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Time-of-flight measurements of the mass-to-charge ratio of positive ion emission accompanying fracture

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When non-metals are fractured, electrons and positive ions are emitted. We report our first time-of-flight measurements of the mass-to-charge ratio (*M/q*) of the positive ion emission (PIE) from the fracture of Kevlar and E-glass fibres and aluminium oxide coatings. Although the uncertainty is relatively large, the *M/q* observed suggest that for these materials PIE is a result of molecular and atomic fragments being produced during fracture.

1. Introduction

A number of particle-emission phenomena have been observed accompanying and following the fracture of materials. These have been collectively termed "fracto-emission" because the propagation of a crack appears to be a prerequisite for their appearance. The types of particles we and others have observed include electrons [1–8], positive and negative ions [1–9], neutral molecules [10], and photons [8, 11]. Positive ion emission (PIE) accompanying tensile deformation of a material was first reported by Rosenblum *et al.* [9] for oxide-covered metals. Dickinson *et al.* [3–5] showed that both PIE and electron emission (EE) from oxidized Al was due to crack propagation in the oxide coating and that the PIE and EE occurred in bursts typically less than 1 μsec in duration and in coincidence with crack growth in the oxide.

In this report, we present results of a preliminary determination of the mass-to-charge ratio (M/q) of the positive ion emission (PIE) emitted from Kevlar-49* and E-glass fibres, and from aluminium oxide coatings. The motivation for these measurements is first to improve our understanding of the origin of PIE and second to enhance the usefulness of fracto-emission (FE) measurements for the understanding of fracture phenomena. The latter is of particular importance if the observed PIE is a product of the molecular and atomic fragments produced in crack propagation. In such a case, the ionic species observed would indicate how fracture occurred in the material. For example, in the fracture of a polymer a simple question is: during fracture, are there fragments of mass less than, equal to, or greater than the monomeric unit? PIE may also be a useful tool for examining loci of fracture in multiphase systems such as ceramics and fibre-reinforced composites.

Similar questions have been raised for epoxy systems using stress-induced mass spectroscopy to monitor the neutral emission. Wolf *et al.* [12] have shown that in the fracture of an epoxy resin, MY720 (Ciba-Geigy) cured with Eporal (diaminodiphenylsulphone, Ciba-Geigy) SO_2 is released which was considered part of the main chain. The uncertainties in our measurements make it difficult to give definitive answers to these questions; however, it will be shown that in the case studied we must consider the emission of atomic/molecular fragments from fracture as strong possibilities.

2. Experimental procedure

The polymer fibres used in this study were 10 μm Kevlar-49 aramid fibres, characterized by high

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*Trade name of E. I. Dupont de Nemours and Co.

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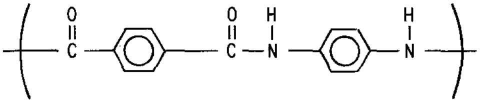
crystallinity, high tensile strength and modulus, and low density. The chemical composition by weight [13] is; 67% C; 15.9% O; 11.2% N; 4.3% H; 0.8% ash (including small quantities of Na and S). The monomer unit, determined by Penn and Larsen [13] is poly(*p*-phenylene terephalamide, PPD-T):



which has a mass of 238 a.m.u. Only trace amounts of unreacted constituents and solvent are expected to be present. Owing to long exposure to the atmosphere there is likely to be H_2O absorption [13], of the order of 1 to 3% by weight, before introduction into the vacuum system. Although a good portion of this moisture should be removed during pump down, some H_2O certainly would remain at room temperature. Other atmospheric gases might be present, also.

The E-glass fibres were untreated and 20 μm in diameter. The chemical composition of E-glass [14] is: 53% SiO_2; 21% CaO; 15% Al_2O_3; 9% B_2O_3; 1.2% Na_2O; 0.3% MgO; 0.3% BaO; 0.1% K_2O. Water is the predominant absorbed molecule in glasses [15]. At elevated temperatures (above the softening temperature) constituents of the glass itself begin to break down and lead to evolution of H_2O (dehydration), CO_2, and sometimes O_2.

The fibre samples were composed of 5–20 fibres adhesively bonded to Al sheet metal shaped to fit into clamps in a vacuum system. To decrease the probability of pull-out of the fibres out of the adhesive, the fibres were stretched across a sharp Al edge, where approximately 90% of them would fracture. The fibre length was 1.5 cm. The diameters were 10 μm for Kevlar and 20 μm for E-glass. By using fibres of various lengths one could spread out in time the fracture events, although multiple breaks within a few microseconds were not uncommon when fibres were allowed to twist or cross in any way.

The aluminium oxide coatings were produced on Al 1350 substrates machined in a dog-bone shape, 0.5 mm thick and with a gauge of 10 mm × 30 mm. The samples were cleaned in a CrO_3–H_2SO_4 solution and anodized in a 0.05 m ammonium tartrate solution at room temperature for 30 min at 230 V. This produced a dense oxide layer approximately 300 nm thick. The structure of aluminium oxides produced by anodization is known to be amorphous in nature with varying degrees of crystallinity, depending on the electrolyte and the anodizing conditions [16]. It is also known that during the anodizing process, the anion and H_2O are incorporated to some extent into the oxide [17–19], which tends to be hydrated. Oxygen gas is evolved at the anode which could be absorbed into the oxide layer. Thermal desorption measurements [10] on similarly grown anodized oxide films on bare Al 2024 yielded the release of O_2 and CO_2 (presumably from the tartrate anion). No evidence of N_2 or NH_3 was found. During fracture of the oxide, intense emission of neutral O_2 and CO_2 was observed [10].

Earlier attempts to determine PIE mass using a standard quadrupole mass spectrometer (QMS) were unsuccessful due to relatively low signal-to-noise, the unknown mass, widely varying ion energy distributions, and most problematic, the transient nature of fracture. A less direct, but more practical method, was developed that takes advantage of (a) the rapid crack growth that occurs in thin fibres and brittle metal oxide coatings, and (b) the fact that both EE and PIE are emitted "simultaneously" from the fracture surfaces. It is basically a time-of-flight (TOF) technique. Its main advantage is that the M/q values can be completely unknown and can be determined without a search.

Fig. 1 shows schematically the experimental arrangement, where two channel-electron-multipliers (CEM) are positioned on two sides of the sample. The electron detector, CEM-EE, is positioned within 1 cm of the specimen and its front end is biased with + 300 V to attract electrons. The TOF of an electron to the CEM-EE in such an E-field is approximately 2 nsec. In order to reach the PIE detector, the ions must pass from the fracture surface through a drift tube, the total flight path being 27 cm. The drift tube is biased with a voltage, $-V$, which determines the TOF of an ion of a given mass through the tube. The front end of the CEM-PIE is biased at -1 kV to ensure efficient PIE detection. Grids are mounted on both ends of the drift tube to prevent electric field penetration. The experiments were carried out in vacuum at a pressure of 10^{-7} Torr. Details of the experimental arrangement are given in [7].

The total TOF distribution is obtained as follows: a multichannel analyser (MCA) set at

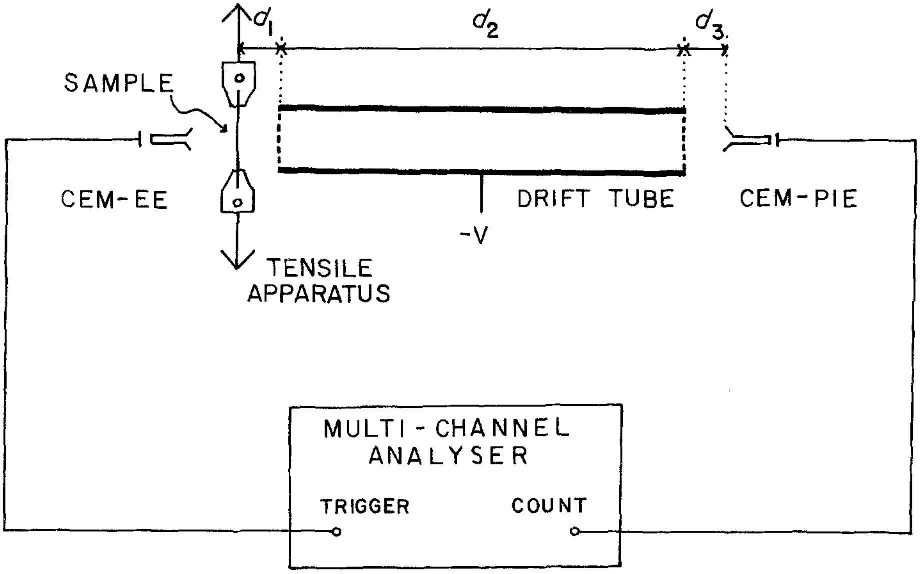


Figure 1 Schematic illustration of the experimental apparatus. The distances are: $d_1 = d_3 = 1$ cm, $d_2 = 25$ cm.

1 μsec/channel is triggered with the first incoming electron. The PIE arriving at the CEM-PIE then produce a distribution of pulses that are accumulated in the MCA at times determined by (a) their time of release from the sample, and (b) their TOF. If fracture produces a burst with a fast leading edge, then the fact that the sample continues to emit for several microseconds will not affect the *leading edge* of the PIE-TOF. It is this feature we use to determine M/q.

The leading edge of the PIE time distribution relative to the first electron detected was examined by removing the drift-tube and positioning the CEM-PIE within 1 cm of the sample. The leading edge of these time distributions did show a finite rise time for Kevlar. This was probably due to the fact that the Kevlar fibres were not fracturing as fast as one might expect. Scanning electron micrographs of fractured Kevlar fibres showed frequent splitting and shredding of the fibres rather than brittle fracture. This type of fracture would take longer to occur, thus leading to the finite rise time of the time distributions. For E-glass, we found that although the bursts reached a peak very rapidly (within 1 μsec), the EE frequently showed emission a few microseconds *before* this rapid rise. This precursor was random and occurred approximately 30% of the time and is believed to be due to crack formation in the strained fibre. The result was a shift in the leading edge of the accumulated time distribution of 1 μsec. These shifts in time were taken into account in the final analysis of the TOF. For the aluminium oxide coatings, the rise times of the PIE time distributions were, within our time resolution, instantaneous and therefore no correction in the TOF was used.

The total TOF, T, consists of the sum of the flight times: $t_1 + t_2 + t_3$ over the regions d_1, d_2, and d_3 shown in Fig. 1. Using Newton's second law, conservation of energy, and simple kinematics, we obtain a relation for T in terms of the ion mass-to-charge ratio M/q, the tube potential V, and the distances $d_1 = 1$ cm, $d_2 = 25$ cm, and $d_3 = 1$ cm. With substitution of these lengths the relation reduces to:

$$T = 20.1\sqrt{\left(\frac{M/q}{V}\right)}, \qquad (1)$$

where T is in μsec. When T is measured for various values of V, M/q can be determined from the slope of plots of T against $1/\sqrt{V}$. Because the emitted ions have an energy distribution, the leading edge of the emitted bursts spreads in time. To increase precision, T was taken to be the value of time corresponding to half way up the leading edge of the time distributions (T at half-maximum). A correction to V for the initial kinetic energy corresponding to this half-maximum was determined for E-glass and Kevlar by measuring the value of T at half-maximum for $V = 0$ (thus no acceleration) and calculating the corresponding energy

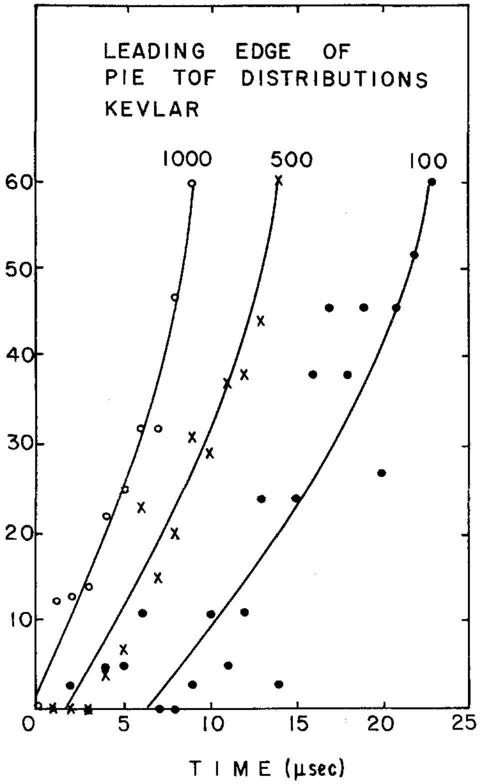


Figure 2 Leading edge of PIE TOF distributions for Kevlar fibres.

using a value of M/q determined from Equation 1 *without* this correction. These corrections were surprisingly small: 2 V for E-glass and 4 V for Kevlar. We were unable to make measurements of T for the oxide coating below − 500 V because the presence of the metal substrate made the collection of both electrons and positive ions more difficult at lower tube voltages. Thus for the oxide coatings we have not made any corrections; we expect, however, that it would not be very significant compared to $|V| \geqslant 500$ V.

3. Results

Figs. 2 to 4 show the leading edges of typical TOF distributions for positive ion emission from Kevlar, E-glass, and anodized Al for various drift tube potentials. For the fibres, each curve represents the fracture of approximately 10 fibres. Five to ten curves like these were acquired for each V and a distribution of T at half-maximum obtained. The average of these results were then plotted against $1/\sqrt{V}$, as shown in Fig. 5. The error in T was estimated to be ± 1 μsec. As mentioned previously, the Kevlar and E-glass T at half-maximum have been decreased to account for the measured shifts in the leading edge occurring in the initial time distributions. These corrections are 1.5 and 0.8 μsec for Kevlar and E-glass, respectively. No measurable correction was found for the aluminium oxide coatings. A least squares fit to these data produced the lines shown in Fig. 5, where all curves have been forced through the origin, in compliance with Equation 1. The slopes of these lines were then used to calculate M/q. The values obtained are:

Material	M/q (a.m.u.)
Kevlar	60 ± 20
E-glass	48 ± 12
Aluminium oxide coating	17 ± 6

4. Discussion and conclusion

Although the uncertainties in these values of M/q are relatively large, we emphasize that the M/q of the PIE accompanying fracture of materials has

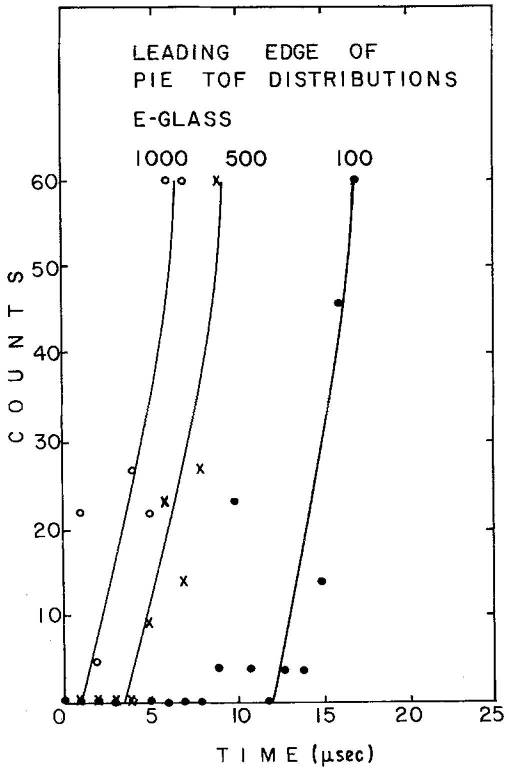


Figure 3 Leading edge of PIE TOF distributions for E-glass fibres.

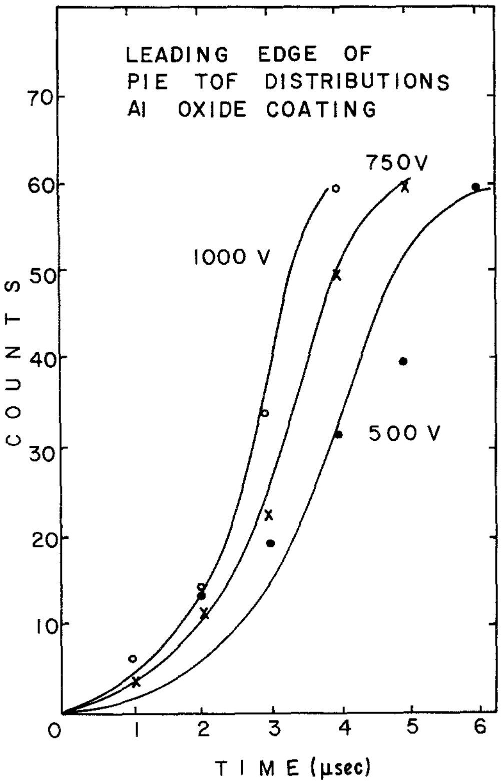
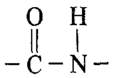


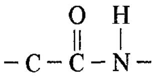
Figure 4 Leading edge of PIE TOF distributions for Al oxide coating.

previously been totally unknown. The technique we have employed here favours the detection of the lightest masses if more than one mass is emitted. Nevertheless, we have some sensitivity to the presence of heavier masses which should show up as a shoulder on the leading edge of the TOF distribution at longer times. Careful examination of a number of TOF distributions for all three materials showed no clear evidence of heavier masses. Therefore, our present results indicate that the PIE accompanying fracture from these materials consists of relatively light ions.

For each material our uncertainties do not allow a unique value of M to be assigned to the observed PIE and therefore there are a number of candidates for each material. For Kevlar, we can rule out absorbed H_2O^+ and ions of common background and atmospheric gases. If we assume $q = 1$, the PIE mass from Kevlar is considerably smaller than a monomer. Likely candidates could involve species like

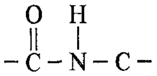


$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$



$$-C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$

or



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-C-,$$

all of which would be produced by main-chain bond cleavage.

For E-glass, if we assume $q = 1$, we can rule out H_2O^+ and O_2^+, but not CO_2^+. Fragments of the components of E-glass which are candidates include Ca^+, K^+, $B_2O_3^+$, MgO^+, and possibly SiO^+. Ohuchi *et al.* [20] have shown that soda-silica glass under electron bombardment (with energies between 1.5 and 10 keV) yielded emission of Na^+ via electron-stimulated desorption (ESD). They estimated the bulk concentration of their samples to be 15% Na_2O and 85% SiO_2. Given the measured value of M/q in this experiment and the strong possibility that fracture induces similar intermediate states produced by ESD, we propose that we are observing Ca^+ or K^+ and note that these elements are originally bonded into the glass "lattice."

The lower M/q obtained for the aluminium oxide coating, assuming $q = 1$, could be one of the following: O^+, H_2O^+, OH^+, N^+, NH_x^+, or CH_x^+. All of the ions listed could be due to species entrapped in the oxide during the anodization process, although the source of O^+ or OH^+ could be from decomposition of the hydrated oxide. Again, we point out that ESD and PSD (photon stimulated desorption) studies on a number of ionically bonded, hydrated oxides [21, 22] show

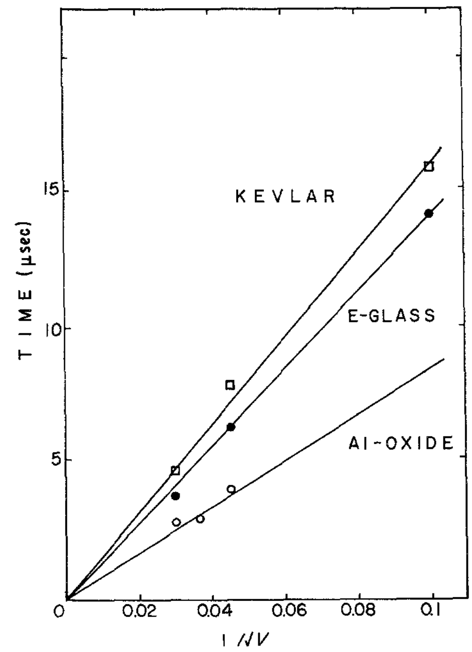


Figure 5 Plot of T at half-maximum against $1/\sqrt{\text{(tube voltage)}}$.

that the predominant species desorbed during electron and soft X-ray bombardment are H^+, OH^+, and O^+. This provides support for the possibility that we are observing either OH^+ or O^+. In either case, these would most likely be quite tightly bound in the oxide structure and either one *could* be considered as a product of fracture of the oxide. (One experiment that suggests itself is to study PIE from pure Al_2O_3.)

In summary, these preliminary measurements of M/q from three different materials first verify that indeed positive ions are a fracto-emission product and not an artefact induced by photon or electron emission. Second, there is a tendency for these fragments to be relatively light (10 to 80 a.m.u.). Third, there is a strong possibility that, for these materials, the PIE observed are fragments of the original matrix. This may be a necessity simply on the basis of energy-transfer arguments: we have proposed [6–8] that PIE is intimately related to the production of high-energy sites on the fracture surface by cleavage and bond breaking. These sites consist of defects in the case of oxides, displaced atoms and ions in the case of glass, and free radicals in the case of polymers. Trapped electrons available for non-radiative electronic transitions also play an important role in all these cases. The chemical reactions and electronic transitions that ensue following crack propagation then lead to ions in anti-bonding surface states, releasing the ions into the vacuum. These steps require relatively close coupling of the high-energy sites and displaced atoms or molecules to be ionized and therefore, it may have to be part of or bonded to the defect structure.

In addition to furthering our understanding of PIE mechanisms, the major goals of future PIE research include: (a) more precise measurements of M/q, and (b) relating PIE to factors such as mode of fracture, material composition and structure, and the microscopic events occurring during fracture. The technique outlined in this paper can be used to determine approximate M/q values for a wide variety of materials. Once such values are known, as in the materials studied here, high resolution M/q measurements can be made with little or no searching using a standard quadrupole mass spectrometer. To resolve questions concerning the source and mechanism of PIE we intend to carry out these studies on better characterized, pure materials.

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References

1. J. T. DICKINSON, P. F. BRAUNLICH, L. LARSON and A. MARCEAU, *Appl. Surf. Sci.* **1** (1978) 515.
2. D. L. DOERING, T. ODA, J. T. DICKINSON and P. F. BRAUNLICH, *ibid.* **3** (1979) 196.
3. J. T. DICKINSON, D. B. SNYDER and E. E. DONALDSON, *J. Vac. Sci. Technol.* **17** (1980) 429.
4. *Idem, Thin Solid Films* **72** (1980) 225.
5. J. T. DICKINSON, E. E. DONALDSON and D. B. SNYDER, *J. Vac. Sci. Technol.* **18** (1981) 238.
6. J. T. DICKINSON and L. C. JENSEN, *J. Polymer Sci. Polymer Physics Ed.* in press.
7. J. T. DICKINSON, E. E. DONALDSON and M. K. PARK, *J. Mater. Sci.* **16** (1981) 2897.
8. J. T. DICKINSON, M. K. PARK, E. E. DONALDSON and L. C. JENSON, *J. Vac. Sci. Technol.* **20** (1982) 436.
9. B. Z. ROSENBLUM, P. F. BRAUNLICH and L. HIMMEL, *J. Appl. Phys.* **48** (1977) 5262.
10. L. A. LARSON, J. T. DICKINSON, P. F. BRAUNLICH and D. B. SNYDER, *J. Vac. Sci. Technol.* **16** (1979) 590.
11. J. I. ZINK, *Acc. Chem. Res.* **11** (1978) 289.
12. C. J. WOLF, D. L. FANTER and M. A. GRAYSON, "Ageing of Polymers and Composites", ONR Final Report MDC-Q 0743, 21 July (1981).
13. L. PENN and F. LARSEN, *J. Appl. Polymer Sci.* **23** (1979) 59.
14. L. L. CLEMENTS, "Properties of Commercial Fibers Used for Filament-Wound Composites", Lawrence Livermore Laboratory Report UCID-17873 (1978).
15. S. DUSHMAN and J. M. LAFFERTY, "Scientific Foundations of Vacuum Technique", 2nd Edn, (Wiley, New York, 1962) pp. 470–500.
16. J. W. DIGGLE, T. C. DOWNIE and C. W. GOULDING, *Chem. Rev.* **69** (1969) 365.
17. J. E. LEWIS and R. C. PLUMB, *J. Electrochem. Soc.* **105** (1958) 496.
18. R. B. MASON, *ibid.* **102** (1955) 671.
19. R. E. HERFORT, "Fundamental Investigations of Anodic Oxide Films on Aluminium Alloys as a Surface Preparation for Adhesive Bonding", US Air Force Technical Report AFML-TR-76-142.
20. F. OHUCHI, M. OGINO, P. HOLLOWAY and C. G. PANTANO, Jr, *Surface Interface Analysis* **2** (1980) 85.
21. M. L. KNOTEK, V. O. JONES and V. REHN, *Surf. Sci.* **102** (1981) 566.
22. H. NIEHUS and W. LOSCH, *ibid.* **111** (1981) 344.

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