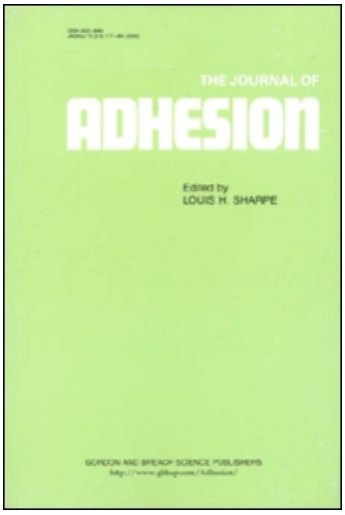

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Preadhesion Laser Treatment of Aluminum Surfaces

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To cite this Article Dodiuk, H. , Buchman, A. , Kenig, S. , Rotel, M. , Zahavi, J. and Reinhart, T. J.(1993) 'Preadhesion Laser Treatment of Aluminum Surfaces', The Journal of Adhesion, 41: 1, 93 — 112
To link to this Article: DOI: 10.1080/00218469308026556
URL: http://dx.doi.org/10.1080/00218469308026556

J. Adhesion, 1993, Vol. 41, pp. 93–112
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Printed in the United States of America.

Preadhesion Laser Treatment of Aluminum Surfaces*

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(Received February 6, 1992; in final form September 1, 1992)

An excimer laser may be used for preadhesion treatment of aluminum alloys. This method presents an alternative to the use of ecologically unfriendly chemicals involved in conventional anodizing pretreatments.

Experimental results indicate that preadhesion laser surface treatment significantly improved the shear strength of modified-epoxy bonded aluminum specimens compared with untreated and anodized substrates. The best results were obtained with laser energy of about 0.2 J/Pulse/cm^2 where single lap shear strength was improved by 600–700% compared with that of untreated Aℓ alloy, and by 40% compared with chromic acid anodizing pretreatment.

The mode of failure changed from adhesive to cohesive as the number of laser pulses increased during treatment. The latter phenomenon has been correlated with morphology changes as revealed by electron microscopy, and chemical modification as indicated by Auger and infrared spectroscopy.

It can be concluded that the excimer laser has potential as a precise, clean and simple preadhesion treatment of Aℓ alloys.

KEY WORDS Adhesion; aluminum; excimer laser; surface treatment; shear strength; FTIR; Auger.

INTRODUCTION

Proper surface treatment of adherends is among the decisive factors determining the final quality and durability of an adhesive joint.

Many treatments have been devised for preparing metal surfaces for adhesive bonding, painting and the like. The general purpose of these preparation procedures is to modify the original surface of the metal (a) to promote development of interfacial bonds to adhesives and (b) to enhance the environmental resistance to moisture and humidity effects.

*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

The pretreatments which are commonly used for aluminum as corrosion resistant coatings or adhesion promoters are: chromate conversion coating, chromic acid anodization (with or without sealing), sulfuric acid anodization (with or without sealing), phosphoric acid anodization (PAA) and chromic-sulfuric etch (FPL).

All these treatments involve the use of acids (sulphuric, nitric, hydrochloric), strong bases or hexavalent chromium compounds.[1] New OSHA and EPA regulations ban such chemicals in industrial operations. UV lasers may offer a chemical-free surface treatment for aluminum adhesion. Furthermore, the use of laser treatment offers a precise, clean and simple pretreatment method.

The potential of a UV laser for prebonding treatment of thermoplastic adherends has been demonstrated in previous investigations.[2,3] The treatment mechanism involves morphological and chemical changes of the surfaces of the adherends, due to conformity of UV laser energy to surface topography modification and to organic bond activation.[4] It has been shown that surface treatment of aluminum by excimer laser results in roughening and oxidation of the surface,[5–7] increase of microhardness[8] and induction of surface melting.[9]

Rigorous characterization of the effect of the various chemical and electrochemical preadhesion treatments on aluminum indicated morphology and chemical composition changes of the surface.[10] Thus laser and chemical pretreatments can be compared.

In the present investigation the application of an excimer UV laser for surface treatment of Aℓ alloy adherends has been studied. The objective of the work is two-fold: firstly, to establish the effect of the excimer UV laser on the surface microstructure of the Aℓ alloy using various spectroscopic methods and, secondly, to correlate the microstructure with the macro behavior as reflected in a shear loading and failure location of adhesively bonded joints using a two-part, rubber-modified epoxy adhesive developed for field repair.[11–13]

EXPERIMENTAL

Laser Treatment

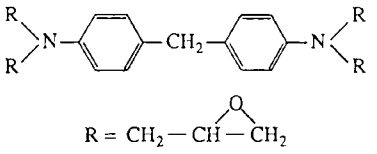
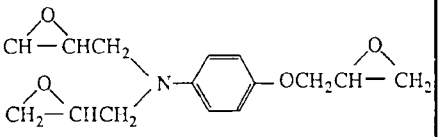
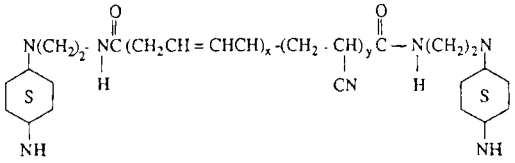
The laser used during the course of this investigation was a UV excimer ArF laser, Model EMG 201 MSC, a product of "Lambda Physik," W. Germany, producing a 2×0.5 cm^2 area beam at 193 nm with a pulse energy of 160–200 mj/Pulse/cm^2 or a concentrated beam (0.3 cm^2) with higher pulse energy (730 mj/Pulse/cm^2). Repetition rate was 30 Hz and the number of pulses ranged between 1–5000.

The specimens were moved under the beam by means of a controlled X-Y table. The laser beam scanned stripes of 0.5 cm wide with an overlap of 0.2 cm (about 40%). The distribution of the laser energy is not homogeneous and reaches two maxima in the center of the stripe. All experiments were conducted at ambient temperature and air environment.

Adherend and Adhesive

The substrate used throughout this work was Aℓ 2024 of nominal composition, Cu

TABLE I
Chemical formula

MATERIALS	CHEMICAL FORMULA	TRADEMARK
EPOXY RESIN EE = 128 gr/eq		MY 720 CIBA GEIGY
EPOXY RESIN EE = 107 gr/eq		ERL510 CIBA GEIGY
CURING AGENT AE^b = 40 ± 3 gr/eq	$_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)NH_2$	TETA MILLER STEPHENSON Chem. Co.
RUBBER ATBN AE - 1160 gr/eq		HYCAR ATBN 1300 X 16 BF GOODRICH Chem. Co.

4.4%, Mg 1.5%, Mn 0.6% and the balance Aℓ. The substrate was wiped with acetone prior to laser treatment.

The adherends were laser treated and bonded by a rubber-modified epoxy adhesive.[11–13] The adhesive is a mixture of two polyfunctional epoxy resins (ERL-510 and MY 721, products of Ciba-Geigy [MY 721 is similar to MY 720 (Table I) but has a lower viscosity]) cured with TETA and modified with ATBN-1300 × 16 rubber product of B.F. Goodrich (Table I). Curing was carried out at ambient temperature for 48 hours.

Testing

The surface of the laser-treated aluminum was examined and compared with untreated adherends using an FTIR (Fourier Transform IR) spectrophotometer (Nicolet 5DX) in an external specular mode, equipped with a horizontal stage in a

near-to-normal incidence and a gold-coated mirror as reference, and by AUGER electron spectroscopy (AES) (Physical Electronics Ind. Inc., model 590A).

Two different sputtering rates were used in the Auger analysis, 15 Å/min and 200 Å/min determined with a Ta_2O_5 standard.

Surface morphology was studied by Scanning Electron Microscopy (Jeol model JMS 840, Japan) equipped with an Energy Dispersive System (EDA, product of Link, model 290).

Adhesive joint properties were determined using Single-Lap-Shear Joints (SLS) according to ASTM D-1002-72. SLS joints are difficult to analyse as they combine shear and opening modes; however, they are a simple design and are usually used for comparative studies. Ten days curing was allowed before loading the SLS specimens in an Instron Model 1185 at a rate of 2 mm/min at 25°C. The mode of failure was determined visually by SEM to be either adhesive or cohesive. Fracture surface morphology was studied by SEM.

Methodology

Two kinds of references were used for comparison with laser-treated specimens: a non-treated, bare Aℓ set and an unsealed chromic acid anodized (according to MIL-A-8625C) Aℓ set of adherends. The latter is a common preadhesion surface treatment for Aℓ alloys.[14] Non-treated Aℓ is not used in high performance applications. However, it was chosen as a reference since it represents the lower limit of SLS strength. The level of adhesion was determined relative to the SLS strength of the anodized and the non-treated specimens for each laser condition studied.

Surface chemical and morphological analysis were performed prior to, and following, laser treatment of the aluminum adherends and on the fractured surfaces of SLS specimens.

In an additional phase of the study the effect of laser treatment on chromic acid anodized Aℓ specimens was investigated and compared with laser effects on bare and chromic acid anodized Aℓ alloys.

RESULTS AND DISCUSSION

Shear Strength and Failure Mode

Table II and Figure 1 give the SLS strengths of the modified epoxy adhesive for UV laser treated and untreated Aℓ 2024 joints at various numbers of laser pulses and laser energy densities. It is evident that UV laser treatment is effective on the Aℓ adherend. The higher the number of laser pulses the greater is the SLS strength (Fig. 1).

At higher laser energy, the lap shear strength is increased by 40% compared with the unsealed chromic anodization treatment and an improvement of 600–700% compared with nontreated Aℓ is achieved.

Increasing the energy density of the laser treatment results in higher SLS strength until an optimum value is reached. More energetic laser treatment (0.73 J/P/cm^2)

TABLE II
The effect of laser pretreatment of aluminum (2024-T3) on single lap shear strength

Sample	Laser energy J/P/cm^2	Repetition rate Hz	No. of pulses	Shear strength MPa**	Failure type c/a/m*
Untreated Aℓ (ref.)	—	—	—	2.03 ± 0.20	a
Anodized Aℓ (ref.)	—	—	—	10.20 ± 0.80	c
Laser-treated Aℓ	0.16	Manual	10	4.17 ± 0.45	m
	0.16	30	1000	7.95 ± 0.20	m
Laser-treated Aℓ	0.185	Manual	1	2.45 ± 0.47	a
	0.185	30	200	12.33 ± 0.5	c
	0.185	30	600	11.59 ± 0.45	c
	0.185	30	1000	11.63 ± 0.57	c
	0.185	30	2000	14.39 ± 0.20	m/c
	0.185	30	5000	14.25 ± 0.30	m/c
Laser-treated Aℓ	0.73	Manual	10	5.11 ± 0.32	m
	0.73	30	200	5.30 ± 0.5	m
	0.73	30	600	4.16 ± 0.4	c
	0.73	30	1000	5.40 ± 0.5	c

*c = cohesive, a = adhesive, m = mixed failure
**five specimens were used for each test

reduces SLS strength probably due to a melting effect.[2] It can be seen that a small change in laser energy (~15%) causes a pronounced improvement in SLS strength. This may be due to the fact that the laser attacks specific chemical bonds, resulting in a very sharp optimum (energy threshold).[15] This mechanism should be further evaluated, but indication of its applicability was found in previous work.[2,3]

Visual inspection of the failure surfaces shows clearly that laser treatment causes a dramatic change in the mode of failure from adhesive (interfacial) in non laser treated adherends to mostly cohesive following laser treatment, indicating that the interfacial adhesion was significantly improved. The strength of joints that fail cohesively varies widely (between 4.2 to 12–14 MPa). This may be due to different failure mechanisms, influenced by the laser surface treatment of the adherends. It can be clearly seen from the SEM photomicrographs that a finer microstructure of the failure surface appears in cases which show higher SLS strength.

The effect of laser treatment on SLS strength of unsealed chromic acid anodized Aℓ 2024 is presented in Table III.

It can be seen that UV laser treatment of the unsealed chromic acid anodized aluminum adherends reduces the strength of the joint at all the laser conditions tested, probably due to destruction of the fine anodized layer microstructure by the laser radiation. Thus, no further study was pursued in this direction.

SEM

SEM micrographs of the Aℓ adherend after laser treatment at low laser energies showed no morphological changes compared with untreated Aℓ (Fig. 2a). In-

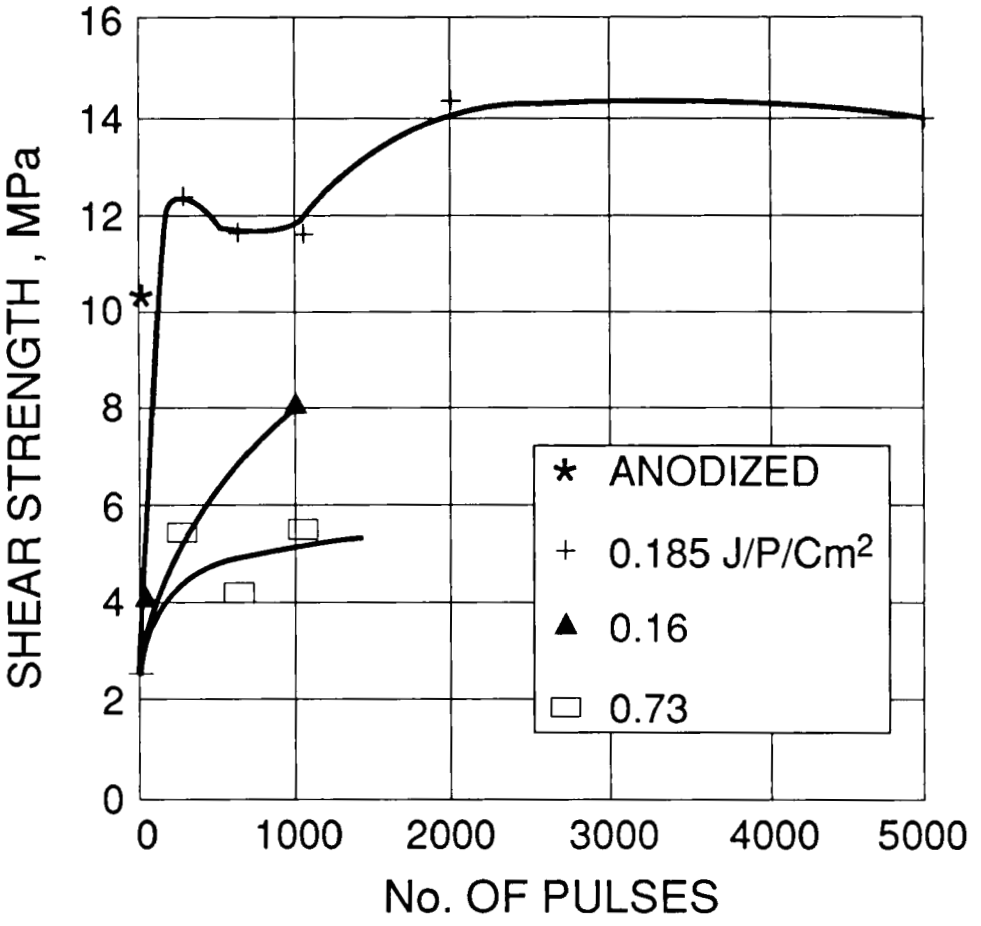


FIGURE 1 Single lap shear strength of laser treated Aℓ as a function of number of laser pulses.

TABLE III
The effect of laser pretreatment of unsealed chromic acid anodized aluminum on lap shear strength

	Anodized Aℓ	
No. of pulses*	Lap shear strength MPa	Failure type
(ref.) 0	10.2 ±0.8	c
100	7.2 ±0.6	a
1000	8.39±0.7	c

*Laser energy 0.185 J/P/cm^2

creasing the laser energy (0.73 J/P/cm^2) reveals a fine microstructue of the treated surface, an array of cracks about 1μ wide and small holes (Fig. 2b).

Increasing the number of pulses results in a finer surface microstructure of the crack nets, larger holes and exposed inclusions. The edges of the holes and cracks are smooth (Fig. 2c).

SEM micrographs of the fractured adhesive surfaces exhibit a smooth adhesive (interfacial) failure in non laser treated adherends and at 1 pulse laser treatment (Fig. 3). Raising the number of pulses to 200 results in a rough cohesive failure typical of the modified epoxy microstructure (filled with spherical rubber particles)[11,13] (Fig. 4a,c).

At a higher number of pulses, *i.e.* 1000–2000 (0.185 J/P/cm^2), the micro fractograph reveals a finer cohesive structure having the same microstructure (Fig. 4b). At 5000 pulses a mixed failure (but still mostly cohesive) is observed (Fig. 5) probably due to surface damage (Fig. 2). Damage to the adherend's surface results in regional melting exposing smooth, rounded areas which are less suitable for adhesion. It also creates weak surface layers which can be easily peeled off by external forces.[2]

FTIR

In addition to morphological modifications at high laser energies, chemical changes were detected by FTIR. The main FTIR absorptions for the various laser treatments on Aℓ 2024 are shown in Figure 6. Untreated Aℓ shows no absorptions due to an oxide layer. The higher the number of pulses applied to the Aℓ surface the stronger are the absorptions of the oxide layer (Fig. 6).

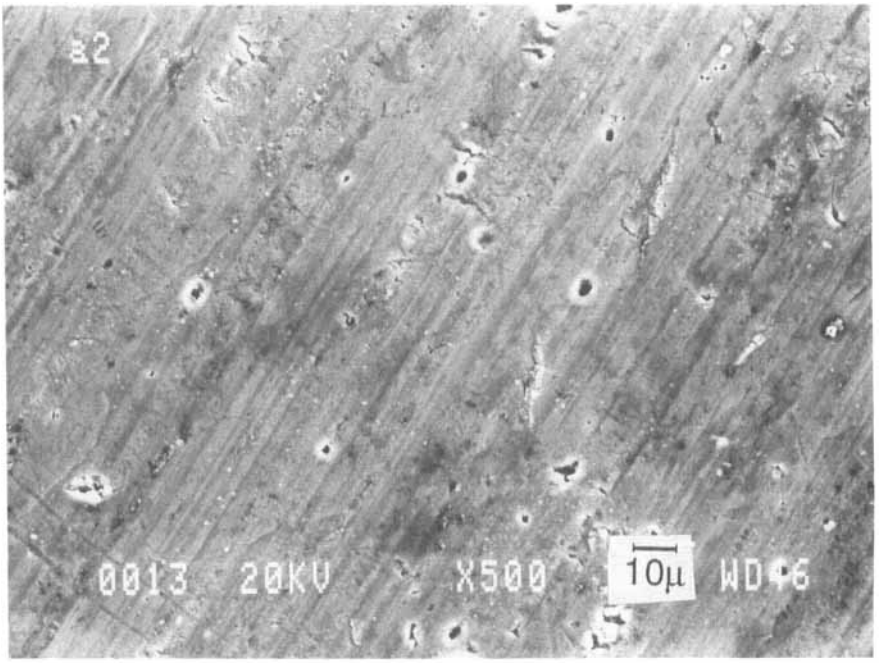
Gradual increase of the laser energy results in a different chemical effect on the Aℓ surface. The absorption peaks at 3600–3700 cm^{-1} are stronger at higher laser energy, probably due to water accumulation at the surface. The absorption peak at 950 cm^{-1} (Aℓ—OH) disappears, and a peak at 1630 cm^{-1} (Aℓ—O + H_2O) appears at high laser energies. These effects are similar to those shown in chromic acid anodization.[10,11] At lower laser energies the IR spectrum of the oxide layer is similar to that of the unsealed chromic acid oxide layer and at higher laser energies to the sealed one.[13]

Auger

Auger surface and depth profiles of laser treated and untreated Aℓ specimens shed more light on the effect of the laser treatment. It can be seen that on the surface of untreated Aℓ, mainly C, Aℓ and O are present and small amounts of Cu and Mg (Fig. 7a). At lower laser energies the surface is cleaned of contaminants such as carbon compounds (Fig. 7b). At a high number of pulses probably a new Aℓ and Mg oxide layer grows (Fig. 7c).

Comparing the depth profile of laser treated and untreated Aℓ (Fig. 8) reveals that the main effect of the laser treatment at a low number of pulses is the removal of the carbon compounds present in the untreated oxide. Carbon content in the

a



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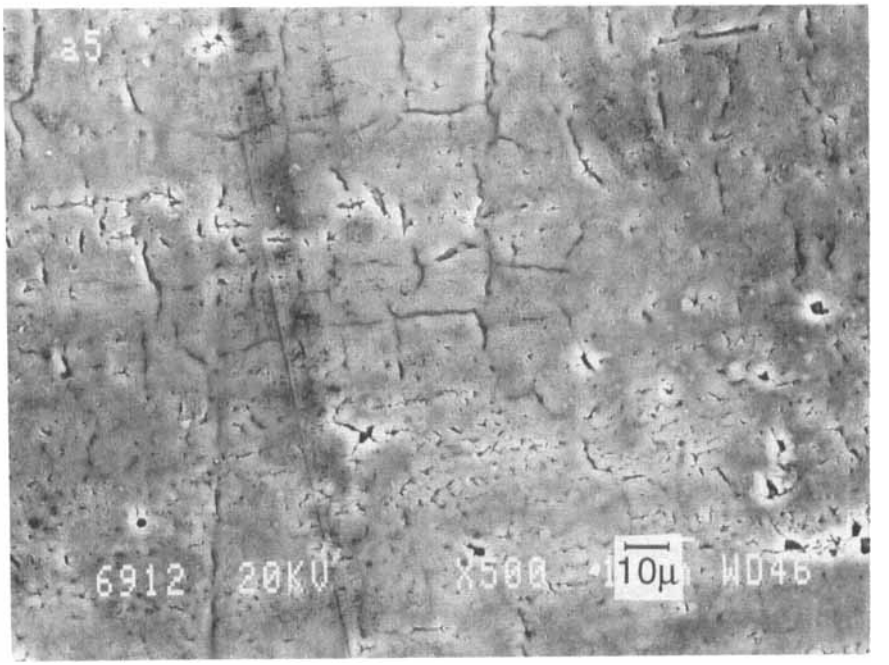


C

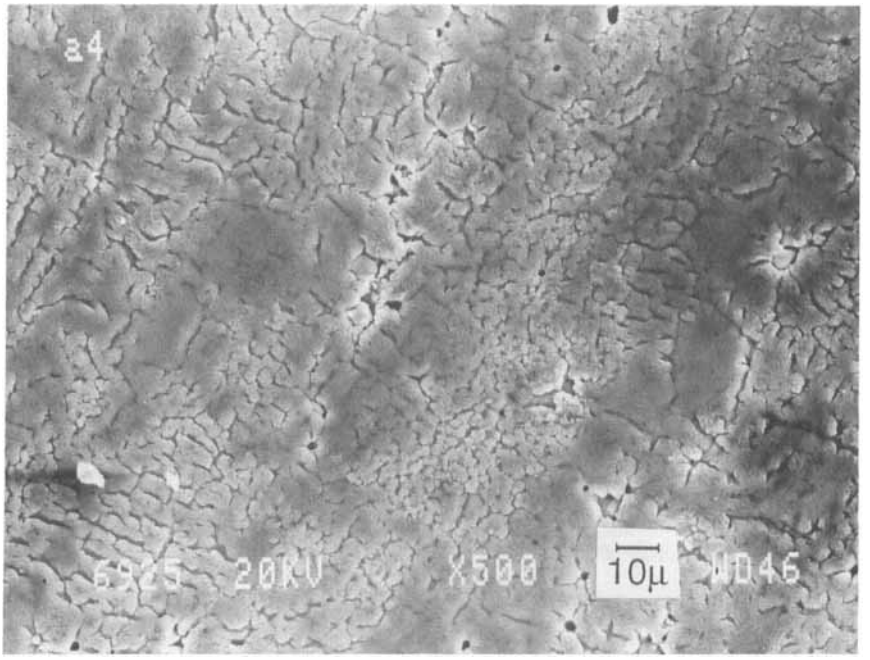


FIGURE 2 SEM micrographs of laser irradiated Aℓ specimens, (a) untreated, (b) 200 P, (c) 2000 P (0.73 J/P/cm^2).

surface of the untreated Aℓ is as high as 55% Atomic Concentration (A.C.) (Fig. 8a) and decreases gradually to 10% A.C. at the depth of 3000 Å (Fig. 8d). For the laser treated Aℓ, carbon content at the surface is only 15% A.C. (Fig. 8b) decreasing to 5% A.C. at the depth of 15 Å (Fig. 8e). At a higher number of pulses an oxide layer is present (Fig. 8c,f). The oxide layer of the untreated Aℓ is 950 Å deep while the new oxide layer grown on the treated Aℓ is only 550 Å thick. Oxide thickness is defined as the points where the Aℓ and O concentration (A.C.) are equal. The oxidized layer of the laser treated, and untreated, Aℓ consists of both Aℓ and Mg oxides. Comparing the relative amounts of O: Aℓ + Mg on the surface reveals that the oxides grown on the laser treated Aℓ are richer with oxygen compared with the untreated ones. (O: Aℓ + Mg = 3:4 for untreated Aℓ, O: Aℓ + Mg = 4.7:4 for 200 P and O: Aℓ + Mg = 4.6:4 at 2000 P treatment). Enrichment of the oxide layer was also mentioned in Ref. 8.

No similar effects were found in the chromic acid anodization treatment.[10]

CONCLUSIONS

An ArF excimer laser, the radiation from which produces chemical and physical effects, provides an effective preadhesion treatment for 2024 Aℓ alloy. The effect of laser treatment depends upon time of exposure and laser energy. High laser

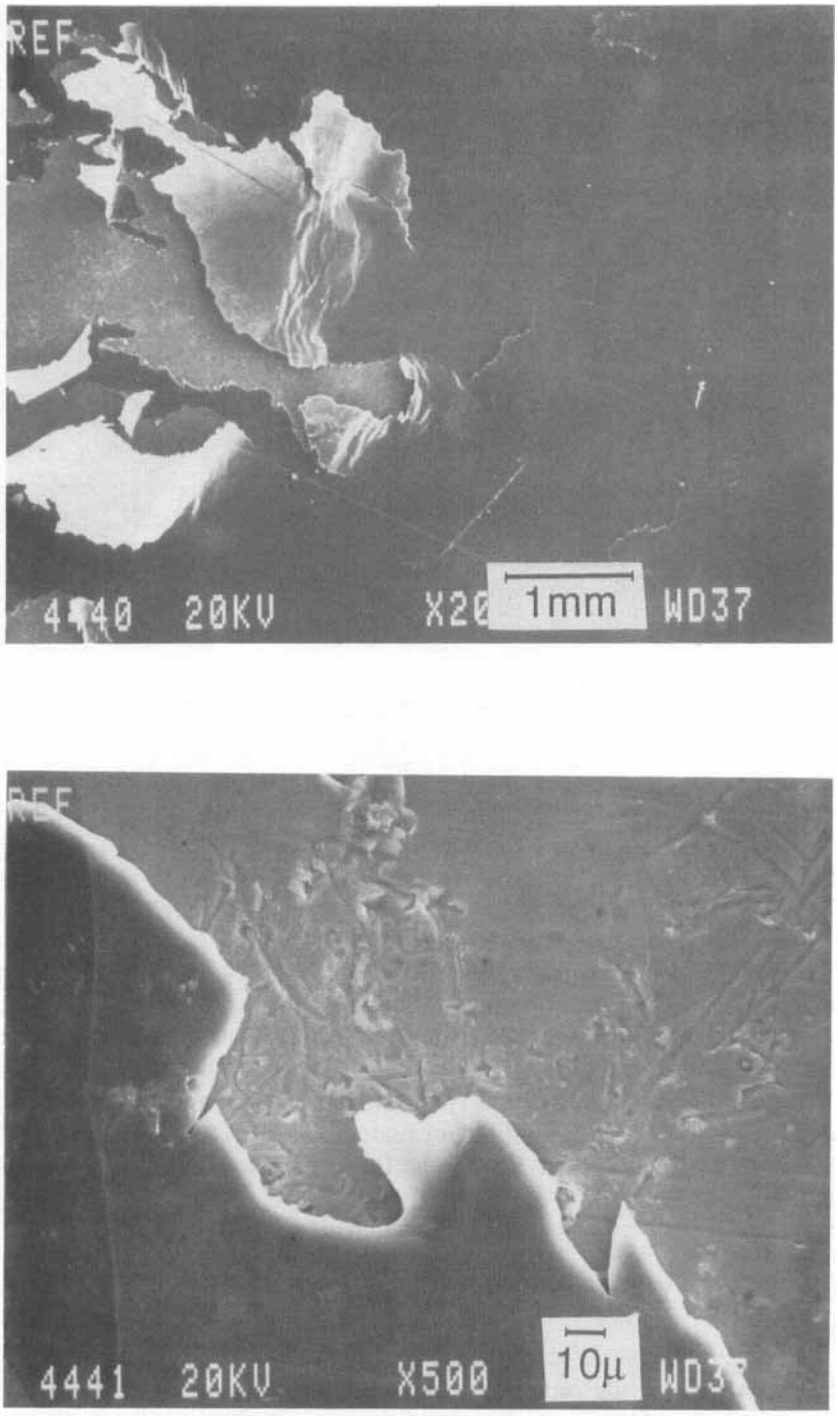
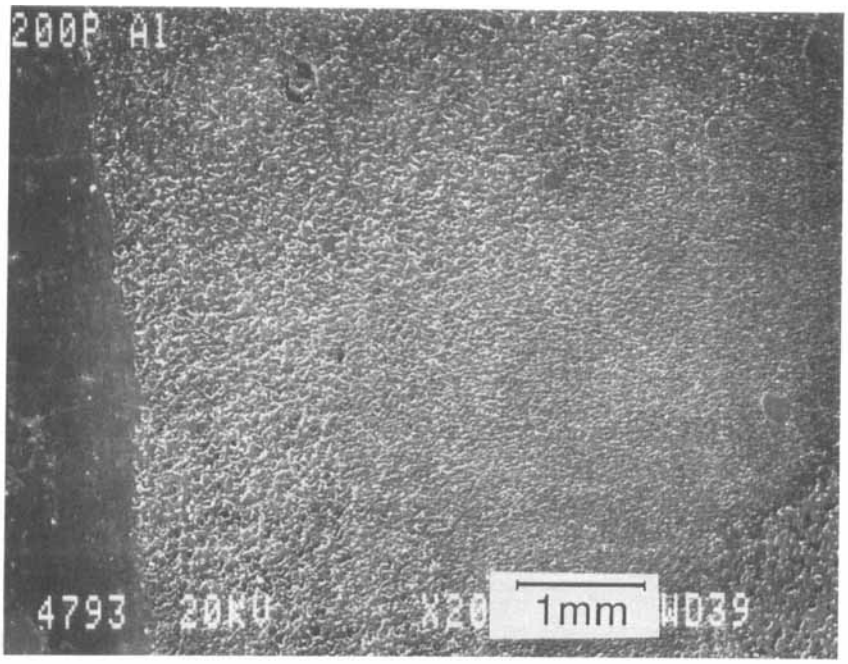


FIGURE 3 SEM micrographs of failure surfaces of untreated Aℓ at two different magnifications.



a

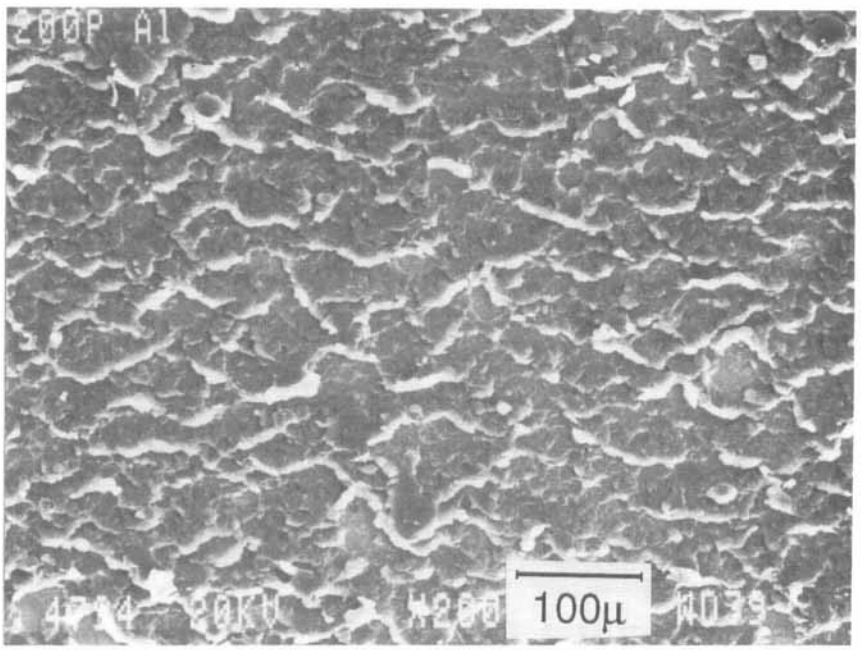
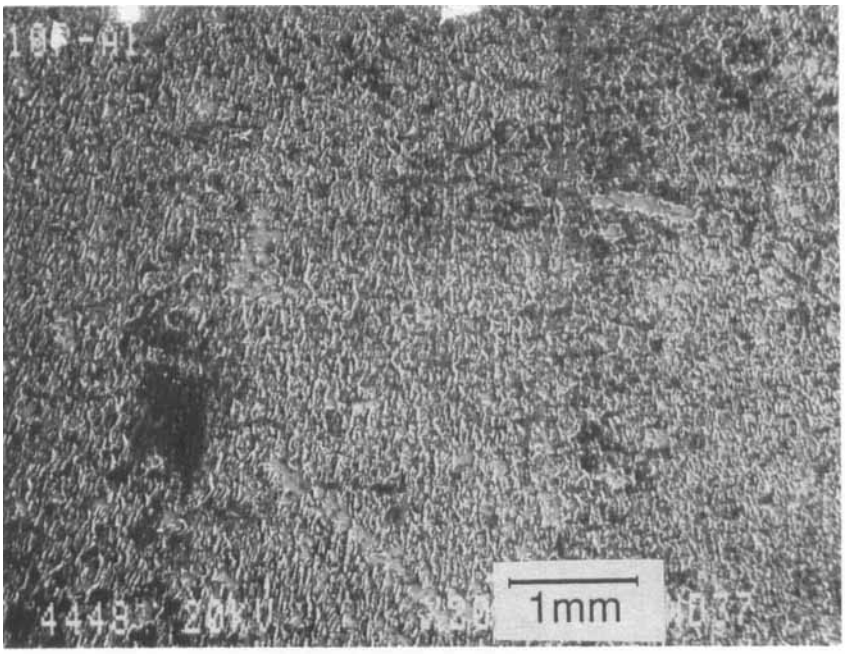


FIGURE 4 SEM micrographs of failure surfaces of laser treated Aℓ specimens, (a) 200 P, 0.25 J/P/cm^2, (b) 1000 P, 0.16 J/P/cm^2, (c) typical cohesive microstructure.



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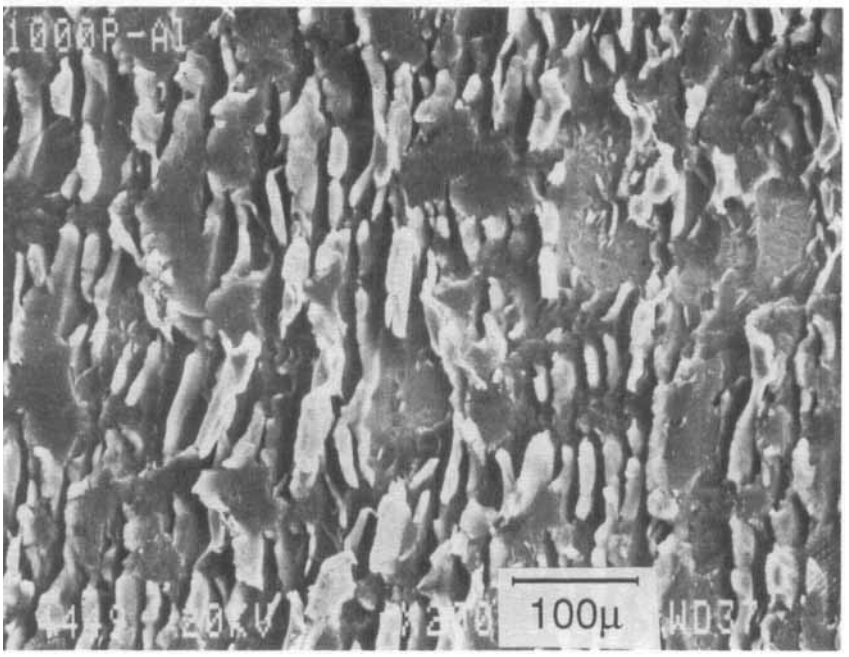


FIGURE 4 *(Continued)*

c

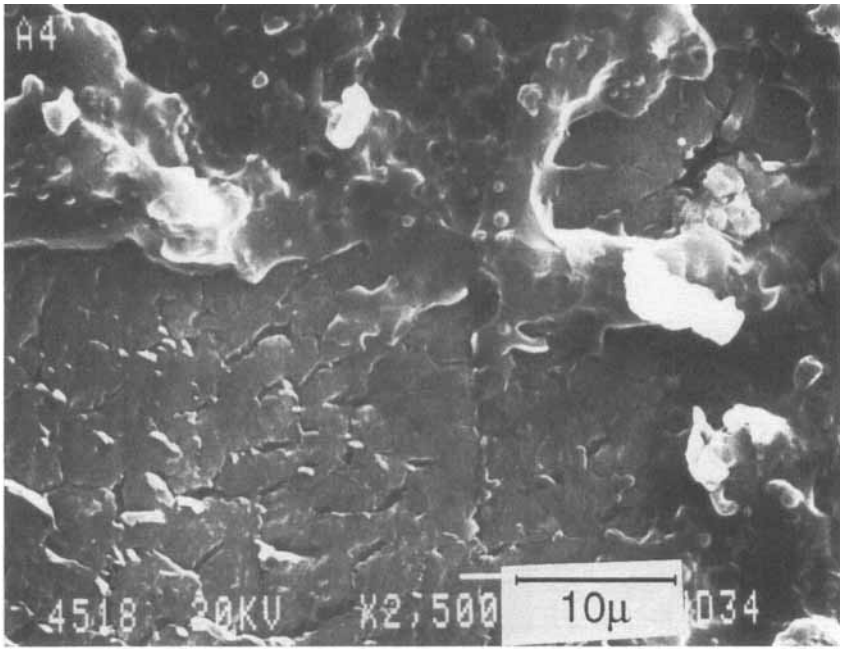


FIGURE 4 *(Continued)*

energy treatment results in high single lap shear SLS strength which, at optimal conditions, (0.185 J/P/cm^2), exceeded that of chromic acid anodized, unsealed, preadhesion treatment of Aℓ alloys.

The enhanced mechanical properties were supported by visual and SEM micrographs indicating a change of failure mode from adhesive (nontreated) to mostly cohesive (laser treated). At a higher number of pulses the changes in Aℓ surface morphology were correlated with the enhanced SLS strength.

FTIR studies revealed chemical changes on the surface including growth of an oxidized layer at optimal laser conditions (0.185 J/P/cm^2) and, probably, sealing of the oxide layer by humidity at high laser energies (0.73 J/P/cm^2).

Auger depth analysis supported the FTIR results in addition to indicating cleaning of the surface.

It can be concluded that ArF laser treatment is feasible and is an effective and clean method for surface pretreatment of aluminum compared with conventional etching and abrading methods. The main advantage of this treatment is ecological, *i.e.* the potential for replacing the use of harsh and dangerous chemicals.

Further study is planned to evaluate the durability of the laser pretreated joints in hot-humid environments, and in other modes of loading (peel and tension).

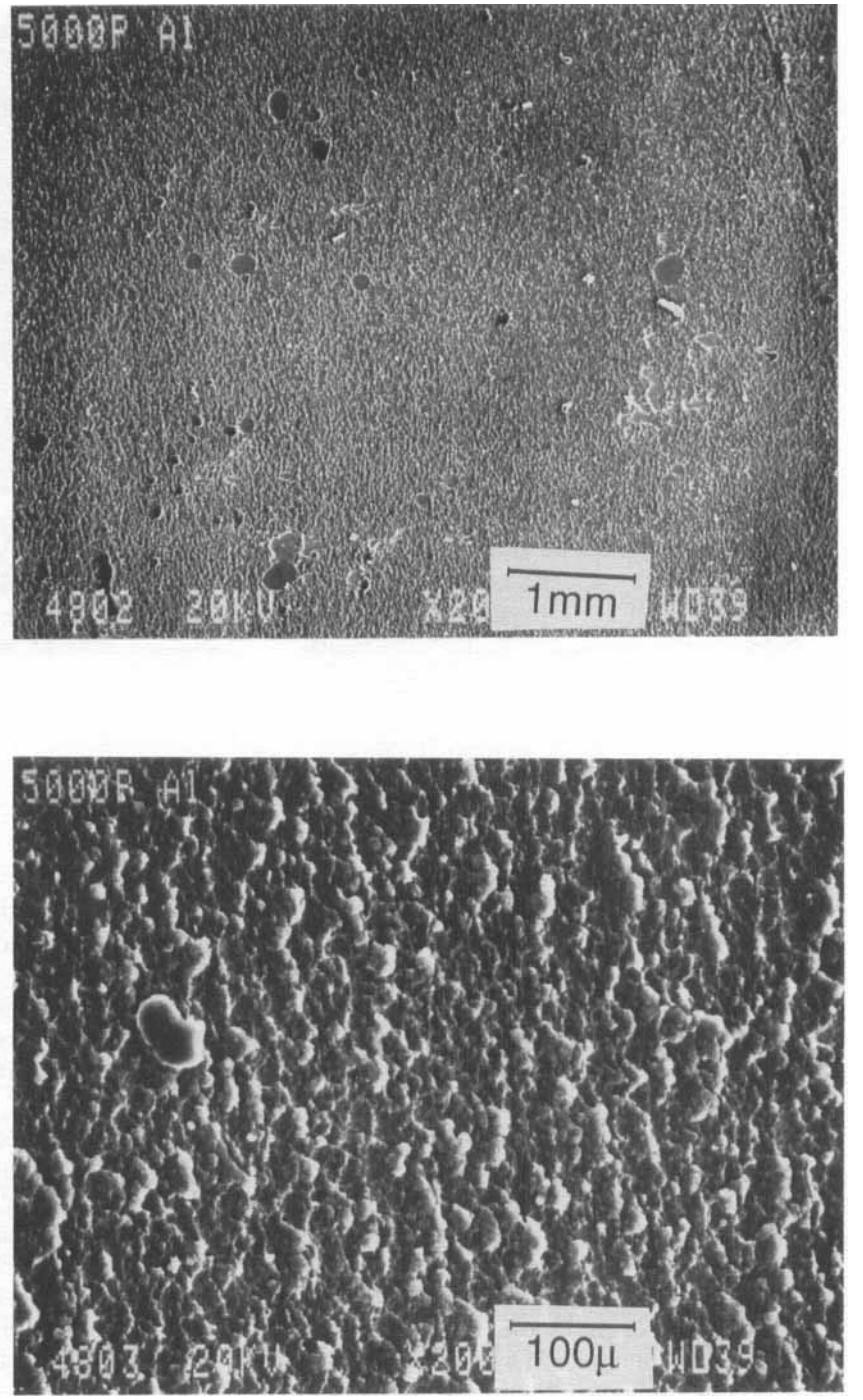


FIGURE 5 SEM micrographs of failure surface of laser treated (5000 P, 0.2 J/P/cm^2) Aℓ specimen at two different magnifications.

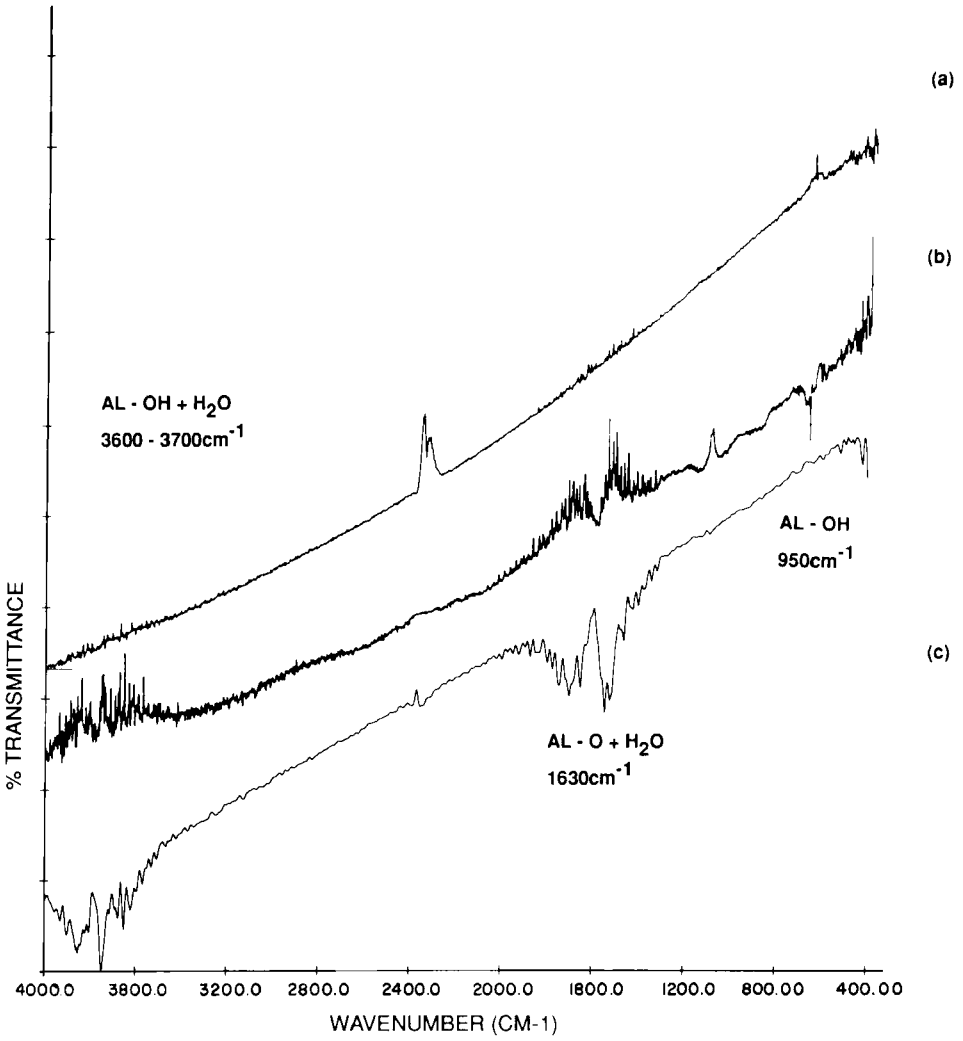
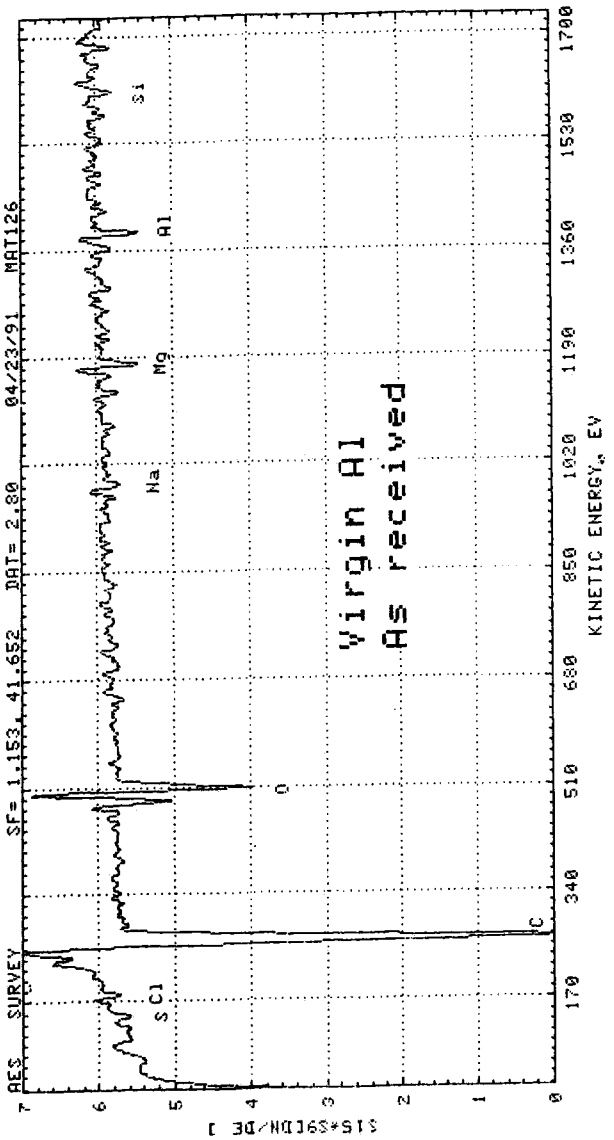
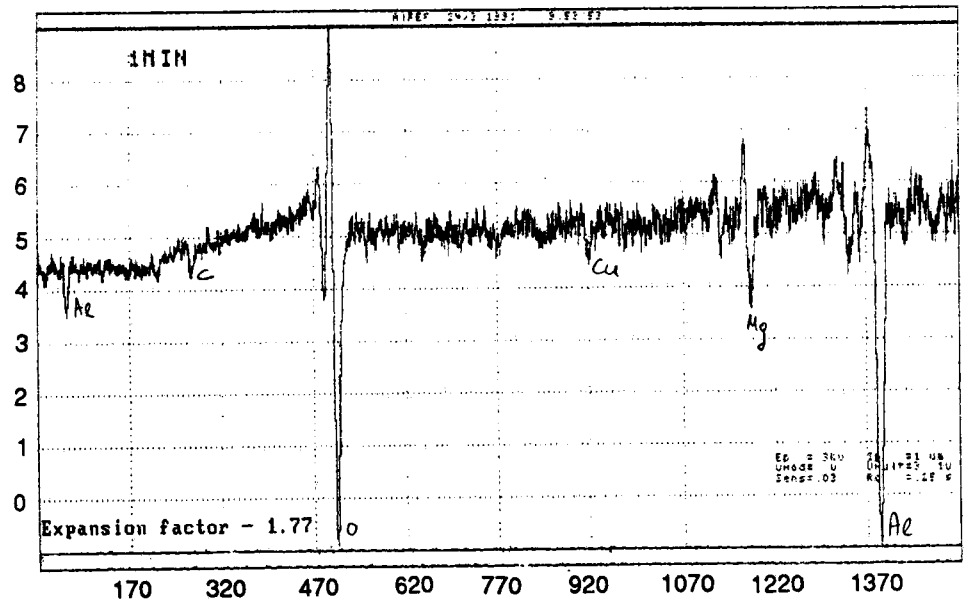


FIGURE 6 FTIR spectra of, (a) untreated Aℓ; (b) of laser treated Aℓ: 200 P, 0.2 J/P/cm^2; (c) of laser treated Aℓ: 200 P, 0.72 J/P/cm^2.





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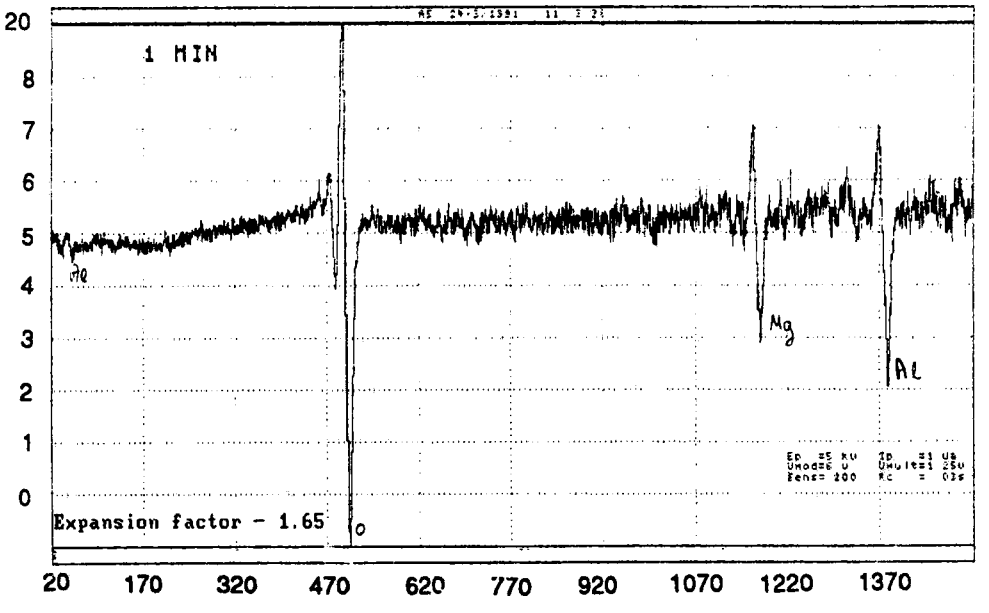


c

FIGURE 7 Auger surface analysis of, (a) untreated Aℓ; (b) and (c), of laser treated Aℓ: 200 P and 2000 P, respectively.

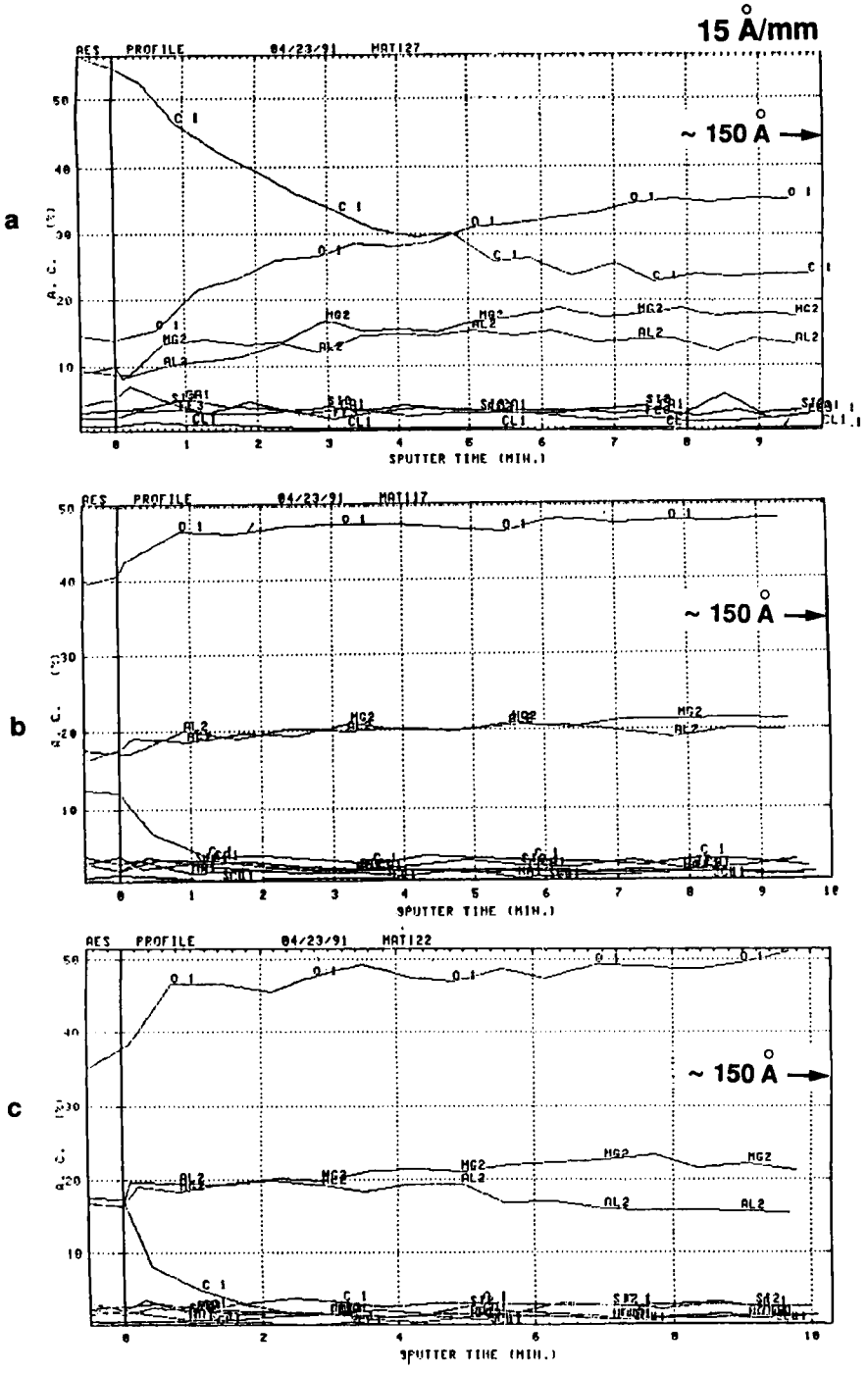
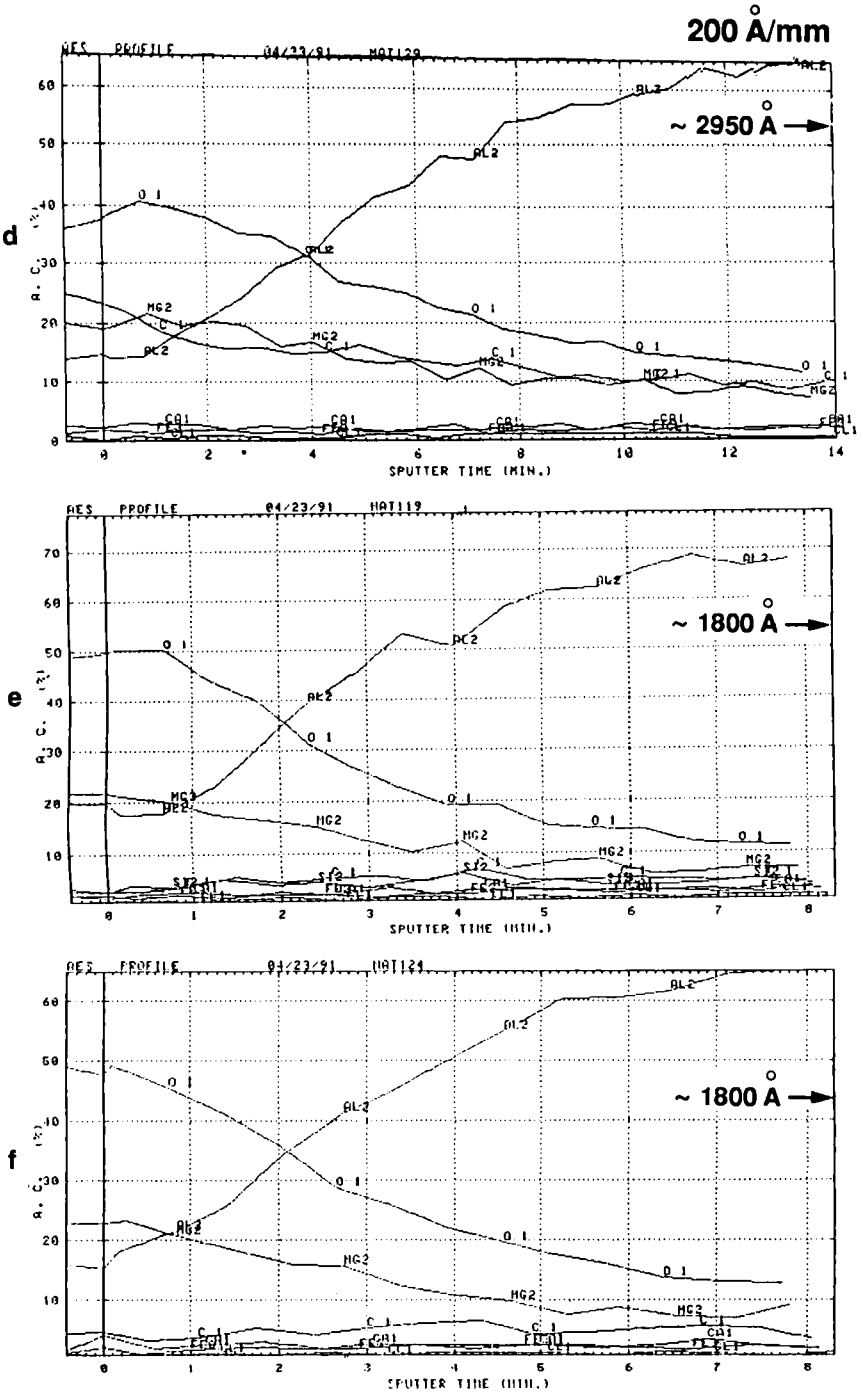


FIGURE 8 Auger depth analysis of, (a, d) untreated Aℓ; (b, e) of 200 P laser treated Aℓ; (c, f) of 2000 P treated Aℓ.



Acknowledgments

The authors would like to thank the United States Air Force for financing the research and for the scientific supervision. They also wish to thank Ms. H. Ziv for the SEM examination, Ms. S. Uziel for running the FTIR tests, and Ms. I. Liran for technical assistance.

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