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# Dip-coating of aluminium by lead

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A study of the problems connected with the coating of aluminium by molten lead has been made. A theoretical approach shows that lead only wets the aluminium surface if the latter is completely free of oxide. Contact of liquid lead with a "clean" aluminium surface may be effected by using an intermediate layer of molten chlorides as a flux and this process has been studied using electrochemical methods. It has been shown that the flux (formed by a eutectic mixture of KCl and $ZnCl_2$) reacts with the aluminium to form a surface layer of various Al—Zn alloys as shown by electron probe microanalysis. After removal of all traces of chlorides, the resulting surface may be readily wetted by molten lead at the appropriate temperature.

## 1. Introduction

Much technological interest in the coating of aluminium by lead has been shown, owing to the favourable specific strength of aluminium alloys and the peculiar electrical properties of both lead and aluminium.

On a flat surface under thermodynamic equilibrium, the surface tensions of the liquid, $\gamma_l$, and solid, $\gamma_s$, phases and of the interface, $\gamma_i$, must verify the Young-Duprè relationship

$$\gamma_s = \gamma_i + \gamma_l \cos\theta\,. \tag{1}$$

If not, a coefficient of spreading, $S$, may be defined [1] as

$$S = \gamma_s - (\gamma_i + \gamma_l)\,. \tag{2}$$

Combination of Equations 1 and 2 gives

$$S = \gamma_l(\cos\theta - 1)\,. \tag{3}$$

Therefore, the condition for obtaining complete wetting ($\theta = 0$) or spreading is:

$$S \geqslant 0\,.$$

However, for the present system, no interfacial energy values are known. Theoretically it is possible to calculate the $\gamma_i$ using, for example, the theory of Good and Girifalco, as presented by Good and Elbing [2]. The following relationship has been proposed

$$\gamma_i = \gamma_l + \gamma_s - 2\phi\sqrt{(\gamma_l\gamma_s)} \tag{4}$$

where $\gamma_l$ and $\gamma_s$ are the surface tensions of the pure components and the parameter $\phi$ can be evaluated by means of the potential energy functions for substances forming the liquid and the solid phases, and it may range between 0.5 and 1.15 (values obtained from experimental data).

As pointed out by Good and Elbing "$\phi$ should be close to unity when the cohesive forces within each separate phase and the forces across the interface are of the same type. Conversely . . . when the predominant forces within the separate phases are unlike . . . low values of $\phi$ are to be expected" [2].

For the system Pb—Al Equation 80 of ref. [2] takes on a very simple form (as the dipolar moments of Al and Pb are zero):

$$\phi = \frac{2(I_l\delta_l I_s\delta_s)^{\frac{1}{2}}}{I_l\delta_l + I_s\delta_s} \tag{5}$$

Here $I_l$, $I_s$ are the ionization energies of lead and aluminium; parameters $\delta_l$ and $\delta_s$ are related to the number of electrons that must be considered in quantum mechanical calculations, and vary between 1 and 2.

Assuming $I_l = 7.414$ eV for lead and $I_s = 5.984$ eV for aluminium [20], we obtain from Equation 5 a value of $\phi$ ranging between 0.9052 and $\approx 1$ when $\delta_l$ and $\delta_s$ assume all values between 1 and 2. Let us take $\phi = 0.9$. Assuming $\gamma_l = 445$ mN m$^{-1}$ for lead at 350°C [3] and $\gamma_s = 1050$ mN m$^{-1}$ for aluminium at the same temperature (the average of the values reported in [4] and [5]), Equation 4 gives a value of $\gamma_i = 270$ mN m$^{-1}$, which, substituted into Equation 2 gives

$$S = +\,335\,\text{mN m}^{-1}\,.$$

A result of similar magnitude ($S = +255$ mN m$^{-1}$) can be obtained with the procedure used by Wassink [7] based on Skapski's theory [8] using the value of $3.3 \times 10^{-4}$ at. % for the solubility of aluminium in lead [6] and a mean molar surface area of $4.7 \times 10^8$ cm$^2$ for the aluminium-lead interface.

From the above discussion it is clear that molten lead must wet the aluminium surface; moreover Fig. 1 shows the dependence of the contact angle, $\theta$, between aluminium and lead on the parameter $\phi$. It is shown that a value of $\phi$ as low as 0.35 should be sufficient to have a contact angle less than 90° and that the spreading coefficient becomes positive for $\phi > 0.65$.

On the other hand, experiments show that lead does not wet aluminium oxide; this can be explained by a mutual repulsive interaction between the surface of the oxide, where oxygen anions predominate, and the electronic cloud of the metal [10, 11]. This leads to an appreciable lowering of the parameter $\phi$ which may assume values much less than one. In fact, assuming a value of $\gamma_S = 630$ mN m$^{-1}$ at 350°C for $Al_2O_3$ [9] it is easy to show, with the same calculations used before, that the parameter $S$ is positive only for $\phi > 0.84$, which is a very high figure for a metal-oxide system.

## 2. Vapour deposition of lead on aluminium

In order to verify the above from a theoretical point of view, a thin layer of aluminium was evaporated onto an aluminium disc which had just been polished, and followed immediately by a thicker layer of lead thus creating a layer-structure of lead-aluminium-aluminium oxide-aluminium alloy. The whole process was carried out in a vacuum above $10^{-5}$ Torr, which was obtained after repeated purgings of the evaporation chamber with a mixture of argon + 5% hydrogen. It was thought that under these conditions it would be possible to drastically reduce the formation of a compact layer of oxide at the lead-aluminium interface. The samples thus prepared were then put in a furnace at 350°C in a hydrogen atmosphere and then examined by an electron scanning microscope.

Fig. 2 shows how the lead on melting assumed the characteristic form of a drop with contact angles of about 30°: wetting had, therefore, occurred, even if there was no spreading. From other details shown in Fig. 3 it could be thought that complete spreading had been prevented by the formation of small areas of very thin oxide, which were present at the aluminium-lead interface despite the precautions taken.

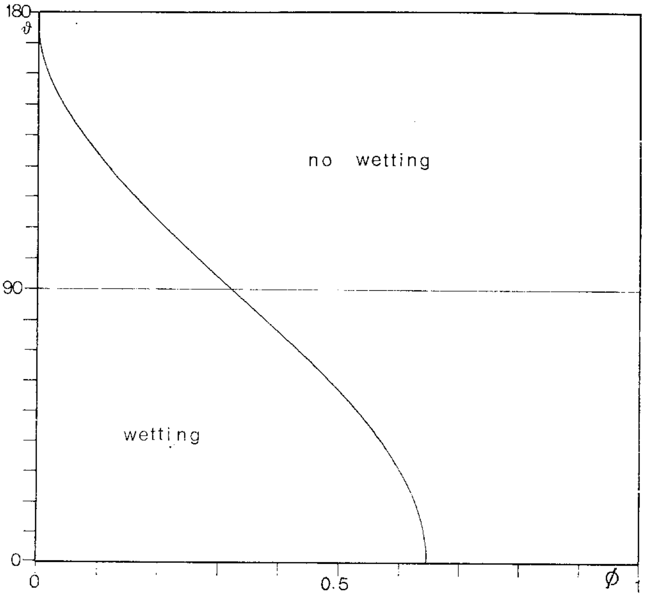

*Figure 1* Dependence of contact angle $\theta$ on the parameter $\phi$ for the system Al-molten Pb.

$$\theta = \arccos\left(\frac{2\phi\sqrt{(\gamma_l\,\gamma_s)}}{\gamma_l} - \mathrm{i}\right)$$

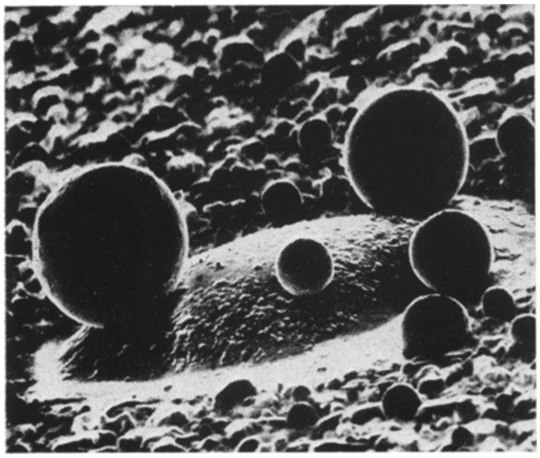

*Figure 2* Drop of lead formed on the aluminium surface after evaporation and heat-treatment. The smaller drops are formed by lead, resulting from reduction by $H_2$ of the lead oxide formed after the vapour deposition (× 3200).

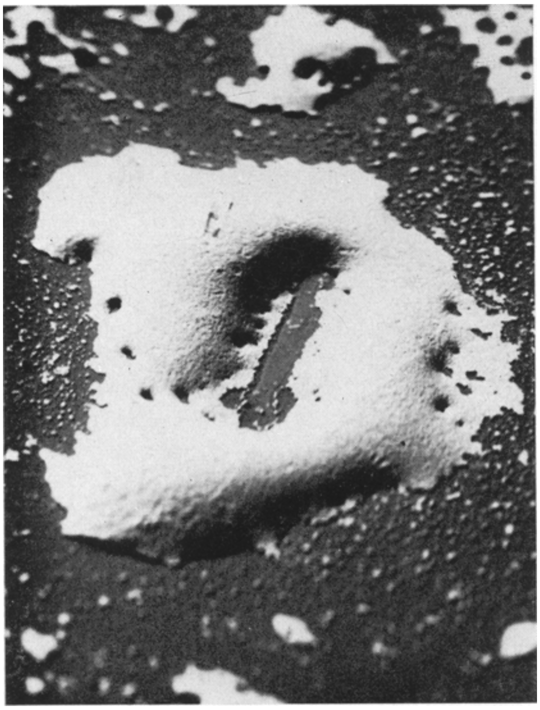

*Figure 3* Drops of evaporated lead not completely wetting the aluminium surface (× 200).

This stage of the work has shown that molten lead can adhere to aluminium, but only if the surface is completely free of oxides. As this can be verified only in conditions that are technologically hard to realize and for extremely short periods of time, the mode of action of fluxes which are in practice used in welding procedures was studied.

## 3. Interaction between aluminium and molten salts

After some preliminary studies, the eutectic mixture formed by KCl and $ZnCl_2$ (46; 54 mol %) [12] was chosen. Its great solubility in water makes it easily eliminated from the surface thus preventing the formation of weak zones and areas of corrosion localized at the lead-aluminium interface.

With this eutectic the following interaction tests on molten salts and aluminium were carried out by means of electrochemical measurements. The lead-aluminium couple in the presence of molten salts constitutes, in fact, an electrochemical system which may be schematically shown in the following way:

$$Pb/KCl - ZnCl_2/Al_2O_3/Al\,.$$

A cell was, therefore, prepared to allow measurements of the potential established between lead and aluminium as a function of temperature and with samples of aluminium at different alloy levels.

### 3.1. Experimental details

The cell was made of Pyrex glass and is shown in Fig. 4. For the preparation of the eutectic it was necessary to follow a very careful procedure of purification and dehydration (using the method proposed in [13] and [14]) because of the hygroscopic nature of $ZnCl_2$.

A quantitative analysis of Zn (with the EDTA) and for chlorine (with $AgNO_3$ and fluorescein as indicator) was then carried out [15]; the composition of the mixture was then modified until it reached the eutectic composition in the vicinity of 0.1%.

The lead electrode was made of Pb BDH 99.999%. The aluminium electrode was made with the following alloys: Al · AP5; Al + 0.5%, 1%, 5% or 10% Zn.

The cell was placed in an electric furnace preset at 250°C; after the introduction of the sample the eutectic was poured into the cell and the temperature was then raised regularly at a speed of about 7°C $min^{-1}$.

### 3.2 Discussion

The behaviour of the potential of the battery described above was followed and for all the

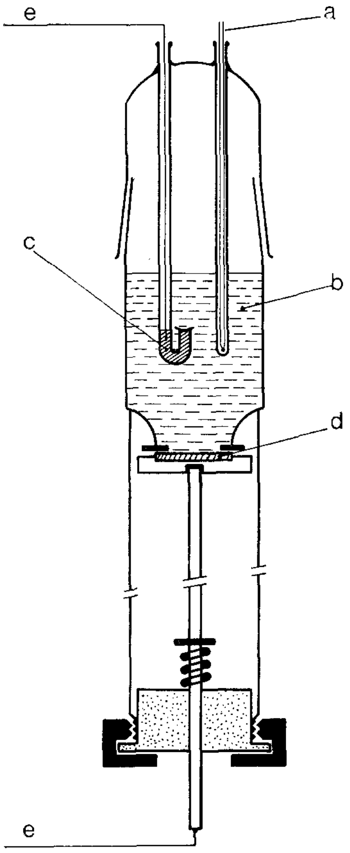

*Figure 4* Cell for measurements of potentials in molten salts. (a) Thermocouple, (b) molten eutectic, (c) lead electrode, (d) aluminium sample, (e) electrical connections (pure iron).

alloys studied the behaviour of the curve $V = f(\text{time})$ was essentially identical. The potential of the battery, after an initial period of scarce significance, increased with fairly regular tendency: this increase was, however, interrupted by two points situated around 327 and 400 to 410°C (Fig. 5). The first point corresponds to the fusion of the lead electrode (mp of lead: 327.4°C) while for the second the explanation is more complex. The action of molten chlorides on aluminium is, in fact, double: they have a high solvent action on the aluminium oxide and at the same time they react with the metal surface. Such interaction may be explained by the different electrode potentials of aluminium and zinc. Values of the electrode potentials assumed by aluminium and zinc in the presence of single chlorides and their mixtures have been reported [16]. Aluminium, in the presence of chlorides, has always a less "noble" behaviour than zinc. The reaction

$$2\,\mathrm{Al} + 3\,\mathrm{ZnCl_2} \rightleftarrows \mathrm{Al_2Cl_6} + 3\,\mathrm{Zn} \qquad (6)$$

is, in fact, decidedly displaced towards the right ($K_\mathrm{p} \approx 10^9$ at 600°C [17]).

At the second transition point of the cell potential, a very strong effervescence due to rapid development of gaseous $\mathrm{Al_2Cl_6}$ can be seen in the molten mass. Fig. 6 shows the temperatures recorded for the beginning of the turbulent phase of the reaction (the second point) and the corresponding tensions. The temperature varies between 390 and 417°C without following in any way the behaviour of the alloy level of the sample examined, whereas the tension increases fairly regularly with the alloy level and assumes reproducible values. Zinc forms a eutectic with the aluminium at 5% Al which melts at 382°C [18]. The zinc which had been deposited following reaction 6 at a temperature

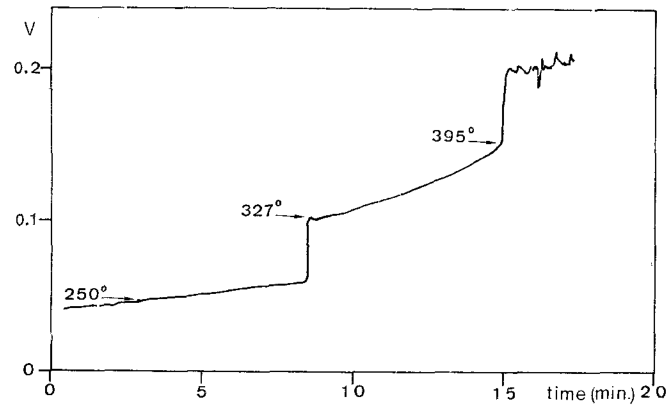

*Figure 5* Dependence of the potential of the battery Pb/Eut/Al on time and temperature.

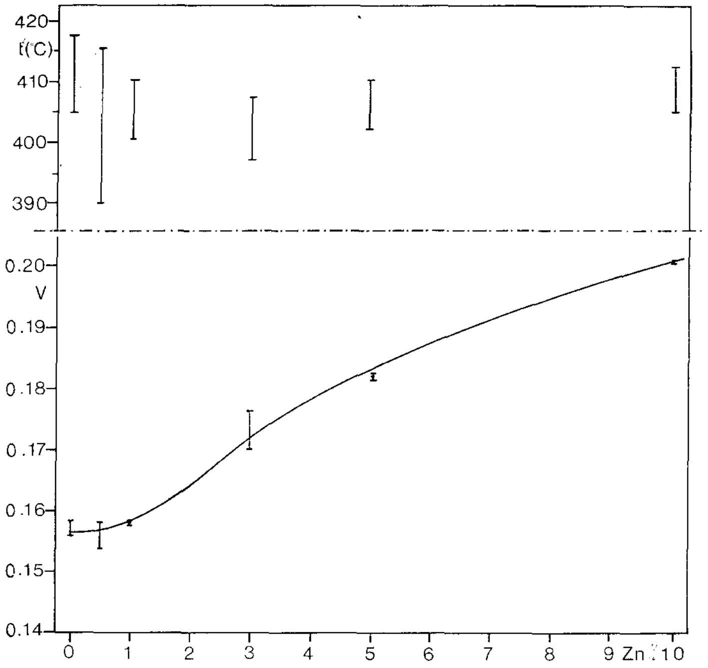

*Figure 6* Temperature (top) and potential (bottom) at the beginning of the second inflection point (see text) as a function of the alloy level of the aluminium sample.

of about 400°C diffuses in support of either aluminium or alloy forming alloy layers which gradually become richer in aluminium content. Eventually these layers melt according to the phase diagram.

Samples removed from the cell just after the beginning of the reaction clearly show the presence of molten masses and the evident trace of intergranular and transgranular attack.

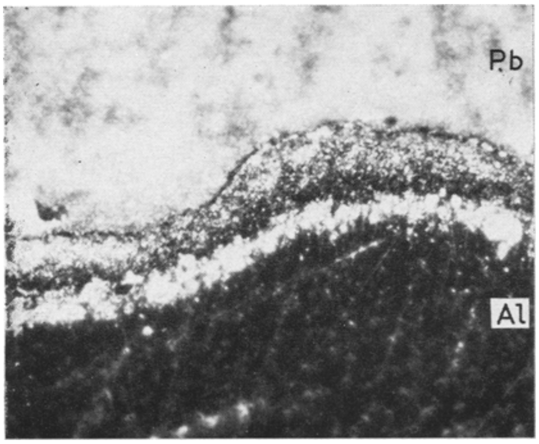

*Figure 7* Interface lead – aluminium 10% Zn (×200).

Metallographic examination carried out on sections of the sample pretreated with molten salts, as described, and then used for the study of the aluminium-lead interactions (see the following section), shows the formation of one or more intermediary phases of variable thickness in the area of lead-aluminium transition, and the complete absence of visible porosity at the interface itself (Fig. 7). The use of the electron microprobe reveals that at the lead-aluminium interface a rich layer of zinc exists. Figs. 8 and 9 show the behaviour of the zinc concentration along a scanning line (Fig. 8) and over the whole area examined (Fig. 9). One can see a fairly regular increase in the zinc content at the interface on the aluminium side followed by a region in which the concentration is nearly constant: the two zones must thus correspond to the phases $\alpha'$ and $\beta$ of the Al—Zn phase diagram.

## 4. Spreading of lead on a pretreated aluminium surface

The "pretreated aluminium-molten lead" interactions have been studied by the "sessile-drop" technique [19] which allows us to follow, over a period, the evolution of the form of the drop of molten lead in contact with the specimen of

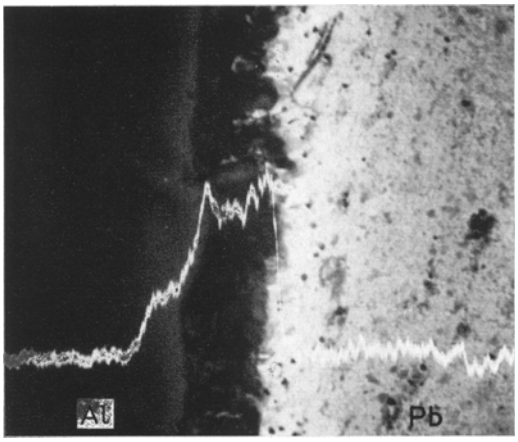

*Figure 8* Zinc distribution along a scanning line (Pb on Al-5% Zn) (× 325).

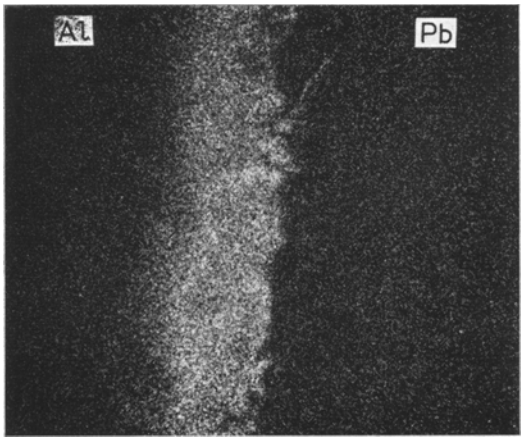

*Figure 9* Zinc distribution over the whole area shown in Fig. 12 (× 325).

aluminium (and its alloys). The experiments were carried out in a tubular furnace made of pyrex glass and cooled by water, so that results could be obtained under vacuum or with an inert atmosphere. The heating element was made up of a susceptor of graphite coupled inductively to a high frequency generator.

The temperature control (± 1 °C) was assured by a low thermal capacity resistance element connected with a regulator. Using this apparatus the work was carried out at a heating rate of about 150 °C $\text{min}^{-1}$ and a cooling rate of about 50 °C $\text{min}^{-1}$.

When the temperature is raised under vacuum, the eutectic which was placed on the top of an aluminium disc, melts forming a drop which does not completely wet the aluminium surface.

As soon as the temperature reaches about 400 °C reaction 6 occurs with a very strong generation of gas and immediate spreading of the eutectic. The furnace is turned off, the sample extracted and washed thoroughly under running water to eliminate every trace of the chlorides and of non-alloy metallic zinc (which is present on the sample as a dust deposit). The sample is then returned to the furnace together with a piece of lead, in the form of a drop premelted in $N_2$, and rapidly heated under vacuum to around 400 °C.

During the increase in temperature, once the lead is molten it does not wet the support. As soon as the temperature reaches 400 to 410 °C complete and instantaneous spreading takes place, due to the fusion of the surface layer of zinc-aluminium alloy, in which the lead itself is soluble.

## 5. Concluding remarks

The study of the molten lead-aluminium system has led to the following conclusions.

1. Molten lead can adhere to aluminium and wet it only if the surface of the latter is completely free from oxide.

2. If a molten mixture of KCl and $ZnCl_2$ in eutectic proportions (46 to 54 mol %) is brought into contact with aluminium (or its alloys with zinc) the oxide dissolves and zinc is deposited. This reaction happens with great speed at the temperature at which a zinc-aluminium alloy in molten state is formed. Study of the difference of potential of the Pb/Eut/Al battery may yield useful information. The function $V = f(\text{time})$ shows a very marked transition point corresponding to the beginning of this reaction.

3. It is possible to remove all the eutectic which has not reacted by washing, and then to cause the spreading of lead on the surface of aluminium (or its alloys), treated as described in point 2), under non-oxidizing conditions (vacuum or inert atmosphere) at the temperature of fusion of the superficial alloy Al—Zn.

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