ELECTRO-DEPOSITION OF TIN-ZINC ALLOY AS A PROTECTIVE COATING OF FERROUS METALS

S. K. RAY

Central Electro-Chemical Research Institute, Karaikudi, India

Abstract

Alloys of tin and zinc are now deposited electrolytically for their high intrinsic resistance to corrosion. The plating of this alloy is intended primarily for the protection of ferrous metals, the protection being considered to be better than with zinc, cadmium or tin alone. According to information and data available on corrosion resistance under salt spray conditions and in cyclic humidity tests, the best protection is obtained from a deposit between the range 75-80 per cent Sn and 25-20 per cent Zn and a coating of 0.0003 in. thickness. Tin-zinc alloy plating has been commercially practised in England and U.S.A. from a bath in which the use of potassium cyanide is essential. Since the cyanide bath is hazardous to operate, investigations are being made of the possibility of replacing the conventional cyanide plating bath by a non-cyanide bath consisting of a mixture of sodium stannate, sodium zincate and excess of caustic soda in solution.

Preliminary observations have been completed on the cathode potential current density curves, separately of tin and zinc in the sodium stannate and sodium zincate solutions respectively. The results show the possibility of the co-deposition of the two metals from the proposed electrolyte.

Further investigations are in progress to ascertain the influences of various factors, e.g. C.D., pH, concentrations, temperature, etc., on the character and composition of the deposits and to arrive at the best operative conditions for the commercial plating from the bath.

TIN-ZINC alloy is electroplated largely nowadays for its high intrinsic resistance to corrosion; and plating of this alloy is intended primarily for the protection of ferrous metals. The protection is said to be better than zinc, cadmium or tin alone¹. The metals tin and zinc are widely used separately as coatings for the protection of steel against corrosions; there are some drawbacks invariably associated with commercial hot-dipped and electro-deposited tin and zinc coatings to ensure more lasting protection of the steel. Tin coatings are almost invariably porous² to an extent depending partially on their thickness, and consequently with all but the thickest coatings rusting occurs sooner or later and spreads from the pore sites. Hitherto no method of ensuring complete freedom from porosity in thin tin coatings has been devised. Zinc protects by sacrificial action, being itself consumed in the process; but although even discontinuous zinc coatings will give protection at the outset, rusting inevitably commences after a certain amount of zinc has been consumed. A reduction in the porosity of tin coatings or in the rate of sacrificial attack of zinc coatings would ensure more lasting protection of steel. A valuable compromise is achieved by resorting to composite coatings containing both metals.

Experience^{1,3,4} has established that electrodeposited tin-zinc alloy coatings of compositions containing 78 per cent Sn and 22 per cent Zn have excellent corrosion resistance properties. Humidity, salt spray, hot-water porosity and outdoor exposure tests have been carried out on steel specimen coated with tin-zinc deposits of various compositions and thicknesses. In every case, the optimum tin content has proved to be 75-80 per cent. 0.0003 in. thickness of this alloy coating gives better protection than the same thickness of cadmium or zinc⁵. It has also been found that alloy coatings containing less than 50 per cent Sn have their corrosion resistance marked inferior to that of the one mentioned. The corrosion

tests showed that under salt-spray conditions the performance of tin-zinc alloy coatings of 75-80 per cent Sn was very good and superior to the 50 tin: 50 zinc composition. Under the conditions in the cyclic humidity, the 80: 20 alloy coating behaved better than 50 tin: 50 zinc. Solderability, which is excellent for the 80 per cent tin alloy, deteriorates steadily with reduction in tin content^{4,5}.

Besides its main use as a protective coating against corrosion of steel, this alloy has been widely used for other purposes. So far, the electrical industry has been the chief user of tin-zinc plate and is turning to the 80 per cent tin alloy as an alternative to cadmium for the protection of radio chassis, loudspeaker frames, valve screens and other components. Since the plate stands up well to marine atmospheres, it is attracting some interest for the protection of ship's fittings, etc. There are many further applications in engineering where it is thought that the new finish will find an outlet.

Tin-zinc alloy was first deposited in the year 1915 by P. Marino⁶ and its process was protected by a patent. From 1915 to 1932 there was little further development, but during 1932 several patents bearing on the deposition of tin-zinc alloys were taken out. P. Marino⁷ claimed the deposition of tin-zinc alloys from solutions prepared by dissolving the tartrates or oxalates of the metals in aqueous ammonia, using tin-zinc alloy anodes of the same composition as the alloy to be deposited. Thompson and Pattern⁸ described a method for depositing alloys on iron, steel and other metals using tin-zinc anodes amalgamated with mercury in a solution containing zinc sulphate, stannous chloride, sodium hydroxide and a sulphonated oil. A few more workers^{9,10,11} made some preliminary attempts to plate the alloy, but no success was made by them on the technical deposition of the type of alloy.

The deposition of these alloys became a practical process when the use of alkaline bath containing sodium stannate, sodium zinc cyanide, sodium hydroxide and free sodium cyanide, and the use of polarized tinzinc alloy anodes was introduced by R. M. Angles¹² and systematic investigations were made by him on this electrolyte. Since that time further work on this subject has been undertaken in the Tin Research Institute. England, and tin-zinc plating has advanced to a stage where it is being developed on an industrial scale by Cuthbertson¹⁴. A thorough investigation of the deposition and properties of tin-zinc plate was made and as a result a practical process for deposition of the more serviceable alloys was developed. All the advancements and improvements were made on the cyanide bath, originally developed by Angles¹³. Tin and zinc were co-deposited in all proportions from the same bath, operated at 65°C., and at a cathode current density, for still solutions, of 10-13 amp./ft.² (1.08-3.24 amp./dm.²) using alloy anodes of the same composition as the alloy to be deposited. The tin content of the solution is maintained at 30 g./l. and the free cyanide at 17.5-20.0 g./l. throughout, and the composition of the deposit is adjusted by varying the amounts of zinc, total cyanide and sodium hydroxide. The most serviceable composition from the veiwpoint of the protection afforded to steel is around 78 per cent tin and 22 per cent Zn. Plate of this composition not less than 0.0003 in. thick is superior in protective value to either cadmium or zinc plate of comparable thickness and moreover is extremely easy to solder.

The serviceable composition of tin-zinc alloys for protective coatings of ferrous metals is usually electro-deposited from the cyanide bath as mentioned, in which the use of cyanide is hazardous for the platers and certain precautions for the operations of the bath are to be observed rigorously. With the object of eliminating cyanide used by previous workers and to study the possibility of replacing the existing cyanide bath in commercial practice by a simpler and cheaper bath, easy to operate, free from hazards and precautions, the problem of depositing tin-zinc alloy from a non-cyanide bath containing sodium zincate, sodium stannate together with caustic soda has been taken up at the Central Electro-Chemical Research Institute, Karaikudi, India. The various conditions and factors that influence the composition of the deposits are being studied to ascertain the operative conditions for the plating of 78 tin: 22 zinc composition. The successful plating of the alloy from this bath will, no doubt, be of immense service and utility to the iron and steel industries of this country as a protective coating of the steel base materials for subsequent finish for longer life and better corrosion resistance instead of galvanizing by hot-dipped or electroplated method.

Theoretical Considerations

Tin and zinc cannot be co-deposited between all compositions from their simple salt solutions as the normal electrode potentials of tin and zinc are -0.136 volt and -0.758volt respectively. A difference of more than 0.6 volt between the static equilibrium potentials is sufficiently large to suggest that co-deposition of the two metals from acid solutions of their simple salts may be impracticable. If two different cations present in a solution have to be electro-deposited simultaneously, their deposition potentials must remain equal or very close to each other throughout a certain range of current densities^{15,16}. Deposition potentials of two metals can be brought nearer to each other by formation of complex ions containing the metal¹⁷. The nature of the cathodic potential-current density curves18 of two metals in their respective solutions determines the possibility of co-deposition of the two metals and also gives an idea about the ratio of the two metals in the deposit when codeposition is possible.

When two different metal ions are present in a solution, they may influence each other's activity and over-voltage and thus alter the relationship between their cathodic potentialcurrent density curves. The above discussion assumes that the deposition of one metal is not influenced by that of the other and that the behaviour of the bivalent system can, therefore, be predicted from that of the separate metals.

Hence, though cathodic potential-current density curves as determined for a metal in a solution of one of its salts cannot give us the exact information about the deposition of an alloy and also about the nature of the alloy deposited, they may, however, throw some light on the possibility of its formation and also help us in finding out conditions for materializing that possibility. It was, therefore, thought desirable to determine the cathode potential-current density characteristics of tin and zinc in solutions of different concentrations of sodium stannate and sodium zincate respectively which were used as the mixed electrolyte for the subsequent electro-deposition.

When depositing tin from a bath containing sodium stannate and free sodium hydroxide, the following reactions occur:

$$Na_2SnO_3 \rightarrow 2Na^+ + SnO_3^-$$

SnO_3^- + 3H_2O \rightleftharpoons Sn^{++++} + 6OH

In zinc-plating practice from the zincate bath, the basic reactions are:

$$Na_{2}ZnO_{2} \rightarrow 2Na^{+} + ZnO_{2}^{--}$$
$$ZnO_{2}^{--} + 2H_{2}O \rightleftharpoons Zn^{++} + 4OH$$

In tin-zinc plating from a mixed electrolyte the possibility of all these reactions taking place must be considered.

Methods and Materials

Electrolyte — The electrolyte was made up of sodium zincate, sodium stannate and caustic soda. Sodium zincate solution was prepared by dissolving zinc oxide in requisite amount of caustic soda solution. B.D.H. make sodium stannate was used. The zincate solution was mixed in appropriate proportions with sodium stannate to give the desired tin : zinc ratio in the electrolyte. An excess of alkali was added, when necessary, to keep the zincate in solution in the mixed electrolyte. The concentrations of tin and zinc in the electrolyte were determined.

Electrodes — A solid cylinder of stainless steel, height 4.5 cm., diameter 2.5 cm., surface area 40.32 sq. cm., was used as the cathode.

An annular cylindrical anode made of tinzinc alloy of approximate composition 78 Sn : 22 zinc, of inner diameter 8 cm. and height 4.15 cm.

Electrolytic Cell — The cell used was of the rotating-cathode type. The electrolyte was taken in a 3-litre pyrex beaker and kept stirred by the rotating cathode placed centrally in the annular cylindrical anode. The current passing through the cell was measured by a direct current ammeter and bath voltage with a Weston voltameter.

Analysis of the Electrolyte and the Deposit — Tin and zinc in the electrolyte and in the deposits were determined according to the methods of Angles¹³.

10 cc. of the electrolyte is heated with concentrated H_2SO_4 till it fumes. The solution is diluted with 100 cc. of water and 50 cc. of HCl is added. The tin is reduced with a nickel foil and titrated with iodine in the usual manner.

cc. of N/10 iodine \times 1.18 =

tin content in grams per litre 10 cc. of the electrolyte is acidified with nitric acid, 10 cc. of sulphuric acid are added, and the solution is boiled. After cooling it is diluted with 50 cc. of water and 20 cc. of 50 per cent citric acid and 10 cc. of 15 per cent ferric nitrate solution are added. (The ferric nitrate solution should contain a few cc. of nitric acid to prevent hydrolysis.)

The solution is then made just alkaline to litmus with ammonia (1:1), diluted to about 200 cc. and heated to boiling. The hot solution is titrated with standard potassium ferrocyanide solution using 50 per cent acetic acid as an external indicator. The ferrocyanide solution should be standardized against a known zinc solution.

The deposit is also analysed for its tin and zinc content. Tin is precipitated as metastannic acid with concentrated HNO_3 and the filtrate containing zinc is estimated volumetrically by ferrocyanide method.

Determination of Cathode Potential-Current Density Relationship - The experimental arrangements adopted for measuring the cathode potentials of tin and zinc in solutions of sodium stannate and sodium zincate respectively at various current densities were practically the same as those used in the electrolytic cell. The cathodic potentials of tin and zinc in the two respective solutions were measured against a saturated calomel half-cell with a Tinsley potentiometer connected to a suspended coil galvanometer fitted with lamp and scale arrangements. A salt bridge with a capillary tip placed nearest to the rotating cathode, but not in contact with it, was connected with saturated calomel half-cell. An annular cylindrical anode of tin and zinc separately, 7 cm. in diameter and of the same height as the cathode, was used in the respective solutions.

Experimental Results

1. The relation of cathode potentialcurrent density of tin and zinc in the respective solutions of a particular composition is represented graphically in Fig. 1.



TABLE 1

Solution A

Volume of the electrolyte,	2000 cc.; Tin	content, 38 g./l.	; Zinc content,	1.9 g./l.; pH,	above 12.5; Ratio of
ti	in/zinc, 20:1;	Anode — An allo	y of tin and zin	nc (78:22)	

NUMBER	CURRENT	CURRENT	DURATION OF	AMOUNT OF	COLOUR OF	TIN IN THE
OF EXPTS.	PASSED, amp.	DENSITY, amp./dm. ²	ELECTROLYSIS, min.	DEPOSIT, g.	THE DEPOSIT	DEPOSIT, %
1	0.3	0.745	45	0.080	Whitish	22
2	0-5	1.244	30	0.385	Greyish white	72
3	1-0	2.488	10	0.240	Whitish	60
4	2.0	4.900	5		Whitish	58

Solution B

Tin content, 30 g./l.; Zinc content, 3 g./l.; Ratio of tin/zinc, 10:1; pH, above 12.5; Anode — An alloy of tin and zinc (78:22)

		1				
NUMBER OF EXPIS.	CURRENT PASSED, amp.	CURRENT DENSITY, amp./dm. ²	DURATION OF ELECTROLYSIS, min.	Amount of deposit	Colour of the deposit	Tin in the deposit, %
1	0-5	1.244	15		Whitish grey	5
2	1.0	2.488	15		Grey	90
3	2.0	4.900	8	1 <u></u> 1	Greyish white	66
4	3.0	7.464	5		Whitish	60
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2. Some preliminary investigations on the influence of current density on the composition of tin-zinc alloy deposits from the electrolytes containing different metal ratios in solutions A and B were made and the results are recorded in Table 1 and represented graphically in Fig. 2.



Discussions

The cathode potential-current density curves (FIG. 1) of tin and zinc as determined in their respective solutions of a particular concentration taken for consideration indicate that co-deposition of two metals is possible.

The effect of variation in current density on the composition of the deposits from electrolytes containing tin and zinc in different proportions as in solutions A and B is shown in Table 1 and respresented graphically in Fig. 2. It is seen that in each solution tin content of the deposit increases with increase in current density, reaches a maximum around a certain current density and decreases thereafter.

It is expected from the cathodic potentialcurrent density curves of the two metals in the respective solutions (FIG. 1) that tin content of the deposits will go on decreasing with increase in current density and low

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current density will deposit an alloy rich in tin. But in actual practice in the study of effect of current density on the compositions of the deposits, some discrepancy is observed where the tin content of the deposit goes on increasing with current density. This can be explained as follows:

$$Na_2SnO_3 \rightarrow 2Na^+ + SnO_3^{--}$$
 (i)

$$SnO_{3}^{--} + 3H_{2}O \Rightarrow Sn^{++++} + 6OH^{--}$$
 (ii)

From the reaction (ii), it follows that an increase in hydroxyl ion concentration leads to a reduction in the concentration of tin ions in the bath and in consequence the deposition potential is raised. Accordingly an increase in the sodium hydroxide content of the bath would be expected to decrease the ionic concentration of tin and thus cause the tin content of the deposit to diminish. The inference is, therefore, that the enrichment of the deposit in zinc resulting from an increase in hydroxide is due, not to the conditions having been made more favourable for the deposition of the zinc, but to the suppression of the deposition of the tin. Similar observation was noted by Angles¹³ in the deposition of the alloy from the cyanide bath containing excess of alkali.

The behaviour of the zincate solution in excess of alkali is quite uncertain and does not exactly follow the reversible ionic phenomenon as it exists in concentrated alkali as a series of readily soluble and highly hydrolysed zincates¹⁹. Moreover, it is noteworthy that Thorne and Ward express²⁰ the view that zincates are not ionic in character and entirely colloidal in behaviour.

Conclusion

So from the observed experimental result it can be concluded that from an electrolyte containing tin and zinc in the ratio of 20:1 in the mixed electrolyte of sodium stannate and sodium zincate, alloys of tin and zinc having 75-80 per cent Sn and 25-20 per cent Zn composition ranges with high corrosion resistance properties can be plated out under suitable current density. The current density range is appreciable for the deposition of the above compositions.

Detailed investigations to study the influence of various factors on the character and composition of the alloys deposited are in progress. Actual plating of the alloy (78:22) to test the corrosion resistance properties of it on steel specimen will be taken up when the above observations are completed.

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References

- 1. ANGLES, R. M., Engineering, 161 (1946), 289.
- 2. MACNAUGHTON, D. J. & PRYTHERCH, J. C., J. Electro-dep. Tech. Soc., 12 (1937), 66.
- KERR, R., J. Soc. Chem. Ind., Lond., 16 (1942), 128.
- 4. Prod. Finish., Lond., 195, 15(4), 22.
- 5. Tin-zinc Alloy Plating (Tin Research Institute) (March 1952), 16-18.
- 6. MARINO, P., British Patent 10,133.
- 7. MARINO, Q., British Patent 405,433.
- 8. THOMPSON, M. M. & PATTERN, J. C., U.S. Patent 1,876,156.
- 9. S. O. COWPER-COLES & FERBRITE LTD., British Patent 420,103.
- 10. HAUEISEN, B. R., U.S. Patent 1,904,732.
- 11. BAIER, S. W. & MACNAUGHTON, D. J., British Patent 525,364.
- LOWRINGER, V. A., ANGLES, R. M. & BAIER, S. W., British Patent 548,009.
- ANGLES, R. M., J. Electro-dep. Tech. Soc., 21 (1946), 45-64.
- CUTHBERTSON, J. W. & ANGLES, R. M., J. Electro-chem. Soc., 94(2) (1948).
- THOMPSON, M. DEKAY, Theoretical and Applied Electro-chemistry (Macmillan & Co., London)
 3rd Edition (1939), 152.
- 16. FAUST, CHARLES L., Trans. Electro-chem. Soc., 81 (1941), 301.
- 17. GLASSTONE, S., The Electro-chemistry of Solutions (Mathuer & Co. Ltd., London) (1937), 459.
- GLASSTONE, S., The Electro-chemistry of Solutions (Mathuer & Co. Ltd., London) (1937). 459, Fig. 33.
- SCHOLDER, R. & WEBER, H., Z. Anorg. Chem., 215 (1933), 355.
- 20. Inorganic Chemistry (Gurney & Jackson, London) (1939).