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The effect of small additions of indium and thallium on the corrosion behaviour of aluminium in sea water

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The effect of small additons of indium and thallium on the anodic behaviour of high purity aluminium (99.999%; 5N) and the anodic and corrosion behaviour of technical purity aluminium (T) was investigated with the aim of confirming the suitability of these alloys for the protection of steel constructions located in sea water. It has been found that the effects of indium and thallium additions on the anodic behaviour are less explicit in technically pure alloys. The effect of thallium on the anodic behaviour of Al–In alloy can be explained by the presence of indium atoms in this alloy and by the high mutual solid solubility of thallium in indium.

The ternary alloy Al(T)–0.1% In–0.1% Tl is uniformly dissolved in sea water and has a potential of – 900 mV (SCE) in the current density region of 1–10 mA cm^{-2}.

1. Introduction

Utilization of aluminium as a protective material against the corrosion of steel constructions located in sea water creates difficulties due to the passivation of aluminium in electrolytes containing sodium chloride. The passivation potential of aluminium decreases from 1.9 to about 0.8 V (SCE) [1].

Among numerous chemical elements having the ability to prevent aluminium passivation, i.e. make the aluminium anode more negative in eletrolytes containing sodium chloride, only some, such as zinc, indium, gallium, tin, etc., can be used without a negative secondary effect on sea water pollution.

The aim of the present work is to investigate the behaviour of new aluminium alloys with indium and thallium [2, 3] used as protective anodes. Corrosion microstructure, distribution of alloying elements in the alloys and anodic behaviour in sea water have been investigated.

2. Materials and experimental procedures

For anodic behaviour and corrosion investigation we have used as-cast alloys Al–0.1% In*, Al–0.2% In, Al–0.2% Tl and Al–0.1% In–0.1% Tl made from high purity aluminium (99.999%; 5N), Al–0.1% In and Al–0.1% In–0.1% Tl alloys made from technically pure aluminium (99.5%; T) and of 99.8% pure indium and thallium alloying additions. Impurity contents for both (5N) and (T) aluminium are given in Table 1.

Corrosion was investigated only on the Al–0.1% In–0.1% Tl alloy made of (T) aluminium. The alloys were melted in a high purity graphite crucible under an inert gas atmosphere and cast in a copper mould. Samples for examination of structure, corrosion and anodic behaviour were machined from all alloys. Before examination the samples were mechanically and electrolytically polished [4].

The polarization curves were recorded in sea water at a potential scan rate of 1000 mV min^{-1}. The working electrode potential was measured with respect to the saturated calomel electrode (SCE), in the potential range – 2000 to – 200 mV, and reversed in the opposite direction.

Corrosion was tested by *in situ* exposure of

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* Concentrations in wt%.

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Table 1. Content of impurities in aluminium

	Cu	*Fe*	*Si*	*Mg*	*Zn*
High purity aluminium (99.999%; 5N) ppm	1.0	2.0	1.5	2.5	in traces
Technical purity aluminium (99.5%; T) wt %	0.01	0.28	0.12	–	–

samples in sea water at the Institute of Science of the Yugoslav Academy of Sciences and Arts in Dubrovnik.

In addition to potentio-dynamic polarization experiments, metallographic and electron microprobe methods were used in the investigation.

3. Results

3.1. *Polarization curves*

Figs. 1–3 show the polarization curves for high purity aluminium (5N) and its alloys. Characteristic data of the anodic behaviour of these materials are given in Table 2. The polarization curve for high purity aluminium (Fig. 1, Curve a) shows a wide passivation region, from − 1610 to − 700 mV. In reversal, the polarization Curve a′ has a plateau at about − 850 mV that is in agreement with the literature data for the potential of aluminium in dilute sodium chloride electrolytes.

Addition of 0.1% In (Fig. 1, Curve b) considerably changes the behaviour of aluminium (5N) in the same potential region, so that it:

1. decreases the passivation region
2. shifts the passivation threshold towards high current densities
3. makes the potential more negative at lower current densities and
4. increases the current density, which becomes, at a potential of − 400 mV, about a thousand times higher than the value for high purity aluminium.

The effect of this addition is even more pronounced in the case of potential reversal during recording (Fig. 1, Curve b′). The plateau of the curve is at about − 1300 mV.

By increasing indium content in the alloy to 0.2% (Fig. 1, Curve c) two changes are observed on the polarization curve:

1. The appearance of new peaks in the passivation region and
2. shifting of the plateau towards more negative potentials during potential reversal, i.e. towards − 1500 mV (as compared to Al(5N)–0.1% In)

Fig. 2 shows the polarization curves for high purity aluminium (5N) (Curve a) and for the alloy with 0.2% Tl (Curve b). As can be seen from the curves, the presence of 0.2% Tl does not essentially change the shape of the curve but shifts the passivation threshold towards higher current densities and increases the current density at a potential of − 400 mV.

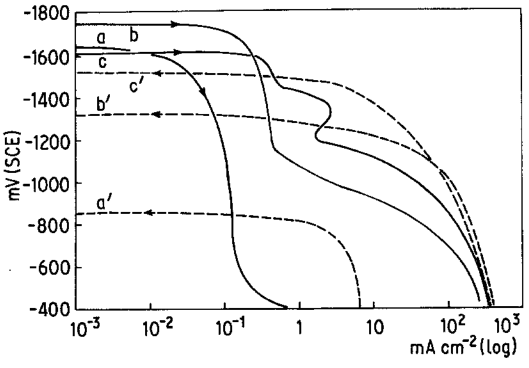

Fig. 1. The polarization curves of high purity Al(5N) and alloys in sea water. (a) High purity Al(5N), (b) Al–0.1% In, (c) Al–0.2% In.

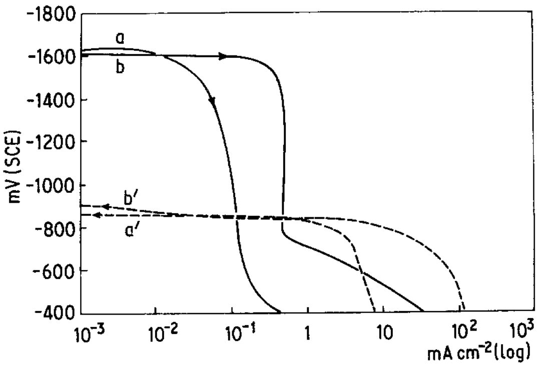

Fig. 2. The polarization curves of high purity Al(5N) and alloys in sea water. (a) High purity Al(5N), (b) Al–0.2% Tl.

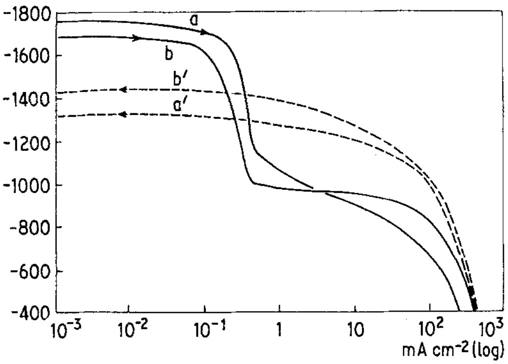

Fig. 3. The polarization curves of alloys Al(5N) in sea water. (a) Al–0.1% In, (b) Al–0.1% In–0.1% Tl.

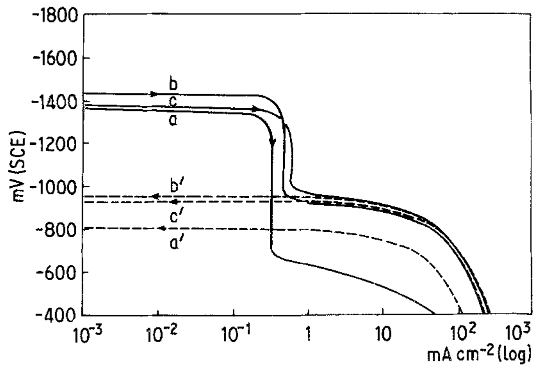

Fig. 4. The polarization curves of technical Al(T) and alloys in sea water. (a) Technical Al(T), (b) Al–0.1% In, (c) Al–0.1% In–0.1% Tl.

During potential reversal (Curve b′) the plateau is the same as that for aluminium (5N) (Curve a′) (see Table 2).

Fig.3, shows the polarization curves of a binary alloy Al(5N)–0.1% In (Curve a) and of a ternary alloy Al(5N)–0.1% In–0.1% Tl (Curve b).

Addition of thallium to a binary alloy does not markedly change the shape of its polarization curve but affects some parameters of the anodic behaviour, i.e. it

1. decreases the potential at lower current densities
2. increases the current density at − 400 mV and
3. makes the potential more negative at reversal of the polarization curve (Curve b′) (see Table 2).

The polarization curves of technically pure aluminium (T), and of the alloys with 0.1% In and 0.1% In–0.1% Tl made with the same kind of aluminium are given in Fig. 4. Data characteristic for the anodic behaviour of these materials are given in Table 3. The polarization curve for technically pure aluminium (T) (see Fig. 4, Curve a), explicitly shows a passivation threshold which is considerably lower compared to that of high purity aluminium (5N), and also shows higher current densities at − 400 mV (see Table 3).

The addition of 0.1% Tl has practically no effect either on the shape or position of the polarization curve, whereas the addition of 0.1% In (Fig. 4, Curve b) narrows the passivation threshold and shifts the whole curve towards more negative potentials and this is also seen in the reversed scan case (Fig. 4, Curve b′). The addition of 0.1% Tl to the binary alloy Al(T)–0.1% In only serves to decrease the passivation range (Fig. 4, Curve c).

Table 2. Characteristic electrochemical data of Al(5N) and alloys in sea water

Materials	*Passivation threshold (mV) (SCE)*	*Potential at zero current (mV) (SCE)*	*Potential at 10 mA cm^{-2} (mV) (SCE)*	*Current density at − 400 mV (mA cm^{-2})*	*Potential on scan reversal (mV) (SCE)*
Al(99.999%; 5N)	− 1610 − 700 > 910	− 1610	–	0.5	− 850
Al(5N)– 0.1% In	− 1750 − 1150 > 600	− 1750	− 900	300	− 1290
Al(5N)–0.2% In	− 1620 − 1150 > 470	− 1620	− 1100	480	− 1500
Al(5N)–0.2% Tl	− 1600 − 750 > 850	− 1600	− 510	38	− 700
Al(5N)–0.1% In–0.1% Tl	− 1680 − 1000 > 680	− 1680	− 950	480	− 1430

Table 3. Characteristic electrochemical data of Al(T) and alloys in sea water

Materials	*Passivation threshold (mV) (SCE)*	*Potential at zero current (mV) (SCE)*	*Potential at 10 mA cm^{-2} (mV) (SCE)*	*Current density at − 400 mV (mA cm^{-2})*	*Potential on scan reversal (mV) (SCE)*
Technical aluminium (T)	$\begin{matrix}-1350\\-700\end{matrix} > 650$	− 1350	− 530	50	− 800
Al(T)–0.1% In	$\begin{matrix}-1430\\-950\end{matrix} > 480$	− 1440	− 880	280	− 950
Al(T)–0.1% In–0.1% Tl	$\begin{matrix}-1360\\-1000\end{matrix} > 360$	− 1370	− 900	300	− 920

3.2. *Corrosion investigation*

The microstructural change of a ternary alloy Al(T)–0.1% In–0.1% Tl after corrosion in sea water is given in Fig. 5. Reaction with the electrolyte becomes evident after 6 h of exposure (Fig. 5a) and is manifested by dissolution at grain boundaries and at isolated inclusions of alloying elements. After 20 h of contact with the electrolyte (Fig. 5b) more intensive reaction is observed at the grain boundaries and on isolated inclusions but without any considerable corrosion of the matrix. After a hundred hours of contact with the electrolyte (Fig. 5c) corrosion of the matrix is also observed, becoming more intensive after 200 h (Fig. 5d) in the same way as the reaction at the grain boundaries. Further exposure to the electrolyte shows uniform dissolution of both the matrix and grain boundaries (Fig. 5e). This behaviour is also demonstrated by the microstructure observed at lower magnification after about 500 h of exposure (Fig, 5f).

4. Discussion

Recent investigations [5] of the utilization of aluminium for corrosion protection, have shown that small additions of gallium, indium and thallium cause the aluminium potential to shift in a negative direction and generally change its electrochemical behaviour. It is already known that indium has very low solubility in solid aluminium (about 0.07 wt% at about 833 K/560°C). By decreasing the temperature the solubility rapidly decreases so that an Al–In alloy in the equilibrium state at room temperature has very low indium concentration which has not yet been exactly determined. However, even this small indium concentration considerably affects the anodic behaviour of aluminium as can be seen in Fig. 1. Increasing the indium concentration from 0.1 to 0.2% in binary Al–In alloys results in a new peak on the polarization curve and shifts the curve in a negative direction at a current density of about 1 mA cm^{-2}.

Due to the low solubility of indium in solid aluminium the total quantity of indium above the solubility limit at a determined temperature is segregated into inclusions predominantly at grain boundaries (Fig. 6), but also within metal grains. Earlier investigations [6] have shown intense corrosion at indium inclusions. This has been demonstrated by electron microprobe investigations (Fig. 7a, b). The negative effect of the above mentioned increase of indium concentration is that it increases the amount of indium inclusions and this is manifested as a peak at − 1350 mV on the polarization curve of a binary alloy Al–0.2% In.

In contrast to indium, thallium is practically insoluble in aluminium in both liquid and solid state so that an Al–Tl system can not be considered as an alloy in the classical sense of the word. The alloy Al–Tl can be obtained by dispersion of thallium in an aluminium melt. Most probably almost all the thallium is separated into inclusions rich in thallium as has been indicated by the microprobe investigation (Fig. 8a, b). However, the addition of 0.2% Tl (see Fig. 1) changes the polarization curve of aluminium but it is still difficult to say whether this phenomenon is a consequence of the presence of thallium inclusions or whether it is caused by a change in the electrochemical properties of the matrix due

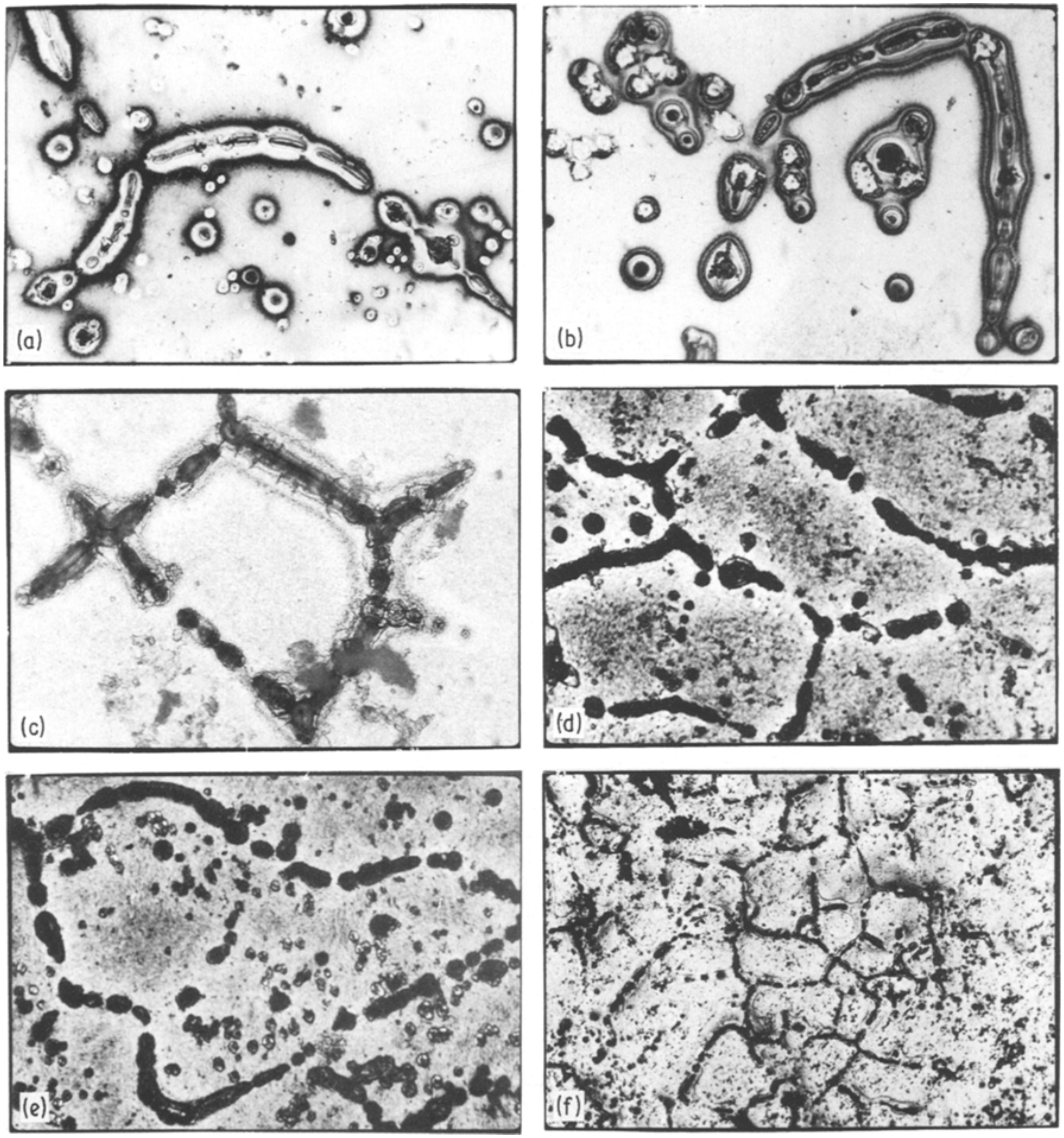

Fig. 5. Corrosion microstructure of Al(T)–0.1% In–0.1% Ti alloy in sea water, (a) After 6 h ×550; (b) After 20 h ×550; (c) After 100 h ×550; (d) After 200 h ×300; (e) After 250 h ×300; (f) After 500 h ×100.

to the presence of thallium even in ppm concentration. This would mean that some effects of the additions of thallium to Al–0.1% In alloy (see Fig. 3) could not be definitely explained at present. The thallium effects in a ternary alloy Al–0.1% In–0.1% Tl, especially on reversal of the polarization curve (see Table 2), can be explained by the incorporation of a certain quantity of thallium into the indium since both metals are mutually very soluble in the solid state [7]. Therefore, it can be assumed that beside separation of an In–Tl compound in the form of inclusions, a certain thallium concentration is also present in solid solution. This would also explain the smaller effects of thallium in alloys not containing indium.

As has been said earlier, corrosion was investi-

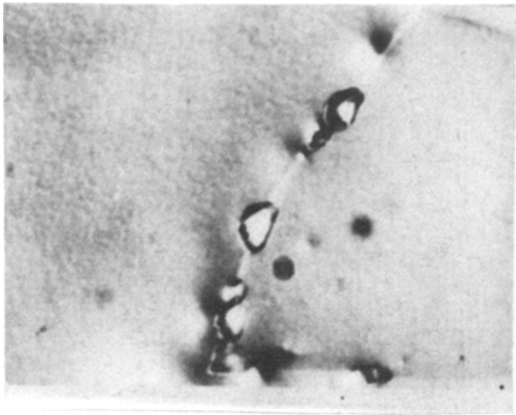

Fig. 6. Al(5N)–0.1% In alloy (interference phase contrast) ×1200.

gated by using alloys based on technically pure aluminium. By comparing the polarization curve of a ternary Al(5N)–0.1% In–0.1% Tl alloy (see Fig. 3, Curve b) with that of a ternary alloy made of technically pure aluminium (see Fig. 4, Curve c) it is seen that alloying effects are considerably lower in alloys made of technically pure aluminium. This is especially evident in the reversed scan curves. The reduced effects of indium and thallium in the latter alloys can be explained by the presence of impurities in technically pure aluminium which would oppose any beneficial effects (see Table 1). However, beneficial effects of alloying with indium and thallium are still considerable at current densities above 1 mA cm^{-2} (see Fig. 4) so that a potential of − 900 mV is achieved at 10 mA cm^{-2} (see Table 3).

It is especially important that a ternary alloy made of technically pure aluminium, Al(T)–0.1% In–0.1% Tl, dissolves very uniformly as can be seen by corrosion microstructures (see Fig. 5). Increased corrosion along grain boundaries is unavoidable in alloys used in the as-cast state due to segregation of alloying elements at primary (dendrite) grain boundaries. However, this corrosion can be characterized as less dangerous than that observed with Al–Ga and Al–In–Ga.

Better uniform dissolution can be achieved also with as-cast alloys if they are annealed before use at about 560°C [8]. Such annealing results in a more uniform distribution of alloying elements and decreases segregation. This can be seen in Fig. 9a, b, by the absence of selective reaction along grain boundaries and by intense dissolution of the matrix.

5. Conclusion

On the basis of the investigation of binary and ternary alloys of aluminium with indium and thallium the following conclusion can be drawn:

1. Addition of thallium has no major effect on the anodic properties and corrosion behaviour of aluminium due to the insolubility of thallium in aluminium.
2. The change in the anodic behaviour of

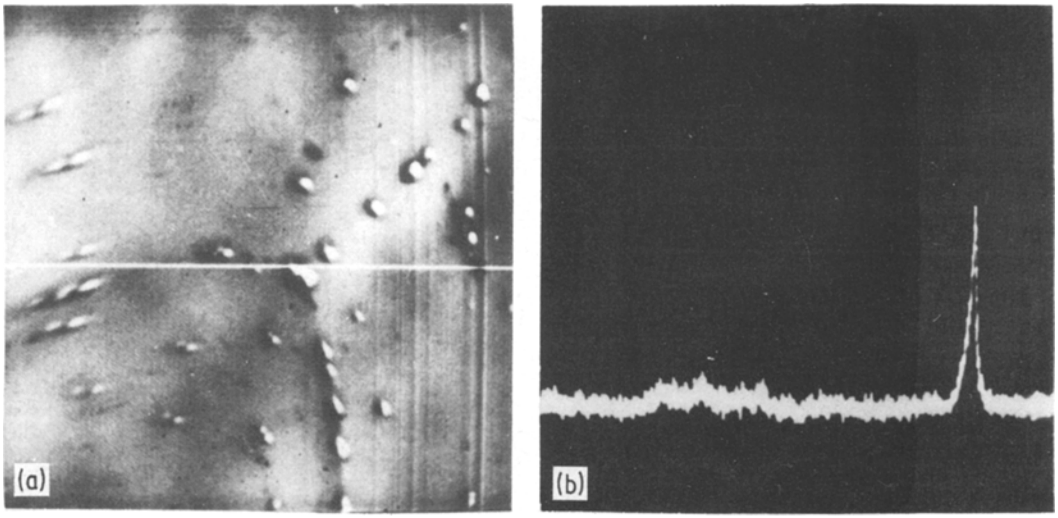

Fig. 7. Al(5N)–0.1% In alloy. (a) Electron micrograph ×600, (b) distribution of In.

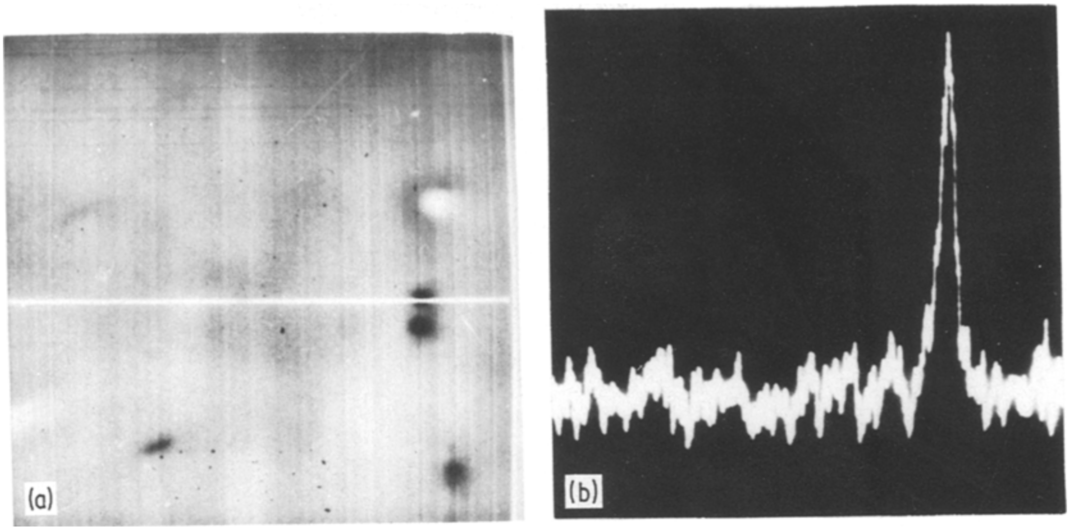

Fig. 8. Al(5N)–0.1% Tl alloy. (a) Electron micrograph ×600, (b) distribution of Tl.

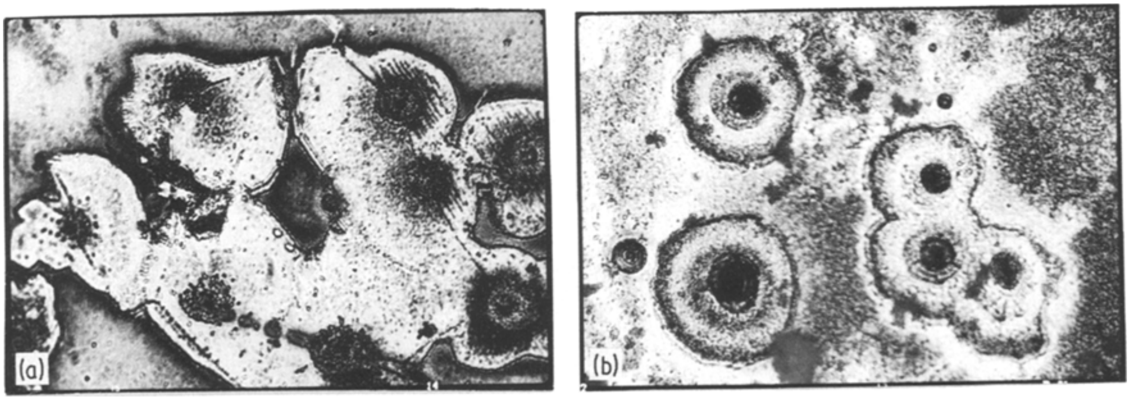

Fig. 9. Corrosion microstructure of Al(T)–0.1% In–0.1% Tl alloy in sea water after annealing (a) After 20 h ×500, (b) after 200 h ×550.

aluminium in ternary alloys Al–In–Tl can be explained by the presence of indium due to the high mutual solubility of indium and thallium.

3. Additions of indium and thallium have considerably lower effects on the anodic behaviour of technically pure aluminium due to the opposing effects caused by impurities present in this metal.

4. The ternary alloy made of technically pure aluminium, Al(T)–0.1% In–0.1% Tl, has a potential of − 900 mV in the current density region from 1 to 10 mA cm^{-2}, and shows uniform dissolution in sea water.

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