Film Growth on Copper in Acidified Cupric Chloride Solutions

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The reaction of copper with cupric ions in chloride containing acid solutions is accompanied by a precipitation of cuprous chloride on the metal surface when the chloride concentration is below a certain limit depending on the cupric concentration. This precipitation and its effect on the above reaction have been studied mainly in 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride by means of rate measurements (quartz helix, intermittent weighing, dissolution of precipitated layers) and potential measurements (corrosion potential). In these solutions, the reaction of copper with cupric ions to cuprous species becomes noticeable at x-values above about 0.01 and gives cuprous chloride precipitation at all x-values up to about 1.5. The reaction rate goes through a maximum around $x = 0.05$ and a minimum around $x = 0.125$ and becomes essentially independent of x at x-values above 1.5. Also the amount of cuprous chloride precipitated on the surface in given times shows a maximum at about $x = 0.05$. These transitions in chloride ion dependence are further reflected in the corrosion potential.

1.0 INTRODUCTION

It is well known that copper in cupric ion containing chloride solutions does not act as a reversible copper/cupric electrode, but as an irreversible and mixed copper/cuprous and cupric/cuprous electrode, the cuprous ions being complexed with chloride ions [1-3]. When copper is immersed in such a solution, therefore, it will react with the cupric and the chloride ions to form various cuprous chloride species.

In a previous work [4], this reaction has been studied mainly under conditions of negligible cuprous chloride precipitation. The pure anodic dissolution reaction in corresponding cupric free solutions has also been studied [5]. The former investigations show that cuprous chloride is precipitated on the copper surface when the cupric concentration is high enough (dependent on the chloride concentration). The present work is aiming at elucidating this cuprous chloride precipitation and its effect on the reaction of copper with cupric ions in chloride solutions. To avoid a concurrent cuprous oxide formation, the investigations have been performed with acid solutions of pH about 1.

Previous work related to this matter is especially due to Cooper *et al.*[6,7], who have studied the formation of cuprous chloride films on copper anodes in hydrochloric acid solutions.

2.0 EXPERIMENTAL

The main part of the experimental work consists in determinations of the weight change of copper sheets in various cupric ion containing chloride solutions (specified below) and of their successive weight loss in 1 N hydrochloric acid. The latter weight loss represents the dissolution of the cuprous chloride layer formed on the sheets during their immersion in the former solutions.

The weight change measurements have been performed both by the semi-continuous quartz helix technique previously described [8] and by intermittent weighing. From quartz helix measurements, it was found that even the thickest cuprous chloride layers encountered were completely dissolved in the 1N hydrochloric acid solution in less than 15 min. A duration of 15 min was therefore chosen for these dissolution runs, whereas the duration of the actual reaction experiments has varred mostly from 2 to 120 min. The dissolution runs were accompanied by blank tests, none of which showed any noticeable dissolution of the copper metal itself. All these experiments have been performed with sheets of 14 cm² total surface area (geometrical) exposed to 500 ml solution. The quartz helix used had a sensitivity of 0.505 mm/mg. Because of buoyancy, no attempts have been made to transfer the helix readings to actual weight changes, whereby these measurements only give semiquantitative indications of the weight changes occurring.

A few corrosion potential measurements have been made in the way previously described [8], and also a few preliminary radio-tracer experiments. The latter experiments have been performed partly with neutron activated copper sheets in chloride solutions of inactive cupric salts and partly under opposite activation conditions. This type of measurements is now being continued and extended and will only be touched upon in the present work. A more complete description of the tracer technique will therefore be postponed.

The same type of annealed and etched sheets of high purity copper as previously described [8] have been used, and the solutions have been made from A.R. quality acids and salts in water distilled from a rather pure tap water. All the experiments have been performed at room temperature (about 22°C) and no stirring have been applied.

3.0 RESULTS

From X-ray diffraction measurements directly on the surface of copper sheets having been immersed in some of the solutions to be mentioned below, clear evidence is found for the presence of cuprous chloride. The diffractograms do not show reflections from any other compound.

The total weight change. The weight change of copper sheets as indicated by quartz helix measurements during their immersion in various cupric and chloride containing acid solutions is shown in Figs. 1 and 2. The zero point position of the quartz helix has in these cases been determined by a somewhat uncertain free hand extrapolation of the readings to zero time in a linear plot. The same uncertainty is thus attached to the ordinate position of the "helix extension"/time curves, but not to the variations shown by these curves from the first reading on.

The curves in Fig. 1 apply to solutions of 0.1 N hydrochloric acid + x M cupric chloride ($x = 1$, 0.3, and 0.1). In all these solutions, the reaction of copper with cupric ions is accompanied by a precipitation of cuprous chloride on the metal. During a first stage, this gives rise to a weight increase of the
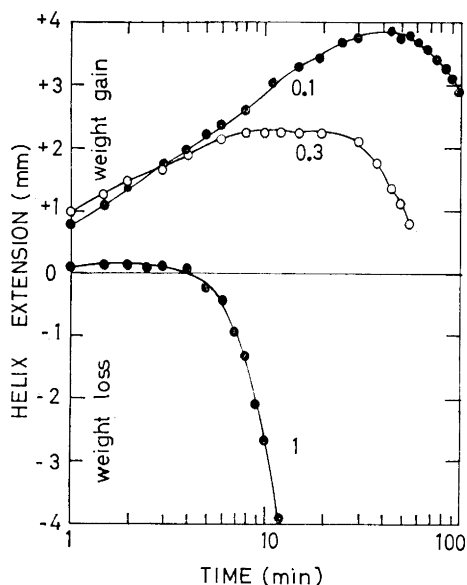
Fig. 1. Helix extension curves for copper
(14 cm²) in 0.1 N hydrochloric acid + x M
cupric chloride at x = 1, 0.3, and 0.1.

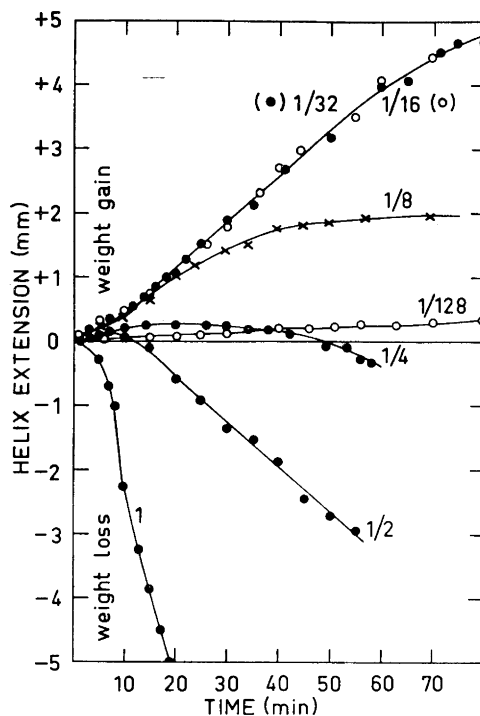Fig. 2. Helix extension curves for copper
(14 cm²) in 0.1 N sulphuric acid + 0.1 M
cupric sulphate + x M potassium chloride
at various values of x.

copper sheets, a weight increase which apparently is not far from obeying a
direct logarithmic time dependence. Successively, however, the weight increase
comes to an end, whereafter the further reaction makes the sheets loose in
weight. In the solutions applied, the initial weight gain is less distinct and the
weight loss starts earlier the higher is the cupric chloride concentration.

The curves in Fig. 2 apply to solutions of 0.1 N sulphuric acid + 0.1 M
cupric sulphate + x M potassium chloride x = 1, 1/2, 1/4, 1/8, 1/16, 1/32, and
1/128). Also in these solutions it is quite clear that a weight influencing precipi-
tation of reaction products occurs on the copper surface. The film growth
seems most pronounced at some intermediate chloride concentrations (1/32 —
1/16 M) and becomes less pronounced to both sides of this chloride range. At
the lower side, there still is a weight increase all over the experimental time
applied, but this increase becomes very slow at low chloride concentrations
(see the curve for x = 1/128). At the higher side, the helix extension curves
are essentially of the same type as described above for the hydrochloric acid
solutions of cupric chloride. The initial weight gain becomes here less and less
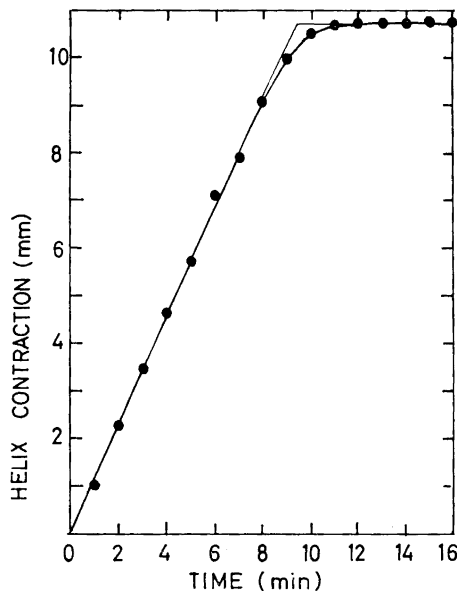distinct with increasing chloride concentration and is not observable at chloride

Fig. 3. Helix contraction curve for the dissolution in 1 N hydrochloric acid of the cuprous chloride layer formed on a copper sheet (14 cm²) during one hours immersion in 0.1 N sulphuric acid + 0.1 M cupric sulphate + 0.05 M potassium chloride.

concentrations above 1 M. Even at 1 M, however, there probably is a rate affecting precipitation on the copper surface. The dissolution rate is here distinctly slower than at higher chloride concentrations at which it becomes independent of the chloride concentration [4]. As is evident from previous results (see especially Fig. 1 in Ref.[4]), the chloride concentration range in which there is a rate affecting precipitation increases with the cupric sulphate concentration in solutions of the type discussed here.

The film growth. Fig. 3 shows a typical example of the weight change of a cuprous chloride covered copper sheet in 1 N hydrochloric acid, as this is indicated by quartz helix measurements. It is there seen that the dissolution rate is essentially constant until it relatively sharply drops to zero. This obviously represents the complete dissolution of the cuprous chloride layer, the weight of which may be determined by weighings before and after the dissolution process.

Results of determinations of this type of the cuprous chloride layer formed on copper during various lengths of immersion in 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride (x = 0.25, 0.125, and 0.05) are given in Fig. 4. It is there seen that, in all these solutions, the layer grows rapidly in the first few minutes of immersion. At the lowest chloride concentration (0.05 M), laying in the above described chloride range of most pronounced film formation, the layer continues to grow relatively rapidly, but the growth rate decreases somewhat with time. This decrease, however, is less than what would correspond to a parabolic time dependence. At the two higher chloride concentrations applied, there is a relatively sharp fall in the growth rate after the
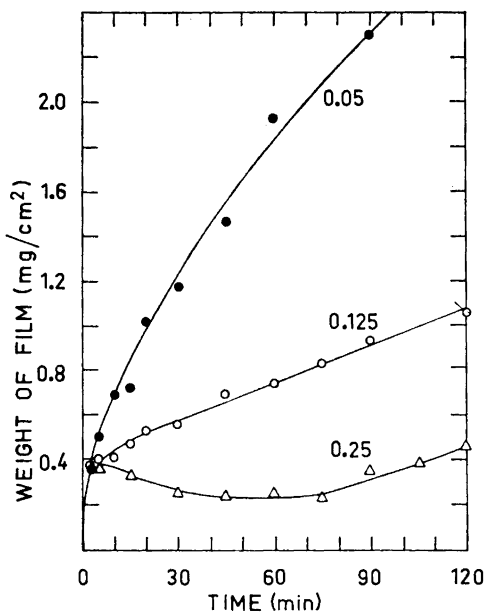
Fig. 4. Growth of cuprous chloride on copper in 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride at x = 0.25, 0.125, and 0.05.
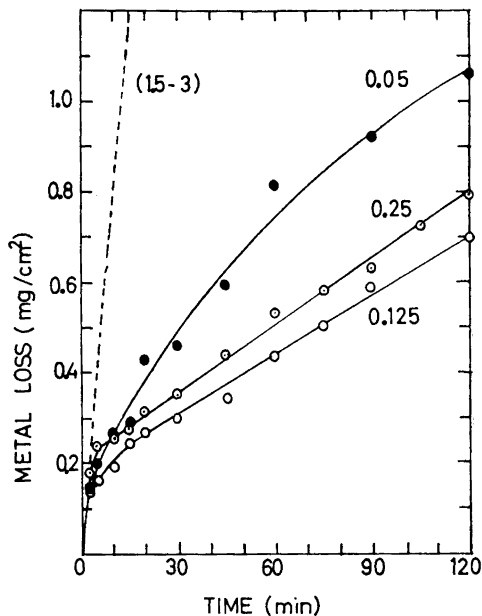
Fig. 5. Total reaction of copper in 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride at x = 0.25, 0.125, and 0.05.

first few minutes, a fall which in the strongest chloride solution goes practically to zero.

Each of the experimental points in Fig. 4 represents the average of at least four experiments. The reproducibility has not always been very good, however. This applies especially to the strongest chloride solution.

The reaction rate. The reaction of copper with cupric ions in the solutions applied does certainly not only lead to cuprous chloride precipitated on the surface, but also to cuprous species in the solution. Besides being obvious, this is also verified by tracer experiments (neutron activated copper sheets). If we by w_0, w_1, and w_2 designate the weight of a copper sheet at the start of the experiment, after immersion in the test solution, and after removal of the cuprous chloride layer, respectively, the metal loss $w_0 - w_2$ should represent the total amount of copper that has reacted with the test solution. Results of such measurements for various lengths of time in solutions of 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride (x = 0.25, 0.125, and 0.05) are given in Fig. 5. The slope of the curves there drawn is a measure of the reaction rate.

In the solution of the lowest chloride content (0.05 M), the reaction rate decreases with time qualitatively in the same way as the rate of growth of

the cuprous chloride layer. Within the experimental times applied, however, the weight increase of the layer (Fig. 4) is always faster than the metal loss (Fig. 5) whereby the total weight of the specimen increases all the time. This is in accordance with the results of the quartz helix measurements in analogous solutions of similar chloride content (Fig. 2).

Also in the solution of medium chloride content (0.125 M), the reaction rate varies with time in very much the same way as does the growth rate of the cuprous chloride layer. A comparison of the rate curve for film growth (Fig. 4) and for metal loss (Fig. 5), shows also in this case reasonable agreement with the quartz helix measurements in the same solution (Fig. 2). It is here further interesting to note that, after an initial period, both the reaction rate and the growth rate becomes essentially independent of time. This may indicate that the increase in thickness of the cuprous chloride layer, when above a certain limit, does not mean very much for the reaction rate. There is at least no inverse proportionality and no other simple relationship between the layer thickness and the reaction rate. This may also be seen by comparing the results in the solutions of 0.125 and 0.05 M potassium chloride, respectively. Even though the cuprous chloride layer (Fig. 4) becomes appreciably thicker in the latter than in the former case, the reaction rate (Fig. 5) remains higher, at least over most of the time period covered.

Also in the solution of the highest chloride content (0.25 M), there is a relatively sharp fall in the reaction rate to a steady value after a short initial period. The steady value is slightly higher than in the 0.125 M chloride solution. There is also in this case relatively good agreement between the specific results in Figs. 4 and 5 with the composite results in Fig. 2.

For comparison, previous results [4] on the reaction of copper with cupric ions in solutions of the same sulphuric acid and cupric sulphate concentration as given above and of high enough potassium chloride content (1.5 — 3 M) to avoid any rate influencing cuprous chloride precipitation, are reproduced by the stipulated line in Fig. 5. This line applies to all chloride concentrations within (and probably above) the range mentioned. The results in Fig. 5 further indicate that the reaction follows this line for a short initial period also at the lower chloride concentrations at which it is accompanied by a cuprous chloride precipitation on the metal surface. It may seem, therefore, that the precipitation does not affect the reaction very much until the surface is covered by an appreciable amount of precipitated cuprous chloride, about 0.3 mg/cm² when judged from the results in Figs. 4 and 5. This amount corresponds to a layer of average thickness around 10^4 Å.

The results in Fig. 5 further show that the steady reaction rate in the 0.125 and the 0.25 M chloride solution is about 5 to 6 percent of the initial rate, and that the reaction rate seems to slow down to a similar value also in the 0.05 M chloride solution during the time period covered.

The corrosion potential. The corrosion potential of copper in solutions of the above described type, 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride with x in the range 10^{-2} — 1, have been measured over periods of about one hour. In all the solutions applied, the corrosion potential was found to be stationary almost from the beginning. Some variation some-
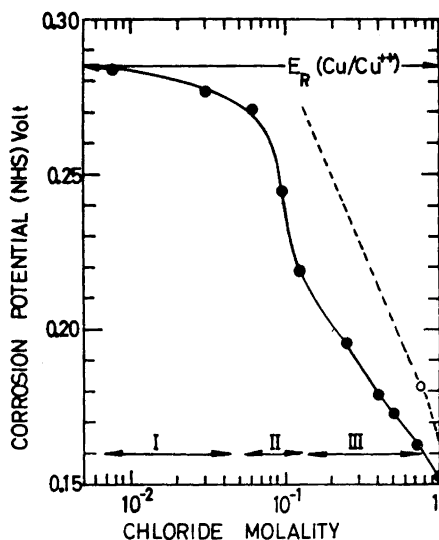
Fig. 6. Corrosion potential of copper in 0.1 N sulphuric acid + 0.1 M cupric sulphate + x M potassium chloride as a function of x.

times observed in the very first minutes of immersion, could very well simply be due to disturbancies introduced by the starting operations. Stirring, for instance, was found to affect the potential.

In Fig. 6, the stationary potentials found are plotted *versus* the chloride concentration of the respective solutions. In the same diagram are also given the value found for the reversible potential of copper at the extreme of no potassium chloride in the solution (horizontal line), and values to be expected for the corrosion potential in the imaginary case of no cuprous chloride preci-pitation (the stipulated line with a break at a chloride molality of about 0.8). These "expected" potentials are estimated by extrapolation of previous results [4] obtained under conditions of no cuprous chloride precipitation in solutions of the same type as here applied, but partly at higher chloride concentrations and partly at lower cupric sulphate concentrations.

The results in Fig. 6 thus show that the potential of copper in the solutions concerned is essentially determined by the reversible copper/cupric exchange reactions at chloride concentrations below about 10^{-2} M, and by the irreversible and mixed copper/cuprous and cupric/cuprous reactions and the effect of the cuprous chloride precipitation on these reactions at chloride concentrations higher than this. That the precipitation on the surface also affects the poten-tial (and not only the rate) is indicated by the distinct deviation of the experi-mental curve from the "expected" one in Fig. 6. It is further interesting that this deviation shows a maximum very nearly at that chloride concentration at which the reaction rate (see Fig. 5) shows a minimum (*i.e.* at about 0.125 M).

The experimental potential curve is clearly composed of three main sections applying to three successive chloride concentration regions. These regions are indicated in Fig. 6, but their boundaries are not well established. In region I (low chloride concentrations), the potential falls somewhat and the reaction

rate increases with increasing chloride concentration. In region II, the potential fall is much steeper and the reaction rate has turned over to decrease with increasing chloride concentration. In region III, the potential fall is again lower and the reaction rate again increases with increasing chloride concentration. Region III terminates at a chloride concentration somewhere between 1 and 1.5 M, above which there is no (or only a negligible) cuprous chloride precipitation and the reaction rate is essentially independent of the chloride concentration (see Ref.[4]). What here is said about the reaction rate is based on the data in Figs. 2 and 5.

Tracer studies. Only a few preliminary tracer experiments have so far been made in some mixed sulphate and chloride solutions of the above type (partly with neutron activated copper sheets and partly with neutron activated cupric sulphate). These measurements show essentially the same features as already mentioned in the above description of the film growth and the reaction rate. They further indicate that the cuprous ions in the precipitated layers originate about half and half from the metal and from the cupric ions in the solution. This work is now being continued, and the detailed description will therefore be postponed until a more complete set of measurements has been made.

4.0 DISCUSSION

The present work clearly shows that the reaction of copper with cupric ions in acid chloride and mixed chloride and sulphate solutions, over a large chloride concentration range (dependent on the cupric concentration [4]), leads to a precipitation of cuprous chloride on the metal surface. It further shows that this precipitation (after an initial period) affects both the potential and the rate of the further reaction, and thereby also the further growth of the cuprous chloride layer. These effects are rather strange, however, as they seem more determined by the conditions (electrolyte composition) under which the reaction (and the precipitation) occurs than of the actual amount of precipitated cuprous chloride on the surface. This is also indicated by the observed constancy in potential and partly also in reaction rate (Fig. 5) even under conditions of relatively rapid growth of the cuprous chloride layer (Fig. 4). It is further interesting to note that the observed potentials are on the *active* side of those to be expected (from extrapolation) for the imaginary case of no precipitation (see Fig. 6). This is the opposite of what is encountered in the formation of passivity films on metals.

The present experiments have mainly been performed in solutions of 0.1 N sulphuric acid + 0.1 M cupric sulphate with various amounts of potassium chloride, and the results indicate three successive chloride concentration regions of different chloride ion effects on the reaction and the precipitation. In the low region, the reaction seems first of all determined by the small amount of chloride ions available, and its rate increases therefore with the chloride ion concentration. The cuprous chloride layers formed in this region, apparently have relatively low protecting properties. However, the protecting properties may seem to increase with the chloride ion concentration at which the layers are formed, successively resulting in a reversal of the chloride concentration

dependence into that encountered in the medium chloride concentration region. The solubility and also the dissolution rate [9] of cuprous chloride increases with the chloride concentration, and the chloride dependence found in the third region is qualitatively what to be expected from these effects to become appreciable. In this region, the precipitation is increasingly diminished and the reaction rate increases with increasing chloride concentration, until no precipitate is formed at all. The reaction rate then becomes independent of the chloride concentration and entirely determined by the cupric ion diffusion [4].

The present work is just comprehensive enough to suggest the above trend, and more work is needed before a more complete account can be given of the cuprous chloride precipitation and its role in the reaction of copper with cupric chloride in acid solutions.

In closing this discussion, it might be appropriate to point out some consequences of the reaction of and precipitation on copper in cupric chloride and bromide [9] solutions. Such solutions have previously been used by several investigators in radiochemical studies on the exchange of copper between the metal phase and aqueous solutions of cupric salts and on the effect of anions on this exchange (see, e.g., Ref.[10]). Some strange conclusions have also been drawn from such measurements as to the exchange reaction [10,11]. It should now be clear, however, that these measurements have little to do with the reversible copper/cupric exchange reaction, but are reflecting partly the irreversible dissolution of and partly the cuprous halide precipitation on copper in these solutions.

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