JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 699–706

The electrodeposition of aluminium on mild steel from a molten aluminium chloride-sodium chloride bath

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Received 24 October 1978

The electrodeposition of aluminium on mild steel from a dry and HCl-free $AlCl_3$/NaCl melt (80 wt% purified $AlCl_3$, 20 wt% NaCl) has been studied. Electropolishing the substrate in the same electrolytic bath produced satisfactory electroplates with almost 100% current efficiency. The quality of the plate has been examined through photomicroscopy of the cross-section, profilometry, electron microscopy, and electron microprobe analysis of the surface of the electroplate. It has been suggested that the greyish colour of the plate is most probably due to the presence of iron as an impurity in the electroplated aluminium.

1. Introduction

The studies on the electrodeposition of aluminium on steel from fused salt baths based on $AlCl_3$ and NaCl are quite extensive [1–7]. One of the conclusions [7] that has emerged from these studies is that the presence of a small amount (0·07%) of hydrogen chloride in the bath is essential for obtaining a smooth aluminium electroplate. This can be achieved either by using a slightly moist bath, as has been the case in most of the studies made in the past, or by introducing dry hydrogen chloride into a moisture-free bath. Some possible mechanisms have also been suggested [7] to explain the role of hydrogen chloride in the deposition process. However, our work with electrodeposition of aluminium on brass [8] clearly shows that very satisfactory electrodeposits of aluminium can be obtained on brass substrates in a dry bath, even in the absence of HCl. This has, therefore, given rise to some doubt regarding the validity of the conclusions arrived at earlier concerning the role of HCl in the deposition process on steel.

We report, in this paper, the results of our studies on the electrodeposition of aluminium on mild steel from the fused salt bath $AlCl_3$ (80 wt%) and NaCl (20 wt%) made with a view to establishing conditions for obtaining satisfactory electroplates from a dry and HCl-free bath and understanding the role of HCl in the deposition process. The effect of the following variables on the quality of the plate have been examined:

(a) surface treatment of the substrate;
(b) cathodic current density;
(c) speed of rotation of the cathode;
(d) duration of electrolysis; and
(e) bath temperature.

2. Experimental

The materials for the electrolytic bath, electrolysis cell, experimental procedures, and the techniques for examination of the electroplate were the same as those reported earlier [8], except that mild steel rods were used as cathodes and the photomicrographs were obtained using a Model OMO-7 Vertical Metallographical Microscope (USSR). The surface structure of the electroplates was studied by making a cellulose acetate–carbon double stage replica of the surface and examining it in an EM-6 electron microscope (AEI, England).

3. Results and discussion

The results of electrodeposition following various surface treatments of the substrate are summarized in Table 1. The results are based on observations

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Table 1. Exploratory electrodeposition of aluminium on mild steel with different surface treatments (bath temperature, 175 ± 2° C; static cathode; cathodic c.d., 18 mA cm^{-2}; plating time: 30 min)

Run no.	*Treatment of cathode surface prior to electrolysis*	*Nature of the electrodeposit*	*Surface roughness (μm)*	*Current efficiency (%)*
1	mechanically polished cathode introduced into a bath not subjected to pre-electrolysis (bath containing dissolved hydrogen chloride)	good plating	0·36	79·5
2	mechanically polished cathode introduced into a dry bath (bath which was subjected to sufficient pre-electrolysis)	rough dendritic deposit	–	–
3	cathode treated with 1 M H_2SO_4 for one minute followed by washing with water and acetone successively and dried at room temperature	rough and dendritic deposit	–	–
4	cathode surface was wiped with glass wool soaked with concentrated HCl just before introduction into the bath	good plating with occasional appearance of rough deposit on small areas	0·36	95·0
5	cathode was exposed to dry HCl gas for two minutes prior to introduction into the bath	loose dendritic deposit	–	–
6	cathode treated for 15 min, at 35° C with a chemical polishing solution [9] consisting of water (80 cm^3), oxalic acid (2·8 g), and 30% H_2O_2 (4 ml). It was then washed and dried as in the case of run 3	good plating in general with dendrites at the upper portion of the electrode	0·51	97·6
7	cathode, electropolished for two minutes at a c.d. of 20 mA cm^{-2} in an electropolishing bath [10] consisting of perchloric acid (10 cm^3) and glacial acetic acid (100 cm^3), maintained at 20° C using a stainless steel cathode; it was then washed and dried as in the case of run 3	rough dendritic deposit	–	–
8	cathode, electropolished in the electroplating bath itself at a c.d. of 18 mA cm^{-2} for one minute; the direction of the current was then reversed for electrodeposition	very good plating	0·36	96·8
9	cathode electropolished in the same way as in the preceding case but for 45 s	good plating with some amount of loose dendrites	–	–
10	cathode electropolished in the same way as in the preceding case but for 30 s	rough dendritic deposit	–	–
11	cathode electropolished in the same way as in the preceding case but at a c.d. of 36 mA cm^{-2}	good plating but lot of loose deposit at the bottom	–	–
12	mechanically polished cathode introduced into a bath which was initially dry, but to which some $AlCl_3$, after exposure to atmosphere for 5 min was added prior to introduction of the electrode	good plating	0·36	82·0

made with two or more specimens electroplated under identical conditions.

It is found that a mechanically polished electrode, without any additional surface treatment, does not produce a satisfactory electroplate from a dry bath (run 2), but when such electrodes are used in a moist bath (bath containing dissolved HCl), good plates can be obtained (runs 1 and 12) with a current efficiency of about 80%. These observations confirm the findings of Howie and Macmillan [7] that the presence of HCl is necessary for satisfactory plating on steel.

Out of a number of surface treatment procedures followed for the specimens used in a dry bath, electropolishing in the same electroplating bath for one minute at a current density of 18 mA cm^{-2} gave the best result (run 8). Improvement in the quality of the electroplate obtained using electropolished specimens can be seen from Fig. 1. This simple treatment procedure involves no additional material or equipment and the treated surface does not come into contact with the atmosphere following the treatment prior to electrode position. Encouraging results were also obtained when the surface treatment consisted of merely wiping the surface with a glass wool swab dipped in concentrated hydrochloric acid (run 4), or when the surface was treated with a chemical polishing solution [9] consisting of oxalic acid and hydrogen peroxide.

The current efficiency of aluminium deposition from a dry bath was found to be close to 100% as has been noted earlier by Howie and Macmillan [7].

The results clearly show that the presence of hydrogen chloride is not essential for obtaining a satisfactory electroplate of aluminium on steel: the same result can be achieved in a HCl-free bath with a suitable surface pre-treatment procedure, such as electropolishing in the same bath as described above. The fact that HCl produces good electroplates, leads to the conclusion that its role lies essentially in producing a suitably chemically polished surface. This simple role appears to be more probable than those suggested by Howie and Macmillan [7]. This is also supported by the fact that mere wiping of the cathode surface with concentrated HCl prior to introduction of the same into the bath also produces good electrodeposits (run 4).

Results of electrodeposition with varying current densities (c.d.) are given in Table 2. It can be seen from the results that although apparently good plating is obtained at low cathode c.d. (6 mA cm^{-2}), the surface roughness is somewhat high. Electroplates, with a higher degree of smooth-

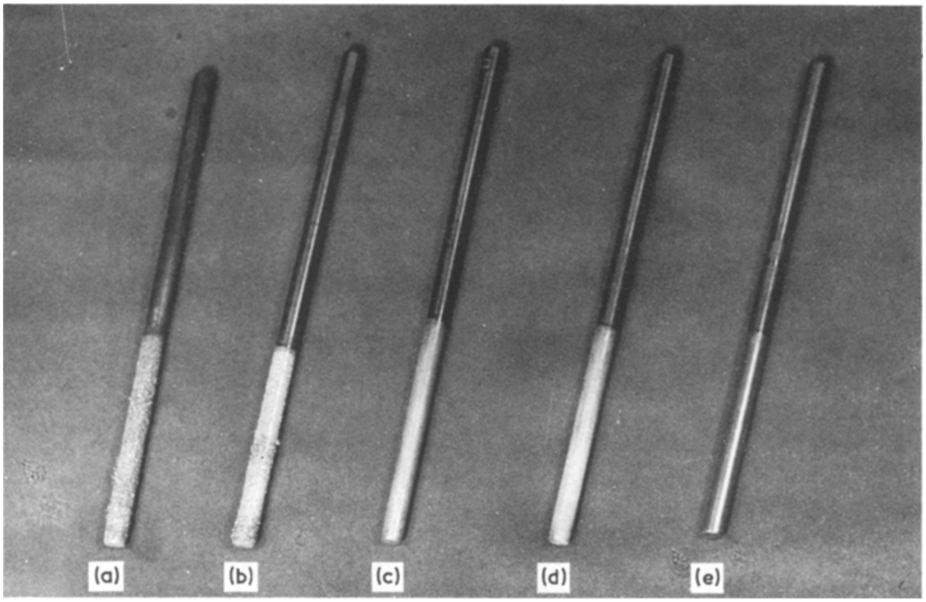

Fig. 1. Photographs of electroplated mild steel specimens obtained during exploratory runs. (a) and (b) deposits from a dry bath on mechanically polished cathodes; (c) a deposit obtained from a dry bath on a specimen cathode electropolished for one minute at a c.d. of 18 mA cm^{-2} in the same bath; (d) a deposit obtained from a bath containing dissolved HCl on a mechanically polished specimen; (e) a deposit on an electropolished specimen obtained under conditions similar to that of (c) but lightly polished with a commercial metal polish.

Table 2. Electrodeposition of aluminium on mild steel at various current densities (bath temperature, 175 ± 2° C; static cathode; substrate surface of electropolished for one minute at a c.d. of 18 mA cm^{-2}; dry and HCl-free bath)

Run no.	*Current density* (mA cm^{-2})	*Plating time* (min)	*Surface roughness* (μm)	*Current efficiency* (%)	*Nature of the electrodeposit*
1	6·06	90	0·89	96·7	good plating, but surface slightly rough
2	6·05	90	0·63	97·5	good plating, but surface slightly rough
3	12·1	45	0·46	98·1	good plating
4	12·1	45	0·63	96·5	good plating
5	18·1	30	0·36	96·8	good plating
6	18·3	30	0·38	97·2	good plating
7	24·0	22·5	–	91·8	good plating on the upper portion, but some dendrites at the lower part
8	24·2	22·5	–	93·6	good plating, but some dendrites at the lower part
9	30·1	18	–	–	dendrites on the lower part having dark appearance
10	29·9	18	–	–	dendrites on the lower part having dark appearance

ness, are obtainable at a higher c.d. in the region of 18 mA cm^{-2}. The dendritic growth threshold current density (DGTCD) for the system is found to be in the region of 20–25 mA cm^{-2}, which is similar to the values found by Howie and Macmillan [7] for mechanically polished cathode specimens in a similarly constituted bath containing dissolved HCl.

The study of the effect of rotation of the cathode on the deposition process (Table 3) shows that rotation brings about a distinct improvement in the quality of the electroplate. The surface roughness values were found to be generally lower on rotating cathodes. Frequently the surface roughness of plates on rotating cathodes is found to be lower (0·14–0·20 μm) than that of the original mechanically polished substrates (0·23–0·28 μm). It is further found that higher c.d.s than 20–25 mA cm^{-2}, which was the DGTCD for stationary electrodes, may be used to obtain satisfactory electroplates on rotating cathodes. Thus it appears that the DGTCD value increases with rotation of the cathode.

Extension of the period of electrolysis from 15 min to 45 min at a more or less fixed c.d. of 18 mA cm^{-2} (Table 4) shows that the quality of the plate deteriorates, becoming rough with increasing thickness of the coating. On the other hand with rotating cathodes, good and thick electroplates could be obtained.

Table 3. Effect of rotation of cathode on aluminium deposition on mild steel (bath temperature, 175 ± 2° C; cathode surface electropolished for one minute at a c.d. of 18 mA cm^{-2}; dry and HCl-free bath)

Run no.	*Rotation of cathode* (rev min^{-1})	*Cathode c.d.* (mA cm^{-2})	*Plating time* (min)	*Surface roughness* (μm)	*Current efficiency* (%)	*Nature of electrodeposit*
1	0	18·1	30	0·36	96·8	good
2	0	18·3	30	0·38	97·2	good
3	112	18·0	30	0·28	97·8	excellent
4	112	18·1	30	0·20	96·3	excellent
5	112	30·8	18	0·28	95·7	excellent
6	112	30·2	18	0·28	90·6	very good plating except for a small area having slightly rough surface
7	112	30·5	18	0·28	94·9	
8	220	31·0	18	0·14	96·5	excellent
9	220	30·9	18	0·18	95·3	excellent
10	220	42·8	13	0·18	93·8	excellent
11	220	42·8	13	0·20	95·8	excellent

Table 4. Effect of duration of electrolysis on aluminium deposition on mild steel with static and rotating cathodes (cathode surface electropolished for one minute at a c.d. of 18 mA cm^{-2}; bath temperature, 175 ± 2° C; c.d., 18 mA cm^{-2}; dry and HCl-free bath)

Run no.	*Plating time* (min)	*Rotation of cathode* (rev min^{-1})	*Surface roughness* (μm)	*Current efficiency* (%)	*Nature of the electrodeposit*
1	15	0	0·28	92·3	excellent
2	15	0	0·28	96·2	excellent
3	30	0	0·36	96·8	good
4	30	0	0·38	97·2	good
5	45	0	1·52–2·54	94·4	rough
6	45	0	0·51–1·78	96·7	rough
7	15	112	0·14	98·2	excellent
8	15	112	0·20	97·5	excellent
9	30	112	0·28	97·8	excellent
10	30	112	0·20	96·3	excellent
11	45	112	0·14	95·7	excellent
12	45	112	0·25	98·8	excellent

Studies on the effect of bath temperature show that (Table 5) on electropolished specimens a good plate is produced at bath temperatures of 175° C and above, but at 155° C dendritic deposits are obtained. However, raising the bath temperature to as high as 205° C is not effective in producing a good electroplate on a mechanically polished specimen.

The current efficiency of aluminium deposition from a dry bath is always found to be high and close to 100% as can be seen from Tables 1–5. These values have been obtained assuming that the total quantity of electricity passed through the cell has been used for depositing aluminium, although some iron enters the bath from the substrate during the electropolishing process and may be included in the deposit. Consequently, the current efficiency values reported here are slight overestimates.

The aluminium electroplate obtained on the mild steel substrate was invariably greyish white and dull in appearance but when the surface of a

Table 5. Effect of varying bath temperature on aluminium deposition on mild steel (static cathode; c.d., 18 mA cm^{-2}; dry and HCl-free bath)

Run no.	*Bath temperature* (° C)	*Surface treatment of the cathode*	*Plating time* (min)	*Surface roughness* (μm)	*Current efficiency* (%)	*Nature of the electrodeposit*
1	175	mechanically polished only	15	–	–	dendritic
2	175	mechanically polished only	15	–	–	dendritic
3	195	mechanically polished only	15	–	–	dendritic
4	195	mechanically polished only	15	–	–	dendritic
5	205	mechanically polished only	15	–	–	dendritic
6	205	mechanically polished only	15	–	–	dendritic
7	155	electropolished*	30	–	80·5	dendritic
8	155	electropolished*	30	–	82·1	dendritic
9	175	electropolished*	30	0·36	96·8	good
10	175	electropolished*	30	0·38	97·2	good
11	195	electropolished*	30	0·30	100·0	good
12	195	electropolished*	30	0·51	96·6	good
13	205	electropolished*	30	0·48	98·2	good
14	205	electropolished*	30	0·36	98·0	good

*At a c.d. of 18 mA cm^{-2} for one minute

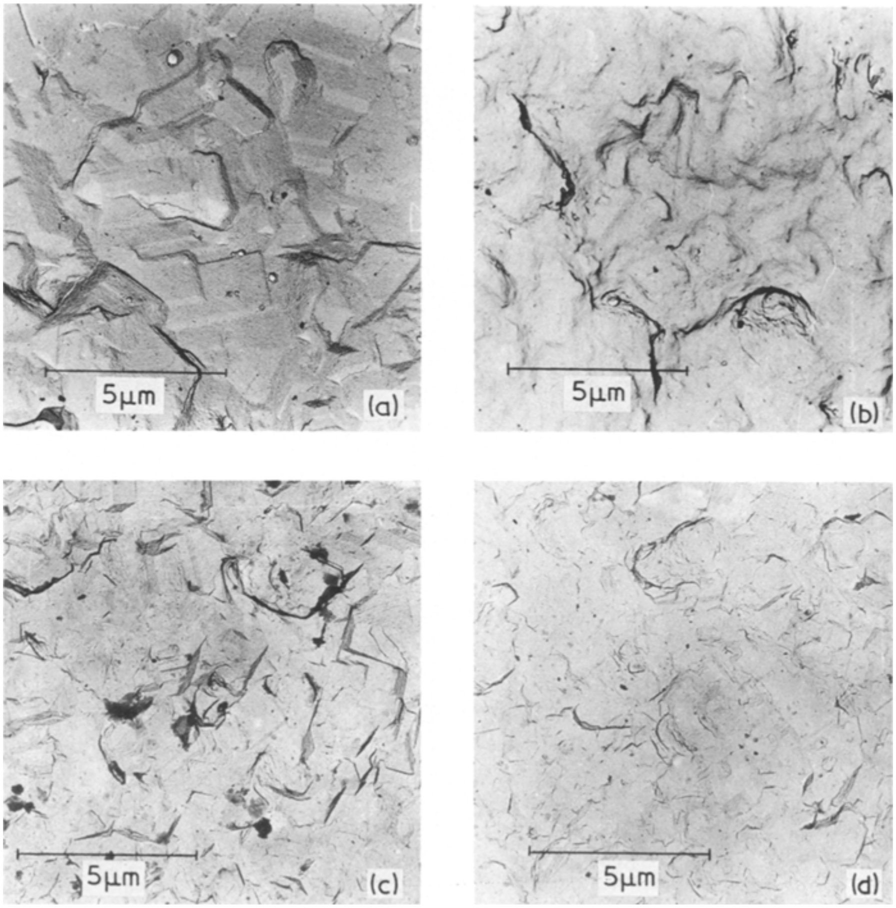

Fig. 2. Electron micrographs of the surface of aluminium electroplates obtained on electropolished mild steel substrates: (a) from a dry bath at 175° C with a static cathode; c.d. 18 mA cm^{-2}; plating time, 30 min; (b) from a dry bath at 175° C with a rotating cathode; speed of rotation, 112 rev min^{-1}; c.d., 18 mA cm^{-2}; plating time, 30 min; (c) from a dry bath at 175° C with a rotating cathode; speed of rotation, 112 rev min^{-1}; c.d., 18 mA cm^{-2}; plating time, 15 min; (d) from a dry bath at 175° C with a rotating cathode; speed of rotation, 112 rev min^{-1}; c.d., 30 mA cm^{-2}; plating time, 18 min.

good electroplate was wiped with a commercial metal polishing paste, a highly reflecting mirror finish was produced (Fig. 1).

The adhesion of the electroplate to the substrate, as tested qualitatively, was found to be good. On bending some plated specimens through almost 180°, no cracks could be seen on the plates indicating that the deposits are highly ductile.

The electron micrographs of the electroplated aluminium surfaces, obtained on an electropolished mild steel substrate (Fig. 2) reveal the structure to be crystalline. The crystal facets of the deposits are more developed at the static electrodes (Fig. 2a and Fig. 2c) than on rotating electrodes where the deposition tends to be more uniform (Fig. 2b and 2d). In Fig. 2a, because of the static nature of the electrode and longer plating time, the crystal facets are well developed and the individual grains can be seen. In Fig. 2c although the growth pattern remains similar, the shorter plating time causes the growth to be less and big facets are consequently absent. The surface of the deposit obtained at a higher c.d. and a rotating electrode (Fig. 2d) appears to be finer due to smaller grain sizes (Fig. 2b). This is in accordance with the observation made earlier while studying the effect of c.d. on the quality of the electroplate (Table 2). The cross-sectional

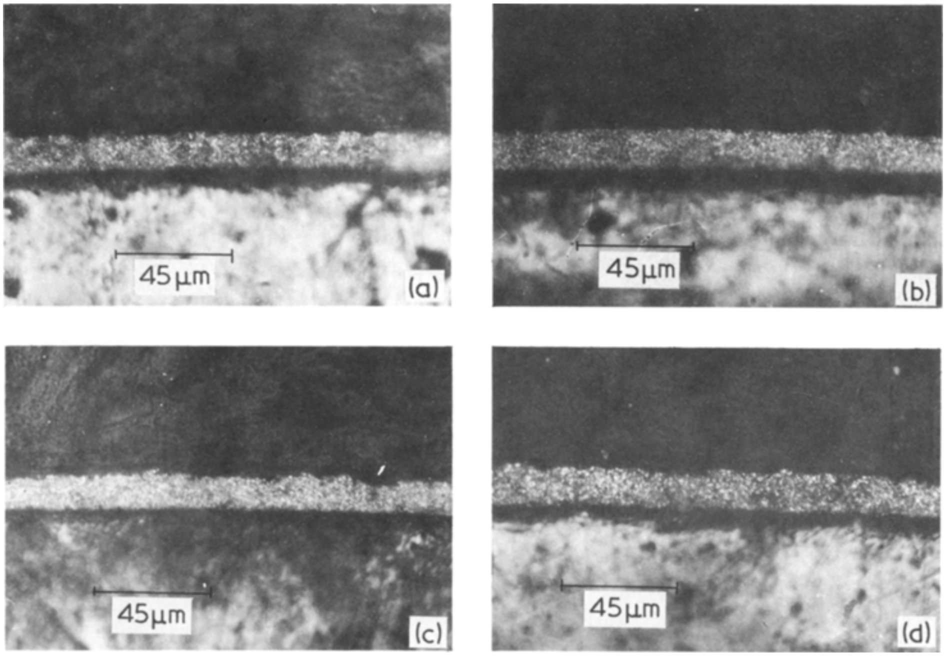

Fig. 3. Photomicrographs (cross-sectional view) of aluminium electroplates obtained: (a) from a dry bath at 175° C with a static electropolished cathode; c.d., 18 mA cm^{-2}; plating time, 30 min; (b) from a dry bath at 175° C with a rotating electropolished cathode; speed of rotation, 112 rev min^{-1}; c.d., 18 mA cm^{-2}; plating time, 30 min; (c) from a dry bath at 155° C with a static electropolished cathode; c.d., 18 mA cm^{-2}; plating time, 30 min; (d) from a bath at 175° C containing dissolved HCl with a static mechanically polished cathode; c.d., 18 mA cm^{-2}; plating time, 30 min.

view of aluminium deposits under a microscope revealed these to be almost uniform, compact and fine grained. The photomicrographs of a few typical samples are shown in Fig. 3. The study shows that the best aluminium electroplate is produced on an electropolished rotating mild steel substrate (Fig. 3b) from a dry bath.

The results of electron microprobe analysis of the surface of some plated specimens are shown in Table 6. The analysis was carried out only for iron and silicon as these are the likely impurities originating either from the bath or the electrode. The plate thickness in each sample was of the order of 11 μm. It is found that while silicon is

Table 6. Impurity levels in electroplated aluminium (static cathode; c.d., 18 mA cm^{-2}; plating time, 30 min)

Run no.	*Bath temperature (° C)*	*Condition of bath*	*Surface treatment of the substrate*	*Percentage (by wt) of*	
				Fe	*Si*
1	195	dry and HCl-free	electropolished at 18 mA cm^{-2} for one minute	1·26	trace
2	175	dry and HCl-free	electropolished at 18 mA cm^{-2} for one minute	1·13	trace
3	155	dry and HCl-free	electropolished at 18 mA cm^{-2} for one minute	0·82	trace
4	175	contained dissolved hydrogen chloride	mechanically polished only	0·92	trace

present only in traces the surface concentration of iron is around 1 wt%.

The surface concentration of iron is found to increase with increasing bath temperature indicating that at least a portion of the iron found on the surface is due to diffusion from the substrate, similar to the diffusion of Cu and Zn from the brass substrates reported earlier [8]. There is not much difference in the surface concentration of iron on an electroplate obtained on a mechanically polished cathode using a bath containing dissolved HCl and that found on the plate obtained from a dry and HCl-free bath using an electropolished cathode, the respective figures being 0·92% and 1·13%. Since the bath, in the latter case, gets contaminated with iron during electropolishing, a much higher iron concentration is normally expected. The fact that it is not so suggests that the iron, entering the bath during electropolishing, gets redeposited preferentially on the cathode prior to aluminium deposition. The greyish appearance of aluminium electroplates on mild steel substrates, which is in contrast to the silver-white appearance of plates obtained on brass [8], appears, in all probability, to be due to the presence of iron. Moreover with an increase of bath temperature, the surface concentration of iron in the electroplate increases and the grey colour is found to deepen.

4. Conclusions

From the information collected here, it is clear that the presence of hydrogen chloride in the $AlCl_3/NaCl$ bath is not essential for obtaining good aluminium electroplates on mild steel as has been concluded by Howie and Macmillan [7]. Indeed, better deposits can be produced in the absence of HCl and with much higher current efficiency (close to 100%) if a suitable surface pre-treatment procedure is used. Amongst various procedures tried, electropolishing the substrate at a c.d. of $18\,mA\,cm^{-2}$ for one minute, in the electrolytic bath itself, was found to be the best, yielding a smooth, fine-grained and strongly adherent deposit.

The rotation of the cathode significantly improves the quality of the electroplate and increases the dendrite growth threshold current density. High bath temperature has a beneficial effect in the overall quality of the plating.

In order to obtain a good electroplate within the shortest possible time, one has, therefore, to rotate the cathode, use a high bath temperature and a current density slightly below the DGTCD.

The aluminium deposited on mild steel cathodes, for all conditions, contains some iron and traces of silicon as impurities, the former appearing possibly through diffusion from the substrate. The presence if iron, which tends to increase with the increase of bath temperature, imparts a greyish tinge to the electroplate, but otherwise does not have any adverse effect on the quality of the electroplate.

Acknowledgements

The authors wish to thank Professor P. G. Mukunda and Dr S. K. Basu for their help in the electron microscopic and electron microprobic analyses, respectively, and one of the authors (M.M.M.) thanks the Sambalpur University and the Ministry of Education, Government of India for the award of a QIP fellowship to him.

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