JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 415–420

The effect of gallium and phosphorus on the corrosion behaviour of aluminium in sodium chloride solution

A. MANCE, D. CEROVIĆ, A. MIHAJLOVIĆ

Institute 'Boris Kidrič'-Vinča, Department of Materials Science, 11001 Beograd, Yugoslavia

Received 15 May 1984; revised 15 August 1984

In order to cause shifting of the potential in the negative direction and to simultaneously control dissolution in sodium chloride solutions, aluminium alloys utilized as anodes in electrochemical power sources contain small additions of alloying elements. This can be achieved with highly pure aluminium alloys. The binary Al–0.2% Ga alloy made of high purity aluminium has a high negative potential ($-1570\,\mathrm{mV}$ at $10\,\mathrm{mA\,cm^{-2}}$), but also a high corrosion rate. The addition of 0.2% P to the above alloy decreases corrosion. Impurities present in technically pure aluminium considerably affect the anodic and corrosion behaviour of the investigated alloys. It was found that corrosion of the Al–0.2% Ga and Al–0.2% Ga–0.2% P is controlled not only by the alloying elements, but also by intermetallic compounds (insoluble in the matrix) which contain alloying elements and impurities (Fe) present in technically pure aluminium.

1. Introduction

The behaviour of special aluminium alloys which can be used as power sources has become the subject of recent investigations [1, 2]. Attempts have been made [3] to use special alloys with small additions of indium, gallium and thallium as the anodic material for potential power sources. In the investigations performed so far, either binary or multi-component alloys of aluminium with indium, gallium and thallium in electrolytes containing sodium chloride [4] have shown a considerable effect of the alloying elements on both the electrochemical and corrosion behaviour [5, 6]. Keeping in mind the possibility of the practical application of these alloys, the question of metal quality choice, i.e. the degree of aluminium purity in the prepared alloys [7, 8], is chemically very important.

The aim of the work presented in this paper was to investigate the anodic and corrosion behaviour of aluminium and its alloys as a function of the purity of the initial aluminium and on the content of alloying elements. The results obtained for the effect of gallium and phosphorus on the electrochemical behaviour and microstructural changes as a function of exposure time with 2 N sodium chloride solution are given in this paper.

2. Materials and experimental procedures

Anodic and corrosion investigations were carried out with highly pure aluminium (5 N) and technically pure aluminium 99,8%). The investigated alloys Al–0.2% Ga and Al–0.2% Ga–0.2% P were prepared using aluminium of both qualities. Metallic gallium and PCl_5 were used as alloying elements. The impurity contents of the technically pure aluminium were: 0.14% Fe and 0.1% Si. The alloys were prepared by casting in a massive copper mould at a cooling rate during solidification of $10^{2}\,^{\circ}\mathrm{C}^{-1}$.

For both structural and microprobe investigations the samples were polished, first mechanically and then electrolytically in a solution of ethyl alcohol, distilled water, glycerine and perchloric acid. The polishing time was 2 s at 40 V. Prior to each use the electrolyte was thoroughly cooled. The samples were then chemically etched in Keller's solution to reveal the structure. For corrosion investigations the samples were also polished both mechanically and electrolytically. For the anodic behaviour experiments the samples were mechanically polished on diamond paste.

---

* all additions in wt %.

0021–891X/85 $03.00 + .12.

Corrosion and anodic experiments were performed in 2 N sodium chloride solution. Polarization curves were plotted in the potential region from − 1800 to − 400 mV, on a *X–Y* recorder, at a rate of potential change of 1000 mV $\min^{-1}$. A 'Tucussel' potentiostat was used to regulate the potential. The potential of the working electrode was measured using a saturate calomel reference electrode (SCE). Corrosion behaviour was studied by immersion of the samples in the electrolyte for several (predetermined) hours and investigation of the microstructural changes.

The distribution of gallium, phosphorus and iron in the alloys was investigated with an electron microprobe SEM-2. At 25 kV acceleration voltage LiF and mica crystals were used, respectively, for $K\alpha$ gallium and iron lines and $K\alpha$ phosphorus lines. The characteristic X-ray radiation of the investigated elements was detected by using xenon and gas-flow proportional counters.

X-ray intensity measurements for phosphorus, gallium and iron performed at determined points did not yield sufficient data for quantitative analysis due to the very small dimensions of the microstructural constituents and the low concentrations of these elements.

3. Results and discussion

3.1. *Alloys made of highly pure aluminium (5 N)*

3.1.1. Anodic behaviour. The polarization curves for highly pure aluminium (5 N) and its alloys, Al–0.2% Ga and Al–0.2% Ga–0.2% P are shown in Fig. 1. Highly pure aluminium has a passivation threshold in a potential region from − 1600 to − 770 mV. The passivation of aluminium completely disappears after the addition of 0.2% Ga. The polarization curve is shifted towards more negative potential values: at a current density of 10^{-2} mA cm^{-2} the potential is − 1700 mV. The addition of 0.2% P to the binary alloy Al–0.2% Ga completely changes the shape and position of the polarization curves of this alloy. It is important to note that the passivation of the anode is restored. Characteristic data are presented in Table 1.

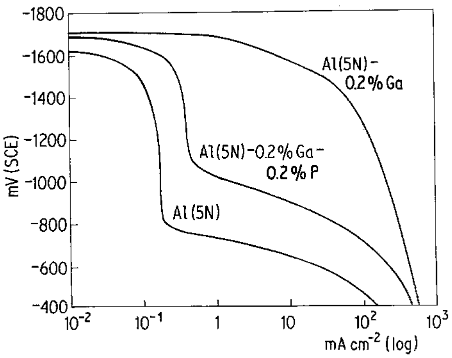

Fig. 1. The polarization curves of high purity aluminium 99.999% (5 N) and alloys in 2 N sodium chloride solution.

3.1.2. Corrosion behaviour. After immersing the alloy Al–0.2% Ga in 2 N sodium chloride solution for a short time (3 h), several typical corrosion phenomena are observed. The most intensive reaction with the electrolyte is observed along grain boundaries. It is interesting to point out that a region of weak corrosion, which follows the boundary lines, is always observed along grain boundaries whereas the central part of some grains is markedly less attacked.

This indicates a decrease in the gallium concentration of the metal grain in the direction from the grain boundaries toward the centre. In spite of the intensive reaction of the binary alloy Al–0.2% Ga, the intensity of corrosion in general is affected by the orientation of the grains. The brighter grains show only slight corrosion pits, whereas other grains already show an intensive reaction with the electrolyte after 3 h.

The above behaviour becomes more intensive after 6 h of contact with the electrolyte. Corrosion on the grain boundaries, Fig. 2, develops further, but general corrosion of the matrix is considerably more intensive. The change of corrosion along grain boundaries with time of immersion in the electrolyte, is manifested as a deeper corrosion penetration into the grain boundaries and a widening of the region of low corrosion observed earlier. The grains less attacked by the electrolyte, owing to orientation or some other so far unknown reason, begin to react during prolonged immersion (10 h), also showing sensitivity to crystallographic orientation by the formation of more or less regular cubicals or parallelopipeds.

After 25 h in the electrolyte the greatest part of the sample surface is attacked so much that microstructural changes can hardly be revealed. General grain and grain boundary corrosion are shown in Fig. 3.

Table 1. Electrochemical characteristic data of Al and alloys in 2 N sodium chloride solution

Materials	*Potential at zero current (mV)*	*Potential at 10^{-2} mA cm^{-2} (mV) (SCE)*	*Passivation threshold from mV to mV (SCE)*	*Passivation peak mV (SCE)*	*Passivation peak (mA cm^{-2})*	*Potential at 10 mA cm^{-2} mV (SCE)*	*Current density at −400 mV(mA cm^{-2})*
High purity Al(5N)	− 800	−1600	−1600 − 770 >830	−1200	0.18	− 630	180
Al(5N)−0.2% Ga	−1325	−1700	−	−	−	−1570	520
Al(5N)−0.2% Ga−0.2% P	−1100	−1680	−1680 −1050 >630	−1400	0.40	− 900	450
Technical purity Al(99.8%)	− 800	−1300	−1300 − 750 >550	−1100	0.20	− 550	40
Al(99.8%)−0.2% Ga	−1500	−1400	−1400 −1100 >300	−1300	0.50	− 980	200
Al(99.9%)−0.2% Ga−0.2% P	− 900	−1450	−1450 − 950 >500	−1100	0.40	− 850	200

The addition of 0.2% P to the binary Al–0.2% Ga alloy completely changes the corrosion behaviour. After 10 to 50 h of contact with the electrolyte no microstructural change is observed as compared to the initial state, with exception only of revealed grain boundaries after 50 h as as shown in Fig. 4. After 500 h of contact with 2 N sodium chloride solution the corrosion behaviour remains unchanged, Fig. 5. Therefore, it can be concluded that the dissolution of the alloy is predominantly uniform.

3.1.3. Investigation with a microprobe. The microprobe was only used for the investigation of the ternary alloy Al–0.2% Ga–0.2% P. It is already known that the determination of low gallium and phosphorus concentrations with this method is difficult due to the low melting point of the first and low atomic weight of the second element. For this reason the results presented in our paper can be accepted only at a qualitative level.

The change of gallium concentration, is indicated by the presence of a maximum, although

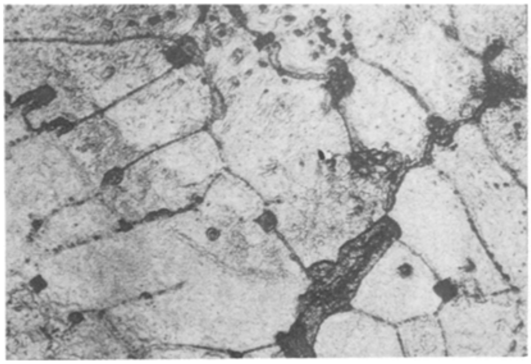

Fig. 2. Corrosion microstructure of Al–0.2% Ga alloy made of high purity aluminium 99.999% (5N) in 2N sodium chloride solution, 6 h (× 150).

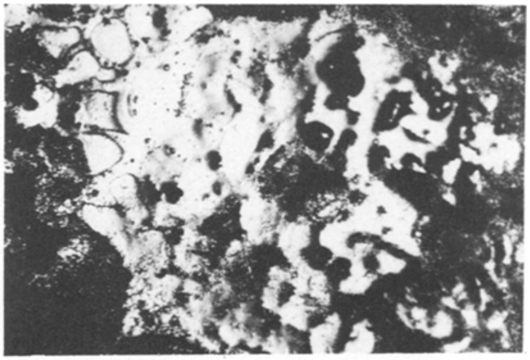

Fig. 3. Corrosion microstructure of Al–0.2% Ga alloy made of high purity aluminium 99.999% (5N) in 2N sodium chloride solution, 25 h (× 150).

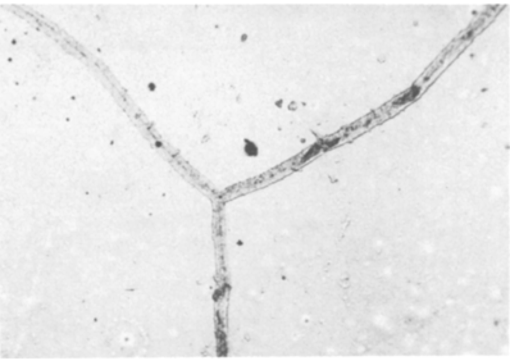

Fig. 4. Corrosion microstructure of Al–0.2% Ga–0.2% P alloy made of high purity aluminium 99.999% (5N) in 2N sodium chloride solution, 50 h (X 400).

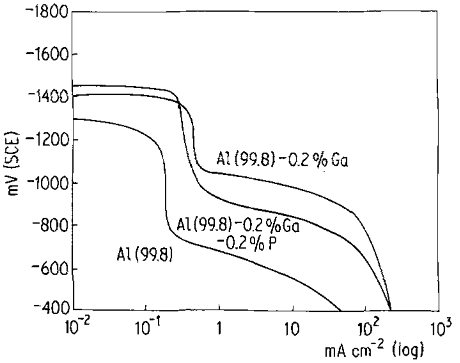

Fig. 6. The polarization curves of technical purity aluminium 99.8% (T) and alloys in 2N sodium chloride solution.

a weak one, at the expected position, i.e. on the grain boundary. The change of phosphorus concentration within the boundary could not be detected.

3.2. *Alloys made of 99.8% technically pure aluminium*

3.2.1. Anodic behaviour. Fig. 6 shows the polarization curves of technically pure aluminium (99.8%) and of the alloys based on this aluminium: Al–0.2% Ga and Al–0.2% Ga–0.2% P. Technically pure aluminium shows passivation in the potential region from −1300 to −750 mV. It is interesting to point out that technically pure aluminium shows considerably smaller current densities at −400 mV (40 mA cm^{-2}) as compared to highly pure aluminium. Actually, the alloys Al–0.2% Ga and Al–0.2% Ga–0.2% P show the same passivation of the matrix as observed with the initial aluminium. It should be especially noted that the addition of 0.2% Ga to technically pure aluminium does not eliminate passivation, in contrast with the same alloy based on highly pure aluminium. Characteristic data are presented in Table 1.

3.2.2. Corrosion behaviour. After immersing the Al–0.2% Ga alloy in the electrolyte for 25 h the dissolution reaction along grain boundaries is not very intensive. Pitting corrosion and crater pits are more evident, Fig. 7.

The addition of 0.2% P to the binary alloy Al–0.2% Ga increases both pitting and corrosion along grain boundaries. After 25 h, the sample surface is completely corroded and it is difficult to follow the change of the structure, Fig. 8.

By comparing microstructural changes of ternary alloys made of both highly pure and technically pure aluminium, it can be seen that the alloys

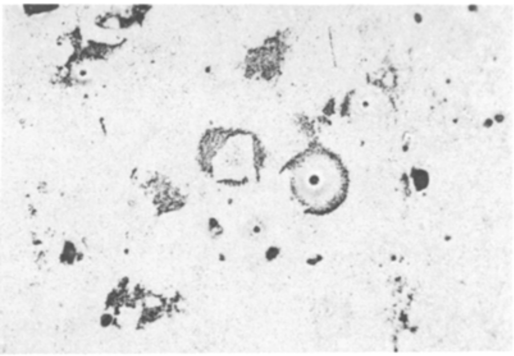

Fig. 5. Corrosion microstructure of Al–0,2% Ga–0,2% P alloy made of high purity aluminium 99.999% (5N) in 2N sodium chloride solution, 500 h (X 400).

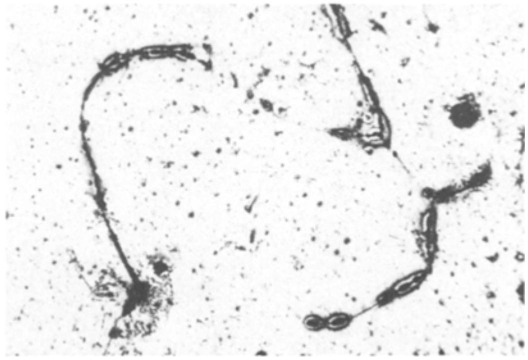

Fig. 7. Corrosion microstructure of Al–0,2% Ga alloy made of technical purity aluminium 99.8% (T) in 2N sodium chloride solution, 25 h (X 150).

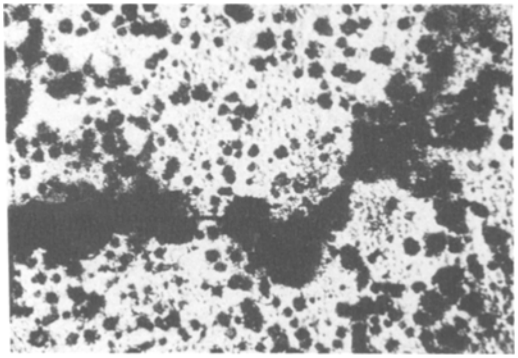

Fig. 8. Corrosion microstructure of Al–0.2% Ga–0.2% P alloy made of technical purity aluminium 99.8% (T) in 2N sodium chloride solution, 25 h (× 150).

made of technically pure aluminium are more susceptible to corrosion in contact with 2N sodium chloride solution. Therefore, it is possible that impurities present, especially a relatively high concentration of iron (about 0.14 wt %), intensify the selective corrosion of alloys based on technically pure aluminium. Although there are no equilibrium diagrams for such multicomponent systems it is already known from corresponding binary diagrams that gallium and phosphorus form the compound GaP with, 30.76% P and that aluminium and phosphorus form the compound AlP with 53.45% P. Furthermore, gallium and iron form a solid solution, but may also form a compound Fe_3Ga. The effect of these intermetallic compounds, and some others which can be formed in a multicomponent system, on the electrochemical and corrosion properties of the investigated alloys is still unknown due to the lack of literature data concerning the basic Al–Ga–P system.

3.2.3. Investigation with a microprobe. The ternary Al–0.2% Ga–0.2% P alloy in the as-cast state has a well defined cellular structure, Fig. 9. Investigation with a microprobe indicated increased concentrations of phosphorus and gallium, both within the grain boundaries and on certain inclusions inside the grains, Figs. 10 and 11. Not being observed in the ternary alloy made of highly pure aluminium, this increase of phosphorus concentration can be ascribed to the formation of Fe_3P, Fig. 12, i.e. the binding of phosphorus with iron contained in technically pure aluminium.

Fig. 9. Results of microprobe electron analysis of Al–0.2% Ga–0.2% P alloy made of technical purity aluminium 99.8% (T), electron micrograph of grain boundary.

4. Conclusions

1. Addition of 0.2% Ga to the highly pure aluminium in contact with 2N sodium chloride solution, causes intensive corrosion, with both pitting and grain boundary attack. Metal grains with suitable crystallographic orientation show relatively high corrosion resistance. Prolonged immersion in the electrolyte causes total 'damage' of the structure, with disintegration of the sample It is characteristic for this alloy to have a high negative potential at the current density of 50 mA cm^{-2}.

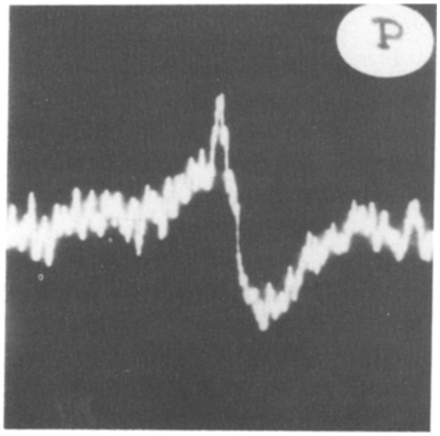

Fig. 10. Results of microprobe electron analysis of Al–0.2% Ga–0.2% P alloy made of technical purity aluminium 99.8% (T), distribution of phosphorus.

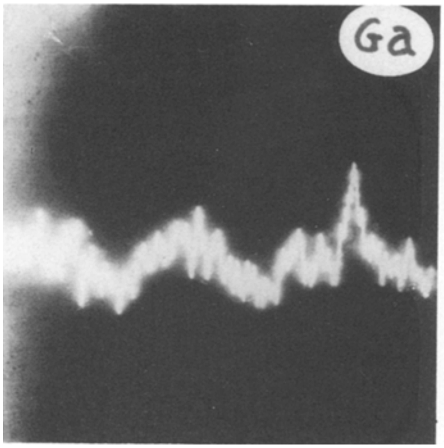

Fig. 11. Results of microprobe electron analysis of Al–0.2% Ga–0.2% P alloy made of technical purity aluminium 99.8% (T), distribution of gallium.

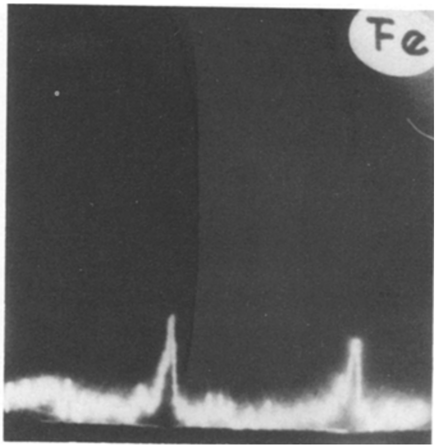

Fig. 12. Results of microprobe electron analysis of Al–0.2% Ga–0.2% P alloy made of technical purity aluminium 99.8% (T), distribution of iron.

2. Addition of 0.2% P to the binary Al–0.2% Ga alloy made of highly pure aluminium decreases corrosion and increases passivation.
3. The binary Al–0.2% Ga alloy made of technically pure aluminium has a passivation region and lower corrosion, as compared to the same alloy made of high purity aluminium.
4. The ternary alloy Al–0.2% Ga–0.2% P made of technically pure aluminium should be treated as a multicomponent system because it contains, besides alloying elements, increased amounts of iron, silicon and copper.
5. Corrosion, with both pitting and grain boundary attack of the binary Al–0.2% Ga alloy made of technically pure aluminium increases after the addition of 0.2% P.
6. Increased corrosion of the ternary alloys made of technically pure aluminium can be explained by the presence of intermetallic compounds and their dissolution reaction with the matrix (galvanic couples).

Acknowledgements

Financial support for this investigation from the Science Foundation of SR Serbia and the Serbian Academy of Sciences and Arts is greatly appreciated.

The authors wish to thank the Academic A. Despić for permission to examine these alloys and for helpful suggestions.

References

[1] C. P. Wales and A. C. Simon, *Electrochim. Acta.* **20** (1975) 895–901.
[2] D. M. Dražić, A. R. Despić and S. K. Zečević, V. Yugoslav Conference of Electrochemistry, Dubrovnik 1–4 June (1977) Commission for Electrochemistry, Yugoslavia, p. 107.
[3] A. Mance, D. Cerović and A. Mihajlović, *J. Appl. Electrochem.* **14** (1984) 459.
[4] A. R. Despić, D. M. Dražić, A. Mihajlović, B. Jovanović, A. Mance and Zh. Georgiev, International Society of Electrochemistry, 29th Meeting, Budapest, August 28–September 2 (1978) p. 998.
[5] A. Mihajlović, A. R. Despić, D. M. Dražić, O. Nešić and B. Jovanović, V. Yugoslav Conference of Electrochemistry, Dubrovnik 1–4 June (1977) Commission for Electrochemistry, Yugoslavia, p. 94.
[6] A. R. Despić, Plenarnij Doklad na V. Vsesojuznom Sovečanii po Electrochimii, Moskva, Janvar (1975).
[7] A. Mance, Proceedings of the XXII Yugoslav Conference, ETAN, V. Yugoslav Conference on Materials, Zadar 12–16 June (1978) p. 61.
[8] A. Mihajlović, International Society of Electrochemistry (ISE), 32nd Meeting, Dubrovnik-Cavtat 13–20 September, Vol. II (1981) p. 859.