AN INVESTIGATION OF SURFACE RE-FORMATION IN THE PRESENCE OF INERTIAL (TRANSIENT) CAVITATION (GR/N30989/01)

P. R. Birkin and T. G. Leighton

1. Background

There is an international need to understand the influence of inertial (transient) cavitation on the erosion of surfaces. Electrochemical data, relevant to this area, has been concentrated on the bulk effects observed for relatively large electrode surface areas (e.g. mm diameters compared to µm diameters as employed here). However, in many of these examples the exact acoustic conditions are not reported at the electrode surface. This is due in part to the diverse nature of sonochemistry, relying on aspects of chemistry, electrochemistry and acoustics. In general the understanding of the acoustic environment of a sonochemical cell is complex and relies on the characterisation of the transducer/cell/cavitation interaction that can be generated within the system as a whole. This fundamental problem often results in poor reproducibility between experiments and laboratories even though the same chemical environment and system is being employed (assuming no differences in the chemistry occur). During this project, the authors set out to systematically and quantitatively identify the sources of these problems and formulated an experimental approach to rectify them considering both the chemistry and acoustics involved.1,2

The project set out to investigate surface erosion caused by cavitation using an acoustoelectrochemical approach to this complex problem. In order to achieve these goals, a controlled and well characterised acoustic cell was employed with the ability to generate inertial and non-inertial cavitation. Within this cell a further series of experiments were undertaken to follow fast surface reformation on a number of different metal/solution interfaces. Two complementary techniques were used to obtain supporting data: High speed imaging; and the quantification and imaging of luminescence produced through so called ‘multibubble sonoluminescence’ [MBSL].

The project was successful in producing and characterising a sonochemical cell, which was then investigated using electrochemical, luminescent and high speed imaging technology with relevance to the study of surface processes. Further to this, a novel electrode (dual electrode) was developed that enabled the assessment of a complex cavitation environment to be investigated for both inertial and non-inertial events. The methodology used in this project relied on microelectrodes (typically 25 µm in diameter) to study surface erosion. This procedure has enabled high temporal and spatial resolution to be achieved. While some results have yet to be published, the authors (PRB & TGL) have produced a series of high quality publications outlining some of the major results of the project (including 5 peer reviewed published papers (or in the process of publishing), with more3-7 [-5] in preparation for high quality journals (e.g. Proc. Royal Soc.)). This success has led to 2 further grant awards to the sum of £110k (including an industrially sponsored grant) all of which rely on well-characterised experimental procedures. In addition to these achievements, while the EPSRC paid for only one PhD student, the grant has (at no extra cost to the EPSRC) provided the platform to support a further PhD student.

2. Key Advances and Supporting material

2.1. SUMMARY: KEY AIMS

There were several key aims of the project. (1) Investigate corrosion kinetics using the erosion of the surface of an electrode as the result of inertial cavitation. (2) Study the effect of cavitation on different oxide layers. (3) Perform a study of the effect of corrosion inhibitors on erosion corrosion transients generated by inertial cavitation events. (4) Perform a study of the effect of a variety of corrosion inhibitors on the re-oxidation transients produced by Ultrasonic erosion of the surface. (5) Investigate the effects of individual cavitation events on the surface of a material using conventional microscopy and scanning electron microscopy (SEM). (6) Investigate a novel mechanical fracture technique. These project aims were all satisfied in full and exceeded. Some key advances relating to these aims will now be summarised as well as highlighting the additional progress made during the project.

2.1.1 A Characterised Acoustic Environment

The need to understand the acoustic environment of sonochemical cells is paramount before any conclusions of sonochemical processes can be drawn (fundamental to all key aims).6 This was achieved by modelling the acoustic field generated by the ultrasonic horn. This involved three key elements6,8: (i) the understanding of the acoustic characteristics of the electrode materials involved; (ii) the modelling of the sound field with respect to the geometry of the cell; and (iii) a pioneering investigation of the invasive nature of the electrode within the sound field produced by both the direct ultrasonic drive signal and the acoustic signal produced by the cavitation process. Important considerations of the materials employed and their effects on bubble dynamics have been suggested.2,8 These papers proposed and verified the importance of the choice of
2.1.2 Acoustoelectrochemical erosion transients
The erosion of a surface using inertial cavitation generated by a 23 kHz sound field was investigated extensively. This study looked at the reformation of a salt covered electrode and electrode passivated with an oxide film after erosion of the interface through inertial cavitation. The kinetics of oxide film growth was investigated for a large number of different erosion/corrosion current time signals. In addition the erosion mechanism was probed using novel electrode arrangements and experimental procedures.

2.1.3 Novel Dual Microelectrode
A new method was developed to detect the presence of inertial and non-inertial cavitation within an environment subjected to cavitation (see key aims 1 & 5). This electrode had the ability to be employed in a complex cavitation environment while producing useful insights into the nature of the events occurring in the vicinity of the electrode surface(s). This idea was extended to investigate material effects relevant to the study of oxide film erosion (see key aims 1 – 4). The exact nature of the erosion process (erosion vs. dissolution) was verified using these novel electrodes. SEM and conventional microscopy images (see key aim 5) were used to characterise the electrodes before and after exposure to inertial cavitation.

2.1.4 Luminescent and Imaging
In order to fully understand the technique employed for the study of surface reformation, a key pre-requisite was the characterisation and understanding of the cavitation environment. This was partially achieved through the physical acoustic analysis of the cell employed (see 2.1.2 and Science and Technology section). However, extra information was obtained through a multi parameter approach to the problem. This included acoustic measurements, luminescent measurements, time correlated measurements, erosion measurements and high speed imaging (see www.soton.ac.uk/~prb2/home.htm and associated web pages) of the cavitation events generated. In many instances simultaneous measurements were recorded. This enabled a comprehensive understanding of the processes involved in the erosion of the surface layers. This is important for the successful deployment and reproducibility of the technique in further studies.

2.1.5 Erosion Transients and Inhibition
Many erosion/corrosion transients were recorded and analysed during this project (see key aim 1 & 2). These transients were captured at a high time resolution (20 MHz) and analysed with respect to the current kinetic theories. The investigation of the effect of inertial and non-inertial cavitation on an inhibitor (see key aim 3

\[ P_A(r,0) = 2 \rho_0 c U_0 \sin \left( \frac{1}{2} kr \left( \sqrt{1 + \left( \frac{a}{r} \right)^2} - 1 \right) \right) \]
was performed with knowledge of the likely effects of each type of cavitation on a particular process. Regions of both surface erosion and mass transfer enhancement were predicted and experimentally verified.\textsuperscript{11}

2.2 SCIENCE AND TECHNOLOGY

The acoustic characterisation of the acoustoelectrochemical cells, employed in many experiments performed on multibubble environments, was shown to be vital in the understanding of the sonochemical effects observed within the system. This concept was extended to the cavitation environment used in this project.\textsuperscript{2}

The acoustic model described the sound field developed by an operating ultrasonic horn (equation 1). Here $c$ represents the speed of sound, $a$ the ultrasonic horn radius, $r$ the axial distance from the surface of the horn, $k$ the wavenumber, $U_0$ the velocity amplitude of the horn and $\rho_0$ the density of the liquid. Under the conditions relevant to the system employed for surface erosion, figure 1 shows the measured pressure profile and fit to equation (1). Note it is difficult to accurately measure the pressure profile close to the tip of the ultrasonic horn as the finite size of the sensing element within the hydrophone will cause spatial averaging. As a result we employed acoustic measurements at extended distance [see figure 1 insert] and then extrapolated using the theoretical pressure amplitude profile [equation (1)] to the region of interest where inertial cavitation existed. This approach shows that the acoustic pressure amplitude produced by the horn falls as the distance is increased between the horn and the electrode. This finding was then correlated to the threshold for inertial cavitation (key to the surface erosion studies). Using a novel dual electrode\textsuperscript{9} the regions of the liquid which contained inertial cavitation were determined to a high degree of accuracy and reproducibility.\textsuperscript{2} The inertial threshold produced using this approach was compared to the theoretical value and that determined from luminescent studies.\textsuperscript{2} Figure 2 shows results from this investigation. These studies revealed that the electrode had a significant role in the type of cavitation event produced by this experimental arrangement. This is shown in figure 3 where the images produced through MBSL output of the system are compared in the presence and absence of the electrode. Figure 3 clearly shows that the electrode contributes significantly to the sound field. This scattering effect was investigated in relation to the erosion of surfaces by cavitation

![Fig 4. Plot showing the relative surface averaged pressure at the surface of a disk as a function of $ka$. Insert shows the pressure as a function of time recorded using a calibrated hydrophone in a water tank above the cavitation threshold.](image1)

![Fig 5. Plot showing the average number of erosion events detected in 0.4 s as a function of axial distance between the electrode and the tip of the ultrasonic horn for glass and epoxy-bodied lead electrodes.](image2)

![Fig 6. Plot showing the current recorded as a function of time for a stainless steel microelectrode (25 µm diameter) exposed to inertial cavitation. Data sampling rate 20 kHz.](image3)

![Fig 7. Plot showing a set of 16 transients recorded in 1 second using a stainless steel microelectrode (25 µm diameter) exposed to inertial cavitation. Insert shows one of the transients showing the data points to illustrate the temporal resolution employed.](image4)
produced by ultrasound. For the first time in electrochemical studies of cavitation the invasive nature of the electrode was considered and quantified with respect bubble dynamics and the acoustics (specifically scattering as a function of the electrode support materials and size). The average pressure amplitude over the surface \( P_T \) of the electrode may be represented by equation (2). Here \( P_i \) is the incident pressure, \( J_i \) is the Bessel function first order and \( K_i \) is the Struve function first order. Figure 4 shows the average pressure amplitude at the surface of the electrode as a function of \( ka \). This analysis indicated that scattering of the drive frequency (~23 kHz) was relatively inefficient (~8%) while scattering of high frequency components (e.g. shockwaves generated by cavity collapse, see figure 4 insert) approached 100%. This approach indicates that the invasive nature of the electrode is related to this high frequency component scattering effect. Shockwaves emitted by bubble (or cluster) collapse close to the horn are then efficiently scattered by the electrode body. The generation of shockwaves were attributed to bubble related phenomena by suppressing cavitation through the employment of castor oil and measuring the acoustic signal generated by the horn. As a result of this shockwave scattering effect, a high pressure region is developed at the surface of the electrode which will cause bubbles which are normally sub-inertial to become inertial. These inertial events are responsible for the extended luminescence and surface erosion detected using the experimental techniques employed. This effect was further investigated with relevance to the materials employed in the construction of the electrodes. It was shown that by varying the electrode substrate (e.g. epoxy vs. glass) a difference in the luminescence and the erosion threshold could be detected (see figure 5). This material effect of the electrode support was verified through accurately investigating the material properties (e.g. speed of sound and density). This investigation showed that the interpretation of studies concerned with surface erosion must consider this scattering/shockwave effect; a consideration lacking in the literature concerning cavitation erosion and the interpretation of sonoelectrochemical data.

Erosion/corrosion transients were recorded for a passivated steel electrode in the presence of inertial cavitation. This was achieved through the employment of high-speed acquisition apparatus programmed in-house. This experimental technique enabled a large number of erosion/corrosion transients to be obtained in a short (~1 s) period of time. Figure 6 shows a set of transients recorded in the presence of continuous ultrasound. Figure 7 shows a set of events recorded at 20 MHz time resolution. This data could then be analysed using standard corrosion kinetic theory. Figure 8 shows analysis of current time erosion/corrosion transients obtained using this inertial cavitation technique. The analysis of the data obtained using this technique indicates that kinetics of film formation under the conditions employed can follow either ion migration or place exchange models. Deep erosion of the passive film, as a result of inertial collapse, results in the kinetics following largely the place exchange mechanism while partial erosion of the upper layer of the film causes an ion migration mechanism to be initiated. Hence there will be a distribution of erosion/corrosion transients and a corresponding distribution of the two mechanisms. This is shown in figure 9 as a range of gradients (from log/log plots of erosion/corrosion events). Large current transients (where the inertial cavitation event punctured the oxide layer) tend to invoke the place exchange mechanism with a correspondingly high gradient of the log/log plot. However, inertial cavitation events which cause damage to the exterior of the passive film cause the ion migration mechanism to be initiated. It was found that there are a range of behaviours which we attribute to the bi-mechanism of oxide growth in tandem with varying erosion characteristics of the inertial cavitation process.

The effect of inhibitors on the corrosion of a steel sample was also investigated. This study benefited considerably from the in-depth and careful characterisation of the sound field employed, and processes occurring in different regions of the liquid, that had been performed. Figure 10 shows how the open circuit potential of a steel sample varied as the distance between the electrode and the sound source was reduced. In the absence of inertial cavitation \((r > 1.0 \text{ mm})\) mass transfer (associated with cathodic processes as an anodic dissolution inhibitor was employed) is accelerated by the exposure to ultrasound. This causes a positive shift in the corrosion potential. While in the presence of inertial cavitation \((r \leq 1.0 \text{ mm})\) the inhibitor is removed from the surface. This causes the potential to shift towards the corrosion potential in the absence of the inhibitor (~700 mV vs. SCE). This demarcation in behaviour is attributed to the erosive effect of inertial cavitation on the surface of the electrode. Lastly a study on a novel guillotine experiment has been performed enabling current time transients to be obtained for the exposure of a fresh electrode surface to the solution (see figure 11). However, SEM analysis of a number of the electrodes post fracture showed that the fracture process was not sufficiently clean to enable this technique to ‘calibrate’ the area of events recorded in the presence of inertial cavitation. In order to circumvent this problem a coulometric analysis was...
Fig 8. Plots of log($i$/A) vs. ($i$)\(^{-1/2}\) for different transients obtained from the inertial cavitation technique. Group A correspond to ‘large’ events and the place exchange mechanism while group B correspond to ‘small’ events and the ion migration model.

Fig 9. Plot showing the gradient of double log plot as a function of peak current. Different symbols denote separate sets of experiments.

Fig 10. Plot showing the corrosion potential as a function of time of a 75 µm radius carbon steel electrode in a solution containing an inhibitor. The solution was sonicated at various horn-to-electrode distances as shown in parenthesis (distances in mm).

Fig 11. Plot showing the current as a function of time for a guillotine experiment on a 25 µm diameter stainless steel microelectrode sealed in glass. The inserted image shows a SEM of a microelectrode post-fracture. The scale bar represents 20 µm.

performed using literature data related to film growth. This enabled the size of the erosion area to be estimated to be of the order of 30 µm\(^2\) per event in agreement with previous studies.\(^{10}\)

2.3 AUXILIARY FINDINGS
As well as the satisfaction of the main project aims, this grant (at no extra cost) helped supply a platform of new ideas and techniques to other PhD students (C. Vian and H. Hirsimaki). These auxiliary projects are investigating the characterisation of acoustic cavitation and laser induced cavitation respectively.

3. Personnel
The project provided funding to support a project student (Douglas Offin) and equipment money to develop the apparatus necessary to measure the erosion transients produced by inertial cavitation above a passivated surface. However, at no extra cost, the ideas developed in the project have been utilised by two other projects. These are the investigation of laser induced cavitation (PhD student H. Hirsimaki, EPSRC GR/S01764/01) and a project sponsored by NPL investigating the quantification of acoustic cavitation (PhD student C. Vian). The project has led to a number of publications either in the public domain, in press or in preparation. Also DGO, PRB and TGL have presented work associated with this project at a number of international meetings (see section 5).

4. Project Plan Review
The original project plan was followed closely throughout the project. However, the research has yielded results beyond the key aims originally suggested.

5. Research Impact
The research impact of this project has been substantial and diverse. A number of papers (5) in international journals have been published (or submitted) and a further 5 publications are in preparation. In addition the results of the study have been publicised within international conferences by a number of the workers. These include a seminar at University of Bangor (TGL), a seminar at University of Cambridge (TGL), a seminar at UCL (TGL), a Royal Society of Chemistry National presentation (PRB, Invited Speaker), an International Conference on Erosive and Abrasive Wear II (PRB, Invited Speaker) and a presentation at the 205th Electrochemical Society Meeting, San Antonio, Texas (DGO). Beneficiaries of the research extend from the general scientific community (where the need for accurate and characterised acoustics in the investigation of surface erosion from inertial cavitation has been highlighted) to the wider community. Again the virtues of acoustoelectrochemistry have been reported in a number of publications. In addition industrially sponsored research is investigating the use of erosion sensors for the characterisation of acoustic cavitation.

6. Further Research and Dissemination Activities

The student (DG0) is in the process of writing up his Ph.D. thesis (the first draft chapters are complete and corrections are being made). It is expected that the thesis will be submitted in April 2005. In addition to the 5 peer-reviewed and, the intention is to publish a minimum of 5 journal papers based on the work funded by this grant. The work has also been disseminated at a number of international meetings (see above). In addition further funding will be sort from both industrial and non-industrial sources while the research continues into other oxide systems (e.g. Aluminium).

7. References

3. T.G. Leighton In The modern acoustics and signal processing series, Bubble acoustics from seas to surgeries; Springer, USA, 2005.