

The Effect of Thermal Annealing on the Adherence of Al₂O₃-Films Deposited by Low-Pressure, Metal-Organic, Chemical-Vapor Deposition on AISI 304

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Thin alumina films, deposited at 280°C by low-pressure, metal-organic, chemical-vapor deposition on stainless steel, type AISI 304, were annealed at 0.17 kPa in a nitrogen atmosphere for 2, 4, and 17 hr at 600, 700, and 800°C. The effect of the annealing process on the adhesion of the thin alumina films was studied using a scanning-scratch tester, type SST-101, developed by Shimadzu. The best mechanical properties were obtained with unannealed samples. After thermal annealing the critical load decreased, proportional to annealing time and/or temperature. This effect was probably due to the presence of a high thermal stress and to preferential segregation of sulfur near the oxide-alloy interface.

KEY WORDS: metal-organic; chemical-vapor deposition (MOCVD); thermal annealing; alumina films; scanning-scratch test (SST); adherence.

INTRODUCTION

Thin oxide films, deposited by a variety of techniques, offer great potential for a large number of possible applications, such as corrosion-protective coatings, optical filters, wear-resisting coatings, and insulating layers.^{1,2} Next to the electrical, optical, or corrosion-protective properties of the layers

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themselves, the mechanical properties of these layers are also of major importance. It is well known that alumina films have excellent chemical properties resisting several types of corrosion.^{1,3,4} On the other hand, alumina is very hard, brittle, and sensitive to thermal shock. Furthermore, it is difficult to deposit alumina films with a high adherence onto metallic substrates, due to the difference of many material properties, such as Young's modulus and the thermal-expansion coefficient, between the alumina and the substrate.⁵

Thin oxide films, deposited by metal-organic, chemical-vapor deposition, may possess high internal stresses.^{1,6} They consist of a thermal and an intrinsic part. The presence of the thermal stress is due mainly to the difference between the deposition temperature and the actual temperature, whereas the intrinsic stress is more related to the deposition mechanism and will be built into the film during the film-formation processes. It was found^{3,7} that postdeposition thermal treatment significantly reduces the intrinsic stress. The thermal stress is still present, due to the difference between the annealing and actual temperatures.

In this study the effect of thermal annealing on the adherence of thin alumina films, deposited on stainless steel AISI 304 by low-pressure, metal-organic, chemical-vapor deposition, was studied by means of scanning-scratch testing. The critical load that causes adhesion failure was determined. AES and EDX were used in order to examine the interface between the metallic substrate and the alumina film.

EXPERIMENTAL DETAILS

Preparation of the Samples

Depositions were performed on stainless steel, type AISI 304 (18% Cr, 8% Ni, 0.08% C, 1% Si, 2% Mn, 71% Fe). The AISI 304 samples (discs: 12- and 20-mm diameter with 1-mm thickness) were ground on SiC paper to a final size of 4000 grit followed by a polishing treatment with Al₂O₃ (3 μm) and subsequently cleaned ultrasonically for 30 min in soap, hexane, and ethanol. Finally, the samples were immersed in Streuer's etching fluid (5% solution of 3 M nitric acid in ethanol) for 15 min, washed with pure ethanol, and dried in hot air.

Low-Pressure MOCVD of Al₂O₃

The Al₂O₃ coatings were deposited by pyrolysis of ATSB (Janssen Chimica) in a LPCVD system.⁴ It consists of a horizontal quartz tube reactor (134 cm long, 10 cm in diameter) in a three-zone furnace (Tempress model Omega Junior). A stream of pure nitrogen gas (Praxair nitrogen 5.0) was

passed through the ATSB precursor in a silicon-oil bath. The ATSB had a vapor pressure of 0.1 kPa (0.8 torr) at 134°C. This saturated gas was diluted with pure nitrogen before entering the reactor. The gas line between the ATSB container and the reactor was heated to 150°C to prevent condensation of the precursor. All gas streams were controlled by electronic mass-flow controllers (Brooks 5850TR). The linear gas velocity in the reactor was 2.6 m/s. The deposition temperature was monitored by three thermocouples which were positioned into the reactor below the specimens. The temperature profile was maintained as flat as possible ($\pm 0.5^\circ\text{C}$) over the length of the specimen load. The reactor pressure during deposition was monitored by capacitive pressure sensors (MKS Baratron type 122A) and kept at the desired value by adding an excess flow of nitrogen to the vacuum pump (Leybold D65BCS). Standard conditions were deposition temperature, 280°C; partial pressure of ATSB, 3.7×10^{-4} kPa (ATSB saturation temperature, 134°C); reactor pressure, 0.17 kPa; film thickness, 0.5 μm .

Thermal Annealing

After the deposition process, the ATSB flow was stopped and the samples were exposed to a nitrogen atmosphere at temperatures ranging from 600 to 800°C, for 2, 4, and 17 hr. After the deposition process the furnace was heated to the desired annealing temperature in 30 min. After finishing the thermal-annealing period, the temperature was lowered below 200°C before the samples were removed from the furnace.

Scanning-Scratch Tests

Scanning-scratch-adhesion measurements were performed with a SST-101 scanning-scratch tester developed by Shimadzu in collaboration with the Kinbara Laboratory in the Engineering Department of Tokyo University. Using the SST-101, the adhesion of thin films is evaluated by the load (critical load), corresponding to the site where the film starts to peel by scratching with a hard stylus. A detailed description of the SST-101 is given elsewhere.³

The specific test parameters for the alumina films were stylus tip radius, 25 μm ; amplitude, 50 μm ; down speed, 1 $\mu\text{m/s}$; stage-drive speed along the *Y* axis, 20 $\mu\text{m/s}$.

Characterization of the Surface Morphology

To characterize the chemical composition and the depth profile, the alumina films were analyzed with a Perkin-Elmer PHI 600 scanning Auger multiprobe. Alternate sputtering and Auger analysis were used for in-depth

analysis. The kinetic energies of the emitted photoelectrons were analyzed with a concentric hemispherical analyzer.

The morphology and the chemical composition of the specimens were also investigated by means of optical and scanning electron microscopy (JEOL M 35 CF), the latter equipped with an EDX analysis system (Kevex Delta, class III).

RESULTS

Scanning Electron Microscopy

Surface scans of the specimens using scanning electron microscopy, before and after the thermal treatment, are shown in Figs. 1a–d. As described above, the thermal treatment was performed in a nitrogen atmosphere at 0.17 kPa, immediately after the deposition and without cooling of the specimens. From these pictures it is clear that no spallation by cracking and delamination was observed after the thermal treatment at mild conditions (up to 700°C during 4 hr; see Fig. 1a). Only after treatment at high temperatures and long exposure times did the alumina films show localized spallation and delamination and were sometimes totally removed from the underlying substrate. After 17 hr at 700°C, only small parts of the alumina films were removed (Fig. 1b), which was more pronounced at 800°C (Figs. 1c,d). Also at longer exposure times, the cracking and delamination behavior intensified. At local sites, see Fig. 2a, where cracks were present, chainlike, manganese-rich chromia (Fig. 2b) was formed. After delamination of the thin alumina film, the surface morphology of the underlying substrate showed a channel-like removal of the substrate material, just on the sites where these chainlike products were formed before delamination occurred. Probably, the internal products were simultaneously removed during the spallation and delamination of the alumina film. The alumina films, which crack and delaminate from the underlying substrate after the thermal annealing procedure, bend convexly. This may be explained by the presence of a stress gradient, compressive at the outer part of the alumina film. No new alumina was formed on the edges and sharp corners of the spalled film or on the uncovered substrate surface.

Auger Electron Spectroscopy and Energy Dispersive X-ray Analysis

Element analysis at the interface between the delaminated alumina film (thermal treatment: 800°C during 4 hr) and the underlying substrate was performed by Auger electron spectroscopy in combination with ion sputtering. From the steady-state Auger spectra (survey scan; see Fig. 3a), it is clear that next to the elements from AISI 304, in this case chromium, iron,

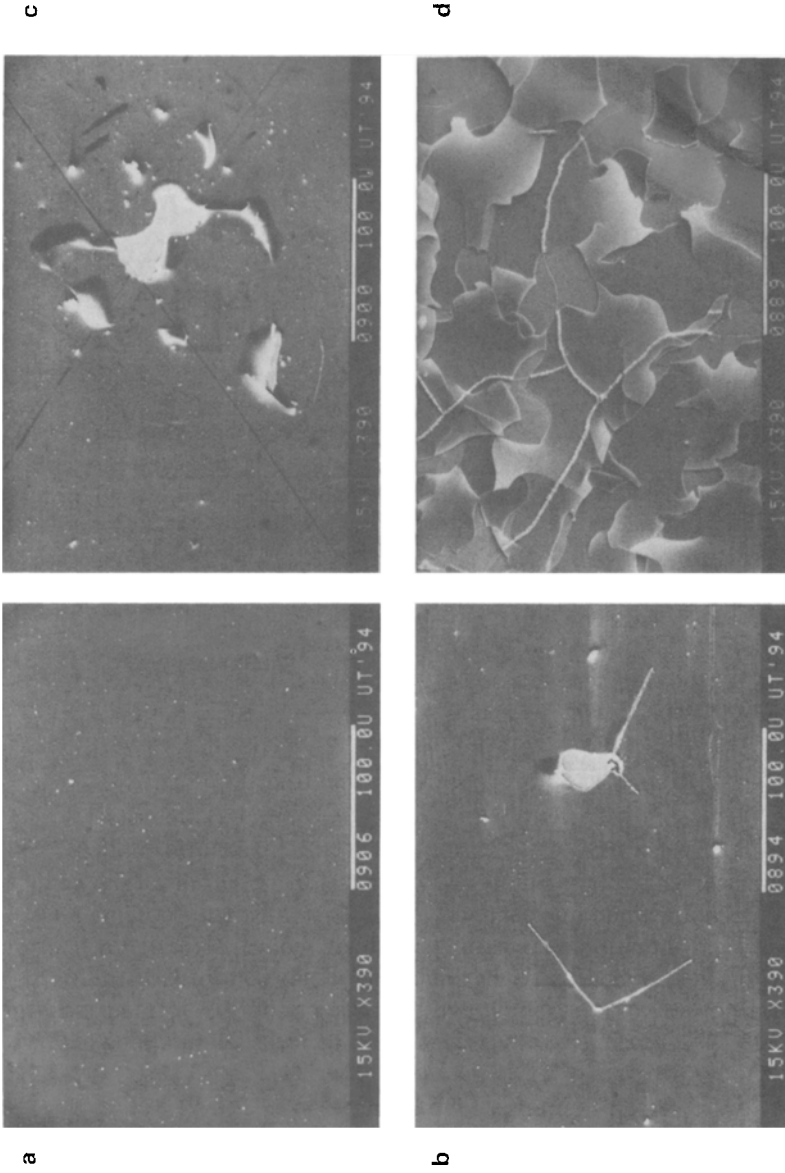


Fig. 1. SEM image of the surface morphology of the specimens after thermal annealing for (a) 4 hr at 700°C, (b) 17 hr at 700°C, (c) 2 hr at 800°C, and (d) 4 hr at 800°C. Reduced 23% for reproduction.

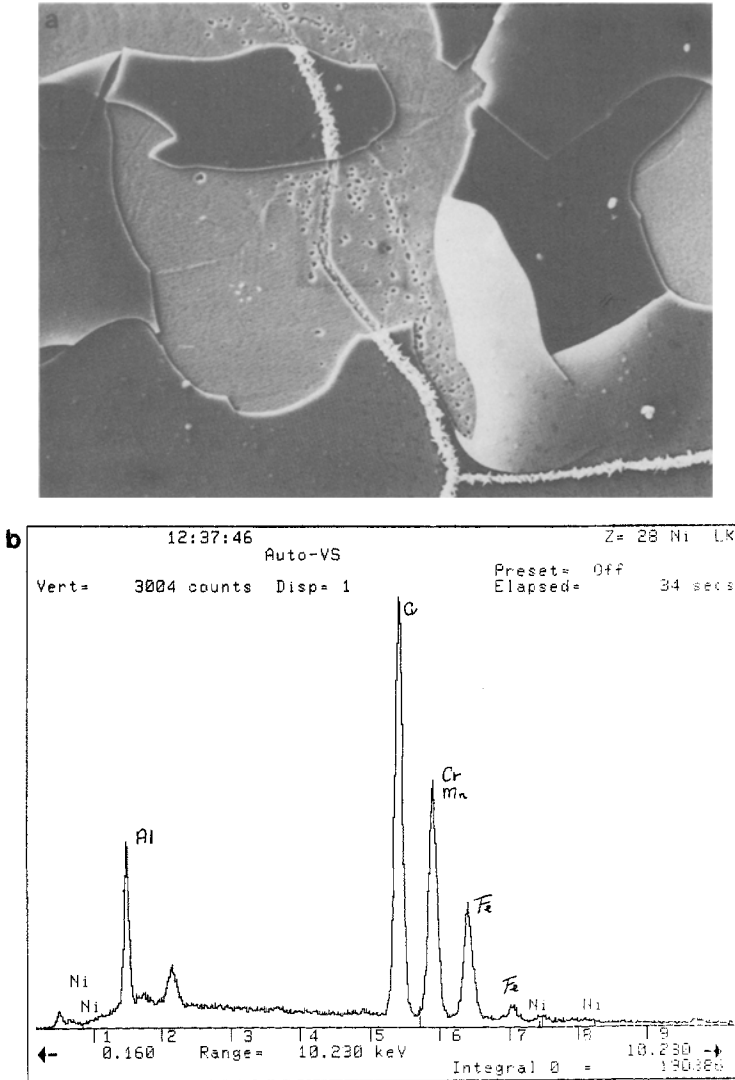


Fig. 2. (a) SEM image of the surface morphology of the specimen after thermal annealing for 4 hr at 800°C. (b) EDX spectrum of the chainlike products formed on the alumina scale.

and nickel, small amounts of sulfur were also detected. After two sputtering cycles (one cycle corresponds to 1-min sputtering at a rate of 1 nm/min) the amount of sulfur decreased below the detection level; see Fig. 3b). Figure 4 shows the AES depth profile of the specimen annealed at 800°C during

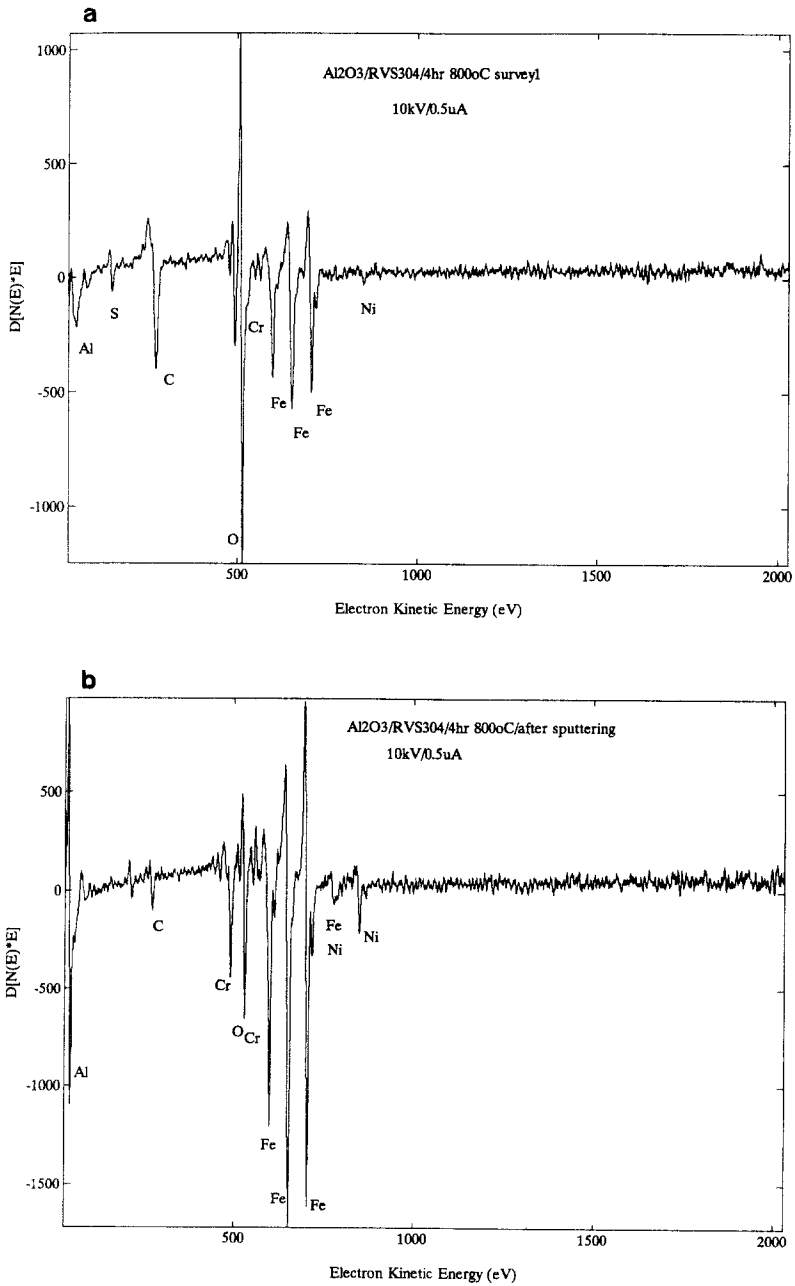


Fig. 3. AES analysis (survey scan) of the alumina-AISI 304 interface (annealed for 4 hr at 800°C) (a) without sputtering, (b) after two sputtering cycles of 1 nm/min.

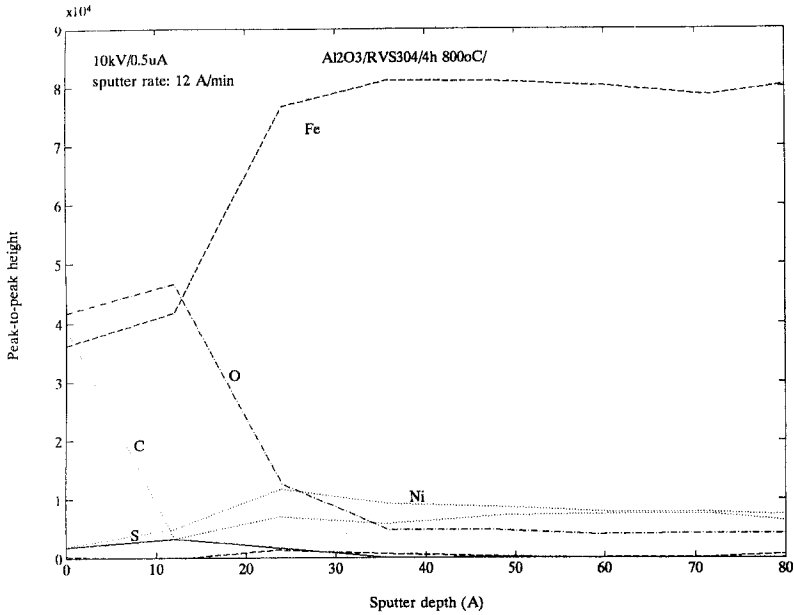


Fig. 4. AES depth profile of the substrate AISI 304, started at the oxide-substrate interface (annealed for 4 hr at 800°C).

4 hr. From these observations it can be seen that the sulfur concentration increases at the interface, compared to the bulk concentration in the stainless steel AISI 304.

In addition to the element analysis by AES, energy dispersive X-ray analysis was performed. Spectra of different parts of the surface are shown in Fig. 5. Three positions were analyzed: (1) the surface of the alumina film (Fig. 5b) at the gas side (after thermal annealing for 4 hr at 800°C), (2) the surface of the substrate (Fig. 5c) after delamination of the alumina film (after thermal annealing for 4 hr at 800°C), and (3) the surface of the substrate (Fig. 5d) without thermal annealing (as received). These spectra showed that after a thermal treatment for 4 hr at 800°C, a detectable increase of sulfur at the alumina-alloy interface was determined.

Scanning-Scratch Tests

Table I shows the critical load (L_c) as a function of the postdeposition thermal treatment for the thin alumina films. The critical loads were obtained from the scratch-loading curves corresponding to the position of the first sudden increase of the output voltage. For each sample at least five scratches were made so that the average and the spread of the critical load could be

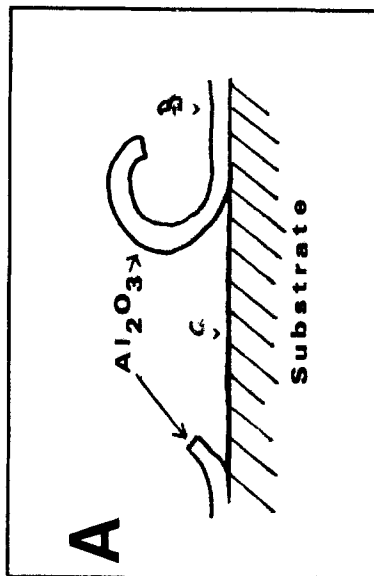
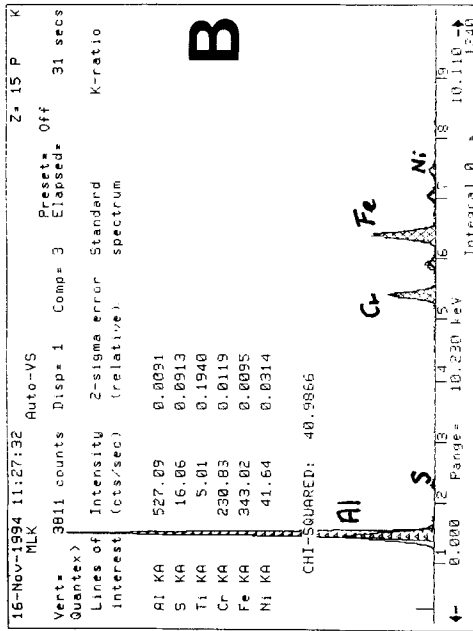


Fig. 5. EDX spectra for different positions of a delaminated Al_2O_3 film on AISI 304 (after thermal annealing for 4 hr at $800^{\circ}C$).

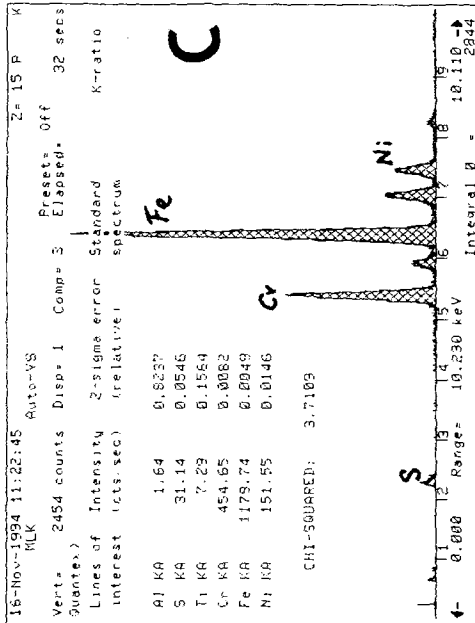
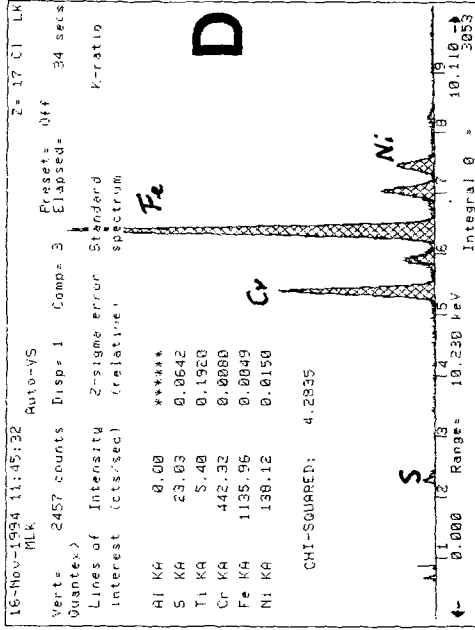


Fig. 5. Continued.

Table I. Critical Loads (mN) for Alumina Films Deposited at Low Pressure on AISI 304 as a Function of the Thermal-Annealing Treatment

| Exposure time (hr) | Thermal annealing at elevated temperatures | | |
|-----------------------|--|-------|--------------------|
| | 600°C | 700°C | 800°C |
| 2 | 99±9 | 73±4 | 51±8 |
| 4 | 84±7 | 67±5 | Local delamination |
| 17 | 58±7 | 75±10 | Local delamination |

calculated. From this table, it is clear that the critical load decreases with increasing annealing time and/or temperature. Under extreme conditions, in this case at least for 4 hr at 800°C, the films blistered and delaminated from the substrate surface. In that case, it was hardly possible to obtain reproducible results. In Fig. 6, the output voltage is shown for three samples as a function of the load, the first without (6a) a thermal treatment, the second (6b) with a thermal treatment at 700°C for 4 hr, and the third (6c) for 2 hr at 800°C. The initial part of the curves, corresponding to low loads, is characterized by a simultaneous deformation of the alumina coating and the substrate. With increasing load the deformation and the friction between the stylus and the film surface both increased. Due to the increased frictional force, the delay in the stylus movement to the cartridge becomes larger, resulting in an increasing cartridge output. In this stage, no spalling or delamination occurs. The first sudden increase of the output voltage is used for the determination of the critical load. From this figure it is remarkable that the effect of a sudden increase in the output voltage is much more pronounced for the thermally annealed specimens than for the specimens without any annealing treatment. This effect of a sharp increase of the output voltage was obtained for all the thermally annealed specimens. From optical and scanning electron microscopy a sudden change of surface morphology was observed at which the delamination of the oxide film starts. Figure 7 shows the scratch morphology of the alumina films, one without (7a) and one with (7b) a thermal treatment (700°C, 4 hr). These SEM pictures also revealed that delamination of the film after reaching the critical load L_c is more pronounced for the annealed specimens.

DISCUSSION

Not only the chemical properties, such as the stability against aggressive compounds, but also the mechanical properties of coatings to be used for corrosion protection are of major importance. A badly adherent oxide film with an excellent chemical resistance against different compounds at high

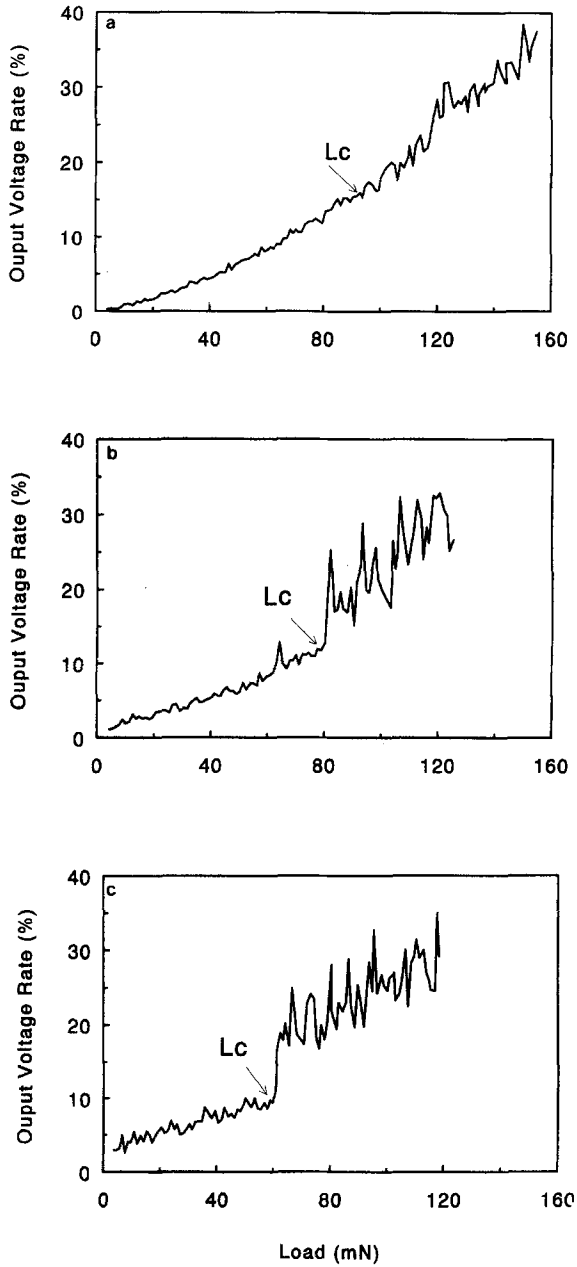


Fig. 6. Output voltages rates (%) of alumina films as a function of the load (mN) (a) without thermal annealing, (b) annealed for 4 hr at 700°C, and (c) annealed for 2 hr at 800°C.

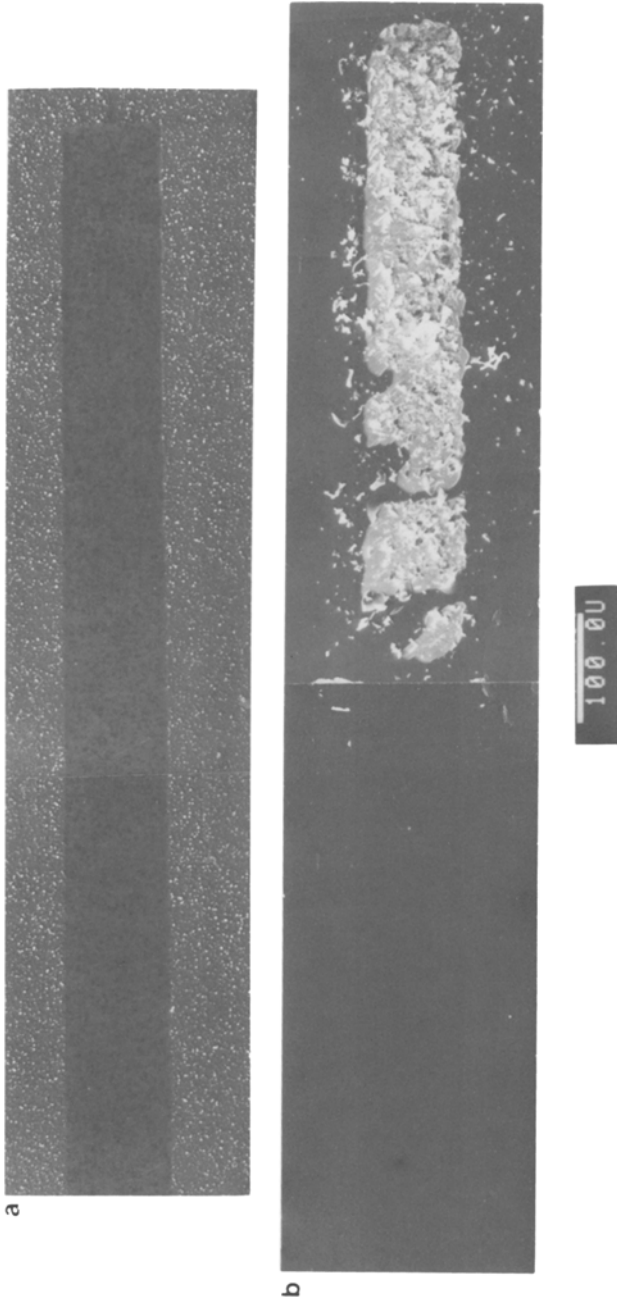


Fig. 7. Scratch morphology of the spalled and delaminated alumina films deposited on AISI 304. (a) Without thermal annealing, (b) annealed for 4 hr at 700°C.

temperatures is very sensitive to any damage caused, for example, by small particles or temperature changes. Therefore, the mechanical aspects of thin alumina films were investigated by means of the scanning-scratch tester SST-101. It was found⁸ that thermal annealing of alumina films on a metallic substrate, AISI 304 stainless steel, had a beneficial effect on the chemical resistance against high-temperature corrosion. Regarding these alumina films, deposited at atmospheric-pressure, metal-organic, chemical-vapor deposition (MOCVD), the crack density was significantly reduced after the thermal treatment. This probably indicates that the susceptibility to crack formation for the alumina films deposited at reduced pressure may also reduce by this postdeposition thermal treatment. Most results are indicated by "very good," "good," "fairly good," or "poor," or by weight gains after thermal-cycling experiments.⁹ In order to measure the strength between the oxide film and the metallic substrate in a more quantitative way, adhesion tests were performed with the SST-101. The adhesion strength is not indicated by the amount of spallation or delamination, or by terms such as "good" or "poor," but is given indirectly by a critical load L_c . The difference in adhesion can now be measured in spite of the fact that oxide spalling neither occurred after the deposition process nor after the postdeposition thermal treatment. For example, SEM analysis revealed that the alumina films show adherence at annealing temperatures up to 700°C and exposure times up to 4 hr, but show initial-crack formation after 17 hr at 700°C or 2 hr at 800°C. From the results obtained only from optical or scanning electron microscopy nothing can be reported on the difference between the adhesion strengths of films annealed at 600°C and different exposure times. Using the SST-101, a lower critical load was found after the thermal treatment for long periods and at high temperatures, indicative of a higher sensitivity of scale failure, for example, spalling or delamination. This reduction of L_c after thermal-annealing processes can be explained as

1. the presence of thermal stresses in the thin alumina films as a result of the difference in the coefficient of thermal expansion of the film and the substrate, and
2. modification or change in the interfacial structure and/or composition.

Assuming that the growth stress has fully disappeared by the thermal treatment,⁸ the total stress is now equal to the thermal stress, which can be calculated by the simplified equation

$$\sigma_{\text{total}} = \sigma_{\text{thermal}} = E_f \Delta T \Delta \alpha \quad (1)$$

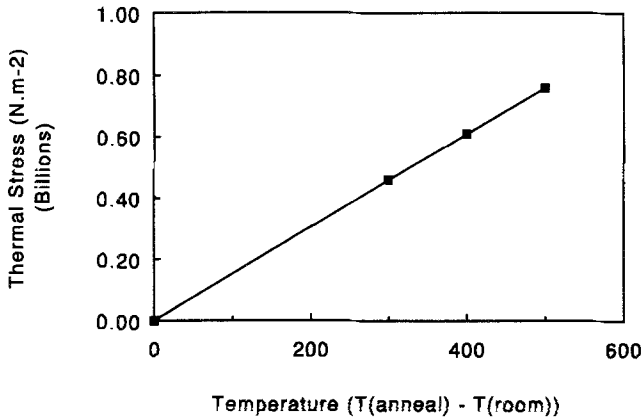


Fig. 8. Thermal stress in the alumina films deposited on AISI 304 as a function of the difference between annealing and actual temperature.

where E_f = Young's modulus of the film

ΔT = difference between deposition and actual temperatures

$\Delta\alpha$ = difference between thermal-expansion coefficients

An increasing difference between the annealing and actual temperatures leads to an increased thermal stress, which eventually will reach the critical stress, resulting in adhesion of the alumina film. Earlier experiments⁶ have shown that metal-organic, chemical-vapor-deposited alumina films at reduced, as well as atmospheric, pressure suffer from internal stress which can lead, under extreme practical circumstances, to cracking and delamination. Furthermore, these films start to crack and to delaminate after passing a critical thickness, caused by a high intrinsic (growth) stress. This may be explained by phase-transformation reactions of boehmite to γ -alumina, which is more pronounced at the interface than at the outer part of the film. This might be explained by a longer residence time of the inner part in the reactor during the deposition process. Thermal-annealing experiments have shown³ that the intrinsic stress was significantly reduced after 4 hr (or longer) at 700°C (or higher). Scale failure after the thermal-annealing processes can only be a result of temperature changes and different values of the coefficients of thermal expansion. It is possible to determine the thermal stress. Considering the thermal-expansion coefficients $\alpha(\text{alumina}) = 8 \times 10^{-6} \text{ K}^{-1}$ and $\alpha(\text{steel}) = 12 \times 10^{-6} \text{ K}^{-1}$ (assuming that the bulk values can also be used here) and the difference between annealing and room temperatures, 300, 400, and 500°C, respectively, the thermal stress in the alumina film on steel can be calculated (Fig. 8). Because the thermal expansion coefficient of the metallic substrates is larger than that of the alumina, the oxide film will suffer from

compressive stress after cooling. Scale failure by the presence of a compressive-stress gradient is often related to the energy required for the production of two new surfaces. This criterion leads to the following equation:¹⁰

$$-\varepsilon_{\text{ox}}^c = [2\gamma_0/E_{\text{ox}}d]^{1/2} \quad (2)$$

where $\varepsilon_{\text{ox}}^c$ is the critical strain in the oxide layer, γ_0 is the surface energy at the site of delamination or spalling, and d is the scale thickness. The critical stress for scale failure, neglecting the Poisson ratio, can be calculated by

$$-\sigma_{\text{ox}}^c = [2E_{\text{ox}}\gamma_0/d]^{1/2} = K_{\text{Ic}}/d^{1/2} \quad (3)$$

where K_{Ic} is the fracture toughness of the oxide-substrate interface. From this equation it is clear that for equal thicknesses of the oxide film, the higher the critical stress for spalling and/or delamination, the higher the fracture toughness of the film-substrate combination.

Next to this effect of thermal stress, which has a detrimental effect on scale adherence, the literature^{9,11-15} reports many theories of changing the scale adhesion or changing the fracture toughness of the interface. For example, the incorporation of reactive elements into oxide scales may (1) improve the scale plasticity, and thus the adherence at high temperatures, (2) reduce the growth rate, resulting in a lower growth stress, (3) eliminate voids at the substrate-oxide interface, (4) promote the growth of oxide pegs, (5) form a compound oxide layer at the substrate-oxide interface, and (6) increase the chemical bonding between the oxide and the metallic substrate. Next to these, an additional theory was developed, based upon sulfur segregation near the interface between the oxide film and the underlying substrate. The sulfur, uncombined in the metallic matrix, diffuses through the matrix to the interface, and may consequently cause spalling. This theory is based upon breaking of the Al—O—Fe bond.¹⁶ Sigler⁹ reported that sulfur segregation can be suppressed by immobilizing sulfur. It was found that alloys with elements from groups III–VI of the periodic table, which are excellent sulfide formers, for example, reactive elements such as Ca, Mg, Y, Ce, and Zr, will provide good oxide adherence of alumina-forming materials. This is in contrast with elements, such as Al, which are not able to form sulfides stable enough to prevent sulfur migration to the interface.⁹ Beneficial effects were also obtained with small amounts of Ti, where the Ti segregates into the alumina scales as either fine alumina-titania particles or in solution, or providing sinks within the scale for the released sulfur.⁹ The effect of Ti on the improvement of the adherence of alumina films on steels was also found by Tosa *et al.*¹⁶ These authors attributed this effect to the formation of TiC into the alumina film, resulting in an anchoring effect. The concentration gradient of TiC near the interface can also relax thermal stress. A third mechanism, proposed by Tosa,¹⁶ is that Al—O—Ti bonding will take place between the alumina film and the precipitated TiC. Deterioration of the

adherence was obtained by graphite precipitation (a local volume expansion of precipitated graphite at the interface will push up the alumina film, causing cracking and delamination of the film).

The mechanism of sulfur segregation was also proposed by Lees *et al.*^{17,18} and Funkenbusch *et al.*¹⁹ According to Lees *et al.*,¹⁸ sulfur segregation can be avoided by the presence of elements, such as yttrium, which associate with the S, or by annealing in hydrogen, which reduces the concentration of sulfur in the metallic matrix. According to Briant and Mulford,²⁰ the sulfur may have an embrittling effect when it segregates at the oxide-metal interface. This theory of trapping S by Y was first proposed by Smeggil *et al.*,^{21,22} who studied the effect of Y for NiCrAl alloys by Auger studies. Sigler¹¹ reported also that void formation at the interface may be due to the presence of sulfur. Due to the weakening of the metal-oxide bond and the locally high sulfur concentration a reduction of the adherence has occurred, forming voids by either vapor transport or surface diffusion.

Next to the incorporation of yttrium into the metallic matrix, as discussed above, also yttria dispersions, for example, oxide-strengthened alloys (ODS), may have a beneficial effect on the adherence of alumina coatings. Ikeda and Yata²³ give an excellent overview of several mechanisms of the "yttria" effect on sulfur segregation, consisting of (1) sulfur trapping by yttria, (2) retardation of diffusion of elements such as manganese and chromium into the alumina films, (3) adhesive effect by the presence of TiC, and (4) increased plasticity of the alumina doped with yttria. From the results it was concluded that mechanisms (1) and (2) are dominant. The alumina films were superficially applied to the ODS alloys by magnetron sputtering. Next to this, oxidation of the ODS alloys also results in an alumina layer with excellent spallation and delamination resistance.²⁴ Due to the presence of a well-adherent alumina formed by the presence of yttria particles, these oxide films can also be used as excellent diffusion barriers against aggressive-gas compounds.²⁵ For example, it was found that preoxidation in air of MA956 produces an alumina scale with excellent resistance against sulfidation.

Other studies were also performed to suppress sulfur segregation at the interface. Smialek²⁶ studied the adherence of self-producing alumina scales on undoped NiCrAl alloys. He found a change from a nonadherent to an adherent alumina scale by repeated oxidation and surface removal. Due to the repeated oxidation and removal of the surface layers by polishing a gradual depletion of the sulfur impurity was observed. Smialek reported that less than 40 cycles will be required to completely remove the sulfur from the alloy.²⁶

Summarizing, from many studies it is clear that sulfur segregation has a detrimental effect on the adherence of oxide scales on metallic substrates. The fracture toughness of the interface is related to the chemical bonds

between the metallic substrate and the oxide film. As already discussed, sulfur can lower the fracture toughness of the composite extensively.

From our results it was clear that spalling of the oxide layer was more pronounced at high annealing temperatures. This can be due to a transformation of boehmite into γ - Al_2O_3 with a higher brittleness. The AES and EDX analyses showed that after the annealing processes the concentration of sulfur was increased at the oxide-substrate interface. No increased concentration of Ti or C was observed. This may indicate that the higher susceptibility for cracking and delamination after thermal annealing is probably due to a higher thermal stress and a higher brittleness caused by an increased amount of sulfur near the interface, lowering the fracture toughness K_{Ic} .

The effect of the substrate composition on the adherence of thin oxide films was also investigated by Hofman.²⁷ Research was focused on the adhesion of silica coatings on different alloys by using the SST-101 (scanning-scratch test). It was found that the critical loads for silica coatings on Incoloy 800H were higher than for silica coatings deposited on AISI 304 stainless steel. This effect was explained by the presence of a chromia scale near the matrix on Incoloy 800H, whereas a spinel-chromia scale with defects was formed near the matrix on AISI 304. In this study nothing was reported about the effect of substrate composition. It is known that the concentration of Ti in Incoloy 800H is about 0.7%. This probably means that the formation of TiC particles, resulting in an enhanced adhesive force due to the anchoring effect, is more pronounced for Incoloy 800H. Next to this higher concentration of Ti, AISI 304 contains a higher concentration of sulfur. It is now well known that sulfur has a detrimental effect on scale adhesion, forming Al-S-M instead of Al-O-M bonds. From these findings, the difference in adhesive force between the silica film and the metallic substrates, may also be partly explained by this "titanium" or "sulfur" effect.

In order to reduce the cracking and delamination susceptibility of the alumina films, other substrate materials have to be used, for example, yttrium or yttria-dispersed alloys or TiC-forming stainless steels. To obtain a better overview of the effect of the underlying substrate, in the near future more research will be performed.

CONCLUSIONS

1. Thermal annealing results in a significant reduction of the intrinsic stress. On the other hand, due to the high annealing temperatures, the thermal stress increases.
2. The critical load measured by the SST-101, the load where the films starts to spall or to delaminate, reduces with increasing annealing time or temperature.

3. This detrimental effect of annealing on the adherence of the alumina films may be explained by an increased thermal stress and sulfur segregation at the metal-oxide interface.
4. The sulfur-effect, currently used in the literature as the major mechanism to scale de-adhesion, proposes that sulfur segregates at the interface, where it has a deleterious effect on the oxide-metal adhesion.

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