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Investigation of the stress corrosion cracking of pure copper

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Newcastle upon Tyne, Great Britain, April 1983

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INVESTIGATION OF THE STRESS CORROSION RESISTANCE OF PURE COPPER

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GENERAL INTRODUCTION

The Swedish KBS project is concerned with the long term disposal of unprocessed radioactive waste. In order to comply with safety regulations, the waste would be encapsulated and the canisters placed in vertically boreholes, drilled from horizontal tunnels in rock 500m below the surface. It is proposed that the space around the canisters would be filled with a buffer mass consisting of compacted bentonite. The latter is intended to inhibit penetration of ground water to the container and to act as a chemical buffer (regulating the pH of the water to between 8.5 and 9), as well as providing a soft, pliable bed sufficient to support the canister.

Although a variety of container materials have been considered, the safety requirement has necessitated a conservative approach to the disposal of the early stocks of waste and therefore a thick copper container has been specified. Copper is a noble metal that is not inherently reactive and its general rate of corrosion in water, even in the absence of corrosion films or insoluble corrosion products, is usually low. The thickness of container being specified - 200mm thick - should be ample to cope with the maximum rate of corrosive attack anticipated. Even allowing for excessive pitting the maximum penetration should be no greater than 60mm in 10^6 years.

Calculation of rates of penetration on a basis of general corrosion, even with due allowance for any pitting that might be expected, would of course become meaningless if there were any likelihood of stress corrosion cracking in the type of environment surrounding canisters. It was therefore essential to obtain information about the susceptibility of copper to stress corrosion cracking in a suitable range of environments. The only method of obtaining such information from a short-term test is by means of slow strain rate testing in tension.

The normal environment that the canisters would be likely to meet in the rock boreholes would correspond to low salinity ground water as specified by an earlier reference group.(1) This was therefore the basis environment chosen for the tests to assess stress corrosion susceptibility of both oxygen-free high conductivity (OFHC) and phosphorus-deoxidised (PDO) copper. The pH of the environment should be in the range 8.0 to 8.5.

Since the maximum temperature expected at the copper-bentonite interface was 80°C, it was decided that the majority of tests at ambient temperature should be backed-up by selected tests at the higher temperature. Although it might be expected that any corrosion of the container was proceeding under de-aerated conditions, because of the slow percolation of water through the ground and the restricted permeation through the bentonite surrounding the canisters, it was decided that susceptibility should be assessed under both aerobic and anaerobic conditions.

There were two main reasons for deviating from the basis ground water in assessing stress corrosion behaviour:

(1) the possibility of accidental contamination of the boreholes by nitrite, as a result of prior blasting, and

(2) concentration of certain anions in the ground water would be possible due to evaporation effects from the surface of the container which could attain a temperature of 80°C.

A further variable that was considered was that of potential, since deviations from the normal free corrosion potential in a particular environment could be introduced by changes in surface condition.

Although the majority of slow strain rate tests were conducted at a nominal strain rate in the region of 2.6×10^{-6}/s, a number of tests involved a faster strain rate of 1.7×10^{-5}/s, since it is known that stress corrosion effects may depend on the particular strain rate involved. It was confidently felt that the absence of significant effects at these strain rates would be a reliable indication of lack of susceptibility to stress corrosion.

Solutions containing sodium nitrite were expected, from other work on copper(2) and 70/30 brass, (3) to promote stress corrosion failure and the work carried out was therefore intended to define a safe upper limit for nitrite contamination.

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INVESTIGATION OF THE STRESS CORROSION RESISTANCE OF PURE COPPER

by

L.A. BENJAMIN, D. HARDIE AND R.N. PARKINS

FIRST PROGRESS REPORT

MAY 1982

INVESTIGATION OF THE STRESS CORROSION RESISTANCE OF PURE COPPER

INTRODUCTION

It is proposed to use pure copper as a material for canisters for the storage of nuclear waste in deep bore holes. In order to assess the likelihood of stress corrosion cracking in the ground water of the bore holes, a programme of slow strain rate testing of the copper in various environments is being carried out.

MATERIAL

So far, only OFHC copper has been used. It was supplied in the form of approximately 4.8 mm diameter rod, from which tensile specimens having a 12.7 mm gauge length of approximately 2.5 mm diameter were machined. When examined metallographically, the copper was found to have an equiaxed grain structure with extensive twinning. The average grain size in the cross section was approximately 44 μm and in the longitudinal section, approximately 77 μm. The respective Vickers hardness, determined with a 5 kg load, were approximately 94 and 74. In a slow tensile test in air at a strain rate of 2.88×10^{-6}/s (Figure 1) the material showed a 0.2% proof stress of ~80 MPa, a UTS of 222 MPa, a plastic elongation to failure of 58.7%, and a reduction in cross-sectional area at fracture of 87%.

METHOD

The test method used has become well established at Newcastle. Hard frame testing machines giving slow tensile strain rates between 2.3 and 2.9×10^{-6}/s were generally employed and minor variations are not thought to be significant. Potentials were measured with respect to a saturated calomel electrode. All the tensile tests so far carried out have been done at room temperature using normally aerated (air saturated) solutions, and potentiokinetic measurements were carried out under the same conditions. The environments examined to date include artificial ground water and a wide range of concentrations of sodium nitrite.

RESULTS

Potentiokinetic sweeps from -200 mV to +300 mV in the artificial ground water at 1 V/min, and at 10 mV/min, resulted in curves that closely followed each other (Figure 2), except where they crossed over at about +75 mV. Substituting 0.1 M or 1.0 M $NaNO_2$ for ground water gave similar results, which do not indicate a specific range in which stress corrosion cracking might be predicted, as happened for a pipeline steel in a carbonate-bicarbonate environment(1). Such predictability requires a high anodic activity during a fast potential sweep reducing to a low value at a slow sweep rate that simulates filmed conditions. These conditions are likely to maintain a sharp stress corrosion crack. The current densities for the ground water are also rather low; the highest value in this potential range being 1 mA/cm^2. The maximum current densities for the 0.1 M and 1.0 M $NaNO_2$ solutions were both over 10 times larger and occurred at +300 mV, where it is thought that general dissolution is occurring.

Slow strain rate tests in the ground water have been done at intervals from -50 mV to +300 mV, including the free corrosion potential. The latter varied sporadically in the range -56 mV to + 8 mV during the test. Failures were invariably ductile and no stress corrosion cracks have been observed.

The reduction in cross-sectional area at fracture was always greater than 80% (Figure 3), i.e. quite similar to the 87% obtained when testing in air.

It was noticeable that raising the potential to high positive values immediately produced bubbling in the cell, and a blue deposit was gradually formed in the solution as the test proceeded. These processes caused an increase in pH from the initial value of 8.0-8.5, to over 10 in certain tests. This is thought to be attributable to the reaction:

$$Cu + 2H_2O \rightarrow Cu(OH)_2 + H_2^{*} \qquad (1)$$

The hydrogen bubbles off and dissociation of the $Cu(OH)_2$ to give free OH^- ions causes an increase in pH. With an applied potential of +250 mV, the pH rose from 8.3 to 10.2. The filtrate from the cell solution after the test was subjected to an X-ray analysis, which confirmed that the blue deposit was mainly $Cu(OH)_2$.

Nominal stress-elongation curves were plotted for all slow strain rate tests conducted in the synthetic ground water and all were similar in shape (Figure 4). Since both the maximum stress and the plastic elongation to failure were slightly less than the values observed in air, it could be argued that the environment has a detrimental effect. It was also decided to "combine" the stress and elongation measurements by using the area under the stress-elongation curve, and so compare the work done per unit volume. For the test in air, this was found to be $104 \times 10^6 J/m^3$ (e.g. $10^6 N/m^2 \times 1\%$ elongation $= 10^4 N/m^2 = 10^4 J/m^3$). When the work done per unit volume in a particular environment is expressed as a fraction of the value obtained in air, there is more variation than was indicated by the reduction in area at failure, but a high degree of ductility was still shown (Table 1).

* The H_2 evolution occurs at the Pt counter electrode

TABLE 1.

Potential (mV)	% Reduction in area	Fracture energy as a fraction of that involved in air
-50	87.3	0.77
+15	87.4	0.86
+50	85.8	0.87
+100	88.4	0.80
+150	87.0	0.82
+200	92.3	0.83
+250	90.9	0.70
+300	84.8	0.76
Free Corrosion Potential	90.0	0.88
in Air	86.9	1.00

Tests have also been conducted in sodium nitrite solutions of various concentrations, in an attempt to assess the critical amount needed for embrittlement. Initially, tests were done in 1M $NaNO_2$, simply because this environment had been reported to give transgranular stress corrosion cracking in pure copper(2) and in 70/30 brass(3). More dilute solutions were then studied. Except with 0.05 M solution, where only two tests have been conducted to date, six potentials were investigated for each concentration of solution: -100 mV, -50 mV, 0 mV, +50 mV, +100 mV and the free corrosion potential. As in the ground water test, the latter fluctuated with time in each case. The effect of the 1M, 0.6 M, 0.3 M and 0.1 M solution on the stress-elongation curves can be assessed by comparing Figures 5, 6 7 and 8. In the more concentrated solutions the potential reduces both the maximum stress and the elongation to failure.

The areas under the curves (the fracture energies) were again measured and compared with that observed in air (Figure 9). There is a general trend towards greater embrittlement as the concentration of solution or the potential is increased, but the effect is irregular and at no potential in this range does the fracture energy continuously fall off with increasing concentration. The measured reductionsin area at fracture show a similar general trend towards embrittlement with increasing concentration and potential (Figure 10).

In the sodium nitrite solutions, as the concentration and/or potential was increased, the specimen became covered with a shiny steel-grey film that became very thick, and dull green in colour, at the highest concentration and potentials. Unlike the ground water tests, there was usually a rise in pH during the test of between 0.5 and 1.0, even at low concentrations and negative potentials. At +100 mV the final pH was always >10, from an initial value of about 7.5. At +100 mV there was also vigorous agitation in the solution as soon as the potential was applied and there was bubbling at both the platinum electrode and the specimen. Filming was immediate and a green deposit was formed in the solution. For the test carried out in 0.6 M $NaNO_2$, the solution was filtered and X-ray analysis showed that the deposit was mainly CuO. Perhaps this is formed by the reactions:

$$Cu + 2H_2O \rightarrow Cu(OH)_2 + H_2^{*} \qquad (1)$$

and $$2Cu(OH)_2 \twoheadrightarrow 2CuO + 2OH^- + H_2^{*} \qquad (2)$$

* The H_2 evolution occurs at the Pt counter electrode

It has proved difficult to measure crack velocities, but some estimates can be made by examining the fracture surface in the SEM (Figure 11) and dividing the extent of stress corrosion cracking by the time to failure. At the high potentials, chemical attack was so vigorous that the crack length was effectively the specimen radius. In these cases the times to failure were ~24 hours and the crack velocity = 2.5/(2 x 24 x 3600) = 1.4×10^{-5} mm/s. In 1M nitrite at the free corrosion potential, CV = 7×10^{-6} mm/s, and in 0.1 M at the free corrosion potential, CV = 3×10^{-6} mm/s. At higher magnification it could be seen that fracture in the stress corrosion region was transgranular (Figure 12).

In those specimens that showed a significantly lower reduction of cross-sectional area at failure, compared to that in air, there was multiple cracking along the gauge length. This multiple cracking became more severe as the reduction in area became less.

CONCLUSIONS

1. Stress corrosion cracking of OFHC copper in the ground water under the conditions tested appears unlikely, but there is a small reduction in the fracture energy.
2. Depending on the precise solution concentration and potential, there is moderate to severe stress corrosion cracking, in the presence of sodium nitrite.

FUTURE WORK

Future work will extend the range of testing to consideration of other factors that might influence cracking and tests will be carried out:

(1) at still lower sodium nitrite concentrations, to establish a safe limit below which cracking does not occur,

(2) with PDO copper,

(3) at 80°C,

(4) with additions of CO_3^{2-} , SO_4^{2-} and Cl^- ions

(5) in deaerated conditions,

and (6) at different strain rates.

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2. S.P. Pednekar, A.K. Agrawal, H.E. Chaung and R.W. Staehle, J. Electrochemical Society, Accelerated brief communications, April 1979, p.701.
3. S.J. Guest, N.J.H. Holroyd and R.N. Parkins, University of Newcastle upon Tyne, Progress Report "Environmental aspects of stress corrosion cracking of brasses", February 1981

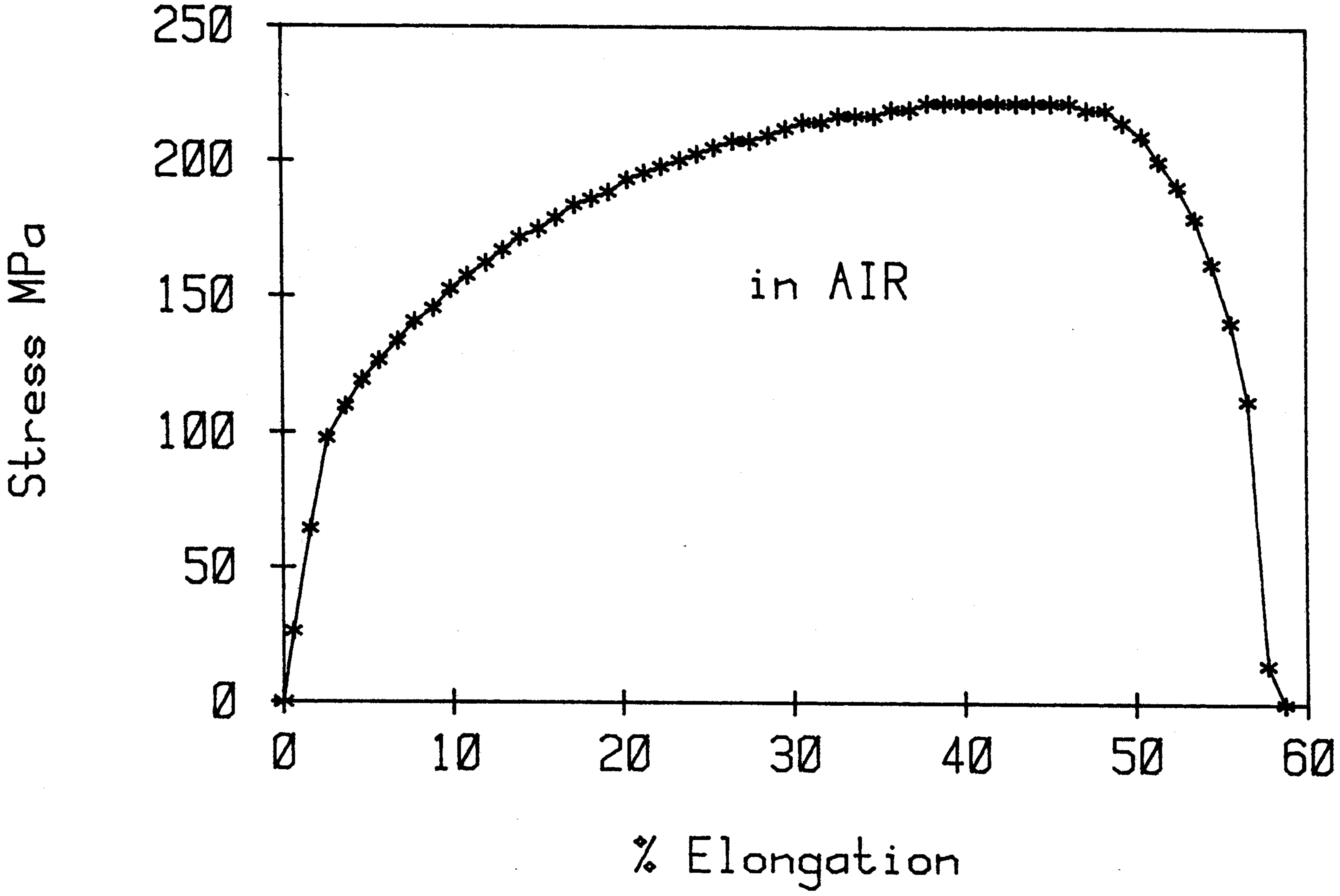

Figure 1. Nominal stress - % elongation for OFHC copper in air.

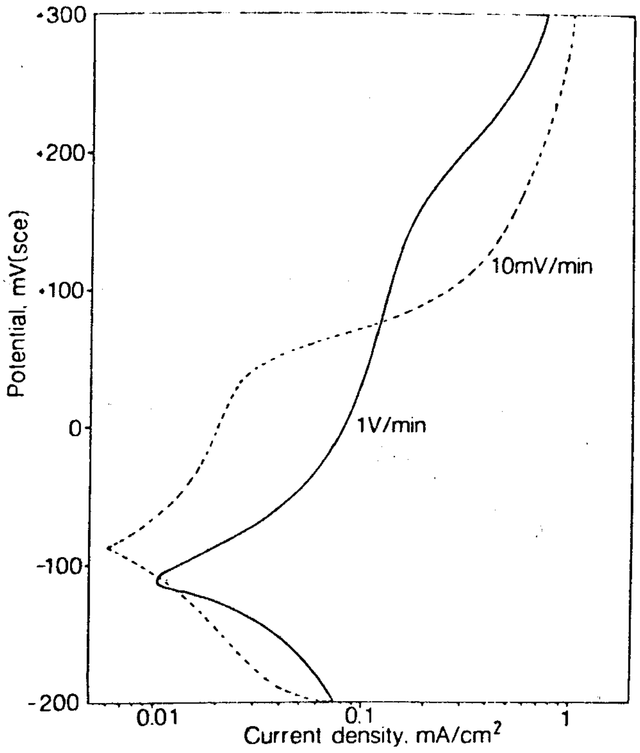

Figure 2. Fast and slow sweep rate polarization curves for OFHC in artificial ground water.

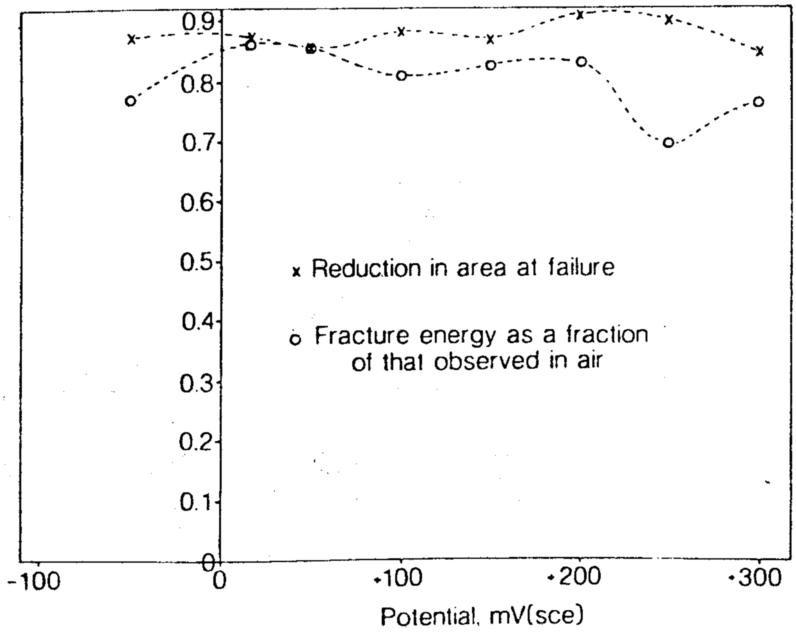

Figure 3. Variation of reduction in area and fracture energy with potential for tests in artificial ground water.

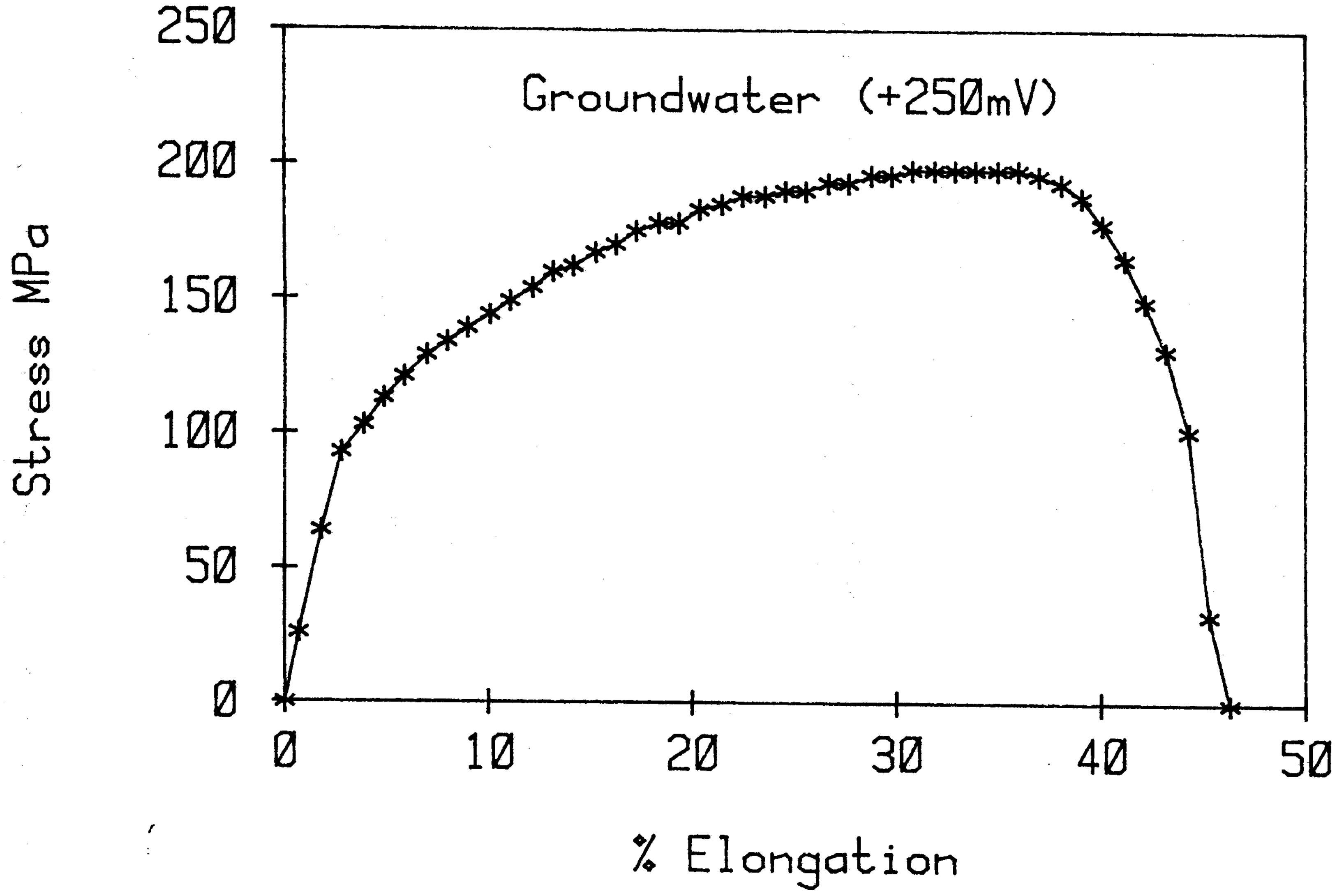

Figure 4. Typical stress - % elongation curve obtained in the ground water (at +250 mV).

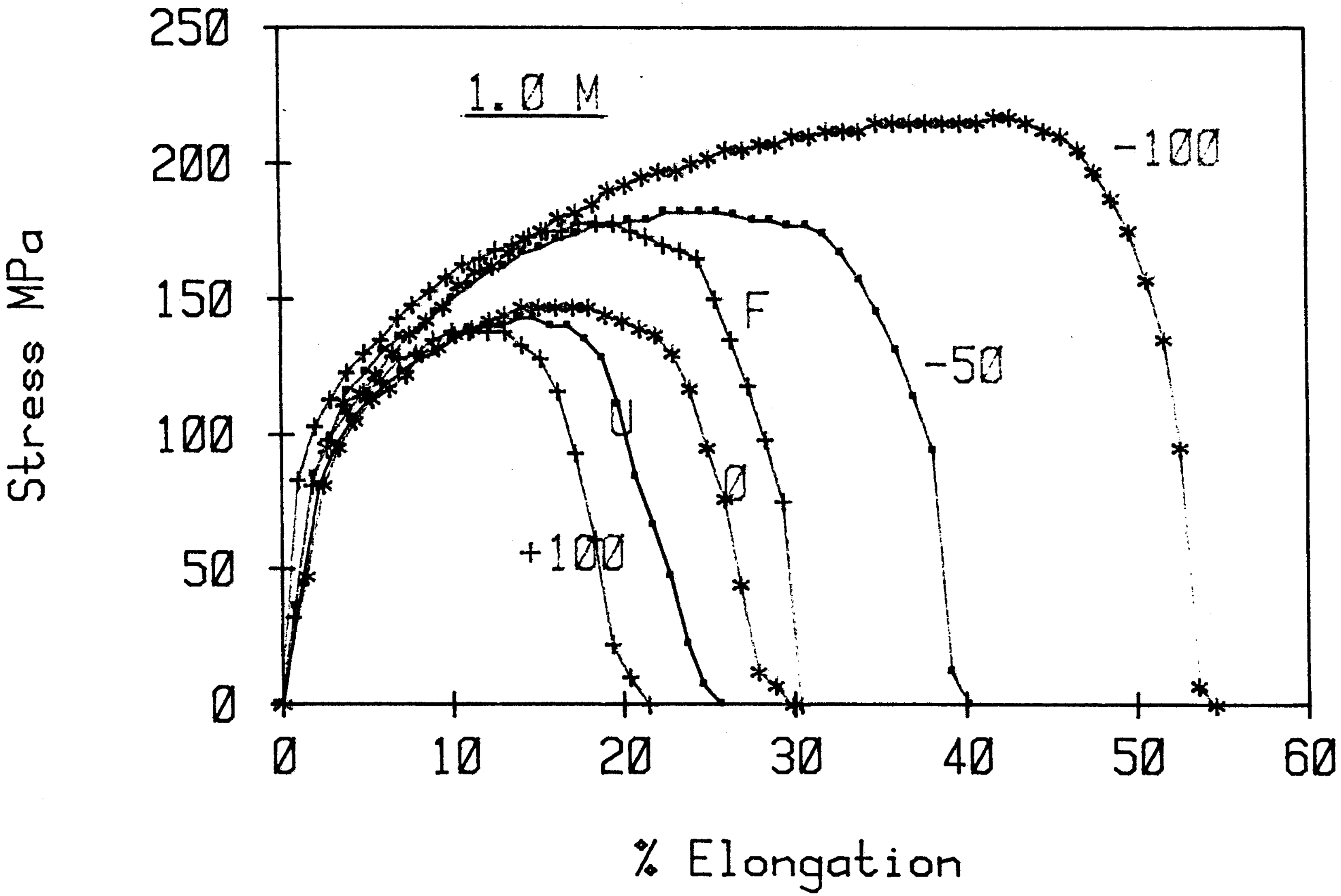

Figure 5. Stress-elongation curves for tests in 1.0 M $NaNO_2$. Figures on curves indicate applied potential in mV (sce); F = free corrosion potential, and U = +50 mV

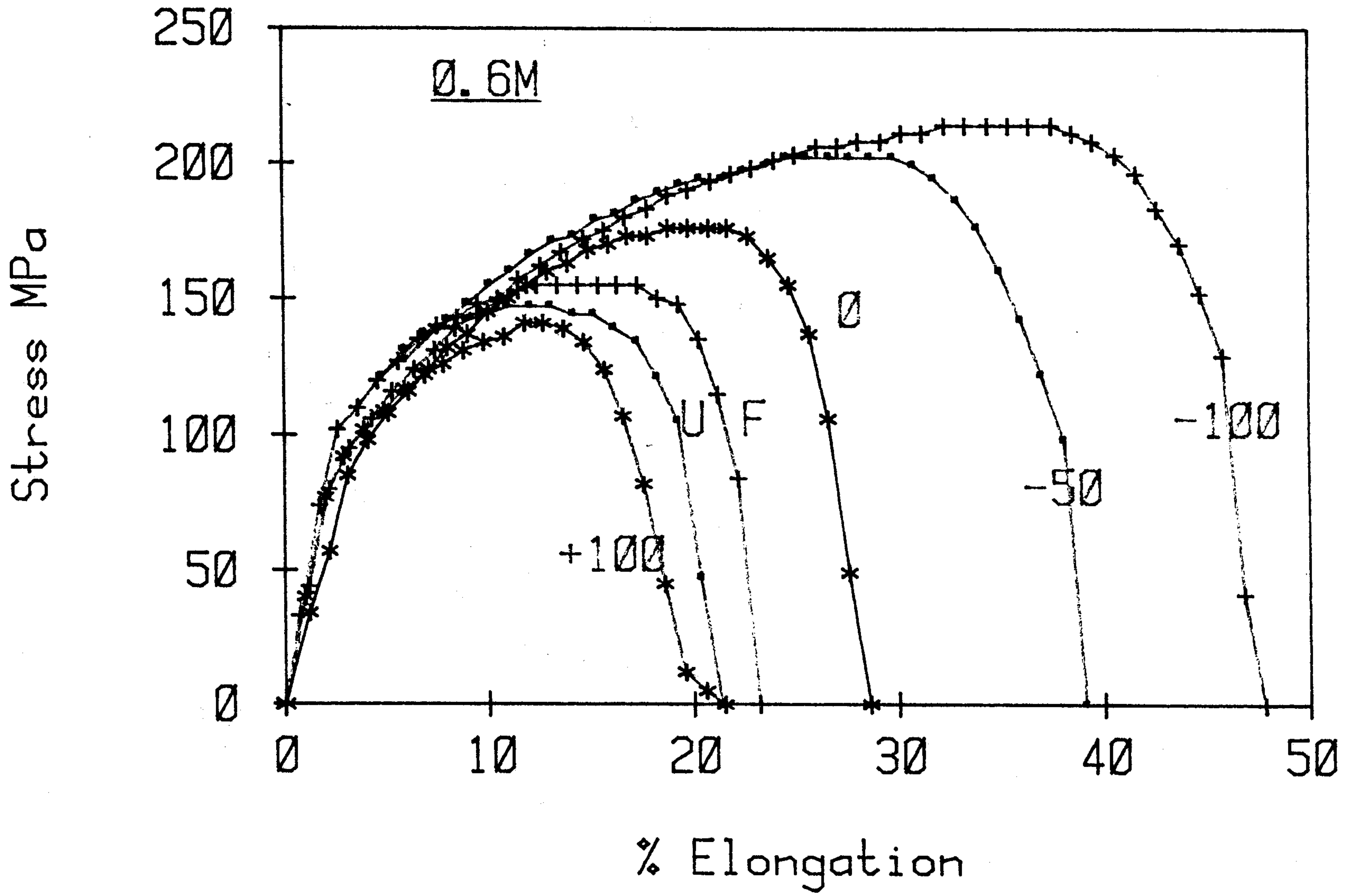

Figure 6. Stress-elongation curves for tests in 0.6 M $NaNO_2$. Figures on curves indicate applied potential in mV (sce); F = free corrosion potential, and U = +50 mV.

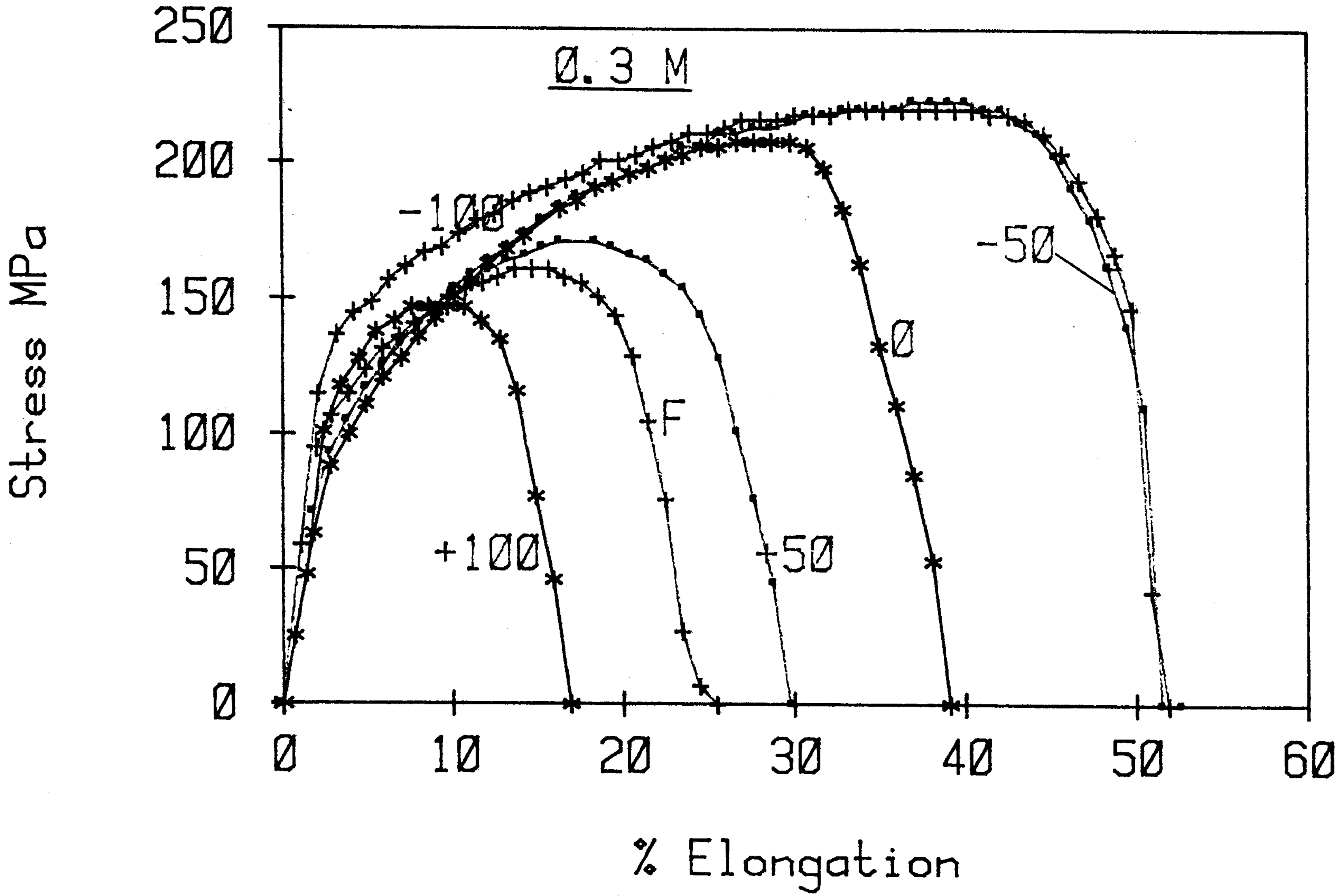

Figure 7. Stress-elongation curves for tests in 0.3 M $NaNO_2$. Figures on curves indicate applied potential in mV (sce); F = free corrosion potential.

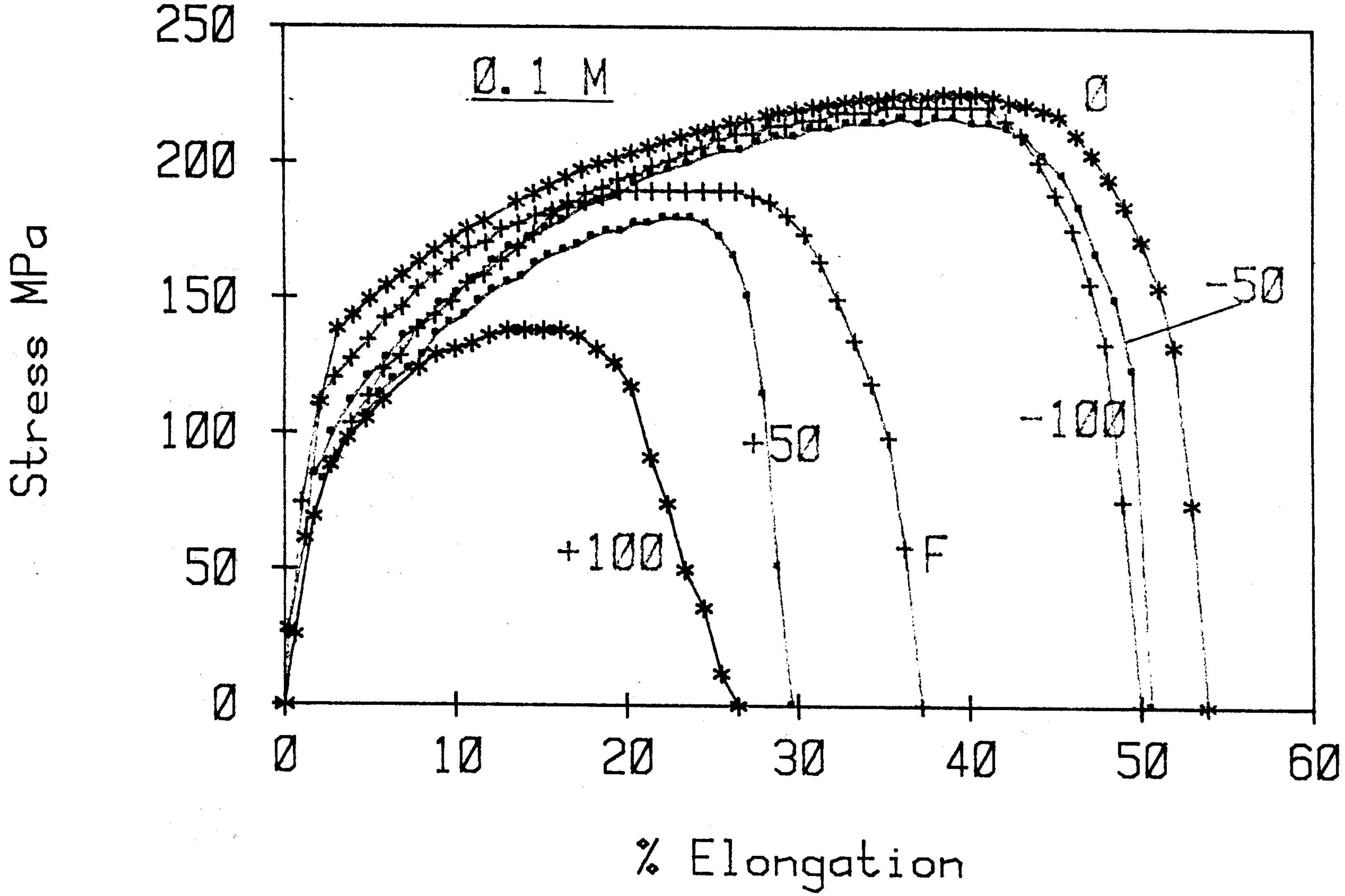

Figure 8. Stress-elongation curves for tests in 0.1 M $NaNO_2$. Figures on curves indicate applied potential in mV (sce); F = free corrosion potential.

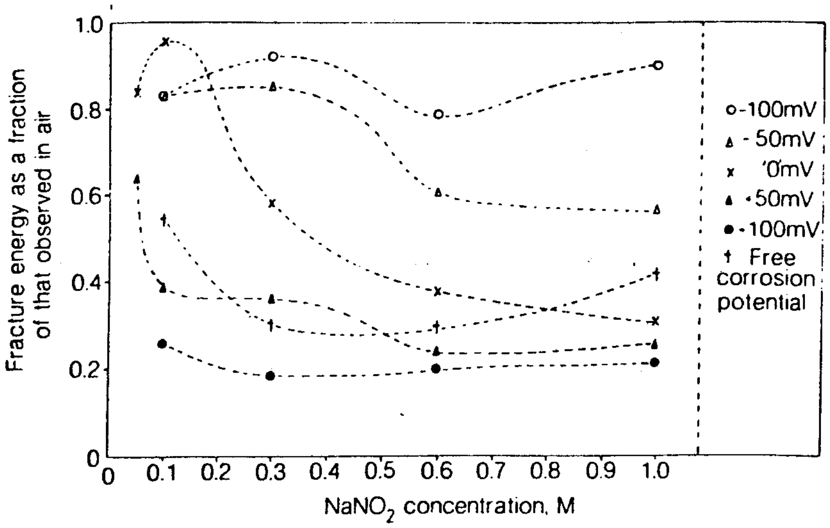

Figure 9. Variation of fracture energy with sodium nitrite concentration and potential.

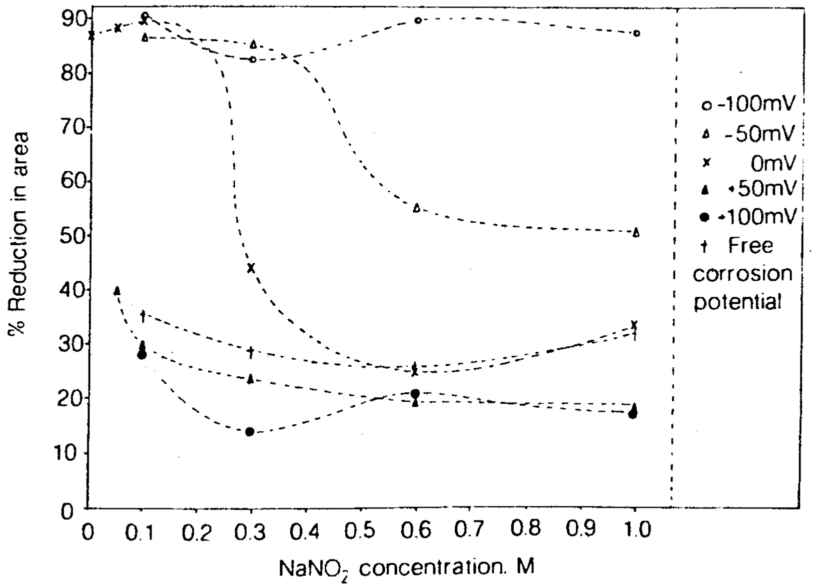

Figure 10. Variation of reduction in area with sodium nitrite concentration and potential.

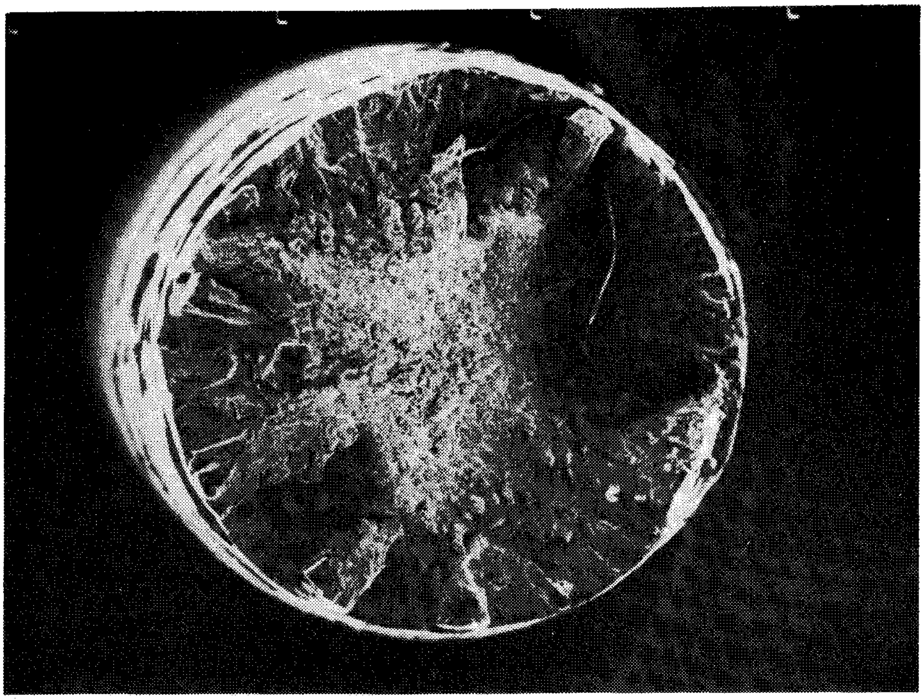

Figure 11. Fracture surface of specimen tested in 1.0 M $NaNO_2$ at the free corrosion potential. x35

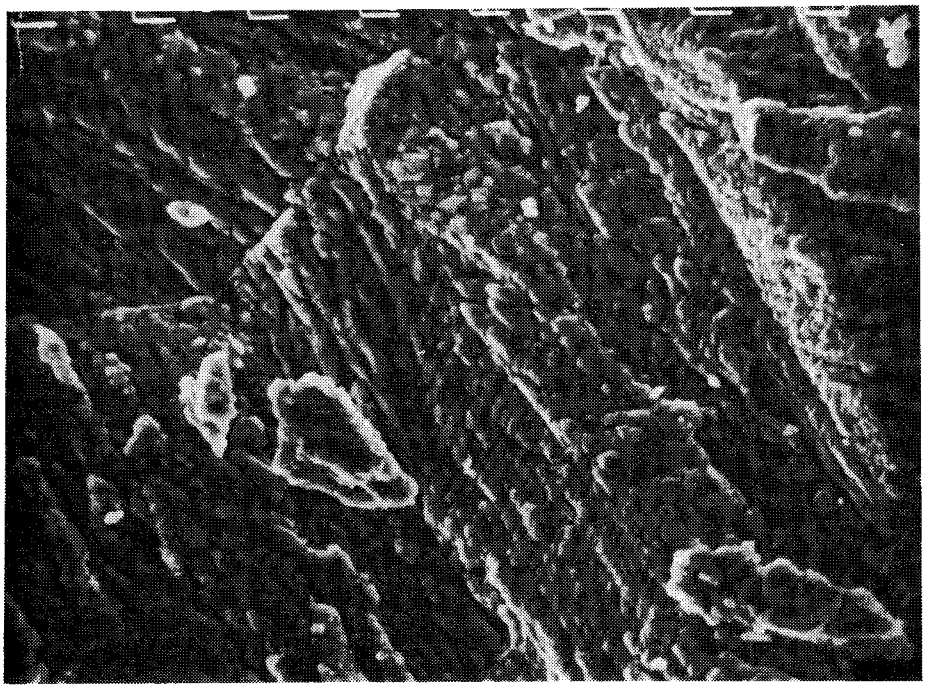

Figure 12. Transgranular stress corrosion fracture of specimen tested in 0.6 M $NaNO_2$, at 0 mV. x1500

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SECOND PROGRESS REPORT

OCTOBER 1982

1. INTRODUCTION

In the first progress report(1) the results of testing Oxygen-Free High Conductivity (OFHC) copper at strain rates between 2.9 x $10^{-6}s^{-1}$ and 2.3 x $10^{-6}s^{-1}$, at room temperature in air saturated solutions of ground water and in sodium nitrite solutions of concentrations between 1.0 and 0.05M, were described. This second report covers similar tests on Phosphorous De-oxidised (PDO) copper, and an attempt to determine a safe limit for sodium nitrite concentration below which stress corrosion cracking does not occur. Further tests have also been performed on both OFHC and PDO copper at a faster strain rate (1.7 x $10^{-5}s^{-1}$) and in de-aerated conditions, with a few tests at 80°C.

2. EXPERIMENTAL TECHNIQUE

2.1. Materials

The physical properties of OFHC copper have already been described(1). The PDO copper was similarly supplied in the form of approximately 4.8mm diameter rod, from which tensile specimens having a 12.7mm gauge length of approximately 2.5mm diameter were machined. In a slow strain rate test in air at a strain rate of 2.9 x $10^{-6}s^{-1}$ (Fig 1) the PDO copper showed a 0.2% proof stress of ≈85MPa, a UTS of 201MPa, a plastic elongation to failure of 56.9% and a reduction in cross-sectional area at failure of 84.4%. When examined metallographically, the PDO copper was found to have an equiaxed grain structure with extensive twinning. The average grain size in the cross-section was 46 μm and in the longitudinal section, 44 μm. The respective Vickers hardnesses, determined with a 5kg load, were approximately 85 and 64.

2.2 Test Methods

Tests at the slow strain rates were conducted in hard frame testing machines similar to those previously described, giving tensile strain rates of either between 2.3 and 2.9 x $10^{-6}s^{-1}$, or 1.7 x $10^{-5}s^{-1}$. Before testing, the specimens were polished to a 5/0 grit finish and degreased with an organic solvent. All potentials were measured with respect to a saturated calomel electrode (sce). Potentiokinetic measurements were carried out at room temperature using normally aerated (air saturated) solutions. Tests under deaerated conditions involved deaeration of the environment before the start of tests and continuously during tests by bubbling nitrogen through the specimen cell. For tests at 80°C, the test cell was heated by a coil wrapped around it. Again, the environments examined to date included the artificial ground water previously prepared and a wide range of concentrations of sodium nitrite. The potentials during free corrosion tests were monitored with a sensitive (± 0.01mV) measuring device using screened leads connected to the specimen and the calomel electrode. Crack velocities were estimated by measuring the longest observed crack in a longitudinal section of the specimen gauge length when mounted metallographically, and dividing this by the test time.

3. RESULTS

3.1. Oxygen-Free High Conductivity (OFHC) Copper

3.1.1 Tests at room temperature in aerated solutions of sodium nitrite

The observation of stress corrosion cracking in OFHC copper at a strain rate of ≃ 2.6 x $10^{-6}s^{-1}$ at room temperature in air saturated solutions of sodium nitrite of concentrations down to 0.1M has already been reported(1). Further tests were done under similar conditions but using 0.05M and 0.025M solutions of sodium nitrite. Five tests were done for each of these solutions: at -50, 0, +50 and +100mV and at the free corrosion potential. As before, the reductions in cross-sectional area at failure and the fracture energy (the area under the nominal stress-elongation curve) were measured.

With 0.05M $NaNO_2$, testing at +100mV resulted in a low reduction in area and a low fracture energy, but in the previous progress report(1) it was pointed out that environmental effects were significantly more severe at +100mV than at less anodic potentials, in solutions containing sodium nitrite. The test at +50mV showed some loss in ductility whereas all other potentials tested showed no such loss (UTS always above 210MPa and more than 45% elongation to failure). The reduction in area at failure, together with the fracture energies as a function of that obtained in a test in air ($104MJm^{-3}$(1)) are listed in Table I.

TABLE I. OFHC copper tested in 0.05 and 0.025 M sodium nitrite.

Potential mV (sce)	% Reduction in area at fracture		Fracture energy as a function of that observed in air	
	0.05 M	0.025 M	0.05 M	0.025 M
-50	91.7	88.2	1.00	0.82
0	88.2	88.4	0.84	0.79
+50	39.1	90.1	0.64	0.74
+100	15.7	22.2	0.24	0.28
FCP	89.0	75.5	0.86	0.86

In the more dilute 0.025M sodium nitrite solution, maximum embrittlement was again observed at +100mV, but the loss of ductility was less than that obtained with the 0.05M solution. The other four tests gave reductions in area above 75% and fracture energy ratios above 0.74, with UTS values above 215MPa and >44% elongation to failure (Table I).

A principle aim of this work is to identify a safe upper limit for sodium nitrite concentration, below which stress corrosion cracking does not occur. Results to date indicate that in the range -100mV to +100mV, cracking is most likely at +100mV and therefore further tests have been conducted at this potential using still lower nitrite concentrations of 0.0125M and 0.00375M, i.e. down to 259mg/litre (Table II)

TABLE II. OFHC at +100 mV with low concentration of sodium nitrite.

Concentration, M	% Reduction in area at fracture	Fracture energy as a function of that observed in air
0.0125	37.3	0.49
0.00375	75.1	0.64

The results indicate that, even at a sodium nitrite concentration of 259 mg/litre, the environment is having a significant effect in reducing the fracture energy. In most other ductile failures (reduction in area 80%) the fracture energy ratios (ratio of fracture energy in test to that observed in air) have been ≥ 0.75.

The stress-elongation curves for OFHC copper at a potential of +100 mV in solutions containing 0.05 M, 0.025 M, 0.0125 M and 0.00375 M sodium nitrite solutions are shown in Figure 2.

The most direct measure of cracking susceptibility, as opposed to more general environmental effects, is the crack velocity. This was assessed in this work by mounting a specimen sectioned longitudinally across a diametral plane, measuring the length of the longest crack and dividing by the test time. The variation of crack velocity with potential and nitrite concentration may then be assessed (Table III).

TABLE III. Crack velocities (10^{-6}mms^{-1}) in OFHC copper at room temperature when strained in air saturated solutions of sodium nitrite at about 2.6 x 10^{-6}s^{-1}.

Environment ($NaNO_2$)	POTENTIAL					
	-100 mV	-50 mV	0 mV	+50 mV	+100 mV	fcp
0.1 M	0	2.0	5.1	6.9	4.8	3.2
0.6 M	0	1.8	4.9	8.1	13.4	5.3
0.3 M	0	0	1.8	4.5	8.2	5.5
0.1 M	0	0	0	3.1	6.3	2.0
0.05 M	-	0	0	0	7.2	0
0.025 M	-	0	0	0	4.7	0
0.0125 M	-	-	-	-	2.5	-
0.00375 M	-	-	-	-	0.4	-

fcp - free corrosion potential

The general effect of reducing concentration and/or potential is to reduce the crack velocity. As mentioned previously(1) no cracking has been observed in the ground water at potentials in the range -50 to +300 mV.

The potential during the free corrosion potential tests was monitored, and the results are shown in Figure 3. There appears to be a slight link between the form of the potential-time curves and cracking susceptibility, at concentrations that are sufficient to cause cracking. The curve for 0.6 M sodium nitrite is moved to significantly higher potentials than that for 1.0 M, and this is associated with a higher crack velocity (Table III). Potentials at 0.3 M are higher still and again there is a slightly higher crack velocity but at 0.1 M both the potential and crack velocity are reduced. At 0.05 M and 0.025 M the potentials are the most positive, but are still only at values that do not cause cracking in fixed potential tests, and this is reflected in zero crack growth. In ground water, the potential is around 0 mV, which did not give cracking in a fixed potential test.

3.1.2 Tests at room temperature in de-aerated solutions at $\dot{\varepsilon}$ 2.6 x $10^{-6}s^{-1}$

A few tests have been done using OFHC copper under de-aerated conditions, but only in solutions containing 0.6 M and 0.3 M sodium nitrite. On a basis of the stress corrosion cracking range observed with air-saturated solutions, it was decided to perform only three tests for each concentration: at 0 mV, +100 mV and the free corrosion potential (Figure 4). The reductions in area at fracture, fracture energy ratios and crack velocities were compared with those observed in aerated solutions (Table IV).

TABLE IV. % reduction in area at fracture, fracture energy ratios (compared with tests in air) and crack velocity for OFHC copper tested at room temperature in deaerated solutions of sodium nitrite (strain rate $\simeq 2.6 \times 10^{-6} s^{-1}$).

Molar Concn	Potential mV (sce)	% Reduction in area		Fracture energy ratio		Crack velocity (10^{-6}mms^{-1})	
		Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated
0.6	+100	20.2	15.5	0.20	0.16	13.4	5.4
	0	24.7	28.4	0.38	0.33	4.9	2.1
	FCP	25.2	49.8	0.29	0.54	5.3	0.7
0.3	+100	13.5	12.0	0.18	0.16	8.2	9.0
	0	43.9	89.6	0.58	0.64	1.8	0
	FCP	28.5	87.2	0.30	0.76	5.5	0

Whenever there was a significant difference between the ductilities for aerated and de-aerated conditions, the difference indicated improved environmental resistance for the de-aerated conditions. It is thought that the marked improvement in ductility at the free corrosion potential is because the potentials are considerably more negative than the corresponding tests under air-saturated conditions (compare Figure 4 with Figure 3). Stress-elongation curves for tests in 0.3 M sodium nitrite are shown in Figure 5, which can be compared with those obtained in the corresponding air saturated tests in Figure 7 in the previous progress report(1).

3.1.3 Tests at 80°C in aerated solutions at a strain rate of $2.6 \times 10^{-6} s^{-1}$

The only solution investigated so far contained 0.6 M sodium nitrite. The reduction in area, fracture energy ratio and crack velocity are compared with those for the corresponding tests at room temperature (Table V).

TABLE V. % Reduction in area at fracture, fracture energy ratio (compared with tests in air at room temperature) and crack velocity for OFHC copper tested in aerated solutions of 0.6 M sodium nitrite at $80^{o}C$ (strain rate ~$2.6 \times 10^{-6}s^{-1}$).

Potential mV (sce)	% Reduction in area		Fracture energy ratio		Crack velocity $10^{-6}mms^{-1}$	
	RT	$80^{o}C$	RT	$80^{o}C$	RT	$80^{o}C$
+100	20.2	10.3	0.20	0.20	13.4	3.5
0	24.7	81.7	0.38	0.69	4.9	0
FCP	25.2	77.6	0.29	0.73	5.3	0

The results in Table V indicate that except for the % reduction in area and fracture energy ratio at +100 mV, raising the test temperature to $80^{o}C$ has the effect of reducing detrimental environmental effects. It might be thought that at the higher temperature the electrochemical processes are more active, but this could be offset by the fact that the metal itself is softer, dislocations are more mobile and recovery from stress is easier. A contributing factor to the enhanced ductility in the test at the free corrosion potential would seem to be the change in the monitored potential to about -90 mV, significantly more cathodic than that at room temperature (Figure 3). The results of tests in all conditions used to date indicate that environmental effects are more likely at more anodic potentials. These tests at $80^{o}C$ produced a dark blue colouration in the test solution at the end of the test and a significant (1-2) rise in pH, as happened in the more aggressive solutions in aerated tests at room temperature. This has been attributed(1) to the reaction:

$$Cu + 2H_2O \rightarrow Cu(OH)_2 + H_2. \qquad (1)$$

The deep blue colour may simply be due to a high concentration of $Cu(OH)_2$, which is light blue in colour$^{(2)}$. Dissociation of the $Cu(OH)_2$ gives free (OH^-) ions that may cause the observed rise in pH. It has also been observed in the tests at +100 mV in air saturated solutions at 80°C, and in de-aerated tests at room temperature, that the initial bubbling at the platinum anticathode on application of the potential is less vigorous than in air saturated solutions at room temperature.

3.1.4 Tests in aerated solutions at room temperature at a faster strain rate ($1.7 \times 10^{-5} s^{-1}$)

Tests have now been done at a faster strain rate, giving failure times of <9 hours instead of the >60 hours obtained with less aggressive solutions at slow strain rates. Since the stress-elongation profiles at this faster strain rate appear somewhat irregular and do not always give such a smooth curve as in the slower strain rate tests, fracture energy measurements are not presented for comparison. However, the reduction in area at fracture gives a good comparison with tests at slower strain rates (Table VI).

TABLE VI. % Reduction in area at fracture for tests on OFHC copper in sodium nitrite solutions at different strain rates: $1.7 \times 10^{-5}s^{-1}$ (fast) and $2.6 \times 10^{-6}s^{-1}$ (slow).

Potential mV (sce)	Sodium nitrite concentration - molar							
	0.6		0.3		0.1		0.05	
	Fast	Slow	Fast	Slow	Fast	Slow	Fast	Slow
-100	86.6	89.1	90.4	90.4	-	-	-	-
-50	88.7	54.4	88.6	85.2	84.7	86.2	-	-
0	71.6	24.7	71.6	43.9	76.9	90.2	-	-
+50	50.1	19.4	40.5	23.2	59.2	29.6	70.0	39.1
+100	37.4	20.2	48.1	13.5	35.6	28.1	44.3	15.7
FCP	85.7	25.2	87.3	28.5	90.8	35.7	91.9	89.0

It is clear that, where environmental effects are present at slower strain rates, the effect of the faster strain rate is to give much increased ductility. This could be due simply to the fact that the environment has less time to act at the faster tests. Environments that produce no embrittlement at the slow strain rates also have no effect at the faster strain rate.

Crack velocities have not yet been presented, but are expected to be lower than those obtained at the slower strain rates.

No tests in these conditions have been done in artificial ground water, because this did not produce stress corrosion cracking at slower strain rates.

3.2 Phosphorus Deoxidised (PDO) Copper

3.2.1 Tests at room temperature in aerated solutions (strain rates about 2.6 x $10^{-6}s^{-1}$)

Preliminary potentiokinetic tests were done in 0.6 and 0.1 M sodium nitrite as well as artificial ground water and the range covered was the same as with OFHC copper, i.e. from -200 mV to +300 mV(1). In ground water (Figure 6) a clear cracking range is not indicated. For this, it is necessary to have high current values with a fast sweep rate (corresponding to an active crack tip) and low current values with a slow sweep rate (corresponding to filmed, passive crack sides). The two curves cross over at about +100 mV, probably because of the pitting involved at slow sweep rates. The curves for 0.1 and 0.6 M sodium nitrite were similar to those in ground water, except that the cross over occurred at about +50 mV and higher current densities were observed in the anodic region.

At the end of the slow sweep rate polarization tests, lasting about 50 minutes, the specimen immersed in ground water was filmed light brown, that in 0.1 M sodium nitrite was filmed a shiny dark grey, and that in 0.6 M sodium nitrite was filmed dull green. Consideration of the observations of Pourbaix(2) suggests that the dark grey film may be CuO, which is a stable substance at pH 8 and potentials more anodic than -42 mV (sce), according to the potential-pH diagram. The other films are more difficult to identify, but are of similar characteristics to others mentioned by Pourbaix.

In slow strain rate tests in the range -50 to +100 mV in artificial ground water, failures were invariably ductile and no stress corrosion cracks have been observed. In the potential range +50 mV to +300 mV, a light blue deposit formed in the solution and the specimen appeared red at the end of the test. The blue deposit resembled that identified as $Cu(OH)_2$ from tests with OFHC copper, and is confirmed by Pourbaix(2). The red colouration could be due to Cu_2O, but is thought to be simply bare copper exposed beneath the initial polished surface. As with OFHC copper under the same conditions, the reduction in area values are comparable to that obtained in air (89.4%) but an environmental effect is indicated by a reduction in the fracture energy (Table VII). The stress-elongation curves were all similar in shape (Figure 7).

Slow strain rate tests have also been conducted in sodium nitrite solutions of various concentrations in the potential range -100 to +100 mV. Since tests with OFHC copper gave similar results for 1.0 and 0.6 M sodium nitrite, the more concentrated solution was not used for testing PDO copper.

TABLE VII. % Reduction in area and fracture energy ratios (compared to that obtained in air) in ground water for PDO copper at room temperature at a strain rate $\approx 2.0 \times 10^{-6} s^{-1}$.

Potential mV (sce)	% Reduction in area at fracture	Fracture energy ratio
-50	83.4	0.83
0	86.1	0.78
+50	80.4	0.81
+100	85.8	0.75
+150	84.5	0.77
+200	90.0	0.76
+250	80.9	0.77
+300	87.2	0.78
FCP	79.4	0.89

TABLE VIII. % Reduction in area for PDO copper at room temperature in aerated solutions (strain rate $\approx 2.6 \times 10^{-6} s^{-1}$).

Molar concn. of sodium nitrite	Potential mV (sce)					
	-100	-50	0	+50	+100	FCP
0.6	86.3	36.3	30.2	17.3	21.4	17.8
0.3	82.9	83.1	47.8	24.4	12.7	41.0
0.1	84.1	84.4	80.8	32.6	19.3	41.8
0.05	-	85.7	89.4	44.8	10.7	83.4
0.0125	-	-	-	-	36.2	-
0.00375	-	-	-	-	72.9	-

Again the general trend is that increasing concentration and potential results in increasing embrittlement (Table VIII). The stress-elongation curves from all these tests have been plotted (as indicated for 0.3 M solutions in Figure 8) and, somewhat surprisingly, in this particular diagram the relative positions of the curves at different potentials was different to that previously observed. This was reflected in the area under the curves, which were measured and expressed as a ratio of that obtained in a test in air (Table IX), which was 94 MJ m^{-3}, slightly less than the 104 MJ m^{-3} of OHFC copper. The crack velocities show similar trends (Table X).

TABLE IX. Fracture energy ratios for PDO copper at room temperature using air saturated solutions of sodium nitrite ($\dot{\varepsilon} \simeq 2.6 \times 10^{-6} s^{-1}$).

Molar concn. of sodium nitrite	Potential mV (sce)					
	-100	-50	0	+50	+100	FCP
0.6	0.92	0.52	0.29	0.24	0.22	0.19
0.3	0.76	0.93	0.54	0.23	0.28	0.34
0.1	0.84	0.87	0.87	0.42	0.44	0.70
0.05	-	0.99	0.84	0.39	0.19	-
0.0125	-	-	-	-	0.56	-
0.00375	-	-	-	-	0.67	-

TABLE X. Crack velocity (10^{-6} mms^{-1}) in PDO copper at room temperature using aerated solution of sodium nitrite at strain rates ≈2.6 x 10^{-6}s^{-1}.

Molar concn. of sodium nitrite	Potential mV (sce)					
	-100	-50	0	+50	+100	FCP
0.6	0	4.3	5.7	4.8	5.2	7.5
0.3	0	0	0.8	8.2	7.4	3.0
0.1	0	0	0	4.0	3.6	1.1
0.08	-	0	0	3.8	8.3	0
0.0125	-	-	-	-	1.7	-
0.00375	-	-	-	-	0.7	-

As with the OFHC copper, a potential of +100 mV causes a greater ductility loss in a 0.05 M solution than in the more concentrated 0.1 M solution and full ductility (80% reduction in area, a fracture energy ratio of 0.8 and zero crack velocity) is not quite attained with this potential even when the solution is diluted to 0.00375 M. Further tests will therefore be necessary.

The stress-elongation curves for tests at a potential of +100 mV in 0.05, 0.0125 and 0.00375 M solutions of sodium nitrite show increasing ductility as the concentration is reduced (Figure 9).

The monitored potential during tests under freely corroding conditions in the four concentrations of sodium nitrite (Figure 10) indicate a link between the position of the curve and cracking susceptibility. The curve at the free corrosion potential in ground water lies between -50 and -60 mV, and this range is clearly passive in a fixed potential test.

Some examination of fracture surfaces in a scanning electron microscope reveals very similar characteristics to those observed for OFHC copper(1). In specimens that showed cracking, there was a rim of transgranular stress corrosion cracking surrounding an inner ductile failure region (Figure 11). Further indication of the transgranular mode of cracking is shown in Figure 12. However, one specimen, (Figure 13) showed some intergranular attack at the extreme edge of the specimen. Rangel et al(3) have observed that cracking of pure copper in 1.0 M sodium nitrite frequently initiates at the grain boundaries and then propagates by a transgranular mode.

In tests in sodium nitrite solutions that showed embrittlement a thin, grey shiny film on the specimen was frequently observed. This is thought to be CuO, as suggested by reference to the Pourbaix diagrams(2), and as observed by Rangel et al(3).

At more anodic potentials in the more concentrated solutions initial bubbling at the platinum anticathode was frequently observed.

3.2.2 Tests at room temperature in de-aerated solutions (strain rates $\approx 2.6 \times 10^{-6} s^{-1}$)

After considering the results of the unsaturated tests, it was decided to perform de-aerated tests at only three potentials: 0 and +100 mV, and the free corrosion potential. So far, only two solutions have been investigated: 0.6 and 0.3 M sodium nitrite. The results (Table XI) indicate that de-aeration results in an increased ductility, i.e. higher reduction in area and fracture energy ratio and lower crack velocity.

TABLE XI. % Reduction in area, fracture energy ratio and crack velocities for PDO copper tested at room temperature in de-aerated solutions of sodium nitrite at $\dot{\varepsilon} \approx 2.6 \times 10^{-6} s^{-1}$.

Molar Concn	Potential mV (sce)	% Reduction in area		Fracture energy ratio		Crack velocity (10^{-6} mms^{-1})	
		Aerated	Deaerated	Aerated	Deaerated	Aerated	Deaerated
0.6	+100	21.4	33.4	0.22	0.31	5.2	4.7
	0	30.2	35.8	0.29	0.33	5.7	4.5
	FCP	17.8	83.7	0.19	0.83	7.5	0
0.3	+100	12.7	11.0	0.28	0.16	7.4	7.1
	0	47.8	79.3	0.54	0.98	0.8	0
	FCP	41.0	85.6	0.34	1.00	3.0	0

As with OFHC copper, this increase in ductility supports the statement that "copper is a relatively noble metal and is not normally attacked by oxygen-free water"(4). The marked rise in ductility at the free corrosion potential can be partly explained by reference to the potential-time curves for the de-aerated tests (Figure 14), which are significantly less anodic than for the corresponding air saturated tests (Figure 10).

3.2.3 Tests at 80°C in aerated solutions (strain rate $\approx 2.6 \times 10^{-6} s^{-1}$)

So far, only tests in 0.6 M sodium nitrite have been done and it was again decided to restrict testing to three potentials: 0 and +100 mV and the free corrosion potential.

It is clear (Table XII) that the effect of the higher temperature in 0.6 M sodium nitrite is to greatly increase the ductility of the PDO copper, perhaps because the material is getting softer and does not easily maintain a sharp crack. The potential during the free corrosion test was about -85 mV (sce), much less anodic than at room temperature.

TABLE XII. % Reduction in area at fracture, fracture energy ratio and crack velocities for PDO copper tested at 80°C in an aerated solution of 0.6 M sodium nitrite at a strain rate $\simeq 2.6 \times 10^{-6}s^{-1}$

Potential mV (sce)	% Reduction in area		Fracture energy ratio		Crack velocity $10^{-6}mms^{-1}$	
	RT	80°C	RT	80°C	RT	80°C
+100	21.4	45.2	0.22	0.57	5.2	1.5
0	30.2	89.0	0.29	0.79	5.7	0
FCP	17.8	79.1	0.19	0.79	7.5	0

3.2.4. Tests at room temperature in aerated solutions at a faster strain rate ($1.7 \times 10^{-5}s^{-1}$)

As with OFHC copper, the stress-elongation curves are rather irregular and neither these nor the fracture energy measurements are presented. However, the reduction in cross-sectional area obtained in solutions of various concentrations of sodium nitrite in the potential range -100 to +100 mV may be compared with results from the slower strain rate (Table XIII).

TABLE XIII. % Reduction in area for PDO copper at room temperature in aerated solutions of sodium nitrite (strain rates: $1.7 \times 10^{-5}s^{-1}$(fast) and $\simeq 2.6 \times 10^{-6}s^{-1}$(slow)).

Potential mV (sce)	Molar concentrations of sodium nitrite							
	0.6		0.3		0.1		0.05	
	Slow	Fast	Slow	Fast	Slow	Fast	Slow	Fast
-100	86.3	87.0	82.9	87.2	84.1	84.3	-	-
-50	36.3	83.4	83.1	85.1	84.4	86.0	85.7	85.9
0	30.2	58.2	47.8	69.7	80.8	79.8	89.4	82.6
+50	17.3	44.1	24.4	61.5	32.6	69.7	44.8	85.0
+100	21.4	40.3	12.7	40.4	19.3	53.1	10.7	59.4
FCP	17.8	77.1	41.0	85.5	41.8	87.8	83.4	83.6

It is clear that under conditions where the PDO copper is not already fully ductile (i.e. >80% reduction in area) at the slower strain rates there is much improved ductility at the faster strain rate, simply because the environment has less time in which to act. There is still some embrittlement at +100 mV in 0.05 M sodium nitrite and further tests at lower concentrations will therefore be necessary. Tests in ground water have not been performed because it was thought that any cracking would be detected under conditions that produced no cracking at faster strain rates. Crack velocities cannot be presented, simply because they have not yet been measured.

CONCLUSIONS

1. Stress corrosion cracking of PDO copper in aerated ground water at room temperature and a strain rate ≈2.6 x $10^{-6}s^{-1}$ appears unlikely in the potential range -50 to +300 mV, but there is a certain reduction in the fracture energy.
2. Depending on the precise solution concentration and potential, there is moderate to severe stress corrosion cracking of PDO copper in the presence of sodium nitrite in aerated solutions at room temperature at a strain rate of ≈2.6 x $10^{-6}s^{-1}$.
3. In both OFHC and PDO copper, there are still some detrimental environmental effects at the aggressive potential of +100 mV (sce) with sodium nitrite concentrations as low as 259 mg/litre.
4. With both OFHC and PDO copper the severity of stress corrosion cracking in sodium nitrite solutions is usually considerably reduced if (a) de-aerated conditions are employed, (b) the temperature is raised to 80°C, or (c) the strain rate is increased to 1.7 x $10^{-5}s^{-1}$.

FUTURE WORK

Future work will further extend the range of testing to consideration of other factors that might influence cracking and such tests will be carried out:

(1) at still lower sodium nitrite concentrations than 259 mg/litre, to identify a safe limit below which cracking does not occur,

(2) at 80°C,

(3) in de-aerated conditions,

(4) with the addition of CO_3^{2-}, SO_4^{2-} and Cl^- ions,

and (5) at different strain rates (there might be some signs of cracking in the ground water at very slow strain rates ($\approx 10^{-7} s^{-1}$) that give the environment more time in which to act.

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2. M. Pourbaix, "Atlas of electrochemical equilibria in aqueous solutions", pp384-392.
3. C.M. Rangel, J. Yu and R.N. Parkins, Fourth Progress Report, "Environmental aspects of the stress corrosion cracking of brasses", February 1982.
4. K.B.S. Teknisk Rapport 90, Final Report 1978-03-31, p9.

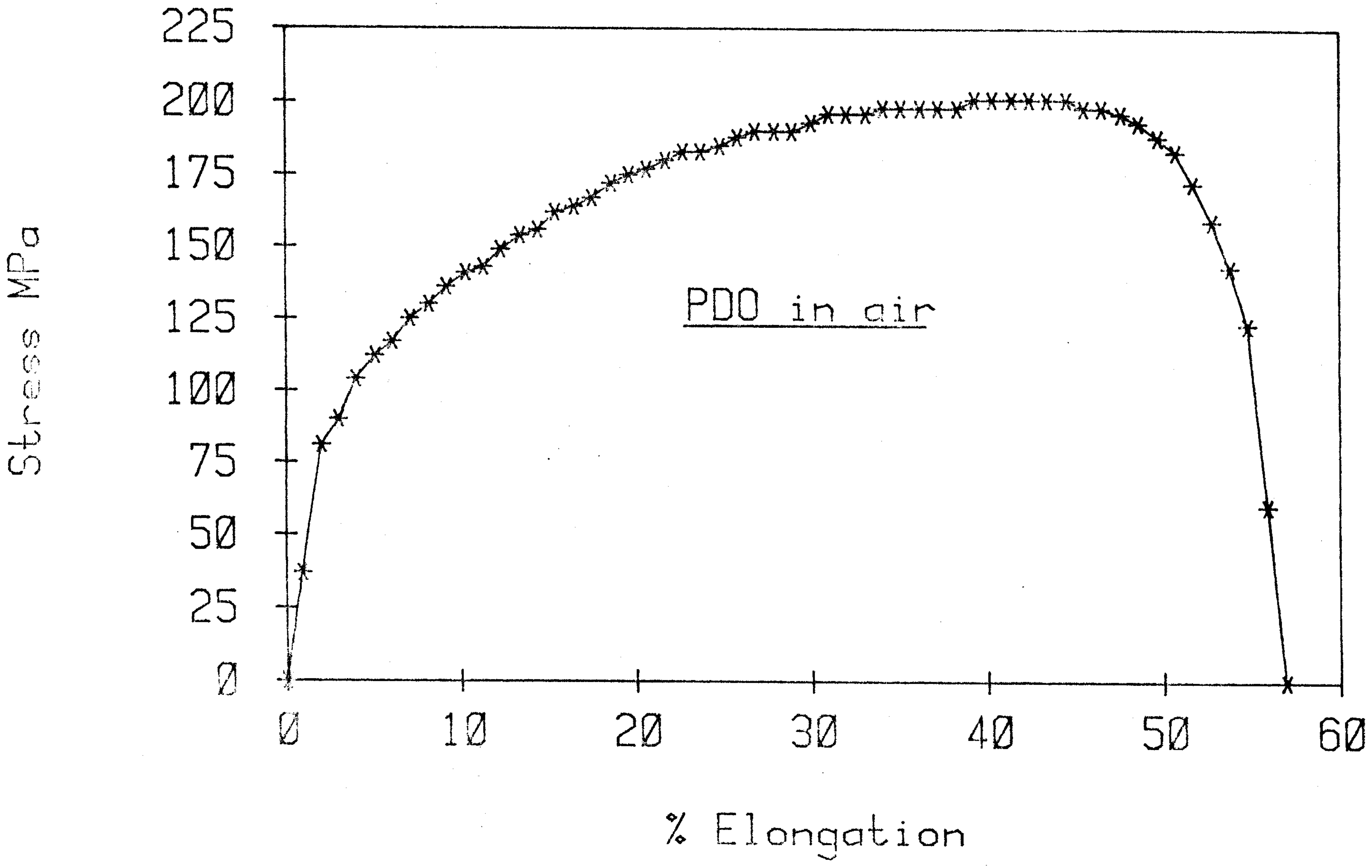

Figure 1. Nominal stress vs elongation for PDO copper strained at ~2.6 x $10^{-6}s^{-1}$ in air.

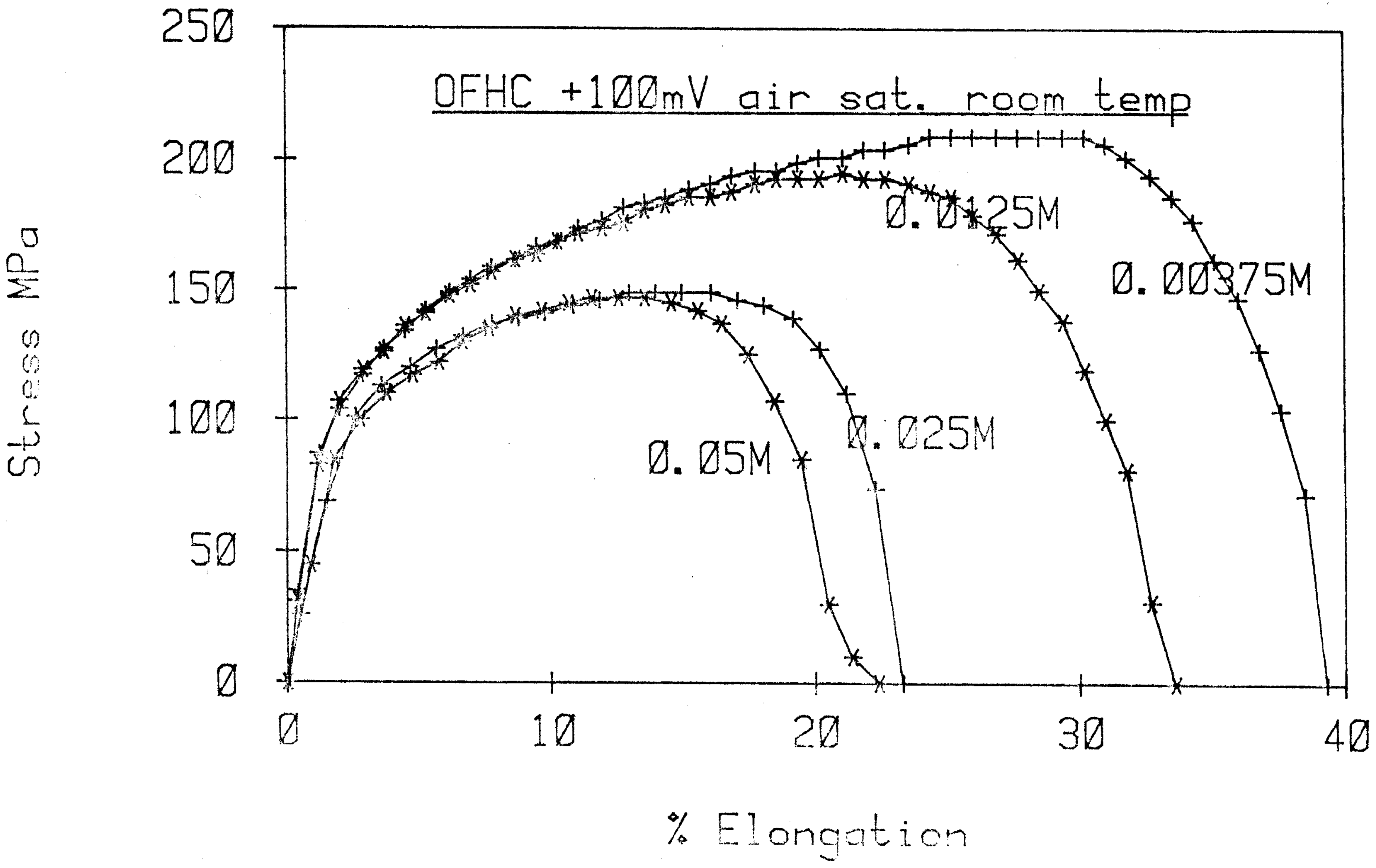

Figure 2. Stress-elongation curves for OFHC copper strained at ~2.6 x $10^{-6} s^{-1}$ in dilute, aerated solutions of sodium nitrite (at concentrations shown) at a potential of +100 mV (sce).

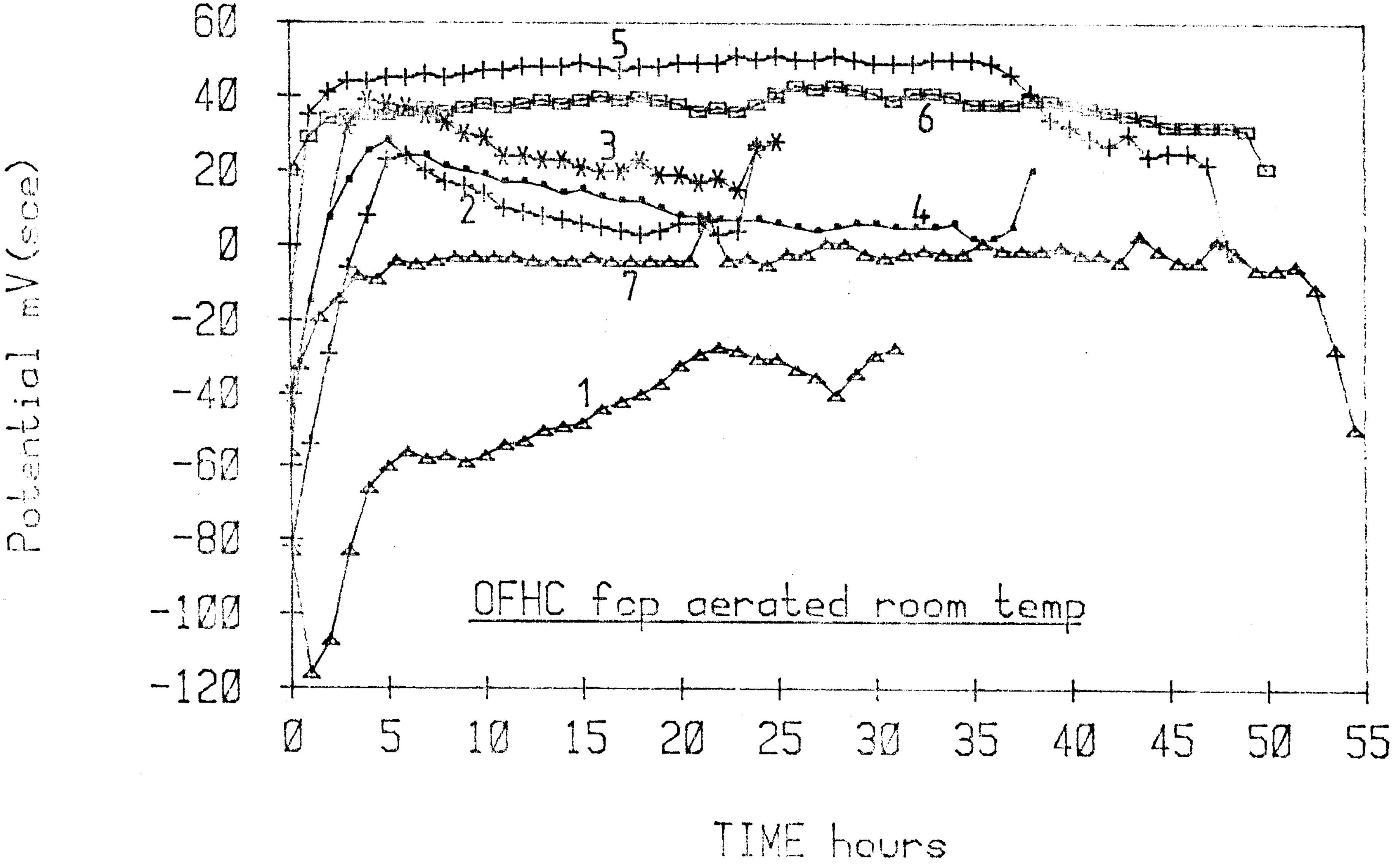

Figure 3. Monitored free corrosion potential for OFHC copper strained at ~2.6 x $10^{-6}s^{-1}$ in aerated solutions at room temperature. 1 = 1.0 M NaNO , 2 = 0.6 M, 3 = 0.3 M, 4 = 0.1 M, 5 = 0.05 M, 6 = 0.025 M and 7 = ground water.

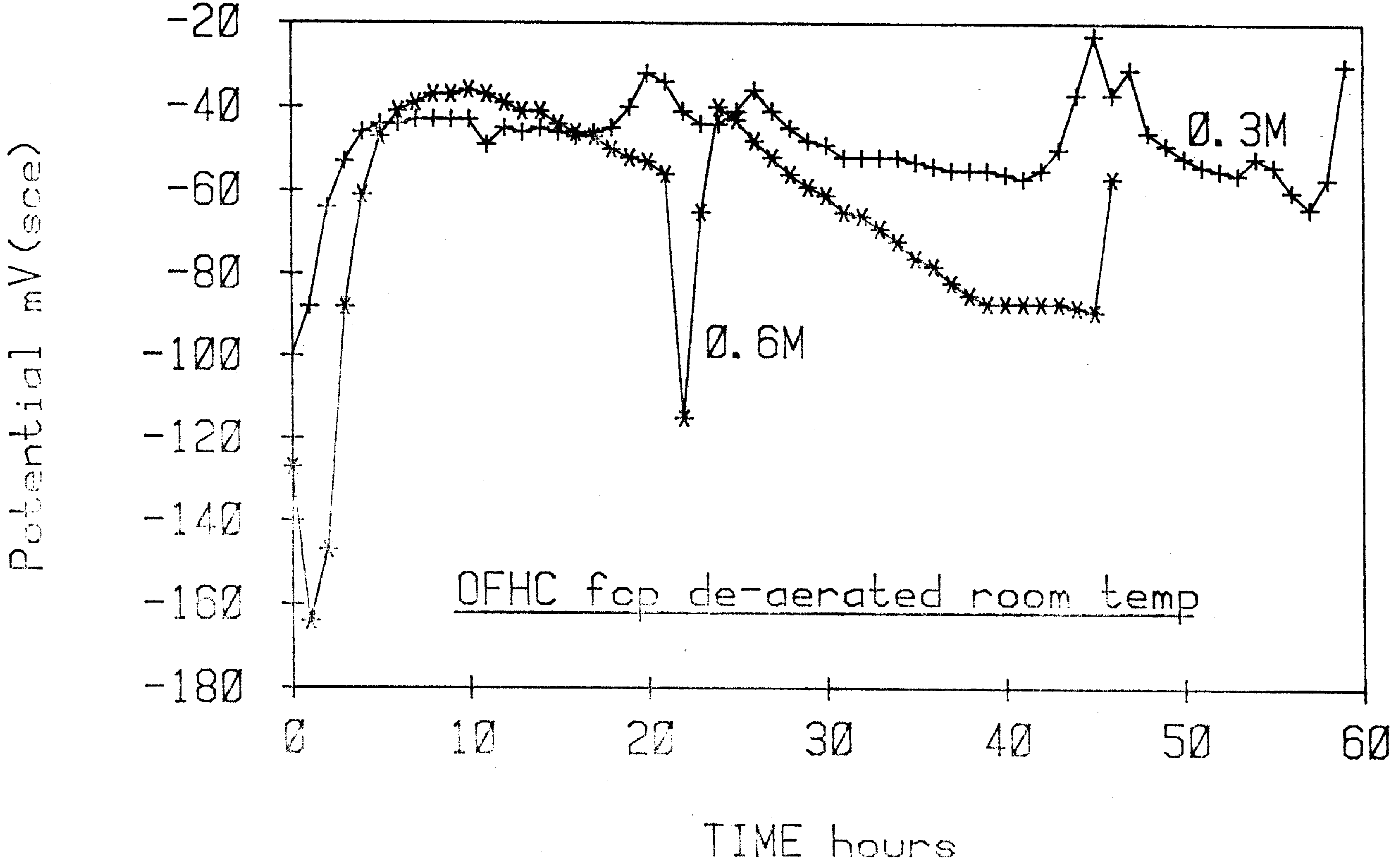

Figure 4. Monitored free corrosion potential for OFHC copper strained at ~2.6 x $10^{-6}s^{-1}$ in de-aerated solutions of sodium nitrite (at two concentrations shown) at room temperature.

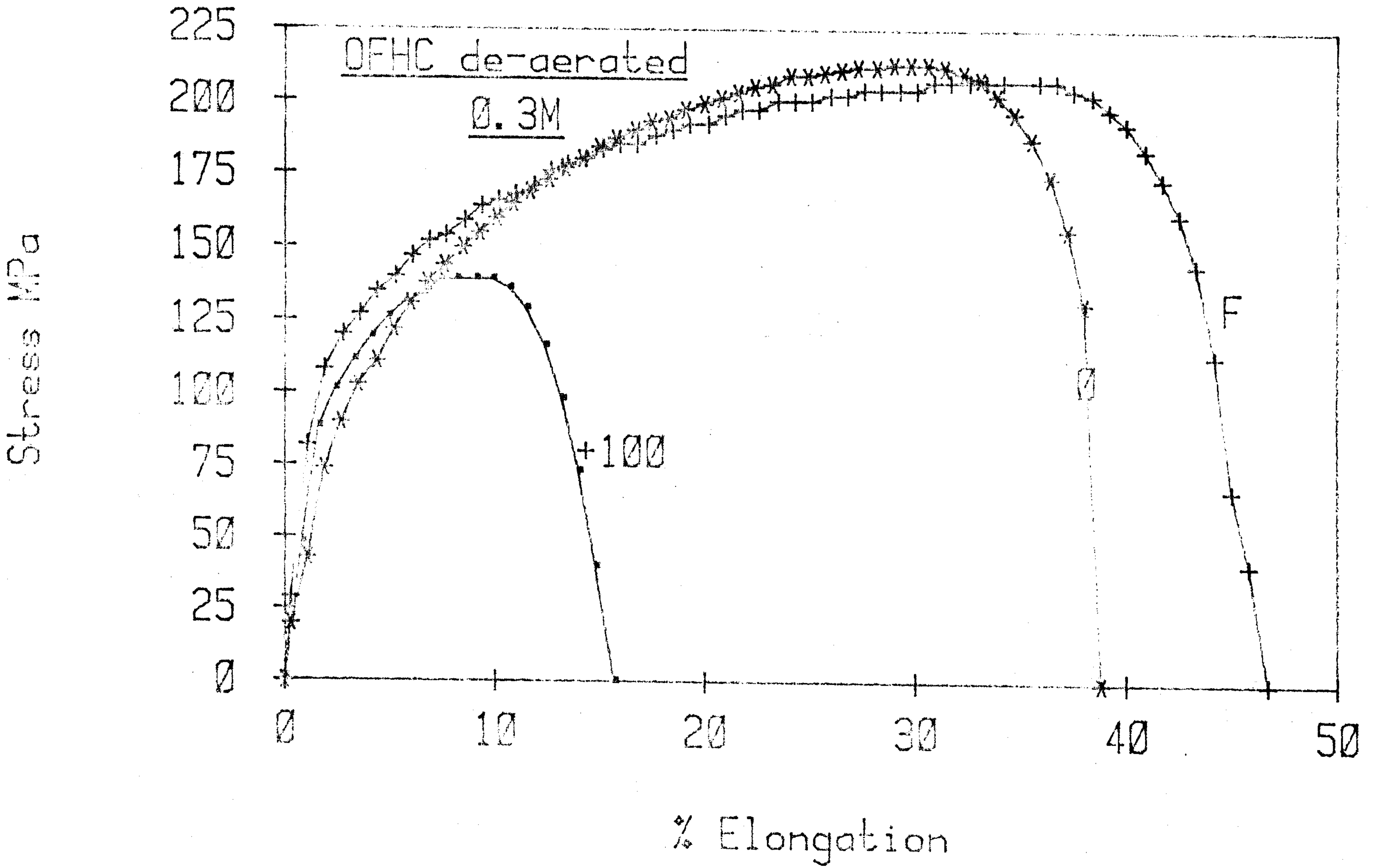

Figure 5. Stress-elongation curves for OFHC copper strained at ~$2.6 \times 10^{-6} s^{-1}$ in de-aerated 0.3 M sodium nitrite at room temperature and at the free corrosion potential (F) and at 0 and +100 mV (sce).

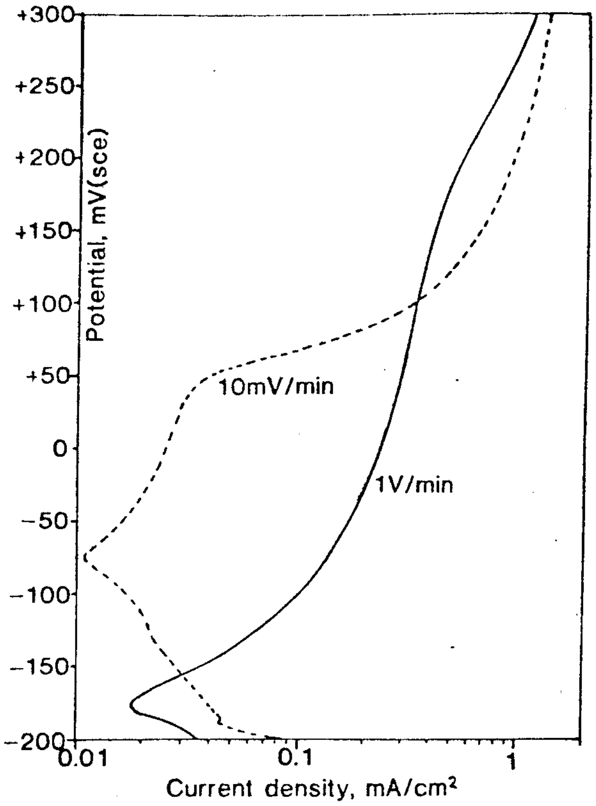

Figure 6. Fast and slow sweep rate polarization curves for PDO copper in aerated ground water at room temperature.

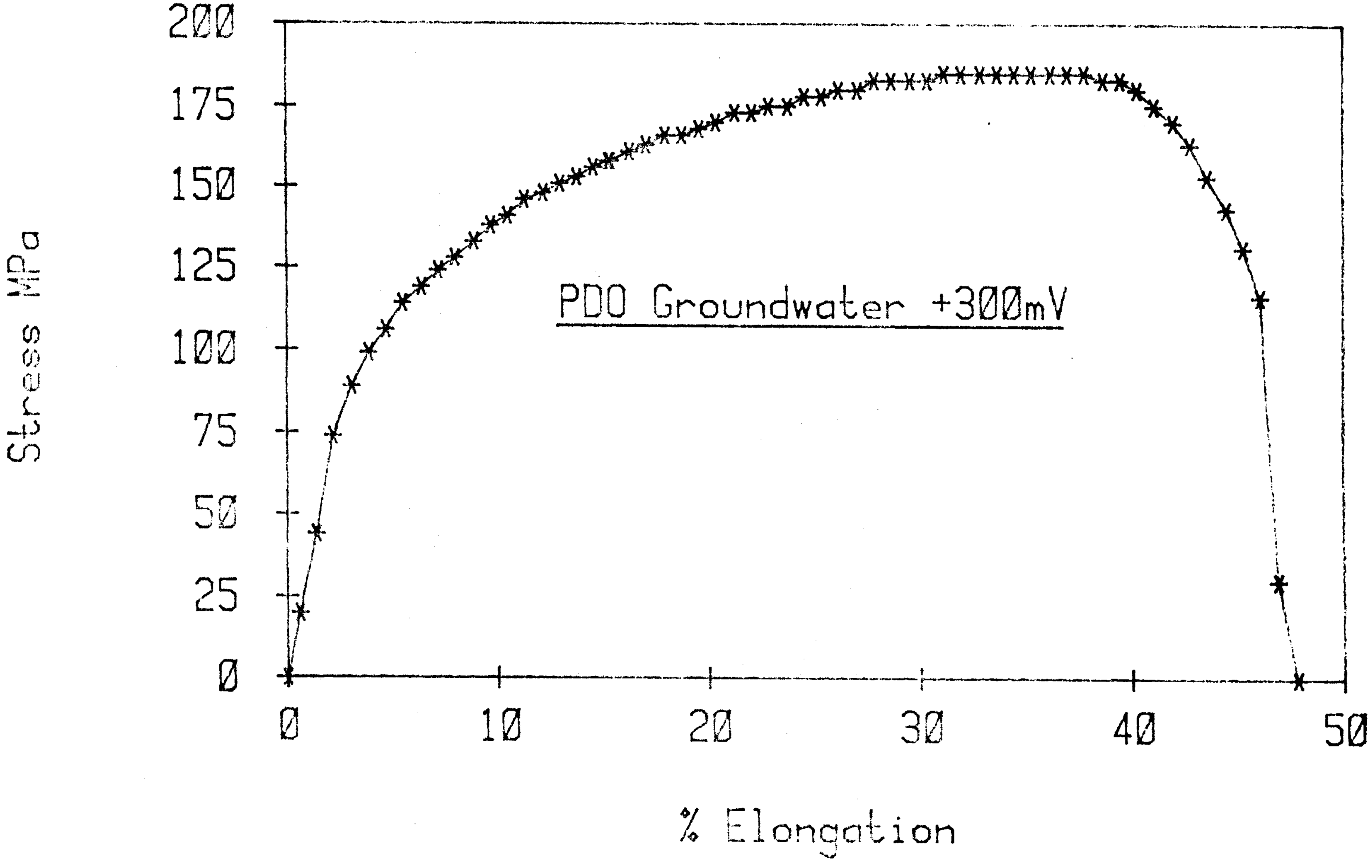

Figure 7. Typical stress-elongation curve for PDO copper strained at ~2.6 x $10^{-6}s^{-1}$ in aerated ground water at room temperature (at +300 mV (sce)).

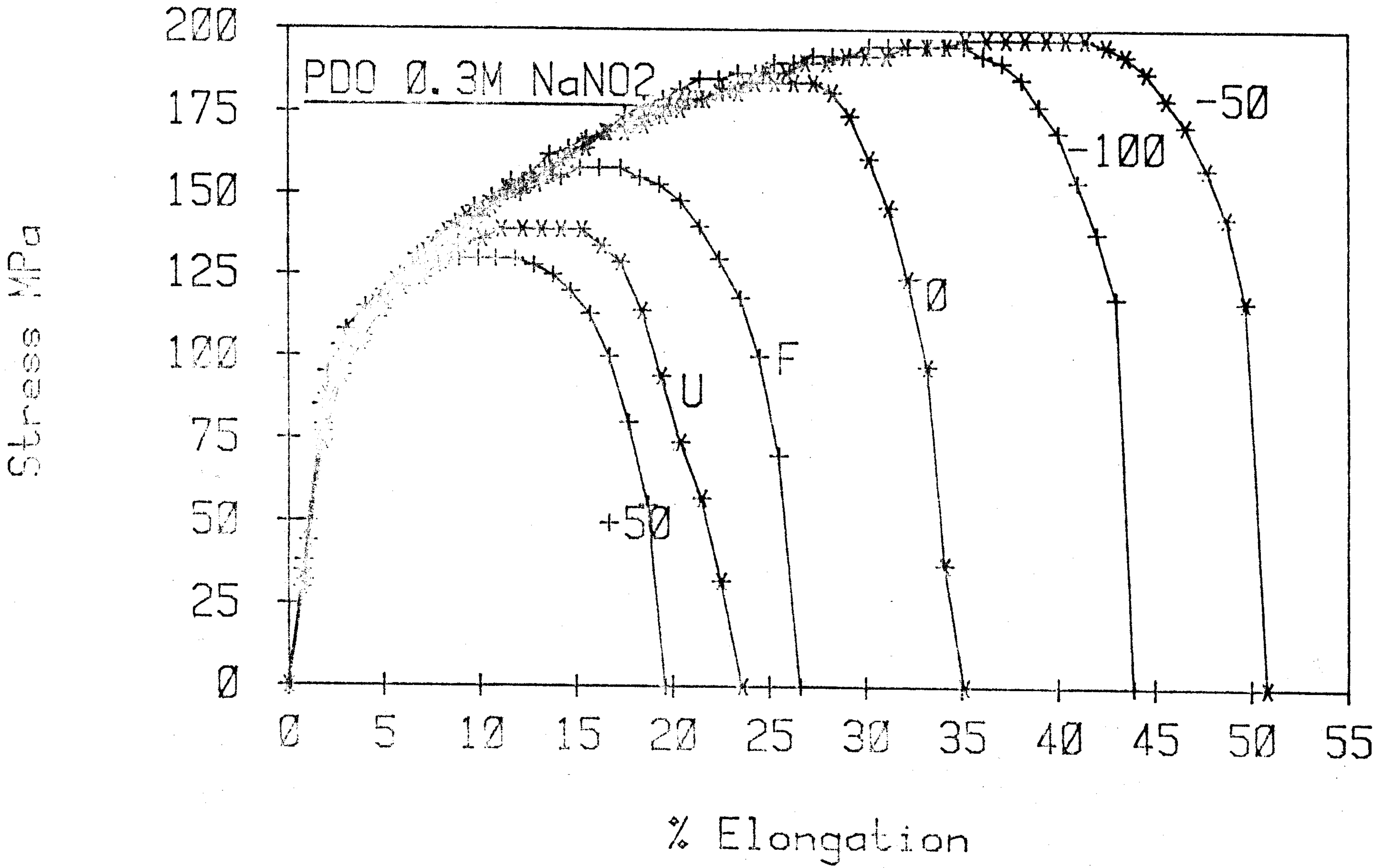

Figure 8. Stress-elongation curves for PDO copper strained at ~$2.6 \times 10^{-6} s^{-1}$ in aerated 0.3 M sodium nitrite at room temperature, at the free corrosion potential (F) and with various applied potentials (mV sce) - U corresponds to +100 mV (sce).

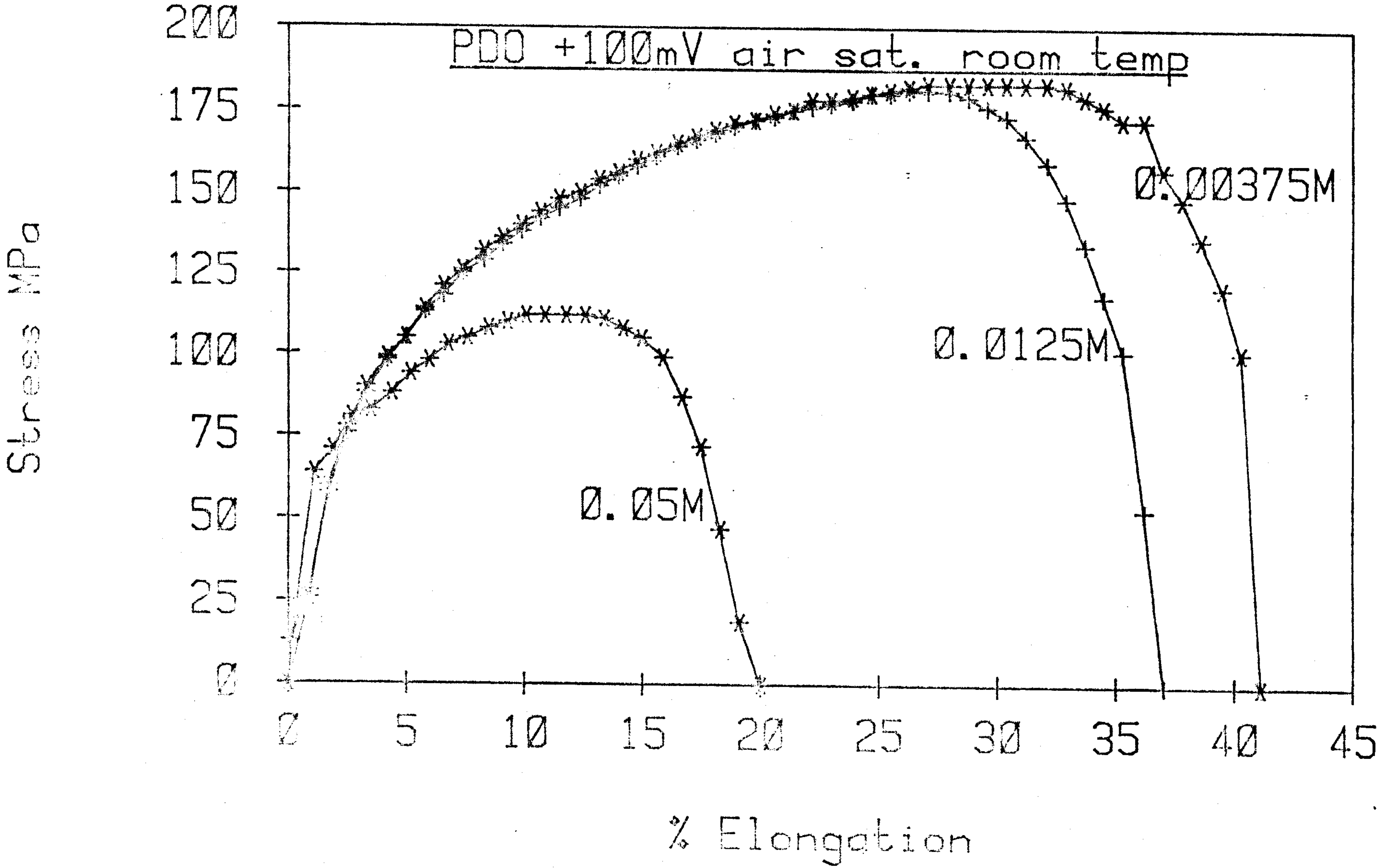

Figure 9. Stress-elongation curves for PDO copper strained at ~$2.6 \times 10^{-6} s^{-1}$ at a potential of +100 mV (sce) in dilute, aerated solutions with various concentrations of sodium nitrite at room temperature.

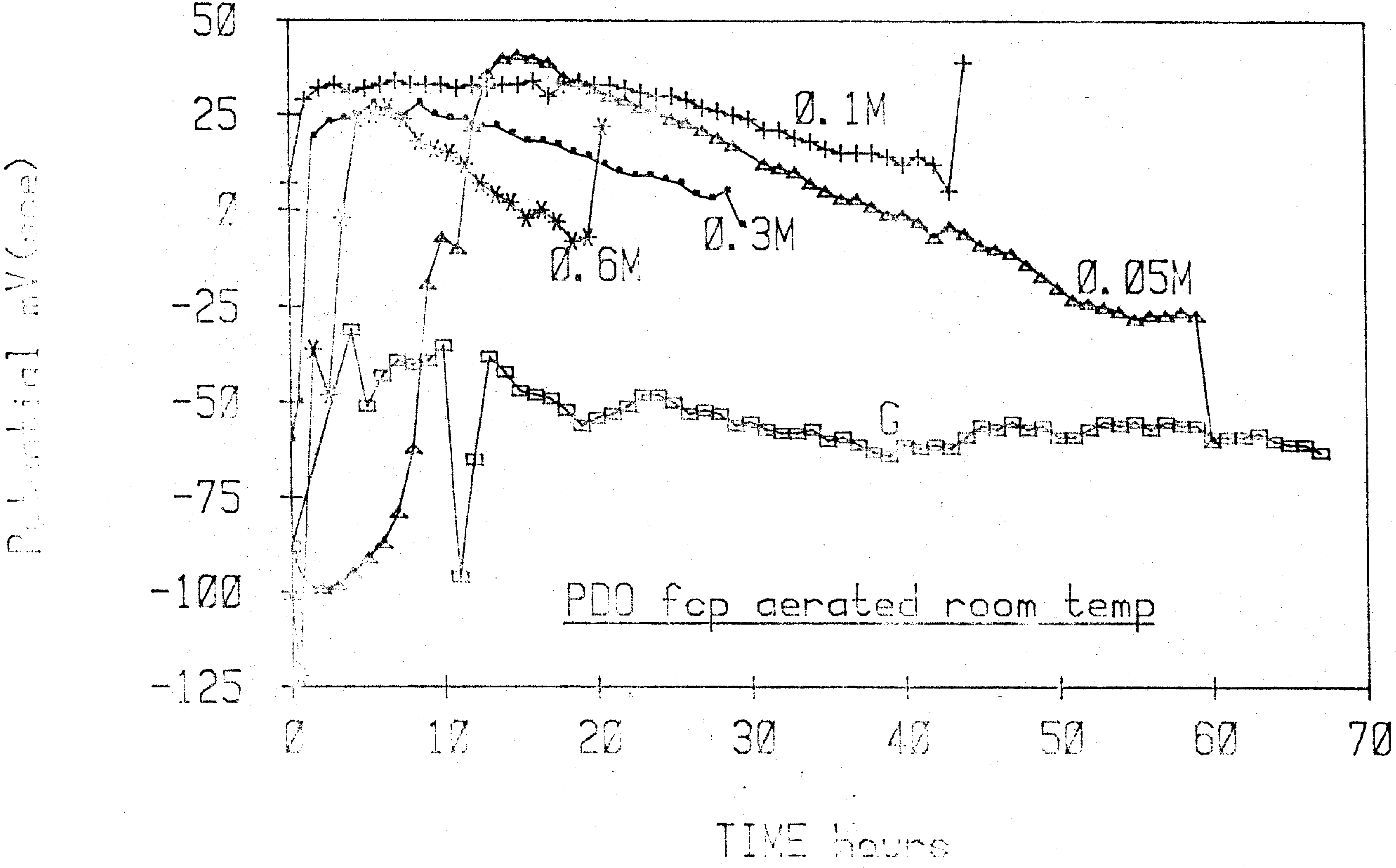

Figure 10. Monitored free corrosion potential for PDO copper strained at ~$2.6 \times 10^{-6} s^{-1}$ in ground water (G) and in aerated solutions containing various concentrations of sodium nitrite at room temperature.

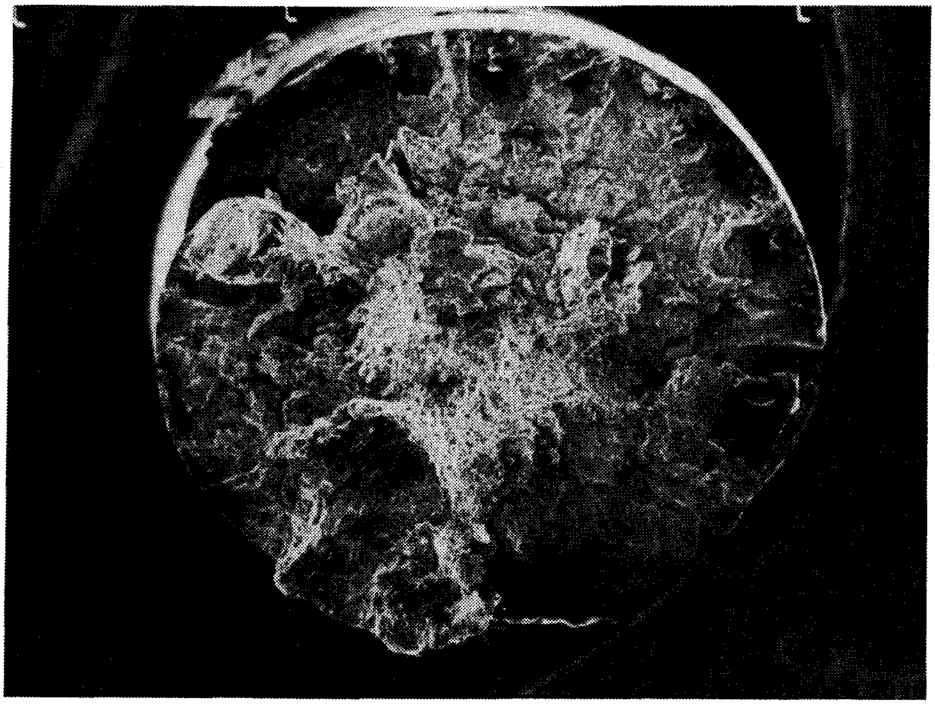

Figure 11. Fracture surface of PDO copper strained at ~$2.6 \times 10^{-6} s^{-1}$ in aerated 0.6 M sodium nitrite at room temperature at the free corrosion potential. x35

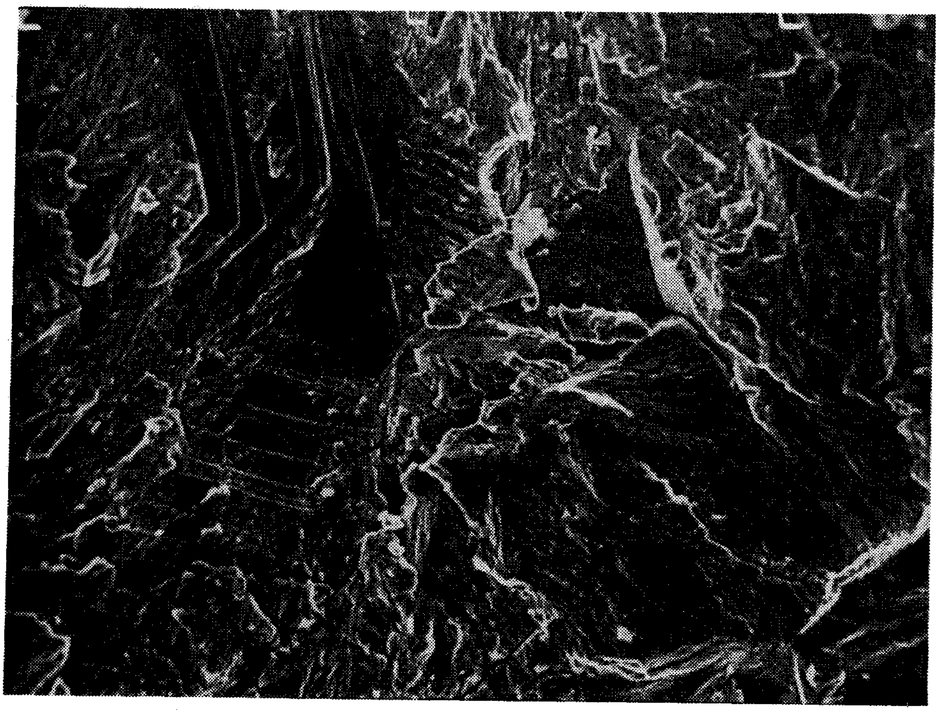

Figure 12. Transgranular fracture of PDO copper strained at ~$2.6 \times 10^{-6} s^{-1}$ in aerated 0.6 M sodium nitrite at room temperature at the free corrosion potential. x500

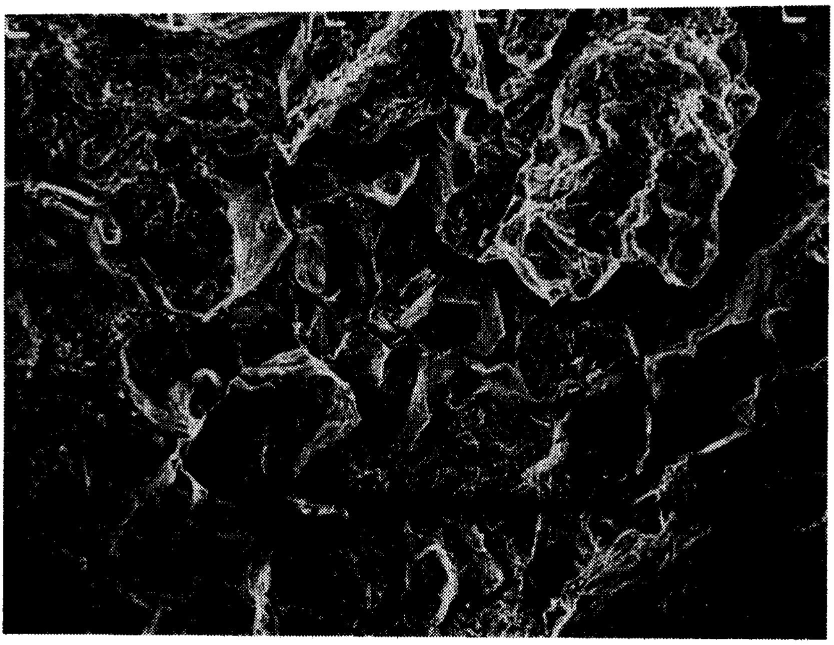

Figure 13. Intergranular attack of PDO copper strained at $2.6 \times 10^{-6} s^{-1}$ in aerated 0.6 M sodium nitrite at room temperature and +50 mV (sce). x200

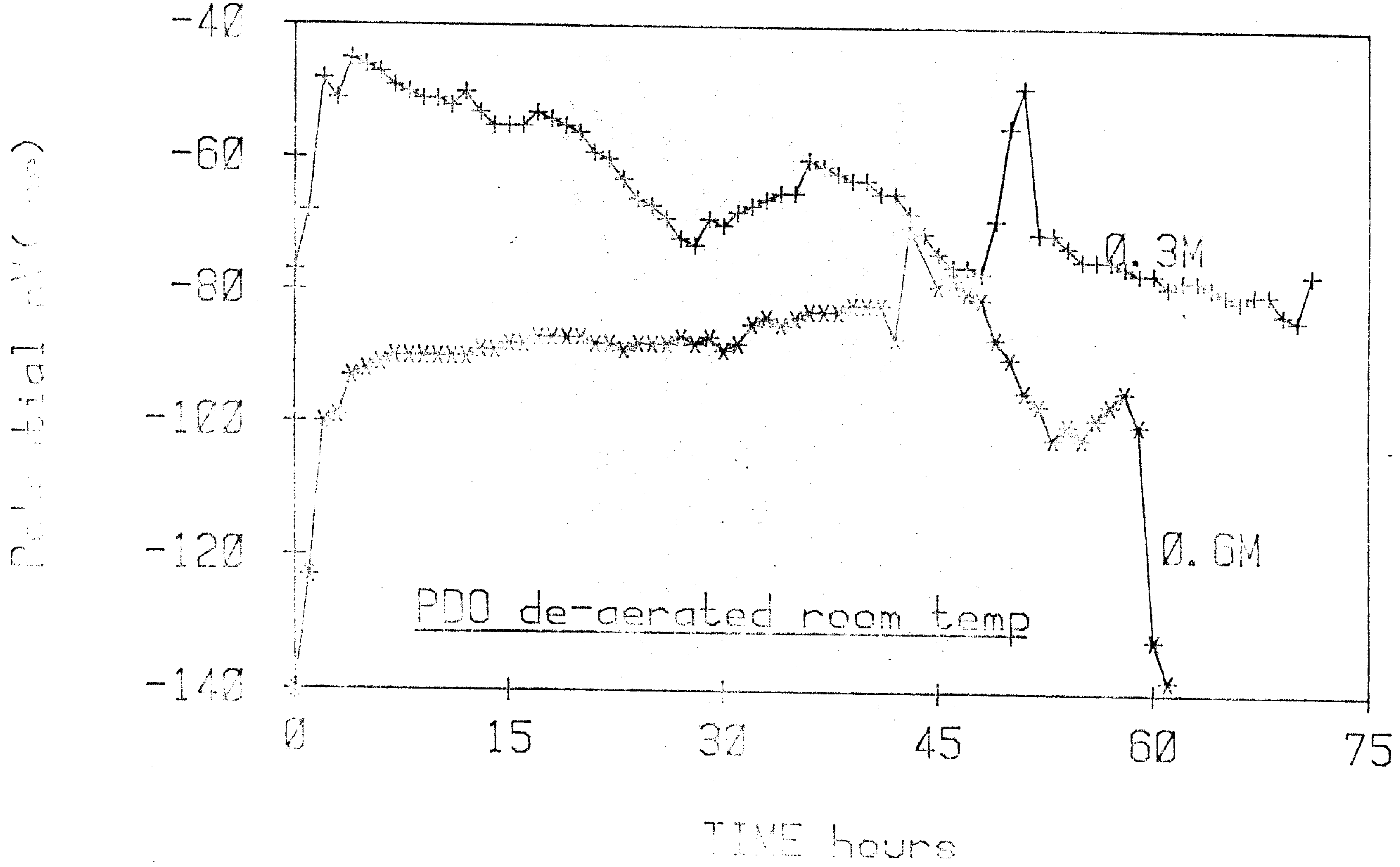

Figure 14. Monitored free corrosion potentials for PDO copper strained at $\sim 2.6 \times 10^{-6} s^{-1}$ in de-aerated sodium nitrite solutions of various concentrations at room temperature.

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INVESTIGATION OF THE STRESS CORROSION RESISTANCE OF PURE COPPER

by

L A Benjamin, D Hardie and R N Parkins

FINAL REPORT

April 1983

1. INTRODUCTION

The first two progress reports (4,5) covered the slow strain rate testing of both oxygen-free high conductivity (OFHC) and phosphorus-deoxidised (PDO) copper and the tests were generally conducted in normally aerated (i.e. air-saturated) solutions at room temperature, using strain rates of $2.6 \times 10^{-6} s^{-1}$ and $1.7 \times 10^{-5} s^{-1}$. The environments involved were synthetic ground water (1) and a solution containing sodium nitrite in concentrations from 1.0M to 0.00375M. A small number of tests were also included using de-aerated solutions or employing a temperature of 80°C.

This final report describes the results of further testing of both OFHC and PDO copper at room temperature using normally aerated solutions based on the synthetic ground water, but with additions of selected anions. Stress corrosion resistance at an even lower nitrite concentration than previously examined was also evaluated. The strain rates employed were $1.7 \times 10^{-5} s^{-1}$, $2.8 \times 10^{-6} s^{-1}$ and $1.8 \times 10^{-6} s^{-1}$.

A few tests were again done at 80°C but no further de-aerated tests could be included in the limited time available.

2. EXPERIMENTAL METHODS

The mechanical properties of both OFHC and PDO copper have been presented in earlier reports and the experimental techniques generally employed have also been described. (4,5) In the latest series of tests, 'fast' strain rate tests were done at $1.7 \times 10^{-5} s^{-1}$ but 'slow' strain rate testing was mainly carried out on new machines and, depending on the available gear ratios, involved strain rates of either $1.8 \times 10^{-6} s^{-1}$ or $2.8 \times 10^{-6} s^{-1}$.

3. RESULTS

3.1. Tests in Laboratory Air

Some tests were done in laboratory air, which may be considered as an inert environment for both OFHC and PDO copper, to establish a basis of comparison between the new slow strain rate machines and those previously employed. The measured parameters that were used in this assessment were: (a) the reduction in cross-sectional area at fracture, (b) the maximum nominal stress, (c) the total elongation to failure and (d) the fracture energy as represented by the area enclosed by the stress-strain curve. As before, (d) was calculated on a basis of

$$1\text{MN/m}^2 \times 1\%\ \text{elongation} = 10^6\text{N/m}^2 \times 0.01 = 10^4\text{N/m}^2$$
$$= 10^4\text{J/m}^3 = 10\text{MJ/m}^3,$$

and this represents the work done per unit specimen volume to produce failure (Table I).

The accumulated results of these tests in air (Table I) were slightly different from those previously reported and this is particularly

TABLE I. Results of tensile tests of OFHC and PDO copper in air at two slow strain rates

Property	Strain rate ($10^{-6}s^{-1}$)			
	2.8		1.8	
	OFHC	PDO	OFHC	PDO
% reduction in area	89.0	82.8	81.8	84.9
Maximum stress (MPa)	216	217	217	208
% Total elongation	53.7	50.7	43.1	46.4
Fracture energy (MJm^{-3})	95	88	76	79

true of the fracture energy (the least dependable parameter) and the elongation at 1.8 x $10^{-6}s^{-1}$, both of which showed a reduction. This is slightly at variance with the earlier belief that slight variations in strain rate (within an order of magnitude) did not produce significant changes in ductility parameters.

3.2. Testing of OFHC Copper in Aerated Solutions at Room Temperature

Here, a variety of environments was studied using OFHC copper specimens strained at the rates already mentioned:

(i) A 0.1M sodium nitrite solution was examined at a more cathodic potential than previously attempted.

(ii) An attempt was made to define a lower limit of sodium nitrite at which no stress corrosion would be observed, by using a 0.001M solution (i.e. 69mg $NaNO_2$ per litre).

(iii) Synthetic ground water was assessed at a potential of -100mV(sce), in order to complete the range of potentials examined from -100mV to +300mV (sce).

(iv) A whole series of solutions based on the synthetic ground water, with individual additions of various anions: Cl^- was added in the form of sodium chloride, using 1.65g NaCl/litre to give 1g Cl^-/litre; the sulphate ion concentration was increased by addition of 148mg sodium sulphate/litre to produce 100mg SO_4^{2-}/litre; and carbonate solutions contained equimolar amounts of CO_3^{2-} and HCO_3^-, giving a total of 1g/litre by weight (achieved by adding 0.88g sodium carbonate/litre - 0.50gCO_3^{2-}/litre, and 0.69g sodium bicarbonate/litre - 0.50g HCO_3^-/litre)

Apart from one test that indicated a reduction in area at fracture of < 80%, a high level of ductility was exhibited by all specimens tested in all of these solutions (Table II) and no stress corrosion cracks were detected.

The free corrosion potentials of all solutions doped with specific anions were continuously monitored during straining. That for the Cl^--doped solution rose steadily from -210 to -155mV (sce) throughout the 50 hours of the test, that for the solution doped with SO_4^{2-} dropped rapidly from around -20mV (sce) then remained constant at -70mV (sce) for most of the test, and that with the CO_3^{2-}/HCO_3^- additions fluctuated about a 'mean' of about -10mV (sce), within a range from -40 to +20mV (sce)

TABLE II. % Reduction in area values for OFHC copper strained at 2.8 x $10^{-6}s^{-1}$ and 1.8 x $10^{-6}s^{-1}$ (*) in aerated solutions based on ground water at room temperature

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	90.5*	-	-	-	-	-
0.1M $NaNO_2$	89.2	-	-	-	-	-	-
0.001M $NaNO_2$	-	-	-	-	83.8*	-	-
1g/l Cl^-	-	86.3*	90.9	89.8*	85.1*	89.4	-
100mg/l SO_4^{2-}	-	-	87.2	91.3*	88.4*	82.6*	90.3*
1g/l CO_3^{2-} and HCO_3^-	-	91.0	88.5	86.2	86.3	87.0	76.9

TABLE III. Fracture energy values (MJm^{-3}) for OFHC copper tested at 2.8 x $10^{-6}s^{-1}$ and 1.8 x $10^{-6}s^{-1}$(*) at various potentials in aerated solutions at room temperature (FCP = free corrosion potential).

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	82*	-	-	-	-	-
0.1M $NaNO_2$	84	-	-	-	-	-	-
0.001M $NaNO_2$	-	-	-	-	83*	-	-
1g/l Cl^-	-	81*	83	81*	69*	80	-
100mg/l SO_4^{2-}	-	-	83	73*	76*	84*	83*
1g/l CO_3^{2-} and HCO_3^-	-	80	97	75	75	74	71

Fracture energy values were measured but, because of uncertainty concerning the effect of strain rate on fracture energy, results quoted (Table III) are given as MJ/m^3 instead of as a fraction of that obtained for a test in air. As has previously been reported, fracture energies show much greater irregular variations than the measured reductions in area. At the slower strain rate ($1.8 \times 10^{-6}s^{-1}$), several fracture energies were observed that were higher than the value of $76MJ/m^3$ observed in air. The low energies observed at more anodic potentials in solutions containing CO_3^{2-}/HCO_3^- ions, and also in the Cl^--doped solution at +100mV (sce), appeared to be due more to low elongation (∿ 42%) than to low stresses.

Tests at the faster strain rate of $1.7 \times 10^{-5}s^{-1}$ were conducted in a slightly reduced range of solutions than that used for the slower strain rate. As in earlier work,(5) fracture energies are not quoted because of the more erratic stress-strain curves obtained with the smaller number of points available over the shorter testing time (readings were still taken at hourly intervals). The results (Table IV) all indicate a high level of ductility and there was a complete absence of stress corrosion cracks.

TABLE IV. % Reduction in area values for OFHC copper tested at a strain rate of $1.7 \times 10^{-5}s^{-1}$ at various potentials in aerated solutions at room temperature.

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	91.2	85.5	87.0	81.4	87.8	85.3
0.001M $NaNO_2$	- -	-	-	-	87.6	-	-
1g/l Cl^-	91.7	87.2	90.7	87.7	86.6	90.9	-
100mg/l SO_4^{2-}	83.4	-	89.5	88.9	91.1	-	-

One constant load test was conducted on a specimen of OFHC copper using an environment of 0.1M sodium nitrite, a stress of 126MPa and a potential of +100mV (sce). Although there was a great deal of corrosion product, the specimen did not fail in 48 days.

3.3. Testing of PDO copper in Aerated Solutions at Room Temperature

Phosphorus-deoxidised copper was tested in ground water specifically contaminated with the same range of anions as used for the OFHC copper. The reduction in area at fracture (Table V) again indicated a high level of ductility in all environments, at both the strain rates involved, and no stress corrosion cracks were observed.

However, as with the OFHC copper, certain erratic and inexplicable variations occurred in the measured fracture energies (Table VI). On this occasion, the low energy observed in the presence of CO_3^{2-}/HCO_c^- ions at +200mV (sce) was associated with a decreased maximum stress (189MPa) and a low elongation (41.7%). The results in the Cl^--doped solution at +100mV (sce) were very similar to this and gave a fracture energy of 61MJ/m^3.

TABLE V. % Reduction in area values for PDO copper strained at $2.8 \times 10^{-6}s^{-1}$ and $1.8 \times 10^{-6}s^{-1}$ (*) in aerated solutions at various potentials at room temperature.

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	83.8*	-	-	-	-	-
0.1M $NaNO_2$	83.8	-	-	-	-	-	-
0.001M $NaNO_2$	-	-	-	-	86.5*	-	-
1g/l Cl^-	-	86.2*	85.9	88.4*	85.7*	84.7	86.0
100mg/l SO_4^{2-}	-	-	86.6	83.9*	83.8*	84.1*	89.5*
1g/l $CO_3^{2-}$and HCO_3^-	-	85.8	86.6	85.0	89.7	84.6	82.9

TABLE VI. Fracture energy (MJm^{-3}) for PDO copper tested at $2.8 \times 10^{-6}s^{-1}$ and $1.8 \times 10^{-6}s^{-1}$ (*) in aerated solutions at various potentials at room temperature.

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	76*	-	-	-	-	-
0.1M $NaNO_2$	92	-	-	-	-	-	-
0.001M $NaNO_2$	-	-	-	-	77*	-	-
1g/l Cl^-	-	85*	94	82*	61*	77	93
100mg/l SO_4^{2-}	-	-	88	85*	81*	76*	74*
g/l CO_3^{2-} and HCO_3^-	-	76	93	85	84	62	78

Since no loss of ductility is apparent in specimens tested in a 0.001M solution of sodium nitrite, this would seem to represent a safe limit for this species if stress corrosion cracking is to be avoided, even though the fracture energy is not as high as that observed in certain other tests.

Again, the free corrosion potentials were monitored: the potential in the Cl^--doped solution slowly increased from around -80mV (sce) to about -50mV (sce), that for the SO_4^{2-}-doped solution lay between -60 and -30mV (sce) and that for the CO_3^{2-}/HCO_3^- additions varied more than the others, rising from -65mV to +10mV (sce) over 59 hours.

Tests carried out at $1.7 \times 10^{-5}s^{-1}$ (Table VII) also indicated high levels of ductility, with no detectable stress corrosion cracking.

TABLE VII. % Reduction in area values for PDO copper strained at $1.7 \times 10^{-5}s^{-1}$ in areated solutions at various potentials and room temperature.

Environment	Potential mV (sce)						
	-500	-100	FCP	0	+100	+200	+300
Ground water	-	81.5	-	84.8	-	-	-
0.001M $NaNO_2$	-	-	-	-	86.5	-	-
g/l Cl^-	84.3	83.8	82.5	88.7	88.0	80.2	-
100mg/l SO_4^{2-}	86.2	-	89.1	86.1	89.0	-	-

3.4. Tests at 80°C in aerated solutions

It was only feasible to carry out a selected number of tests at an elevated temperature, because of the limited availability of machines with a heated environmental cell. The behaviour of both OFHC and PDO copper was very similar (Tables VIII and IX). Although there were some reductions in area of less than 80%, which indicates that the increase in temperature does have a small effect in reducing ductility, there was no sign of any stress corrosion cracks. The fracture energies are

TABLE VIII. % Reduction in area values for tests on OFHC and PDO copper tested at 2.8 x 10^{-6}s^{-1} in aerated solution at 80°C.

Environment	Potential mV (sce)					
	FCP		0		+100	
	OFHC	PDO	OFHC	PDO	OFHC	PDO
Ground water	74.0	78.8	-	-	-	-
1g/l^{-1} Cl$^-$	-	-	87.0	74.0	-	-
100mg/l SO$_4^{2-}$	-	-	80.7	83.7	-	-
1g/l CO$_3^{2-}$ and HCO$_3^-$	76.3	81.8	75.3	84.6	77.3	84.1

TABLE IX. Fracture energy values (MJm^{-3}) for failure of OFHC and PDO copper strained at 2.8 x 10^{-6}s^{-1} in aerated solutions at 80°C.

Environment	Potential mV (sce)					
	FCP		0		+100	
	OFHC	PDO	OFHC	PDO	OFHC	PDO
Ground water	80	70	-	-	-	-
1g/l Cl$^-$	-	-	60	47	-	-
100mg/l SO$_4^{2-}$	-	-	69	72	-	-
1g/l CO$_3^{2-}$ and HCO$_3^-$	70	75	82	71	70	70

generally lower than might intuitively be expected, and indicate that both varieties of copper are considerably weakened by the combined effect of the environments and the increase in temperature. The particularly low values in the presence of Cl^- ions result from low maximum stresses (∿ 168MPa) combined with low elongations (∿ 40%). Monitoring of the free corrosion potentials during high temperature tests indicated values between -100 and -150mV (sce), except for one sample of PDO copper which showed a potential of about -45mV (sce).

3.5. Chemical Effects

During the latest series of tests, certain chemical effects were observed, in terms of the formation of deposits in the environmental cell and the occurrence of surface films on certain specimens, and these are useful in providing some indication of the various chemical reactions involved. The behaviour of OFHC and PDO copper in this respect was naturally similar when being strained in comparable environments.

During tests in solutions at room temperature, a shiny brown film invariably formed on the copper specimens at the more cathodic potentials (i.e. -100mV, the free corrosion potential and 0mV (sce)). This film varied in tone from a dark brown to a yellowish-brown but was usually shiny and adherent. Under such conditions, the environment usually remained quite clear until the end of the test. Since the tests were invariably conducted at a pH close to 8, reference to the Pourbaix diagram(6) indicates that this brown film is cupric oxide (CuO). At -500mV (sce), which corresponds to -258mV on the hydrogen scale, conditions correspond to the metallic copper region of the diagram and any brown film observed was very patchy.

As the potential was raised (i.e. at +100, +200 and +300mV (sce)) bubbling was observed at the platinum counter-electrode immediately the potential was applied, although this bubbling was never as vigorous as that observed in the more concentrated sodium nitrite solutions described earlier. Under such conditions, a blue deposit occurred in the solution as the test proceeded. The same form of deposit had been obtained earlier(5) and was then identified as $Cu(OH)_2$. Usually such deposition was accompanied by a dull red colouration in patches on the surface of the specimen, that was distinctly different from the cupric oxide. Since cuprous oxide (Cu_2O) should not occur at this potential, according to the Pourbaix diagram, the colouration is thought to be attributable to the exposure of bare copper as a result of oxidation to $Cu(OH)_2$. Any $Cu(OH)_2$ that was actually formed on the surface of the specimen proved to be non-adherent and was inevitably brushed off in pulling the specimen through the close-fitting rubber bung at the bottom of the environmental cell at the conclusion of the test.

At the faster strain rate ($1.7 \times 10^{-5} s^{-1}$) the ground water with enhanced Cl^- content frequently gave rise to a greenish-blue colouration in the cell, and a dusty yellow film formed on the specimen, both of which could be attributable to cuprous oxide or Cu(OH). The deposits in the test cells and the films on the copper specimens generally occurred within the first few hours of straining, so that tests at $1.7 \times 10^{-5} s^{-1}$ (which only took about 10 hours) showed the same environmental effects, though to a lesser extent, as those at the slower strain rates that lasted up to 3 days.

At 80°C, the environment in the test cell frequently became brown as the test proceeded, sometimes accompanied by a small amount of brown deposition, and the specimen itself also often had a brown surface film.

4. GENERAL CONCLUSIONS

1. There is moderate to severe stress corrosion cracking of both OFHC and PDO copper in the presence of sodium nitrite, but cracking is eliminated when the sodium nitrite concentration is as low as 0.001M (69mg/l). The stress corrosion cracking in nitrite becomes more severe as the nitrite concentration is increased particularly if the testing potential is raised to more anodic values (i.e. in the range 0 to +100mV (sce)).

2. Stress corrosion cracking of both OFHC and PDO in ground water based solutions does not occur (at strain rates from 1.8×10^{-6} to $1.7 \times 10^{-5} s^{-1}$) in the potential range -500 to +300mV (sce) over the temperature range 20 to 80°C, although there is a certain amount of dissolution at the more anodic potentials. In all conditions there appears to be some weakening of the metal, leading to a drop in the energy required to cause fracture and this seems to be particularly noticeable in solutions with a high chloride content at 80°C. This phenomenon does not however produce actual cracks and the material should be safe for use provided the stresses are kept sufficiently low to avoid any plastic deformation.

3. De-aerated conditions increase the environmental resistance of the material in aggressive environments (i.e. 0.6M and 0.3M solutions of sodium nitrite).

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INVESTIGATION OF THE STRESS CORROSION RESISTANCE OF PURE COPPER

APPENDIX

In order to cover the possibility of fabricating copper canisters by using a joining technique involving isostatic pressing, a number of tests were carried out using

(i) rods having joints produced by an isostatic pressing technique

and (ii) rods containing oxygen levels such as might be encountered in such joints (up to 5000 ppm).

Three rods were provided having an isostatically pressed joint 110 mm from one end and another three that had been produced by sintering together two fractions of copper powder and machining the product to rods.

Stress corrosion test specimens of the standard dimensions previously employed were machined from all of the specimens provided, but the rods containing the joints were polished and etched in ferric chloride to positively locate the narrow band of fine grain in the fusion zone before machining, so that this would be included in the offset gauge length.

Once machined, and the gauge length polished and degreased in the usual way, specimens were strained to failure using an initial strain rate of 2.5×10^{-6}/s. Two of each type of rod were tested in the synthetic ground water for comparison with the copper samples previously tested, and the third was strained in 0.001 M sodium nitrite (69 mg/litre) i.e. the concentration chosen from previous results as the maximum permissible level of contamination by this species.

All but one of the specimens showed extensive ductility before failure (Table A1) and no indication of stress corrosion cracking. One of the two welded specimens tested in ground water showed a significant loss in ductility, as indicated by the reduction in area at failure. However, since the other specimen in ground water and that in the dilute nitrite both showed good ductility, it is felt that the failure was more attributable to a poor quality weld than to any tendency to stress corrosion.

TABLE A1. Maximum stress, % total elongation and % reduction in area for welded copper and powder copper specimens strained at 2.5 x 10^{-6}/s in various environments.

Specimen	Material	Environment	Maximum Stress MN/m^2	% Total Elongation	% Reduction in Area
4	Welded Cu	Ground water pH9.7	231	43.5	34.9
5	"	" pH8.2	234	30.3	89.5
1	"	0.001 M $NaNO_2$	234	43.6	92.0
3	Powder Cu	Ground water pH9.6	230	33.8	55.6
6	"	" pH8.2	232	37.1	53.5
2	"	0.001 M $NaNO_2$	223	35.1	64.3

The results indicate that rods prepared from sintered powders have intrinsically less ductility than either the extruded rod or that satisfactorily welded by isostatic pressing. However, all materials tested indicate no susceptibility to stress corrosion cracking in either ground water or a solution containing 0.001 M sodium nitrite.

Examination of a metallographic section cut parallel to the tensile axis through the fracture surface showed regions close to the fracture of the specimen having low reduction in area that had a different structure (probably fine-grained) - Figure A1. This suggests that fracture of this specimen was very closely associated with the weld.

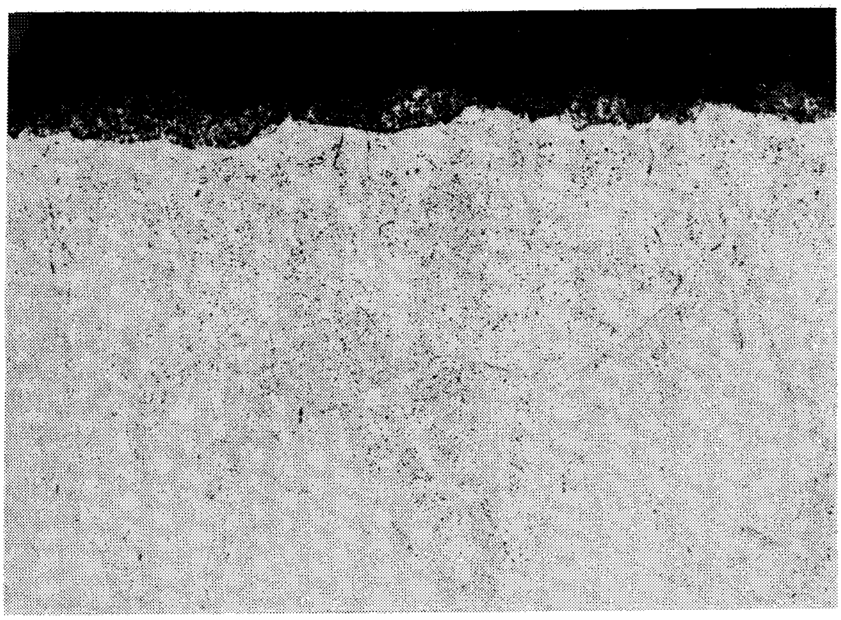

Figure A1. Section through the welded specimen 4 (etched in ferric chloride) showing the differential etching close to the fracture surface.

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