THE POTENTIODYNAMIC BEHAVIOUR OF COPPER IN NaCl SOLUTIONS STUDIED BY AUGER AND PHOTOELECTRON SPECTROSCOPY

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Abstract The potentiodynamic behaviour of copper in brine solutions was studies. Auger and photo-electron spectroscopy were used together with electrochemical methods. It is demostrated that the passivation observed in potentiodynamic curves is due to a surface film formation on a copper electrode. It is concluded that this film must be copper (I) chloride in nature. Effect of different factors on potentiodynamic curves has also been investigated.

چکیده دراین مقاله روند پتانسیو دینامیکی مس در آب دریا مورد بررسی قرار گرفته است استفاده از اسپکتروسکوپی الکترون اوژه و فتو الکترون اشعه X همراه با سیستم الکترو شیمیایی در بررسی منحنیهای پتانسیودینامیکی در ناحیه غیرفعال بیانگر تشکیل لایه‌های سطحی برروی الکترود مس میباشد. نتیجه‌گیری نهائی بررسی این‌لایه سطحی مربوط به‌ترکیب کلرور مس یک‌ظرفیتی میباشد. همچنین دیگر عوامل موثر در قسمت‌های مختلف منحنی‌های پتانسیودینامیکی نیز مورد بررسی قرار گرفته است.

INTRODUCTION

Although there are a relatively large number of publications dealing with the electrochemical behaviour of copper in different solutions [1-5], until now the knowledge of the process is rather limited. Although electrochemical investigations are mainly used to study these processes, it is not always easy, to obtain meaningful and reproducible results in such measurements. This is perhaps the reason for using a surface sensitive technique in conjuction with the electrochemical methods.

X-ray photo-electron spectroscopy (XPS or ESCA) and Auger spectroscopy (AES) have been shown to be powerful techniques for surface studies and, have the capability to provide a wealth of information about the nature of the surface films such as passivation layers etc [6-9]. A potential drawback lies in the fact that it is not possible to study the surface films in situ at the metal-solution interface, since both XPS and AES are UHV (Utra High Vaccum) techniques. There also exists a transfer problem in any experimental programme. However, these techniques were used successfully in recent studies of copper electrolyte systems.

In the present study, the potentiodynamic behaviour of copper has been studied, using the potentiostat together with ESCA (or XPS) and AES to investigate the nature and mechanism of the film formation.

EXPRIMENTS

Copper electrodes were prepared from copper sheets (99.99%) obtained from BDH company Ltd.

Only one surface of the electode was exposed to the solution, using an epoxy resin (Araldite) to cover most of the electrode. No contaminations from epoxy resin was observed. Electrodes after being polished

with diamond pastes, (with the last one being Iu) were introduced into a diluted nitric acid solution for a short period of time, followed by washing with triply distilled water. ESCA examination of the surface treated in this way, revealed no residue remained due to HNO_3 treatment [6]. A platinum auxiliary electrode was used and the electrochemical cell was enclosed in a thermostatic bath. A saturated calomel electrode was used as a reference electrode and triply distilled water was used to prepare the electrolytes. Reagents were AR grade and obtained from the BDH Company. All copper electrodes prepared for this study were exposed to the solution pior to measurement for an hour.

XPS and AES spectra were obtained with the Physical Electronics (PHI Model 550) spectrometer. The instrument was equipped with both Auger and X-ray-photoelectron spectrometer and additional accessories of SAM, SIMS and UPS. The binding energy scale was chosen in such away that the C(1s) level rising from surface contamination was 285. O eV.

RESULTS AND DISCUSSION

Figure (1) shows a voltagram of a copper electrode in a IM NaCl solution at 25°C. This starts from extreme cathodic overpotentials (i.e. 4.0 Volts) and runs up to +2.0 volts at 0.001 Vs^{-1}, under repetitive tringular potential scan. The voltagram shows a sharp peak [1] at −0.2 V with a small shoulder. At 0.7 V, copper electrodes were taken from the solution at both 0.2 V and 0.7 V, and were examined by XPS and AES. Figure (2a) shows an Auger spectrum of the sample taken at 0.2 V and Figure (2b) shows the spectrom of the sample taken at 0.7 V. The main difference between the two spectra is clearly the lack of peak due to the chlorine in the first spectrum. The presence of a strong oxygen peak in Figure. (2a) clearly shows that the shoulder is due to oxide formation and the strong chlorine peak in Figure (2b) is an indications of copper, chloride formation. This must be stated,that although the Auger spectra gives detailed information about the elements present on the surface, it yields very little information about the chemical states of the elements. X-ray photo-electron spectroscopy (XPS or ESCA) gives valuable information; not only about the presence of elements on the surface, but also their chemical states. Figure (3a) and (3b) show XPS spectra of the samples mentioned above. In the 2P region, the binding energy calculation and also the lack of any shake-up satellite (which are associated with Cu^{2+} species) suggests that both the oxide and chloride that formed on the surface of the electrodes are monovalent copper compounds. [6, 10].

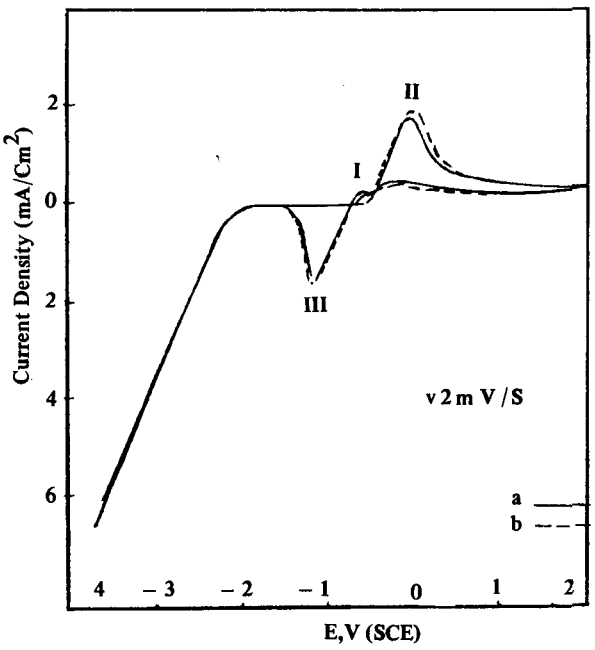

Figure 1. The potentiodynamic curves of copper electrode in 1 M., NaCl solution at 25°. Heavy line shows the first scan and dashed line shows the second Both curves were obtained at a speed of 2 mV/S.

Examination of the electrolyte by the use of atomic absorption spectro-photometer showed no copper in the solution at 0.7 V. In contrast to the second point i.c. cuprous chloride formation.

The passivation expercised by CuCl layer, is responsible for the low current density anodic curve in Figure (1). That is to say, if there were no passivation the current density (and hence the corrosion rate) would have a much higher value.

During the cathodic scan a well defined cathodic current peak occurs in the vicinity of the free corrosion potential. This is due to rapid electrodissolution of the film which is formed during the anodizing period.

The factors affecting the shape and occurence of the current peaks are numerous. Among the factors that have the greatest

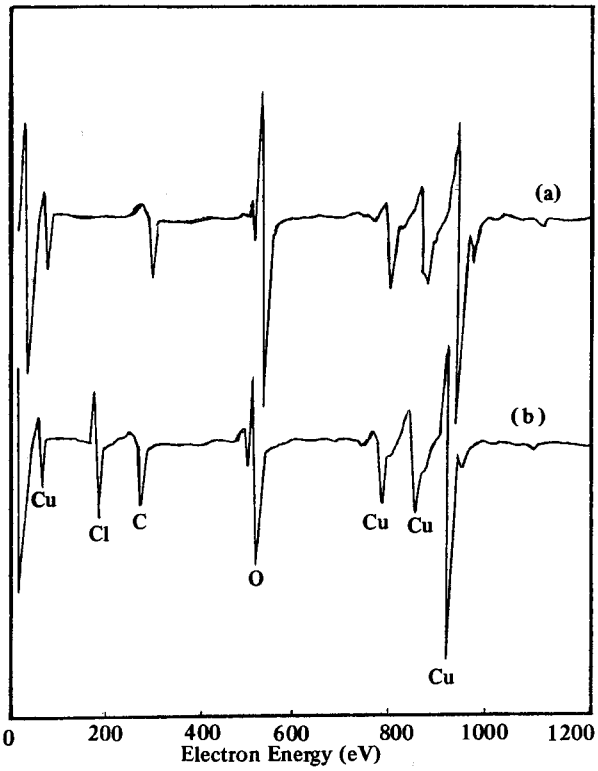

Figure 2. Auger electron spectra of copper electrodes electrochemically polarized at 0.7 V (2a) 0.2 V (2b).

effect are the anodic and cathodic maximum overpotentials, rate of potential perturbation (the number of scans when repetitive triangular potential scans are used) and the concentration of NaCl in electrolyte. Figure (3) shows the effects of cathodic overpotential and number of scans on the potentiodynamic curves of the copper electrode. The great effect of scan rate, particularly on current peak due to CuCl formation, indicates that the process is highly time dependent and and rather slow.

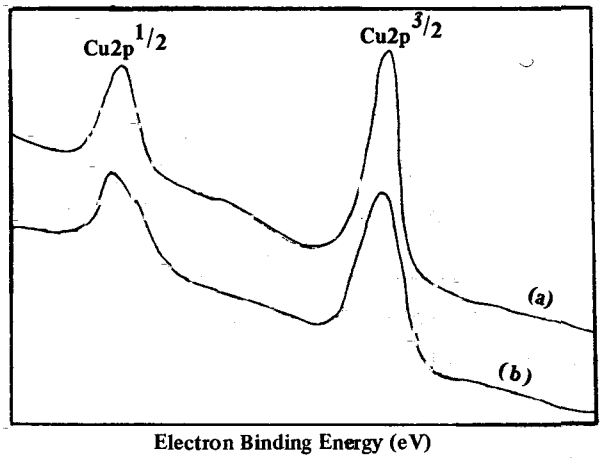

Figure 3. X-ray photo-electron spectra of copper electrodes electrochemically polarized at 0.7 V (2a) and 0.2 V (2b).

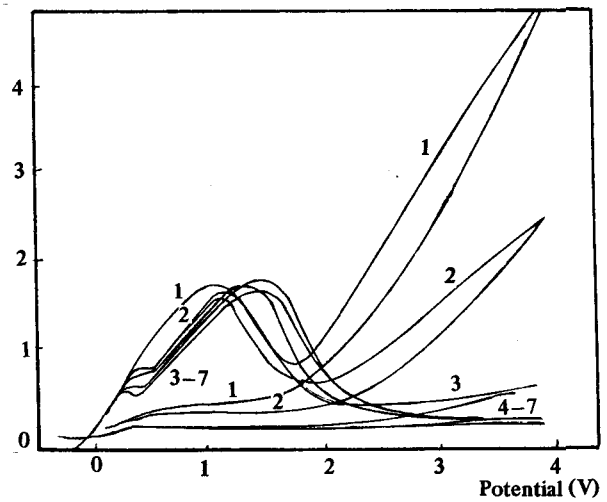

Figure 4. The potentiodynamic curves of copper electrodes in NaCl solution at a speed of 20 mV/S. Successive scans are numbered. All curves were taken at 25°C.

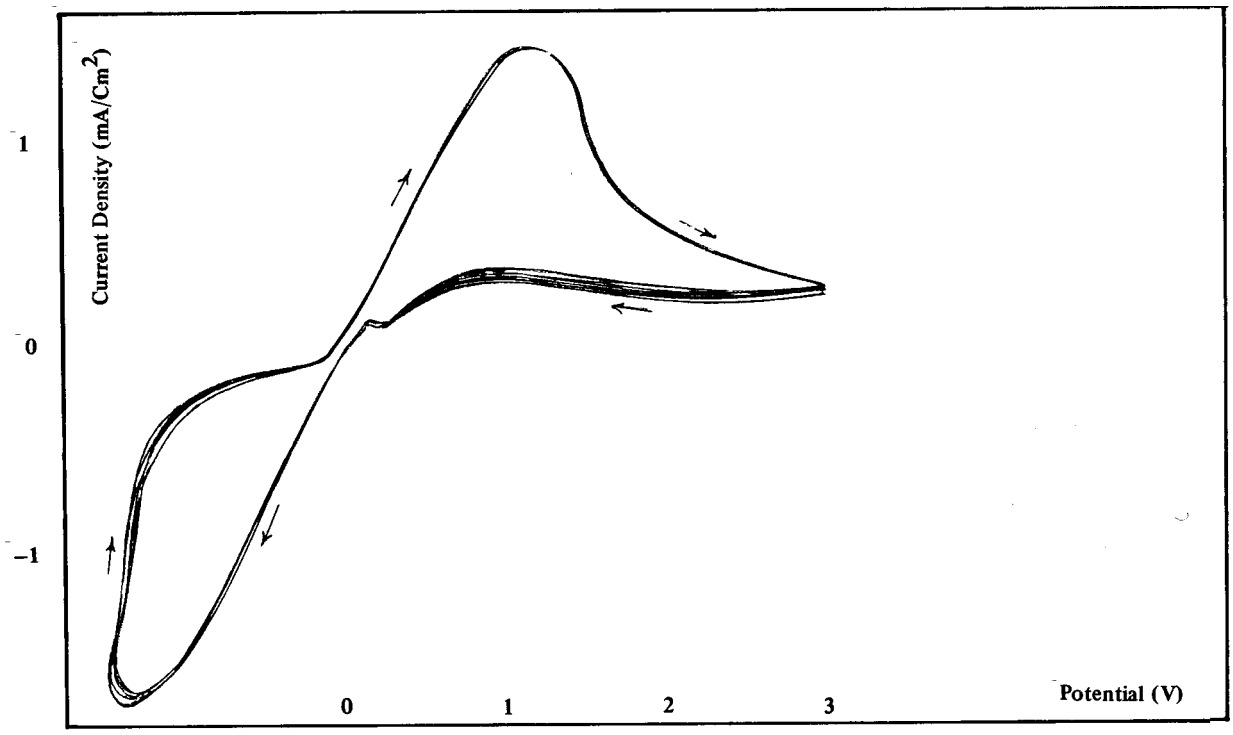

Figure 5. The potentiodynamic curves of platinum electrode. Note the similiarity between the two sets of curves in Figure 4 and Figure 5.

Figure (4) shows a series of potentiodynamic curves for a copper electrode left in the solution for an hour, after being under cyclic polarization with a speed of 500 Vs^{-1} for 2 minutes. Almost the same behaviour was observed when two similar platinum electrodes for both working and auxiliary electrodes (Figure 5) were used.

Using proper overpotentials and speed,one can always eliminate the effect of the number of scans on potentiodynamic curves(Figure 6).

The above results show that in the anodic region, the main processes are cuprous oxide and at higher overvoltages cuprous chloride formation. Copper dissolution takes place via Cu^{+} ions, which in contact with the solution containing chloride ions, forms insoluble CuCl. This soon reaches its limit of solubility and as a result, precipitates onto the surface. The mechanism of passive film formation, therefore, is concluded to be a dissolution

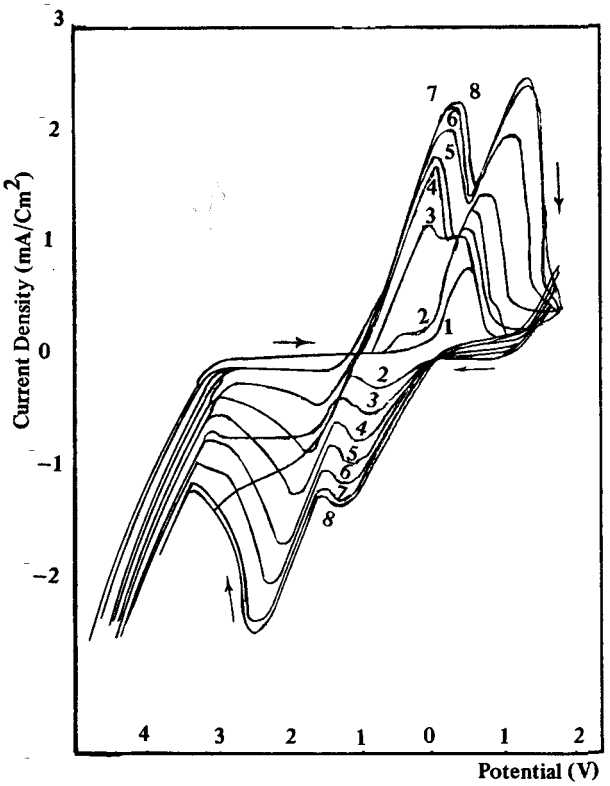

Figure 6. The potentiodynamic cerves for copper electrode at a speed of 20 mV/S. Cathodic and anodic overpotential were chosen to eliminate the effect of overpotential and curves at successive scans.

precipitation mechanism suggested by Miller [11]. This is in contast to the nucleation and growth mechanism [12, 13].

CONCLUSIONS

The conclusions reached in this work are listed below:

1. The surface sensitive new physical techniques such as Auger and photo-electron spectroscopy (AES and XPS) together with electrochemical methods, form an, ideal combination for such studies.
2. The passivation observed in potentiodynamic curves of copper electrodes in brine solutions is due to a formation of a CuCl surface layer formation.
3. The mechanism by which the passivation takes place is in fact a dissolution-precipitation mechanism.

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