Internal Stress in Electrodeposited Metals

By

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This paper is concerned with the mechanism responsible for the internal stress in the electrodeposited metals. Metals such as nickel, chromium, copper, etc., exhibit tensile stress during their electrodeposition, whereas zinc and cadmium show compressive stress. When the electrodeposited metals are kept in air by removal from their electrolytes after electrodeposition, they release a certain amount of hydrogen and the stress in them becomes more tensile. When hydrogen is electrodeposited on the surface of electrodeposited metals and hydrogen occlusion takes place in the electrodeposits, stress in metals is changed to compressive. From the results obtained, the authors have arrived at a conclusion that one of the factors responsible for creating internal stress in the electrodeposited metals is the release or introduction of hydrogen in the electrodeposited metals.

Introduction

It is a well known fact that internal stresses are produced in some electrodeposited metals. This, in turn, causes the deposit to contract or expand during and after electrodeposition.

The magnitude and kind of internal stress depend on the kind of electrodeposited metals and electrolytic conditions.[1)2)3)]

The stress produced in electrodpeosited metals during electrodeposition may be classified in the following three groups:
(1) tensile stress, (2) compressive stress and (3) either tensile or compressive depending on the electrolytic conditions.

Concerning the internal stress in electroposited metals, various theories have been proposed by many investigators. So far the theories are as follows:

(1) Hydrogen theory[4)5)]
(2) Excess energy theory[6)7)]
(3) Parasitic water theory[8)9)]
(4) Dislocation theory[10)]

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Despite these different theories, concrete explanations have not yet been given about creating the stress in the electrodeposited metals. The authors have, therefore, made an attempt to investigate the magnitude and kind of stress in electrodeposited metals with a view to finding some explanations about its source and its nature.

Experimental Procedure

The deflection of the cathode was measured by a contractometer in a manner similar to that employed by V. Kohlschütter and E. A. Viulleumier.[4]

Anode and cathode, each 50 mm $\times$ 10 mm, were suspended vertically and parallel to each other at a distance of 50 mm apart. The cathode was in the form of a thin flexible plate made of annealed platinum, one side of which was coated with polyvinyl chloride so that deposition took place only on the other side.

The anode and cathode were suspended on a fixed stand. The electrolytic bath could be raised or lowered easily away from the electrodes without touching them. Thus, we were able to measure also the deflection of the cathode after electrodepostion.

The schema of the experimental apparatus is shown in Fig. 1.

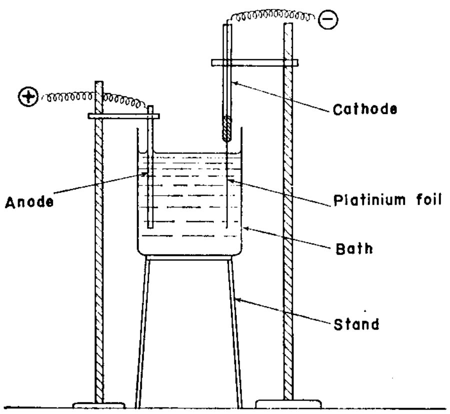

Fig. 1. Schema of experimental apparatus.

Results

1. Deflection of electrodeposited metal during and after electrodeposition.

By means of a contractometer we measured the deflection of the cathode and found that nickel, chromium and copper contract during electrodeposition as shown in Figs. 2 to 4.

When the cathode was taken out of the bath and was kept in air after electrodeposition, these metals were contracted as more shown in Figs. 2 to 4.

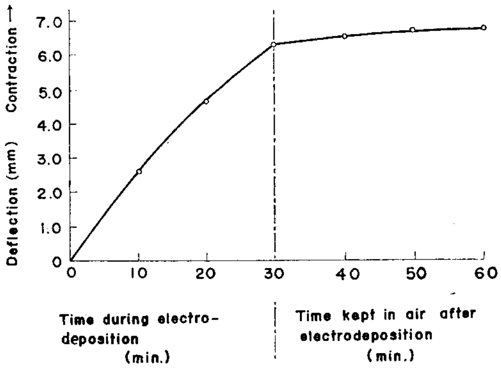

Fig. 2. Deflection of electrodeposited nickel from sulfate bath during electrodeposition and kept in air after electrodeposition.

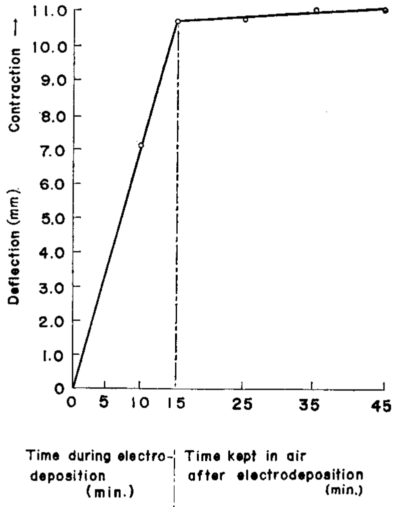

Fig. 3. Deflection of electrodeposited chromium from chromic-acid bath during electrodeposition and kept in air after electrodeposition.

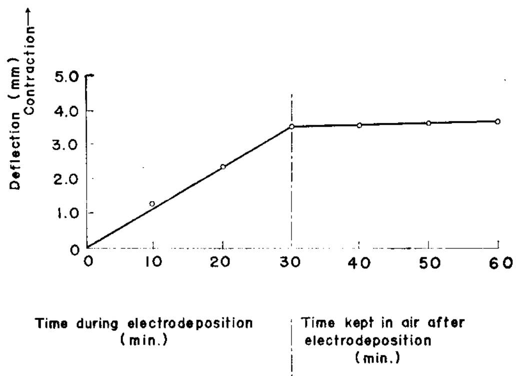

Fig. 4. Deflection of electrodeposited copper from sulfate bath during electrodeposition and kept in air after electrodeposition.

Zinc electrodeposited from a sulfate bath, copper from a sulfate bath containing glue and lead from a fluosilicic acid bath containing glue, all expand during the electrodeposition as shown in Figs. 5 to 7.

As shown in Figs. 5 to 7 the deflection (the direction of expansion) of the electrodeposited metals diminished to zero by having the deposits kept in air and in some cases, the electrodeposits had some contraction.

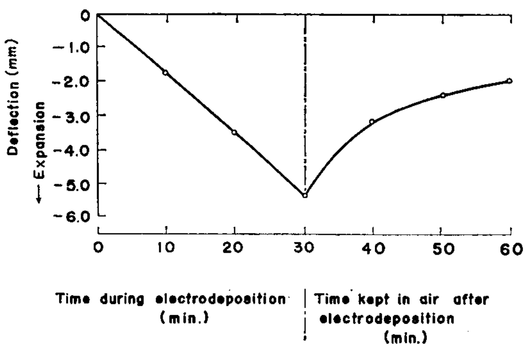

Fig. 5. Deflection of electrodeposited zinc from sulfate bath during electrodeposition and kept in air after electrodeposition.

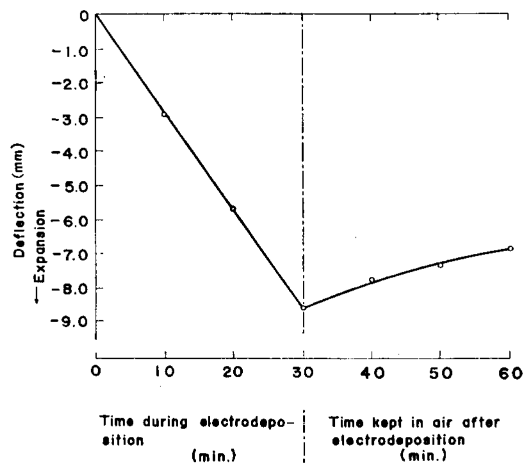

Fig. 6. Deflection of electrodeposited copper from sulfate bath containing glue during electrodeposition and kept in air after electrodeposition.

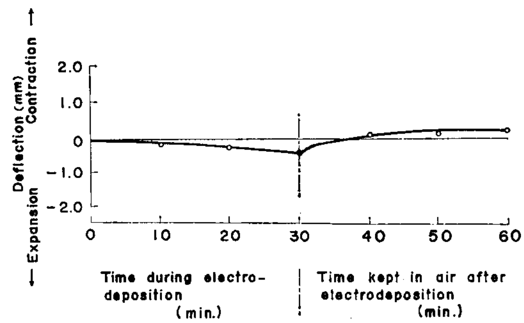

Fig. 7. Deflection of electrodeposited lead from fluosilicic bath containing glue during electrodeposition and kept in air after electrodeposition.

2. Hydrogen gas occluded in electrodeposited metals.

Measurement was taken by a gas analyser on the content of gases occluded in the electrodeposited metals after electrodeposition. The results are shown in Tables 1 and 2. The electrodeposited nickel and copper occluded a certain amount of hydrogen and the amount of hydrogen gas occluded in nickel and copper was apparently reduced when they were kept in air after electrodeposition.

Table 1. Gases in the electrodeposited nickel after electrodeposition.

Keeping time in air (day)	Total gas (cc/100 g Ni)	Composition (cc/100 g Ni)				
		H_2	CO_2	CO	O_2	Residue
0	13.98	11.51	0.35	1.89	0.18	0.05
7	13.25	10.79	0.34	1.88	0.18	0.06
14	12.75	10.27	0.35	1.88	0.18	0.07
21	12.17	9.72	0.34	1.85	0.19	0.08
28	11.84	9.37	0.33	1.89	0.17	0.06
49	11.17	8.76	0.33	1.88	0.17	0.03

Table 2. Gases in the electrodeposited copper after electrodeposition.

Keeping time in air (day)	Total gas (cc/100 g Ni)	Composition (cc/100 g Ni)				
		H_2	CO_2	CO	O_2	Residue
0	15.25	11.68	1.75	0.60	0.56	0.77
7	13.72	10.01	1.95	0.53	0.62	0.59
14	12.58	8.91	1.80	0.50	0.50	0.79
21	11.74	8.28	1.68	0.50	0.48	0.75
28	10.58	7.39	1.56	0.50	0.43	0.68
56	9.72	6.53	1.53	0.54	0.52	0.64

3. Effect of hydrogen electrodeposited on the surface of the electrodeposited metals.

We attempted to investigate further concerning what changes could be observed in stresses if hydrogen is introduced into electrodeposits. As a method for carrying out this investigation, we placed electrodeposited metals as a cathode, and platinum plate as an anode in a bath containing one normal solution of sodium sulfate, then hydrogen was electrodeposited on the surface of cathode.

Here we presumed that some hydrogen might have introduced into the metal. Figs. 8 to 11 show the change of the deflection made in electrodeposited metals during electrodeposition of hydrogen on the surface of the electrodeposited metals and during kept in air after electrodeposition of hydrogen.

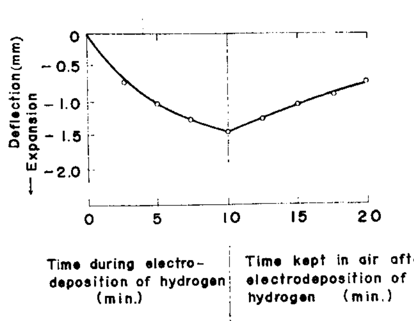

Fig. 8. Deflection of electrodeposited nickel during electrodeposition of hydrogen and kept in air after electrodeposition of hydrogen.

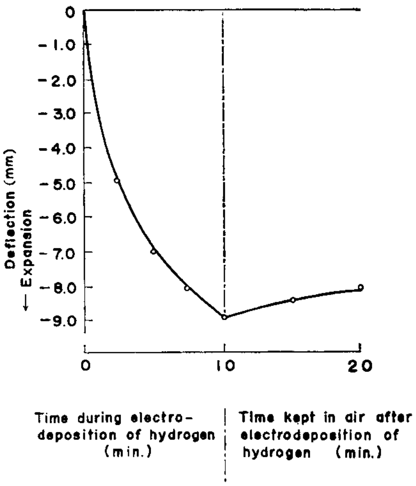

Fig. 9. Deflection of electrodeposited chromium during electrodeposition of hydrogen and kept in air after electrodeposition of hydrogen.

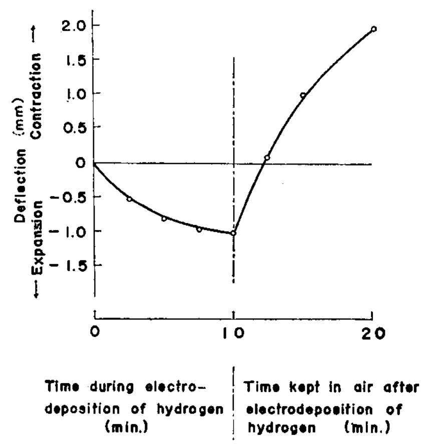

Fig. 10. Deflection of electrodeposited zinc during electrodeposition of hydrogen and kept in air after electrodeposition of hydrogen.

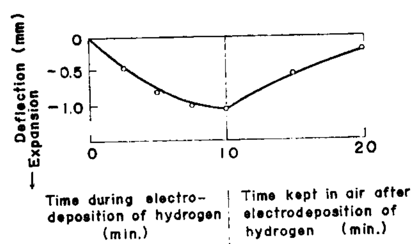

Fig. 11. Deflection of electrodeposited copper from sulfate bath containing glue during electrodeposition of hydrogen and kept in air after electrodeposition of hydrogen.

As shown in Figs. 8 to 11, during electrodeposition of hydrogen, the deflection of expansion was observed in all cases, though in certain cases we noticed that deflection diminished after the cathode was taken out of the sodium sulfate bath and was kept in air.

4. The Change of Direction of Deflection under Various Conditions

We selected out nickel and chromium as metals having deflection of contraction during electrodeposition and zinc as a metal having deflection of expansion.

Then we made a series of measurements in the following order: electrodeposition, keeping in air, hydrogen deposition on the surface of electrodeposited metal in the sodium sulfate bath and again keeping in air. The results are shown in Fig. 12.

In Fig. 12 it is clear that nickel and chromium contract during the deposition period while zinc expands. However, the electrodeposited nickel, chromium and zinc deflect in the direction of contraction, when they are kept in air.

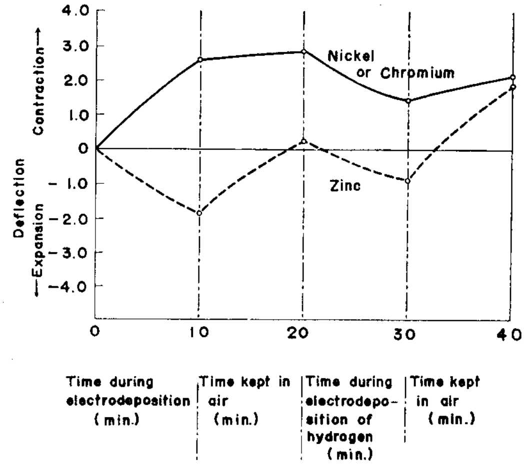

Fig. 12. Change of deflection under various conditios.

And then they deflect in the direction of expansion during the hydrogen deposition in the sodium sulfate bath. They deflect again in the direction of contraction when they are kept in air.

It is only during the electrodeposition that nickel (or chromium) and zinc show different kinds of direction of deflection.

Discussion

Nickel, chromium and copper deflect in the direction of contraction during electrodeposition, whereas zinc electrodeposited from the sulfate bath, copper from the sulfate bath containing glue and lead from the flouosilicic acid bath with glue deflect in the direction of expansion during electrodeposition.

These deposits, however, all deflect in the direction of contraction when they are kept in air after electrodeposition.

On the other hand, as shown in Table 1 and 2, contents of hydrogen in electrodeposited metals appraently decreased when they were kept in air after electrodeposition.

So it seems electrodeposited metals deflect in the direction of contraction when a part of hydrogen in electrodeposited metals is released.

When hydrogen is introduced into electrodeposited metals by electrodeposition of hydrogen on the surface of the electrodeposited metals, the electrodeposited metals deflect in the direction of expansion. (as shown in Figs. 8 to 11).

Therefore we presume as follows:

Some amount of hydrogen is co-deposited with electrodepositing metals during electrodeposition and the electrodeposited metals do not deflect in any direction soon after their deposition.

When a part of the hydrogen co-deposited with electrodepositing metals (Ni or Cr) is released from electrodeposited metals during electrodeposition, thin films of electrodepositing metals deflect in the direction of contraction.

When some amount of hydrogen is introduced into the surface of electrodepositing metals (Zn or Cd), metals deflect in the direction of expansion during electrodeposition.

We used thin flexible plate as a cathode, so the electrodeposited metals deflect in the direction of contraction or expansion. But when we use thick rigid plate as a cathode, internal stress would hold in the electrodeposited metals.

In this time tensile stress is created when some amount of hydrogen in electrodeposited metals is released from deposits and compressive stress is created when hydrogen is introduced into the electrodeposited metals.

Conclusion

We are convinced that the behavior of hydrogen is really one of the factors responsible for internal stress in electrodeposited metals. Release of hydrogen from the electrodeposited metal gives rise to tensile stress. On the other hand compressive stress is produced when hydrogen is introduced into the electrodeposited metals.

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