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Influence of Ultrasound on the Corrosion of Aluminium

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Abstract: The influence of ultrasound on the electrochemical behaviour of aluminium in chloride solution was studied using an ultrasonic probe placed above the metal surface. Enhanced mass transport and cavitation phenomena were shown to remove the protective layer from aluminium and increase the rate of corrosion and of pit formation. Various parameters were studied using measurements of open circuit potential and polarisation curves. The order of importance was found to be: Area of the probe tip < [Cl^-] < Distance between probe tip and metal < Ultrasound power.

Introduction

Ultrasonic radiation can have a significant effect on processes occurring at or near the surface of solid objects immersed in liquid solutions. A high mass transport of solution in the vicinity of the surface and cavitation phenomena near the solid liquid interface, can be accompanied by a change in the mechanism of interfacial reactions, a reduction in the amount of adsorption of species from solution and continuous in situ activation of the surface. All these factors are of importance in influencing corrosion processes.

The ways in which ultrasound can be utilised in electrochemistry have been summarised [1]. The significant and reproducible increase of mass transport can increase the measured current in analytical experiments e.g. [2], improve quality of electroplating e.g. [3] and form a basis for electrode pre-treatments [4]. Additionally, the cavitation process leads to the formation of microbubbles, which collapse on colliding with the electrode surface causing erosion. It is thus interesting to investigate the influence of ultrasound on corrosion processes in which mass transport plays an important role and which can be influenced by erosion of the corroding area.

In this study the influence of ultrasound on the corrosion of aluminium in aqueous chloride solution, which can promote pitting corrosion of aluminium [5] was investigated and how insonation affects the properties of the protective oxide layer.

Experimental

Experiments were carried out in a one-compartment electrochemical cell. Pure aluminium (99.99%) disk electrodes were mounted in epoxy resin, the surface of which was freshly polished with alumina down to 1 μm particle size before each experiment. The cell also contained a platinum counter electrode and saturated calomel electrode as reference. The cell was thermostatted at 25ºC.

A Vibra cell 501 model 20 kHz sonic horn (Sonics & Materials Inc) was employed with titanium tipped probes of 3 mm and 10 mm diameter. Power levels up to and including 44 W cm^{-2} were used, The aluminium electrode was oriented vertically facing upwards to face the horn tip and the distance, *d*, regulated.

Experiments were carried out in KCl solutions of 0.01 M, 0.1 M and 1 M concentration made from analytical grade reagent and MilliQ ultrapure water (resistivity > 18 MΩ cm). Ultrasound was applied after 15 min immersion during 5 minutes, usually following an optimised scheme of 2s on and 1s off.

Open circuit potential and polarization curve measurements were carried out using a Potentiostat PAR 273A (EG&G) controlled by M352 Corrosion Analysis Software which was also used for Tafel analysis.

Results and Discussion

Open Circuit Potential The open circuit potential, OCP, was measured as a function of time. Two different diameter ultrasound probe tips were used (3 mm and 10 mm), and the ultrasound power was varied; the method of application (continuous or different kinds of pulses) was also investigated. The distance between probe tip and electrode was changed and different chloride concentrations were employed as described in the experimental section.

First experiments were designed to examine the most efficient way of applying the ultrasound over a 5 minute period, between 15 and 20 minutes after immersion when the value of the OCP was almost constant, indicating that a protective oxide layer had already been formed, in agreement with previous investigations [5]. Various schemes were tried with 2s pulses of radiation followed by different rest periods of 1s, 2s, 10s, 18s off in which the temperature variation was monitored as well as the variation of potential. It was found that the temperature rose less than 1ºC using a 1s off period and this was the most efficient so was used in all subsequent experiments.

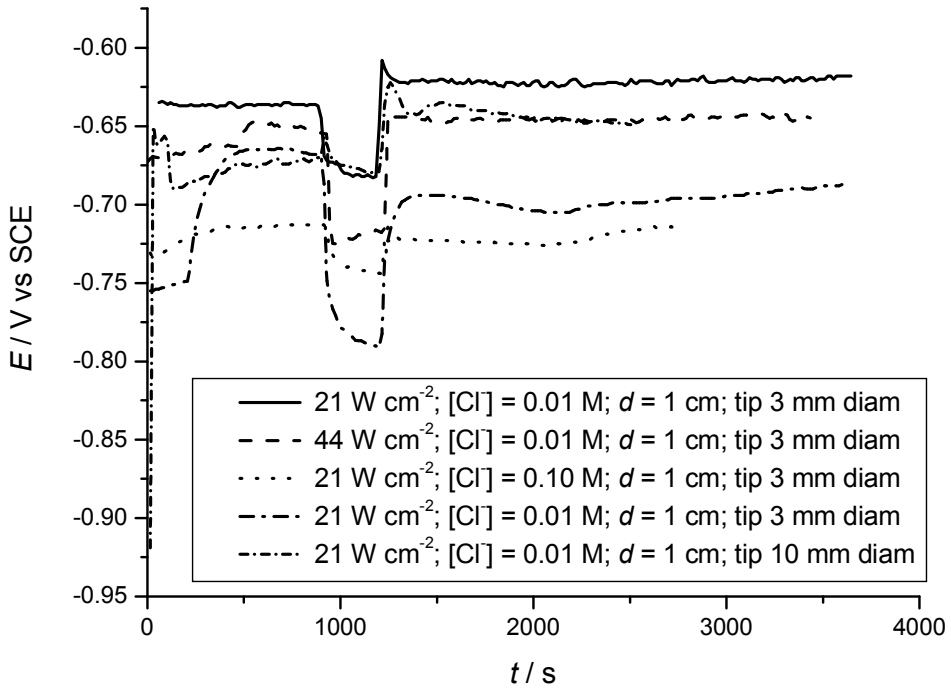

Fig 1 –Summary of the influence of experimental conditions on the variation of OCP of pure aluminium

An example of the variation of some of these parameters is shown in Fig.1. Application of ultrasound leads to a sharp variation of potential in the negative direction. This can be attributed first to the cavitation process leading to the formation of bubbles and their collapse on the surface giving rise to erosion and destruction of the passive oxide layer, and secondly to the increased mass transport. Immediately following the ultrasound is stopped, the value of the OCP begins to return to the values before insonation and there is repassivation.

Considering the various factors separately, in particular their influence on the difference of OCP on applying ultrasonic radiation:

Probe tip diameter: the larger tip leads to a more homogeneous corrosion of the surface and the smaller tip leads to deep hemispherical pits. This can be attributed to the mass transport streamlines and direction of the cavitation.

Chloride ion concentration: the higher the chloride ion concentration the less the effect of

ultrasound on the values of OCP, showing that the effect of chloride ion on pitting corrosion is dominant.

Distance between horn tip and aluminium surface: the less the distance between the tip and the electrode the more efficient is the ultrasound except at very small distances when there is a shielding effect from the tip.

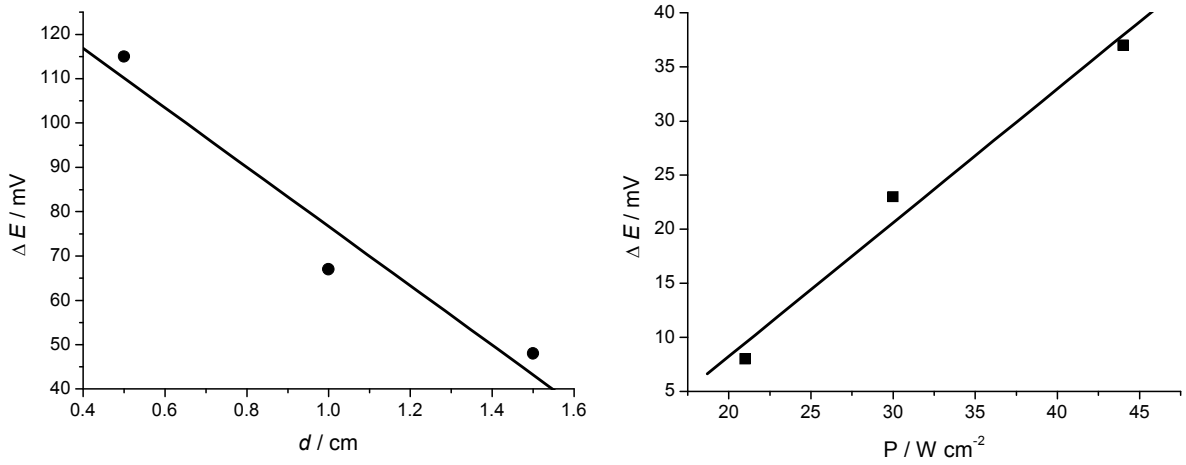

Fig.2 Influence of horn tip – aluminium electrode distance and of ultrasound power on the change in open circuit potential immediately after commencing radiation with ultrasound.

Ultrasound power: as expected, increasing power increases the rate of removal of the protective oxide layer.

The linear variation of change in OCP on commencing insonation with the last two parameters is shown in Fig.2.

Polarisation Curves Polarisation curves were registered over a range of -200 to +200 mV from the OCP at a scan rate of 5 mV s^{-1}, see examples in Fig.3. Tafel analysis was then carried out by computer adjustment, Table 1. These were recorded after 10 min immersion, i.e. when the steady-state had been reached before application of ultrasound; after 25 min. when the system had appeared to reach a steady state after finishing applying ultrasound; and after 1 h, in order to probe any differences due to formation of a thicker oxide layer during the period following application of ultrasound.

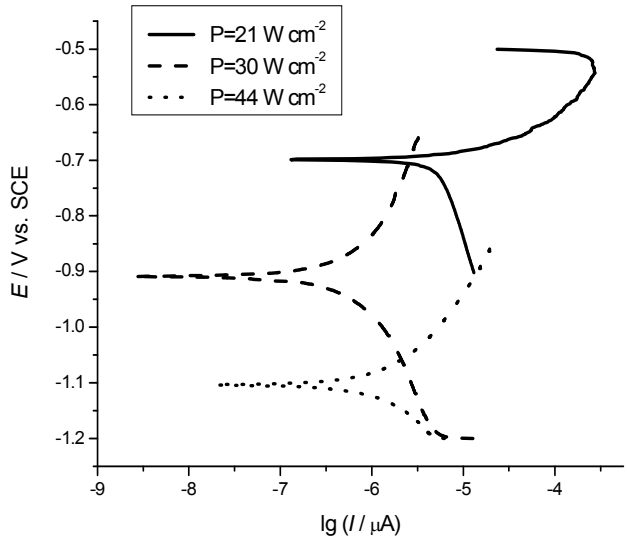

Fig.3 Polarisation curves showing the influence of ultrasound power after 25 min. immersion. [Cl^-] = 0.01 mol dm^{-3}, d = 1 cm, 3 mm tip

Table 1 – Values of E_{cor} and I_{cor} obtained by Tafel analysis of the polarisation curves

		E_{cor} / V vs. SCE			I_{cor} / μA cm^{-2}		
		10 min	25 min	60 min	10 min	25 min	60 min
Tip diameter / mm	3	-0.921	-0.862	-0.885	1.2	4.9	0.7
	10	-0.843	-0.729	-0.724	4.0	5.1	5.5
Power / W cm^{-2}	21	-0.921	-0.862	-0.885	1.2	4.9	0.7
	30	-1.025	-0.907	-0.838	2.9	7.2	1.1
	44	-0.726	-0.694	-0.676	3.1	5.8	2.0
Tip - electrode	1	-0.921	-0.862	-0.885	1.2	4.9	0.7
distance / cm	1.5	-0.940	-0.880	-0.908	0.5	1.6	0.3
[Cl$^-$] / mol dm^{-3}	0.01	-0.921	-0.862	-0.885	1.2	4.9	0.7
	0.1	-0.915	-0.902	-0.877	3.0	4.9	4.3
	1.0	-1.012	-1.057	-1.070	0.2	8.7	5.3

It can be seen that the variation of corrosion current parallels that of the corrosion potential and the latter is in reasonable agreement with the values of open circuit corrosion potential. In general, there are large reductions in corrosion current between 25 min and 60 min immersion, demonstrating that, although from the corrosion potentials it appears that a steady state has been reached 5 minutes after application of ultrasound has ceased together with reformation of the oxide layer, in reality a longer time is necessary for a fully formed oxide protective layer. This period for oxide growth has been investigated before in chloride media [5].

Observation of the pits formed by scanning electron microscopy demonstrates that they are deeper and the inner surface is irregular, with no evidence of crystallographic etching, as occurs in the absence of ultrasound, e.g. [5]. This is in agreement with the erosion effect of ultrasound contributing to the pitting process as well as causing an increase in mass transport.

Conclusions

It has been shown that ultrasound increases the rate of corrosion of aluminium destroying the passive layer and promoting the formation of pits.

Analysis of the results obtained for variation of open circuit potential and from polarisation curves lead to the following order of influence of the ultrasound parameters on the rate of corrosion:

Area of the probe tip < [Cl$^-$] < Distance between probe tip and metal < Ultrasound power.

The possibility of using ultrasound as a method for accelerating corrosion and as a corrosion diagnostic for quality control has been demonstrated.

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