Technical Section

Measurement of the Thickness of Electroplates by Electrolytic Stripping Method: Stripping Solution for Chromium over Mild Steel

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INTRODUCTION

THE routine testing of the electroplates for control purpose in development and production is usually carried out by magnetic method[1], B.N.F. Jet test[2], drop test[3] or anodic stripping method[4], as these methods are simple and quick for thickness measurements. The magnetic method is applied only to systems where either the plated or the basis metal is of magnetic nature. B.N.F. jet test is highly dependent on the temperature and the nature of the deposit-fine, coarse, porous, soft and hard. The detection of the end point in this test is rather crude and less accurate. The drop test suffers from more or less the same defects as the jet test. Anodic stripping method seems to have greater precision and wider scope of applicability as the time of stripping is not influenced by temperature fluctuations and can be controlled by controlling the current, and the end point indication is given by an instrument such as voltmeter or magic eye.

The anodic stripping method consists in dissolving out a plated metal from a small area by using a constant current and a proper stripping solution which may have hundred per cent current efficiency and show a marked change in anodic potential and give a uniform and good spot at the end point of stripping. Knowing the stripping time 't', the thickness 'T' of the electroplates can be calculated out by applying Faraday's laws and using the following equation:

$$T = \frac{W.C}{d.A} t$$

where 'W' is the electrochemical equivalent and 'd' the density of the plated metal, 'C' the current used for dissolution and 'A' the area of the stripped spot. In order that the equation may hold the current efficiency of the stripping solution should be hundred per cent, and the area of the stripped spot 'A' and the current 'C' should remain constant. The important problems in this method are: (*a*) to obtain stripping solutions which may have hundred per cent anodic current efficiencies, (*b*) to design a proper stripping cell with a constant stripping aperture, and (*c*) to design a simple thickness testing instrument which may give constant currents within a desired range. In earlier communications, the testing instrument[5] and a stripping cell[6] have been described.

Stripping Solutions

It has been observed that stripping solutions are specific not only with respect to the plated metal but also with respect to basis metals. So, unless the stripping solutions for each of the industrial combinations of plated and basis metals are worked out the anodic stripping method, although simple, cannot be adopted for testing the thickness of electroplates. Proper stripping solutions for most of the industrial combinations of plated and basis metals are not reported in literature.

Francis[4] has suggested the use of the 10 per cent NaOH as anodic stripping solution for testing the thickness of electroplates of alkali soluble metals such as tin, lead, zinc and chromium, and a 10 per cent potassium cyanide solution for cadmium, copper, silver, gold and brass. Our investigations have, however, shown that although these solutions are good chemical solvents for various metals, they do not show hundred per cent anodic current efficiency in electrolytic stripping at high current densities and fail to give properly stripped spots, besides showing inconsistency in observed potential. In earlier communications stripping solutions for nickel[7] plated over copper, silver[8] over copper, brass, mild steel and nickel, cadmium[9] over copper and mild steel, copper[10] over mild steel, and zinc[11] over mild steel and copper base metals have been reported[12].

Stripping Solution for Chromium Plated over Mild Steel

In literature two stripping solutions are found to be reported for chromium electroplates Anderson and Mannel[10] suggested a solution of 1N Na_3PO_4 + 1N Na_2SO_4, and Francis[4] recommended 10 per cent NaOH solution. Our investigations have shown that none of these solutions satisfy all the necessary conditions of a good anodic stripping agent. Caustic soda solution showed a low anodic current efficiency about 80 per cent. Phosphate-sulphate solution, however, satisfies current efficiency condition but shows chemical action on electroplate, and more pronounced over thin electroplates. It is found to be far better than 10 per cent NaOH solution. However, on the consideration of the high cost of this solution and also the chemical action over plated metal it is desirable to work out a better and cheaper solution for testing the thickness of chromium electroplate over mild steel.

For the anodic current efficiency of a solution to be hundred per cent, the necessary conditions are that besides the metal dissolution reaction, there should not occur any other side reaction at the anode, nor should the stripping solution chemically attack the plated metal. A mixture containing 0.5 per cent KCl and 2 per cent HNO_3 has been found to satisfy the necessary conditions of a good stripping solution for testing the thickness of chromium electroplates over mild steel.

Experimental

Experimental arrangements are made as described in earlier communications. Current within a range of 10 to 25 milliamps has given satisfactory results over a stripping area of 0.074 sq. cm. For a current of 10, 15, 20 and 25 milliamps, the initial and final voltages are respectively: 1.8, 2.36; 2, 2.56; 2.1, 2.76; 2.26, 2.9 volts. The instrument described earlier has been used to adjust the current and also to balance the initial voltage of the cell system. A coated cell described elsewhere[7] has been used in order to avoid cathodic gassing in close vicinity of the anode surface. Large size gas bubbles produced in the narrow region of the bottom part of the cell shield the anode surface and this increases the current density over the unshielded area, and thus results in the gradual increase in voltage. When gas bubble leaves the surface, the current distribution over anodic surface becomes uniform and the voltmeter needle flies back. With a cell stopped off in the bottom region with a suitable insulating material the to and fro type of fluctuations in the voltmeter needle have completely been checked.

Results

The stripping solution reported here gives a sharp spot completely free from plated metal A nicely polished surface is seen when the stripping is just completed. The change in voltage is sharp at the end point of stripping. The effect of current density on stripping and the chemical action of the solution on electroplate are studied. The results presented in Table I indicate that the current efficiency is close to 100 per cent in the current density range 10-25 milliamps.

The solution contained in a stainless steel stripping cell is kept in contact with the electroplate for some time without passing the current, and then the current is passed and stripping time is noted. The time for keeping the solution in contact with the plate when current is not passed, the time of electrochemical stripping and the calculated thickness values in various experiments are tabulated in Table II. The results show that the chemical action of the stripping solution on the electroplate is negligible, as the time of stripping does not decrease regularly with the increase of time of contact of the solution with the electroplate. From the literature also it was found that chromium is not attacked by KCl and HNO_3 at ordinary temperatures[14].

The accuracy of the anodic stripping test for chromium over mild steel with the stripping solution reported here is within ± 5 per cent.

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TABLE I

Current Efficiency

Current milliamps	*Thickness in thou*					
	PLATE 1		PLATE 2		PLATE 3	
	Time secs.	*Thickness (thou)*	*Time secs.*	*Thickness (thou)*	*Time secs.*	*Thickness (thou)*
10	264	0.382	278	0.403	78	0.113
			277	0.401	74	0.107
					78	0.113
15	178	0.387	193	0.419	49	0.106
					48	0.104
					50	0.108
20	135	0.391	140	0.406	37	0.107
					38	0.110
					37	0.117
25	107	0.383	113	0.409		

TABLE II

Chemical Action

Time of contact of solution with electroplate, mins	PLATE 1		PLATE 2	
	Time of stripping secs.	*Thickness (thou)*	*Time of stripping secs.*	*Thickness (thou)*
0	61	0.133	68	0.148
	65	0.143	73	0.159
10	63	0.137	66	0.143
	66	0.143	72	0.156
20	65	0.141	71	0.154
	67	0.146		