

ALUMINIUM-LITHIUM ALLOY BY FUSED SALT ELECTROLYSIS

M KAMALUDEEN, N G RENGANATHAN, M SUNDARAM and K I VASU

Central Electrochemical Research Institute, Karaikudi-623 006

Laboratory scale investigations on the preparation of aluminium-lithium alloy containing 11% lithium by the electrolysis of a molten mixture of LiCl + KCl + LiF at 670° - 700°C, employing molten aluminium cathode were carried out and the results are reported. The applications of Al-Li alloy and the advantage of the electrochemical alloying method have been indicated. An outline of the electrolytic cell with rocking motion employed for the experiment has been given.

Key word: Al-Li alloy, fused salt electrolysis, molten Al cathode

INTRODUCTION

Electrodeposition of metals from molten salts employing molten metal cathodes is a competitive procedure of alloy making, especially with reactive metals. The process of preparing Al-Li alloy by the electrolysis of molten LiCl - KCl - LiF mixture with molten aluminium cathode has been described in this paper.

In recent years metallurgists have shown special attention to the preparation and properties of Al-Li alloy which has tremendous potentialities in aircraft, defence and battery industries. The requirement of high yield strength combined with low density structural components for aircraft for increasing the payload as well as reducing the fuel cost could be satisfactorily met by Al-Li alloy containing other elements like Cu, Mg, Zn, Si and with little Zr to increase ductility without impairing its yield strength [1].

A 3% drop in density and 6% increase in modulus of elasticity could be achieved by incorporating 1% lithium in aluminium alloys to a maximum of 4% lithium.

The mechanical properties of X2020 Al-Li alloy containing 1.2%Li, 4.45Cu, 0.21Cd, 0.16Fe, 0.08Si, 0.51Mn, 0.06Ti and balance Al are compared with 70 75 alloy with yield strength of 520 MPa with about 10% elongation [2]. The strength is maintained even at higher temperature than standard aircraft alloys [3].

The increase in strength is associated with the magnitude of resistance by δ' Al₃Li precipitate to dislocation motion. The phase diagram of Al-Li in Fig.1 indicates the formation of various age hardenable alloys.

In the development of high energy and power density molten salt lithium batteries with FeS, FeS₂, TiS₂ cathodes, solid electrolyte and thermal batteries, the use of Al-Li alloy as anode has added advantage over lithium metal as such because of the high reactivity of molten lithium with almost all the ceramic separators or insulators and its solubility in molten LiCl-KCl electrolyte [4] (0.13 mol % at 400°C) leading to self discharge. The problem could be overcome by employing Al-Li alloy anode without affecting the performance characteristics of the battery. The electrochemical stability of Al-Li alloy permits its use as reference electrode in molten systems containing lithium salts.

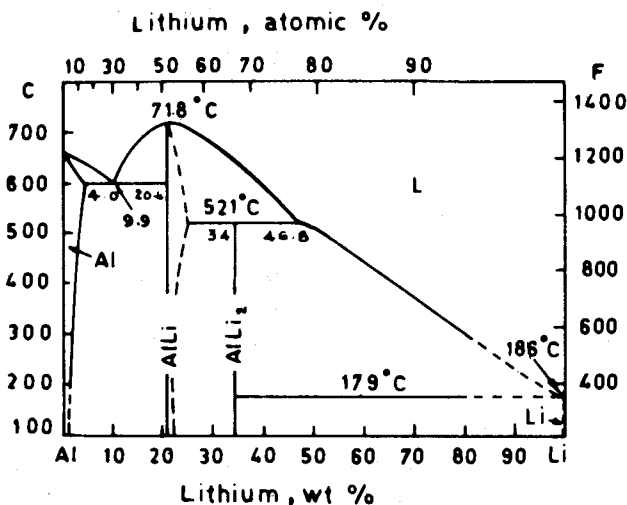


Fig.1 Al-Li phase diagram

Though the direct alloying procedures like ingot melting, powder melting under suitable flux and atmospheric conditions have been followed in the preparation of the alloy, the electrochemical route seems to have an edge over them because of the fact that the deposition of lithium and in situ alloying takes place simultaneously under protective covering of molten electrolyte which would have otherwise been difficult in direct alloying due to the vast difference in densities (Li-0.53, Al-2.7 g/cc) and in addition to the susceptibility of lithium to oxidation and nitration.

EXPERIMENTAL

Electrolytic set up

The electrolytic cell is shown in Fig.2. The cell consisted of a rectangular mild steel vessel lined internally with magnesite refractory so as to form an inner rectangular cavity of 15 × 11 × 23 cm. The cathode lead for molten aluminium was 11.5 cm wide, 3 mm thick 'L' shaped stainless steel plate introduced through one side bottom of the cell. Except the contact area the remaining portion was protected from direct contact with molten electrolyte by suitable refractory insulation with magnesia bricks.

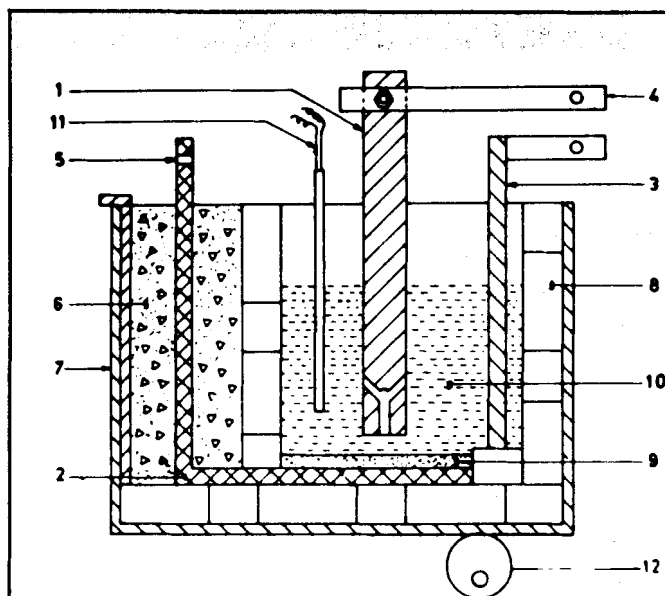


Fig.2:Electrolytic cell set up

- | | |
|------------------------------------|----------------------------|
| 1. Graphite anode | 7. Rectangular m.s. vessel |
| 2. S.S cathode | 8. Refractory lining |
| 3. S.S. rods for a.c. heating | 9. Molten aluminium |
| 4. Anode connection | 10. Molten electrolyte |
| 5. Cathode connection | 11. Thermocouple |
| 6. High temperature cement packing | 12. Rocking cam |

The anode was 7.5 cm dia graphite rod introduced from the top. The slanting holes of 1 cm dia provided at the bottom of the rod [5] facilitate easy circulation of electrolyte and free passage of chlorine away from the cathode vicinity, thus avoiding the danger of recombination with cathode product, resulting in lowering the current efficiency. An interelectrode distance of 5 cm was maintained and no diaphragm has been introduced.

The initial melting of the electrolyte and its subsequent maintenance in molten condition throughout the electrolysis was accomplished by internal A.C. resistor heating arrangement [6] by means of impressing A.C. at 10-12V, 200-250A across two 2.5 cm stainless steel rods introduced from top. The electrolyte consisted of a mixture of 1 : 1 LiCl + KCl with 5% LiF. The operating temperature was maintained at 670°C - 700°C and measured with an alumina sheathed Chromal-Alumal thermocouple. In this procedure enhancement of mixing of the deposited lithium with molten aluminium for hastening the diffusion process so as to attain faster homogeneity was aimed at and in view of this a rocking motion arrangement to the whole cell has been attached and was performed once in 10 mts during electrolysis.

In most of the fused salt electrolysis especially with hygroscopic salts the presence of moisture even at 500°C not only affects the electrolyte and electrodes but also has an adverse effect on current

efficiency due to hydrolytic decomposition. Increase of oxide content in bath results in sludge formation. The removal of moisture from the electrolyte is a matter of primary concern before electrolysis. Slow melting of the LiCl + KCl mixture under vacuum for extended period of time (8- 10h) followed by bubbling dry HCl gas has been indicated [7].

A faster rate of removing moisture by bubbling dry Cl₂ for 2 hours followed by argon for 30 minutes has been recommended [8].

If the moisture is not removed, hydrolysis occurs upon fusion as indicated by $\text{Cl}^- + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{OH}^-$. By passing dry Cl₂



The OH⁻ ion is thus removed without contamination. O₂ and HCl gases are swept out by chlorine which is easily removed by flushing argon. The latter procedure was followed in our experiments.

Electrolysis experiments

Dried mixture of 1:1 LiCl + KCl with 5 W/o LiF was slowly melted in the cell by the AC resistor heating arrangement in which molten electrolyte itself acted as resistor except at the initial stages.

After suitable depth of melt has formed dry Cl₂ was bubbled through the melt for 2 hours followed by argon for 30 mts. The temperature of the bath was then slowly raised to 670-700°C. 1.5 kg of aluminium in the form of pieces were fed into the bath which formed a molten cathode layer at the bottom over stainless steel contact plate. The graphite anode was slowly introduced into the bath and held in position with suitable external frame so as to maintain 5 cm gap from the molten aluminium surface.

Electrolysis was carried out by impressing direct current of 150A at 6-8 volt for 6 hours with anodic and cathodic current densities of 3.5 and 1A/cm² respectively. Throughout the electrolysis the temperature was maintained at 670-700°C. The liberated chlorine at the anode was sucked off by means of blower with jet arrangement. After the electrolysis, the alloy was ladled out and cast into ingots.

The alloy was analysed by flame photometry and found to contain 11.14% lithium and 0.0028% potassium. This works out to a current efficiency of 75% with energy consumption of 5-6 kwh per kg of the alloy formed.

CONCLUSION

The possibility of preparing Al-Li alloy with 11% lithium by electrochemical alloying has been realised. The liquid nature of the cathode and the mechanical mixing facilitate faster rate of diffusion of the lithium atom, resulting in the possibility of obtaining alloy with high content of lithium.

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