THE SPRING RESEARCH AND MANUFACTURERS' ASSOCIATION

AN INVESTIGATION INTO THE REMOVAL OF HYDROGEN EMBRITTLEMENT BY BAKING

by

J. Desforges, B. Met.

Report No. 292

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SUMMARY AND CONCLUSIONS

The degree of hydrogen embrittlement caused by zinc and cadmium electroplating was measured, using a slow bend test, for strip material of three hardensses. After plating, batches of strips were baked for various times to determine the time necessary to reduce embrittlement to a minimum.

It was found that zinc plating reduced the mean bend angle to failure by just over 50% for the hardest material and by 30% for the other two materials. In the case of cadmium plating, the bend angle to failure was reduced by 30% for the hardest material and by 10% for the other two samples. In addition it was found that all the strips required only two hours baking after zinc plating. After cadmium plating the hardest material required two hours baking, while the amount of embrittlement in the other two materials was not reduced by baking. Although as much embrittlement as possible was removed by these treatments, the ductility of the plated strips was still lower than that of unplated strips.

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1. INTRODUCTION

Following the conclusions of the literature survey on the subject of hydrogen embrittlement of martensitic steels carried out recently at SRAMA[1], work has been carried out which attempts to answer one of the questions raised in that review i.e. how long is it necessary to bake after electroplating in order to remove hydrogen embrittlement?

Preliminary work was carried out in the laboratory using a small rack plating set-up, but there was too much scatter in the results obtained to enable any confidence to be placed on them. In order to increase the sample size to a point where the results could be statistically analysed, and also in view of the fact that, commercially springs are usually barrel plated, it was decided that more meaningful results would be obtained using a commercial barrel plating set-up.

As the relevant specifications[2,3] recommend different baking times for materials of different tensile strengths, hardened and tempered spring steel strip at three differenct hardnesses was used in this investigation. These were plated from zinc and cadmium cyanide baths and batches were baked for various times to determine the time necessary to reduce embrittlement to a minimum.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Hardened and tempered spring steel strips of the three following hardness levels were used for this investigation:-

a) CS80 strip, hardness 562 HV, thickness 0.76 mm, width 13 mm

b) CS80 strip, hardness 465 HV, thickness 0.76 mm, width 19 mm

c) CS80 strip, hardness 364 HV, thickness 0.81 mm, width 13 mm

Each strip was cut into test pieces approximately 90 mm long.

The test specimens produced from the 364 HV material had a notch ground in the centre of both edges to a depth of 0.5 mm at an angle of 90 degrees. This was done because in the unnotched condition these strips were capable of being bent through an angle of 180° without breaking and were therefore unsuitable for slow bend tests. The test specimensat the other two hardnesses were tested in the unnotched condition.

2.2 Cleaning

As the strips used in this investigation were bright polished, they required no pretreatment in either an acid or alkaline solution. Therefore the only cleaning process which they were subjected to was a degreasing treatment in tricthoroethylene immediately before plating.

2.3 Electroplating

Electroplating was carried out in one of the two barrel plating baths, a low cyanide zinc bath and a conventional cyanide cadmium bath, the approximate analyses of which are given below:-

a) Zinc

Zinc	-	12 g/l
Total sodium cyanide	-	20 g/l
Sodium hydroxide	-	75 g/l

b) Cadmium

Cadmium	-	25 g/l
Total sodium cyanide	-	85 g/l
Sodium hydroxide	-	20 g/l

Half the specimens were zinc plated at a current density of approximately 0.5 A/dm^2 to an average thickness of 0.0025 mm, which was less than recommended in BS 1706: 1960. The other half were cadmium plated at a current density of 1 A/dm^2 to an average thickness of 0.01 mm as recommended for Class B conditions in BS 1706: 1960.

2.4 De-embrittlement

Baking was carried out at 190-200°C within 30 minutes of completion of electroplating. Two batches of each hardness, one zinc plated and one cadmium plated, were not baked; similar sets of batches were baked for 2, 4, 8, 16 and 24 hours.

2.5 Bend Tests

The angle at which the strips broke when bent around a 3.175 mm diameter mandrel at a rate of 0.6 degrees/sec was used as a measure of ductility. The tests were carried out using the slow bend test machine described in an earlier report(4).

Batches of each unplated type of strip were tested to give a measure of the original ductility of the strip. The strips which had been plated but not baked were in all cases tested within 3 hours of the end of the plating process.

3. RESULTS

The mean values and standard deviation of the bendtest results for the zinc plated strips are given in Tables I, III and V and those for the cadmium plated in Tables VII, IX and XI.

Student 't' tests were carried out to determine the significance of any difference between the mean bend angle of the different batches. The results of these tests and the conclusions which can be drawn from them are given in Tables II, IV, VI, VIII, X, XII. In these tables 'not significant' refers to a level of significance less than 95%.

4. DISCUSSION

Both zinc and cadmium plating caused a highly significant reduction in the ductility of the strips of all three hardnesses, with the greatest percentage reduction in bend angle occurring for the 562 HV material. This confirms the generally accepted view that, as the tensile strength of the material increases, the quantity of hydrogen required to cause failure will decrease, i.e. a given quantity of hydrogen will cause failure at a lower bend angle for a hard material than for a softer one. Zinc plating reduced the mean bend angle to failure of the hardest material by just over 50% and cadmium plating by just over 30%. The percentage reductions in bend angle for the other two strips were similar, about 30% after zinc plating and 10% after cadmium plating. For all three materials therefore the zinc plating caused a greater loss in ductility than the cadmium plating. This is surprising since it would be expected that the low cyanide solution from which the zinc was deposited would have a higher efficiency than the high cyanide solution from which the cadmium was deposited, and thus more hydrogen would be absorbed during the latter than the former.

For all three zinc plated materials, baking for two hours at 190-200^{o}C caused a highly significant recovery of ductility due to the diffusion of hydrogen either out of the steel or to 'safe' sites throughout the material. Increasing baking time up to a total of 24 hours did not result in any further significant increase in bend angle in any of the three materials.

For the cadmium plated 562 HV material baking for two hours caused a highly significant recovery of ductility. Baking had no effect, however, on the 465 HV material, and the 364 HV material showed a slight decrease in bend angle. This decrease was significant only at the 95% level (i.e. these results would occur once by chance if the test was repeated 20 times). Increasing the baking time had no effect on the two harder strips but the ductility of the 364 HV material increased to a similar level to that of the strips which had been plated but not baked.

From the bend test results after plating it is evident that all the ductility is not recovered by baking. The final bend angles were 5-10% lower than the initial bend angle and this difference was found to be statistically significant for all three materials after both zinc and cadmium electroplating.

The hardnesses of the three test materials were chosen so that one fell into each of the three tensile strength ranges included in the specifications i.e. 1000 to 1400 N/mm^2, 1400 to 1800 N/mm^2, and over 1800 N/mm^2 (corresponding approximately to 310 - 430 HV, 430 - 540 HV and over 540 HV). The recommended baking times for these categories in the M.O.D. Standard[(2)] are a minimum of 4, 18, and 24 hours for both zinc and cadmium plating, and BS 1706: 1960 recommends 2 hours at 200°C for tensile strengths up to 1400 N/mm^2 and 4 hours for higher tensile strengths.

From our results it appears that the two hour baking treatment is sufficient for the three zinc plated materials and for the hardest cadmium plated material, the post-plating bake having no effect on the other two cadmium plated materials. Thus the times recommended in the specifications appear to be longer than we have found to be necessary in this case. Any evidence to suggest that baking times may be safely reduced will, of course, be welcomed by the spring industry but it is important to realise that there are many variables which may effect the amount of embrittlement occurring and the necessary baking time. Variations in the composition of the base steel, cleaning process, plating bath composition, brightening additions and current density may all effect the degree of embrittlement and so may alter the baking time necessary to reduce this embrittlement to a minimum. We therefore feel that, before we can draw any general conclusions from this work a similar programme of work should be carried out in a number of different plating shops where conditions may vary. From the data thus obtained we would then be able to make some general recommendations for baking steel of various strengths after zinc and cadmium electroplating.

5. CONCLUSIONS

1. Zinc electroplating reduced the mean bend angle to fracture by just over 50% for the hardest material and by 30% for the two materials with a lower hardness.

2. Cadmium electroplating reduced the mean bend angle to fracture by 30% for the hardest material and by 10% for the other two materials.

3. A post-plating baking treatment of two hours was found to be sufficient for the material zinc plated by the process used in this investigation.

4. A post-plating baking treatment of two hours was found to be sufficient for the cadmium plated material of the greatest hardness. In the case of the two materials with lower hardnesses the ductility was not improved by the post-plating baking treatment. It should be remembered however that in these two cases the ductility was only reduced by 10% by the plating process.

5. Baking after zinc and cadmium electroplating does not completely restore the ductility of any of the materials.

REFERENCES

1. HEYES, P.F. and DESFORGES, J. 'Hydrogen embrittlement - A Literature Review' SRAMA Report 257, March 1976.

2. Def. Stan. 03-4/1, 1971. 'The Pre-Treatment and Protection of Steel Parts of Tensile Strength Exceeding 1400 N/mm^2'.

3. B.S. 1706: 1960. 'Electroplated Coatings of Cadmium and Zinc on Iron and Steel'.

4. MEE, J.E. 'The Hydrogen Embrittlement of Electroplated Cold-Worked Steels'. SRAMA Report 150 July 1964.

TABLE I SLOW BEND TEST RESULTS FOR ZINC PLATED STRIP, HARDNESS 562 HV

BATCH	BAKING TIME (hours)	NO. OF TESTS	MEAN BEND ANGLES (degrees)	STANDARD DEVIATION
A	Unplated	16	109.06	1.18
B	0	16	52.06	4.84
C	2	16	104.00	8.70
D	4	16	104.63	3.36
E	8	16	105.19	1.47
F	16	16	103.30	2.80
G	24	16	102.31	3.00

TABLE II STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE I

BATCHES COMPARED	t VALUE	LEVEL OF SIGNIFI-CANCE	CONCLUSIONS
A + B	44.5	>99.9%	Zinc plating caused a highly significant reduction in ductility
B + C	20.2	>99.9%	Baking for 2h gave a highly significant increase in ductility
C + D	0.26	Not Signifi-cant	Increasing baking time from 2h to 4h had no significant effect on ductility
C + E	0.37	Not Signifi-cant	Increasing baking time from 2h to 8h had no significant effect on ductility
C + F	0.30	Not Signifi-cant	Increasing baking time from 2h to 16h had no significant effect on ductility
C + G	0.71	Not Signifi-cant	Increasing baking time from 2h to 24h had no significant effect on ductility
A + C	2.23	95%	After baking for up to 24h the ductility of the plated strips was significantly lower than that of the unplated strips
A + G	8.13	>99.9%	

TABLE III SLOW BEND TEST RESULTS FOR ZINC PLATED STRIP, HARDNESS 465 HV

BATCH	BAKING TIME (hours)	NO. OF TESTS	MEAN BEND ANGLES (degrees)	STANDARD DEVIATION
A	Unplated	20	97.20	2.19
B	0	20	64.00	5.54
C	2	20	90.40	1.85
D	4	20	89.80	2.09
E	8	20	90.15	2.70
F	16	20	89.25	2.05
G	24	20	89.65	1.31

TABLE IV STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE III

BATCHES COMPARED	t VALUE	LEVEL OF SIGNIFICANCE	CONCLUSIONS
A + B	24.2	>99.9%	Zinc plating caused a highly significant reduction in ductility
B + C	19.7	>99.9%	Baking for 2h gave a highly significant increase in ductility
C + D	0.94	Not Significant	Increasing baking time from 2h to 4h had no significant effect on ductility
C + E	0.33	Not Significant	Increasing baking time from 2h to 8h had no significant effect on ductility
C + F	1.82	Not Significant	Increasing baking time from 2h to 16h had no significant effect on ductility
C + G	1.44	Not Significant	Increasing baking time for 2h to 24h had no significant effect on ductility
A + C	10.30	>99.9%	After baking for up to 24h the ductility of the plated strips was significantly lower than that of the unplated strips
A + G	13.02	>99.9%	

TABLE V SLOW BEND TEST RESULTS FOR ZINC PLATED STRIP, HARDNESS 364 HV

BATCH	BAKING TIME (hours)	NO. Of TESTS	MEAN BEND ANGLE (degrees)	STANDARD DEVIATION
A	Unplated	20	127.05	8.96
B	0	20	87.70	6.51
C	2	20	118.37	8.51
D	4	20	115.35	3.72
E	8	20	116.00	5.07
F	16	20	119.15	4.73
G	24	20	121.13	7.06

TABLE VI STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE V

BATCHES COMPARED	t VALUE	LEVEL OF SIGNIFICANCE	CONCLUSION
A + B	18.0	>99.9%	Zinc plating caused a highly significant reduction in ductility
B + C	12.5	>99.9%	Baking for 2h gave a highly significant increase in ductility
C + D	1.42	Not Significant	Increasing baking time from 2h to 4h had no significant effect on ductility
C + E	1.04	Not Significant	Increasing baking time from 2h to 8h had no significant effect on ductility
C + F	0.35	Not Significant	Increasing baking time from 2h to 16h had no significant effect on ductility
C + G	1.07	Not Significant	Increasing baking time from 1h to 24h had no significant effect on ductility
A + C	3.06	99.9%	After baking for up to 24h the ductility of the plated strips was significantly lower than that of the unplated strips
A + G	2.26	95%	

TABLE VII SLOW BEND TEST RESULTS FOR CADMIUM PLATED STRIP, HARDNESS 562 HV

BATCH	BAKING TIME (hours)	NO. OF TESTS	MEAN BEND ANGLE (degrees)	STANDARD DEVIATION
A	Unplated	16	109.06	1.18
B	0	16	84.94	6.9
C	2	16	101.25	4.8
D	4	16	103.25	3.62
E	8	16	103.87	1.96
F	16	16	102.94	1.88
G	24	16	103.75	1.73

TABLE VIII STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE VII

BATCHES COMPARED	t VALUE	LEVEL OF SIGNIFI-CANCE	CONCLUSIONS
A + B	13.33	>99.9%	Cadmium plating caused a highly significant reduction in ductility
B + C	7.52	>99.9%	Baking for 2h gave a highly significant increase in ductility
C + D	1.29	Not Significant	Increasing baking time from 2h to 4h had no significant effect on ductility
C + E	1.96	Not Significant	Increasing baking time from 2h to 8h had no signficant effect on ductility
C + F	1.27	Not Significant	Increasing baking time from 2h to 16h had no significant effect on ductility
C + G	1.89	Not Significant	Increasing baking time from 2h to 24h had no significant effect on ductility
A + C	4.79	>99.9%	After baking for up to 24h the ductility of the plated strips was significantly lower than that of the unplated strips
A + C	9.83	>99.9%	

TABLE IX SLOW BEND TEST RESULTS FOR CADMIUM PLATED STRIP, HARDNESS 465 HV

BATCH	BAKING TIME (hours)	NO. OF TESTS	MEAN BEND ANGLE (degrees)	STANDARD DEVIATION
A	Unplated	20	97.20	2.19
B	0	20	89.15	2.41
C	2	20	88.70	2.81
D	4	20	90.20	1.99
E	8	20	90.00	2.10
F	16	20	89.90	1.83
G	24	20	89.20	1.79

TABLE X STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE IX

BATCHES COMPARED	t VALUE	LEVEL OF SIGNIFI-CANCE	CONCLUSIONS
A + B	10.73	>99.9%	Cadmium plating caused a highly significant reduction in ductility
B + C	0.53	Not Signifi-cant	Baking for 2h had no significant effect on ductility
B + D	1.48	Not Signifi-cant	Baking for 4h had no significant effect on ductility
B + E	1.15	Not Signifi-cant	Baking for 8h had no significant effect on ductility
B + F	1.09	Not Signifi-cant	Baking for 16h had no signficiant effect on ductility
B + G	1.07	Not Signifi-cant	Baking for 24h had no significant effect on ductility

TABLE XI SLOW BEND TEST RESULTS FOR CADMIUM PLATED STRIP, HARDNESS 364 HV

BATCH	BAKING TIME (hours)	NO. OF TESTS	MEAN BEND ANGLE (degrees)	STANDARD DEVIATION
A	Unplated	20	127.05	8.96
B	0	20	114.55	5.72
C	2	20	110.95	4.42
D	4	20	115.30	3.31
E	8	20	112.75	6.54
F	16	20	113.85	5.73
G	24	20	115.20	7.11

TABLE XII STATISTICAL SIGNIFICANCE TESTS ON RESULTS IN TABLE XI

BATCHES	t VALUE	LEVEL OF SIGNIFICANCE	CONCLUSIONS
A + B	5.12	>99.9%	Cadmium plating caused a highly significant reduction in ductility
B + C	2.17	95%	Baking for 2h caused a significant reduction in ductility
B + D	0.49	Not significant	Baking for 4h had no significant effect on ductility
B + E	0.90	Not significant	Baking for 8h had no significant effect on ductility
B + F	0.38	Not significant	Baking for 16h had no significant effect on ductility
B + G	0.31	Not significant	Baking for 24h had no significant effect on ductility