A Study of the Films Produced by the Aluminum/Water Reaction Using Rutherford Backscattering Spectroscopy

Reed L. Shilts

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A STUDY OF THE FILMS PRODUCED
BY THE ALUMINUM/WATER REACTION USING
RUTHERFORD BACKSCATTERING SPECTROSCOPY

by

Reed L. Shilts

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Western Michigan University
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A STUDY OF THE FILMS PRODUCED
BY THE ALUMINUM/WATER REACTION USING
RUTHERFORD BACKSCATTERING SPECTROSCOPY

Reed L. Shilts, M.A.

Western Michigan University, 1981

This work compares the action of pure water to various aqueous electrolytes on aluminum surface film formation at about 100°C. The electrolytes were pure water with various inhibitor ions added. The ions were nitrate, tungstate, borate, molybdate, silicate, phosphate, a mixture of nitrate and molybdate, and a mixture of silicate and molybdate. The investigative technique was Rutherford backscattering spectroscopy (RBS) using 2 MeV alpha particles with an annular detector set at 180 degrees for maximum elemental resolution. RBS was chosen for this investigation because it offers in an easily interpretable manner a relatively fast and semi-quantitative method of analysis of surface films a few microns thick. Since RBS was new to the WMU HVEC tandem Van de Graaff accelerator laboratory, the implementation and use of all aspects of this tool are described.
ACKNOWLEDGEMENTS

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I would also like to thank my beautiful wife, Dawn, for her support in concluding this project.

Reed L. Shilts
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CHAPTER I

INTRODUCTION

The shift to lighter weight automobiles has resulted in a renewed interest in the use of aluminum heat exchangers. Due to the highly specific action of corrosion inhibitors, presently used inhibited coolants are not satisfactory for aluminum radiators. The main reaction taking place in aluminum-based heat exchangers is that between aluminum metal and water which forms an aluminum-hydroxide film at the interface. This aspect of the problem has been the focus of considerable research and is the subject of an extensive review by Alwitt (1976).

Since the form and degree of surface corrosion are determined by this nominally aluminum-hydroxide surface film, the characteristics of this film must be determined. Many of the standard techniques for studying surfaces (Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), low energy ion scattering spectrometry (ISS), etc.) are limited in their ability to depth profile the thick films characteristic of the aluminum and water reaction. To profile these films, the aforesaid techniques require concurrent sputter etching.
Sputter etching has the drawbacks that it often requires long data collection times and it results in limited depth resolution due to artifacts associated with the sputter process.

The technique used in this study, Rutherford backscattering spectroscopy (RBS), has the advantage of an elemental depth profile of the overall film in a relatively fast and nondestructive manner. Rutherford scattering is a two-body elastic scattering process which, for acceptable data collection times, requires a particle accelerator. The RBS technique is not new to the analysis of aluminum films, as in Brown (1973). Brown's work exemplifies the simplicity and flexibility of RBS for thick film analysis.

In this work, the incident ions were 2 MeV alpha particles supplied by the WMU HVEC tandem Van de Graaff accelerator. The backscattered alpha particles were energy analyzed using an annular surface barrier detector placed at 180°. The films analyzed were those which form on an 1199 aluminum substrate during immersion in boiling water, either pure or with various radiator coolant additives. The additives to the distilled-deionized water were the following ions, in concentrations typical of the commercially available coolants: nitrate, tungstate, borate, molybdate,
silicate, sulfate, phosphate, a mixture of nitrate and molybdate, and a mixture or silicate and molybdate. The films were analyzed only as to their physical thickness and chemical composition as a function of depth. No measurements were made on the effects of aggressive ions to the films, the effect of ambient pH on the film, etc.

The technique was tested using a sapphire crystal standard and anodized films of known thickness which were made at Ford Motor Company. The RBS results compared favorably to those from other techniques.

The composition, order of magnitude thickness, and growth rate for pure water grown films compared very favorably to previously published data. The relative amount of the inhibitive action is that expected when there are published data for comparison. The aim of this study is to demonstrate that RBS can be used to easily and non-destructively characterize films which would otherwise require complicated and time-consuming analyses. Such characterizations have not appeared previously in the literature.
Rutherford Scattering

Rutherford scattering is simple Coulombic, binary, elastic scattering of the projectile and target nuclei. Rutherford backscattering spectroscopy (RBS) uses Rutherford scattering at angles of nearly 180 degrees as an elemental spectroscopic technique. Rutherford scattering is well known and the pertinent equations can be found in any text on modern physics (e.g., Eisberg & Resnick, 1974). The following is a brief review of the salient features of RBS (Foti, 1977; Mayer, 1975).

Consider a helium ion scattered from a nucleus in the matrix of the target. A target nucleus of high mass would have a small recoil energy and the scattered ion would have almost all of its original kinetic energy. A target of low mass would recoil with a larger amount of energy and the scattered ion would have only a small kinetic energy. Thus, by measuring the energy of the scattered ion, RBS is used as a spectroscopic technique that is sensitive to the mass of the target nuclei.
For Brehmott scattering, the energy of the scattered ion is:

$$E = \alpha E_x$$

where \( \alpha \) = kinematic factor:

$$\alpha = \left( \frac{m \cos \theta + \sqrt{m^2 - m_s^2 \sin^2 \theta}}{m + m_s} \right)^2$$  \( \text{(3)} \)

\( E_x \) = incident energy in lab coordinates

\( \theta \) = scattering angle in lab coordinates

\( m \) = incident particle mass

\( m_s \) = target particle mass

The probability of scattering at a given angle is the scattering cross-section, which for BSS is given by:

$$\frac{d^2 \sigma}{d\Omega dE} = \frac{\alpha^4}{4 \pi^2} \left( \frac{E_x^2}{2m \sin^2 \theta} \right)^2 \frac{s \cos \theta + \left[ 1 - \frac{m_s}{m} \sin^2 \theta \right] \frac{\hbar \omega \eta}{E_x} \left[ 1 - \frac{m_s}{m} \sin^2 \theta \right]^{1/2}}$$  \( \text{(4)} \)

Where:

\( S_1 \) = S of the projectile

\( S_2 \) = S of the target

\( \hbar \) = Planck constant

\( \eta \) = charge of an electron

Scattering angles near 180° (i.e., backscattering) were used because it may be shown that at 180° the energy resolution \( \Delta \phi / \phi \) is maximum. Also, it is observed from equation 3 that the scattering cross-section is dependent
upon \(1/E^a\) where \(E\) is the energy of the projectile immediately before scattering. It is important to realize this is the energy immediately before scattering because as the incident ion traverses the target, small amounts of energy will be lost in collisions with the electrons of the target material. These energy losses are so small and numerous that the loss appears for all intents and purposes to be continuous. This energy loss is termed stopping power or \(dE/dx\) loss. As a result of these losses, one can see a concentration versus depth profile for the top few microns of the material.

The procedure to find the elemental composition and thickness of a film is straightforward. Of the incident beam at energy \(E_0\), there will be scattering near the very top of the surface with essentially no energy losses. The energy of these scattered particles will be \(\propto E_0\). As the incident particles move through the film, as in Figure 1, they experience \(dE/dx\) loss, which will decrease the incident energy from \(E_0\) to \(E_1\), where \(E_1\) depends upon composition and depth. When the projectile, now at energy \(E_1\), is scattered, the energy of the scattered ion will be \(\propto E_1\). As the ion backscatters through the film, it again experiences energy loss until it leaves the film surface. The energy of a particle emerging from a depth \(X\) below the surface is thus given by an equation of the
Figure 1. Geometry of ion scattering within a film. The incident ion beam is normal to the film surface and the scattering angle approaches 180°.
form (Brown, 1973):

\[ E' = \alpha \left[ E_0 - \int_0^X \frac{dE}{dX} \, d\ell \right] - \int_X^0 \frac{dE}{dX} \, d\ell \]  

(3)

Where the first and second integrals are, respectively, the energy losses along the ingoing and outgoing trajectories. Since the ingoing trajectory is normal to the surface and the outgoing is virtually normal to the surface, using just the depth X for the distance travelled is an excellent approximation.

If the shape of the peak is roughly gaussian, the areal mass density (n) is given by:

\[ n = \frac{N_0}{I} \frac{M}{N_a} \left[ (\Delta \Omega) \frac{d\sigma}{d\Omega} \right]^{-1} \]  

(4)

where

- \( N_0 \) = incident number of particles
- \( I \) = area of peak
- \( \Delta \Omega \) = solid angle of detector
- \( N_a \) = Avogadro's number
- \( M \) = molecular mass

If the density, \( \rho \), of the film is known, the film thickness, \( T \), can be determined by the expression

\[ T = n / \rho \]
Three special cases can be examined to demonstrate the interplay of these effects: 1) A thin, uniform, self-supporting film of multi-elemental composition 2) A thick film of uniform multi-elemental composition and 3) A film of non-uniform composition, which incorporates some of the substrate material into the film.

Figure 2 is a typical energy spectrum for case (1). Note that the tops of each of the three peaks slope upward with decreasing energy. This reflects the energy dependence of the cross-section; that is, as the energy decreases, the cross-section increases. From this spectrum one can find:

1. The film thickness from $\Delta E_1$, $\Delta E_2$ or $\Delta E_3$; or, if the line shape is roughly gaussian, the film thickness from the line's area.

2. The masses of the target constituents from $E_1$, $E_2$, and $E_3$.

3. After normalization for cross-section differences, the relative concentration of the constituents of the target from the heights.
Figure 2. RBS spectrum produced by a homogenous, three-element thin film.
The relative concentration of element 1 to element 2, for example, can be found from the expression:

$$\frac{N_1}{N_2} = \left[ \frac{d\sigma}{d\Omega} \right]_1 \left[ \frac{d\sigma}{d\Omega} \right]_2^{-1} \frac{H_1}{H_2}$$

(5)

Where $H_{1,2} = \text{height of plateau}$

$$\frac{N_1}{N_2} = \text{atomic ratio of element 1 to element 2}$$

For case (2), a thick film of uniform density consisting of three component elements, the single element spectra in the top of Figure 3 show how the resultant spectrum can be generated from the addition of these three pure elemental spectra. When mass$_3 >$ mass$_2 >$ mass$_1$, the edges will be displaced by the kinematic factor $\alpha_3, \alpha_2, \text{and } \alpha_1$. Since these film components have essentially infinite thickness, the low energy edges are at zero energy. When the low energy edge of a film component is at essentially zero energy, this usually points to a component which is the substrate or a portion thereof. The bottom spectrum is the result of the addition of the top three individual spectra. Because each element's height is simply added to whatever amount is already at that energy and in this case, an edge is present for each element which is characteristic of that particular element. After correction for cross-sections, the edge heights will correspond to the concentrations. From this spectrum, one can obtain the same information as for a thin film by performing the reverse of the above.
Figure 3. A three-element thick film spectrum showing that the resultant spectrum is the addition of the individual spectra.
spectrum building i.e., spectrum stripping.

Figure 4 is the hypothetical spectrum for case (3), that of a substrate with a two-component film, in which one of the components is substrate material. This spectrum shows the non-uniformity, again with height dependent upon concentration and cross-section. Since the RBS cross-section is a smooth function of energy, the bump on the highest energy distribution i.e., that due to the heaviest element, points to an increase in concentration towards the middepth of the film, which is also reflected by the dip in the shelf of the substrate material, which is the substrate material in the film. Here the shelf in the light element spectrum has a definite width because the amount of substrate material in the film is less than the amount in the pure substrate. The energy width of this shelf can yield the thickness of the film, as can the width of the heavier element's spectrum.

Some data which demonstrate these effects are shown in Figure 5, which contains the spectra of both a pure aluminum substrate and that of a polished sapphire crystal (Al₂O₃) cut along a random plane. The sapphire is coated with a thin layer of copper to reduce sample charging effects. For the sapphire, the oxygen plateau is on top of the aluminum plateau, just like case (2).
Figure 4. Hypothetical RBS spectrum for a non-uniform thick film, the substrate being incorporated into the film with the heavier element.
Figure 5. Typical RBS spectra for a clean aluminum surface and sapphire (Al₂O₃) coated with copper.
The thin layer of copper is shown by the gaussian copper spectrum, a classic example of case (1) in the extreme. This is an extreme example because the film is extremely thin, thus there is no flat top to the copper spectrum, just a gaussian peak with its width dependent upon detector resolution. Also the area of the peak is simply dependent on the areal mass density of the thin copper layer.

It is important to consider the stopping power (dE/dx loss) phenomena in compounds. Stopping power values are well documented for the elements, but for compounds the values are not well known. An approximation to the stopping power for compounds is given by the Bragg Additivity Rule (Bourland, 1971). Bragg additivity is simply the addition of the individual stopping powers for the elements in the compound according to the fractional amount of the element in the compound, that is:

$$\frac{dE}{dx}(A_mB_n) = m \frac{dE}{dx}(A) + n \frac{dE}{dx}(B)$$

where $\frac{dE}{dx}(A)$ and $\frac{dE}{dx}(B)$ are the stopping powers for elements A and B respectively, and $\frac{dE}{dx}(A_mB_n)$ is the total stopping power in the compound with the stoichiometry $A_mB_n$. However, Bragg additivity is only an approximation. There still is no algorithm, theoretical
or empirical, which yields totally accurate results for the stopping powers of compounds. Also Bragg additivity does not consider the density of atoms, only the fraction of atoms in a compound. A further complication with dE/dx loss is that the loss is strongly dependent upon energy (Ziegler, 1977). This limits the ease of using RBS to find the depth or the thickness of films.

Aluminum Corrosion

Aluminum has many modes of corrosion. These modes vary from an amorphous, passive oxide layer formed upon exposure to air at room temperature and pressure to the extremely hard corundum formed only under conditions of high temperature and pressure (Alwitt, 1976). The corrosion processes which are discussed in this work are the reactions between aluminum of relatively high purity and various aqueous electrolytes near temperatures of 100°C. These reactions are of interest because aluminum components used in automotive engines and heat exchangers will be in contact with essentially aqueous electrolytes at elevated temperatures. These electrolytes contain numerous components which are designed not only to produce an anti-freeze, anti-boil condition, but also to inhibit the localized forms of corrosion on internal surfaces, (e.g. pitting).
The primary hydroxides of aluminum formed in these conditions are bayerite and pseudoboehmite. Bayerite $[\text{Al(OH)}_3]$ has a temperature of formation ranging from about $20^\circ$ to $90^\circ$C. The morphology of bayerite is that of well developed crystals of diverse shapes, e.g., cone, wedge, rod, and hourglass figures.

Pseudoboehmite (also called gelatinous boehmite) is the initial crystalline product formed over the temperature range $90^\circ$ to $130^\circ$C. Pseudoboehmite has a poorly crystallized, even fibrous structure. It is much more hydrated than boehmite, and can be transformed to boehmite at $240^\circ$C or to $\text{Al}_2\text{O}_3$ by slow heating to $600^\circ$C (Alwitt, 1976, pp.179).

When the growth of the pseudoboehmite begins, the hydroxide particles align into chains with a length of several hundred angstroms (Alwitt, 1976, pp.200). These chains then coalesce to form very thin sheets, or platelets. These platelets then coalesce, completely covering the surface after about one minute. The process continues, but the growth is largely at the base of the platelets, yielding a film that is coherent and dense after about three minutes. The rate of film growth is rapid in the first few minutes, followed by a continually slowing rate as the film thickens, see Results and Discussion.

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Two types of corrosion prevail in the aluminum and water reaction: an ubiquitous, self-regenerating, self-limiting, almost passive protective layer that the pseudoboehmite produces; and in the presence of aggressive ions (e.g. Cl\textsuperscript{−}), a pitting attack that can lead to catastrophic failure of the component (e.g. actual perforation). If the aluminum is protected with a non-regenerating film (i.e. Teflon, anodized layer, etc.), any flaw in the film would become susceptible to a localized pitting attack from the aggressive anions in the electrolyte. Once pitting begins, a crater is formed which has an environment with higher concentration of the aggressive anion than the electrolyte as a whole (concentration cell corrosion), thereby speeding the corrosion until perforation occurs. However, if the protective film could regenerate and limit the transport of the aggressive anions through the film, or alter the local solution make-up to make the pitting chemically unfavorable, the aluminum would be protected.

The protective film is essentially an intentional corrosion of the surface and concurrent precipitation of the corrosion products. This paper reports on a study of the effect which inhibitors and buffers, added to the electrolyte to inhibit corrosive attack, have on formation of the passive layer (nominally
pseudoboehmite). Effective corrosion protection optimizes the beneficial aspects of the protective layer and minimizes the likelihood of pitting attack.

The beneficial aspects here may be seen as providing a physical barrier to the onset of pitting attack through the growth of the surface film. On the other hand, once formed, the film may actually accentuate pit growth (as described) or even result in a poorly adherent coating which may be lost from the surface under conditions of extreme turbulence (e.g. cavitation attack).
Sample Preparation

The material utilized for this investigation was aluminum of 99.99% purity (type 1199) supplied by the ALCOA company. The procedure for preparing each sample was, in order, mechanical polishing, electro-chemical polishing, etching, and finally film formation in boiling distilled, deionized water containing the various buffers and inhibitors of interest.

The mechanical polishing of each sample was performed at the Ford Motor Company Scientific Research Labs in Dearborn, Michigan. This procedure consisted of first removing the mill finish and deburring with 600 grit silicon carbide paper. The initial polishing was done with a 1-micron aluminum-oxide (Linde C) and the final mechanical polishing was done with a .3-micron aluminum-oxide (Linde A) compound. The samples were rinsed in alcohol and water.

The samples were then electrochemically polished to a specular surface in a perchloric acid-alcohol bath as described in Appendix A, which was cooled to six degrees.
Celsius. A potential of 12 VDC was applied to do the actual polishing with a current density of about 0.07 A/cm². The polished samples were then cut into samples of 1.2 cm square with a small hole punched in a corner for support in the particular electrolyte bath.

Since the samples were prepared in large batches, the desired films were not grown until weeks later. Over this extended period, a passive oxide film formed from exposure to the air. This passive oxide film had to be removed before the desired film could be grown. This was accomplished by etching each sample in a 50 gram/liter sodium hydroxide solution at 50° to 60°C for a few minutes to remove this passive oxide film. Each sample was then rinsed in distilled water, then methanol, then distilled water again.

Finally, the desired films were created by immersing the prepared aluminum sample into boiling water, either pure or to which various compounds had been added. The boiling was performed in a specially prepared aluminum beaker. An aluminum beaker was used because previous work has shown that silicate may leach from glass vessels which would cause spurious results.
The aluminum beaker was prepared by cleaning it in a laboratory detergent with vigorous scrubbing or a chromic-phosphoric acid bath (2% chromic acid and 5% phosphoric acid) at 85°C for 5 to 10 minutes (Bernard, 1960). Distilled water was then boiled in the beaker for 30 minutes to build a protective layer. This was done to create a passive environment in the beaker and to prevent cross-contamination. Apparently, this was only partly successful for there was some cross-contamination, see Results and Discussion.

The additives were ions of nitrate, tungstate, borate, molybdate, silicate, sulfate, phosphate. Also tested was a mixture of nitrate and molybdate and a mixture of silicate and molybdate in concentrations typical of the commercially available coolants (Wiggle, Hospadaruk, and Styloglou, 1980). The inhibitors are reported as grams/liter of the specific ion under investigation. This method disregards the waters of hydration and cations, usually sodium, present. The pH was generally unadjusted. Appendix C contains the table of the stock chemicals used, concentrations, and representative pH values.
Data Acquisition

The samples were analyzed on the WMU HVEC tandem Van de Graaff accelerator using a 2 MeV helium beam in a 1+ charge state. It was initially desired to use the 2+ charge state, and hence a final energy of 3 MeV, in the analysis in order to obtain more beam current. However, initial spectra indicated that the RBS oxygen cross-section near 3 MeV was anomalous. This was due to the $3.04 \text{ MeV } ^6\text{O}(\alpha,\alpha)^6\text{O}$ resonance (Cameron, 1953). Because of this nuclear resonance, when alpha particles near 3.04 MeV scatter from oxygen, the cross-section is much greater than that predicted by Rutherford theory which takes into account only the Coulomb interaction. For this reason 2 MeV incident particles were used, since the use of 3 MeV particles would require additional calibration. It should be pointed out that this anomaly does suggest a way in which to detect trace amounts of oxygen. By using such a nuclear resonance, an otherwise small oxygen peak is easily resolved from the background, thereby improving the lower limit of detection. The current lower limit of detection for anodic films was about 150 Å.
Figure 6. Experimental geometry at full scale.
Another anomaly was the low energy rise below 470 keV. This effect is suspected to be caused by the oxygen stripping canal poisoning the alpha particle beam. The poisoning is because as the helium beam traverses the stripping canal, it also strips and accelerates some of the oxygen stripping gas. Since the terminal voltage was 1 MeV, it accelerated both the 2 MeV helium beam and a small 2 MeV oxygen beam in a 2+ charge state. Because the magnetic rigidity of 2 MeV helium in a 1+ charge state is the same as 2 MeV oxygen in a 2+ charge state, the analyzing magnet would not differentiate between the two, thereby yielding a small oxygen beam on the target.

The scattering chamber used was an Ortec 43.2 cm diameter chamber with the sample targets at the center, using the geometry in Figure 6. The detector was mounted with a tantalum disk on the back with a tantalum tube through the annulus. Because the targets appear to have infinite thickness to the ion beam, they will act as their own Faraday cup for purposes of determining total incident charge. The low energy secondary electrons being emitted from the target were returned to the target using a suppressor shield biased at a negative 300 VDC.

The detector was an annular surface barrier detector set at 180 degrees to obtain maximum elemental resolution. The detector geometry was typically defined
by a 1.9 cm diameter aperture located 7.0 cm from the target. For 2 MeV alpha particles, the system resolution is about 18 keV FWHM.

Data Analysis

The data analysis utilized five computer programs: RBSAN1, KINMAT, THICK, ELOSS1, and ELOSS2, which will be described below. KINMAT, ELOSS1 and the basic idea for RBSANL were by Dr. S. M. Ferguson. The programs were written in Fortran 4 and Fortran 10 on WMU's dual KL10 computer system.

Three basic parameters are utilized to describe the overall film characteristics from RBS spectra. For thick films, as in Figure 4, the thickness may be deduced from plateau width, where a composition could be calculated, and a density assumed from tabulated data. For thin films, or a thin film component producing a gaussian profile, the areal density may be deduced from calculated cross-sections, yielding the thickness for an assumed density. The atomic compositions are calculated from the plateau heights.

KINMAT is a nuclear kinematics program. This program calculates the energies of helium scattered from various elements for a set of initial conditions.
RBSANL calls the spectra from disk and finds the heights and energies of all the edges, defined in Appendix B, and the areas of all the peaks from the appropriate fitting function. RBSANL also performs many other functions such as spectrum smoothing, spectra subtraction, calibration and generating graphical data.

If the line shape is gaussian, the area computed from RBSANL is put into THICK (listing in Appendix D) which calculates the film thickness of this component using equation 4 from chapter 2. If finding the film thickness from energy loss calculations is more appropriate, the programs ELOSS1 and ELOSS2 will be used.

ELOSS1 is used for elementary films, whereas ELOSS2 (listing is Appendix E) uses Bragg additivity for two element compounds. These programs are based on equation 3 from chapter 2. The calculation begins with a simple numerical integration of the energy loss of a projectile as it goes in through the film. Then the program computes the kinematic factor in a collision. Finally, there is a numerical integration for the energy loss of the projectile as it comes back out through the film.
The functional form of the stopping power \((S(E)\) or \(dE/dx\) loss) follows that proposed by Ziegler (1977), which is:

\[
\begin{aligned}
S(\text{Low}) &= A(1) E^{A(2)} \\
S(\text{High}) &= \frac{A(3)}{E} \ln \left[ 1 + \frac{A(4)}{E} + A(5)E \right] \\
S(\text{Total}) &= \frac{S(\text{Low}) \cdot S(\text{High})}{S(\text{Low}) + S(\text{High})}
\end{aligned}
\]  

(6)

where \(A(i)\) is dependent upon target element and incident ion. The units for stopping power are usually \(\text{eV/atom/cm}^2\), \(\text{keV/\mu m}\), or \(\text{eV/\mu g/cm}\).

Standard Sample Analysis

In this study, the RBS technique was tested against a series of anodic barrier films and a sapphire crystal supplied by Ford Motor Company.

The thickness measuring capability of RBS was tested using the anodic films. The accepted thicknesses of the anodic films were measured by microtoming and examination with a transmission electron microscope (TEM), a destructive and time consuming technique.
For the anodic films, using the energy width of the oxygen peak and assuming the film to be $\gamma$-\text{Al}_2\text{O}_3$ at a density of 2.8 g/cm$^3$, RBS yields a reliable thickness gauge for films thicker than 500 Å. Figure 7 is a comparison of the RBS measured thickness and the accepted TEM thickness. The line in Figure 7 represents an exact agreement between RBS and TEM. This figure shows that the RBS technique with Bragg additivity is a good measure of thickness for an aluminum-oxide film at this energy.

The atomic ratio as given by RBS was measured with a sapphire crystal. A typical RBS spectrum for sapphire is shown in Figure 5. The calculated atomic ratios (equation 5, chapter 2) were 36% aluminum atoms in the aluminum-oxygen compound. This compares favorably to the 40% that is expected for Al$_2$O$_3$. 

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Figure 7. Comparison of anodized film thickness as measured by a Transmission Electron Microscope (TEM) and as measured by RBS using a stoichiometry of $\text{Al}_2\text{O}_3$ and a density of 2.8 g/cm$^3$. The straight line corresponds to perfect agreement.
Typical RBS spectra for a series of water grown films are shown in Figure 8. The magnitude of the thickness follows that tabulated by Alwitt (1976). It is observed from Figure 9 that the pseudoboehmite film quickly thickens to about 3200 Å after only 10 minutes, then levels off to about 4300 Å after 30 minutes which agrees well with Baker & Balser (1976). Water films are also the thickest with the exception of molybdate, which is still unresolved. The calculated stoichiometry for pseudoboehmite is similar to that published, three oxygen atoms to each aluminum atom, or \( \text{Al(OOH)} + 3\text{H}_2\text{O} \), an entire mole of water to each mole of \( \text{Al(OOH)} \).

Figures 9 and 10 are a comparison of the film thicknesses formed by the various electrolyte modifiers to each other and to water. Below is a brief description of the modification of both thickness and composition to the film surface created by the action of each additive.

Nitrate (1.0 g/l of \( \text{NO}_3^- \)) shows a behavior similar to distilled water, with a maximum thickness of about 3100 Å.
Figure 8. Typical RBS spectra for films grown in boiling water for the times indicated.
Figure 9. Comparison of film growth for water to that of nitrate, tungstate, and borate inhibitors, assuming the principle product to be hydrated pseudoboehmite $\text{AlOOH} \cdot \text{H}_2\text{O}$ at a density of 2.4 g/cm$^3$. 

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Figure 10. Comparison of film growth for water to that of silicate, sulfate, and silicate/molybdate, assuming the principle product to be hydrated pseudoboehmite AlOOH·H₂O at a density of 2.4 g/cm³.
The silicate (1.0 g/l of SiO$_2$) spectra suggest the slowly growing, thin film. This is to be expected because silicate is an excellent film inhibitor (Wiggle, Hospadaruk, and Styloglou, 1980).

Borate (0.9 g/l of B$_4$O$_7$) has the unusual (but expected) behavior of actually decreasing in thickness over time. This so-called "borate effect" was detected earlier using other techniques (Alwitt, 1976, pp.211).

Sulfate (2.0 g/l of SO$_4$) films have an indefinite behavior, beginning at a constant 800 Å for the 5 and 10 minute films, then slowly increasing to at least 2200 Å after 40 minutes. This apparent constant thickness for the thinner films (800 Å) may be due to experimental error.

The tungstate (2.0 g/l of WO$_4$) spectra (Figure 11) show an unusual (and unconfirmed) behavior. For the 5 and 10 minute films, the tungstate appears to be a thinly adherent film on the surface, whereas the 20 and 40 minute films suggest that the tungstate is forming a compound with the aluminum surface and the pseudoboehmite.

The molybdate (4.5 g/l of MoO$_4$) films (spectra in Figure 12) show an interesting, although unconfirmed, effect. For the 5 to 30 minute films, the amount of
Figure 11. RBS spectra for films grown in a tungstate inhibited electrolyte for the indicated times.
Figure 12. RBS spectra for comparison of the films grown in straight molybdate and mixtures containing nitrate / molybdate and silicate / molybdate for the indicated times.

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molybdate on the surface stays constant and appears to be plated on the surface. However the 40 minute film shows a tail of molybdate into the aluminum substrate. Also the molybdate in the film is very thick, on the order of 200 \( \mu g/cm^2 \).

The phosphate (4.5 g/l of PO\(_4^3\)) caused very little detectable modification of the aluminum surface. The spectra show a small phosphorus peak and little or no oxygen confirming that phosphate is a good inhibitor. The data are difficult to interpret both because of the small amount of phosphorus uptake by the film and the presence of chlorine and potassium contaminates.

A silicate and molybdate mixture (1.0 g/l of SiO\(_2\) and 4.5 g/l of MoO\(_4^2\)) produced the most interesting synergistic effect (spectra in Figure 12). With the silicate, which strongly inhibits a film, and the molybdate, which forms an extremely thick layer, the film is on the order of 14 to 18 \( \mu g/cm^2 \) thick for 5 and 30 minute respectively, as compared to the 200 \( \mu g/cm^2 \) for molybdate. While the data are intriguing, possible cross contamination confuses the interpretation.

The film made in a nitrate and molybdate mixture (1.0 g/l of NO\(_3^-\) and 4.5 g/l of MoO\(_4^2\)) shows the molybdate being incorporated into a film with the oxygen and
aluminum, whereas the films formed in just a molybdate mixture showed little aluminum in the film itself.

The film growth for the 50% and 75% (by volume) ethylene glycol are compared in Figure 13. The films were as expected with ultimate thicknesses of about 3100 Å and 1800 Å, respectively. In calculating the thickness of the ethylene glycol films, a density of 2.4 g/cm³ and a stoichiometry of one aluminum to every three oxygens, as given by an atomic ratio computation, were assumed. These results are somewhat uncertain because there are small amounts of impurities in the solution.
Figure 13. Comparison of film growth for 50% and 75% ethylene glycol, with the principle product as hydrated pseudoboehmite AlOOH·H$_2$O at a density of 2.4 g/cm$^3$. 

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CHAPTER V

CONCLUSIONS

As expected, the pure water formed the thickest films, with silicate being the strongest film growth inhibitor. The silicate slowed the uptake of the molybdate, a strong film former. Both the molybdate and tungstate first adhered to the surface, then formed a compound with the aluminum and oxygen.

Overall, these results are very encouraging. We have demonstrated that RBS is an acceptable qualitative method of nondestructive surface analysis. This technique gives a spectrum, often easily interpretable, in a short amount of time. RBS is a reliable thickness gauge for anodic films greater than 500 Å and the atomic ratios determined were all in the expected range.

A problem encountered in this study was with cross-contamination in the sample preparation, leading to many tempting but disputable conclusions about these film modifiers. A remedy to this problem may lie in use of a more stable container; or "seasoning" the aluminum beaker with the desired electrolyte before immersing the sample. With cleaner sample preparation techniques, further application of RBS will help in the ultimate
understanding of the surface corrosion of aluminum in an aqueous electrolyte.
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Eisberg, R., & Resnick, R. Quantum physics of atoms, molecules, solids, nuclei, and particles. New York: John Wiley & Sons, 1974


Ziegler, J.F. Stopping powers and ranges in all elements. New York: Pergamon, 1977
APPENDIX A

Perchloric acid electrolyte operation *

1. 300 ml absolute ethanol, 29 ml distilled water, 229 ml 2-Butoxyethanol

2. Mix in this order and hold at zero degrees C in a clean glass beaker.

3. Add 65 ml of 70 percent perchloric acid slowly to the above solvent.

4. Polishing should be done with bath held at zero degrees C. Temperatures in excess of 35° C must be avoided.

5. Mixture is flammable; avoid all sparks or open flames.

6. Perchlorates have a moderate explosion hazard when shocked, exposed to heat, or by chemical reaction. They should not be associated with carbonaceous materials or finely divided metals.

* Courtesy of General Services, Safety operations section Ford Motor Company, June 1979
Perchloric acid use, handling, and storage

1. Rubber protective equipment should be used in handling the mixture and cleaned promptly after contamination with the acid.

2. Perchloric acid should be stored away from all flammable materials.

3. Perchloric acid solutions should not be used to polish alloys containing bismuth, as an explosive compound may be formed.

4. Perchloric acid solutions should not be used in contact with organic materials.

5. "Bakelite" or "Lucite" mounting materials and cellulose-base insulating lacquers and materials should not be used in perchloric acid solutions.

6. Cooling and stirring arrangements may be necessary to maintain the temperature of the solution below 35°C to avoid possible combustion or explosion.

7. Provisions should be made for adequate ventilation wherever perchloric acid mixtures are used.
Whenever one measures something in nature, the limits on resolution will affect the data taken. Since in the present study there is a non-zero system resolution of about 18 keV FWHM, the "true" spectra will be different from the spectra taken. The spectra taken are the "true" spectra convoluted with the 18 keV instrument function. Figure 14 shows how the "true" spectra and the convoluted spectra compare. The first spectrum is for a rectangular plateau, the following are for plateaus with differing features.

From analyzing these spectra, it is apparent that the leading or trailing edges of the "true" spectra fall at the half-height of the convoluted spectra. Also one sees that if there is a small kink in the "true" spectra, then the convolution process smears this into an edge with only a bit less slope.
Figure 14. Comparison of various "true" spectra and their convoluted products. The "true" spectra are the solid lines and the convolution product is dotted. The width of the feature of interest is reported in multiples of the standard deviation of the gaussian instrument function.
This appendix is a listing of the basic compounds analyzed for this work. All chemicals used were reagent grade.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Concentration</th>
<th>Chemical Form</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>B&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.9 g/l</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;·10H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>7.5</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>2.0</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;·10H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>6.0</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1.0</td>
<td>NaNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6.6</td>
</tr>
<tr>
<td>MoO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>4.5</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;MoO&lt;sub&gt;4&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>9.0</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1.0</td>
<td>40% Na&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>---</td>
</tr>
<tr>
<td>PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;</td>
<td>4.5</td>
<td>NaH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;·H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.6</td>
</tr>
<tr>
<td>WO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>2.0</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;WO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>NaOH to dissolve</td>
</tr>
</tbody>
</table>

8.2
APPENDIX D

This appendix gives the listing of a program which calculates the areal mass density of a film component that has a gaussian spectral profile. The areal mass density is given by equation 4 in chapter 2.

C THICK.FOR  RFRD THICKNESS PROGRAM
C REED SHILTS  JULY 1980
C WESTERN MICHIGAN UNIVERSITY
C KALAMAZOO, MI  49007
C (616) 383-1870
C
C CALCULATES THE THICKNESS OF A MATERIAL USING
C THE 212 EQS.
C INPUT: PROJECTILE/TARGET Z,AMU
C DETECTOR ANGLE,SOLID ANGLE
C N-INC AND N-SCATTERED
C ION ENERGY
C OUTPUT: E-SCATTERED
C AREAL DENSITY
REAL M1,M2,NCTD,NINC,NSQC,NA
NA= 6.022 E23
C
1 FORMAT(2G)
C *** GET THE PARAMETERS ***
TYPE 4
TYPE 5
4 FORMAT('  RFRD THICKNESS CALC')
5 FORMAT(' DATA UNCHANGED ON CR>/ NEG PROJ Z TO EXIT')
110 TYPE 6
6 FORMAT('  PROJ Z,AMU')
ACCEPT 1,T1,T2
IF (T1.LT.0)GOTO 999
IF(T1.GT.0)Z1=T1
IF(T2.GT.0)M1=T2
TYPE 7
7 FORMAT('  TRGT Z,AMU')
ACCEPT 1,T1,T2
IF(T1.GT.0)Z2=T1
IF(T2.GT.0)M2=T2
TYPE 8
8 FORMAT('  ANGLE IN DEGREES: ')$
ACCEPT 1,T1
IF(T1.GT.0) PH=T1
TYPE 20
20 FORMAT(' DETECTOR SOLID ANGLE IN SR: ', $)
ACCEPT 1, T1
IF(T1.GT.0) SA=T1
TYPE 10
10 FORMAT(' ION ENERGY IN MEV: ', $)
ACCEPT 1, T1
IF(T1.GT.0) E=T1
TYPE 25
25 FORMAT(' INCIDENT ELECTRONIC CHARGE STATE: ', $)
ACCEPT 1, T1
IF(T1.GT.0) CSZ=T1
TYPE 30
30 FORMAT(' COULOMBS OF INCIDENT CHARGE: ', $)
ACCEPT 1, T1
IF(T1.GT.0) TC=T1/1.602E-19
NINC= TC/CSZ
TYPE 40
40 FORMAT(' COUNTS IN PEAK BEING MEASURED: ', $)
ACCEPT 1, T1
IF(T1.GT.0) NCTD=T1

C *** NOW ACTUALLY DO SOME COMPUTING ***
C
CALL CBSCA(E,PH,Z1,Z2,M1,M2,EOBS,OBSIN)
C EOBS= SCATTERING ENERGY MEV
C OBSIN= X-SECTION IN MB/STR
C MULT BY 1E-27 TO GET CM2/STR
C
C NSQC = NUCLEI PER SQUARE CENTIMETER
C TP = AREAL DENSITY
C
OBSIN= OBSIN* 1E-27
NSQC= (NCTD/NINC)/(SA*OBSIN)
TP= NSQC*M2/NA
C CONVERT TO MICRO-GRAMS
TP= TP* 1E+6
WRITE(20,100) E,EOBS,PH
WRITE(20,150)M1,M2
WRITE(20,200)NINC,NCTD,TP
100 FORMAT(' E-INCIDENT='F6.3' MEV E-SCATTERED='F7.4
 1 ' MEV ANGLE= 'F6.2)
150 FORMAT(' PROJECTILE MASS='F7.3' TARGET MASS='F7.3)
200 FORMAT(' PARTICLES: INCIDENT='G' PEAK='G,
 3 ' AREAL DENSITY='G' MICRO GRAMS/CM2')
GOTO 110
999 TYPE 1000
1000 FORMAT(' LOOK FOR RESULTS IN FOR20.DAT')
CALL EXIT
END
C

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SUBROUTINE CBSCA(EI, PH, Z1, Z2, M1, M2, EOBS, OBSIN)
REAL M1, M2
A = ((M1 + M2) / M2)
PI = 3.14159
B = A * ((Z1 * Z2) / EI)
THETA = PI * PH / 180. + ASIN(M1 * SIN(PI * PH / 180.) / M2)
CMIN = (SIN(THETA * 0.5)) ** 4
CMIN = 1.296 * B * B / CMIN
CMANG = (THETA * 180.) / PI
ERAT = 1. - (2. * M1 * M2) * (1. - COS(THETA)) / (M1 + M2) ** 2
G = (M2 / M1) ** 2 - (SIN(PH * PI / 180.)) ** 2
G = M1 * M2 * SQRT(G)
R = ((M1 + M2) ** 2) * ERAT
OBSIN = (R * CMIN) / G
EOBS = ERAT * EI
RETURN
END
This appendix gives the listing of a program which calculates the thickness of a two element film utilizing Bragg additivity.

```fortran
C ELOSS2.FOR ENERGY LOSS FOR RBS
C AUTHOR: REED SHILTS JULY/AUGUST 1980
C WESTERN MICHIGAN UNIVERSITY
C KALAMAZOO, MICHIGAN 49007
C (616) 383-1870
C USES BRAGG ADDITIVITY RULE FOR A 2 ELEMENT COMPOUND
C CHAPT 2C IN ZIEGLIER NEW USES OF ION ACCELERATORS
C BRAGG RULE ONLY WORKS ON THE ATOMIC SCALE
C DE/DX UNITS = EV/1E15 ATOMS/CM2
C DX= E15 MOLECULES/CM2
C FAC= E15 MOLECULES/CM2 PER ANGSTROM
C T= THICKNESS IN ANGSTROMS
C REL1= RAT(1)= NUMBER OF ELEMENT PER MOLECULE
C REL2= RAT(2)= NUMBER OF ELEMENT PER MOLECULE
C
C FROM BASE OF ELOSS,F4 BY SMF AND REED
DIMENSION EP(1000),E1(0:100),TMASS(2),RAT(2)
COMMON ASL1,BSL1,ASL2,BSL2,ASH1,BSH1
COMMON ASH2,BSH2,ASH3,BSH3
C ADV NUMBER = AN
AN= 6.022E23
99 TYPE 3
3 FORMAT('RBS COMPOUND ENERGY LOSS PROGRAM')
TYPE 4
4 FORMAT('ENTER PARAMETERS SEPERATE BY COMMAS')
TYPE 6
6 FORMAT('ENTER DENSITY IN GRAMS/CUBIC CENTIMETER:')$)
READ(5,10)RHO
10 FORMAT(3G)
C MAX THICKNESS IN A
TYPE 13
13 FORMAT('ENTER MAX THICKNESS IN ANGSTROMS:')$
READ(5,10)TMAX
C PRO MASS
TYPE 20
20 FORMAT('ENTER PROJECTILE MASS:')$
READ(5,10)PMASS
C TRGT MASS
TYPE 25
25 FORMAT('ENTER TARGET MASS ELEMENT 1:')$
```

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READ(5,10) TMASS(1)
TYPE 27
27 FORMAT(' ENTER TARGET MASS ELEMENT 2: ')
READ(5,10) TMASS(2)
C SCATTERING ANGLE IN DEG
TYPE 30
30 FORMAT(' ENTER SCATTERING ANGLE: ')
READ(5,10) THETA
C INCIDENT ENERGY IN KEV
TYPE 35
35 FORMAT(' ENTER INCIDENT ENERGY IN KEV: ')
READ(5,10) E0
TYPE 40
40 FORMAT('RATIO OF ELEMENTS; ELEMENT 1, ELEMENT 2: ')
ACCEPT 10,REL1,REL2
RAT(1)= REL1
RAT(2)= REL2
FAC= RHO*AN/((REL1*TMASS(1))+(REL2*TMASS(2)))
FAC= FAC/ 1E23
C FAC= E15 MOLECULES/CM2 PER ANGSTROM
TYPE 50
50 FORMAT(' REFER TO STOPPING POWERS BY ZIEGLER, VOL.4')
C ELEMENT 1
TYPE 60
60 FORMAT('INPUT THE 2 NUMBERS FOR S-LOW ELEMENT 1')
READ(5,10) ASL1,ASL2
C ELEMENT 2
TYPE 70
70 FORMAT('INPUT THE 3 NUMBERS FOR S-HIGH ELEMENT 1')
READ(5,10) ASH1,ASH2,ASH3
C ELEMENT 2
TYPE 77
77 FORMAT('INPUT THE 2 NUMBERS FOR S-LOW ELEMENT 2')
ACCEPT 10,BSL1,BSL2
C ELEMENT 2
TYPE 79
79 FORMAT('INPUT THE 3 NUMBERS FOR S-HIGH ELEMENT 2')
ACCEPT 10,BSH1,BSH2,BSH3
C ***** MAINLINE ******
C
DO 900 MEL=1,2
C
TYPE 110
110 FORMAT(' ***** THINKING *****')
C
ES= E0
DX= TMAX* FAC/1000
C
C ** PATH IN **
DO 100 I=1,1000
EP(I)=ES-DEDX(ES,REL1,REL2)*DX/1000
100 ES=EP(I)
C KINEMATIC FACTOR
CS=COSD(THETA)
SN=SIND(THETA)
SQR=SQRT(TMSS(MEL)**2-PMASS**2*SN**2)
AK=((PMASS*CS+SQR)/(TMSS(MEL)+PMASS))**2
EI(0)=AK*EO
CS=COSD(180-THETA)
WRITE(20,250)
250 FORMAT('1')
WRITE(20,5)E0,THETA,RHO
5 FORMAT(' INC E =F7.0 KEV ANGLE=G DENSITY=G)
C
C ***** PATH OUT *****
DO 200 I=10,1000,10
II=I/10
EI(II)=EP(I)*AK
DO 190 J=1,I
190 EI(II)=EI(II)-DEDX(EI(II),REL1,REL2)*(DX/CS)/1000
200 CONTINUE
WRITE(20,80)PMASS,TMSS(MEL),RAT(MEL)
WRITE(20,1)
1 FORMAT(' El5 MOLECULES/CM2 ANGSTROM E IN KEV
DEL E IN KEV')
80 FORMAT('PROJECTILE MASS= ',F9.4,' TARGET MASS= 'F9.4,/  
   ' NUMBER/MOLECULE= ',F4.2)
   DO 220 I=0,100,2
   X=I*DX*10
   T=X/FAC
   DELE=EI(0)-EI(I)
220 WRITE(20,2)X,T,El(I),DELE
2 FORMAT(3X,F9.2,11X,F6.0,4X,F7.1,5X,F7.1)
C
900 CONTINUE
C
TYPE 85
85 FORMAT(' WANNA DO ANOTHER CALC??????')
READ (5,90)ANS
90 FORMAT(A3)
IF(ANS.EQ.'YES'.OR.ANS.EQ.'Y') GOTO 99
TYPE 300
300 FORMAT(' LOOK FOR RESULTS IN FOR20.DAT')
END
FUNCTION DEDX(E, REL1, REL2)
C E=ALPHA ENERGY IN KEV
C DEDX = STOPPING POWER IN EV/1E15AT/CM2
C HELIUM, STOPPING POWERS AND RANGES IN ALL ELEMENTS
C ZIEGLIER VOL 4
COMMON ASL1, BSL1, ASL2, BSL2, ASH1, BSH1
COMMON ASH2, BSH2, ASH3, BSH3
ASL = ASL1 * (E**ASL2)
BSL = BSL1 * (E**BSL2)
ASH = (ASH1/E) * ALOG(1. + ASH2/E + ASH3*E)
BSH = (BSH1/E) * ALOG(1. + BSH2/E + BSH3*E)
S1 = (ASL*ASH)/(ASL+ASH)
S2 = (BSL*BSH)/(BSL+BSH)
DEDX = ((REL1*S1) + (REL2*S2))
RETURN
END


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