The corrosion of zircaloy 2 in anaerobic synthetic cement pore solution

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SUMMARY

Measurements have been made of the corrosion rates of Zircaloy 2 tubes in anaerobic synthetic cement pore solution of pH 12.0-13.8. The samples were tested in the as-received condition by the polarization resistance technique using a Tafal constant of 52 mV/decade and, for all pH values, corrosion rates of $\sim 3.10^{-5}$ A/m^2 (~ 0.03 μm/yr) were determined. These corrosion currents are at the lower limit of the experimental detection range of the technique used.

Some samples were then held at a low electrochemical potential, namely -1850 mV SCE, for several days but this treatment had only a minor effect on the behaviour of the Zircaloy: the value of corrosion rate was increased by a factor of ~ 3 and the free potential was temporarily lowered but drifted towards more positive values after the applied potential was removed.

Attempts were made to remove the passive film from the surface of the samples by electrochemical reduction. For practical, experimental reasons, this was not successful and, instead, the effect of removing the film by scratching the surface was investigated. At both the free potential and at applied cathodic potentials, an anodic current was detected immediately the surface was scratched but, in all cases, the scratched area repassivated within a few seconds and the anodic corrosion current fell accordingly.

Thus, it may be concluded that active corrosion of Zircaloy 2 in anaerobic concrete will not occur and, by comparison with measurements on steel, it is likely that the passive corrosion rates will be even lower in concrete than those measured in the synthetic pore solution.

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INTRODUCTION

The aim of the project was to measure the corrosion rate of Zircaloy 2 in anaerobic synthetic cement pore solutions in order to determine whether or not any significant amount of hydrogen evolution could be expected to occur when Zircaloy tubing is cast in concrete and buried under ground.

The Pourbaix diagram[1] for zirconium shows a potential independent transition from passive to active corrosion at a pH of approximately 13, which is around the normal pH for cement pore solution. The Pourbaix diagram, however, gives the theoretical, thermodynamic limits of passivity and it has been shown experimentally[2] that the passive region can extend up to pH = 14. It is not clear, however, whether the latter experiments were carried out in anaerobic or aerobic conditions. It was decided, therefore, that the corrosion rates should be experimentally determined in anaerobic solutions of 4 different pH values, 2 in the theoretical passive region and 2 in the theoretical active region of the Pourbaix diagram for zirconium. The experiments should be conducted on samples in the "as recieved" condition (ie. already passivated) and on samples which are first de-passivated.

SAMPLE PREPARATION

Ten tubes of Zircaloy 2 of the nominal composition given in Table I, were received from SKBF. The tubes had an outer diameter of 12 mm and a wall thickness of 1.0 mm. From these, samples 100 mm long were cut and a single strand copper wire was spot welded to the inner surface of each as an electrical lead. The Zircaloy tubes were filled with epoxy so that only the outer surface would be exposed to the solution and the weld joint was covered.

TABLE I

Composition of Zircaloy 2 (supplied by ASEA-ATOM)

Sn   1.50%

Fe   0.10%

Cr   0.10%

Ni   0.07%

O   1400 ppm

Remainder: Zr

MEASUREMENTS ON AS-RECIEVED SAMPLES

Four electrochemical cells such as that illustrated in Figure 1, were set up with solutions of sodium hydroxide, potassium hydroxide and calcium hydroxide corresponding to the pH values given in Table II.   Deaerated nitrogen gas was bubbled through the solutions for two days and then polarization resistance measurements were made on each of the samples. Values of corrosion rate were calculated from the polarization resistances using a Tafel constant of 52 mV/decade. This is the value used for passive steel in concrete and agrees reasonably well with the value

estimated from a polarization curve determined for one of the Zircaloy samples. The corrosion rates are given in Table II and are at the lowest limit of our detection range and should be regarded as the maximum values. It could well be that the actual corrosion rates are even lower.

TABLE II

pH	E_R mV SCE	i_{corr} A/m^2
12.0	-401	2.10^{-5}
12.6	-533	3.10^{-5}
13.1	-562	3.10^{-5}
13.8	-473	4.10^{-5}
13.8	-1045	9.10^{-5}

Sample cathodically polarized prior to testing.

Two extra cells with the highest and lowest pH, resp., were also set up and the samples in these were held at the lowest potential possible with the potentiostats, namely -1850 mV SCE, for several days. After approximately two days at this potential, hydrogen bubbles were seen to evolve from the Zircaloy surface. The applied potential was then removed and the following day a polarization resistance measurement was carried out. The free potential of the sample in a solution of pH 12 was very unstable and it was not possible to obtain a corrosion rate for this sample. The value for the sample in solution of pH 13.8 is included in Table II and is slightly higher than the corresponding value for samples which were not previously cathodically polarised. It should be noted that it is not unusual for free potentials to fluctuate in passive metals because there is no

specific free potential corresponding to a particular electro-chemical reaction, and is a problem well known to investigators of stainless steel.

CORROSION MEASUREMENTS ON DE-PASSIVATED SAMPLES

According to the Pourbaix diagram, at pH = 13, an applied potential of -2565 mV SCE is necessary to completely reduce the passive film on zirconium. Several attempts were made to accomplish this. Firstly, the potentiostat was modified so that it could apply -3 V. Secondly, the plastic tubing for the nitrogen gas was replace with copper tubing to remove any possibility of oxygen diffusing into the system. Thirdly, when the sample is polarized cathodically, the counter electrode is automatically polarised anodically and oxygen can evolve from its surface. Therefore, the counter electrode was placed in a tube with an agar gel connection to the electrolyte. Unfortunately, these measures were not successful: the current output at high applied potentials was (a) higher than the limit of the potentiostat and (b) sufficient to heat the electrolyte to a level where the agar gel melted! A commercial potentiostat was then modified to apply -3V and the agar gel was replaced with a glass frit. This too was unsuccessful because the potentiostat suffered the same limitations as the KC one and, secondly, the glass frit dissolved in the pH 13.8 solution, despite the fact that it was of alkali resistant glass. Moreover, the hydrogen evolution was so violent that it was not practical to continue.

Attempts to reduce the passive film electrochemically were, therefore, given up. Instead, we decided to determine whether the metal was stable in the de-passivated state if the passive film were removed mechanically. A glass rod was introduced into the electrochemical cell and nitrogen was bubbled through the system for two days. The free potential was then measured and the potentiostat was set to hold the sample at that potential.

While held at this potential, the current was measured at 450 ms intervals and recorded by computer. At the free potential, the net current is, of course zero. The surface of the Zircaloy was then scratched with glass rod and the resulting current recorded automatically. This experiment was conducted in a solution of pH 13.6 and with two samples, one virgin sample and one which had previously been held at a low potential for many days and had been exposed to violent hydrogen evolution and could be expected to be essentially saturated with hydrogen.

It was expected that if the samples were in a thermodynamically active region of the Pourbaix diagram, active corrosion would continue after the passive film was mechanically removed. On the other hand, if the region of passivity actually extends up the high pH values, the samples should re-passivate fairly rapidly. In fact, the latter behaviour was observed for both samples as illustrated in Figs. 2 and 3. Very high corrosion rates were briefly observed but re-passivation occurred within a few seconds and there was no observable difference in behaviour between the virgin sample and that which had been cathodically polarized. The higher corrosion rates in the latter sample may, to some extent, be attributed to the internal hydrogen contributing to the anodic current, but is predominantly due to the fact that this sample was scratched harder than was the virgin sample.

The free potentials of these samples were rather high, namely around -150 mV SCE, despite the fact that O_2-free nitrogen was continously bubbled through the cells. In order, therefore, to ascertain whether or not repassivation would occur as rapidly at lower potentials, the second sample was first held at -1500 mV SCE for 3 days and, after the applied potential was released, the shift in potential was monitored and is illustrated in Fig. 4. When the potential had become reasonably stable, at -550° mV, the scratching experiment was repeated and the data were found to be similar to the previous ones as shown in Fig. 5.

More and more negative potentials were applied and the scratching experiment repeated at each value of the potential. The data for a potential of -800 mV SCE are given in Fig. 6. At lower potentials, the anodic current peak decreased in height with increasing (ie. more negative) cathodic potential, as would be expected.

SUMMARY AND CONCLUSIONS

1. The corrosion rate of Zircaloy 2 in anaerobic synthetic pore solutions is of the order of 2.10^{-5} A/m^2 and is independent of the pH within the measuring capability of the experiment.

2. Cathodically polarizing the sample for several days prior to measurement lowered the free potential and raised the corrosion rate by a factor of 3-4, presumably because the passive film was thinner. It should be noted that the free potential did not remain at the low value given in Table II but drifted slowly towards more positive values.

3. It did not prove possible to remove the passive film electrochemically.

4. When the passive film was removed mechanically, the scratched area repassivated within a few seconds, demonstrating that the passive film is stable even at pH = 13.6.

5. It may be concluded that active corrosion of Zircaloy 2 in concrete will not occur. Moreover, by comparison with measurements on steel, it is probable that the corrosion rate of Zircaloy 2 in concrete will be significantly lower than that in pore solutions. Consequently, even if the potential were to fall to a negative level, the rate of hydrogen evolution would be correspondingly small.

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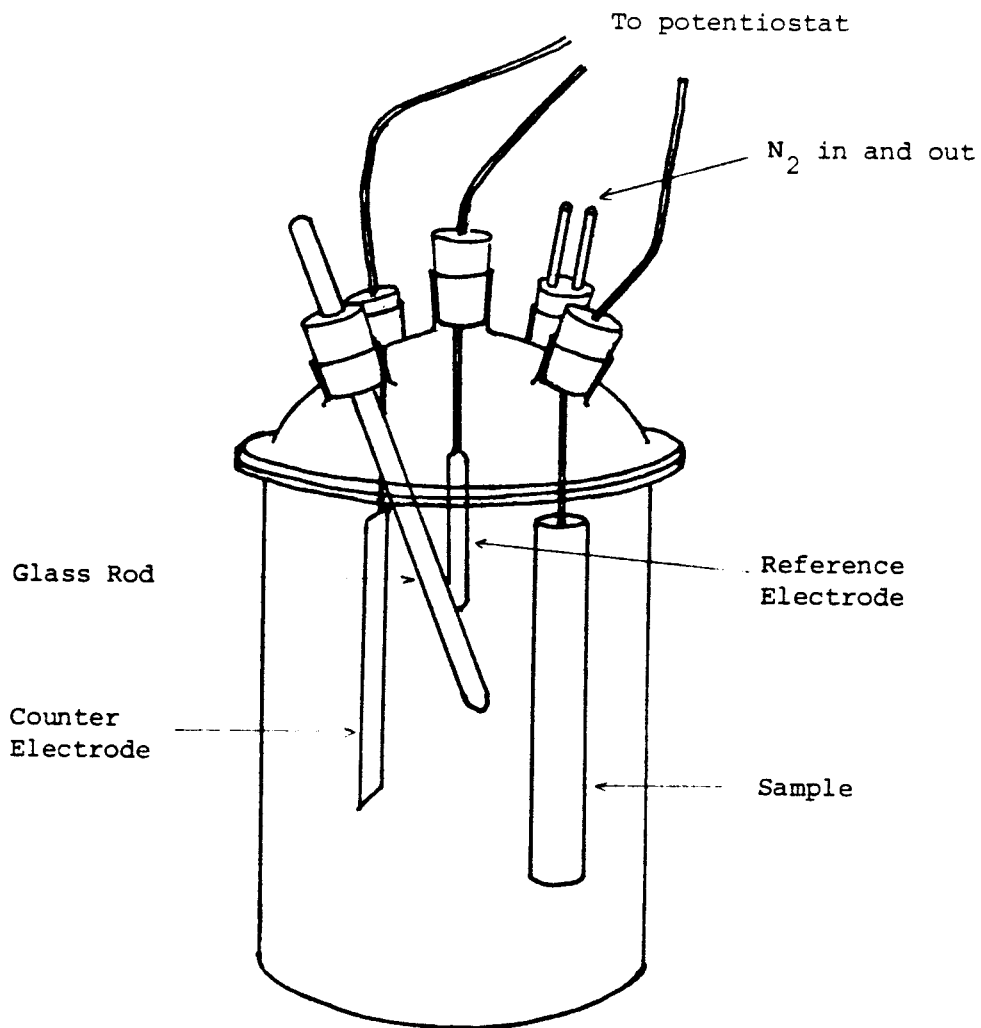
Fig. 1. Experimental arrangement for electrochemical
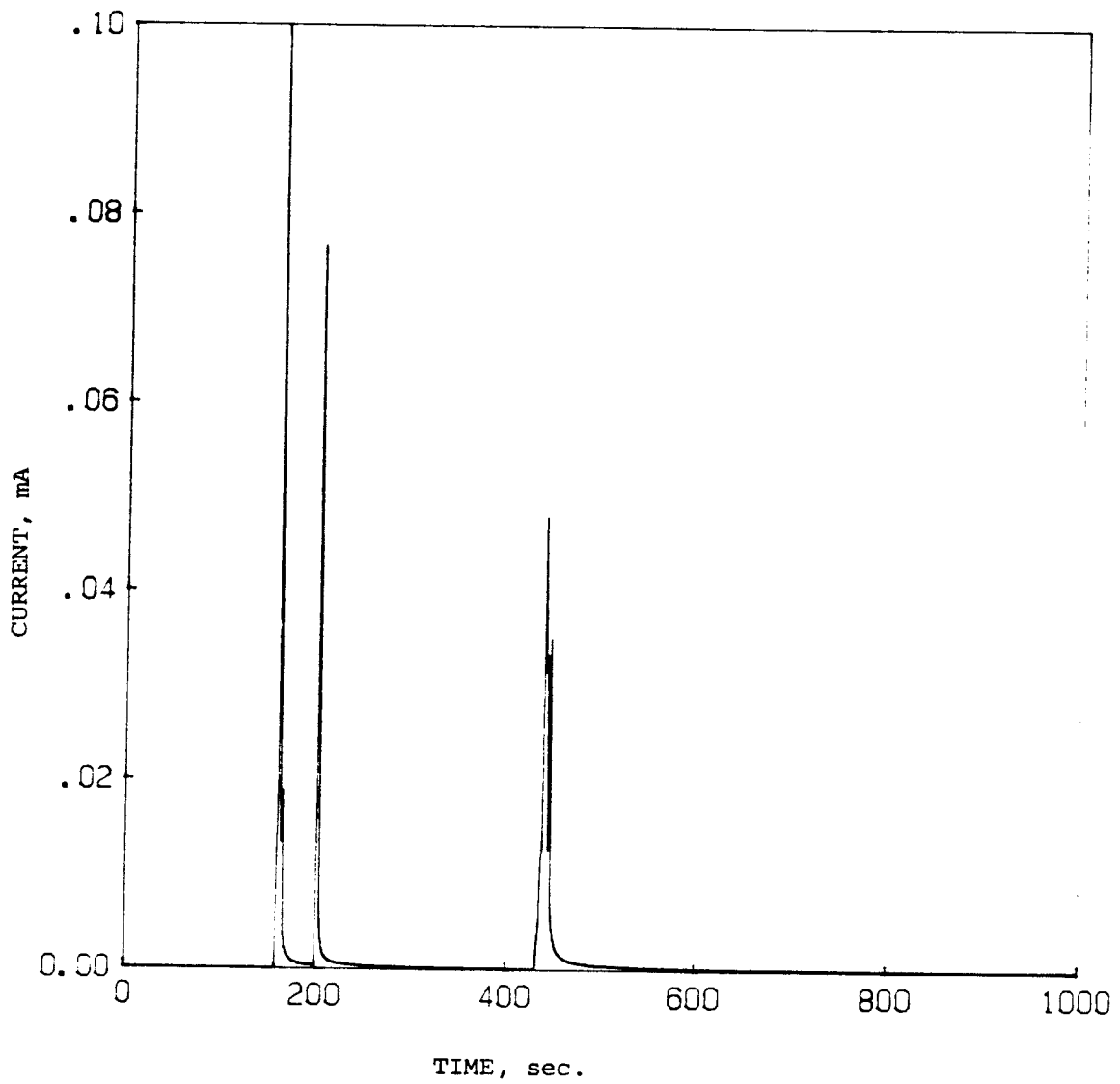Measurements of Zircaloy 2 in synthetic cement
pore solution

Fig. 2. Current peaks resulting from scratching the surface
of a virgin Zircaloy 2 sample potentiostatically held
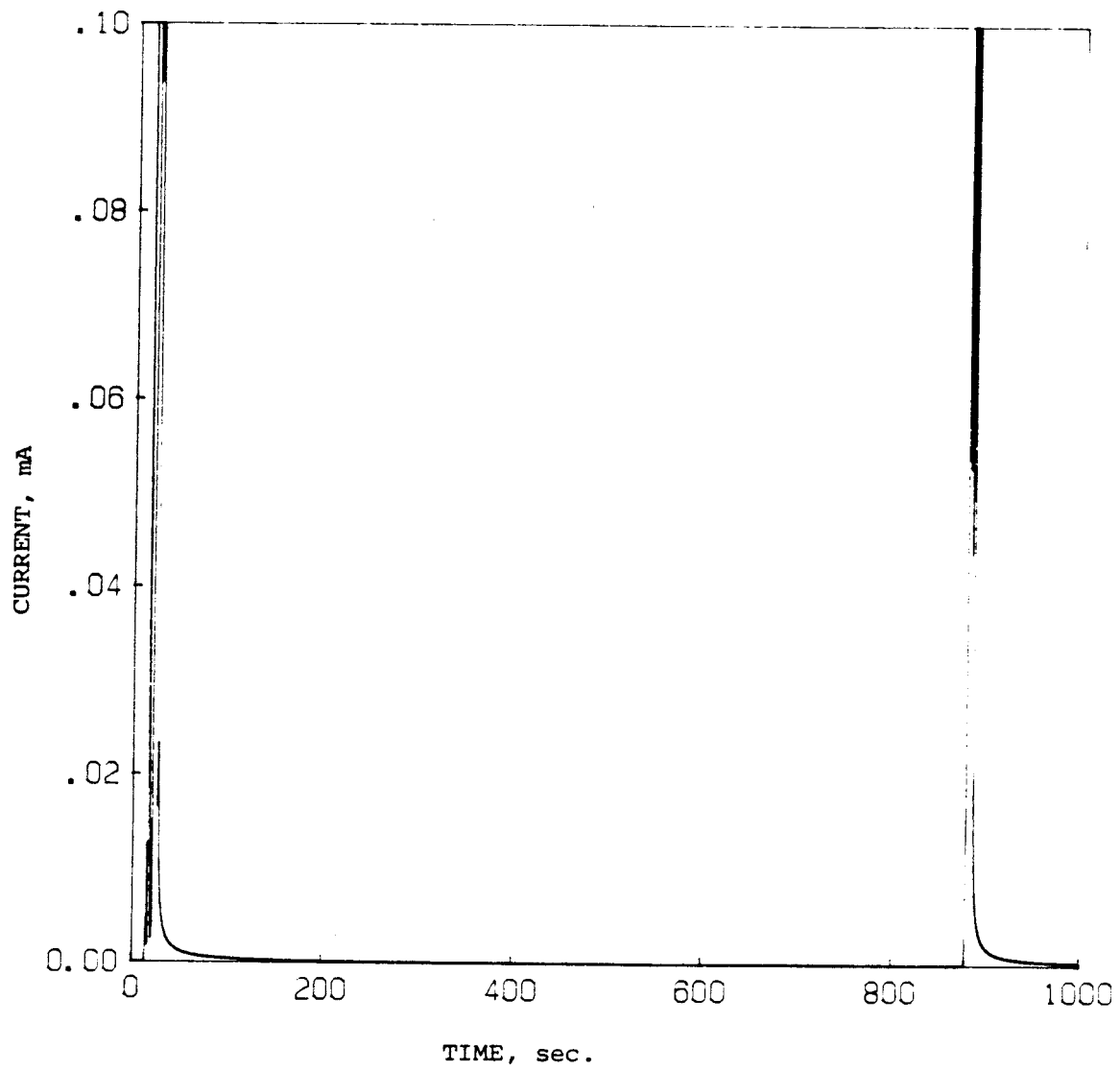at its free potential.

Fig.3. Current peaks resulting from scratching the surface of
a Zircaloy 2 sample which had previously been cathodically
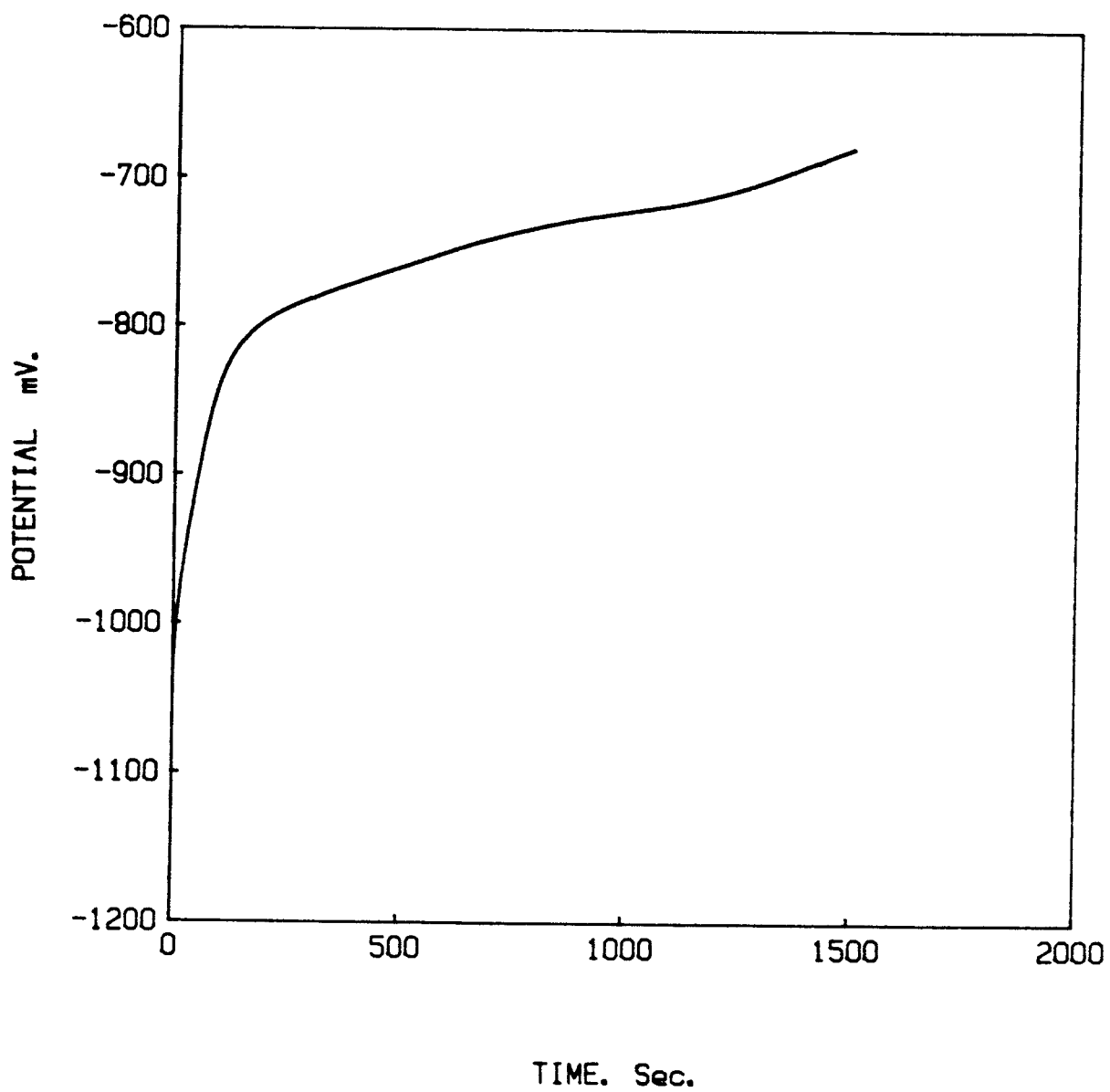polarized and, thereby, exposed to hydrogen.

Fig. 4. The potential (vs. SCE) of the same sample as that represented in Fig. 3, measured as a function of time after the applied potential of -1500 mV SCE was removed.
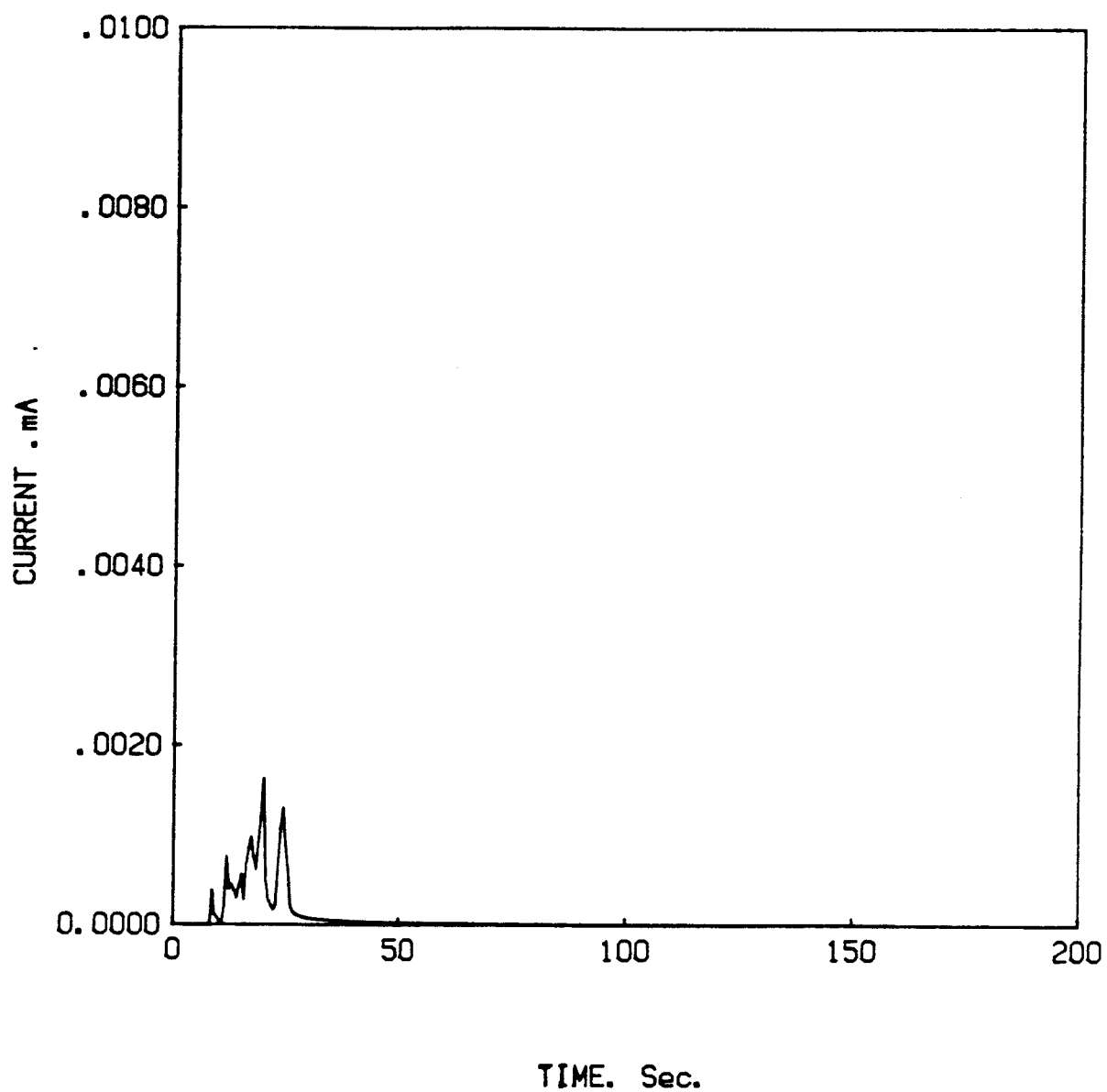
Fig. 5. Current peaks resulting from scratching the surface of the Zircaloy 2 sample represented in the two previous figures. The sample was held at its free potential of -550 mV SCE. Note that the ordinate scale is different from those in Figs. 2 and 3.
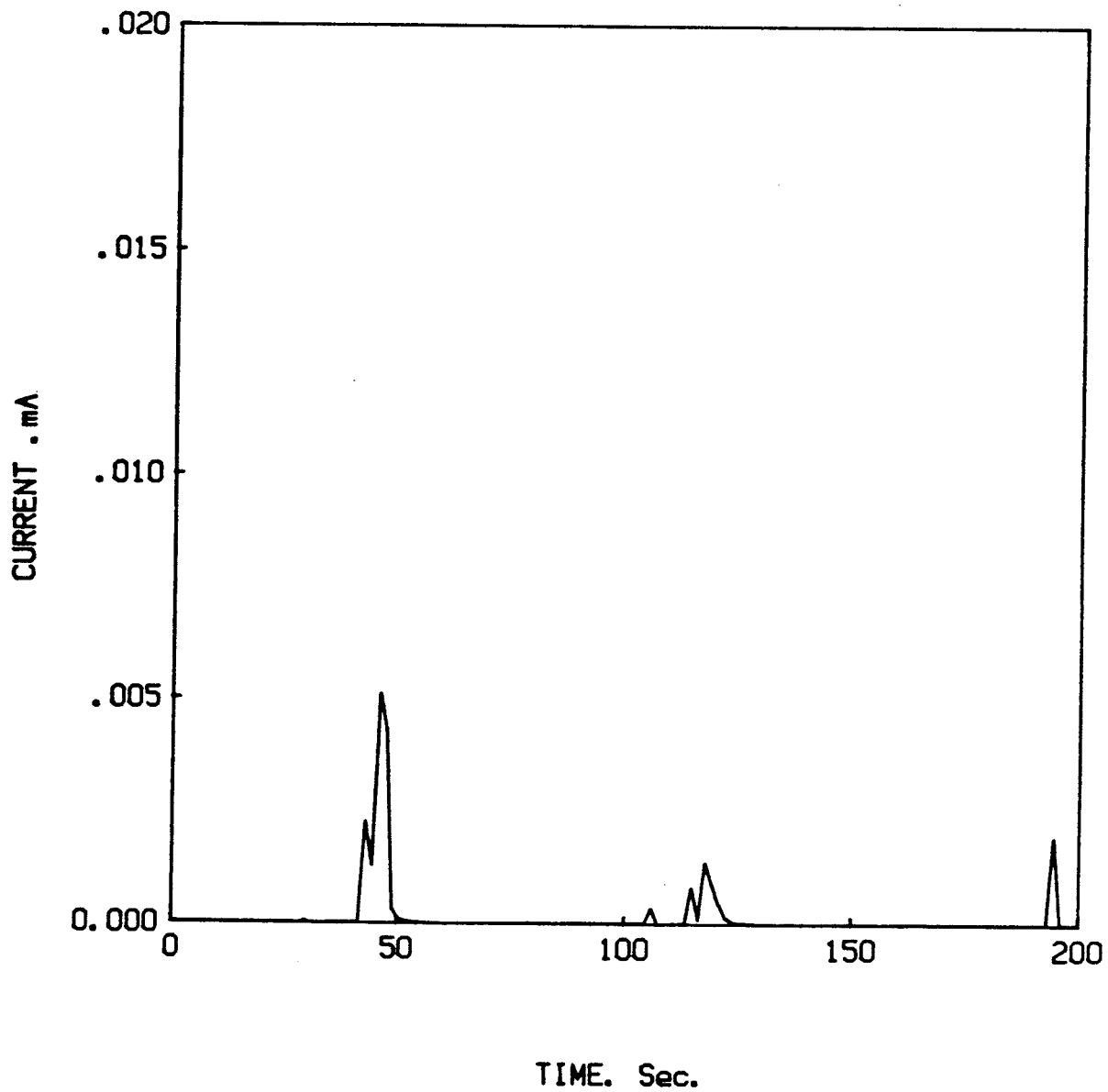
Fig. 6. Current peaks resulting from scratching the surface of the Zircaloy 2 sample held at a potential of -800 mV SCE.

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