A.E.S. STUDIES OF SURFACE COMPOSITION OF Al-Sn AND Al-Cu LIQUID ALLOYS
L. Goumiri, P. Laty, J. Joud, P. Desre

To cite this version:

HAL Id: jpa-00220299
https://hal.archives-ouvertes.fr/jpa-00220299
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
A.E.S. STUDIES OF SURFACE COMPOSITION OF Al-Sn AND Al-Cu LIQUID ALLOYS

L. Goumiri, P. Laty, J.C. Joud and P. Desre

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques (associé au CNRS L.A. 29)
E.N.S.E.E.G., Domaine Universitaire, B.P. 44, 38401 Saint Martin d'Hères, France.

I - INTRODUCTION.

The application of surface thermodynamic principles to multicomponent systems readily shows that in equilibrium the surface composition may be markedly different from the bulk composition. In this way, statistical approaches have been developed\(^1\)\^-\(^5\) to evaluate surface compositions of different types of systems. Auger electron Spectroscopy (AES) provides a means to measure directly the composition of the topmost atomic layers. The purpose of this work is first to determine surface compositions of Al-Sn and Al-Cu alloys at respectively 973K and 1048K by this technique. In another way, we compare them with those predicted by the monolayer models and the surface composition obtained from Gibbs adsorption formula using experimental data of surface tension.

II - THERMODYNAMIC BASIS AND STATISTICAL APPROACHES

The Gibbs adsorption equation which results from a thermodynamic treatment of the variation of surface tension with composition, states that \( d\sigma = -\sum \Gamma_i d\mu_i \) where \( \mu_i \) and \( \Gamma_i \) are respectively the chemical potential and the surface adsorption (defined as the excess surface concentration in moles/cm\(^2\)) of the component i. Thus using monolayer representation of the surface and Gibbs-Duhem formula we deduce the surface composition from the corresponding equation \( X_A^S = X_A - \omega(1-X_A) d\sigma/d\mu_A \). For the system Al-Sn which is characterized by associations between atoms of the same type, consistent with tendency to phase separation, the surface tension isotherm present a strong and negative concentration coefficient (\( d\sigma/dX_{Sn} \))\(^\\frac{1}{X_{Sn}=0} \) in the dilute solution. Interpretations based on structural and thermodynamic aspects have been offered previously\(^6\) which correlate this thermodynamic behaviour with strong surface segregation. The solute-solvent interactions and the size effect (the difference between the surface average area occupied per atom A and B) are responsible for the strong fall in the surface tension isotherm and the surface saturation by Sn species.

In the opposite way the Al-Cu system has strong chemical heteroatomic interactions consistent with the existence of numerous stable intermediate phases observed in phase diagram. Indeed the liquids surface tension in such systems exhibit inflection points\(^7\) and strong indications make the existence of clusters in the liquid and its surface layer highly probable. Recently theoretical works have been published\(^5,8\) in an attempt to analyse these phenomena. Selected properties and parameters of Al-Sn and Al-Cu systems are shown in Table I.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Al-Cu</th>
<th>Al-Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1373</td>
<td>810 - 1343</td>
<td>862 - 500</td>
</tr>
<tr>
<td>(\omega(\text{cm}^2/\text{mole}))</td>
<td>4.3x10(^3)</td>
<td>4.68x10(^3) - 6.32x10(^3)</td>
</tr>
<tr>
<td>(\delta\omega^S(\text{Kcal}))</td>
<td>[-16.6] - [-8.67]</td>
<td>[1.93] - [3.66]</td>
</tr>
</tbody>
</table>

Table I: Selected properties and thermodynamic data for Al-Sn and Al-Cu systems.

III - EXPERIMENTAL.

III.1 - Apparatus and samples preparation:

The samples were studied in U.H.V. apparatus under a total pressure less than 10\(^{-7}\) torr at 973K. The temperature was monitored by a chromel-alumel thermocouple and the constancy was better than 6K at this temperature. Auger spec-
tra were recorded using a cylindrical mirror analyser in the following conditions: $E_p = 2 \text{keV}$, $I_{\text{target}} = 10 \mu \text{A}$, modulating tension = 2v.

Six alloys consisting of 99.999% Al and Sn both from JMC (chemically analyzed as 0.62, 0.88, 1.34, 2.52, 8.62, and 10.53 weight % Sn) and four alloys of 99.999% Al (JMC) and 99.999% Cu (Asarco) (chemically analyzed as 19.7%, 33.3%, 50.1%, 60.9% weight % Cu) were used in the present study. The cleaning treatment and the experimental apparatus used for the Al-Cu system has been described previously. For Al-Sn system, flash-heating to 873K following by 30 mn Ar bombardments ($Z_{kv}, 15 \mu \text{A/cm}^2$) are necessary to reduce C, O, S Auger peaks to the noise level. The ultimate aim of eliminating all contaminants was never quite achieved. Data were collected only after measurements showed that C and S Auger peaks were sufficiently reduced.

III.2 - Normalization of Auger spectra:
A calibration of Auger measurements is necessary for quantitative interpretations. The spectra of the pure elements Sn and Al were first examined at 973K under identical experimental conditions in order to estimate the relative sensitivity factor. The Auger spectra of pure liquid Al and Sn were found to be identical with those obtained in solid state. Thus, aluminium exhibits only a strong peak, located at 68 ev, which is associated with an L$_{2,3}$VV Auger transition. For Sn specimen the important doublet located at 430-437 ev is obtained. So it was decided to select for calibration the peak to peak intensity ratio of the aluminium 68 ev and the tin 430 ev transitions. Then changes in this intensity ratio are used to estimate surface composition of liquid alloys whose typical spectrum is given in Fig. 1.

For Al-Cu system, such experimental measurements of pure standards were impossible (due to the vapor pressure of Cu at melting point). So as a rough estimate of the sensitivity factor; peak to peak intensity ratio of aluminium 68 ev and copper 920 ev transitions is selected from the Handbook of solid standard Auger spectra.

Fig. 1 Typical spectrum of Al-Sn alloy at 973K.

IV - RESULTS AND DISCUSSION.-

IV.1 - Al-Sn system:
We suppose that tin atoms (surface active species) cover a fraction $X$ of a practically pure aluminium substrate. The quantification is considered with reference to spectra from bulk standards. Data on Inelastic mean free path (IMFP) in solids and backscattering correction have been used to determine the composition of the surface atom layer. Hence according to Seah and Co the intensities of the characteristic transition are given by:

\[
I_{\text{Sn}} = I_{\text{Sn}}^0 X (1 + r_{\text{Al}}) \left(1 - \exp \left(-\frac{m}{0.74 \lambda_{\text{Al}}} \right) \right)
\]

and

\[
I_{\text{Al}} = I_{\text{Al}}^0 \left(1 - X + X \exp \left(-\frac{m}{0.74 \lambda_{\text{Al}}} \right) \right)
\]

where $I_{\text{Al}}^0$ and $I_{\text{Sn}}^0$ are the signals from the pure bulk standards, $r_{\text{Al}}$ and $\lambda$ are respectively the backscattering contribution and the IMFP (in monolayers units) of Auger electron, $m$ is the number of monolayer for-
Because of the repulsion of nearest neighbour interactions (Al-Sn bonds not preferred) and the excess size solute atoms Sn, the surface is considerably richer in this element than the bulk as shown in Fig. 2. Furthermore the plotted curves (statistical model and Gibbs treatment) are in good qualitative agreement with the Auger data obtained from a monolayer model (m = 1).

Fig. 2: Tin surface enrichment deduced from statistical model, Gibbs treatment and Auger measurements assuming m = 1, 2 or 5 layers for Al-Sn system.

IV.2 - AI₂CU SYSTEM:

Here we treat ordering alloys with the same method and within the same approximations. Results presented in table II, reveal surface enrichment in Al obtained from statistical model, Gibbs adsorption relation and Auger measurements assuming m = 2, 3 and 10 layers. We observe a qualitative agreement between the different estimations. Nevertheless a weak variation of surface composition with number of monolayers is deduced for Al-Cu Auger estimation comparatively to Al-Sn system. This last point is mainly due to the fact that in Al-Cu system the solvent is also the segregating element.

<table>
<thead>
<tr>
<th>Bulk molar fraction</th>
<th>Surface molar fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X'_A )</td>
<td>( X'_{Al} ) Auger</td>
</tr>
<tr>
<td>m = 2</td>
<td>m = 3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>0.602</td>
<td>0.93</td>
</tr>
<tr>
<td>0.702</td>
<td>0.98</td>
</tr>
<tr>
<td>0.823</td>
<td>0.98</td>
</tr>
<tr>
<td>0.903</td>
<td>0.98</td>
</tr>
</tbody>
</table>

V - CONCLUSION.-

In this work A.E.S. measurements have been performed on liquid Al-Sn and Al-Cu alloys at respectively 973K and 1048K. The corresponding surface compositions are deduced from classical expression of Auger intensity. Compositions are calculated assuming various surface layer thickness and compared with thermodynamical estimations (statistical models or Gibbs treatments of surface tension data). For both systems which exhibit opposite thermodynamic behaviours we obtained a fairly good agreement between the different estimations of surface enrichment. In particular we can emphasize the direct verification by A.E.S. of Gibbs adsorption equation. In addition results indicate a localized segregation for studied systems at thermodynamical equilibrium.

REFERENCES
2 - I. PRIGOGINE, the molecular theory of solutions, North Holland, Amsterdam (1957).
8 - L. GOUMIRI, J.C. JOUD et P. DESRE, to be published.