JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 465–469

The effect of certain ions on the internal stress of bright copper electrodeposits

R. E. GANA, M. G. FIGUEROA, R. J. LARRAÍN

Departamento Electroquímica Aplicada, Instituto de Ciencias Químicas, Pontificia Universidad Católica de Chile, Santiago, Chile

Received 20 April 1978

The effect of low concentrations (0–100 mg l^{-1}) of F, Cl, Br, I, As, Sb, Bi, Ni, Zn, Fe, Ag, Te, Se, Pb, and S on the internal stress of bright copper electrodeposits was studied. The following solution containing 30 mg l^{-1} of thiourea as a brightening additive was used as the electrolyte: $CuSO_4 \cdot 5H_2O$ (225 g l^{-1}), H_2SO_4 (60 g l^{-1}). It is shown that the internal stress of copper electrodeposits can be considerably reduced by addition of Se(IV), Cl, Br, or I to the above electrolyte.

1. Introduction

The internal stress of an electrodeposit can be defined as a set of forces (generated during electrodeposition) tending either to contract or expand the thin layer of electrodeposited metal. In the first case, the stress is named contractile, tensile or positive, while in the second case expansive, compressive, or negative.

If the internal stress is very high, partial or even total, peeling of the deposit might occur. Also, bending of the base metal was observed in several experiments.

Internal stress is a very serious problem in industrial electroplating. Although a great deal of work has been carried out and several theories have been put forward, the phenomenon is not yet understood.

From the reviews of Vagramian [1], Subramanian [2], Weil [3] and Newell [4] among others, it would seem that the most relevant factors in the generation of internal stress are the following:

(a) variation of the lattice parameters;

(b) variation of the distance between crystals;

(c) occlusion of foreign substances in the electrodeposit (hydrogen, hydrolysis products, chemical combinations, etc.).

In practice, it would seem likely that more than one of these factors are responsible for the generation of internal stress.

The additives used in the preparation of bright electrodeposits (among them thiourea and its derivatives) are usually responsible for the generation of internal stress. To counteract this side effect, numerous additives such as disulphonaphthalene, phenol, formalin, dextrin, diethylamine, oxalic acid, benzotriatole and other, have been proposed [4–6].

During the course of studies in our department, using industrial electroplating solutions, it was found that the internal stress of the electrodeposits was dependent on the methods used to purify these solutions. Normally these solutions were treated with activated charcoal, followed by electrolysis using a corrugated copper cathode between copper anodes. On one occasion, where blister copper anodes were used (instead of the usual electrolytic anodes), a marked decrease in the internal stress of the electrodeposit was observed. This finding led us to study the effect of the common impurities of blister copper on the internal stress of copper electrodeposits. This study was extended to include the effect of other impurities normally contaminating the industrial electroplating solutions, and also the halogen family. The halogen family was studied in order to compare the relative effect of its members; chloride ion, widely studied in our department, is an effective agent for decreasing the internal stress of electrodeposits resulting from the use of thiourea as a brightening agent [7].

0021–891X/79/040465–05 $02·50/0

2. Experimental

2.1. *Tensiometer*

The internal stress of the electrodeposits was measured using a tensiometer built in our department according to the specifications of Stoney [8] and Tzareva, Vagramian and Demin [9]. The method is based on measuring the deflection of the cathode free end. The values given in the present publication are expressed in relative units (r.u.) and they represent the average between two or more measurements with a deviation of less than 5% between measurements. A plus sign is used for positive stress, while a minus sign is used for negative stress.

The relative values measured in our instrument can be approximated into absolute values using the equation of Stoney [8]. In Table 1, a list of some equivalences is given.

2.2. *Electrolyte*

The following standard electrolyte was used in all experiments: $CuSO_4 \cdot 5H_2O$ (225 g l^{-1}), H_2SO_4 (specific gravity 1·84, 60 g l^{-1}). To this, 30 mg l^{-1} of thiourea was added as a brightening additive. Merck reagents of analytical grade were used.

2.3. *Electrodes*

The cathodes were: sheets of laminated copper of 5 cm^2 (5 × 1 cm) and 0·1 mm thick.

The following pretreatment procedure was employed: (a) heat at 500° C, (b) dip in 1 : 2 HNO_3 : H_2O, (c) polish with 600 mesh emery paper, (d) blank off the back face, (e) degrease and treat with 10% H_2SO_4.

The anodes were sheets of laminated electrolytic copper of 13 cm^2 (5 × 2·6 cm) and 2 mm thick. They were degreased and then treated with 10% sulphuric acid.

Table 1. Some equivalences between relative and absolute units of internal stress

Relative units (r.u.)	*Absolute units* (kg cm^{-2})
1	1100
2	1570
3	2130
4	2590

*Table 2. Experimental conditions used for copper electroplating**

cathodic current density	2·6 A dm^{-2}
temperature	20 ± 0·5° C
electrolysis time†	15 min
initial spacing between electrodes	3·5 cm
stirring	none

* Internal stress (30 mg l^{-1} thiourea added) without contaminants: 2·8 ± 0·1 (r.u.).

† Thickness of the deposit around 8 μm.

Table 2 illustrates the experimental conditions, and Table 3 those compounds which were tested for their effect on the internal stress of copper electrodeposits. The concentration of these compounds was varied between 0–100 mg l^{-1}, expressed as the weight of the main element per litre of solution.

3. Results

The effect of thiourea on the internal stress of copper electrodeposits can be seen in Fig. 1. Between 30–60 mg l^{-1} of thiourea a maximum of about 3 relative units is reached. It is also in this region where maximum brightness is achieved. Suggestions for a mechanism to explain the action of thiourea are offered by Valentelis [6], Turner and Johnston [10] Gudin [11], Javet and Hintermann [12] and others.

Under identical conditions to the ones described above, but where thiourea was replaced by commerical brightening agents (Udilyte and Schering), a positive stress of between 0·5–0·7 relative units was found.

The effect of increasing the concentrations of chloride, bromide, iodide and fluoride ions is shown in Fig. 2. It can be seen that relative to the other halide ions, the chloride ion decreases the internal stress of copper electrodeposits most effectively. At about 40 mg l^{-1} chloride ion the stress has diminished to a null value at which it remains until at least 100 mg l^{-1} of chloride ion (as proved by other experiments where concentrations up to 150 mg l^{-1} of chloride ion were tested). Bromide and iodide ions are less efficient than chloride ion in that higher concentrations are required to achieve low values of internal stress.

Table 3. Compounds tested for their effect on the internal stress of copper electrodeposits

Main element	*Oxidation state of the main element*	*Type of compound used**
F, Cl, Br, I	1–	sodium salts†
As, Sb, Bi	3+	oxide
Ni, Zn, Fe	2+	sulphate
Ag	1+	sulphate
Te	6+	oxyacid
Se	4+	sodium selenite
Pb	2+	oxide‡
S	2–	sodium sulphide‡

* Analytical grade reagents.
† Sodium has no significant effect on the internal tension of electrodeposits.
‡ Concentration equal to the solubility products of the compound.

By contrast, fluoride ion has very little effect in the range studied.

The remarkable decrease of internal stress observed upon addition of chloride ion to the solution occurs when thiourea is present in the electrolyte. On the other hand, it is interesting to note that the internal stress increases when chloride ion is added to acidified copper sulphate solution in the absence of thiourea, which has been reported by Newell [4] and Fedot'ev [13].

The diverse behaviour of chloride ions in the presence of thiourea can be explained in terms of the formation of copper(I) complexes with the general formula $Cu(Tu)_nCl$ [14–17].

Different experiments reported by Ke and coworkers with the radio-tracer thiourea-S^{35} [18] have shown that using acid copper sulphate solutions the thiourea molecules are adsorbed strongly on the surface of the copper metal. Llopis and co-workers [19] have postulated a mechanism involving hydrolysis and reduction of thiourea to form copper sulphide on the surface of the cathode. The copper sulphide may interfere with crystal growth by inhibiting the surface diffusion of copper adatoms to growth sites. Copper sulphide may even block a growth site and force re-nucleation.

On the other hand, Gauvin and Winkler [20] have postulated the adsorption of CuCl on the cathode when an acidified solution of copper sulphate contains chloride ions. This adsorption phenomenon produces changes in the properties of the deposit. The authors of the present work

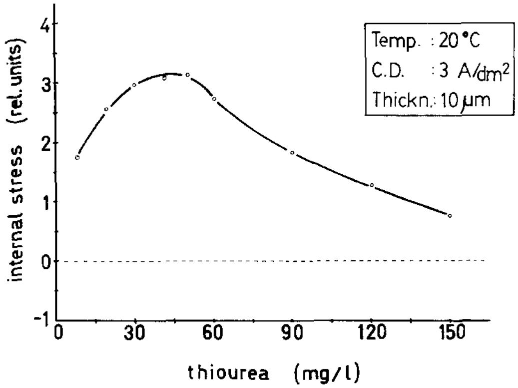

Fig. 1. The effect of thiourea on the internal stress of copper electrodeposits. Electrolyte: standard $CuSO_4$–H_2SO_4.

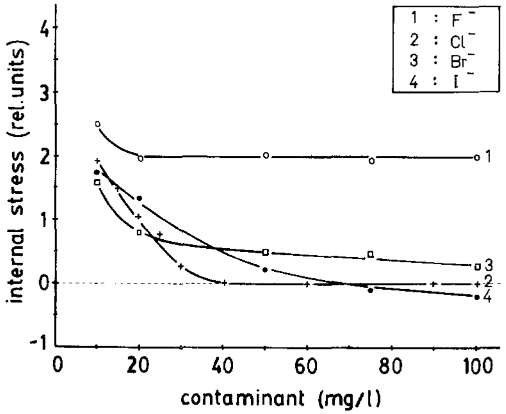

Fig. 2. The effect of F^-, Cl^-, Br^-, and I^- on the internal stress of copper electrodeposits. Electrolyte: standard $CuSO_4$–H_2SO_4 (30 mg l^{-1} thiourea added). Internal stress without contaminants 2·8 ± 0·1 (r.u.).

have observed changes in the reflectivity of copper deposits (brightness synergesis) upon addition of chloride ions to $CuSO_4$–H_2SO_4 solutions containing thiourea [21]. The brightness synergesis observed in the presence of chloride ions can be attributed to the influence of complexes like $Cu(Tu)_nCl$ and/or CuCl on the growth sites.

Based on the available information it is reasonable to postulate that the complexes $Cu(Tu)_nCl$ can be partially adsorbed onto the cathode in the form of copper sulphide and copper chloride. The adsorption of both compounds produces copper deposits with different properties in regard to reflectivity, physical appearance, hardness and internal stress compared to the deposits obtained from $CuSO_4$–H_2SO_4 solutions containing only thiourea (adsorption of CuS) or only chloride ions (adsorption of CuCl) as additives.

The behaviour of iodide and bromide ions can be explained in terms of adsorption of CuI and CuBr, respectively. Under the conditions studied a correlation is not observed between the properties of the halogens (ionic radius, electronegativities, etc.) and the values obtained for the internal stress. The small influence of fluoride ion on the internal stress can be attributed to the fact that copper does not form the sparingly soluble compounds with fluoride ion that are characteristics of the other halide ions.

The effect of Sb(III), Bi(III) and As(III) is illustrated in Fig. 3. The first two lead only to a very moderate reduction in stress, while the last, is responsible for keeping the internal stress at high values.

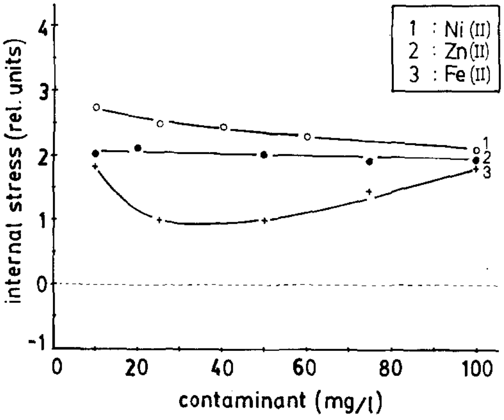

Fig. 4. The effect of Ni(II), Zn(II) and Fe(II) on the internal stress of copper electrodeposits. Electrolyte: standard $CuSO_4$–H_2SO_4 (30 mg l^{-1} thiourea added). Internal stress without contaminants: 2·8 ± 0·1 (r.u.).

Fig. 4 shows that Ni(II) and Zn(II) tend to keep internal stress at a high, almost constant value in the range studied, whilst Fe(II) is responsible for a minimum of about one relative unit at 30 mg l^{-1}.

In Fig. 5 the effect of Ag(I), Te(VI) and Se(IV) is presented. Ag and Te decrease stress, but high concentrations are required to reduce it to a low value. The use of Ag(I) is only of theoretical interest since the concentration of this ion is continuously changing due to its discharge at the cathode. On the other hand, most of the electrolytes used in industrial electroplating contain chloride, which would reduce the concentration of Ag(I)

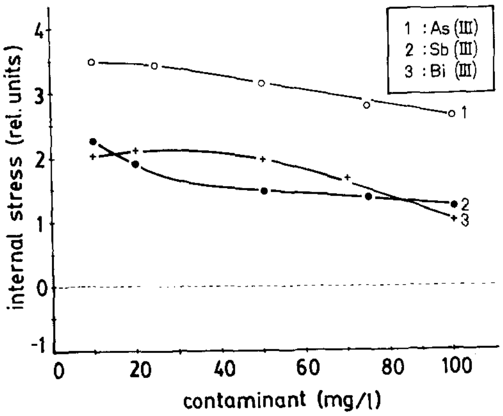

Fig. 3. The effect of Sb(III), Bi(III) and As(III) on the internal stress of copper electrodeposits. Electrolyte: standard $CuSO_4$–H_2SO_4 (30 mg l^{-1} thiourea added). Internal stress without contaminants: 2·8 ± 0·1 (r.u.).

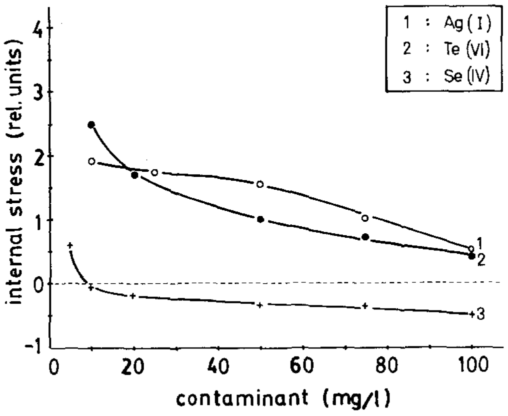

Fig. 5. The effect of Ag(I), Te(VI) and Se(IV) on the internal stress of copper electrodeposits. Electrolyte: standard $CuSO_4$–H_2SO_4 (30 mg l^{-1} thiourea added). Internal stress without contaminants: 2·8 ± 0·1 (r.u.).

to a very low value due to the formation of AgCl ($K_{sp} = 1{\cdot}8 \times 10^{-10}$ at 20° C).

Of all the species studied, Se(IV) is the most efficient in decreasing stress. Indeed, only 10 mg l^{-1} are required to reduce the internal stress of the electrodeposit to a slightly negative value; − 0·5 relative units when the concentration of Se(IV) is set to 100 mg l^{-1}.

In another group of experiments, either PbO or Na_2S was added to the electrolyte. Since the concentration of Pb^{2+} and S^{2-} was governed by the formation of $PbSO_4$ and Cu_2S respectively, only one value of internal stress per species was obtained. The average value for Pb^{2+} and S^{2-} was 2·1 and 1·1 relative units respectively.

The variation of internal stress produced by the metallic contaminants studied can be explained in terms of the adsorption of these elements on the copper cathode. This contamination by adsorption has been widely proved in industrial refining processes. The presence of some of these elements in the cathode is due either to the discharge of those that have a potential similar or more electropositive than copper (i.e. arsenic and silver) or to the formation of complexes with thiourea which have been reported by Yoe and Overholser [22]. According to this reference of the contaminating elements studied, Se(IV) in the form of SeO_3^{2-} is the only one that forms an insoluble compound with thiourea in acidic media. In this case the compounds of selenium can arrive at the cathode by an electrophoretic effect.

In the present work we do not postulate any explanation for the different behaviour of the elements or compounds that are adsorbed on the cathode with respect to the internal stress of the deposits.

4. Conclusions

The following conclusions were reached:

(a) In the concentration range 0–100 mg l^{-1}, most of the ions studied tended to decrease the internal stress of copper electrodeposits (where 30 mg l^{-1} of thiourea had been added as a brightening agent). However, only Cl^-, Br^-, I^- and Se(IV), the last one being added as Na_2SeO_3, could be considered as being potentially useful in diminishing internal stress.

(b) Among the halides, Cl^- has the advantage of keeping stress to a null value over a wide range of concentrations (40–150 mg l^{-1}). This is particularly useful considering the synergetic effect of Cl^- over some brightening additives normally used in the preparation of bright copper electrodeposits.

(c) Of all the species studied, Se(IV) showed the greatest tendency to decrease stress. Indeed, even below 10 mg l^{-1} this species allowed the preparation of bright copper electrodeposits with a very low internal stress.

References

[1] A. T. Vagramian and Z. A. Solovieva, 'Le dépot électrolitique des Métaux', Dunod, Paris (1958).

[2] R. Subramanian, C. Balansingh and B. A. Shenoi, *Metal Finishing* **65** (1967) 101.

[3] R. Weil, *Plating* **2** (1971) 137.

[4] I. L. Newell, *Metal Finishing* **58** (1960) 56.

[5] R. Weil, *Plating* **1** (1971) 50.

[6] L. Iu. Valentelis, I. Iu. Kamyntavichene and Iu. Iu. Matulis, *Proceedings of the Lithuanian Academy of Sciences. Series B* **1** (1969) 55.

[7] R. Gana and E. Gálvez, *VIII J. Chilevas de Quimica Santiago* (1976) IV4.

[8] G. G. Stoney, *Proc. Roy. Soc.* **A82** (1909) 172.

[9] A. T. Vagramian and Z. A. Solovieva, *ibid* A82 (1909) 136.

[10] D. R. Turner and G. R. Johnston, *J. Electrochem. Soc.* **109** (1962) 798.

[11] N. V. Gudin, Y. Y. Gerenrot and M. S. Shapnik, *Ukrain. Chem. Journal* **33** (1967) 854.

[12] Ph. Javet and H. E. Hintermann, *Electrochim. Acta* **14** (1969) 527.

[13] N. P. Fedot'ev, *Plating* **53** (1966) 309.

[14] N. W. Sidwick, 'Los elementos químicos y sus compuestos' Aguilar, Madrid (1954) Vol. 1, p. 158.

[15] C. B. Knolber, Y. Okaya and R. Pepinsky, *Z. Krist.* **111** (1959) 385.

[16] W. A. Spofford and E. L. Amma, *Chem. Commun.* 7 (1968) 405.

[17] J. Frost, M. Lawson and G. M. McPherson, *Inorg. Chem.* **15** (1976) 940.

[18] B. Ke, Y. Hoekstra, B. Sison and D. Trivich, *J. Electrochem. Soc.* **106** (1959) 382.

[19] Y. Llopis, J. M. Gamboa and L. Arizmendi, *C.I.T.C.E. Meeting* Paris (1951) p. 448.

[20] W. H. Gauvin and C. A. Winkler, *J. Electrochem. Soc.* **99** (1952) 71.

[21] R. Gana, E. Gálvez, A. M. Edwards and V. Silva, *XII Congreso Lat. Quimica* Quito (1976) p. 4.

[22] J. H. Yoe and L. G. Overholser, *Ind. Engn. Chem* **14** (1942) 435.