

CHEMISTRY / ELECTROCHEMISTRY OF THE SULPHUR TARNISHING OF COPPER

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CHÉMIA / ELEKTROCHÉMIA STMAVNUTIA POVRCHU MEDI V DÔSLEDKU PRÍTOMNOSTI SÍRY

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Abstrakt

Stmavnutie povrchov medi je v tomto príspevku definované ako dôsledok sulfidov medi, čo je esteticky alebo technicky nežiaduce v mnohých odvetviach priemyslu a obchodu ako napr v elektronike, klenotníctve a stomatológii.

Mnohé publikácie zaoberajúce sa testovaním tmavnutia povrchov necitujú mnohé vedecké poznatky z oblasti vlastností tuhých látok a správania sa sulfidov medi, úlohu chemo- a fotokatalýzy v systéme plynná síra-voda-kyslík, význam prenosu hmoty v testoch v plynnej fáze a vodných prostrediach. Tieto budú uvažované v tomto príspevku kladúc dôraz na elektrochemický priebeh v procese tmavnutia povrchov vo vzťahu k anodickým a katodickým reakciám, chémie/elektrochémie systému síra/voda a mechanizmu tvorby sulfidov medi.

ABSTRACT

Tarnishing of copper surfaces is defined here primarily as the formation of copper sulphides, which are aesthetically and/or technologically undesirable in many areas of industry and commerce, such as in electronics, jewellery and dentistry. Many of the publications dealing with tarnish testing do not cite the large body of scientific knowledge describing the solid-state properties and behaviour of copper sulphides, the role of chemical- and photo-catalysis in the gas phase sulphur-water-oxygen system, the importance of mass transport in gas phase tests and aqueous environments. These will be considered here, laying emphasis on the electrochemical behaviour of the tarnish process in terms of coupled anodic and cathodic reactions, the chemistry/electrochemistry of the sulphur/water system, the mechanism of formation of the copper sulphide phases.

Key words: copper tarnishing, copper sulphides, sulphur, hydrogen sulphide, electrochemistry

1. INTRODUCTION

The systematic application of scientific methodology to the results obtained in the accelerated testing of electrical contacts and similar components, as also the metals and alloys of which these are fabricated, is now about a quarter of a century old; some of the accelerated tests themselves are much older still.

Successive papers have revealed shortcomings in the techniques of some earlier workers and have highlighted the experimental difficulties of carrying out steady-state measurements with mixed gases at extremely low concentrations. Thus, it is clear, as several workers have pointed out [1,2] that inlet and outlet concentrations are rarely identical, or that chamber loading [1,2] and the location of test samples in the chamber [2] can affect results. Abbott [1] has suggested that some of the apparent dependence of tarnish rates on gas flow, may in fact be spurious and attributable in fact to decreasing depletion effects as higher gas flow rates are used through the chamber.

Many workers have followed tarnish film formation by electrical contact resistance measurements. This method, while a direct method of measuring the very parameter of importance to the industry, is not a reliable guide to film thickness, since the contact resistance is a function of parameters such as load, prevailing (as opposed to chamber) humidity and the chemistry of the tarnish film.

The emphasis, throughout, has been on the electrical side. Only a few workers in the field have considered what chemical reactions are actually responsible for the tarnish mechanisms, a slightly large number having been content to reduce the process, whatever its chemistry, to an empirical parametric equation. To the extent that mechanisms or rate-determining steps have been proposed, these do not in all cases seem fully consistent with experimental observations either those of the proponents themselves or of other workers.

Possibly the single most remarkable omission from the considerable body of literature, is the apparent absence of any suggestion that the tarnishing processes might involve electrochemical reactions. That corrosion, both in the liquid and the gas-phase, is based on coupled electrochemical processes, is accepted without question. Saving only the fact that tarnish films are largely sulphides, rather than oxides, it is hard to understand why the same theories have seemingly not been applied. Nor should the analogy be restricted to the superficial resemblance, since there is much information relating to anodic and cathodic reactions involving the reactants and products of tarnishing. At least one of the major tarnishing reactions - the sulphidation of Cu - has been studied (admittedly at much higher temperatures) by workers who recognised the electrochemical nature of the process. In what follows, an attempt has been made to examine critically the experimental data and the proposed mechanisms for the tarnishing of copper by elemental sulphur and by hydrogen sulphide.

2. THERMODYNAMIC DATA AND EQUATIONS

2.1 Copper-gas systems

Critically assessed thermodynamic data [3] were used to calculate the equations that provided predictions for the kinetic behaviour of copper-sulphur-oxygen and copper-sulphur-water-oxygen systems, which are of relevance to gas- and aqueous-phase tarnishing processes.

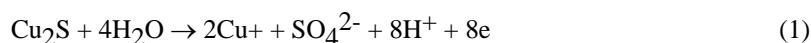
However, this information is more digestible in the graphical form of predominance area diagrams, giving the predominant phases as function of gas compositions. These are shown in Figs.1-4 for the systems Cu/H₂S-O₂-saturated H₂O, Cu/S₈-O₂-saturated H₂O, Cu/SO₂-O₂-saturated H₂O and Cu/SO₂-O₂, respectively. Comparison of Figs.3 and 4 shows that the increased stability of hydrated copper sulphate increased its predominance area slightly compared with the anhydrous salt.

All the diagrams predict that under typical atmospheric conditions of 0.21 oxygen partial pressure, metal sulphate phases should predominate. However, this is not in line with experimental results, indicating a large kinetic barrier for the formation of those phases.

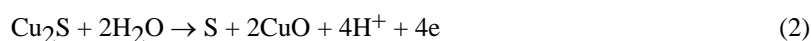
2.2 Copper-aqueous-gas systems

The aqueous chemistry of sulphur is complex, with both truly stable oxidation states species (VI - $\text{H}_2\text{SO}_4 / \text{HSO}_4^- / \text{SO}_4^{2-}$), (0 - S) and (-II - $\text{H}_2\text{S} / \text{HS}^-$) and many metal-stable species with oxidation states between -1 and "+8" (H_2SO_5). The chemistry of such systems may be summarised conveniently in the form of potential-pH diagrams, calculated from Gibbs energies of formation of the various species considered. If S(VI) species are excluded, a meta-stable diagram is obtained in which sulphy species have areas of predominance. If all sulphur species with oxidation states > 0 are excluded, then polysulphides (S_x) have areas of predominance at high pH; such a diagram is a good predictor for the oxidation of sulphide by dissolved oxygen in aqueous solutions.

Potential-pH diagrams for Cu-S- H_2O systems predict that Cu_2S could oxidise by the reaction [4]:



In electrochemical experiments, little, if any, sulphate is formed even at high anodic potentials, with elemental sulphur being the kinetically favoured product, together with $\text{CuO}/\text{Cu}(\text{OH})_2$ or Cu^{2+} ions depending on the pH:



Hence, the kinetic hindrance of copper sulphate formation in aqueous solutions is congruous with its behaviour in the sulphur-containing gas phases. Meta-stable predominance diagrams for the Cu-S-O system could be constructed merely by excluding the sulphate from consideration.

2.3 Water vapour pressure



$$\Delta G^{\circ} (\text{H}_2\text{O} (\text{g})) = -228.589 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ} (\text{H}_2\text{O} (\text{g})) = -238.915 \text{ kJ mol}^{-1}$$

$$S^{\circ} (\text{H}_2\text{O} (\text{g})) = 0.188715 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^{\circ} (\text{H}_2\text{O} (\text{l})) = -237.178 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ} (\text{H}_2\text{O} (\text{l})) = -285.830 \text{ kJ mol}^{-1}$$

$$S^{\circ} (\text{H}_2\text{O} (\text{l})) = 0.06991 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^{\circ} = (-228.589 + 237.178) = 8.589 \text{ kJ mol}^{-1}$$

$$\log P_{\text{H}_2\text{O} (\text{g})} = -1.505$$

$$P_{\text{H}_2\text{O} (\text{g})} = 0.0313$$

3. SULPHUR TARNISHING OF COPPER

While most gaseous sulphur-containing species have been shown to react with metallic copper to form tarnish films, the reaction of this metal with elemental sulphur is not only the simplest stoichiometrically, but also kinetically. The rate of metal sulphide formation is, apparently without exception, linear as a function of time, whereas other sulphur-containing species frequently show parabolic growth rates.

In addition to the simplicity of its kinetics, the rate of metal sulphide formation has been shown by several authors [5,6] to be substantially independent of water vapour pressure (relative humidity), only Chiarenzelli [7] dissenting somewhat from this finding. The reaction product, in the case of copper, has been many times shown to be Cu_2S and, in addition to this sulphide, a range of non-stoichiometric sulphides can form.

In spite of this apparent simplicity, a rigorous mechanistic and kinetic analysis of the sulphur tarnishing of copper has yet to be published and while the use of elemental sulphur for accelerated environmental testing of electronic components is not widespread, sulphur itself is almost universally

invoked as a reaction intermediate in flowing mixed gas tests based on H₂S. For this reason alone, these reactions deserve the closest possible scrutiny.

Published data are summarised in Table 1 below. In spite of the fact that all workers obtained linear kinetics, the experimental conditions varied widely. Most of the data relate to static as opposed to flowing gas tests. Almost all workers have seemingly ignored the important finding that even modest levels of illumination accelerate the reaction. In this case ("Laboratory Illumination") the rate was doubled.

Table 1 Summary of Sulphur Tarnishing Kinetics of Cu

S - Static test ; F - flowing gas test or forced circulation

Because of the very low vapour pressure of elemental sulphur at ambient temperatures, the tarnishing of copper in this way is undoubtedly a process in which diffusion in the gas-phase is the rate determining step and this conclusion has been reached by several workers from different reasoning.

Thus Sinclair [5] and Reagor and Sinclair [6] have derived simple diffusion equations which, when solved, support this contention.

3.1 Additional Comments on Published Data

Some doubts exist as to whether Chiarenzelli [7] carried out this work at 126°F or 140°F (both temperatures are cited). Using XRD, copper sulphides and also copper oxides were identified. Using lead acetate paper, no H₂S was detected. Absence of water inhibited tarnishing.

With Cu, 21 - 32% of film was oxide, the rest, sulphide. Film morphologies were different for S and H₂S - loose and sooty in the former case. (Assumed that "thickness" measured by coulometric techniques is actually "equivalent thickness"). All workers except for Chiarenzelli [7] report the sulphur-tarnishing of Cu to be relatively unaffected by moisture content.

The effect of illumination, reported by Crossland and Knight [10], who also quote Bennett [11], appears not to have been noted by subsequent workers although Sinclair [5] does show its effect on the tarnishing kinetics of organo-sulphur vapours. The origin of this effect is not clear. Crossland et al. [10] propose a "photo-assisted solid-state diffusion" mechanism. There appear to be two difficulties here. Firstly, since the tarnish mechanism is gas-phase diffusion limited, one would not expect effects in the solid-state diffusion process to alter the overall kinetics, this not being the rate-determining step. In the second place, the hypotheses advanced by these workers as to the band-gap of the metal sulphide is not in line with most recent information.

There seem only two broad explanations, the first based on photochemical action on the flowers of sulphur itself, the second based on gas-phase reactions which, by producing alternative forms of sulphur, increase the total vapour pressure of all sulphur-containing species and thus permit increased flux densities of this element to the copper surface.

3.2 Relation of Tarnishing Data to Other Studies

Several workers have studied the reaction of sulphur vapour with Ag or Cu in the temperature range 200 to 400°C, including Rickert [12-18], Schmalzried [19,20], Valensi [21,22], Wagner [23], Corrish and Ward [24] and Reye [25].

4. THE TARNISHING ACTION OF HYDROGEN SULPHIDE AND MIXED GASES

Tarnishing of Cu and alloys, including these metals by H₂S in air of varying relative humidity in the concentration range 2% down to ppb, has been studied by various authors. In the main, when oxidising gases are absent, the rates appear to follow a parabolic law. Exceptions to this statement are the data of Chiarenzelli [7], for which we can find no explanation, and some experiments [26-29] at very low H₂S concentrations, for which gas-phase mass-transport limitation could be responsible.

Explanation of the parabolic kinetics is not easy. The process is clearly not gas-phase diffusion limited, since there would then be no reason why the initial high rates should be sustained. The obvious alternative is that the mechanism is solid-state diffusion limited and indeed this has been proposed. The objection to this is that the composition, if not the morphology, of the film, has been reported several times (Table 2) to be the same as that found with elemental sulphur tarnishing. In the case of elemental sulphur, if that film can sustain transport rates of the order shown in Table 1 up to thicknesses also indicated there, why should such films behave differently in the case of H₂S? One must also consider the undisputed effect of relative humidity, which increases the tarnish rate, and also the largely overlooked observations of Pope et al. [28] that certain metals, notably Fe, can catalyse the tarnish rate, not only when deposited in sub-monolayer quantities on a metal surface but also when, as a wire gauze, the H₂S containing mixture is allowed to flow over them before entering the tarnish chamber. Finally, cognisance must be made of the fact that addition of an oxidising agent, such as chlorine or NO₂ (but not SO₂) at concentrations broadly comparable to that of the H₂S, transforms the parabolic kinetics into linear relationships.

Table 2 Reaction Products Formed in Tarnish Tests

Pope et al. [26,27] state that moisture accelerates the reaction, as does SO₂ and Fe individually; SO₂ nullifies Fe catalysis.

Guinement and Fiaud [29] cite other work where CuS was determined. Suggest that product distribution and mechanism is related to [H₂S] : [Cl₂] or [NO₂]. Postulate gas-phase reaction: H₂S + Cl₂ → 2HCl + S moisture catalysed.

Chiarenzelli [7] does not explicitly mention Cu product valence states.

Study by [32] on techniques and methodology of product identification shows that CuO only appears later in the process. Mixed product not identified further.

In all cases, excepting system of ref. [32], air is present in 99% to 99.99% and R.H. is of about 75%.

5. PROPOSED REACTION MECHANISMS

If neither gas-phase mass-transport nor solid state diffusion are to be invoked as rate-limiting steps, there would seem to be only interfacial reactions at the gas-solid interphase to be considered, including under this the existence of a thin film of water. Before taking this further, a summary of mechanistic proposals and reactions is given here. Only Crossland and Knight [33] appear to have given thought to the thermodynamic aspects of such proposed reactions.

Campbell and Thomas [34] have suggested that H₂S is oxidised by SO₂ or Cl₂ to form elemental sulphur. This idea is dismissed by Crossland and Knight [33] on the grounds that, although energetically permitted, there are no reasons why the oxidation should stop at this stage, rather than carrying on to the SO₂ or SO₃ state. The same authors dismiss the reaction on kinetic (collision probability) grounds also. Such a dismissal is premature, since a number of authors, going back as far as Dalton in 1808, have considered this reaction. Murthy and Rao [35] studied the reaction and the effect of humidity and heterogeneous catalysis on its rate.

Thiosulphurous acid, then hydrogen sulphoxide are proposed intermediates.

Abbot [36] considers two reactions:



Quoting unpublished work, he suggests that this reaction is very slow and so dismisses it. Alternatively:



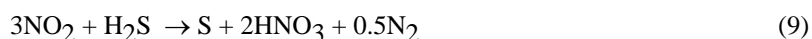
has been found to be fast in Russian work which is cited. Both reactions, it is stated, are accelerated in presence of Bronstead bases, e.g. water. Elsewhere [31] he has proposed:



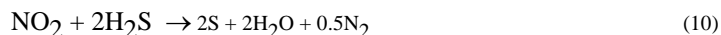
Simon et al. [37] again propose elemental sulphur as an intermediate, writing:



or

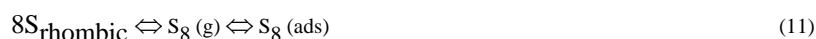


or



suggesting that tarnishing may thus be controlled by the concentration of the NO_2 . Graedel et al. [38] while not writing equations, describe how H_2S builds a sulphide layer above cuprous oxide, showing this duplex structure. However, elsewhere, the same authors propose the absorption of H_2S (dissolution) by a surface layer of water. It then ionises to form HS^- ions, which react with Cu ions in the first step of Cu_2S formation. Such a mechanism, they state, would give a low activation energy in line with their observed value of 7 kcal mol^{-1} . They suggest the protons might form molecular hydrogen.

In summary, with one exception noted above, the universal model for tarnishing by H_2S with or without added oxidants, appears to rest on the formation of elemental sulphur as an intermediate. What is seemingly suggested nowhere, apart from a passing comment by Simon [37], is an electrochemical mechanism such as:



with sulphur molecules acting both as a source of sulphide and an oxidant, so that the overall reaction is:



Oeste [39] has demonstrated that the reaction of oxygen with H_2S over a carbon catalyst does indeed proceed on this basis. By construction of a divided cell, containing carbon in each compartment, the one side purged with air, the other with H_2S , he was able to draw a substantial current. Depending on the pH, elemental sulphur or sulphuric acid were the main products. The analogy with gas-phase tarnishing is close and to take it one degree further, Oeste shows that addition of ferric oxide (which would be reduced to FeS_2/FeS), both catalyses the reaction and promotes sulphuric acid, rather than elemental sulphur formation. Thus, a graph shows conversion to sulphuric acid to be 0% in the absence of iron, increasing to 40% with 3% ferric oxide.

Oeste [39] states that at $\text{pH} < 2$, catalysis is inhibited because the H_2S protonates to the electro-inactive H_3S^+ ; however, this species has not been reported elsewhere in the literature, and the observed effect is more likely to have been due to H_2S desorption from the electrolyte. Further important observations relate to formation of S chains of up to 20 units long, which then break down to CS_2 -soluble S_8 . Cutting off the gas supply leads to catalyst deactivation which is explained in terms of alternative forms of sulphur.

Formation of sulphuric acid as described here, leads to acid concentrations of 60% or more. Around this point, the sulphuric acid reacts with H_2S to form SO_2 and elemental sulphur. However, in this case, the element is insoluble in CS_2 , but can partly be washed out of the carbon using water.

However, iron (or its compounds) can lead to other effects. Knotkova-Chermakov and Vichkova [40] measured the pH of thin films of moisture under an SO_2 atmosphere, as well as their $\text{SO}_2/\text{SO}_4^{2-}$ compositions. The lowest pH values were found on glass (about 3), on Cu values between 4.1 and 4.9 prevailed, while on steel the highest values were found (5.5 to 6). Such a "buffering effect" taken with the observations of Oeste [39], might be invoked to explain some of the findings of Pope and Moss [26-28].

It is seen (Table 2) that addition of either iron or SO_2 increase the rate of Cu_2S formation, but that when both together are present, they cancel each other out. The reaction of H_2S with SO_2 is not, as has been seen, one which has much effect on pH. The presence of iron, however, can work in two directions, the one promoting, the other inhibiting, formation of very acid surface layers.

A major unexplored element in the chemistry or tarnishing is thus, it is proposed, the different forms of elemental sulphur, some of which are capable of reacting with metals such as others being largely inert, electrically insulating and also hydrophobic. Production of sulphur of this kind (not to be confused with S_8), would result in a passivating layer being formed on the surface and also, to a lesser extent, being incorporated into the growing tarnish film. The first effect would inhibit the surface reaction involving decomposition of the H_2S , the second, a reduction in the transport rate of Cu^+ ions through the now non-stoichiometric sulphide layer. There can be no argument that, under suitable conditions, such elemental sulphur is formed. It might well be asked, if this were the case, why would it not be detected ?

As an electrochemically inert species, it would not be revealed in the electrochemical reduction methods used for film thickness measurements and characterisation. It might just be possible that, in extreme cases, such sulphur could be visually observed in a colloidal form after the electrochemical reduction. Nor would elemental, as opposed to combined, sulphur be readily observed by the more sophisticated methods such as AES or ESCA, unless it was being specifically sought. The main support for such an idea comes from the known fact (viz: Oeste [39]) that such sulphur is indeed formed. However, an intriguing observation reported by Crossland and Knight [33] is as follows. These authors measured tarnish formation rate not only by electrometric methods but also using radio-labelled sulphur. In a number of cases, the two methods were in close agreement. In other cases, the radiotracer method gave many times as much sulphur, a fact the authors were unable to explain. They could only conclude that sulphur was deposited on the surface in a form inaccessible to cathodic reduction.

Addition of oxidising agents such as Cl_2 or NO_2 would be expected to modify conditions on the surface such that formation of elemental sulphur was unfavoured, higher oxidation states such as SO_2 or SO_3 being thermodynamically predicted. Apart from such predictions, analysis of tarnish films indicate that this is indeed the case (Table 2). The "passivating action" would thereby be eliminated and in addition, the tarnish film with its altered chemical composition (in all probability a highly inhomogeneous structure) would be expected to have quite different ionic transport properties.

The foregoing facts allow an explanation of the results of Pope and Moss [28]. Increase in tarnish rate when an iron gauze was interposed in the gas-stream, one explains by a partial conversion of H_2S to S_8 , the latter, a species capable of reacting with Cu. Iron on the Cu surface would also act the same way. An alternative explanation is that given above, as shown by Oeste [39], which is that the iron catalyses oxidation of the H_2S past the $\text{S}(0)$ stage to sulphuric acid. This would not only avoid the blocking action of bulk elemental sulphur but also increase the number of electrons in the overall reaction, thus effectively increasing its rate. A concurrent effect would be to decrease the pH although, as has been seen, this might not inevitably increase the reaction rate. Whether the iron acts as a redox catalyst, cycling between alternative valence states, can be predicted.

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