

Quantitative acoustic microscopy of anodized and coated aluminium at frequencies up to 1 GHz

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Quantitative acoustic microscopy (QAM) has been used to measure surface wave velocities on polished, anodized and coated aluminium substrates, these materials being representative of those used for adhesive bonding in the aerospace industry. Good quality acoustic measurements were obtainable at frequencies between 225 and 980 MHz, despite the inhomogeneous nature of the oxide layer produced by phosphoric acid anodization (PAA). Good agreement was obtained between the surface acoustic wave dispersion measured on aluminium coated with 0.2 and 1.0 μm PMMA, and that calculated by a simple isotropic layer model. The anodized aluminium was modelled as a transversely isotropic oxide layer on an aluminium substrate. At 0.2 μm , the oxide layer was too thin for the comparison between measurement and calculation to be conclusive, but the calculations suggest that a change in porosity of 10% in a 0.6 μm oxide layer, as obtained with an industry standard PAA treatment, should be readily detectable. The highly dispersive nature of some of the surface acoustic wave modes makes QAM extremely sensitive to small changes in the material parameters.

1. Introduction

Adhesive bonding has been used extensively for many years in the aerospace and other high-technology industries. It is attractive because it distributes stress over the entire bond area and thus avoids the stress concentrations which can occur with mechanical fasteners. With good design, it can also yield significant weight savings. However, in spite of its potential advantages, the use of adhesive bonding in primary structures has been limited by a lack of adequate non-destructive testing procedures [1]; without such procedures, the reliability of a structure cannot be guaranteed.

There is also considerable uncertainty about the mechanism of adhesive bonding and, in particular, the changes occurring during environmental attack which greatly reduce the bond strength [2]. This lack of understanding hampers the development of better adhesive systems and also makes the development of non-destructive testing methods very difficult because it is not certain what properties should ideally be measured.

Surface pretreatments are usually employed prior to bonding because these have been found to improve the resistance of the joint to environmental attack. The standard surface pretreatments used on aluminium adherends in aerospace applications produce a honeycomb-like oxide structure on the adherend surface [2], and the adhesive (or primer if one is used)

penetrates some distance into the honeycomb cells, the depth of penetration depending on the pretreatment used and on the viscosity of the primer or adhesive. The overall thickness of this "interlayer" between the bulk adhesive (or primer) and the bulk adherend in a typical aluminium-epoxy joint is typically only of the order of 1 μm and, even over this distance, its properties may be a function of depth depending on the adhesive penetration and the honeycomb structure. It is therefore extremely difficult to measure the mechanical properties of the interlayer.

In this study, the major interest is in gaining more information about the mechanical properties of the interlayer, and so an adherend/adhesive combination is examined rather than a full joint. This allows the use of much higher frequencies than would be possible for non-destructive inspection. Quantitative acoustic microscopy (QAM) was chosen because the technique is very sensitive to the near-surface mechanical properties of a material. Operation of the microscope is possible at frequencies up to 1 GHz, where the acoustic wavelength approaches 1 μm . If these measurements could be carried out on samples with the complex structure found in the interlayer of adhesive joints, it should be possible to measure the velocity of a wave whose energy is predominantly contained within the interlayer. This opens up the possibility of measuring the properties of the interlayers produced by different surface preparations, and also of

monitoring the changes which occur during environmental attack.

Most previous QAM of multilayer systems has been done at frequencies around 200–400 MHz, and has for the most part been limited to relatively simple, low attenuation systems such as gold-plated silicon wafers. It was therefore necessary to demonstrate that satisfactory measurements could be obtained on the much more complex structures found in adhesive joints where a honeycomb oxide structure is partially penetrated by an attenuative polymer (the adhesive or primer). In order to do this, tests have been carried out using 225, 820 and 980 MHz centre frequency lenses on plain, polished aluminium, polished aluminium coated with thin layers of polymer, anodized aluminium and anodized aluminium coated with polymer. The results of this preliminary study are reported here.

The ultimate goal of the work is to use acoustic microscopy to provide the adhesion science community with more information about the mechanical properties of the interlayer between the adhesive and the adherend and how they change during environmental attack, so facilitating the development of improved adhesive systems. The measurements will also provide information on the properties which must be measured in a non-destructive test. Although attenuation in the adherend precludes the use of acoustic microscopy in non-destructive inspection, it may be possible to develop lower frequency methods building on the work of, for example, Wang and Rokhlin [3] and Cawley and Pialucha [4, 5].

2. Quantitative acoustic microscopy

Progress in the field of acoustic microscopy has been rapid since the first instrument was built by Lemons and Quate [6]. In the standard reflection arrangement, a single spherical lens is used to focus acoustic waves on to the specimen and detect the subsequent reflection (Fig. 1). The acoustic microscope initially attracted attention because of its ability to depict inhomogeneity in near-surface elastic properties with high spatial resolution. It was quickly recognised that surface acoustic waves (SAWs) play a fundamental role in the generation of contrast within the acoustic image. The particle displacements in a SAW decay exponentially into the material, so that most of the energy is concentrated within a wavelength of the surface. In typical materials, the wavelength can be varied from about 15 μm at 200 MHz to 3 μm at 1 GHz. In the case of an isotropic infinite halfspace, the surface wave is called a Rayleigh wave; when layers are present, a variety of dispersive surface wave modes may exist. A coupling fluid, usually water, is required between the lens and the specimen, because the attenuation of waves in air is prohibitively high at these frequencies.

Once the mechanism for the contrast in the image had been understood, the possibility of quantitative measurement became apparent [7]. In this mode of operation, shown schematically in Fig. 1, the "reflected" output from the lens is measured as a function of

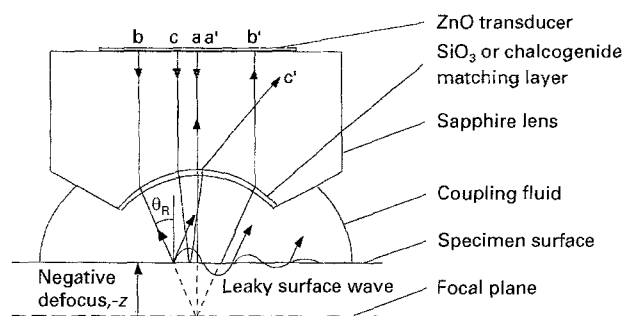


Figure 1 Schematic diagram of the defocused acoustic lens. In this ray model picture, two rays are of fundamental importance. Ray aa' is incident normally on to the specimen and is reflected back along the same path. Ray b is incident at an angle such that it excites a Rayleigh wave along the surface. This wave leaks back energy into the fluid, and the particular ray b' is incident normally on to the transducer. The two rays aa' and bb' change phase at different rates as the z -position of the specimen is altered and hence can produce oscillations at the transducer output. The majority of other rays, such as cc' , either fall on to the transducer obliquely, or miss it altogether.

the lens–specimen separation, over a fixed point on the specimen. Oscillations are frequently observed in the output signal, which is known as the $V(z)$ (see, for example, Fig. 2). The oscillations are intimately related to the excitation of surface waves, and the velocity of these waves can be ascertained from the periodicity of the oscillations. Because the SAW velocity depends on the stiffness and density of the material, it is possible to obtain quantitative values for one or more of the mechanical properties of the near surface region.

Initially, all lenses had spherical cavities, and hence averaged the properties over all directions in the surface. An important development therefore came with the design of a lens containing a cylindrical cavity, which focuses cylindrical wavefronts on to a line on the specimen surface [8]. The line focus beam (LFB) acoustic microscope can therefore measure directly anisotropy in materials, albeit at the expense of spatial resolution.

Quantitative acoustic microscopy (QAM) has been applied to a wide range of coated materials, making use of the dispersive nature of the SAW in such cases to determine an unknown material property. In the vast majority of cases, the substrate and also usually the coating have been smooth and homogeneous, and the frequency has been below 400 MHz. Early applications were to thickness measurements for coatings with known elastic constants, such as gold or tungsten silicide on substrates of silicon or fused quartz [7, 9, 10]. Since then, attempts have been made to invert the elastic constants of coatings from measurements of SAW frequency, thickness or angular dispersion [11–14]. There have also been attempts to study the adhesion of coatings [15–17], but the only successes have been for the case of complete delamination, where there is a large change of impedance at the interface. There has been relatively little $V(z)$ work at high frequencies, mainly because the measurements are more difficult, and the accuracy is much poorer. Briggs *et al.* [18] presented results on glass at 1 GHz

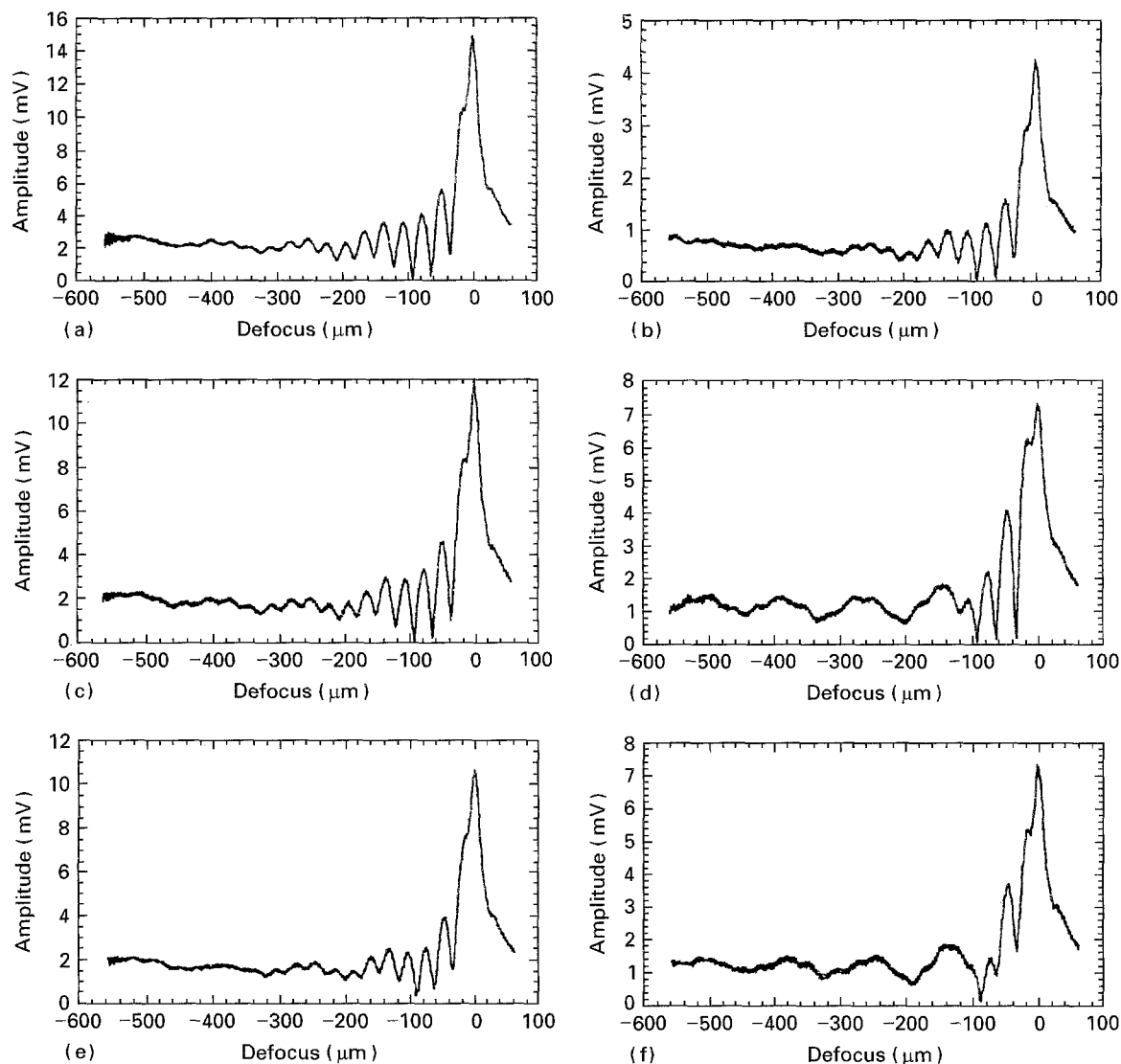


Figure 2 $V(z)$ s at 225 MHz on (a) polished, and (b–f) anodized and or coated aluminium 8090 specimens, (b) 8090 + 0.2 μm oxide, (c) 8090 + 0.2 μm PMMA, (d) 8090 + 1.0 μm PMMA, (e) 8090 + 0.2 μm oxide + 0.2 μm PMMA, (f) 8090 + 0.2 μm oxide + 1.0 μm PMMA.

obtained with the Ernest Leitz scanning acoustic microscope (ELSAM) [19], whilst Walikainen [20] studied very thin metallic coatings on fused quartz also at 1 GHz.

3. Experimental procedure

3.1. Choice of specimens

Because most QAM has been done at frequencies around 200–400 MHz, and has been limited to relatively homogeneous materials with low attenuation, it was necessary to demonstrate that satisfactory measurements could be obtained on the more complex structures found in adhesive joints, where a honeycomb oxide structure is partially penetrated by an attenuative polymer (the adhesive or primer). In order to do this, tests have been carried out using 225, 820 and 980 MHz centre frequency lenses on plain, polished aluminium, polished aluminium coated with thin layers of polymer, anodized aluminium and anodized aluminium coated with polymer.

3.2. Sample preparation

An aluminium/lithium alloy (Grade 8090) was used as the substrate for the experiments. QAM requires a good surface finish, ideally with local flatness to within a tenth of a wavelength, or about 0.3 μm at 1 GHz. It was therefore necessary to polish the aluminium prior to measurement.

For the experiments on coated samples, it was desirable to use specimens coated with a small, well-controlled thickness of polymer. This was most readily achieved by spin coating polymethyl methacrylate (PMMA) on to a polished aluminium substrate, rather than by attempting to bond a very thin layer of adhesive to the substrate. Various concentrations of PMMA dissolved in toluene were spin coated on to polished aluminium substrates. Adhesion to the substrate was not found to be a problem, and the resultant coating was reasonably uniform, with PMMA concentrations of 3% and 10% yielding coating thicknesses of approximately 0.2 and 1 μm , respectively. These thicknesses were estimated by measuring the reflection spectrum of the samples in and around the

visible region using a Perkin–Elmer Lambda 9 spectrophotometer. Measurements were repeated over different regions of the specimen to assess the variability in PMMA thickness, which was found to be about 5% at most.

Polished aluminium substrates were treated by phosphoric acid anodization (PAA), because this method is well suited to the production of controlled oxide thicknesses. For the sample materials produced for this study, the oxide thickness was approximately 0.2 μm . The thickness was determined by taper polishing, where the specimen is polished at a known small angle, which effectively magnifies the oxide layer so that it may be seen in an optical microscope. This measurement was checked by examining the cross-section in the scanning electron microscope. Specimens were also produced with a layer of PMMA spin coated on to the anodized aluminium.

3.3. Acoustic microscopy

Measurements were taken using three different acoustic lenses, with central frequencies of 225, 820 and 980 MHz. The 225 MHz lens had a cylindrical cavity, while the other two lenses were of the point focus variety. When using the higher frequency lenses it was necessary to heat the water used as couplant to about 50 °C, in order to reduce the attenuation. Twenty five measurements were made at each frequency over a small area of the specimen, and this enabled an assessment of the accuracy at each frequency, as well as giving an indication of the scatter due to the inhomogeneity of the samples.

4. Results

4.1. General results

It had initially been thought that the highly inhomogeneous nature of the oxide might preclude acoustic measurements, but it was found that good quality $V(z)$ s were easily obtainable between 225 and 980 MHz. A second potential source of difficulty, namely the attenuative nature of the PMMA coating, was not significant for the thicknesses of coating employed. Fig. 2a–f show $V(z)$ curves obtained with the 225 MHz lens for polished aluminium, anodized aluminium, polished aluminium coated with a 0.2 μm layer of PMMA, polished aluminium coated with a 1.0 μm layer of PMMA, anodized aluminium coated with a 0.2 μm thick layer of PMMA and anodized aluminium coated with a 1.0 μm thick layer of PMMA respectively. Fig. 3 shows the corresponding results obtained with the 980 MHz lens. The signal–noise ratio is much poorer on the $V(z)$ curves at 980 MHz, but satisfactory analyses could still be carried out.

There are two main qualitative differences in the raw data between the various specimens. The first is a difference in the periodicity of the oscillations near focus: the oscillations are associated with various types of acoustic wave propagating along the surface, and a change in the periodicity represents a change in the velocity of the wave. This effect is small for most of the specimens, and not easily detectable by eye. The

second difference is much more striking, and may be seen by comparing $V(z)$ s on aluminium coated with 0.2 and 1 μm layers of PMMA (Fig. 2c and d). A second mode with a larger periodicity begins to dominate the $V(z)$, particularly at higher negative defocus. This mode is called a pseudo-Sezawa wave, and is characteristic of certain coating–substrate combinations [21]. The pseudo-Sezawa wave is highly dispersive, and QAM is therefore extremely sensitive to changes in the thickness or elastic constants of the layer when this mode is strongly excited. The dispersive nature of the pseudo-Sezawa mode has previously been employed in ultrasonic spectroscopy to measure the thickness of coatings [22].

Fig. 4 shows the velocities of the mode closest to focus, i.e. the Rayleigh-type mode, obtained as a function of position within a small area for a selection of the specimens. One reason for the scatter in velocity is the polycrystalline nature of the substrate. At 225 MHz, the insonified area averages over approximately ten grains at average values of defocus. When the frequency is increased to 980 MHz, the insonified area is comparable to that of a single grain. This indicates the sensitivity of the technique, because the error at each individual point is usually much smaller than the overall scatter. Aluminium is only weakly anisotropic, and any effects due to texture are not noticeable for this orientation of 8090. Summaries of the Rayleigh-type mode velocities measured at each frequency are presented in Table I. The scatter in velocity is quite high for some of the materials, and this can result from surface roughness, weak excitation of the SAW, or non-uniformities in the layer thickness. These effects are discussed in more detail in the next section. Provided that measurements at the higher frequencies were averaged over grains with different orientations, it might be expected that the Rayleigh wave velocity on the polished aluminium should not vary over the relatively narrow frequency range used in these experiments. The differences in velocity between the measurements at 225, 820 and 980 MHz exceed the estimated error bands due to random effects. Although it is possible that a thin surface layer with different mechanical properties could arise as a result of the production process, it is much more likely that the variations are due to a small systematic difference between the measurements made with the three lenses.

4.2. Errors in QAM

The best figures quoted for line-focus beam acoustic microscopy at 225 MHz are a relative error of 0.01% and an absolute accuracy of 0.05% in the velocity [23]. Such figures apply only to ideal single-crystal materials, and the errors are considerably higher for the inhomogeneous materials studied here. One cause of increased error is surface roughness. An extreme example of this may be seen by comparing $V(z)$ s taken on polished and surface-ground alumina wafers in Fig. 5. Li [24] has calculated the effect of periodic surface roughness on Rayleigh wave velocities as would be measured at 225 MHz in the LFB acoustic microscope. He found that the change in velocity from

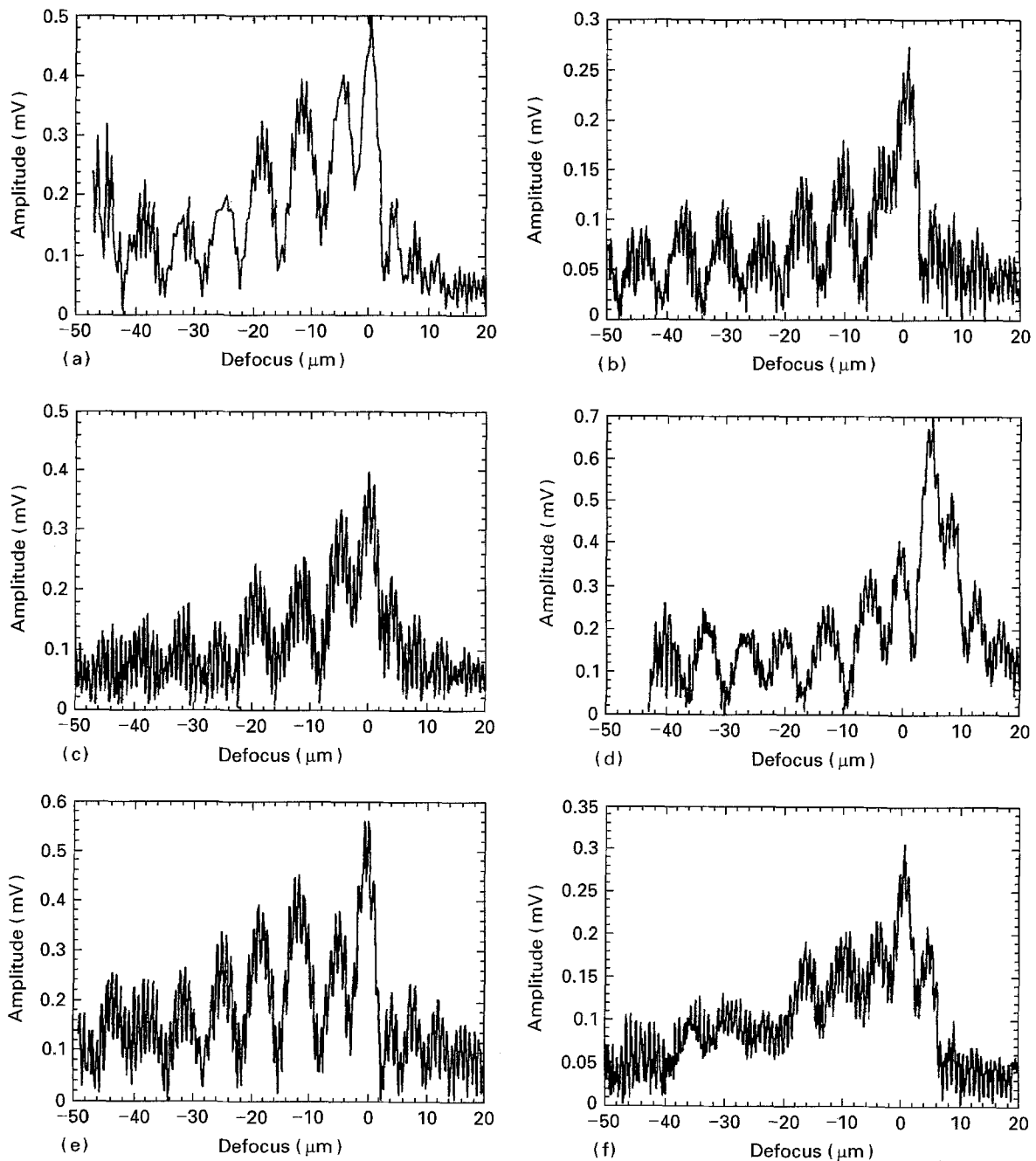


Figure 3 $V(z)$ s at 980 MHz on polished, anodized and coated aluminium specimens. (a-f) as in Fig. 2.

that for a smooth surface varied from 0.2% for a height/period ratio of 0.1 with 1 μm period, to 3% for a height/period ratio of 0.3 with 3 μm period. It seems unlikely, however, that any useful quantitative information could be obtained from a $V(z)$ such as that shown in Fig. 5b, which was obtained for a ground alumina wafer where the surface has random roughness.

A second cause for increased errors is inhomogeneity, because this increases scatter in the near-surface region. In mild cases, the predominant effect is to increase the attenuation of the SAW. This effect can be seen by comparing $V(z)$ s on two different polished aluminium alloys (Grades 8090 and L165) in Fig. 6. The L165 alloy is more porous than the 8090 alloy. Porosity causes scattering of the acoustic wave, and therefore a higher degree of attenuation. If the attenuation is sufficient to reduce the number of oscillations

to two or three, then the errors in the estimation of the velocity can become as high as a few per cent. A similar effect can arise when more than one mode is present in the $V(z)$. An example is shown in Fig. 2f, where the Rayleigh-type mode, i.e. the mode closest to focus, is not the predominant mode at 225 MHz. Only two or three oscillations associated with this weakly excited mode are present in the $V(z)$, and this can lead to large systematic errors in the analysis as mentioned. Although it is possible to correct for the peak position in the Fourier transform of a highly attenuated sinusoid [8], this is again only really effective on reasonably homogeneous materials.

The difficulties with inhomogeneity and roughness tend to increase as the frequency is increased, and there are two reasons for this. Firstly, the wavelength is decreased, and secondly, a smaller area is insonified by the acoustic lens, because the focal length of the

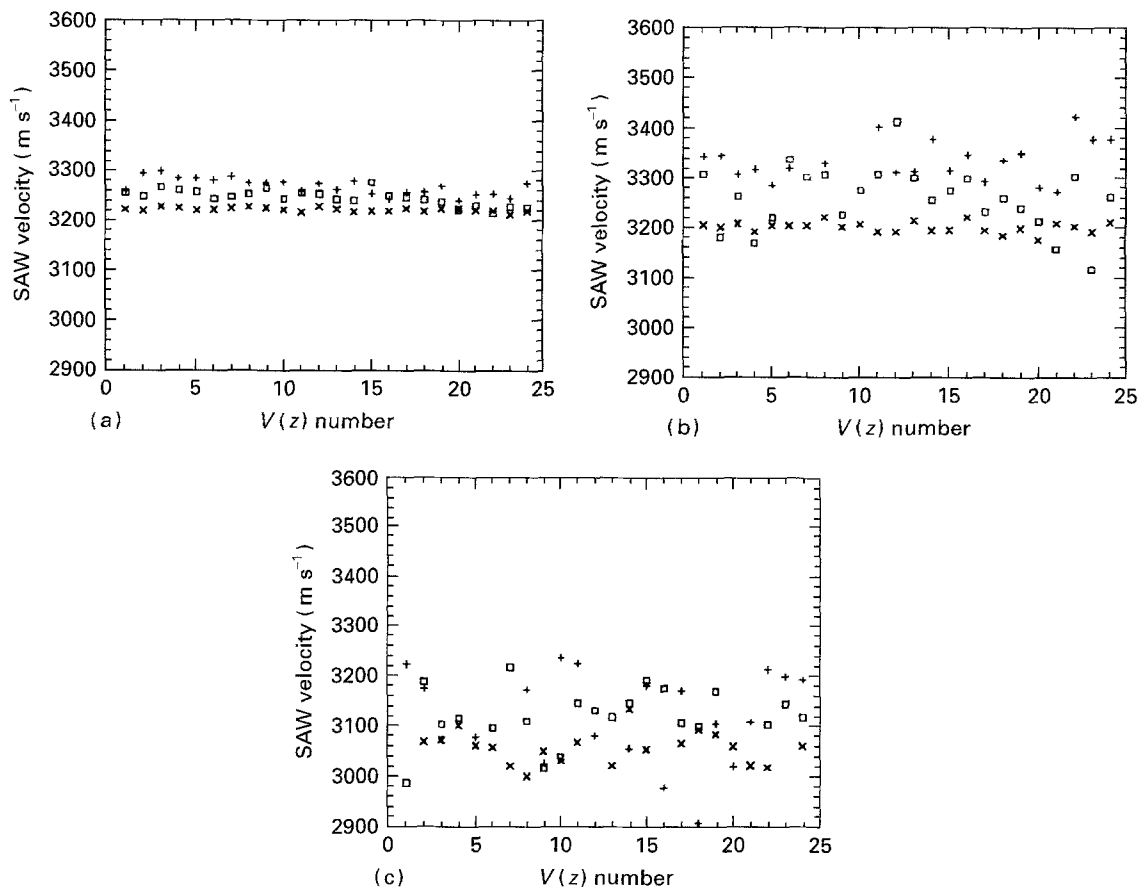


Figure 4 Measured SAW velocities at 25 positions in (a) a 4 mm² area of plain, polished aluminium 8090, (b) a 1 mm² area of anodized aluminium 8090, (c) a 1 mm² area of anodized aluminium 8090 coated with 1 µm PMMA. (×) 225 MHz, (□) 820 MHz, (+) 980 MHz.

TABLE I Summary of measured SAW velocities. The quoted errors refer to the scatter across the material, and do not include systematic errors in the analysis

Specimen	SAW velocity		
	225 MHz	820 MHz	980 MHz
Polished aluminium (8090)	3225 ± 5	3250 ± 15	3275 ± 20
Polished aluminium + 0.2 µm PMMA	3215 ± 5	3120 ± 55	3285 ± 30
Polished aluminium + 1.0 µm PMMA	3140 ± 25	–	3180 ± 90
Anodized aluminium (PAA)	3205 ± 10	3270 ± 100	3320 ± 40
Anodized aluminium + 0.2 µm PMMA	3175 ± 10	3165 ± 75	3205 ± 100
Anodized aluminium + 1.0 µm PMMA	3060 ± 25	3200 ± 200	3100 ± 150

lens must be reduced owing to higher attenuation in the water at high frequencies. The shorter focal length means that less negative defocus is available. This, in turn, can result in fewer oscillations being available, which decreases the accuracy of the analysis. Particularly at high frequencies, the combination of two modes, roughness and inhomogeneity can make the $V(z)$ extremely difficult to interpret. An attempt was made to quantify the errors for the Rayleigh mode on a polished aluminium substrate, and the results are given in Table II.

The relative error in Table II refers to a series of 25 $V(z)$ s taken at the same point on the specimen. At high

frequencies, the values are considerably greater than at 225 MHz because the measurements themselves are considerably noisier, and a smaller range of negative defocus is available. The absolute accuracy refers to uncertainty in the analysis for a single $V(z)$, and has been estimated by conducting the analysis using windows of different shapes [25], and over different regions of the $V(z)$. Temperature effects and differences between the lenses, which might result in an offset in the velocity are not included in these figures. The accuracy is lower at 820 MHz than at 980 MHz because the range of negative defocus is the same for both lenses, and hence fewer oscillations are available for analysis at 820 MHz. The scatter has been estimated by taking 25 $V(z)$ s in an area of between 1 and 4 mm², and is higher at high frequencies because averaging is only over one or two grains for any single measurement, and reflections from grain boundaries are more significant. All the figures in Table II are approximately two to three times higher than on a more uniform material such as glass.

4.3. Modelling SAW measurements

On an infinite isotropic substrate, the Rayleigh wave is composed of shear vertical and longitudinal components, and has a fixed velocity. The presence of a layer on the substrate introduces a characteristic dimension into the problem, and so SAWs become dispersive, i.e. their velocity varies with the thickness of the layer or the frequency. Various different modes can be excited,

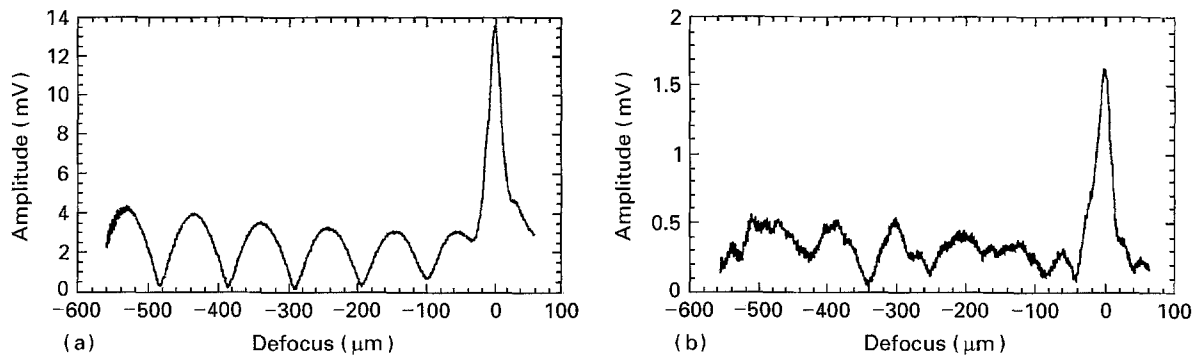


Figure 5 $V(z)$ s on (a) polished and (b) surface-ground alumina.

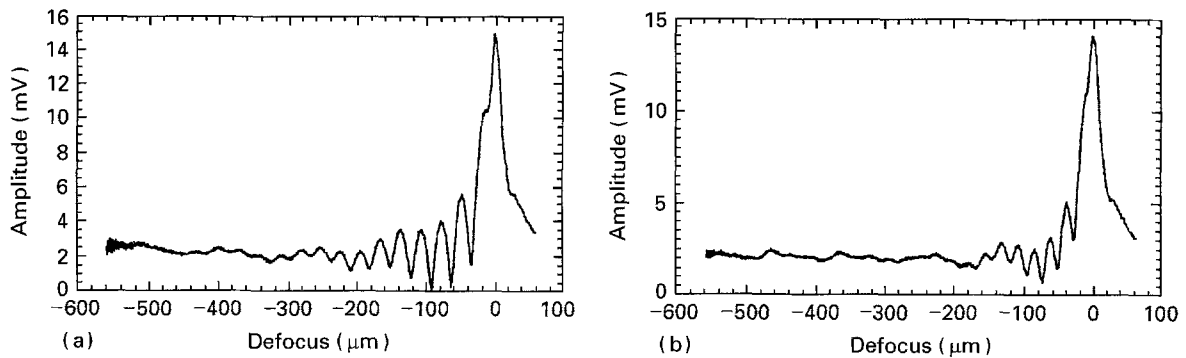


Figure 6 $V(z)$ s on two different aluminium alloys: (a) 8090, (b) L165 at 225 MHz.

TABLE II Estimated standard deviations in velocity for $V(z)$ analysis on polished aluminium

	225 MHz	820 MHz	980 MHz
Relative error at a single point (m s^{-1})	2.0 (0.06%)	10 (0.3%)	8 (0.25%)
Absolute accuracy (m s^{-1})	10 (0.3%)	40 (1.2%)	30 (0.9%)
Scatter along specimen (m s^{-1})	3.5 (0.1%)	15 (0.5%)	18 (0.6%)

and their polarization also varies with the thickness or frequency. Because the acoustic microscope uses a liquid couplant, shear horizontal behaviour cannot be excited in the material, and the microscope excites shear vertical displacements most strongly. The velocity of SAWs in a coated substrate was modelled using a code based on that of Farnell and Adler [26], adapted to allow for modes that can leak energy into the fluid (leaky modes), and/or into the substrate (pseudo modes).

4.4. PMMA on polished aluminium

The aluminium substrate and PMMA coating were modelled as isotropic materials using the values for the elastic constants and density shown in Table III. The calculated SAW dispersion is shown by the solid and dashed lines in Fig. 7, whilst the measured velocities are marked by crosses and squares for frequencies of 225 and 980 MHz, respectively.

The pseudo-Sezawa mode in Fig. 7 begins with a predominantly longitudinal polarization, and is

TABLE III Materials properties used for surface acoustic wave velocity calculations

	c_{11} (GPa)	c_{44} (GPa)	Density (kg m^{-3})
Aluminium (Grade 8090)	139	32	2695
PMMA	8.6	2.1	1185

excited fairly weakly. However, the shear vertical component increases quickly with increasing frequency or thickness, so it becomes strongly excited in the acoustic microscope. The measurements agree well with the calculated dispersion curve.

4.5. Anodized aluminium

Fig. 8 shows calculated SAW dispersion curves for an oxide layer on aluminium, where the predictions for different levels of oxide porosity were made using the model described by Wang and Rokhlin [27] and also used by Cawley and Pialucha [4]. Fig. 8b shows the Rayleigh-type mode, and Fig. 8a shows the next highest mode in the cases where it can be excited. At 30% porosity, the layer is “faster” than the substrate, under which condition there is only a single Rayleigh-type mode, and this begins to attenuate once beyond the substrate shear velocity. The dispersion curve at 60% porosity is markedly different in character because, unlike the case of 30% porosity, a pseudo-Sezawa mode can be excited (see Fig. 8a). At 80% porosity, the oxide layer is much “slower” than the substrate, and the dispersion curves in Fig. 8a and b are typical of

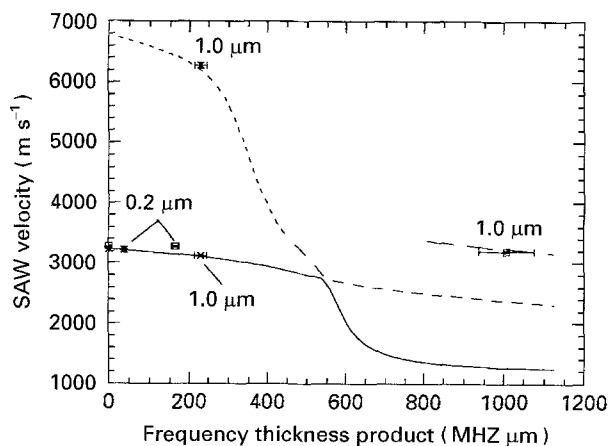


Figure 7 SAW dispersion for PMMA coatings on 8090. (—) First Rayleigh mode, (---) pseudo-Sezawa mode, (-.-) Sezawa mode, (—) third Rayleigh mode, at (x) 225 MHz and (□) 1 GHz.

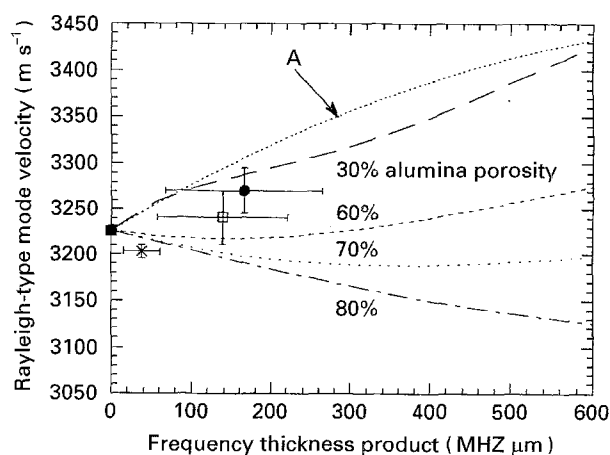
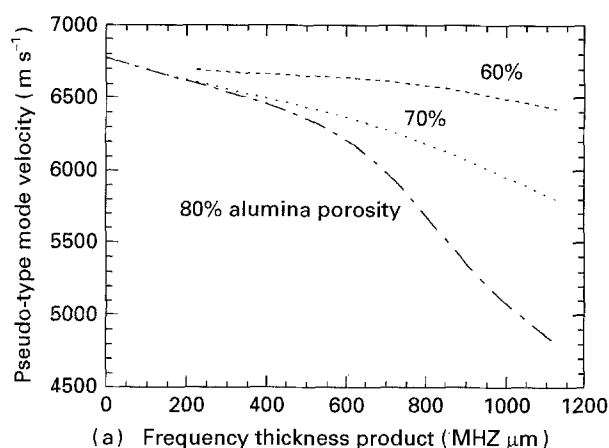
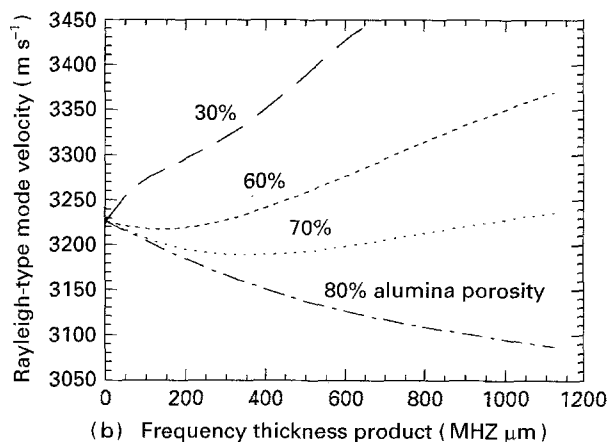


Figure 9 Measured SAW dispersion for 0.2 μm oxide layer on 8090. The curve labelled A was obtained using the properties which were found to fit best to the properties of a 43 μm thick sulphuric acid anodized (SAA) oxide layer [5]. (x) 225 MHz, (●) 980 MHz, (□) 820 MHz.



(a) Frequency thickness product (MHz μm)



(b) Frequency thickness product (MHz μm)

Figure 8 Calculated SAW dispersion for oxide layers of various porosity on 8090. (a) Pseudo-Sezawa mode, (b) Rayleigh-type mode.

this situation. The Rayleigh-type mode velocity decreases monotonically with increasing frequency, whilst the pseudo-Sezawa mode shows strong dispersion over the range of frequency plotted.

Measurements made on a 0.2 μm PAA oxide layer on 8090 are plotted in Fig. 9 as crosses, squares and circles for frequencies of 225, 820 and 980 MHz, respectively. The curves for porosities between 30% and 80% were calculated using the model of Wang and

Rokhlin [27], and are the same as those shown in Fig. 8b. The curve labelled A was obtained using the properties which were found to fit best to the properties of a 43 μm thick sulphuric acid anodized (SAA) oxide layer [5]. As mentioned earlier, it is assumed that the variations in velocity on the plain, polished sample obtained at the different frequencies are due to systematic differences between the measurements made with the three lenses. As a result, the measured velocities at 820 and 980 MHz have been reduced by 25 and 50 m s^{-1} , respectively, on all specimens, in order to make the results with the three lenses the same on the plain, polished sample (the zero frequency–thickness points). The large error bars in the frequency–thickness direction for the measurements on the anodized sample are due to uncertainties in the thickness of the oxide layer which varied from its average 0.2 μm in the region of grain boundaries.

It can be seen that the measured velocities are not consistent with any of the calculated curves. However, the predictions as a function of porosity were made using cell-wall properties corresponding to pure, fully compacted alumina, whereas the cell-wall material formed during anodization is more likely to be a relatively open array of amorphous alumina microcrystallites, permeated by molecular water and with the surfaces of the crystallites carrying hydroxyl ions or groups [28]. The material is also likely to contain as much as 12%–15% by weight of acid anions. Some discrepancy with the predictions would also be expected because the model assumes that the oxide cell structure is uniform with all the cells oriented normal to the interface. However, this is unlikely to be the case [28]. Therefore, it is not surprising that the acoustic measurements do not give good agreement with the calculations. The measurements also do not correspond to the predictions using the properties measured on an SAA oxide layer. However, the SAA layer on which the earlier results were obtained was 43 μm thick compared with the 0.2 μm thick layer tested here, and phosphoric, rather than sulphuric, acid

anodization was employed in the current tests. The morphology and composition of the oxide layers can vary significantly with the anodization conditions [29], so good agreement with the earlier work would not necessarily be expected. It is proposed to obtain high-resolution transmission electron micrographs of the oxide layer in order to obtain more information about its morphology, and also to test a variety of oxide layers formed under different conditions.

It should be noted that the actual oxide layers produced by standard pretreatments are somewhat thicker than that studied here, so that the distinction between different layer porosities will be increased. For example, the industry standard PAA treatment gives a 0.6 μm oxide layer. Looking at Figs 8a and b, a change in porosity of 10% in a 0.6 μm thick oxide layer ought to be readily detectable with measurements over the frequency range from 225–980 MHz. A standard chromic acid anodization treatment yields an oxide thickness of 3.5 μm , and in this case the degree of excitation of the pseudo-Sezawa mode at 225 MHz could provide a sensitive measure of the porosity.

5. Conclusion

Quantitative acoustic microscopy has been used to measure surface wave velocities on polished and anodized aluminium substrates, both with and without PMMA coatings spun on to the surface. Good quality $V(z)$ s were obtained at frequencies between 225 and 980 MHz, and demonstrated the sensitivity of the technique to the presence of a 0.2 μm oxide layer and a 1.0 μm PMMA coating. It was thought initially that the anodized surface might be too rough or the PMMA coating too attenuative for successful measurement at 980 MHz, but neither of these effects has proved problematic. The highly dispersive nature of the pseudo-Sezawa mode excited on some of the coatings means that QAM is extremely sensitive to small changes in the material parameters.

Good agreement has been obtained between the SAW dispersion measured on the PMMA-coated aluminium, and that calculated by a simple isotropic layer model. The work on the anodized aluminium has highlighted the need for improved measurements of oxide morphology. Early calculations have modelled the anodized aluminium as a transversely isotropic oxide layer on an aluminium substrate. At 0.2 μm , the oxide layer was too thin for the comparison between measurement and calculation to be conclusive, but the calculations suggest that a change in porosity of 10% in a 0.6 μm oxide layer, i.e. the thickness obtained with a standard PAA treatment, should be readily detectable.

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References

1. C. C. H. GUYOTT, P. CAWLEY and R. D. ADAMS, *J. Adhes.* **20** (1986) 129.
2. A. J. KINLOCH, "Durability of Structural Adhesives" (Applied Science, London, New York, 1983).
3. W. WANG and S. I. ROKHLIN, *J. Adhes. Sci. Technol.* **5** (1991) 647.
4. P. CAWLEY and T. P. PIALUCHA, in "Review of Progress in QNDE", Vol. 13, edited by D. O. Thompson and D. E. Chimenti (Plenum Press, New York, 1994) p. 1523.
5. *Idem*, submitted.
6. R. A. LEMONS and C. F. QUATE, *Appl. Phys. Lett.* **24** (1974) 163.
7. R. D. WEGLEIN, *IEEE Trans. SU* **27** (1980) 82.
8. J. KUSHIBIKI and N. CHUBACHI, *ibid.* **32** (1985) 189.
9. G. M. CREAN and A. WAINAL, *Electron. Lett.* **22** (1986) 53.
10. J. KUSHIBIKI, T. UEDA and N. CHUBACHI, in "Proceedings of 1987 Ultrasonics Symposium" (IEEE, New York, 1987) p. 817.
11. J. KUSHIBIKI, T. ISHIKAWA and N. CHUBACHI, *Appl. Phys. Lett.* **57** (1990) 1967.
12. J. O. KIM and J. D. ACHENBACH, *Thin Solid Films* **214** (1992) 25.
13. Z. YU and S. BOSECK, *Optik* **88** (1991) 73.
14. Z. SKLAR, P. MUTTI, N. C. STOODLEY and G. A. D. BRIGGS, in "Advances in Acoustic Microscopy", edited by G. A. D. Briggs (Plenum Press, New York, in press) Ch. 6.
15. R. C. BRAY, C. F. QUATE, J. CALHOUN and R. KOCH, *Thin Solid Films* **74** (1980) 295.
16. A. K. MAL and R. D. WEGLEIN, in "Review of Progress in QNDE", Vol. 7B, edited by D. O. Thompson and D. E. Chimenti (Plenum Press, New York, 1988) p. 903.
17. N. NAKASO, Y. TSUKAHARA, J. KUSHIBIKI and N. CHUBACHI, *Jpn J. Appl. Phys.* **28** (1989) 263.
18. G. A. D. BRIGGS, J. M. ROWE, A. M. SINTON and D. S. SPENCER, in "Proceedings of the 1988 Ultrasonics Symposium" (IEEE, New York, 1988) p. 743.
19. A. ATALAR and M. HOPPE, *Rev. Sci. Instrum.* **57** (1986) 2568.
20. D. WALIKAINEN, *J. Vac. Sci. Technol.* **A10** (1992) 290.
21. G. A. D. BRIGGS, "Acoustic Microscopy" (Oxford University Press, 1992).
22. Y. TSUKAHARA, N. NAKASO, J. KUSHIBIKI and N. CHUBACHI, *IEEE Trans. UFFC* **36** (1989) 326.
23. J. KUSHIBIKI, T. KOBAYASHI, H. ISHII and N. CHUBACHI, *Appl. Phys. Lett.* **61** (1992) 2164.
24. Z. L. LI, *IEEE Trans. SU* **40** (1993) 680.
25. A. H. NUTTAL, *IEEE Trans. ASSP* **29** (1981) 84.
26. G. W. FARNELL and E. L. ADLER, in "Physical Acoustics", Vol. 9, edited by W. P. Mason and R. N. Thurston (Academic Press, New York, 1972) Ch. 2.
27. W. WANG and S. I. ROKHLIN, *J. Acoust. Soc. Am.* **94** (1993) 2721.
28. G. E. THOMPSON, R. C. FURNEAUX and G. C. WOOD, *Trans. Inst. Metal Finish.* **55** (1977) 117.
29. G. E. THOMPSON and G. C. WOOD, in "Corrosion: aqueous processes and passive films", edited by J. C. Scully (Academic Press, London, 1983) p. 205.

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