

## EFFECT OF PLASTIC DEFORMATION ON CORROSION OF CADMIUM IN 0.1M SODIUM SULPHATE SOLUTION

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### تأثير التشكيل اللدن على تآكل الكاديوم في محلول كبريتات الصوديوم

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يدرس هذا البحث تأثير التشكيل اللدن ودرجة خشونة السطح على تآكل فلز الكاديوم في محلول ٠.١ م من كبريتات الصوديوم عند درجة حرارة ٢٥م وقد تم ضغط عينات إسطوانية من الكاديوم إلى درجات متفاوتة من التشكيل تصل إلى ١٠٪ وتم إعداد ٣ مستويات لخشونة أسطح العينات هي ١٢٠ ، ٣٢٠ ، ٦٠٠ . وقد أوضحت النتائج أن معدل التآكل الأنودي يقل بزيادة التشكيل في المدى من ٣٠ إلى ٦٠٪ . على حسب درجة خشونة السطح . وبزيادة التشكيل عن هذه القيمة يميل معدل التآكل إلى التزايد ويعزى هذا السلوك إلى التغيرات التي تحدث في التركيب المجهرى إضافة إلى إعادة التبلور المصاحب لتشكيل العينات ، وقد لوحظ إرتفاع معدلات التآكل بإزدياد خشونة السطح .

*Key Words:* Plastic deformation, Corrosion, Cadmium

#### ABSTRACT

The present investigation was carried out to study the influence of prior plastic deformation and surface finish on the corrosion behaviour of pure cadmium in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at 25° C. Cylindrical specimens were deformed by compression to different levels of deformation up to 90% reduction in height (RH). Three surface finishes were examined, namely, 120, 320 and 600 grits. The results obtained indicate that the cathodic corrosion rate decreases with deformation up to 30-60% RH, depending on the surface finish. Further deformation tends to increase the corrosion rate. This behaviour is related to microstructure changes and dynamic recrystallization due to plastic deformation prior to corrosion testing. Relatively higher corrosion rates were observed for coarser surface finishes.

#### INTRODUCTION

Plastic deformation changes the internal structure of a metal and therefore changes its properties, including its corrosion behaviour. When an annealed material is heavily cold worked, energy may be stored in the material as a result of the increased dislocation density and point defects. etc. This energy increase may provide a driving force for corrosion. It was suggested that the kinetics of various anodic and cathodic processes could be quite different on annealed and cold worked surfaces (Shreir, 1979). This would result in significantly different corrosion rates between annealed and cold worked metals. Furthermore, it has been observed that cold work markedly increases corrosion rates of steel and aluminium in acids (Shreir, 1979). Several authors suggest that the increased corrosion rate is due to increased dislocation density. On the other hand, (Foroulis and Uhlig, 1964) suggest that the increased corrosion rate is due to the segregation of carbon and nitrogen to dislocations, and that the cathodic (hydrogen evolution) reaction is kinetically easier at these sites. (Dayal, Parvathavarthini and

Gnanamoorthy, 1984) studied the influence of cold work (up to 20% reduction in thickness) on crevice corrosion of austenitic stainless steels in 0.5 M NaCl solution. Their results indicate that the corrosion resistance decreases with cold work up to 5-15% but that further increase in cold work has a negligible effect. It was concluded that increases in the number of defect sites and changes in texture produced by cold work markedly influence the corrosion behaviour of the examined materials. The effect of cold work may not be very significant for cadmium at 25°C because of its low melting point. At 25°C (298 °K), diffusion processes may allow recovery and perhaps recrystallization.

The purpose of the present investigation is to study the effect of plastic deformation on the corrosion behaviour of cadmium in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at 25°C using the polarization resistance technique. Furthermore, since the surface finish affects corrosion behaviour (Kandeil and Mourad, 1989), the influence of deformation was examined at three different levels of surface finish.

## EXPERIMENTAL

## A) Preparation of specimens

Small cylindrical specimens (dia 15 mm), were machined from pure cadmium bars (BDH, 99.99%). Plastic deformation was introduced by compression between parallel platens in a universal testing machine. The original heights of the specimens were varied to give different amounts of reduction in height upon compression to a final height of 4 mm. The amount of plastic deformation measured as a reduction in height ( $\Delta h/h_0$ ) was varied between 0 (as-received) to approximately 85%. The microstructure of the as-received cadmium material is shown in (Fig. 1).

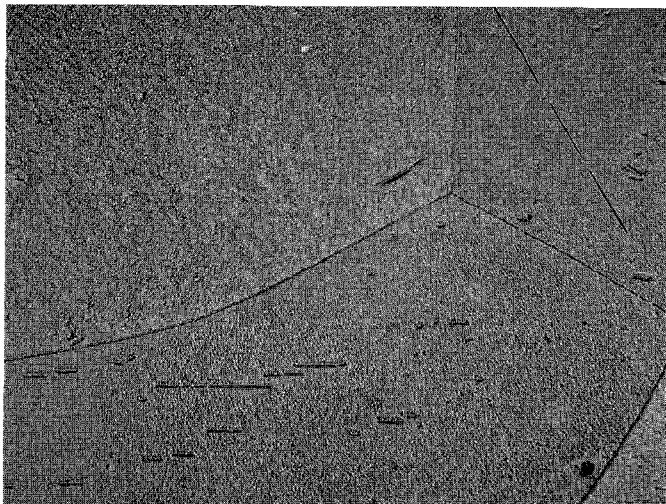


Fig. 1: Microstructure of the as received cadmium material (x 260).

Three groups of plastically deformed samples were mechanically polished using silicon carbide abrasive papers with decreasing grain sizes of: 240, 320 and 600 grit. Water cooling was used during polishing to reduce overheating of the specimens. The polished, as-received and deformed samples were subjected to corrosion testing as described below.

## B) Corrosion system

For performing the polarization measurements the specimens were degreased by washing with acetone, then fitted into a flat specimen holder. The holder contained a sealing washer made of Karlez which exposes 1 cm<sup>2</sup> of the specimen surface to the test solution. A corrosion cell (model K 47 - EG & G Princeton Applied Research - USA), which contained two counter electrodes made of high density graphite was used. A Corrosion Measurement System (model 350 A - EG & G Princeton Applied Research - USA) was used and the potential was measured with reference to a saturated calomel electrode. The experimental measurements were conducted in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at 25°C.

## C) Polarization resistance technique

The polarization resistance technique is a non-destructive and reproducible method for the evaluation of the instantaneous corrosion rate and has been employed extensively (Prazak, 1974). The technique is performed by applying a controlled-potential scan over a small range, typically  $\pm 10$  mV with respect to  $E_{\text{corr}}$  at a scan rate of 1

Mv/sec. The resulting current is linearly plotted versus potential. The slope of this potential-current function at  $E_{\text{corr}}$  is identical to the polarization resistance ( $\pi$ ), which is used together with the Tafel constants to determine the instantaneous corrosion rate of cadmium,  $i_{\text{corr}}$ , using the Stern-Geary equation (Stern and Geary, 1957; Stern 1958):

$$i_{\text{corr}} = \frac{b_a \cdot b_c}{2.3 (b_a + b_c)} \cdot \frac{\Delta i}{\Delta E} = \frac{B}{\pi} \quad (1)$$

where  $b_a$  and  $b_c$  are the anodic and cathodic Tafel constants respectively and  $\Delta i/\Delta E$  is the reciprocal of the polarization resistance. The Tafel constants were determined from the measured plots by scanning the anodic and cathodic regions in a single run beginning with an initial potential that is nominally -150 mV and ending at a final potential of +150 mV (both  $E_{\text{corr}}$  related).

The polarization resistance technique has practical limitations and complications, that chiefly concern the accuracy of the calculated corrosion rates. Possible sources of measurement error include the effect of curvature in the polarization curves close to the corrosion potential (Oldham, Mansfeld, 1971; Callow, Richardson and Dawson, 1976) I.R. drops due to surface films and/or poorly conductive solutions, (Callow, Richardson and Dawson, 1976) anodic processes other than metal dissolution (Reeve and Bech - Nielsen, 1973) non-uniform corrosion, (Reeve and Bech-Nielsen, 1973) corrosion potentials near equilibrium potentials (Mansfeld and Oldham, 1971) and spontaneous changes that occur at the corrosion potential (Callow, Richardson and Dawson, 1976). Furthermore, the Tafel slope values are either not known (LeRoy, 1977) or are obtained from high polarization data which may not be applicable at the corrosion potential (Walter, 1975).

However, the technique is extremely rapid. Additionally, since the applied potential is never far from the corrosion potential, the surface of the specimen is not materially affected by the experiment and the possible error from this source is reduced to negligible levels.

## RESULTS AND DISCUSSION

Fig. (2) shows the potential-time curves measured under open circuit conditions for mechanically polished cadmium electrodes (grit 600) at different amounts of plastic deformation in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution at 25°C. It is evident from the curves that initially negative potentials ranging between -702 and -746 mV, are first obtained upon immersion. Thereafter, the potential of the cadmium quickly changes with time towards negative values until a steady state corrosion potential  $E$  is attained. Similar observations were made for electrodes mechanically polished with grit 120 and 320. It is worth noting from (Fig. 3) that corrosion potential increases for small values of deformation (RH) and then decreases with further deformation as will be explained later. RH is the reduction height calculated from the equation:

$$RH = \frac{h_0 - h_f}{h_0} \times 100 \quad (2)$$

where  $h_0$  and  $h_f$  are the initial and the final heights, of the deformed samples.

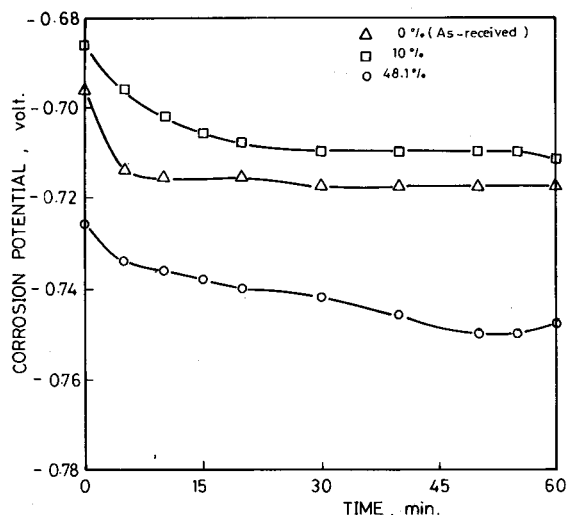


Fig. 2: Variations of corrosion potential with time for plastically deformed cadmium (Grit 600).

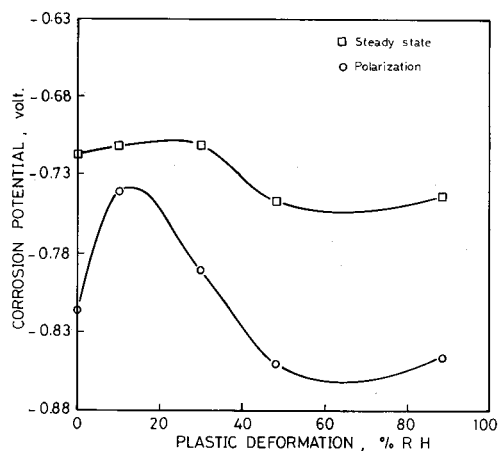
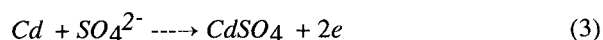


Fig. 3: Effect of plastic deformation on corrosion potential of cadmium.

Fig. (4) shows a typical set of polarization resistance curves for cadmium in the as-received condition as well as for samples deformed to different amounts of reduction in height. All samples were polished with grit 600 prior to corrosion testing. the variation of corrosion parameters with the amount of deformation is given in Table (1) for samples polished with different grits.

The experimental data (Fig. 5) indicate that increasing the amount of plastic deformation, decreases the instantaneous corrosion rate until a minimum value is reached, beyond which it tends to increase with further deformation. Furthermore, the position of the minimum value is shifted towards higher values of deformation as the grit size increases (i.e. as surface roughness increases). These changes in the corrosion rate are accompanied by opposite changes in polarization resistance as shown in (Fig. 6).

The corrosion of cadmium in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution is generally considered to be an electrochemical process that results in the formation of macro-galvanic cells. Metal loss and the build up of corrosion products occurs at the anodic areas of corrosion cells. Metal loss and the build up of corrosion products occurs at the anodic areas of corrosion cells. The chemical reactions that occur at the anode (corroding area) are believed to be as follows:



The cathodic reaction of the electrolysis of water due to the emergence of electrons that are generated at the anode (Eq. 2) and travel through the cadmium to the cathode, as follows:



The negative shift in corrosion potential and the decrease in the corrosion rate with increasing plastic deformation can be explained by the construction of Evan's diagram (Mourad, Abd El-Wahaab, Soliman and El-Gaber, 1988). Fig. (7) shows that an increase in deformation leads to a decrease in

Table 1

Effect of percentage reduction in height on corrosion parameters for mechanically polished cadmium in 0.1M Na<sub>2</sub>SO<sub>4</sub> solution at 25°C

| Grid   | 120    |        |        |        | 320    |        |        |        | 600    |        |        |        |        |        |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|  | 0.0    | 50     | 73     | 83.9   | 0.0    | 10.3   | 44.8   | 66.7   | 83.3   | 0.0    | 10     | 30     | 48.1   | 88.3   |
| <i>E<sub>c,o</sub></i> (volt)                                    | -0.716 | -0.726 | -0.718 | -0.718 | -0.716 | -0.722 | -0.728 | -0.746 | -0.754 | -0.718 | -0.712 | -0.712 | -0.748 | -0.744 |
| <i>E<sub>c,p</sub></i> (volt)                                    | -0.773 | -0.800 | -0.770 | -0.777 | -0.798 | -0.810 | -0.815 | -0.840 | -0.820 | -0.816 | -0.742 | -0.791 | -0.860 | -0.846 |
| <i>b<sub>∞</sub></i> (volt/decade)                               | 0.76   | 0.069  | 0.078  | 0.082  | 0.087  | 0.078  | 0.111  | 0.091  | 0.115  | 0.101  | 0.123  | 0.063  | 0.076  | 0.202  |
| <i>b<sub>c</sub></i> (volt/decade)                               | 0.211  | 0.061  | 0.249  | 0.206  | 0.131  | 0.110  | 0.165  | 0.137  | 0.184  | 0.122  | 0.159  | 0.138  | 0.120  | 0.126  |
| <i>R<sub>p</sub></i> (Ωcm <sup>2</sup> )                         | 367.6  | 981.9  | 2080   | 1644   | 222.6  | 295.1  | 1081   | 793.8  | 1655   | 215.3  | 528.6  | 1250   | 832    | 1099   |
| <i>i<sub>corr</sub></i> × 10 <sup>-4</sup> (nA/cm <sup>2</sup> ) | 6.6    | 1.240  | 1.240  | 1.549  | 10.20  | 6.72   | 2.67   | 2.99   | 1.853  | 11.15  | 4.566  | 1.502  | 2.429  | 3.068  |

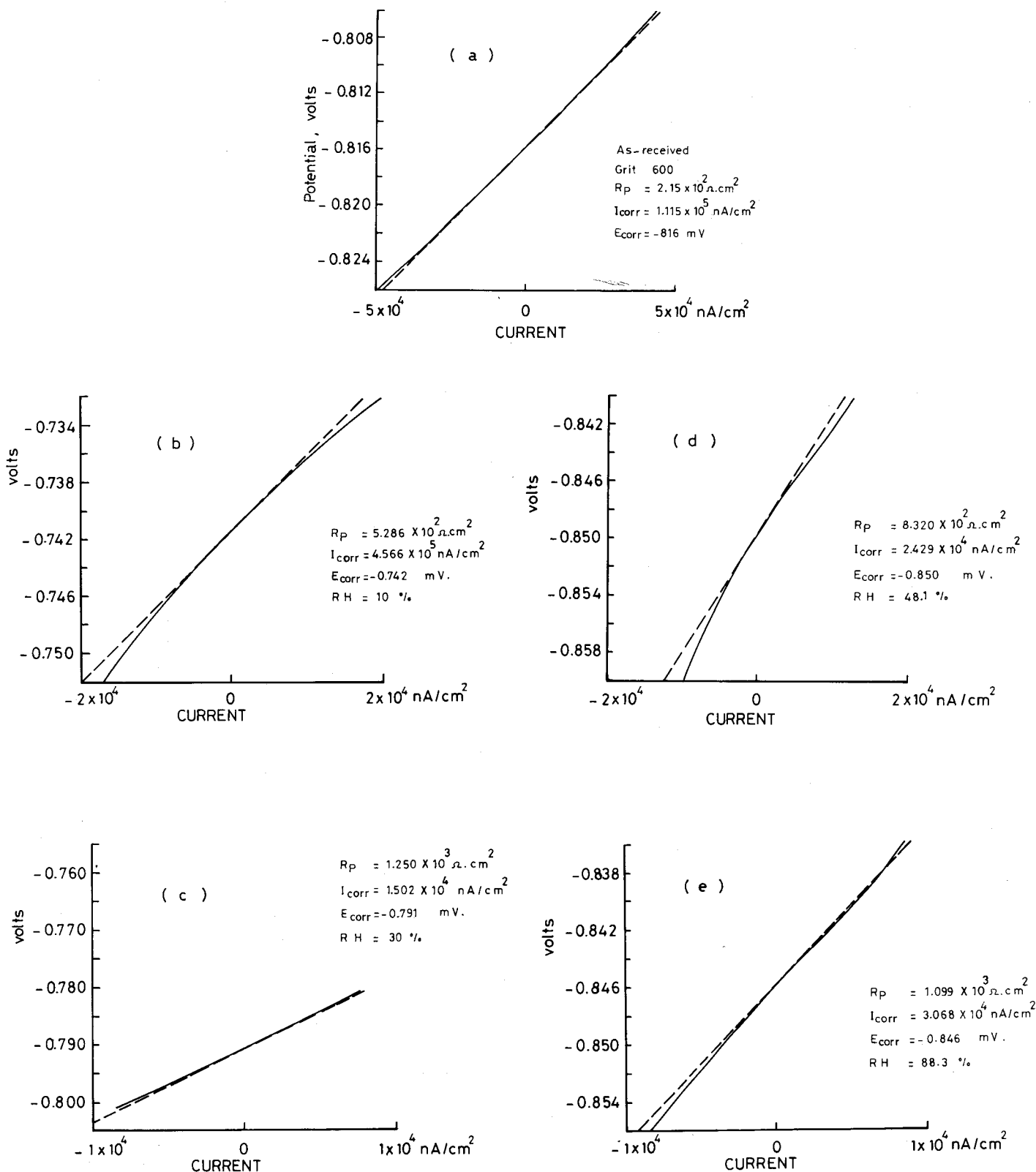


Fig. 4: Polarization resistance curves for cadmium

- (a) As-received
- (b) 10% RH
- (c) 30% RH
- (d) 48.1% RH
- (e) 88.3% RH

corrosion current from  $I_{C0}$  to  $I_{C1}, I_{C2}$  and further to  $I_{C3}$ . Accordingly, the corrosion potential shifts to more negative values from  $E_{C0}$ , to  $E_{C1}$  to  $E_{C2}$  and further to  $E_{C3}$ , respectively. It may be concluded that the corrosion of cadmium in solution is mainly cathodically controlled.

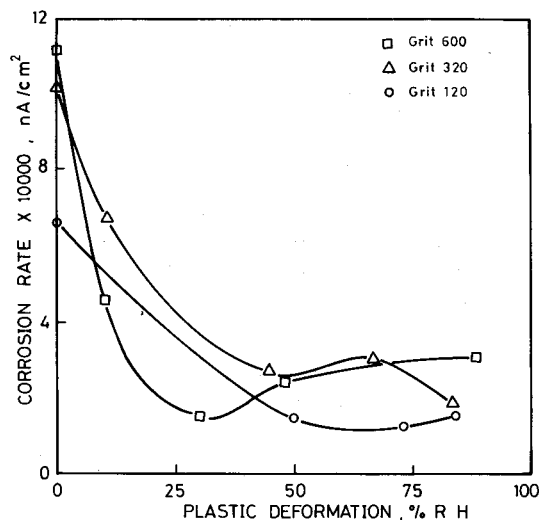


Fig. 5: Effect of plastic deformation on corrosion rate of cadmium with different surface finishes.

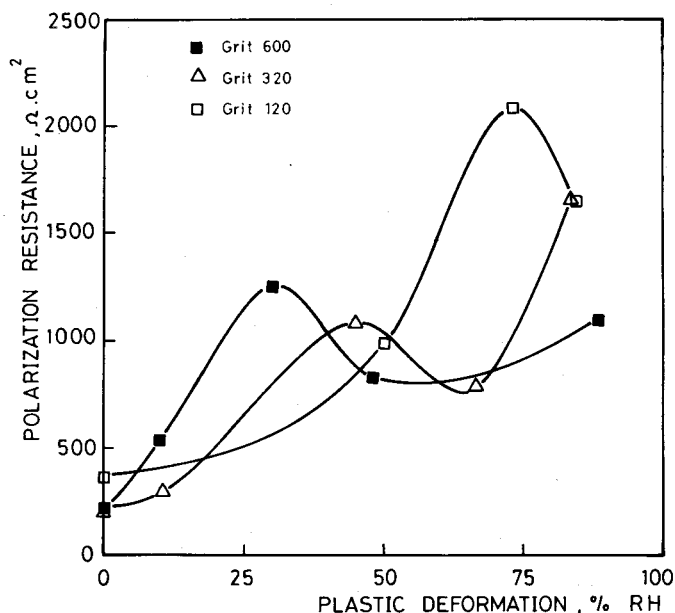


Fig. 6: Effect of plastic deformation on polarization resistance of polished cadmium.

A series of deformed specimens were sectioned parallel to the loading direction. These sections were mounted, polished and etched for metallographic examination. Fig. (8) shows a series of microphotographs for cadmium specimens deformed to different amounts of plastic deformation up to 88%. The as-received material, Fig. (8a), is included for comparison.

It is evident from (Fig. 8) indicates that dynamic recrystallization, in isolated regions, starts at an early stage of deformation as shown in (Fig. 8b, e, & f). It is further observed that the refined grain size and the volume fraction of the recrystallized grains, shown in (Fig. 9), correlate well with the changes in corrosion rate shown in (Fig. 4).

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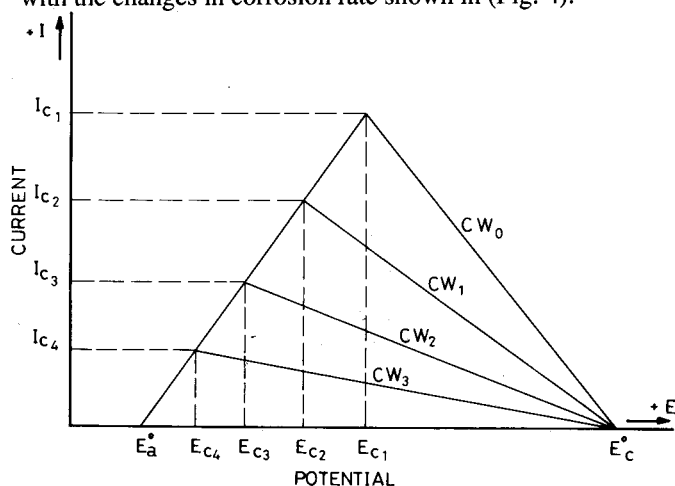


Fig. 7: Evan's diagram showing the effect of plastic deformation on corrosion of cadmium in  $Na_2SO_4$  solution.

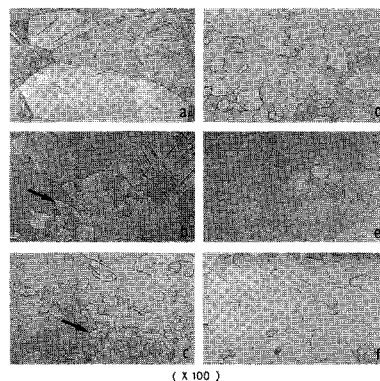


Fig. 8: Microphotographs of cold-worked cadmium specimens, (x 345).

- (a) As-received
- (b) 13% RH
- (c) 30% RH
- (d) 48.1% RH
- (e) 73% RH
- (f) 88.3% RH

Several factors are believed to contribute to the behaviour of cadmium shown in (Fig. 5). Some have opposite effects. Firstly, the dislocation density and point defects change with early deformation until a critical density is attained; beyond which the metal starts to recrystallize grains are free from internal stresses and smaller in size. Recrystallization may start at different locations of the specimen, depending on the local strain and temperature distributions. The volume fraction of the recrystallized grains increases with further deformation until the entire metal recrystallizes and a steady state grain size is obtained at higher values of deformation. Also, deformation is inhomogenous. This leads to variations in microstructure and orientation of the grains that affects the corrosion potential at the different sites of the specimen. Furthermore, there is the possibility of overheating during polishing that accelerates recovery and annihilation. Although

water cooling was applied during polishing, process may occur that allow recovery and recrystallization and hence affect the corrosion behaviour of cadmium.

#### CONCLUSIONS

1. The rate of corrosion of pure cadmium decreases markedly with plastic deformation up to 30-60%, then tends to increase slightly with further deformation.
2. Metallographic examinations indicate that these changes in corrosion rate are due to changes in microstructure and recrystallization of cadmium to a finer grain structure during deformation prior to corrosion testing.
3. Rough surfaces tend to increase corrosion rate for as-received and plastically deformed cadmium. However, this effect tends to diminish at higher values of plastic deformation.
4. Further work is required to fully understand the mechanisms of corrosion in deformed cadmium.

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