Dissolution of Copper in Acidified Ferric Sulphate Solutions

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Measurements have been made on the dissolution rate (i_c) and the mixed potential (E_c) of copper in unstirred sulphuric acid solutions of ferric sulphate at 21°C. These quantities have been found to be very nearly independent of time and to obey the following relationships:

$i_c = 0.011c$ A/cm^2

$d\,E_c/d \log i_c = 2.303RT/2F$

where c is the ferric sulphate molarity. The mixed potential has moreover been found to be very nearly equal to the pure anodic dissolution potential of copper at equal dissolution rates.

1.0 INTRODUCTION

Following previous work [1,2] on the kinetics of the anodic dissolution and cathodic deposition of copper in acid sulphate solution under conditions of amperostatically applied currents, studies have been made on the depolarized dissolution of this metal in acidified ferric sulphate solutions.

In the former case, the dissolution reaction is electronically balanced by the applied current and is essentially the only reaction occurring at the copper anode. In the latter case, however, it is accompanied and electronically balanced by a simultaneous reduction of ferric ions at the same metal surface.

The main purpose of the present work is to compare the polarization characteristics of the dissolution reaction in these two different cases.

2.0 EXPERIMENTAL

The experimental work consists in the determination of the dissolution rate (corrosion rate) and the mixed potential (corrosion potential) of copper in unstirred 1 N and 0.1 N sulphuric acid solutions of ferric sulphate (0.001—0.2 M) at 21°C (room thermostated to ±0.5°C).

High purity copper (2 ppm Fe, 2 ppm Ag, 1 ppm Ni, 1 ppm Si, 1 ppm Na, and less than 1 ppm each of Ca and Mg, other metallic elements and the elements O, S, Se, Te, and P — if present — being below the limits of detection by the spectrographic, chemical, and metallographic methods applied) has been used in the form of sheets of thickness about 0.05 mm and apparent area (both sides) of 14 cm^2 for the rate measurements and about 2 cm^2 for the potential measurements. Prior to use, the sheets were vacuum annealed
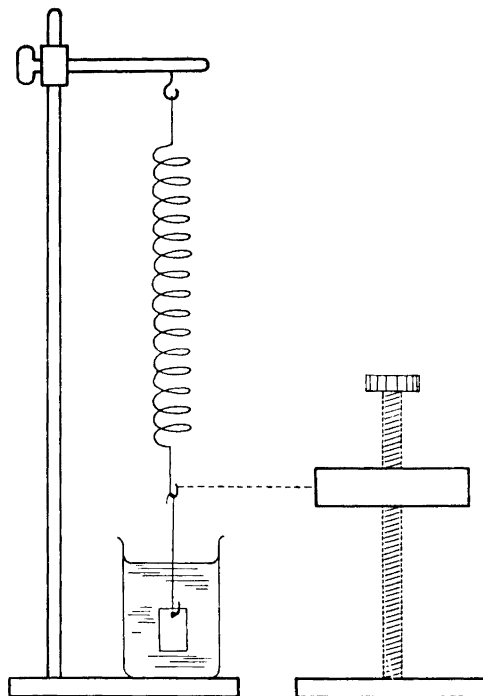
Fig. 1. The quartz helix technique for weight change measurements.

for about one hour at about 700°C, mechanically polished, etched in dilute nitric acid, and washed in running water, distilled water, and acetone (A.R.)

The solutions were prepared from A.R. quality ferric sulphate and sulphuric acid in water distilled from a "pure" and soft fresh water. No attempts were made to free these solutions of dissolved oxygen, and the experiments were performed with the solutions exposed to air.

The rate measurements were carried out by means of a semi-continuous quartz-helix technique as sketched in Fig. 1. This is standard technique for taking up rate curves in the field of high-temperature oxidation of metals. To our knowledge, however, it has not previously been used in the field of low-temperature electrochemical corrosion, even though this technique in many such cases has obvious advantages over the intermittent weighing usually applied. The quartz helix used in the present work, showed a linear extension of 0.505 mm per mg increase in load over a load range including and being much broader than the one covered by the actual experiments (about 0.2 to 0.3 g). It was calibrated for each run through weighings of the copper sheets on a Mettler semi-micro balance. The changes in the quartz helix extension were measured by means of a Fuess cathetometer allowing vertical displacements to be read to less than 0.01 mm. The whole set up was thus sensitive to weight changes of less than 5 μg and, for sheets of 14 cm², less than 0.36 μg/cm². The copper sheets were suspended by means of thin quartz hooks, which were cleaned in chromic acid and in a flame. The reaction took place in 600 ml beakers filled with the test solution. The experimental time varied from one hour to about one day depending on the reaction rate.

The potential measurements were carried out as sketched in Fig. 2 by means of a Cambridge pH-meter and saturated calomel electrodes. The copper electrodes were here exposed with an area of about 2 cm² to about 100 ml of the test solution. Potential readings
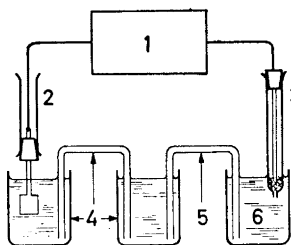
Fig. 2. The technique for potential measurements. 1, potentiometer; 2, test electrode; 3, saturated calomel electrode; 4, test solution; 5, potassium chloride saturated agar-agar bridge; 6, saturated potassium chloride solution.

were made over periods corresponding to those for the rate measurements. In transforming these readings to values on the normal hydrogen scale (NHS), a value of 0.244 V has been used for the saturated calomel electrode.

3.0 RESULTS

Examples of the rate curves and of the potential-time curves obtained are shown in Figs. 3 and 4, respectively. These curves apply to 0.1 N sulphuric acid solutions of ferric sulphate, but are representative also for the types of
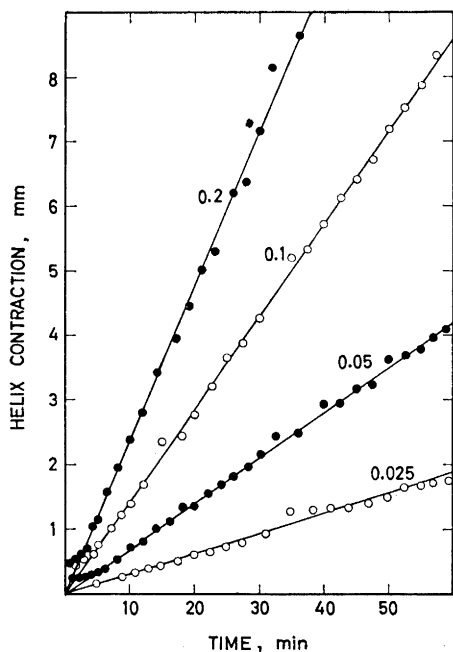

Fig. 3. Dissolution/time curves for copper in 0.1 N sulphuric acid solutions of ferric sulphate at various ferric ion molarities (21°C, helix sensitivity 0.505 mm/mg).
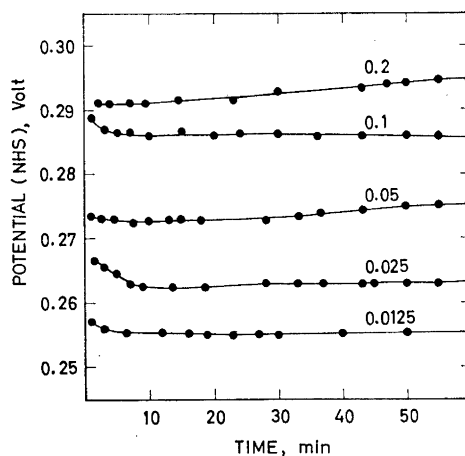
Fig. 4. Potential/time curves for copper in 0.1 N sulphuric acid solutions of ferric sulphate at various ferric ion molarities (21°C).
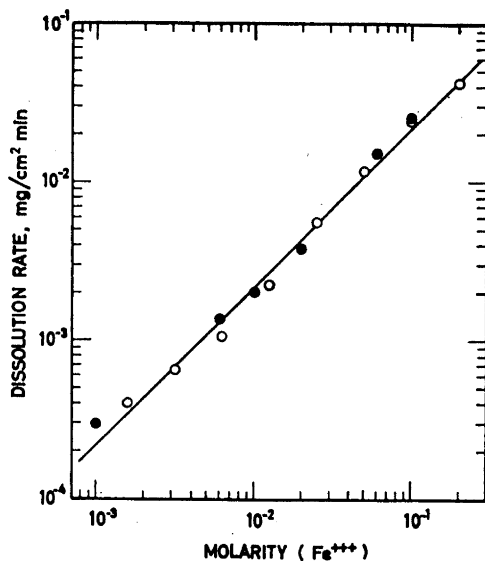
Fig. 5. Dissolution rate of copper in 1 N (closed circles) and 0.1 N (open circles) sulphuric acid solutions of ferric sulphate *versus* ferric ion molarity (21°C).

curves obtained in the 1 N sulphuric acid solutions. It was generally found that both the rate of dissolution and the corrosion potential of copper in any one of the solutions applied were quite nearly independent of time.

In Fig. 5, the average values found for the dissolution rate in the various solutions are plotted as a function of the ferric ion concentration. The results show that the dissolution rate is essentially independent of the sulphuric acid concentration and increases approximately linearly with the ferric sulphate concentration. The straight line drawn in Fig. 5 corresponds to the following relationship:

$$i_a = 0.22c \ mg(Cu)/cm^2min \tag{1}$$

which on the basis of 100 % cupric ion formation and electronic balancing gives:

$$i_a = i_c = 0.011c \ A/cm^2 \tag{2}$$

where i_a is the rate of copper dissolution, i_c the rate of ferric ion reduction, and c the ferric ion molarity.

In Fig. 6, the values obtained for the potential of copper in the various solutions are plotted as a function of the dissolution rate in the same solutions. No corrections have been made for possible liquid junction potentials between the test solutions and the saturated potassium chloride solution. In the same diagram (Fig. 6) is also given the *uncorrected* polarization curve previously [1] obtained from amperostatic measurements on the anodic dissolution of the
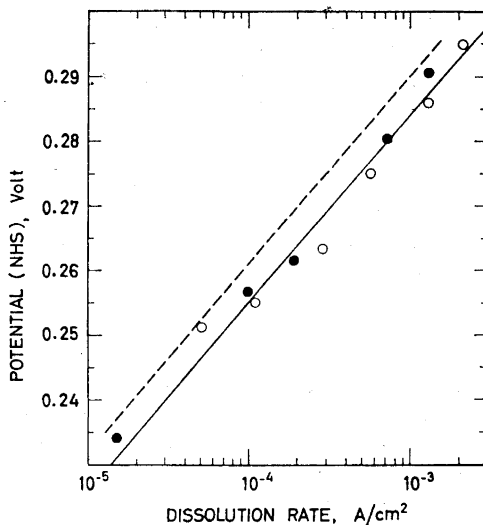
Fig. 6. Potential *versus* dissolution rate of copper in 1 N (closed circles) and 0.1 N (open circles) sulphuric acid solutions of ferric sulphate (21°C). The broken line represents the pure anodic dissolution potential of copper in 0.1 N sulphuric acid at 20°C (Ref.[1]). The potentials include liquid junction potentials between the test solutions and a saturated potassium chloride solution.

same type of copper in 0.1 N sulphuric acid at 20°C. The relatively small difference in position of these two curves may be due partly to the difference in temperature (20 and 21°C) and partly to possible differences in the liquid junction potential. The results do thus indicate that the anodic dissolution reaction of copper is nearly independent of it being electronically balanced by an impressed current or by a simultaneous reduction of ferric ions at the dissolving surface.

It is also of interest to note that the present results strongly support the amperostatically obtained ones [1,2] in showing a Tafel slope of:

$$b_a = 2.303 \; RT/2F \tag{3}$$

(0.029 V at 21°C) for the anodic dissolution of copper under stationary conditions.

4.0 DISCUSSION

The present finding that the rate of dissolution of copper in acidified ferric sulphate solution is proportional to the ferric ion concentration, is in agreement with previous results [3,4] and is analogous to what has been found for a number of other metals less noble than copper [3-7]. It is further qualitatively in accordance with what is to be expected for the rate when entirely controlled by diffusion of ferric ions to the metal surface. The rate data obtained are also quantitatively in agreement with this model, provided the diffusion coefficient of ferric sulphate under the present conditions is about 0.6×10^{-5} cm^2/sec.

According to Kortüm and Bockris [8], namely, the limiting diffusion current for one electron exchanging ions with a diffusion coefficient of 1.3×10^{-5} cm²/sec should be about $0.025c$ A/cm² in unstirred solutions (as compared to the here found rates of $0.011c$ A/cm²). No direct data have been found for the diffusion coefficient of ferric sulphate, but the above value is probably not unreasonable. Zinc sulphate and magnesium sulphate, for instance, have diffusion coefficients of about 0.7×10^{-5} cm²/sec in dilute solutions at 25°C [9].

The present results further show that the rate of dissolution of copper in acid sulphate solution is very nearly the same function of the electrode potential regardless of this being a pure copper dissolution potential (applied anodic current) or a mixed copper dissolution and ferric reduction potential. This indicates that the ferric/ferrous reaction does not interfere very much with the copper dissolution reaction, but tells nothing as to a possible interference of the latter with the former. An interference at the electrode surface will namely be of little importance for the rate of a diffusion controlled reaction. It is further known that an electrode reaction very well may interfere with another without this necessarily being mutual. An example is provided by the dissolution of iron under simultaneous hydrogen evolution in acid chloride solution [10]. Also in that case, the dissolution reaction is independent of whether it occurs alone or together with the cathodic reduction reaction. The latter reaction, however, is clearly stimulated by a simultaneous occurrence of the former.

The present results on copper are quite analogous to recent results of similar experiments on nickel [7].

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