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CAVITATION, SHOCKWAVES AND ELECTROCHEMISTRY – AN EXPERIMENTAL AND THEORETICAL APPROACH TO A COMPLEX ENVIRONMENT

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ABSTRACT
The investigation of bubble events generated and driven in an acoustic environment is reported. An electrochemical approach is combined with a number of other chemical and physical observations of the systems studied. In particular laser scattering through the bubble cloud, high-speed imaging and luminescent measurements of multibubble sonoluminescence (MBSL) within the environment below an operating ultrasonic transducer (specifically a piston like emitter operating at ~ 23 kHz) is discussed in detail. The investigation of this complex environment highlights the contribution to the system from cluster events, shockwaves, transient bubble clouds and the electrochemical sensors employed in their investigation. Implications for the chemical and physical properties of the unusual environments explored will be highlighted with the need for a combined approach to these systems emphasised. In addition, the inertial zone, created by the sound source employed, is used to study erosion/corrosion processes at a stainless steel microelectrode.

INTRODUCTION
The influence of acoustic energy, and in particular the generation of cavitation, on chemical and physical processes has been the topic of an intense multidisciplinary research effort. This is in part due to the highly unusual conditions which prevail inside a liquid which is essentially under ambient conditions yet posses unusually high (estimated in the 1000's K [1]) local and transient temperatures. Hence it is possible to drive unusual chemical and physical processes using acoustic energy concentrated by bubble action. However, even though this fascinating research area has yielded many startling phenomena (for example sonoliuminescence [2] and radical chemistry [3]), it remains a complex environment. This is due to the physical, acoustic and chemical properties of a media where cavitation is generated. This work highlights the need for a multi-sensor approach to the investigation of this media in order for accurate conclusions to be drawn. In addition we show that once an understanding of the cavitation environment has been gathered, the system can be used to study surface erosion/corrosion processes [4]. Indeed 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) [5]. However, this results in an averaged response, both spatially and temporally (since the characteristic response time of an electrode to an erosion/corrosion event has been shown to be dependant on the electrode surface area). Also, in many of these examples the exact acoustic conditions (which are paramount in determining the behaviour of cavitation bubbles) are not reported at the electrode surface. This is due in part to the diverse nature of Sonoelectrochemistry (or alternatively 'Acoustoelectrochemistry' [6]), 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). Clearly these complex systems need a complete approach to be adopted before the correct interpretation of the results obtained from these studies is obtained. This manuscript sets out to show that a

multi-sensor approach can be used to gather useful information on the nature of a cavitation environment which in turn is then used to investigate surface erosion caused by cavitation. In order to achieve this, a controlled and well characterised acoustic cell was employed with the ability to generate inertial and non-inertial cavitation [2, 7]. Within this cell a series of experiments were undertaken to follow the cavitation process and fast surface reformation on a passivated stainless steel surface. In order to understand the acoustic environment of sonochemical cells, modelling of the acoustic field generated by the ultrasonic horn employed has recently been reported. These studies showed that as well as the direct and reverberant sound field produced by the ultrasonic source and cell respectively, the acoustic signal produced by bubble collapse had a significant influence on the results observed from the electrochemical apparatus employed [7, 8]. In brief, shock waves produced by bubble collapse were considered, and shown to be effectively reflected from the solid/liquid interface of the electrode support. These reflected waves could have a significant influence on the fate of bubbles within the locality of the electrode. Bubbles that were previously non-inertial (stable) could be driven to inertial behaviour by these reflected pressure waves. Hence, the electrode can be considered to be invasive under these conditions. Using the experimental setup reported previously, the erosion of a surface as a result of inertial cavitation generated by a 23 kHz sound field was investigated extensively. These experiments have shown that there is a region within the liquid where inertial events can be detected through their erosive characteristics. This region is at an axial distance of < ~2 mm from the centre of the emitter face plate of the ultrasonic source employed [7, 8]. Clearly the ability to position an electrode within an environment where transient erosion can be expected will be extremely useful in the study of the kinetics of oxide film growth. The use of inertial cavitation to remove oxide films has some unique characteristics that make it a suitable erosive mechanism. First, cavitation erosion can be expected to operate in a μs time scale. This is sufficiently fast compared to the oxide film formation to be considered as spontaneous. In addition to this, only small quantities [4] of material are thought to be removed after each erosive event (e.g. ~100 μm^2 and the thickness of the passivating layer). This is one order of magnitude less than reported fracture techniques [9]. Hence the currents and ohmic losses will be significantly less. Also, it is expected that a large number of events can be recorded in a short space of time. These advantages, along with the considerable experience already gained in characterising the experimental and theoretical considerations of the ultrasonic apparatus, indicate that the study of oxide reformation kinetics within an inertial cavitation field would be extremely worthwhile.

EXPERIMENTAL

The acoustoelectrochemical and laser scattering setup employed in this work has been described elsewhere [7, 10]. Briefly, in the electrochemical experiments a 'face-on' arrangement was used. The position of the ultrasonic horn was fixed in the horizontal plane but was controlled in the vertical direction by a micrometer and stage. Ultrasound and cavitation were generated by means of a Grundig Digimess FG 100 function generator, Brüel & Kjær Type 2713 power amplifier and ultrasonic transducer fitted with a 3 mm diameter titanium tip (Adaptive Biosystems). Stainless steel (25 μm diameter, type 302 stainless steel wire, Goodfellow) were sealed in soda. A three electrode setup was used with a Pt gauze counter electrode and a saturated calomel reference. All solutions were made up using water from an USF Elga Purelab Option E10 water purification system. Potassium carbonate (Hogg Laboratory Supplies, 99%) and sodium sulphate (BDH, AnalaR) were used as received. All experiments were performed under aerobic conditions. Acoustic pressure measurements were made using a Brüel & Kjær type 8103 hydrophone and type 2635 charge amplifier.

RESULTS

The investigation of the environment below an operating ultrasonic horn (or piston like emitter) is aided by the employment of a high-speed camera system. This has the advantage of imaging the bubble activity, and if sufficiently fast frame rates are employed, the growth and collapse of these events in 'real time'. In turn this data can be compared to other physical parameters (for example pressure fluctuations, erosion of electrodes, light emission etc.) gained through the employment of other invasive or non invasive sensors and apparatus. Figure 1 shows a sequence of frames taken using a high-speed camera of the bubble activity below an operating ultrasonic horn. This sequence shows a large mass of bubbles which grow and collapse periodically in time. It should be noted that this sequence of events results in a periodic clearing of the solution in front of the ultrasonic horn (see Figure 1, frame (c)) followed

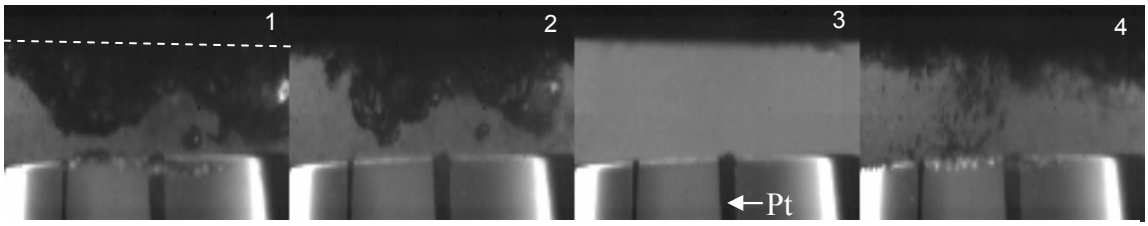

Figure 1. Images recorded in the space below an operating ultrasonic horn. Images recorded at 0, 30, 60 and 70 μs. Note scale from 125 μm Pt electrode. The dotted line in frame 1 indicates the surface of ultrasonic horn.

by a burst of small transient bubble events which can be seen in Figure 1 frame (d). In addition this process was observed to be periodic but at a lower frequency (at ~7.7 kHz [7]) compared to the ultrasonic driving frequency (in this case 23.1 kHz). While this high-speed imaging system is extremely useful, it is desirable to record the bubble population in this environment as a function of time at higher temporal resolution (note in the data shown in figure 1, a frame rate of 100000 frames per second still results in a 10 μs frame to frame time lapse). Hence a simple laser scattering [11] system was developed with the ability to record the presence of bubbles and bubble clouds within the region of interest (in the space directly below the sound source in this case). This system consisted of a laser diode shone through the liquid below the ultrasonic horn (at a defined distance from the piston face) and photo diode system placed directly in the path of the laser at the exit of the cell employed. In the absence of scattering by an object, the photodiode records its maximum (in this case the most negative voltage output) response. However, if an object, such as a bubble, is produced in the path of the laser, the resulting scattering of light causes the output from the photodiode to fall towards 0 V. There are several advantages to this system in comparison to high-speed imaging alone. First, the output of the photodiode can be recorded with μs resolution. Hence more detailed information on the sequence of events in the space below the operating ultrasonic horn can be gathered. Second, the path of the laser/photodiode detector can be adjusted to probe the bubble activity as a function of distance from the ultrasonic source. Figure 2 shows a set of data gathered from the laser scattering system. Note that figure 2 shows the scattering from the bubble events produced under the ultrasonic horn recorded as a function of time with the output of hydrophone placed within the liquid. Here 0 V represents almost complete scattering of the laser beam while approximately -1.1 V represents a clear solution. At approximately -45 μs, the solution has cleared (denoted by the most negative photodiode output, see figure 1 frame (3)). At this point the response from the photodiode spikes towards 0 V (labelled 'A'). This corresponds to strong transient scattering of light from events produced below the ultrasonic horn. This data ties in with the burst of events shown in frame (4) of figure 1. Figure 2 shows that these events are rapid in nature existing for between 5-10 μs. After this time the solution appears to become more opaque over a period of ~60 μs. The sequence of bubble cloud clearing and then transient bubble events is then repeated (data reported elsewhere [10, 12]). In addition to this laser scattering data, the hydrophone trace also shows a transient pressure spike at ~ 0 μs (labelled 'B', note the oscilloscope is triggered from the hydrophone trace).

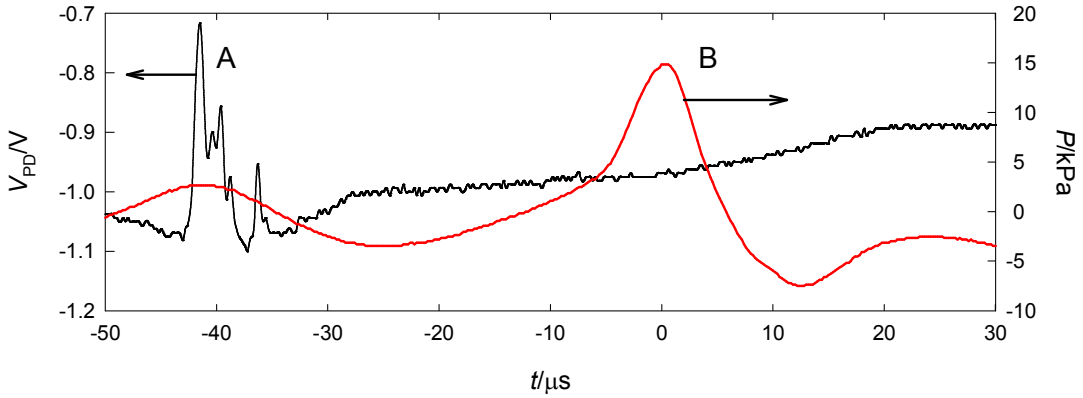

Figure 2. Plot showing the output from the photodiode (—) and hydrophone (—) as a function of time. Ultrasonic source 23.1 kHz, 56 ± 5 W cm^{-2}. Distance between tip and hydrophone was 52.2 mm.

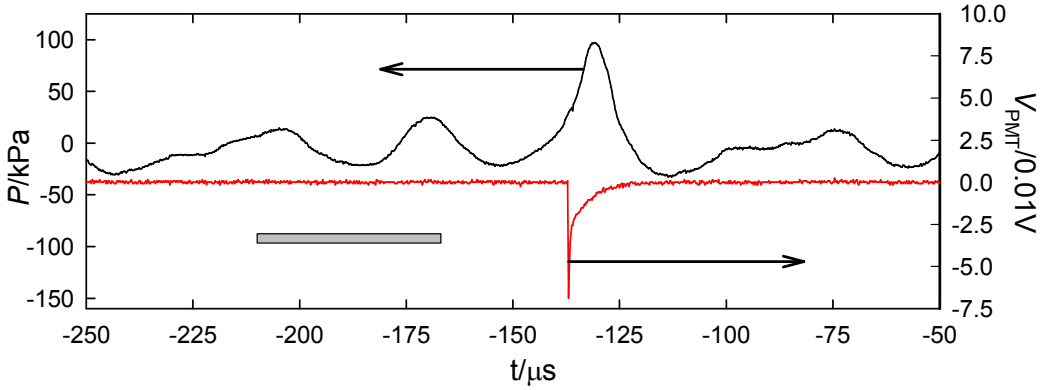

Figure 3. Plot showing the output from the hydrophone (—) and PMT (—) as a function of time. Ultrasonic source 23.1 kHz, 56 ± 5 W cm^{-2}. The solution contained 0.75 M Na_2SO_4. Scale bar indicates period of ultrasonic source.

This was found to be related to the transient spike in opacity of the solution by measuring the time delay between the two events ('A' and 'B' in figure 2) as a function of distance between the sound source and the hydrophone. A direct linear relationship between the two events was noted. Pressure shocks generated through the process of 'cavity collapse' have been detailed in the literature [13]. These pressure pulses or shocks are important in understanding the nature of sensors (whether electrochemical or acoustic etc.) immersed within this environment [8]. In brief, the short wavelength of these waves results in strong reflection from the disk like immersed body (for example the electrode). Further evidence for these shockwaves and their interaction with electrodes, for example, can be found elsewhere [8]. While the preceding section and published work shows evidence for shocks and transient bubbles clouds, it is interesting to investigate other phenomena associated with cavitation. In particular we focus on the emission of light from multibubble sonoluminescence (MBSL). Images of the tip of the piston like emitter show that there is a region under the tip of the ultrasonic probe where MBSL output is detected [8]. However, it should be noted that in order to obtain these images, the exposure time is relatively long (10 minutes) and hence no temporal resolution can be gathered. In an attempt to record the temporal nature of the MBSL event, a photomultiplier tube (PMT) was used to measure the MBSL flash while a hydrophone immersed in the light was used to measure the shocks generated by the cavitation process. Figure 3 shows the simultaneous hydrophone and PMT response. Interestingly flashes of MBSL light are only seen when a shock is generated in the liquid (by the cluster collapse event described previously). The period of the ultrasonic driving wave was 43 μs (shown as a scale bar on figure 3). These results indicate that as well as the transient bubble cloud, the shock is associated with the emission of light. However, assigning the light emission to either the cluster collapse or transient bubble cloud is a non-trivial matter requiring further investigation. Nevertheless it is clear that these events (cluster collapse, shock emission and transient bubble cloud) are important in understanding the cavitation process within this environment. While the previous section outlines a set of results investigating the cavitation process itself, it is possible to employ this system (once thoroughly characterised) to study other equally important phenomena. Here the investigation of erosion/corrosion of a stainless steel microelectrode (25 μm diameter) was studied by positioning the electrode within a region of liquid below to an operating ultrasonic horn where inertial cavitation was known to exist. The location of this 'inertial zone' generated using this apparatus has been investigated thoroughly through the use of MBSL imaging and electrochemical mass transfer/erosion sensors [8]. The results of these studies are detailed elsewhere. Briefly, the inertial zone was found to be within ~2 mm of the tip of the ultrasonic emitter. For the study reported here it is necessary to expose the surface of the microelectrode to this inertial cavitation zone in order to study the repassivation of the surface post erosion. Hence the microelectrode was positioned at a distance of 0.65 mm from the surface of the sound emitter. In this position the exposure of the passivated surface to inertial cavitation results in a series of current time transients of differing magnitudes. Figure 4 shows a series of these events recorded at high temporal resolution (in this case 4 MHz sample rate – see figure 4 insert). In addition to showing the range of current maxima recorded, figure 4 also indicates that the transient current time decays can have different time constants. This is significant as the shape of the current time transient can indicate a difference in the passivation kinetics at the

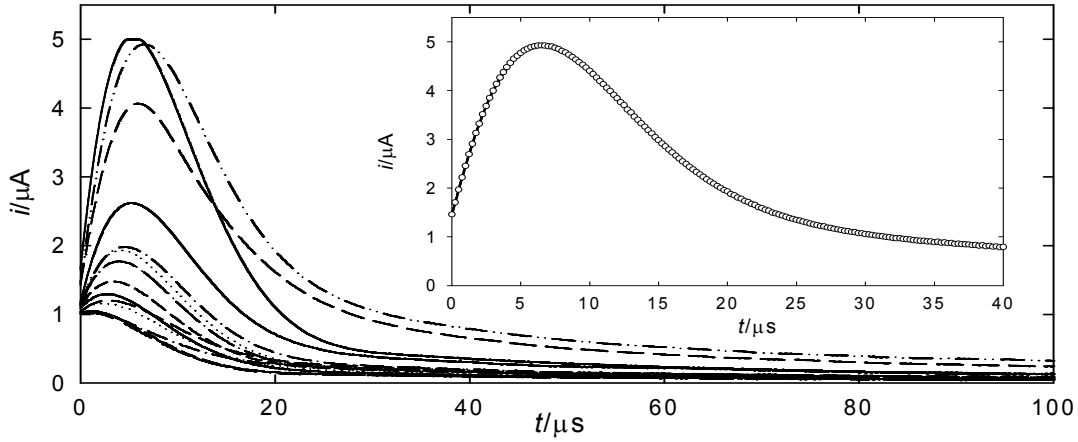

Figure 4. Plot showing a set of 16 transients recorded in 1 second using a stainless steel microelectrode exposed to ultrasound at a horn to electrode distance of 0.65 mm. The trigger current was 1 μA and the solution contained 0.5 M K_2CO_3. Microelectrode was held at +0.25 V vs. SCE. Insert transients showing the data points to illustrate the temporal resolution.

surface of the metal. Under high electric fields the growth of an oxide is thought to occur through two different mechanisms. These are termed 'ion migration' [14] and 'place exchange' [15] respectively. Growth under ion migration is controlled by the transport of cations across the thin film. The growth is self limiting; as the film thickens the electric field strength across the film decreases. In contrast, the place exchange mechanism suggests that film growth occurs through the adsorption of oxygen into the metal surface, which then undergoes a place exchange with the underlying metal atoms. Here, the activation energy associated with place exchange increases as the film thickens, limiting the film growth. The place exchange mechanism is thought to be physically reasonable for the first few atomic layers only [16]. It is possible to distinguish the mechanisms through analysis of the current time transients [17]. Figure 5 shows two different transients (shown by ● and ▼ symbols) recorded in the manner described above plotted as log(i/A) *vs.* $(it)^{1/2}$ analysis (at t > 15 μs) where i represents the current and t time. Although it is difficult to determine the gradients accurately, it can clearly be seen that they vary from a positive finite value (see the data denoted by ▼ and the illustrative line the line shown by (— · —) in figure 5). This indicates that the passivation mechanism of film growth is not fixed to either ion migration or place exchange and may be related to the penetration depth achieved by each erosion event. Log/log analysis (not shown) also supports this. Supporting evidence for the initiation of differing mechanisms depending on the penetration depth (initial film thickness) has been reported by Cho *et al* [16]. These authors studied the repassivation of a steel electrode using a scratched electrode technique. It was found that place exchange initially controlled film growth. However, as the film thickened ion migration became the dominant growth mechanism. We have been unable to observe this

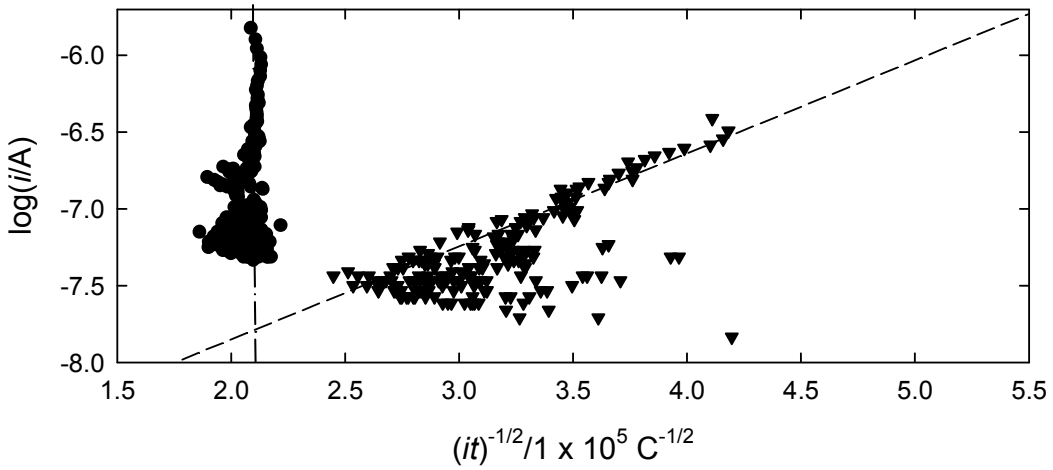

Figure 5. Plots of log(i/A) vs. (it)-1/2 for two transients obtained from the inertial cavitation technique erosion/corrosion technique. The event denoted by ● exhibits the place exchange mechanism while the transient shown by ▼ displays ion migration kinetics

changeover. However, this is not surprising, as the time scale for observing the film growth using the technique described here is restricted to the time interval between erosion events. Cho *et al.* found that the change in growth mechanism occurred after a period of ~10 ms. However, under the conditions used here the time window available to study erosion/corrosion is limited to 120 μs, after which time subsequent erosion events are likely to be observed in the continuous ultrasonic field employed. This is a potential disadvantage of this technique and requires further experimental development to extend this time window through the use of, for example, pulsed systems or the generation of single cavitation events.

CONCLUSIONS

The environment below an operating ultrasonic horn is complex in nature. As well as the acoustic field generated by the sound source and cell, the cavitation process (either through cluster collapse or transient bursts of bubbles) significantly contributes to the processes observed. The investigation and employment of such media require a combined sensor/measurement approach which considers all these effects and the possible invasive nature of the systems involved. However, once a thorough understanding of the system has been attained, it can be used to study other equally important phenomena here the study of erosion/corrosion kinetics. The mechanism for surface reformation was shown to vary from event to event.

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