Auger Electron Spectroscopy (AES) has been used to study the surface of aluminium-Lithium alloy (Al-3.49wt%-Li). In this work, the surface atomic composition as a function of temperature was followed. A great amount of Chemisorbed oxygen and carbon induce the Li segregation and shows that oxygen reacts first with the segregated Li, then with both Li and Al. The carbon adsorbed forms the lithium carbonate which decomposes to form a lithium oxide. The formed Li oxides have been characterised using the activation energy of Li segregation determined experimentally. The heat of the Li₂CO₃ formation and the Li oxide layer formed have been estimated.

Key words: Al-3.49wt.%Li, Li segregation, segregation energy, Li₂CO₃.

1. INTRODUCTION

The good electrochemical properties of Al-Li alloy, more attractive than for the pure Li, have motivated several researchers [1, 2] to develop new battery anodes used as power source for the propulsion of electrical vehicles. In this area, AES measurements made in [3] on clean lithium surfaces after exposure to O₂, CO₂ and N₂ showed that the reactions with the lithium surface occur much more rapidly for O₂ and CO₂ than N₂. The CO₂ reaction indicates that the oxide and carbide of Li are formed. Guorong Zhuang et al. [4] have characterised, with the XPS technique, the reactions of tetrahydrofuran and propylene carbonate with a Li thin film at the surface of an Al substratum. Near its bulk melting temperature of 220 K, essentially all of the propylene carbonate remaining on the surface has reacted with Li to form an alkyl carbonate. In our earlier studies [5, 6], lithium segregation on Al-3.49wt%-Li alloy oxidised surface has been analysed by AES. The surface has been studied in the presence of small both chemisorbed oxygen and graphitic carbon impurity. These two impurities showed a few effect on the segregation energy of Li.

In this paper which is a continuation of our works [5, 6], the study is made on samples of Al-3.49wt%-Li oxidised and contaminated respectively by a great
amount of oxygen and carbon at open air and at ambient temperature during several days. The concentrations evolution as a function of temperature on the alloy surface has been followed by AES technique. We showed that the reaction, at high temperature, of a great amount of carbon and oxygen increase the segregation energy of Li and contribute to form Li carbonate. The carbon adsorbed forms the lithium carbonate and decomposes to form a lithium oxide, in agreement with earlier studies. The oxides formed have been characterised. The heat of the Li$_2$CO$_3$ formation has been estimated.

2. THEORETICAL STUDY

The theoretical calculation of the segregation energy of Li has been given in the earlier work [5]. From the formula (2) [5] and taking into account of two values of $\Delta G^0$(str) and of $\Delta G^0$(sol, id), $\Delta G^0$(seg) takes four values:

\[
\begin{align*}
\Delta G^0_{\text{seg}}^{\text{min1}} &= -0.29 -0.825 = -1.115 \text{ kcal/mole} \\
\Delta G^0_{\text{seg}}^{\text{min2}} &= -1.6 -0.825 = -2.425 \text{ kcal/mole} \\
\Delta G^0_{\text{seg}}^{\text{max1}} &= -0.29 -1.65 = -1.94 \text{ kcal/mole} \\
\Delta G^0_{\text{seg}}^{\text{max2}} &= -1.6 -1.65 = -3.25 \text{ kcal/mole}
\end{align*}
\]

$\Delta G^0_{\text{seg}}^{\text{max1}}$ ($-1.94 \text{ kcal/mole}$) has been considered as the theoretical value ($\Delta G^0_{\text{seg}}^{\text{theo}}$). It has been imposed by the most acceptable agreement in respect with the experimental data obtained from AES spectra [5].

3. EXPERIMENTAL PROCEDURE

The apparatus was a scanning Auger microprobe, of RIBER Type, equipped with a cylindrical mirror analyser (CMA). The experimental conditions and the sample tested are given in [5].

4. RESULTS AND DISCUSSION

4.1. CARBON EFFECT

After preliminary cleaning, a first sample has been left in a box, during several days, in open air. The Auger spectrum (Fig. 1) was recorded just after its introduction in UHV. We detected the Auger transitions LVV (41 eV, 56 eV), KLL (272 eV) characteristic of alumina, chemisorbed carbon and O K$_{\alpha}$V$_{\alpha}$V$_{\alpha}$ (507 eV) Auger transitions of interband type. It has been found that the surface
layer naturally formed at room temperature on the Al-Li sample consists of an alumina film contaminated by carbon in the carbide form. There is no Auger transition characteristic of Li on the surface.

Fig. 2a shows the evolution of atomic surface concentrations calculated from Auger line heights of chemical elements as a function of temperature. From 320°C, the temperature begins to activate the segregation of Li and of the dissolved carbon in the bulk. Oxygen concentration grows and the aluminium concentration decreases. However, we interpreted the concentration evolution of Auger line located at 41 eV in this way:

i) From ambient temperature to 280°C, O and C concentrations increase slightly and aluminium concentration decreases. At 280°C, the main peak of carbon is preceded by very fine structures at energies 252 eV and 267 eV. They are very close to values obtained by A.B. Chritle [8] for tungsten carbide. These fine structures correspond respectively to inter-atomic transitions $K_{\text{carb}} ^{\text{Li}} L_{\text{ox}} ^{\text{LII,IIIox}}$ and $K_{\text{carb}} ^{\text{LII,IIIox}} L_{\text{II,IIIox}} ^{\text{LII,IIIox}}$. The Auger peak located at 41 eV is characteristic of $K_{\text{Li}} ^{\text{LII,IIIcarb}} L_{\text{II,IIIcarb}} ^{\text{LII,IIIox}}$ transition. This last transition shows that the peak located at 41 eV characterised the Li mixed to carbon and to oxygen. The oxygen peak and the carbon peak evolved in the same way. The concentration ratio (Al/Li) is 3/2. It corresponds to the Al$_{3}$ Li$_{2}$ phase.

ii) In the range of 320°C to 400°C, the Li concentration increases. At 320°C, there is appearance of a new peak located at 34 eV. It has been attributed to Li concentration strongly oxidised (symbolized in Fig. 2a by Li$_{\text{ox}}$). The Al (51 eV) concentration decreases. It has been totally attenuated at 400°C.

iii) In the range of 400°C to 500°C, the alloy surface has been coated by a layer of oxidised Li and Li allied to the carbon oxide. The shape of the CKLL
emission has revealed the presence of fine structures located at 246 eV, and 261 eV (Fig. 2b). These structures are interpreted in term of lithium carbonate (Li$_2$CO$_3$) as reported in [7]. At 490°C, the relative concentration to Li$_{ox}$ increases jointly with oxygen concentration and reaches a maximum. The concentrations ratio of (Li$_{ox}$/ C) and (O/C)), at 490°C and 500°C, are equals to 2. Also, Li$_{ox}$/O ratio is equal to 1. The Auger spectra and the concentration ratio indicate the formation of mixed oxide of Al, Li and C.

The temperature effect and the presence of carbon and oxygen at the alloy surface have favoured the Li oxidation. The thermal energy and the content in oxygen have shifted the oxidised Li peak from 41 eV to 34 eV. We notice that the surface remains stable during the progressive decrease of the temperature. The alloy surface is finally coated with a corrosion layer composed of Li carbonate and of Li oxide.

We calculate the segregation energy of Li. The quasi-equilibrium corresponding to the reaction of segregation is determined by the formula (1).

$$\frac{X^S_B}{X^S_A} = \frac{X^b_B}{X^b_A} \exp[-\Delta G^0(\text{seg})/kT]$$  \hspace{1cm} (1)

$\Delta G^0(\text{seg})$ is the standard free enthalpy for the segregation reaction, and the subscripts b and s refer to bulk and surface respectively.

At 450°C, the concentrations of chemical elements at the surface are: Li$_{ox}$ (42%at.); Al (0%at.); O(41%at.) and C(17%at.).

We calculate the segregation energy of Li in using the formula (1) and the data from Fig. 2a. The choice of temperature (450°C) and the calculation details are given in our works [5]. The concentrations are $X^b_{Li} = 42\%$, $X^b_{Al} = 12\%$at. and $k = 1,3806 \times 10^{-23}$ J/deg. The experimental segregation energy of Li has been evaluated to:

$$\Delta G^0_{\text{exp}}(\text{seg}) = -2.4 \text{ kcal/mole}.$$  

$\Delta G^0(\text{seg})_{\text{max}} = -1.94 \text{ kcal/mole}$ has been considered as theoretical energy [5]. We interpreted the difference between the theoretical value and the experimental value in term of ($\Delta G(\text{chem})$) chemical energy, due to exothermic adsorption of oxygen and carbon which have reacted with the two components of the alloy. The following expression (2), explained in [5], has been used.

$$\Delta G(\text{chem}) = Z_B E_{Bx} \theta_B + Z_A E_{Ax} \theta_A$$  \hspace{1cm} (2)

We calculate $\Delta G(\text{chem})$ using data from Fig. 2a and the adsorption heat of O with Al (Al$_2$O$_3 = 266.4$ cal/mole) and O adsorption with Li (Li$_2$O = = 284.8 cal/mole) [8]. The surface coordination number are $Z_A = 2/3$ (2 atoms of Al for 3 atoms of O) and $Z_B = 2$ (2 atoms of Li for one atom of O).

Before the Li segregation, there are Al$_2$O$_3$ and Li$_2$O. For Al oxide $\theta_{Al} = = (0.3/0.34)-0.3$ and for Li oxide $\theta_{Li} = (0.17/0.34)-0.17$. 
ΔG(chem)1 = -(0,3/0,34) – 0,3(2/3) – 0,2664 – (0,17/0,34) = -0,047 = -0,095 kcal/mole.

After Li segregation, at 450°C there are Li\textsubscript{0x} and Li respectively strongly and partially oxidised. Oxygen content at the surface is distributed between Li\textsubscript{0x}, Li and C. Therefore, using data from Fig. 2a and Auger peaks, the concentrations are: Li\textsubscript{0x} (38.9%at.), Li(7.6%at.), Al(0%at.), O(37.85%at.) and C(15.31%at.). Li\textsubscript{0x} corresponds to Li\textsubscript{2}O. 

ΔG(chem)2 = -(0.389/0.378) – 0.389 – 0.2848 – (0.076/0.378) = -0.076 – 2.0.2848

\begin{equation}
ΔG^0 \text{exp(seg)} = ΔG^0 \text{(seg)max1} + ΔG(chem)1 + ΔG(chem)2
\end{equation}

The difference between the two values has been attributed to Li carbonate formed at the surface. We can say that the carbon adsorbed in open air has formed Li carbide that is oxidised in Li\textsubscript{2}CO\textsubscript{3} under the temperature effect. A part decomposes to form a Li oxide and a small amount of Li carbonate is remained at the surface, as reported in [4]. We do not have found anywhere the E\textsubscript{i} (Li\textsubscript{2}CO\textsubscript{3}) heat of the Li\textsubscript{2}CO\textsubscript{3} formation. We can calculate it from this difference between the two values.

\begin{equation}
ΔG^0 \text{exp(seg)} = 2.1577 = Z \cdot θ \cdot E_i (\text{Li}_2\text{CO}_3) = -2.4 + 2.1577 = -0.2422 \text{kcal/mole}
\end{equation}

At 450°C:

\begin{equation}
(0.389/0.3785) \cdot 0.389 \cdot (2/3) \cdot (1/0.153) \cdot E_i (\text{Li}_2\text{CO}_3) = -0.2422 \text{kcal/mole}
\end{equation}

E\textsubscript{i} (Li\textsubscript{2}CO\textsubscript{3}) has found equal to -139 cal/mole.

4.2. OXYGEN EFFECT

After heating, the second sample has been cleaned by argon ion bombardment. The carbon has been totally removed but the oxygen is remained at the surface. We take up again the study of the sample. At ambient temperature, the Auger transitions are located at 41 eV and 34 eV, 56 eV and 507 eV (O) (Fig. 3a). At 380°C the Auger transition located at 56 eV is shifted to 51 eV. This peak is characteristic of Al\textsubscript{2}O\textsubscript{3} oxide. After a progressive heating until 470°C, the Li, Al and O concentrations evolved in the same way than the first sample.

There is a repulsive interaction between Li and oxygen (Fig. 3b). We see well, when Li concentration increases this one of O decreases. We calculate the experimental segregation energy of Li using data from Fig. 3b and formula (1), in the same experimental conditions that the first sample. At 450°C, X\textsubscript{L1} is equal 43%at.
\[ \Delta G^0 \exp(\text{seg}) = -2.46 \text{ kcal/mole}. \]

We notice that the segregation energy is greater than in the case of the first sample. \( \Delta G(\text{chem}) \) energy has been calculated, in the same way that the first sample. This value has been analysed in three stages:

In the first stage, only the Auger peaks characteristic of Li, Al and O located respectively at 41 eV, 56 eV and 507 eV have been considered in our calculation of concentrations. Li (41 eV) corresponds to the more intense Auger peak of Li. This is the way to calculate the concentrations in the case of metallic alloy. In order to follow the Li evolution in comparison with Al and O, Fig. 5b has been drawn.

Before the Li segregation, the surface is coated with \( \text{Al}_2\text{O}_3 \) and \( \text{Li}_2\text{O} \).

\[
\Delta G(\text{chem})1 = - (0.06/0.48) \cdot 0.060(2/3) \cdot 0.2664 = -0.0013 \text{ kcal/mole}
\]
\[
\Delta G(\text{chem})2 = - (0.46/0.48) \cdot 0.46 \cdot 2 \cdot 0.2848 = -0.251 \text{ kcal/mole}
\]

After segregation at 450°C, for \( \text{Al}_2\text{O}_3 \):

\[
\Delta G(\text{chem})3 = - (0.09/0.48) \cdot 0.09 \cdot (2/3) \cdot 0.2664 = -0.003 \text{ kcal/mole}
\]

\[
\Delta G(\text{chem})4 = - (0.43/0.48) \cdot 0.43 \cdot 2 \cdot 0.2848 = -0.22 \text{ kcal/mole}
\]

\[ \Delta G^0 \exp(\text{seg}) = \Delta G^0 (\text{seg})\text{theo} + \Delta G(\text{chem}) \]

\[ \Delta G^0 \exp(\text{seg}) = -1.94 -0.475 = -2.41 \text{ kcal/mole} \]

It is very close to experimental value with a relative error of 2%. This error is due to \( \text{Li}_\text{ox} \) concentration strongly oxidised which has been ignored in our calculations.

We considered in this second stage the \( \text{Li}_\text{ox} \) concentration. The concentrations as a function of temperature are given in Table 1.

\[ \Delta G^0 \exp(\text{seg}) = \Delta G^0 (\text{seg})\text{theo} + \Delta G(\text{chem}) \]

\[ \Delta G^0 \exp(\text{seg}) = -1.94 -0.475 = -2.41 \text{ kcal/mole} \]

We considered in this second stage the \( \text{Li}_\text{ox} \) concentration. The concentrations as a function of temperature are given in Table 1.

\[ \Delta G^0 \exp(\text{seg}) = \Delta G^0 (\text{seg})\text{theo} + \Delta G(\text{chem}) \]

\[ \Delta G^0 \exp(\text{seg}) = -1.94 -0.475 = -2.41 \text{ kcal/mole} \]

\begin{table}[h]
\centering
\caption{The concentrations as a function temperature}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{Li}_\text{ox} (34 eV) & Li (41 eV) & \text{Al (56 eV) and Al (51 eV)} & O (507 eV) & \text{Temp [°C]} \\
\hline
27.7 & 33.32 & 4.22 & 34.68 & \text{T}_{\text{amb}} \\
35.94 & 19.60 & 4.97 & 39.47 & 260 \\
44.56 & 12.99 & 9.8 & 32.62 & 290 \\
41.77 & 13.24 & 8.06 & 36.92 & 330 \\
28.6 & 28.6 & 7.45 & 35.33 & 380 \\
30.46 & 30.46 & 6.17 & 32.89 & 420 \\
26.89 & 31.49 & 5.59 & 36.01 & 450 \\
31.66 & 43.94 & 2.75 & 21.64 & 470 \\
\hline
\end{tabular}
\end{table}
We have considered that the surface is coated only with Li$_2$O and Al$_2$O$_3$; that is to say, Li$_{ox}$ corresponds also to Li$_2$O. Calculating $\Delta G(\text{chem})$ using data from Table 1.

At ambient temperature, there are Li$_{ox}$, Li and Al$_2$O$_3$:

\begin{align*}
\Delta G(\text{chem})1 &= -(0.277/0.3468) \cdot 2 \cdot 0.277 - 0.2848 = -0.126 \text{ kcal/mole} \\
\Delta G(\text{chem})2 &= -(0.333/0.3468) \cdot 2 \cdot 0.333 - 0.2848 = -0.1821 \text{ kcal/mole} \\
\Delta G(\text{chem})3 &= -(0.0422/0.3468) \cdot 0.0422 \cdot (2/3) \cdot 0.2664 = -0.0009 \text{ kcal/mole}
\end{align*}

At 450°C, after segregation:

\begin{align*}
\Delta G(\text{chem})4 &= -(0.2689/0.36) \cdot 0.2689 \cdot 2 \cdot 0.2848 = -0.114 \text{ kcal/mole} \\
\Delta G(\text{chem})5 &= (0.3149/0.036) \cdot 0.3149 \cdot 2 \cdot 0.2848 = -0.1568 \text{ kcal/mole} \\
\Delta G(\text{chem})6 &= -(0.056/0.36) \cdot 0.056 \cdot (2/3) \cdot 0.2664 = -0.0015 \text{ kcal/mole}
\end{align*}

$\Delta G^0 \exp(\text{seg}) = \Delta G^0 (\text{seg}) + \Delta G(\text{chem})$

we found the following result:

$\Delta G^0 \exp(\text{seg}) = -1.94 -0.581 = -2.52 \text{ kcal/mole}$.

The difference between the experimental value ($-2.46 \text{ kcal/mole}$) and the theoretical values ($-2.41 \text{ kcal/mole}$ and $-2.52 \text{ kcal/mole}$) has been interpreted in term of oxidation stage. Li$_{ox}$ can be the first stage of an oxide formation, other than Li$_2$O which may be Li$_2$O$_2$, taken account of the oxygen content. This has been reported in [9]. In this area, Ilmars Dalins et al. [10] have reported that adsorption of oxygen molecule (O$_2$) occurs in the case of a violent oxidation.

We consider here (third stage) that Li$_{ox}$ corresponds, at high temperature, to Li$_2$O$_2$ which are less stable in comparison with Li$_2$O. In our new calculations, $\Delta G(\text{chem})4$ must be divided by 2. The value of the segregation energy of Li becomes:

$\Delta G^0 \exp(\text{seg}) = -1.94 -0.524 = -2.464 \text{ kcal/mole}$

We obtain exactly the same result that the experimental value with an error estimated at 0.16%. The Auger peak located at 34 eV (at 450°C), corresponds, so, to Li$_2$O$_2$. The very good agreement between the two values confirms, so, the data reported in [9, 10]. There is formation of Li$_2$O$_2$ oxide at high temperature.

4.3. REACTION OF OXYGEN WITH SEGREGATED Li

Analysing the data given in the Table 1. In the temperature range, ambient temperature to 290°C, the Li and Li$_{ox}$ concentrations change as a function of temperature. The Al concentrations increase but its Auger peak remains always
located at 56 eV. The \( \text{Li}_{\text{ox}} \) concentration increases and this one of Li (41 eV) decreases. Oxygen reacts so first with the oxidised non-segregated Li. Li (41 eV), less oxidised than \( \text{Li}_{\text{ox}} \), decreases because an amount of this one has been more oxidised and shifted at 34 eV.

In the range of 330°C to 470°C, Li and \( \text{Li}_{\text{ox}} \) concentrations increase regularly. It is the segregated Li which is oxidising. The Al concentration decreases slightly. From 380°C, Al Auger line is shifted at 51 eV. Its concentration is written in bold in Table 1. Al is so more oxidised.

The concentrations evolution and evolution of Al Auger line energy indicate that oxygen reacts first with Li, then with both Li and Al, in agreement with literature [11, 12]. The total attenuation of Al Auger Line (at 470°C), permits us to calculate the Li oxide layer formed at the surface. It is greater than the electron escapement depth of Al (LVV) transition which is very close to 5 Angstrom [13]. The surface is coated with a Li oxides layer estimated, from Auger line intensities, at 22,38 Angstrom.

5. CONCLUSIONS

The calculations and analysis conducted so far are summarized as follows:

- The calculation shows that the segregation is qualitatively and quantitatively explained by a combination of different segregation models as it has shown in our earlier works [5].
- The heat of formed \( \text{Li}_2\text{CO}_3 \) and the Li oxide layer segregated on the Al-Li surface have been evaluated. In the case of the first sample, carbon is combined to form Li carbide. Near 400°C, carbon and oxygen present on the surface have reacted with Li to form the Li carbonate. Under the temperature effect, a part of the Li carbonate decomposes to form a Li oxide. The part remaining has been used to calculate the heat of \( \text{Li}_2\text{CO}_3 \). The segregation energy of Li calculated shows that \( \text{Li}_2\text{O} \) and \( \text{Li}_2\text{O}_2 \) have been formed under strong oxidation. The concentrations evolution as a function of temperature has shown that oxygen reacts first with Li, then with both Li and Al, in agreement with literature [12].

In all cases of oxides, \( \Delta G(\text{chem}) \) must be calculated from all Auger lines (small and main) which characterise the surface.

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Fig. 2 – (a) Concentration as a function of temperature derived from the Auger peaks; (b) Spectrum of Al-Li alloy at 400°C (fine structures of C and Auger peak of Al attenuated).
Fig. 3 (a) Spectrum of the surface no contaminated with C; (b) Concentrations evolution as a function temperature.