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EXTRACTION METALLURGY DIVISION

Reprinted from Electrochemical Technology,
Vol. 6, No. 1-2 Jan.-Feb. 1968

Reprint Series RS 63

Price 25 cents

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ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1968

Preplating High-Strength Steels with Copper to Prevent Embrittlement During Chromium Plating[1]

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High-strength steel Types 1062, 4037, and E4340 are severely embrittled when electroplated with chromium by a standard procedure. However, no significant embrittlement occurs when these steels are (a) given a special acid treatment and (b) electroplated with copper in a stable cyanide bath, prior to the chromium plating.

Chromium is highly resistant to many ordinary types of corrosion. When it is electroplated on other metals, it can have an unusually high hardness. Unfortunately, when it is electroplated directly on high-strength steels by present-day methods, the steels become severely embrittled.

During this research, it was demonstrated that this embrittlement can be prevented by the use of recently developed methods of treating the steel surfaces and electroplating them with copper, prior to the chromium plating.

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Raymond R. Rogers received his M.A. degree in electrothermics at Toronto University in 1926, and his Ph.D. in electrochemistry at Columbia University in 1933. He continued there as instructor and research supervisor until 1941. In 1944, he was placed in charge of research in corrosion and its prevention and in pyrometallurgy at the Canadian Dept. of Energy, Mines, and Resources.

In 1961, Beck and Jankowsky reported attempts which they had made to plate copper on high-strength steel, and chromium on the copper, without embrittling the steel (1).

In 1961, Read (2) stated that "there is little or no agreement on what causes hydrogen embrittlement, on methods of testing for it, or on ways and means of avoiding or removing it." Since that time, this situation has been improved due partly to research on the embrittlement of high-strength steels performed in this laboratory (3-5). However, much more work is required before all of the various aspects of hydrogen embrittlement in these steels have become completely understood.

One unsolved problem has been the electroplating of high-strength steels with chromium without embrittlement occurring in the steels. Much hydrogen is evolved during chromium plating by standard methods.

In 1935, Rogers (6) showed that the acidity of the standard chromic acid-sulfuric acid bath can be substantially decreased by the addition of sodium hydroxide without affecting the nature of the chromium deposit. In unpublished research, the present authors recently showed that the embrittlement of high-strength steels is not appreciably decreased when the latter are plated in a comparatively low-acid bath of this kind, rather than in a standard chromic acid-sulfuric acid bath.

It occurred to the authors that this problem might be solved by plating the steel with copper and then with chromium, the steel being first treated by a special embrittlement-eliminating procedure which had been developed earlier (4). The copper plating would be done in the stable cyanide bath (5) referred to in Table II since such baths do not produce significant embrittlement in steels during plating.

Experiments performed in the hope of proving the soundness of this idea were successful. The electroplated copper acted as a barrier which prevented hydrogen produced during the chromium plating from entering the high-strength steel and embrittling it. It is noteworthy that baking, which is time consuming, expensive, and not always reliable, was not required to free the plated steels from significant embrittlement.

The Steels As Received.—The high-strength steels to be plated were of Types 1062, 4037, and E4340

Table I. Analyses of steels (%)

Elements	Type of steel (AISI) 1062	4037	E4340
C	0.64	0.40	0.38
Mn	1.03	0.76	0.78
P (max)	<0.02	<0.02	<0.02
S (max)	0.02	0.02	<0.01
Si	—	0.31	0.31
Ni	—	—	1.71
Cr	—	—	0.77
Mo	—	0.26	0.21

Table II. Analysis of copper-plating bath

Constituent	Normality
Cuprous cyanide	0.65
Sodium cyanide	1.84
Sodium hydroxide	0.40
Sodium carbonate	Trace*
Copper	0.65
"Free" cyanide	0.40**

* Depends on purity of chemicals used.
** Determined after electrolyzing bath for 3-4 hr.

having the analyses given in Table I, and they were received in the form of pins of 0.4 cm diam. The pins of Type 1062 were 8.3 cm long and had been austempered in the bainitic range giving a Rockwell C hardness of 52-56 and an ultimate tensile strength of 257-279 kpsi. When received, they were covered with a uniform, thin, blue scale of iron oxide. The pins of Type 4037 were 6.7 cm long and had been quenched and tempered giving a Rockwell C hardness of 51-55. When received, they were covered with a thin, very porous film of copper together with smutty black material. The pins of Type E4340 steel were 6.7 cm long and had been hardened in a neutral salt bath at 816° ± 14°C for 30 min, quenched in oil at 24°-60°C, and then washed in water. Then they had been tempered at 204° ± 6°C for 4 hr and air-cooled, resulting in a Rockwell C hardness of 52-54. They became covered with rust during storage. The surfaces of all three types of pins contained many small pits and grooves with sharp overlapping edges.

Experimental Equipment.—The following equipment was of particular importance in this work: (*a*) Sonogen ultrasonic generator LG-150, 25 kc, 150v, equipped with an LT-60 transducerized tank. Branson Ultrasonic Corp.; (*b*) Hounsfield tensometer Type W, using a modified bending jig to give a maximum bend of 135° in 11 min.

Chemical Pretreatment of Pins.—Since there was a considerable difference in the nature of the undesirable material (oxides, *etc.*) on the different types of steel in the "as-received" condition, it was necessary to use different chemical procedures to remove this material from them prior to plating.

After the pins of Types 1062 and E4340 had been degreased in trichlorethylene vapor, they were immersed for 1 and 2 min, respectively, in 18% hydrochloric acid while under the influence of ultrasonic vibrations. Then they were rinsed in water. After the pins of Type 4037 steel had been degreased in the same way, they were immersed for 5 min in a solution containing equal parts by volume of 70% nitric acid, 99.7% acetic acid, and 85% phosphoric acid (later referred to as NAP solution), and then rinsed in water.

All three types of pins then were treated by the following procedure which had been developed previously (4). They were copper coated by immersion in a 10% solution of copper sulfate ($CuSO_4.5H_2O$) at a *p*H of 2.6, and water rinsed. Then they were immersed in an aqueous solution containing 17.5% nitric acid and 35% acetic acid by volume (NAW solution) for 5 min, rinsed in water while under the influence of ultrasonic vibrations, and finally rinsed in distilled water.

In the case of some of the pins, the greatest part of the original undesirable material (oxides, *etc.*) on the surface was removed mechanically prior to plating. This was done by polishing them with "O" grit emery paper. The rest of this material was removed by degreasing in trichlorethylene vapor, cleaning in hydrochloric acid for 10 sec, rinsing in water (but not drying), treatment in NAP solution for 5 min, rinsing in water, ultrasonic rinsing in water, and rinsing in distilled water. The NAP solution did not appreciably attack the mechanically polished surfaces; however, the NAW solution somewhat roughened them.

Copper Plating

During this operation, the steel pin was immersed between two copper anodes in a plating bath having a volume of 2 liters. This bath was a stable one having the requirements which were given in an earlier paper (5), *i.e.*

$$\text{OH normality} = \text{"free" CN normality}$$
$$\frac{\text{total CN Normality}}{\text{Cu normality}} \text{ between 2.6 and 2.9}$$

It was operated at 60°C and slowly agitated.

Some of the pins were plated with copper to a thickness of 2 mils, rinsed, dried, and then plated with chromium. In these cases, both the copper and chromium films were dull in appearance. Other pins were plated with copper to a thickness of 4 mils and then treated with NAP solution at 50°C, which brightened the copper and reduced its thickness to 2 mils. In such cases, the final chromium films were bright also. Some of the pins were chromium plated but not copper plated, for the purpose of comparison.

Chromium Plating

During this operation, the pin to be chromium plated (whether previously copper plated or not) was immersed inside a cylindrical lead anode in a bath having a volume of 280 ml. This bath was a standard one containing 250 g/liter of chromic acid (CrO_3) and 2.5 g/liter of sulfuric acid of sp gr 1.84. The plating was done for 10 min at a cathode current density of 16.1 amp/dm^2 (32.2 amp/dm^2 for the first 10-15 sec in the case of the Type 4340 steel, regardless of whether it was copper coated or not) and a temperature of 50°C. Fresh plating solution was used for each pin so that the results would not be complicated by changes in bath composition. Prior to each experiment, the anodes were electrolytically coated with lead peroxide to insure uniformity in this regard.

Results of Bend Testing

After plating with chromium or copper + chromium, all of the pins were allowed to stand in the air for 30 min before being tested. At the end of that time, they were bent in the Hounsfield machine and the angle of bend at fracture was recorded. When this angle was comparatively small, the pin had been severely embrittled during plating. On the other hand, when the pin was not broken after bending through 135°, it had not been significantly embrittled. The results of the bend tests are given in Table III.

Discussion

The results of these experiments present a very clear picture. In the experiments in which the chromium was plated directly on the high-strength steels, fracture occurred when the pins were bent through an angle of 46° or less in the case of the Type 1062 steel, or an angle of 18° or less in the cases of the Type 4037 and E4340 steels. In the experiments in which there was a 2-mil layer of copper between the steel and the chromium, none of the pins was broken after they had been bent through 135°. This is true whether the copper layer had a dull or bright surface or

Table III. Degree of embrittlement of chromium-plated steel with and without a copper undercoat

Expt. No.	Steel type	Metal undercoat	No. of pins tested	Angle of bend at fracture (degrees)	Proportion of pins passing 135° bend angle (%)
1	1062	—	18	13-46	0
2	4037	—	15	10-17	0
3	E4340	—	15	10-18	0
4	1062	Dull copper	16	>135	100
5	4037	Dull copper	16	>135	100
6	E4340	Dull copper	15	>135	100
7	1062	Bright copper	6	>135	100
8	4037	Bright copper	6	>135	100
9	E4340	Bright copper	6	>135	100
10	*1062	Bright copper	6	>135	100
11	*4037	Bright copper	6	>135	100
12	*4340	Bright copper	6	>135	100

* Steel surfaces mechanically polished to a "0" grit finish.

whether the undesirable materials originally on the steel surface were removed by chemical or mechanical and chemical means.

The slow bend test for the embrittlement in steels has been used frequently in this laboratory because of the ease and rapidity with which large numbers of tests can be performed. In the opinion of the authors, it may well prove to be even more severe, and thus even more useful, than the tests which now are used more frequently for this type of work.

Conclusions

Experiments with three typical high-strength steels, Type 1062, 4037, and E4340, showed that:

1. They are seriously embrittled when chromium is plated directly on them by a standard procedure.

2. They are free from significant embrittlement when copper is first plated on them according to the procedure described in this paper, and then chromium is plated on the copper.

The copper is done in the following two stages:

(*a*) The steel is chemically pretreated to remove oxides, *etc.*, without the occurrence of significant embrittlement, and to eliminate any embrittlement which may have occurred previously.

(*b*) The steel is plated with copper in a stable cyanide bath.

3. Equally satisfactory results may be obtained with steel which has been pickled (*i.e.*, chemically treated) to remove oxides, *etc.*, or with steel which has been mechanically polished and then pickled.

Manuscript received April 13, 1967.

Any discussion of this paper will appear in a Discussion Section to be published in the Nov.-Dec. 1968 issue.

REFERENCES

1. W. Beck and E. J. Jankowsky, "Hydrogen Embrittlement in Metal Finishing," Ed. by H. J. Read, Chap. 7, p. 163, Reinhold Publishing Corp., New York (1961).
2. H. J. Read, *ibid.*, Chap. 9, p. 183 (1961).
3. W. Dingley and J. Bednar, *Tech. Proc. Am. Electroplaters Soc.*, **50**, 71 (1963).
4. J. Bednar, W. Dingley, and R. R. Rogers, *This Journal*, **4**, 497 (1966).
5. W. Dingley, J. Bednar, and R. R. Rogers, *Plating*, **53**, 602 (1966).
6. R. R. Rogers, *Trans. Electrochem. Soc.*, **68**, 391 (1935).