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Surface oxidation studies of Al–2 wt% Li thin films

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Abstract. Thin films of Al–2 wt% Li alloy are prepared on well-cleaned glass substrates by vacuum evaporation at room temperature. Electrical conductivity studies of both alloy Al(Li) and pure Al films show that they obey the logarithmic rate law during the initial period of oxidation. The addition of lithium, however, increases the oxidation rate considerably during the initial period of oxidation. Surface analysis by laser Raman spectroscopy indicates the existence of LiO_2 and Al_2O_3 as the most probable oxide components.

Keywords. Al(Li) logarithm; electrodes; Raman lines; electropositive; selective oxidation; polycrystalline; amorphous; thermochemical.

1. Introduction

Li–Al alloys have been extensively investigated for their interesting electronic properties. They have very high ionic conductivity different from that of pure aluminium, and therefore much importance is attached to resistivity change studies of alloy films with time to explain their oxidation behaviour (Kishio *et al* 1981). The additional metal lithium present in these alloys is said to have significant effect on the oxidation of the alloy as compared to pure aluminium (Kurtasova and Polyanskii 1983).

In this paper we report resistance variation studies of Al–2 wt% Li thin films with time and as compared to that of pure aluminium thin films. The surface analysis of these films after oxidation is also done using laser Raman spectroscopy.

2. Experimental

Thin films of Al(Li) were prepared by the vacuum evaporation method (pressure 10^{-5} torr) into clean Blue star microslides of size $75 \times 14 \times 2{\cdot}85\ mm^3$. Several samples of about 10 nm thickness were prepared under the same conditions. Silver electrodes of matching thicknesses were used and the resistance of each film at room temperature was measured using a digital multimeter within a few seconds of starting the oxidation and continued for about 30 min. The experiment was repeated for pure aluminium films.

Using a SPEX RAMALOG-5 spectrometer, the Raman spectra of Al(Li) thin films oxidized at 303, 478, 508 and 533 K were recorded. The Raman lines were used to identify the oxides present in the film.

3. Results and discussion

3.1 *Resistivity studies*

Figure 1 shows the change in resistance with log(t) of Al(Li) and Al thin films, due

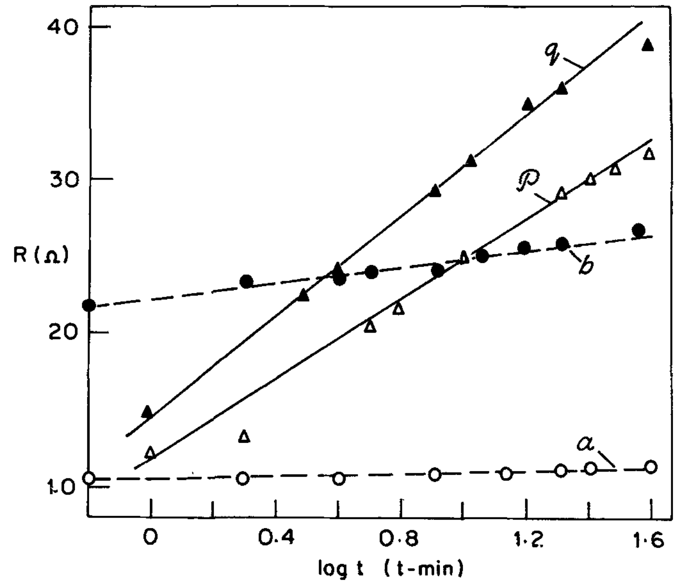

Figure 1. Oxidation kinetics of thin films of Al(Li) and pure Al thin films. Al with initial resistance (*a*) 10·6 and (*b*) 21·4 ohm; Al(Li) with initial resistance (*p*) 12 and (*q*) 14·7 ohm.

to oxidation at room temperature for about 30 min. These curves show that for the initial period of oxidation, the resistance varies linearly with the function of log time.

In the Al(Li) film, lithium atoms are more active than aluminium atoms due to selective oxidation. The occurrence of oxide film causes an excess of vacancies at the metal oxide boundary. These vacancies diffuse into adjacent areas of the metal. In lithium oxide the self-diffusion coefficient of the Li ion is smaller than that of the O_2 ion and the vacancies are easily saturated with oxygen. Thus, the composition of the alloy determines the oxidation rate (Ando *et al* 1986). Pure aluminium thin films are polycrystalline and provide numerous grain boundaries (Bhavani and Vaidyan 1979). Diffusion into the boundaries blocks the oxide formation leading to a slower oxide growth rate. Also aluminium is more protective than alkali metals, hence alloys containing more electropositive materials increase oxide growth. Both alloying elements oxidize simultaneously to give LiO_2 and Al_2O_3, the oxygen pressure in the atmosphere being greater than the equilibrium dissociation pressure of both oxides (Wallwork 1976).

3.2 *Identification of oxides*

The observed Raman shifts at four different temperatures viz. one at room temperature and other three near the melting point of lithium (459 K) (figure 2) are identified (Grow and Pitzer 1977; Andrews and Smardzewski 1973; Thirumalavan and Kumar 1986) and are given in table 1. It is found that as temperature increases the intensity of lines also increases but the peak intensity decreases from 478 to 508 K. This comparison from the table indicates the formation of more oxides at

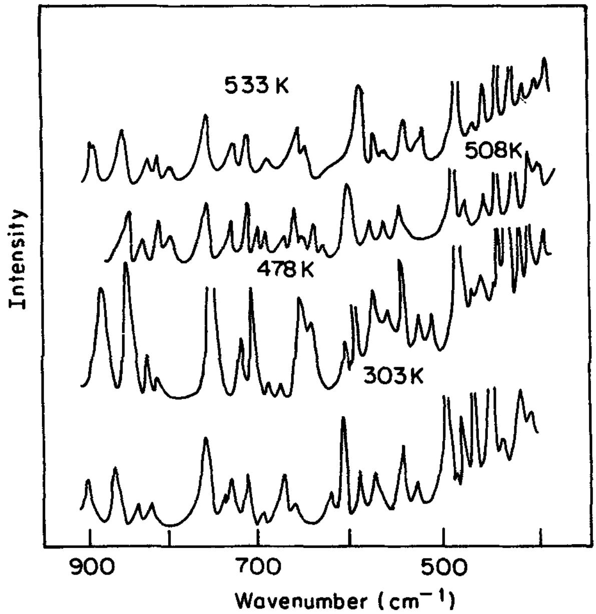

Figure 2. Reflectance Raman spectra of oxidized Al(Li) alloy films at 303, 478, 508 and 533 K.

Table 1. Raman frequencies of oxidised Al(Li) thin films.

Raman frequency (cm^{-1}) at				
303 K	478 K	508 K	533 K	Identification
411	411	410	410	Al_2O_3
440	440	440	440	Al_2O_3
451	448	449	450	Al_2O_3
460	460	458	462	Al_2O_3
495	495	495	495	LiO_2
500	500	500	500	LiO_2
545	545	545	530	?
555	555	555	555	?
570	570	570	572	Al_2O_3
595	595	595	595	?
610	610	610	610	Al_2O_3
675	675	675	678	Al–O vibration
—	—	—	685	LiO_2
710	700	700	705	LiO_2
740	740	740	740	LiO vibration
750	750	750	750	AlO_2
770	770	770	770	Li_2O
825	815	825	810	Li_2O

higher temperature. Also the peaks get broadened as temperature increases and as grain size decreases (Fauchet 1985). The discrepancy in intensity variation at temperatures 478 to 508 K is attributed to the protective scaling of the polycrystalline aluminium oxides.

At room temperature, the oxides formed on the films are Li_2O, LiO_2, Al_2O_3 and AlO_2, the more probable ones being Al_2O_3 and LiO_2. The concentration of LiO_2 is found to increase with increase in temperature. Also, thermochemical data indicate that the formation of Li_2O is more probable than LiO in an alloy (Hildenbrand 1972).

4. Conclusions

The oxidation of Al–2 wt% Li alloy thin films (thickness ~ 10 nm) prepared by vacuum evaporation on clean glass substrates is found to obey the logarithmic rate law of oxide growth as in the case of pure aluminium films but with higher rates of oxidation. Laser Raman surface studies show that the more probable oxides are Al_2O_3 and LiO_2.

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