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Improvement of adhesive bonding strength in sealed anodized aluminium through excimer laser prebond treatment

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The feasibility of using an excimer laser as a prebond treatment of sealed anodized aluminium alloys has been demonstrated. Irradiation of sealed chromic acid anodized aluminium by means of pulsed ultraviolet laser (193 nm wavelength, energy density of 0.2–7 J cm^{-2} per pulse and duration of 24 ns) improved bonding strength by more than 100% compared to that of the sealed anodized but non-treated alloy (using modified epoxy adhesive). The influence of laser treatment on the sealed anodic layer was investigated by various techniques, including scanning electron microscopy, X-ray diffraction and Fourier transform–infrared spectroscopy. Various phenomena, such as morphological changes, ablation, crater formation, melting, gas evaporation, water removal and crystallization, were observed following the laser treatment. The magnitude of these changes was found to depend on both laser-beam energy density and number of pulses.

1. Introduction

For many years, anodization was one of the most effective surface preparation treatments for adhesive bonding of aluminium alloys using polymeric adhesives. In order to increase the resistance to corrosive conditions of the anodic-coated alloy, a sealing process is applied. This results in the formation of a stable alumina monohydrate [AlO(OH)], called boehmite, which seals the pores of the anodic film [1–3]. However, at the same time, the anodizing process became less suitable for adhesive bonding, because the sealing produces weak adhesively bonded joints [4–6].

Adhesive joints under an aggressive environment (heat, humidity) deteriorate and the mode of failure is adhesive when moisture penetrates to the metal–adhesive interface [6, 7]. Venables [4] investigated anodized aluminium–polymer bonds and found that the failure of the adhesive bonding in wet environments was due to the conversion of aluminium oxide to hydroxide (boehmite). Because the adhesion of the hydroxide to aluminium is poor, joints under load or ageing may separate, causing bond failure.

Ultraviolet pulse lasers generate extremely high heating and cooling rates at the surface and at the outer layer, of the order of $(10^8–10^{10})$ °C s^{-1} with an energy density of 0.3–5.0 J cm^{-2} per pulse [8]. These extreme conditions can cause chemical changes, morphological changes, ablation, melting, phase transformations and other phenomena.

Juckenath *et al.* [9, 10] irradiated various metals with an excimer XeCl laser and showed that the roughness increases with the energy density and the number of pulses. Badekas *et al.* [11] obtained similar results by treating plasma-sprayed Al_2O_3 with excimer KrF. Other investigators [4, 12, 13] found that the microscopic roughness of the oxide surface is important in determining bondability, because a mechanical interlocking of the adherend with the adhesive causes stronger bonds on rough surfaces than on smooth ones.

The purpose of this research was to improve the adhesive bonding strength of sealed anodized aluminium surfaces by a new technique of laser prebond treatment. This method has already been proved for bare aluminium alloy [14] and for polymeric adherends [15].

2. Experimental procedure

2.1. Laser parameters

The specimens were irradiated in air with an ArF excimer laser, Lambda Physik model EMG-201-MSC using 193 nm laser pulses within the energy range 160–250 mJ, for the duration of 24 ns and a repetition rate of 30 Hz at various numbers of pulses. In most cases, the emerging beam was concentrated by a fused SiO_2 lens to yield a rectangle with dimensions controlled by the distance between the lens and the target, which varied in the range 0.04–0.80 cm^2.

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The excimer laser energy density at the specimen surface varied within 0.2–7 J cm^{-2} per pulse and the number of pulses within 1–1000.

2.2. Substrate and adhesive

The specimens were sealed chromic acid-anodized aluminium 2024-T3. The chemical composition of the aluminium alloy was (wt %): 4.16% Cu, 1.5% Mg, 0.61% Mn, 0.27% Fe, 0.13% Zn, 0.08% Si, 0.04% Ti, 0.01% Cr and the balance aluminium. Anodizing conditions were 40 ± 1 V, 38 ± 2 °C, 40 min, 4 mA cm^{-2}, 4–5 wt % chromic acid solution. The anodic film thickness was ~ 5 μm. Sealing conditions were 88–96 °C, pH of water ~ 6.3.

The adhesive used throughout this work was a basic formulation comprised of a high functionality aromatic epoxy resin consisting of two components, an aliphatic polyamine curing system and an elastomeric toughening agent. The formulation included a tetrafunctional (MY-721) and a trifunctional (ERL-510) epoxy resins, both products of Ciba-Geigy, cured with (triethylene tetraamine) TETA and modified with (amino-terminated-butadiene acrylanitrile) ATBN 1300*16, products of B. F. Goodrich. This formulation is used for field repair of composites having reduced curing temperature and elevated service temperature [16, 17].

The specimens were bonded at room temperature (50% RH) and cured for 7 days. No primers nor any other surface treatments were used.

2.3. Surface analyses

The morphology of the specimens before and after laser treatment was examined by means of a Jeol model JSM-840 scanning electron microscope operated at 20 keV.

X-ray diffraction patterns before and after laser irradiation were taken by a Philips X-ray diffractometer PW1820, moving in steps of 0.02° and a sampling time of 10 s. Fourier transform–infrared spectroscopy (FT–IR) was applied on the adherend surface following laser treatment in order to determine chemical changes in the anodic layer. The FT–IR spectra were obtained on a Nicolet 5DX in the 4000–400 cm^{-1} range. The spectrometer was operated in an external specular mode, equipped with a horizontal stage, at near-normal incidence and a gold-coated mirror was used as a reference.

2.4. Shear strength tests

Comparative adhesion shear strengths were determined by a single-lap shear joint test (SLJ) according to ASTM D-1002-72. Each set of adherends was irradiated under the same laser conditions and was then bonded. Each irradiation condition was tested by several samples using an Instron tensile machine model 1185.

3. Results

3.1. Morphology

Irradiation of the sealed anodized specimens caused morphological changes which depended on the laser energy density and on the number of pulses. Fig. 1a and b show scanning electron micrographs of the untreated specimens. No cracks were observed at the surface, except for small pits which arose from the imperfect anodization process.

Fig. 2a and b show the effect of the number of pulses on the morphology of the surface at a constant energy density of 0.7 J cm^{-2} per pulse. Fig. 2a shows the surface of a specimen irradiated with 10 pulses. Open bubbles, resulting probably from water removal (see FT–IR results in Section 3.2), some spherical droplets of Al_2O_3 due to splashing and condensation (caused by laser ablation of Al_2O_3 which occurs at a laser energy density above the threshold [18, 19] of 0.6 J cm^{-2}) and cracks could be observed. After 37 pulses (Fig. 2b), most of the area was covered with crystalline Al_2O_3 which had probably been solidified from the molten amorphous anodic layer. It can be concluded that the morphological changes became more pronounced as the number of pulses increased.

The morphology also depended on energy density. At low energy densities (0.2 J cm^{-2}) no change in the morphology was observed even after 1000 pulses, while at 0.7 J cm^{-2}, changes in the morphology were already obtained at 10 pulses (Fig. 2a). At much higher energy densities, such as 6.7 J cm^{-2}, there are dramatic changes even after 10 pulses (Fig. 3), including intensive ablation and dehydration. There is clear evidence of gas (water molecule) breakout and laser destruction of the anodic layer by crater formation.

3.2. Chemistry

Chemical changes that occurred as a result of laser treatment were analysed by FT–IR. Fig. 4a shows the

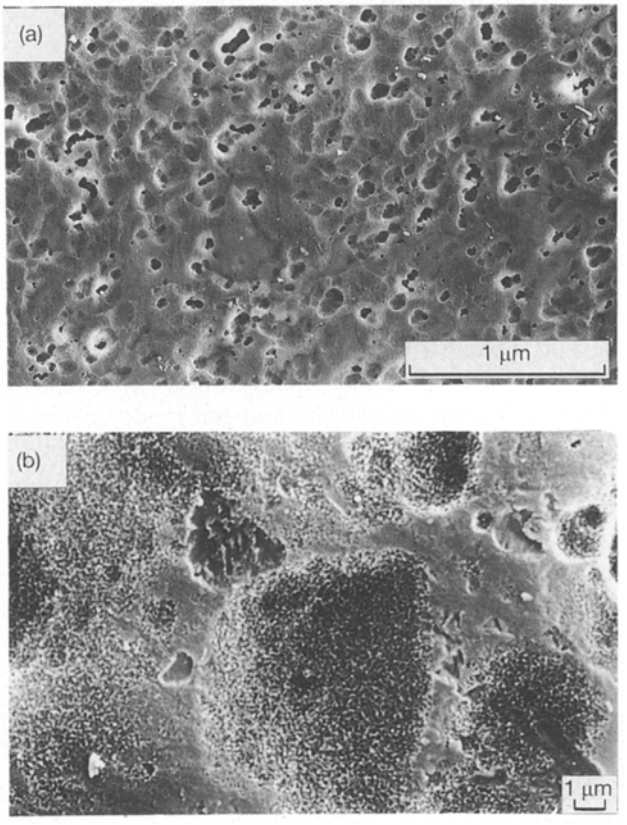

Figure 1 Scanning electron micrographs of the specimen as-received, at two magnifications.

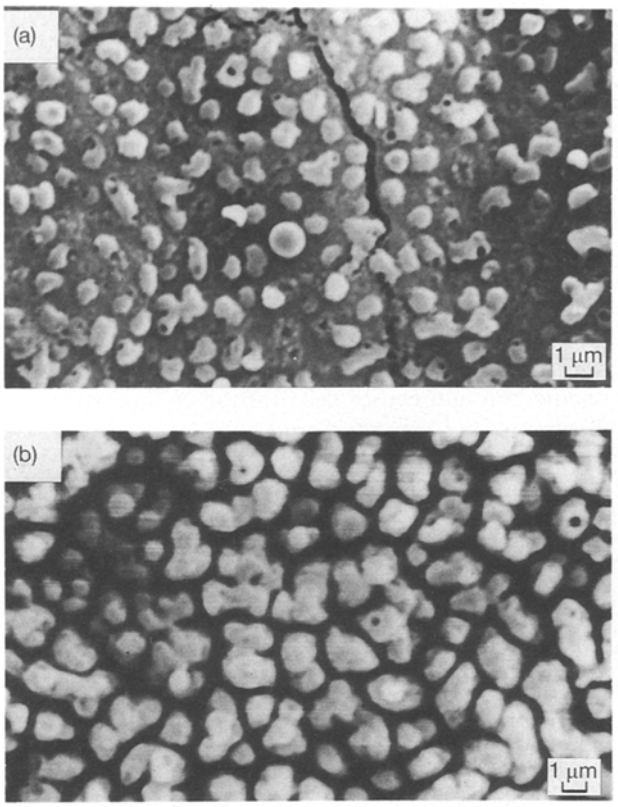

Figure 2 Scanning electron micrographs of the specimen after laser treatment with a pulse energy of 0.7 J cm^{-2}. (a) 10 pulses, (b) 37 pulses.

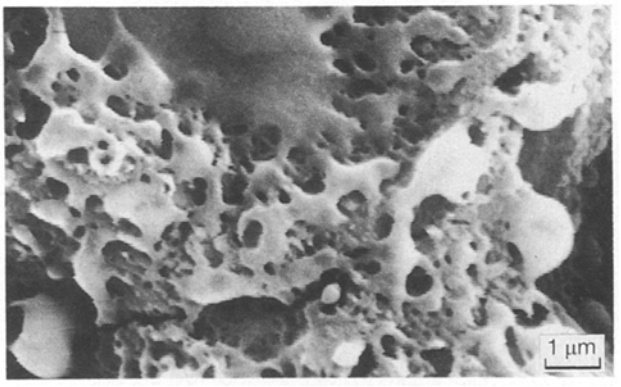

Figure 3 Scanning electron micrograph of the specimen after laser treatment at 6.7 J cm^{-2}, 10 pulses.

FT–IR spectrum of a specimen in the as-received condition. There are two large absorption peaks due to water [20]: AlO↔H(stretch) + H_2O at 3450 cm^{-1}, indicating structural and absorbed molecules, and AlO↔H_2O (stretch) at 1637 cm^{-1}, indicating absorbed water molecules in the anodic film.

Four other peaks belong to free boehmite [21]: 474, 632, 742 and 1070 cm^{-1}. The spectrum in Fig. 4b refers to a specimen irradiated at 0.8 J cm^{-2}, 100 pulses (Fig. 4b), and shows a significant reduction of the boehmite peaks, a small reduction of the water peaks and the appearance of a small peak at 885 cm^{-1} due to Al–O–Al (stretch), in comparison to the as-received specimen.

At a higher energy density of 1.9 J cm^{-2}, already at 10 pulses (Fig. 4c) significant changes occur. All four

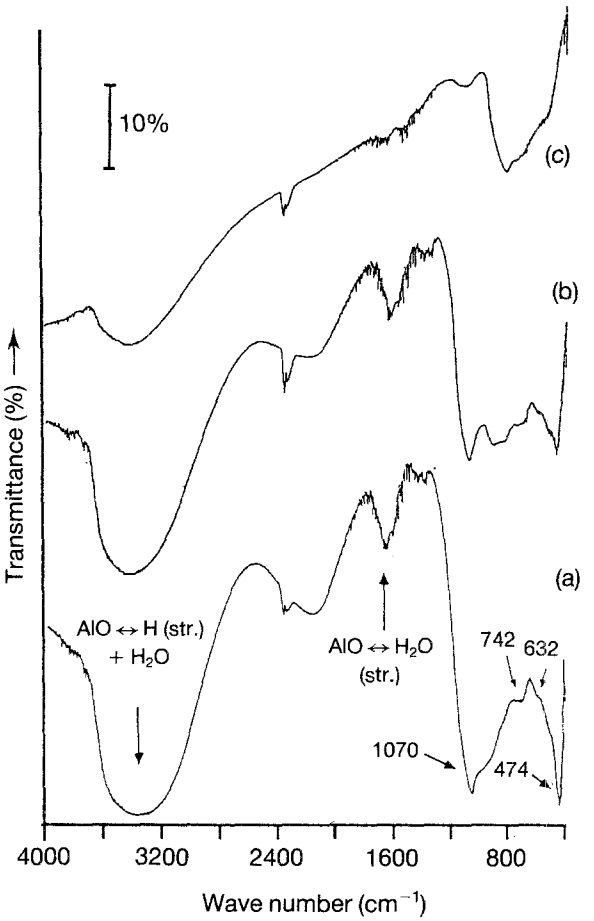

Figure 4 FT–IR spectra of the specimen (a) as-received, (b) irradiated with 0.8 J cm^{-2}, 100 pulses and (c) irradiated with 1.9 J cm^{-2}, 10 pulses.

boehmite peaks disappear, those of structural and absorbed water molecules are reduced to near zero, a new peak at 810 cm^{-1} appears due to Al–O [22], and the peak at 885 cm^{-1} disappears.

3.3. Crystallography

Fig. 5 shows an XRD spectra of the aluminium alloy with sealed chromic acid anodization, before and after laser treatment. Part of the amorphous aluminium oxide was transferred to a mixture of crystalline phases of alumina such as δ-Al_2O_3 and γ-Al_2O_3.

3.4. Adhesive bonding

Fig. 6 shows the shear adhesive strength as a function of the number of pulses of laser irradiation at two levels of energy density, 0.8 and 1.9 J cm^{-2}. The adhesion shear strength of laser-treated adherends was improved to the range 5.8–11.1 MPa depending on (but not necessarily proportional to) the energy density and the number of pulses. Comparison of the adhesive shear strength of laser-treated specimens with that of the non-treated ones (4.5 MPa) indicates that the laser treatment improves the shear strength at all energy density levels in the tested range, 0.2–7 J cm^{-2}.

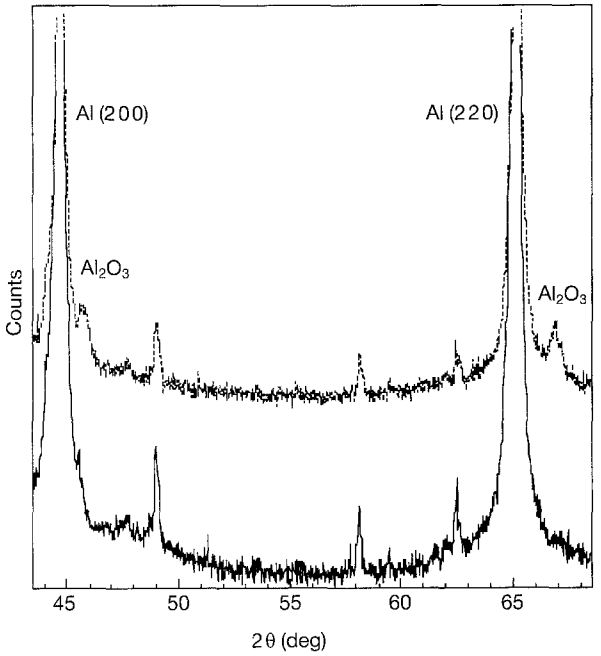

Figure 5 XRD spectra of the specimen (a) as-received and (b) irradiated with 1.3 J cm^{-2}, 180 pulses.

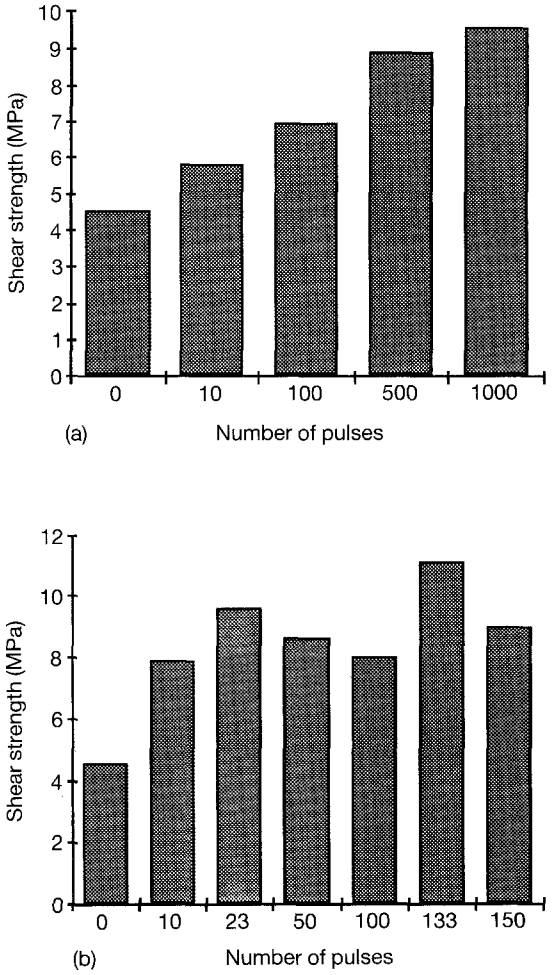

Figure 6 Shear strength of sealed anodized specimens after laser treatment: (a) 0.8 J cm^{-2}, and (b) 1.9 J cm^{-2}.

4. Discussion

4.1. Changes in the anodic film

The absorption depth of ultraviolet radiation in alumina is low, about 100 nm [23, 24], thus the excimer laser treated only the outer layer of the anodic film without damaging or causing any changes in the interface between the aluminium and the anodic film, and without changing the mechanical properties of the aluminium substrate.

Irradiation of the sealed anodized specimens caused various morphological changes depending on the laser energy density (at a constant number of pulses) and on the number of pulses (at a constant energy density). These changes were observed only above an energy density threshold of 0.6 J cm^{-2}.

The FT–IR spectra show that the laser removes absorbed and structural water molecules from the anodic film and causes dehydration of the hydroxide (boehmite) to aluminium oxide.

The formation of the metastable crystalline phases was probably a result of the rapid quenching of the melted surface. The spatial inhomogeneity of the laser beam and the different cooling rates at different depths could result in a mixture of crystalline phases. The molten Al_2O_3 layer is thin, i.e. a very small volume underwent phase transformation from amorphous to crystalline Al_2O_3, resulting in weak peaks of the crystalline Al_2O_3. Furthermore, alumina has a variety of metastable crystal structures, some of which are distinguished only by a change in a few lines of their X-ray diffraction pattern and most of them have the same typical peaks such as 0.139–0.140 or 0.197–0.198 nm. These peaks are the fingerprints of the crystalline alumina and they enable identification of crystallization without defining the exact metastable phase. The main typical crystalline peaks were observed at the XRD spectra, but the weak peaks of the crystalline Al_2O_3, those that distinguished between the different polymorphous, were not observed.

4.2. Adhesive bonding

The improvement in shear strength could be attributed to the changes in surface morphology (increasing surface roughness) indicated by SEM, and to the dehydration of the anodic film indicated by FT–IR. Infrared spectroscopy indicated dehydration of the boehmite to Al_2O_3, and removal of structural and absorbed water molecules. This may contribute to stronger adhesion because boehmite and water molecules deteriorate the adhesive bonding strength [4–6].

Surface roughness, as previous studies [12, 13] have shown, controls the degree of mechanical interlocking between the anodized aluminium and the polymer, which is an important factor in determining initial bond strength and long-term durability. Furthermore, increasing surface roughness may contribute to other adhesive bonding mechanisms (such as chemical or van der Waals bonds), because increased surface roughness means an increase in the bonded area.

In addition, the crystallization of the amorphous anodic film, which was observed in XRD spectra, can contribute to the improvement of the adhesive bonding durability in humid and hot environments [4].

Dodiuk *et al.* [14] found an adhesive bonding shear strength of 10.2 ± 0.8 MPa for chromic acid unsealed anodization (using the same adhesive). Therefore, the bonding strength that was observed in this study after

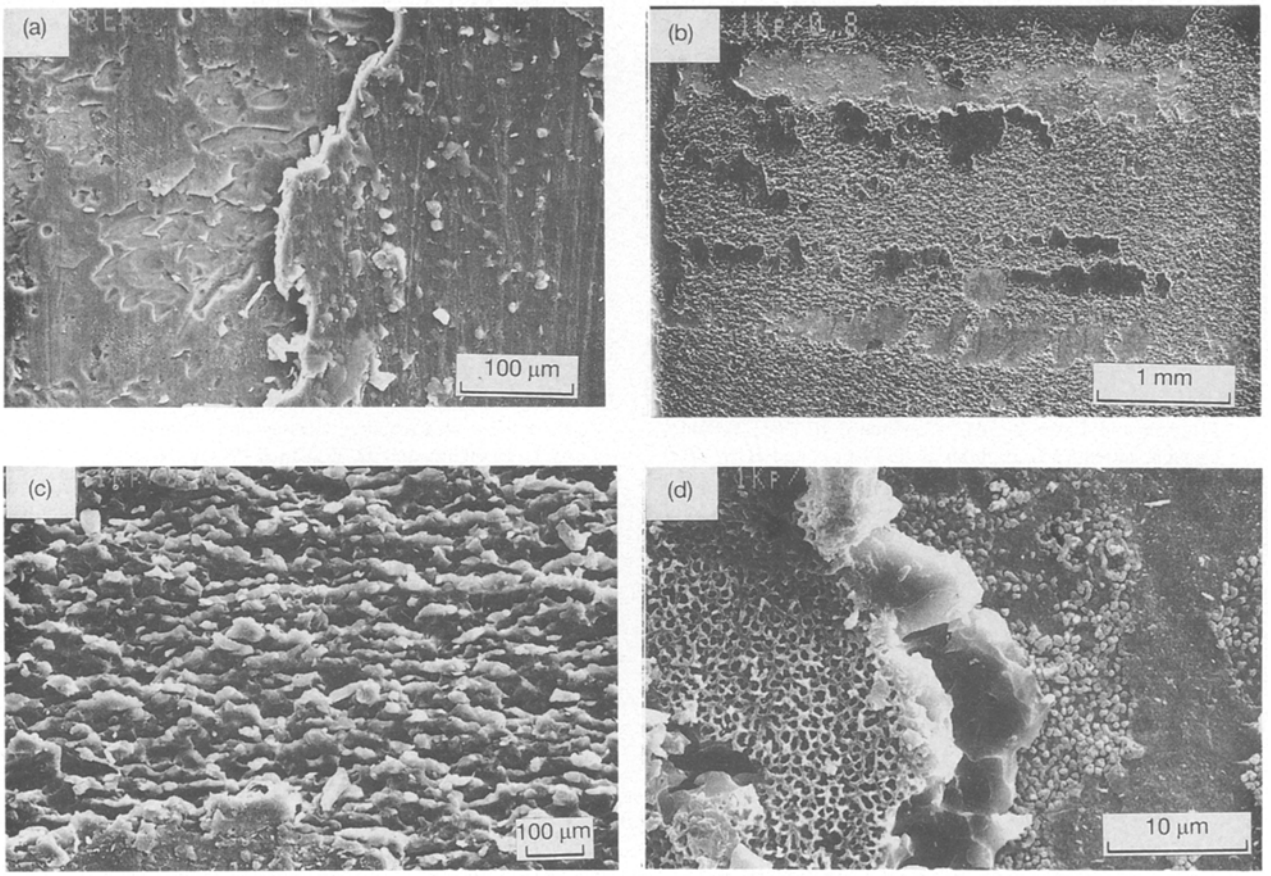

Figure 7 Scanning electron micrographs of adhesive/cohesive failure in the SLJ test. (a) Adhesive failure in untreated specimen; (b–d) specimen treated with 0.8 J cm^{-2}, 100 pulses, (b) general view of mixed adhesive/cohesive failure; (c) cohesive area; (d) granular features of the adherend surface formed due to laser treatment.

laser treatment (5.8–11.1 MPa), is in the same order of magnitude as the bonding strength of unsealed anodization.

The SEM study of the adhesive joints after failure (Fig. 7) reveals the nature of the bonding failure. It was adhesive type at low laser energy densities (Fig. 7a) and cohesive type at the higher ones (Fig. 7b–d). Fig. 7d clearly shows the mechanical interlocking of the adhesive between the granular features of the adherend surface formed by the laser treatment. These results support the assumption that laser prebond treatment improves adhesive bonding strength by morphological and chemical changes in such a way that the adhesion between the sealed anodized aluminium and the modified epoxy became stronger than the adhesive itself (cohesive failure).

5. Conclusions

1. Laser irradiation of sealed anodized aluminium was found to improve bonding adhesion strength up to 150% compared to untreated specimens.

Improvement of the shear strength is due to water removal and dehydration of the boehmite, morphological changes and crystallization.

2. The bonding strength after laser treatment is similar to the bonding strength of unsealed anodization, the conventional treatment for adhesive bonding, and the failure became cohesive. After laser treatment, most of the hydroxide (boehmite) converted to oxide and was removed from the pores. The result is an anodic film with empty pores, quite similar to the anodic layer before the sealing process.

3. The increased surface roughness due to laser irradiation further improves the mechanical interlocking between the anodized aluminium and the adhesive.

4. Ultraviolet irradiation affects only the outer surface of the anodized layer, without damaging the aluminium–anodic film interface.

5. Laser preadhesion surface treatment for field repairing of structural parts already treated with sealed anodization (in order to prevent corrosion), could replace the conventional treatments that involve complicated masking and standard coating processes which are less durable.

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