Some Problems Concerning Aluminium Electro-plating in Molten Salts

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Aluminium plating of iron and steel in molten $AlCl_3$ containing $NaCl-KCl$ mixtures was investigated. The influence of the co-deposition of Mn, Sn and Pb was studied. Also the influence of the addition of some surface active compounds was determined.

Electrolytic metal-plating in molten salts as an alternative to the commonly used hot-plating and galvanic metal plating in aqueous solutions has been discussed elsewhere.[1−3]

Compared to the hot-plating methods, the main advantages of the electrolytic metal plating in molten salts appear to be the possibility of a more exact control of the plating process, saving of the plating metal and, in most cases, also a substantially lower operating temperature. The advantages of electro metal-plating in molten salts over the galvanic methods are higher efficiency of the plating process, better bonding between the base and the deposited metal, better quality (corrosion resistance) of the deposited layer and especially the possibility to deposit protective layers of metals which cannot be deposited in aqueous solutions.

Aluminium-plating appears to be one of the most effective methods for surface protection of iron (steel) bases, mainly against reactions caused by humidity and sulfur compounds.

In the last two decades several papers dealing with aluminium-plating in molten salts have been published. A review of these works has recently appeared.[4] As the fundamental electrolyte chloride melts containing $AlCl_3$ have been suggested in all cases. Mostly melts of the binary system $AlCl_3-NaCl$ or of the ternary system $AlCl_3-NaCl-KCl$ with additions of alkaline earth chlorides or of alkali fluorides were tried.

In most cases, the electrolysis was carried out in the temperature range 150−180 °C and at current densities of 2−5 A dm^{-2}. The possibility of improving the quality (the corrosion resistance) of aluminium layers by a co-deposition of another metal (Mn, Sn, Pb) has also been investigated.

The common inadequacy of all the described procedures appears to be the high concentration of the extremely hygroscopic and highly volatile aluminium chloride. The concentration of $AlCl_3$ in all cases varied from 75 to 80 wt% which led to a strong evaporation of the electrolyte (the major component of the vapours being $AlCl_3$) and to hydrolysis of aluminium chloride in the gaseous phase. This consequently imposed stringent and expensive requirements to the construction of the plating device. At concentrations below 75 wt% $AlCl_3$, coherent aluminium layers were deposited only at very low current densities (below 0.1 A dm^{-2}), while at higher current densities aluminium was deposited in the form of a powder or as dendrites.

From the above analysis it follows that the research in the field of aluminium-plating should be aimed at the fundamental theory of the following problems:

1. The possibility of increasing the current density with electrolytes containing 75−80 wt% $AlCl_3$.

2. The possibility of depositing uniform high-quality aluminium platings from electrolytes containing less than 75 wt% $AlCl_3$, preferably close

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to 70 wt% $AlCl_3$ (*i.e.*, 50.6 mol% $AlCl_3$) when the electrolysis could be carried out in the temperature range 150 – 180 °C with practically all $AlCl_3$ being bound in the form of the stable complex of $NaAlCl_4$ with a lower hydroscopicity and lower vapour pressure.

3. The determination of the conditions for the formation of brittle intermetallic compounds Fe – Al at the phase boundary between the iron (steel) base and the aluminium layer.

4. The possibility of increasing the quality of the protective aluminium layer by co-deposition of other metals.

The problems 1 and 2 may be reduced to finding an electrolyte containing new surface active components (analogous with the galvanic metal plating in aqueous solutions where a substantial increase of the quality of the deposited layers can be achieved by additions of surface active compounds). The formation of an intermetallic compound which can deteriorate the binding between the base and the deposited aluminium layer, was investigated separately as well as the improvement of the quality of the protective layer mentioned in problem 4 above.

In the present work, several series of investigations have been undertaken. In the first series, the published results were reinvestigated, and the results obtained have been treated in the subsequent investigations.[4]

In the second series, the diffusion processes at the phase boundaries Fe/Al were studied.[5] The results give the formation range of intermetallic compounds of iron and aluminium. The co-deposition of aluminium with other metals, especially Sn, was investigated in a third series of experiments. The last series dealt with the influence of surface-active components on current density, and the influence of $AlCl_3$ concentration on the properties of the deposited aluminium layer.

EXPERIMENTAL

Electrolysis was carried out in the apparatus described by Paučirová and Matiašovský.[4] Due to the high hydroscopicity of $AlCl_3$, the preparation of samples, as well as the electrolysis, were carried out in an atmosphere of dry argon. Steel sheets with an active surface of approximately 2 cm^2 were used as cathodes. The source of aluminium was an aluminium anode (Al rod, $d=4$ mm, 99.99 wt% Al).

The fundamental electrolyte consisted of binary $AlCl_3$ – NaCl mixtures containing 70 – 80 wt%

(50.6 – 63.7 mol%) $AlCl_3$ and ternary mixtures $AlCl_3$ – NaCl – KCl containing 70 – 80 wt% $AlCl_3$ and 20 – 30 wt% of a 50:50 wt% mixture of NaCl and KCl. When investigating the influence of NaBr and NaI, part of the NaCl was replaced by this addition which was added in a concentration of 2 – 10 wt%. Tetraalkylammonium halides were added to the fundamental ternary electrolyte in concentrations of 0.5 – 2.0 wt%.

Electrolysis was carried out at a temperature of 180±2 °C, except for the runs where the temperature influence on the quality of the deposited Al layer was studied. Here the temperature varied from 150 to 250 °C. When using the additives NaBr and NaI, the current density was varied in the range 1 – 10 A dm^{-2}, while with the additions of tetraalkylammonium halides it varied from 1 to 20 A dm^{-2}. Electrolysis was carried out for 10 to 40 min depending on the current density and the required thickness of the aluminium layer.

The deposited aluminium layers were investigated both microscopically and by means of an electron microprobe. The thickness of the aluminium layer and the composition of the sublayer at the phase boundary between the base metal and deposited aluminium were determined by means of a JXA-5A electron microprobe analyser.

RESULTS AND DISCUSSION

Fundamental electrolyte. With the binary $AlCl_3$ – NaCl mixtures as electrolyte and a current density up to 5 A dm^{-2}, aluminium was deposited in the form of a dull, non-uniform layer, whilst at higher current densities the formation of dendrites was observed.

When using the ternary electrolyte $AlCl_3$ – NaCl – KCl, it was confirmed that the quality of the deposited Al layer depended on the $AlCl_3$ content of the electrolyte. The optimum concentration was in the range 76 – 80 wt% $AlCl_3$, preferably closer to the higher value. The aluminium layers deposited at lower $AlCl_3$ concentrations (close to 76 %) were silvery bright and macroscopically apparently coherent, uniform and dense. However, microscopic evaluation revealed that they consisted of individual grains. Aluminium deposited in an electrolyte with an $AlCl_3$ content of 80 wt% had a polycrystalline structure and formed a dense compact layer (Fig. 1).

It was found that in the range 150 – 250 °C, the temperature had little effect on the quality of the Al

Fig. 1. Surface of the Al layer deposited in an electrolyte containing 80 % $AlCl_3 + 10$ % NaCl $+ 10$ % KCl at 180 °C at a current density of 3 A dm^{-2}.

layer deposited in an electrolyte containing 80 wt % $AlCl_3$ while the current density had a pronounced effect. At current densities up to 5 A dm^{-2}, aluminium was deposited in the form of a fine-crystalline layer. About 7 A dm^{-2}, however, the layers were irregular and porous, and above 10 A dm^{-2} the formation of dendrites was observed.

The thickness of the deposited Al layer, including the diffusion layer (sublayer), varied from 10 to 50 μm depending on the current density and the duration of electrolysis. Fig. 2 shows the line scan
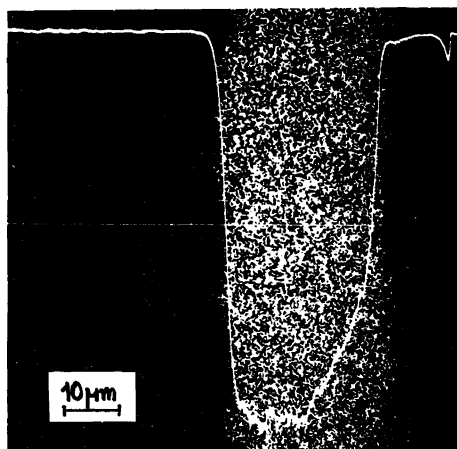

Fig. 2. Distribution of Al in a cross-section of the cathode and the line scan for $Al - K\alpha$.

for aluminium and the distribution of aluminium in a cross-section of an iron cathode with a deposited aluminium layer. The sublayer is apparently only formed by a solid solution of aluminium in iron, without any intermetallic compounds. However, according to the phase diagram of the Fe — Al system,[6] the formation of intermetallic compounds cannot be excluded. Thus, it may be assumed that the thickness of the respective layers, if they exist, is below the limit of the resolving power of the electron microprobe used.

Diffusion at the phase boundary Fe — Al. In order to explain the observed phenomena, the diffusion in the system Fe — Al was studied. In the literature numerous data have been published on the diffusion and the formation of intermetallic compounds in the system Fe — Al at temperatures above 500 °C which is normally used in the hot-plating process.[5] An extrapolation of these values from temperatures above 500 °C down to temperatures about 200 °C yields values which mainly disagree with the diffusion layer thicknesses as determined experimentally in the present work. Thus, the determination of the diffusion coefficients in the system Fe — Al in the temperature range 200 — 600 °C would appear to be of importance.

The concentration distribution of aluminium and iron was determined by means of an electron microprobe. The diffusion coefficients obtained were used to calculate the thickness of the diffusion layers which are formed during electrolysis. In addition to the electron microprobe, a new method[7] based on the anodic dissolution of the deposited layers in molten $AlCl_3 - NaCl - KCl$ mixtures was used to determine the thickness of the deposited aluminium layer and of the diffusion layer.

The distribution of aluminium and the $AlK\alpha$ line scan in a sample of the system Fe — Al that had been thermally treated for 3 h at 500 °C is shown in Fig. 3. It is evident that there is a clear indication of intermetallic compounds, most probably Fe_2Al_5 and $FeAl_3$, while no intermetallic compounds were detected at lower temperatures <400 °C).

The dependence of the diffusion coefficient, D, on temperature was calculated by the procedure of Lubyová *et al.*[8]

It can be expressed by two Arrhenius dependences: in the temperature range 200 — 400 °C
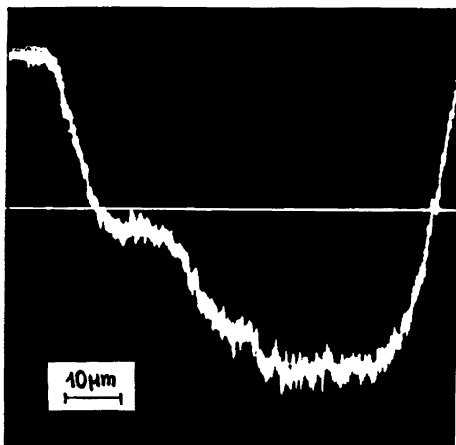
$$D = 6.5 \times 10^{-11} \exp(-2685 \, K/T)$$

Fig. 3. Line scan Al$K\alpha$ for a sample of the system Fe – Al thermally treated at 500 °C for 3 h.

and in the temperature range 400 – 600 °C

$$D = 6.6 \times 10^{-6} \exp(-10466 \, K/T)$$

In addition, the diffusion coefficients describing the formation of intermetallic compounds at 500 °C were determined to be approximately

$$D_{(Fe_2Al_5)} = 7.4 \times 10^{-9} \, cm^2 \, s^{-1}$$

$$D_{(FeAl_3)} = 6.3 \times 10^{-10} \, cm^2 \, s^{-1}$$

From this it may be concluded that under our conditions for aluminium electro-plating no intermetallic compounds are formed.

Deposition of aluminium with other metals. In this series of experiments the co-deposition of Mn, Sn and Pb with aluminium was investigated. The respective metals were either added directly to the electrolyte in the form of chlorides, or subsidiary anodes of the respective metals were used. The second method which enabled a better control of operating conditions, was found to be more appropriate.

As might be expected from the E.M.F. series in the AlCl$_3$ – NaCl and AlCl$_3$ – NaCl – KCl mixtures,[9-10] there were no problems with the co-deposition of Al and Mn while in the case of Sn and especially Pb the experimental conditions had to be strictly equilibrated. It was confirmed that the deposited Sn reacts with the Fe base under the formation of an intermetallic compound,[11] but no

intermetallic compounds[12] were found in the system Al – Sn.

The co-deposition of aluminium with other metals was not found to influence favourably the quality of the layer.

Addition of surface-active compounds. In the last series of experiments the possibility of affecting the electrolytic deposition of aluminium layers by additions of surface active substances was investigated. As surface active agents both inorganic substances, NaBr and NaI, and organic compounds like tetraalktlammonium halides, were applied.

When using NaBr and NaI, the salts were added to the electrolyte at concentrations of 2 to 10 wt%, with an adequate decrease of the NaCl concentration. It was found that the quality of the aluminium layer was improved with increasing concentration of these salts up to a concentration of approx. 5 wt%, while a further increase did no affect the quality of the aluminium layer. With a concentration of 5 wt% NaI, the effective current density could be increased up to 7 A dm^{-2}, the deposited aluminium layers being silver-bright, non-porous and finely crystalline. The composition of the underlayer was the same as with the ternary electrolyte, *i.e.,* no formation of brittle intermetallic compounds was observed.

Still better results were obtained with applications of organic ionic salts like tetraalkylammonium halides which are thermally
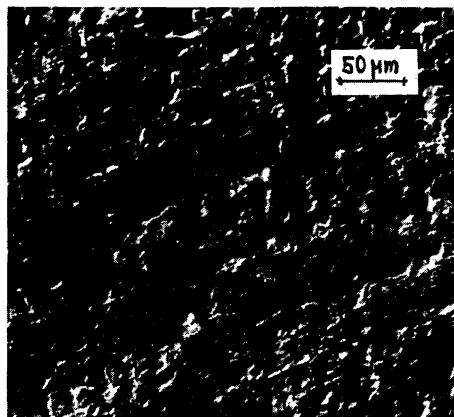

Fig. 4. Surface of the Al layer deposited in an electrolyte containing 70 % AlCl$_3$ + 15 % NaCl + 15 % KCl with an addition of 1 % (CH$_3$)$_4$NCl at 180 % C and a current density of 6.5 A dm^{-2}.

stable for the low-temperature chloride electrolysis. For example, an addition of $0.5-1.0$ wt% $(CH_3)_4NCl$ into the ternary electrolyte containing 80 wt% $AlCl_3$ makes it possible to increase the effective current density to 17 A dm.$^{-2}$ i.e., approximately three times that practical for the fundamental ternary electrolyte. From the technological aspect, however, it is even more interesting that the addition of those materials makes it possible to decrease substantially the concentration of $AlCl_3$ in the electrolyte. For example, the addition of tetraalkylammonium chloride to the ternary electrolyte containing 70 wt% (50.6 mol %) $AlCl_3$ makes it possible to carry out the electrolysis at a current density up to 7 A dm^{-2} while obtaining silver-bright polycrystalline homogeneous aluminium layers (Fig. 4). For this composition most of the $AlCl_3$ is bound in the form of the nonvolatile complex compound $NaAlCl_4$.

The mechanism by which the addition of tetraalkylammonium halides affects the formation of the aluminium layer has not yet been resolved. The experimental results obtained in the investigation of the double layer capacity,[13] however, indicate that the tetraalkylammonium cations are adsorbed on the surface of the cathode and this may affect the electrocrystallization of aluminium.

REFERENCES

1. Matiašovský, K., Lubyová, Z. and Daněk, V. *Electrodeposition Surf. Treat. 1* (1972) 43.
2. Galopin, M. and Daniel, J. S. *Electrodeposition Surf. Treat. 3* (1975) 1.
3. Wurm, J. *Galvanotechnik 70* (1979) 420.
4. Paučirová, M. and Matiašovský, K. *Electrodeposition Surf. Treat. 3* (1975) 121.
5. Fellner, P., Chrenková-Paučirová, M. and Matiašovský, K. *Surface Technology 8* (1979) 501.
6. Taylor, A. and Jones, R. M. *J. Phys. Chem. Solids 6* (1958) 16.
7. Chrenková-Paučirová, M., Fellner, P. and Matiašovský, K. *Hutn. Listy 34* (1969) 431.
8. Lubyová, Z., Fellner, P. and Matiašovský, K. *Z. Metallkd. 66* (1975) 179.
9. Delimarskii, Yu. K., Bereblyum, L. S. and Sheiko, Yu. N. *Ukr. Khem. Zh. 16* (1950) 254.
10. Verdieck, R. G. and Yntema, L. F. *J. Phys. Chem. 48* (1944) 268.
11. Ehret, W. F. and Gurinsky, G. H. *J. Iron. Steel. Inst. London 16* (1943) 543.
12. Losana, L. and Carozzi, E. *Gazz. Chim. Ital. 53* (1923) 546.
13. Fellner, P., Chrenková-Paučirová, M., Silný, A. and Matiašovský, K. *Electrochim. Acta 25* (1980) 189.