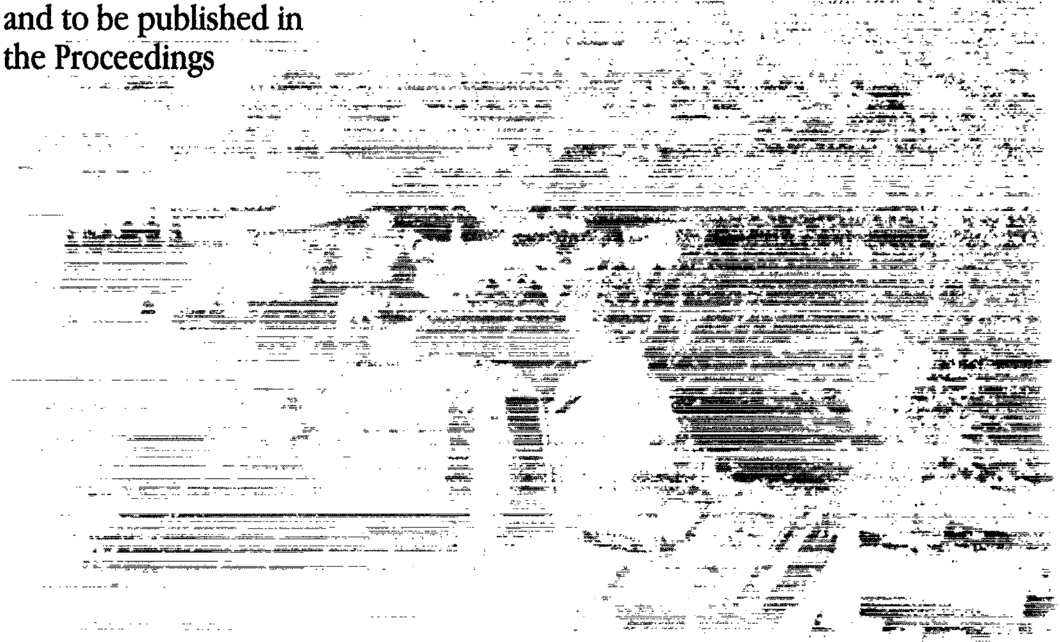

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Sulfur Segregation to Oxide/Metal Interfaces: a Comparison of Thermally Grown and Plasma Deposited Al_2O_3

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Abstract

The segregation of sulfur to oxide/metal interfaces was studied using Scanning Auger Microscopy after removal of the oxide film in ultra high vacuum. Two types of alumina films were investigated. One formed as a result of oxidation at 1000°C on a Fe-28at%Al-5at%Cr alloy; the other was deposited on the same alloy via a plasma synthesis technique, where Al was co-deposited with O to form an amorphous Al_2O_3 film, 0.2 or 0.8 μm in thickness. Subsequent heat treatment of the deposited film at 1000°C caused it to slowly transform to α-Al_2O_3, and the transformation took place at the film/alloy interface. Sulfur segregated to the interface during heat-treatment. The amount increased with heat-treatment time but was much less than that observed with scales formed by oxidation. Furthermore, not all of the film/alloy interfaces contained sulfur; the behavior was different from the uniform sulfur coverage found under thermally grown scales. Sulfur segregation to the film/alloy interface seems to be controlled by the availability of interfacial sites rather than by bulk diffusion rates.

Introduction

The detrimental effect of sulfur on oxide scale adhesion was first proposed about a decade ago.[1] The proposal later gained strong support from oxidizing sulfur free, or very low sulfur, alloys, where excellent scale-to-alloy adhesion could be obtained upon removal of sulfur on otherwise poorly adherent scales.[2,3] Sulfur, as a common impurity in the alloy, is believed to either facilitate interfacial void formation by segregating to the void surface, thus reducing its free energy of formation,[4] or by segregating to the scale/alloy interface and weakens the bonding between the scale and the substrate.[1,5] The enrichment of sulfur at the scale/alloy interface after oxidation has been demonstrated previously by Auger studies.[6,7] However, it is still not clear if sulfur should segregate to an intact oxide/alloy interface. From charge and size considerations, the segregation of sulfur to such an interface seems improbable.[4] Furthermore, the amount of sulfur found at interfaces that appeared to have good scale-to-alloy contact could be a result of interface sweeping, where sulfur in the alloy is accumulated at the moving interface as a result of scale growth. Although successively removing the surface oxide after each thermal cycle could decrease the amount of sulfur in the specimen[2], suggesting that sulfur diffused outward towards the scale. The experiment does not directly support segregation of sulfur to the interface. Moreover, since high void densities were always associated with higher bulk sulfur contents, the removal of sulfur may again be a result of segregation to interfacial void surfaces. It is therefore important not only to answer the question whether sulfur will segregate to an intact interface, but also to determine if it will take place on a non-growing interface. In this paper, results of sulfur segregation to a deposited film/alloy interface during heat-treatment are reported. The purpose is to answer the above questions and to compare the degree of segregation to that of thermally grown scales and to free surfaces.

Experimental

The alloy used for this study was Fe-28at%Al-5at%Cr, containing 37 ppm of sulfur. It was prepared by arc melting and casting, followed by hot rolling to a final thickness of 1.3 mm. Specimens, typically 10mm x 10mm, were cut from the sheets with one of the main faces polished to a 1 μm finish and cleaned prior to deposition or oxidation experiments.

For deposition of the alumina film, an aluminum metal plasma was first created, then aluminum oxide deposited onto the polished surface of the substrate with the presence of a background oxygen pressure in the deposition chamber.[8,9] A high ion energy (2000 volts) was used initially so as to atomically mix the film into the substrate, and a lower, but optimized, ion energy (200 volts) was used during the bulk of the film growth so as to add an 'ion assist' to the deposition. The latter stage is similar to an ion beam assisted deposition, or IBAD, process. Total thickness of the film was controlled by the deposition time. Two batches of specimens were deposited at a film thickness of 0.2 or 0.8μm.

After deposition, the specimens were heat-treated at 1000°C in a vacuum furnace back-filled with high purity He. To avoid oxidation of the deposited film, the specimen was placed on a flat piece of 99.8% alumina with the coated side facing down. The heating chamber was first evacuated to 10^{-6} torr, flushed and back-filled with He, then the whole process repeated again at 300°C before it was heated at a constant rate of 20°C/min to 1000°C. The specimen was held at 1000°C for a desired time, then slowly furnace cooled, within about 45 minutes, to room temperature.

Oxidation of the specimen was carried out in flowing dry oxygen at 1000°C with the specimen placed in an alumina boat. After the desired oxidation time, it was quickly pulled out of the furnace to cool.

Characterization of the thermally grown scales and the deposited films, in as-deposited and heat-treated conditions, were carried out using X-ray diffraction (XRD), Rutherford Backscattering spectroscopy (RBS) and Auger and Scanning Electron Microscopy (AES and SEM). In the ultra high vacuum Auger chamber, the specimen surface could be scratched with a micro-indenter to cause numerous fractures that exposed the film/alloy interface.[10] A 0.4 μm diameter electron beam was then used to study the composition of these interfaces. Some preliminary examinations of sample cross-sections by transmission electron microscopy (TEM) were also carried out to determine its microstructure.

Results

The as-deposited films were amorphous. Both the outer surface and the film/alloy interface were extremely flat. The outer portion of the film appeared featureless under TEM observations, but very fine crystallites existed in the inner 100 nm portion next to the film/alloy interface. RBS analysis of the film before and after heat-treatment is given in Table 1. The film is seen to be slightly enriched with oxygen, and film thickness varied across the specimen to about 5%. The heat-treatment was successful in preventing any oxidation. The film thickness appear to remain the same, but the film/alloy interface became rougher with heat-treatment time. TEM investigation of the 0.2 μm, 2h specimen indicated that locally, film thickness could increase or decrease by a factor of two from its original value, probably due to film crystallization.

SEM images of the film surface before and after the 0.5h heat-treatment are shown in Figure 1. In each case, the film had been scratched in the ultra high vacuum chamber for Auger analysis. A scratch mark and some scratch-induced interfacial fractures are therefore seen on some of these micrographs. The 0.8μm film after heat-treatment showed numerous channeling cracks on the film surface (Fig. 1b). These are believed to be developed during the heating cycle of the heat-treatment. As the specimen was heated, the alloy expanded more than the film due to their difference in thermal expansion. A tensile stress therefore existed in the film to cause these cracks. As expected, the thinner film (0.2μm) was more resistant and did not crack under the same conditions (Fig. 1c). Heat-treatments for 2 hours showed the same results in terms of film cracking. All of the films remained adherent after the heat treatments. Spallation only occurred after scratching.

Magnified views of the film and the film/alloy interface after heat-treatments are shown in Figure 2. After 2 hours, crystallites at the film/alloy interface can be seen with SEM. Glancing angle X-ray diffraction indicated the presence of α-Al_2O_3, but metastable Al_2O_3, particularly γ-Al_2O_3, was also detected. With the thinner film, these crystallites can be seen from the top surface (Fig. 2c), but on the thicker film, they are only apparent on the underside of the film (Fig. 2d). Fracture of the film caused some of the crystallites to remain on the substrate surface, while others were removed with the film, leaving small faceted pits at the interface. These crystallite formations are not as apparent from Figs. 2a and 2b of the shorter heat-treatment times. Preliminary TEM studies showed that the crystallites at the scale/alloy interface were α-Al_2O_3. Small pores could be found next to these α-Al_2O_3 grains, which probably developed as a result of the volume contraction associated with the phase transformation.

Compositions of the film/alloy interface are presented in Figure 3. Analyses were made on alloy surface after pieces of the film had been scratched off under ultra high vacuum. For each scratch, 8-10 different interfacial areas similar to those shown in Fig. 2 can be analyzed. Fig. 3a shows a typical spectrum of the as-deposited film/alloy interface. Some oxygen remained, which may be the oxygen implanted into the alloy during the initial high voltage deposition. The aluminum peak had the kinetic energy of the metal, not the oxide. Small amounts of common surface impurities, such as Si, P, S, Cl seems to be present, but their signals are not much stronger than that of the background. After heat-treatment, sulfur began to be enriched at these interfaces, and the amount increased with heat-treatment time (Figs. 3c and d). This was true for both film thicknesses. However, noticeable variation in the sulfur content could be found within one sample (Figs. 3b and 3c). Attempts were made to correlate these variations with the interfacial morphology, particularly in relation to the void-like features. Probing on or next to these voids did not show any indication that these areas had higher or lower sulfur contents. The variation in sulfur appeared random in relation to the microstructures. At least this was so under the resolution limit of the SEM on the Auger system, which was about 6000 times.

The amount of sulfur present at the thermally grown oxide/alloy interface was studied on a specimen after one hour of oxidation. By weight gain measurements, the scale was calculated to be 0.3 μm. Spontaneous spallation took place during cooling (Fig.4a), but enough scale adhered to carry out the scratch and the Auger study. The interface at this stage was almost entirely void-free. A typical Auger spectrum is shown in Fig. 4b. Variation of the sulfur concentration at these interfaces was small.

The average sulfur content for each sample and its standard deviation, represented by the error bars, are presented in Figure 5. Specimens with the 0.2 μm film had significantly higher standard deviation compared to the other samples, this being a result of varying sulfur contents found on different areas at the interface. The cause for this behavior is however not yet clear. On the same figure are also plotted the equilibrium segregation data to free surfaces of a high purity Ni-20Cr-12.5Al alloy[11] and a commercial 304 stainless steel[12] for comparison. The data for the 304 ss was converted from S/Fe peak height ratio to at% by estimating a 1/1 ratio to be equal to 10 at%. Although the concentration may not be correct, the faster rise to saturation is still valid. The saturation concentration reported by Funkenbusch et al[1] on their Ni-20Cr-12Al alloy, which contained less than 50 ppm sulfur, was as high as 19-20 at%, and this saturation was achieved in less than 0.17 hours. Compare to these surface segregation results, segregation to the film/alloy interface seemed slower and with a lower surface coverage.

Discussion

Sulfur, as an impurity in the iron-aluminide alloy, has been shown to segregate to an alumina film/alloy interface during high temperature anneal. The film did not oxidize during the heat-treatment. Therefore, the amount of sulfur found at the interface must have arrived from segregation rather than accumulation as a result of interfacial sweeping. Since the film was deposited amorphous, crystallization took place during annealing and nucleation of α-Al_2O_3 occurred at the film/alloy interface. This undoubtedly requires atomic movements at the film/alloy interface as the original amorphous film transforms into crystalline grains. It is possible that this crystallization process, which must alter the original film/alloy interface, may have an effect on sulfur segregation. For if sulfur would not segregate to a static, intact oxide/metal interface, it may very well segregate to a dynamic interface where atoms in the oxide film and perhaps also in the substrate are rearranging themselves. This is of course different from interface sweeping, whereas the interface moves upon sulfur atoms in the bulk and collects them. The dynamic nature of the interface would be even more dramatic in the case of a growing oxide. Future work will be performed on α-Al_2O_3 coatings to study the behavior of interfacial segregation without the complication of film crystallization.

Small faceted void-like features were always found on the alloy surface beneath the film, and they increased in size with longer heat-treatment time. However, sulfur concentration was not higher at or near these features. Instead of interfacial voids, they appear to be the sites of crystallites that formed at the film/alloy interface and was pulled out with the fractured film. If interface rearrangement caused by film crystallization may enhance sulfur segregation, as suggested in the previous paragraph, one would expect more sulfur at these faceted pits. However, this was not true. In fact, the variation of sulfur content at various interfacial locations cannot be related to microstructures that are resolvable under the SEM. Nevertheless, these variations are important, because they suggest that the interface has different sites on which the tendency of segregation varies. This may be related to different orientations and cohesiveness between the film and the substrate. Unfortunately, these films are unstable under the electron beam of the TEM, so correlation between S contents and detailed microstructural analysis could not be made.

It is useful to compare the rate and degree of this interfacial segregation to that of surface segregation. Although the most reliable comparison should be made with the same alloy under the same microscope, the results presented in Fig. 5 provides a semi-quantitative view. It is seen that the interfacial segregation reported here was slower than any of the surface segregation found at 1000°C. Furthermore, if one uses a sulfur diffusivity of 4.8×10^{-10} cm^2/s at 1000°C, which is lower than that in pure γ-Fe or pure Ni,[13] and a simplified McLean law,[14] $C_s = 2\, C_o (D\, t / \pi)^{1/2}$, where C_s and C_o are the surface and bulk concentration respectively, the calculated C_s after 30 minutes is 3×10^{15} atoms/cm^2 for the 37 ppm S alloy studied here. This level is high enough for a saturation coverage, if saturation corresponds to 1/2 a monolayer. Therefore, segregation to the film/alloy interface seems to be site controlled, rather than diffusion controlled. This conclusion is also supported by the fact that the sulfur content varied from different locations on the interface. Much faster and more uniform segregation occurred on the interface between the thermally grown scale and the alloy. The reason may be a combination of interface sweeping and the presence of energetically more favorable sites for segregation.

Conclusions

Segregation of sulfur to oxide/alloy interfaces has been demonstrated with a deposited alumina film on an iron aluminde substrate. High temperature anneal at 1000°C in an inert atmosphere was able to prevent any film growth, but caused sulfur to slowly segregate to the interface. The rate of segregation appeared slower than segregation to the free surface or to thermal scale/alloy interfaces. The process was suggested to be controlled by the availability of interfacial sites rather than by bulk diffusion rates. Nucleation of α-Al_2O_3 took place at the film/alloy interface during the anneal. It is not clear how this process would affect the segregation behavior. Future studies will be performed on α-Al_2O_3 films to better determine the behavior of impurity segregation to non-growing oxide/metal interfaces.

Acknowledgment

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Figure Captions:

1. SEM micrographs of the film surface before and after annealing at 1000°C in He for 0.5 hrs. (a) 0.8 μm, as-deposited, (b) 0.8 μm, after anneal and (c) 0.2 μm, after anneal. A scratch mark made to cause film fracture is present on all the samples.

2. Magnified view of the film and the film/alloy interface of a (a) 0.2 μm film, annealed 0.5 hr., (b) 0.8 μm film, annealed 0.5 hr., (c) 0.2 μm film, annealed 2 hrs. and (d) 0.8 μm film, annealed 2 hrs. Part of the fractured film in (d) shows the film underside.

3. Auger analysis of the film/alloy interface after removal of the film under ultra high vacuum. (a) as-deposited, (b),(c) after 0.5h anneal, different areas of the sample and (d) after 2h anneal.

4. (a) Morphology of the oxide scale and the scale/alloy interface after oxidation at 1000°C for 1 hour. (b) Composition of the interface by AES.

5. Concentration of sulfur segregated to the film/alloy interface and to the thermal scale/alloy interface compared with other free surface segregations.

Table 1: Summary of RBS analysis of the deposited alumina films before and after annealing

Sample		Thickness (x10^{18} atoms/cm^{2})	Composition	Comment on interface
0.8 µm	as-dep. center	7.0	$Al_{0.35}O_{0.65}$	sharp
	as-dep. top	7.35	$Al_{0.37}O_{0.63}$	sharp
	as-dep. bottom	6.65	$Al_{0.37}O_{0.63}$	sharp
	1000°C, 0.5 hr	7.3	$Al_{0.40}O_{0.60}$	rough
	1000°C, 2 hr	7.2	$Al_{0.40}O_{0.60}$	very rough
0.2 µm	as-deposited	2,05	$Al_{0.38}O_{0.62}$	sharp
	1000°C, 0.5 hr	1.95	$Al_{0.40}O_{0.60}$	slightly rougher
	1000°C, 2 hr	2.1	$Al_{0.40}O_{0.60}$	very rough

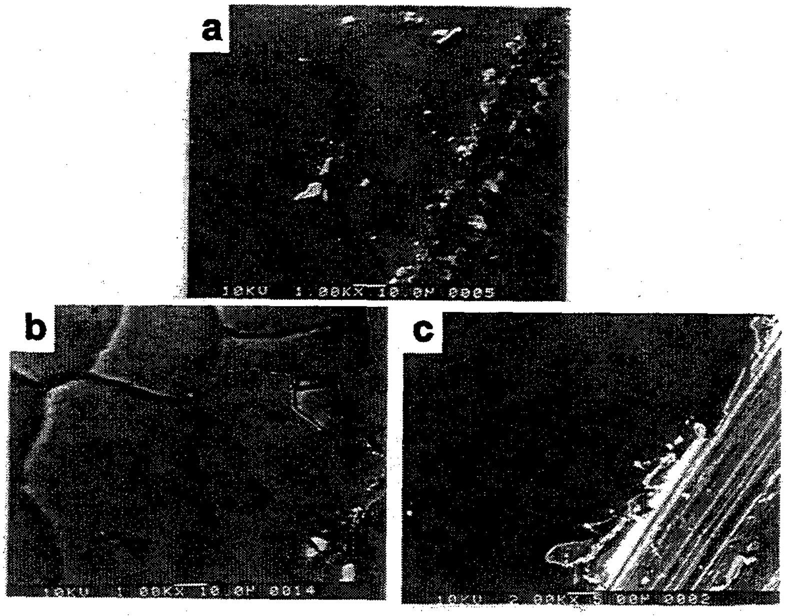
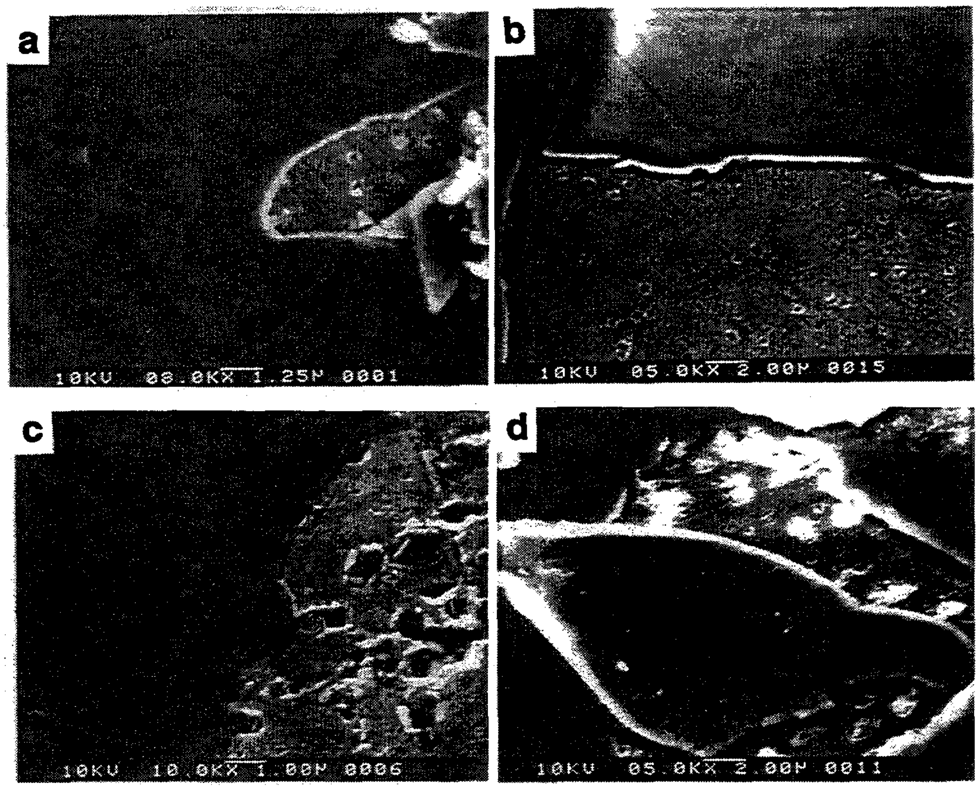


Figure 1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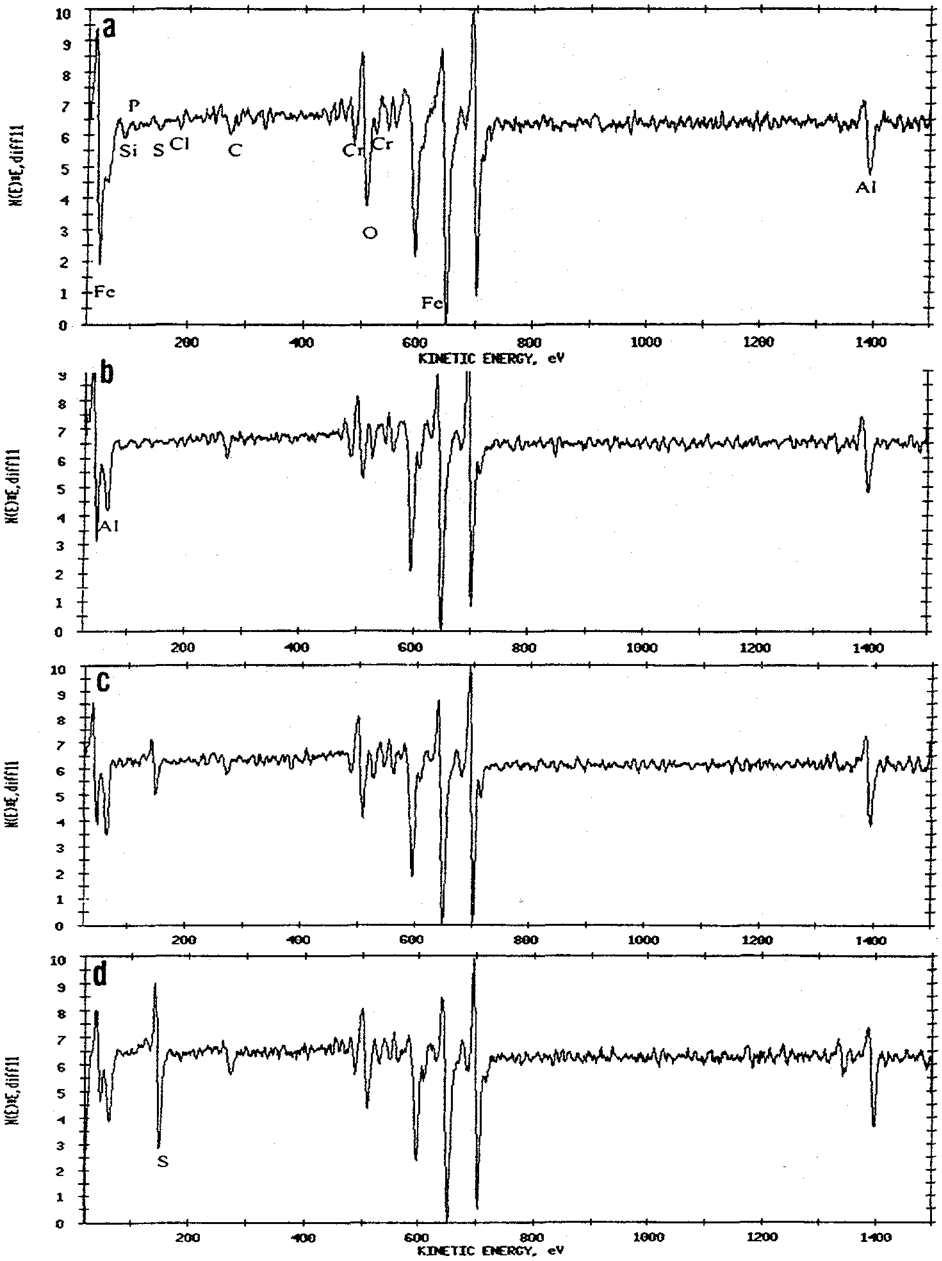
b
10KV 05.0KX 2.00µ 0015
c
10KV 10.0KX 1.00µ 0006
d
10KV 05.0KX 2.00µ 0011

Figure 2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b
c
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Fe
Si
P
S
Cl
C
Cr
Cr
O
Fe
Al
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Figure 3

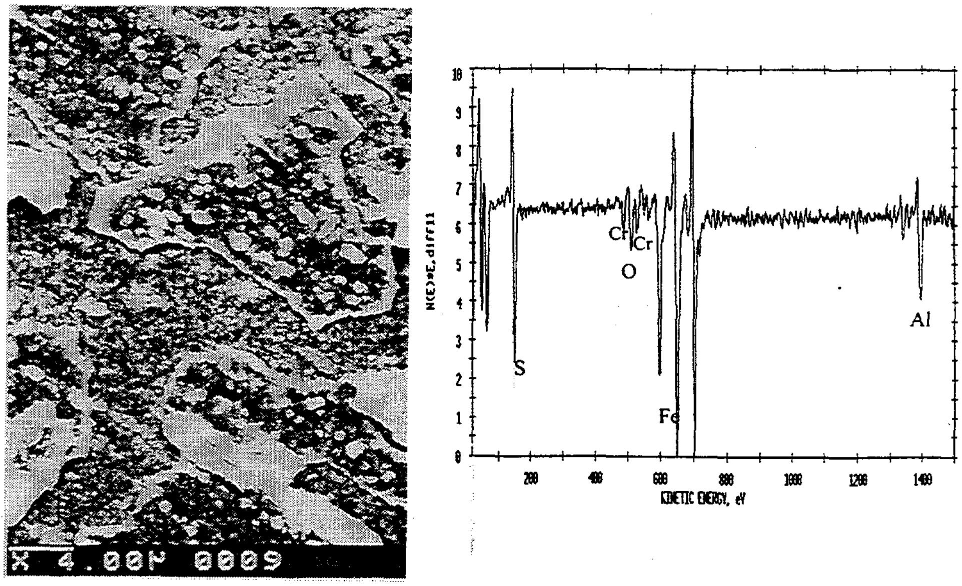

Figure 4

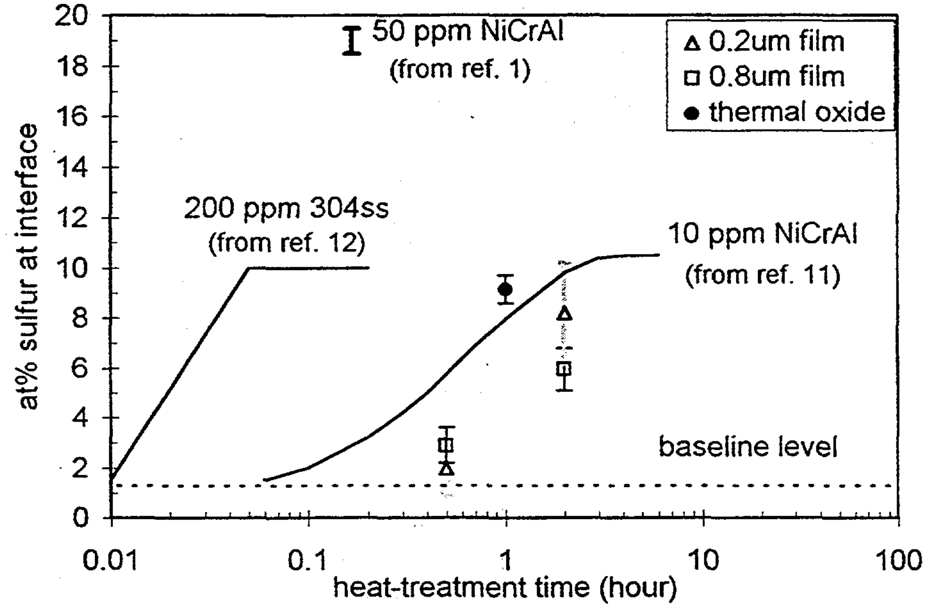

Figure 5