Electronic Structure of Al-Li Alloys by Means of Electron Microprobe

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By means of an electron microprobe the lithium–K- and aluminium–K- X-ray emission lines of Al–Li alloys were studied. The Li-line can be well described by the calculated emission line. The evaluation yields the transfer of electrons from the Li-s- to the Al-p-band during alloying. The charge transfer is enhanced by heat treatment. The dependence of the elastic modulus on the charge transfer is discussed.

I. Introduction

Aluminum–lithium alloys are of technical interest because of their low specific weight and their good mechanical behaviour [1]. According to [2] the improvement of the elastic modulus depends strongly on the electronic structure, i.e. the density of states \( N(E) \). It was our intention to determine \( N(E) \) by means of an electron microprobe in a similar way as shown in an earlier paper [3]. Therefore it was necessary to determine precisely the shapes of the Al- and Li-X-ray emission lines. Since the available electron microprobe could not detect the Li–K-radiation (\( \lambda = 22.8 \) nm; \( E = 54.3 \) eV) our instrument (Jeol Superprobe JXA 733) had to be modified by mounting an XUV-spectrometer (Minuteman 302 VM) which allows to measure the Li–K-emission.

The electron microprobe allows to investigate the partial density of states within small areas with diameters down to 1 \( \mu m \) or less, i.e. local, which is unique.

II. Theoretical Fundamentals

Concerning the theoretical fundamentals we refer to [3] and repeat three equations.

The relationship between the intensity \( I(E) \) of the X-ray emission and the density of states \( N(E) \) can be written as [4]:

\[
I(E) = E^3 P(E) N(E),
\]

where

\( E \) = quantum energy of X-rays,
\( P(E) \) = quantity which is proportional to the transition probability.

Thus from the shape of \( I(E) \) with \( E < E_{\text{Fermi}} \) we obtain a picture of the local partial density of occupied states.

A measure of the type and strength of the chemical bonding between atoms of different species is given by the so-called charge transfer. According to [5] the relative variation of the number of electrons in the 3p-band of aluminum within a sphere around the specific atom can be calculated from emission spectra:

\[
\Delta n_{3p}/n_{3p} = R_K - 1.
\]

This means that the change \( \Delta n_{3p} \) of the number of 3p-electrons is related to the corresponding number \( n_{3p} \) of 3p-electrons of pure aluminum.

The relative charge transfer \( R_K - 1 \) of the 3p-electrons follows from

\[
R_K = \frac{I_{K_{\text{Al}}}^{\text{int}}}{I_{K_{\text{Al}}}^{\text{int}}} \frac{I_{K_{\text{Al}}}^{\text{int}}}{I_{K_{\text{Al}}}^{\text{int}}'} = \frac{n_{3p \text{ alloy}}}{n_{3p \text{ Al}}},
\]

with

\( I_{K_{\text{Al}}}^{\text{int}} \) = integrated intensity of the Al–K\(_p\)-emission line,
\( I_{K_{\text{Al}}}^{\text{int}}' \) = integrated intensity of the Al–K\(_x\)-emission line.

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III. Experiments

1. Specimen Preparation

Al–Li alloys were produced in the concentration range of 11 to 17, 25, and 50 a/o Li from ultrapure aluminum ("Kryal-R"; 99.999%; VAW) and lithium (99.9%; Ventron). The Li was filled into hollow Al-cylinders and closed by an Al-screw. Induction melting was done within Al₂O₃ crucibles in argon atmosphere (10⁻⁵ bar). Within this atmosphere also casting into steel molds was done. The specimens thus obtained were cleaned by zone melting, finally annealed at 540 °C within closed SiO₂-crucibles, and quenched in ice water.

These starting alloys were used to produce specimens by melt-spinning, sputtering, and high vacuum evaporation. Furthermore, the starting alloys were heat treated in bulk form in order to grow the coherent \( \delta' \)-(Al₃Li)-precipitates which are the origin of the increase in strength and specific stiffness. By X-ray small angle scattering \([6]\) could be shown that the growth of \( \delta' \)-precipitates can be well described by the MLSW (Modified Lifshitz-Slyozov-Wagner)-theory \([7, 8]\).

2. Electron Microprobe

The X-ray spectrometers supplied with the electron microprobe (JXA 733, Jeol, Tokyo) allow to investigate the energy range from 14.5 keV down to 100 eV. To detect the Li–K-radiation (54.3 eV; 22.8 nm) an XUV-spectrometer must be applied which covers the range of wavelengths from 20 up to 100 nm. An osmium coated holographic concave grating (2400 g/mm) is used in a Seya-Namioka geometry which allows tuning of the wavelength by a simple rotation of the grating. The dispersion amounts to 2 nm/mm and the reflectivity to less than 10% at 22.8 nm. The detection was done by a channel electron multiplier (Valvo X959AL). To achieve low noise, the vacuum within the XUV-spectrometer was better than 10⁻⁶ mbar and the channeltron was protected from backscattered and secondary electrons by an electrostatic filter.

The main problems in XUV-spectroscopy of Li–K-radiation are the very small fluorescence yield of less than 1%, the very small quantum efficiency of the detector \([9]\), and the contamination of the specimen surface caused by cracking of residual hydrocarbons by the primary electrons which were accelerated by 1 to 5 kV.

IV. Results and Discussion

1. Li-Spectroscopy

Figure 1 shows Li–K-emission lines as obtained from pure lithium. In the upper part the results of the present investigation are presented: the first order line \((n = 1)\) as solid and the second order line \((n = 2)\) as dashed curve. We also present the corresponding fourth derivations \(I^{(4)}\) for better recognition of details, i.e. of the pronounced knee at the high energy side of the peak. Both emission lines were obtained using a primary electron energy of 1 to 5 keV and probe currents of some \(10^{-7}\) A. The lower part of Fig. 1 shows Li–K-lines as obtained by different workers \([10, 11, 12]\). Skinner \([13]\) was the first to measure the Li–K-line using X-ray excitation on areas of some mm². The first electron microprobe investigation of a Li–K-line of pure lithium was performed by \([11]\) using a 2m-grazing incidence spectrometer.

In Table 1 different parameters characterizing the emission lines are presented. These are the resolution \(\Delta E\), the maximum position \(E_m\), the approxi-
Table 1. Li-K-emanation lines from pure Li.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\Delta E$ [eV]</th>
<th>$E_m$ [eV]</th>
<th>$\Delta E_0$ [eV]</th>
<th>$P_{B_{0.5}}$ [eV]</th>
<th>$E_k$ [eV]</th>
<th>$\Delta E_k(2/8)$ [eV]</th>
<th>$\Delta E_k$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[10]</td>
<td>0.07</td>
<td>54.02</td>
<td>3.4</td>
<td>1.52</td>
<td>54.65</td>
<td>0.33</td>
<td>0.69</td>
</tr>
<tr>
<td>[11]</td>
<td>0.88</td>
<td>54.24</td>
<td>3.3</td>
<td>1.82</td>
<td>54.91</td>
<td>0.61</td>
<td>1.08</td>
</tr>
<tr>
<td>[12]</td>
<td>0.17</td>
<td>53.65</td>
<td>3.2</td>
<td>1.81</td>
<td>54.25</td>
<td>0.53</td>
<td>0.94</td>
</tr>
<tr>
<td>[14]</td>
<td>0.04</td>
<td>54.14</td>
<td>3.6</td>
<td>1.80</td>
<td>54.76</td>
<td>0.44</td>
<td>0.82</td>
</tr>
<tr>
<td>Present</td>
<td>0.2</td>
<td>54.5</td>
<td>3.1</td>
<td>1.64</td>
<td>55.0</td>
<td>0.42</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Fig. 2. Pure Li: Li-K line. (----) experimental curve; (-----) calculated according to [16] with a lifetime corresponding to $\Gamma = 16$ meV; (-----) calculated according to [16] with a lifetime corresponding to $\Gamma = 12$ meV.

The high energy side of the Li-K line shows a knee which is characteristic for a partially filled band and which is most pronounced in the dashed curve of Fig. 1a and in the solid curve of Figure 1b. The position of the knee lies at 54.73 eV in the ($n = 1$)-spectrum and at 54.57 eV in the ($n = 2$)-spectrum.

According to recent theories [15, 16] the experimental run can be well-described: In Fig. 2 we compare the measured ($n = 1$ from Fig. 1a) with calculated lines reported by Almlbladh [16] as obtained using a phonon - electron hole - interaction-theory. The two calculated curves differ in the lifetime 0.34 psec and 0.26 psec of the electron holes corresponding to the energies $\Gamma = 12$ meV and 16 meV, respectively. We learn from Fig. 2 that by convenient choice of $\Gamma$ good agreement in shape and position of the experimental and calculated lines can be achieved. The small peak at $E - E_F = -2$ eV is caused by the contamination of the specimen surface [17].

On the right hand side of Fig. 2 the experimental Li-K-absorption edge as reported in [16] is shown.

Figure 3 shows the Li-K line as obtained from LiF applying 4 keV-electrons and a current density of 2000 A/m². Compared to Fig. 1 we state a shift of the Li-K-emanation line from 54.5 to 54.9 eV, the same half width of both lines, and the pronounced symmetry of the line in Figure 3. The strong intensity increase at 50 eV belongs to the Li⁺-peak [18], the peak at 50.5 eV emerges from oxidized Li (Li₂O), the peak at 53.5 eV is the contamination peak, and the origin of the peak at 57 eV is yet unknown.

Figure 4 shows the Li-K-emanation lines as obtained from pure Li (1), the as cast alloy Al₈₃Li₁₇ (2), the Al₈₃Li₁₇ alloy annealed at 250 °C/168 h (3), and
the Al$_{83}$Li$_{17}$-alloy annealed at 250 °C/336 h (4). In Table 2 the different parameters which characterize the emission lines are compiled. $m_k$ means the slope in the middle of the high energy edge. $I^\text{int}_r$ means the relative integral intensity of the main peak without the alloy peak at about 52 eV and normalized to the peak of the unannealed Al$_{83}$Li$_{17}$-alloy. The subtraction of the alloy peak was done by Lorentz-curve fitting. Compared to the Li–K–line from pure Li we state a shift of the line maximum to a lower energy by 0.8 eV. Annealing causes a shift back to higher energies. Alloying causes broadening $\Delta E_{\text{b}}$ of the emission line by 0.54 eV, and annealing causes additional broadening by 1.12 eV. By alloying the Li–K–line becomes more symmetrical. From the decrease of $I^\text{int}_r$ we learn that during annealing a charge transfer from Li to the Al valency band must occur. This seems to be the main effect during annealing.

In a first approach, Inglesfield [19] has presented theoretical calculations of the density of states in Al–Li alloys.

2. Al-Spectroscopy

The spectroscopy of the Al–K–emission lines was performed using a TAP-crystal in the X-ray spectrometer supplied with the electron microprobe. Concerning the Al–K$_{\alpha \gamma}$-lines obtained from Al–Li alloys no alteration could be observed when we compared them with the Al–K$_{\alpha \gamma}$-lines obtained from pure Al. Al–K$_\gamma$ shows a shift after alloying with Li by +0.2 up to +0.5 eV. In the case of Al–K$_{\alpha}$ the shift amounts to −0.6 eV and it is smaller in the case of Al–K$_{\alpha}$, whereas the shifts of Al–K$_{\alpha}$ and −K$_{\alpha}$ during alloying are negligible. For further details of the Al–K$_{\alpha}$-lines and satellites see [6].

Figure 5 shows the Al–K$_\gamma$-emission and absorption lines as obtained from pure Al and an Al$_{89}$Li$_{11}$-alloy before and after heat treatment, respectively.

The main maximum of the solid emission line shows the nearly vertical edge behaviour to be expected with metals. The Fermi-level according to [20] is placed at the middle of the edge ($E_F = 1559$ eV), according to [21] it is obtained by extrapolation of the edge and thus yields $E_F = 1560.45$ eV. The position of the main maximum is designed with $E_m$. The low energy end of the Al–K$_\gamma$-band was obtained according to [21] by extrapolation at $E_F = 1549.1$ eV. Apparently the main maximum shifts to smaller energies during alloying and also during heat treatment. Furthermore we observe the occurrence of an Al–K$_\gamma$-satellite at 1541 eV which is caused by alloying and which has been explained according to [22]. Heat treatment causes the relatively large shift of 4 eV towards smaller energies.

The significant parameters describing the Al–K$_\gamma$-emission spectra are compiled in Table 3. $PB_{0.5}$ means the full width at half maximum. The total band width is $\gamma_1 = E_F - E_{F_1}$ or $\gamma_2 = E_F - E_{F_2}$, respectively, $\varepsilon_1 = E_F - E_m$, $\varepsilon_2 = E_F - E_m$, and the asymmetry number $AN = (E_m - E_{\beta 0.5})/(E_{\beta 0.5} - E_m)$ · $E_{\beta 0.5}$ and $E_{\beta 0.5}$ mean the energies which correspond to the half maximum height with $E_{\beta 0.5} > E_{\beta 0.5}$.

During alloying the position of Al–K$_\gamma$ is shifted to smaller energies and the asymmetry number becomes smaller. By annealing these effects are enhanced and the band width becomes larger. A measure for the binding energy is $\varepsilon_1$ which increases during alloying and during heat treatment. Hydrogen solution, however, leads to smaller $\varepsilon_1$.

Table 2. Li–K–emission lines from pure Li, LiF, and Al–Li alloys; $^a$ (250 °C; 168 h); $^b$ (250 °C; 336 h).

<table>
<thead>
<tr>
<th></th>
<th>$E_m$ [eV]</th>
<th>$\Delta E_\alpha$ [eV]</th>
<th>$PB_{0.5}$ [eV]</th>
<th>$E_\gamma$ [eV]</th>
<th>$\Delta E_\gamma (2/8)$ [eV]</th>
<th>$m_k$ [eV]</th>
<th>$I^\text{int}_r$</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>54.5</td>
<td>3.10</td>
<td>1.64</td>
<td>55</td>
<td>0.42</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>54.9</td>
<td>3.94</td>
<td>1.58</td>
<td>55</td>
<td>0.90</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{50}$Li$</em>{50}$</td>
<td>54.0</td>
<td>3.04</td>
<td>1.79</td>
<td>55</td>
<td>0.83</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{52}$Li$</em>{48}$</td>
<td>53.3</td>
<td>4.13</td>
<td>2.39</td>
<td>54.64</td>
<td>1.59</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{83}$Li$</em>{17}$</td>
<td>53.7</td>
<td>3.61</td>
<td>2.18</td>
<td>54.69</td>
<td>0.93</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{83}$Li$</em>{17}$</td>
<td>54.0</td>
<td>4.00</td>
<td>2.63</td>
<td>55.15</td>
<td>1.20</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Al$<em>{83}$Li$</em>{17}$</td>
<td>54.1</td>
<td>4.34</td>
<td>3.30</td>
<td>55.21</td>
<td>1.18</td>
<td>0.53</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Al–K$_\gamma$-emission lines in second order. (—–) pure Al; (––) Al$_{89}$Li$_{11}$ as cast; (–•–) Al$_{89}$Li$_{11}$ annealed (250 °C/336 h). The designations $E_{F_1}$, $E_m$ etc. refer to the solid line.
Table 3. Significant parameters of Al–Kα spectra.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>E_m [eV]</th>
<th>PB [eV]</th>
<th>E_F⁻ [eV]</th>
<th>E_F⁺ [eV]</th>
<th>γ⁺ [eV]</th>
<th>γ⁻ [eV]</th>
<th>ε₁ [eV]</th>
<th>ε₂ [eV]</th>
<th>AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>1558.1</td>
<td>6.26</td>
<td>1559.6</td>
<td>1560.5</td>
<td>1549.1</td>
<td>10.5</td>
<td>11.4</td>
<td>1.53</td>
<td>2.35</td>
</tr>
<tr>
<td>AlₓLi₁₄ as cast</td>
<td>1557.0</td>
<td>6.36</td>
<td>1559.5</td>
<td>1561.2</td>
<td>1549.1</td>
<td>10.4</td>
<td>12.1</td>
<td>2.51</td>
<td>4.25</td>
</tr>
<tr>
<td>AlₓLi₁₄ (250 °C, 168h)</td>
<td>1556.7</td>
<td>6.50</td>
<td>1559.5</td>
<td>1561.0</td>
<td>1549.1</td>
<td>10.4</td>
<td>11.9</td>
<td>2.88</td>
<td>4.23</td>
</tr>
<tr>
<td>AlₓLi₁₄ (250 °C, 336 h)</td>
<td>1557.1</td>
<td>8.60</td>
<td>1560.0</td>
<td>1561.7</td>
<td>1546.7</td>
<td>13.3</td>
<td>15.0</td>
<td>2.95</td>
<td>4.63</td>
</tr>
<tr>
<td>AlₓLi₁₇ as cast</td>
<td>1557.8</td>
<td>6.05</td>
<td>1559.4</td>
<td>1560.1</td>
<td>1546.4</td>
<td>13.0</td>
<td>13.7</td>
<td>1.60</td>
<td>2.30</td>
</tr>
<tr>
<td>AlₓLi₁₇ (250 °C, 336 h)</td>
<td>1556.7</td>
<td>8.40</td>
<td>1560.1</td>
<td>1561.6</td>
<td>1546.2</td>
<td>13.9</td>
<td>15.4</td>
<td>3.38</td>
<td>4.91</td>
</tr>
<tr>
<td>AlₓLi₁₇ melt-spun</td>
<td>1557.8</td>
<td>5.74</td>
<td>1559.5</td>
<td>1560.7</td>
<td>1549.1</td>
<td>10.4</td>
<td>11.6</td>
<td>1.70</td>
<td>2.86</td>
</tr>
<tr>
<td>AlₓLi₁₇ melt-spin  and hydrogen-loaded</td>
<td>1557.8</td>
<td>6.12</td>
<td>1559.3</td>
<td>1560.7</td>
<td>1548.9</td>
<td>10.4</td>
<td>11.8</td>
<td>1.50</td>
<td>2.86</td>
</tr>
<tr>
<td>Lital B</td>
<td>1558.2</td>
<td>5.90</td>
<td>1559.8</td>
<td>1560.9</td>
<td>1549.3</td>
<td>10.5</td>
<td>11.6</td>
<td>1.65</td>
<td>2.74</td>
</tr>
<tr>
<td>B11-alloy melt-spun</td>
<td>1557.8</td>
<td>5.90</td>
<td>1559.8</td>
<td>1561.0</td>
<td>1549.0</td>
<td>10.8</td>
<td>12.0</td>
<td>2.01</td>
<td>3.17</td>
</tr>
</tbody>
</table>

3. Charge Transfer

For a number of Al–Li alloys the relative charge transfer $Δn_{3p}/n_{3p}$ according to Eqs. (2, 3) was evaluated and presented in Figure 6. Positive charge transfer means increase of the number of Al-3p-electrons and correspondingly a decrease of Li-s-electrons.

Figure 6a shows the dependence of the charge transfer from the heat treatment at 250 °C. It should be stressed that annealing for 336 h causes a considerable increase of the Al-3p-electrons especially with the alloys containing 4 and 5 weight % Li, respectively. This result is in good accordance with the results obtained by Li-spectroscopy (see above). The difference in the charge transfer between Al–Li alloys produced in different ways is shown in Figure 6b. Apparently the charge transfer has its maximum and minimum with the specimens produced by high vacuum evaporation and melt-spinning, respectively. Furthermore we recognize at the MSH-curve that loading the specimen with hydrogen causes an increase of the charge transfer at small Li-concentrations and a decrease of the charge transfer at the larger Li-content.

4. Charge Transfer and Elastic Modulus

In Fig. 7 we show the change $ΔE_{mod}$ of the elastic modulus versus the charge transfer for three samples with different Li-content, i.e. different content of the $\delta'$-phase. $ΔE_{mod}$ means the change of the elastic modulus compared to the modulus $E_{mod}^{0}$ which is composed from that of pure Al (66 GPa) and that of the solid solution (12 GPa) [2]. The
elastische Moduln der Legierungen wurden aus der Literatur abgeleitet [2, 23, 24, 25].

Die untere gerade Linie in Fig. 7 ist auf unannealtes Material zurückzuführen und bezieht sich auf den Beitrag des $\delta'$-Phasen. Die obere gerade Linie in Fig. 7 ist auf annealtes Material zurückzuführen und enthält nur das $\delta'$-Phasen, jedoch zuverlässigere Kristallelemente als Al und die Lösung.

Die Beiträge des $\delta'$-Phasen zum Elastizitätsmodul beliefen sich mit dem unbehandelten Material auf 2.8 bis 5.9 GPa und stiegen durch Annealing auf 2.5 bis 4.7 GPa.

Offensichtlich besteht ein lineares Verhältnis zwischen der Änderung $\Delta E$ des Elastizitätsmoduls und der Ladungsübertragung $\Delta n/n$ für das unbehandelte sowie das annealte Material. Die drei Pfeile in Fig. 7 zeigen die Änderung $\Delta E$ und $\Delta n/n$ in den drei Proben durch den Anheizprozess.

Daher ist der Ladungsübertrag nach Fig. 7 ein Maß für den Elastizitätsmodul einer Probe, die ihre thermische Geschichte berücksichtigt.

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