Zirconium Solubility in Aluminum Alloys

C. Sigli

Alcan, Centre de Recherches de Voreppe, BP27 - 38341 Voreppe Cedex, France

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Abstract

It has been reported in the literature that major alloying elements can have a very strong effect on the precipitation behavior of Al3Zr. This paper proposes a model that describes these effects: the strong zirconium-aluminum interaction within the solid solution induces large variation of the zirconium solubility from one alloy to another. The detail of these variations also depends on all the other interactions between the elements in solid solution. The interactions have been evaluated by a thermodynamic fitting procedure of phase diagrams or by first principle ab-initio calculations.

1. Introduction

Zirconium is added to aluminum alloys in order to prevent recrystallization. It can precipitate in two forms having the same Al3Zr chemistry but different structure: D023 and L12 (see Figure 1). The stable structure is D023; it forms semi coherent or incoherent precipitates in the aluminum matrix. The metastable L12 structure is found commonly in 7xxx alloys. After homogenizing it is fully coherent within the aluminum solid solution and has a dense and fine distribution. The L12 phase is responsible for the effectiveness of Zr to control recrystallization in aluminum alloys.

The solubility limits of the stable D023 phase and of the metastable L12 phase are presented in Figure 2. The solvus of the stable phase can be found in the compilation of Phillips [1]. The solvus of the metastable L12 phase is less well known. At 660°C, values of 1wt% and 0.7 wt% have been calculated by, respectively, Saunders [2] and Murray [3]. More recently, Clouet [4] has used an ab initio approach and found the metastable solubility limit to be 0.87 wt% at 660°C. Clouet’s metastable solvus has been adopted in this study and is presented in Figure 2.

A typical 7xxx homogenizing temperature is 480°C. Considering an alloy containing 0.1wt% Zr and the concentration gradients generated after casting, the L12-Al3Zr precipitate free zones should occupy at least 70% of the volume (see Figure3). This prediction is in contradiction with observations on 7xxx alloys that indicate that the PFZ fraction lies in a 20 - 30% range. The objective of this paper is to show that the zirconium solvus (stable and metastable) is very sensitive to Li, Zn, Cu, Mg... additions and to propose a model that describes this effect. A prediction of the metastable zirconium solvus is then presented for some industrial alloys.
2. Generalized Solubility Product Concept

The general expression of the molar Gibbs free energy of a solid solution in a regular solution model is given by the following expression:

$$G^\alpha = \sum \sum x_i^{\alpha} x_j^{\beta} \Omega_{ij}(T) + RT \sum x_i^{\alpha} \ln \left( x_i^{\alpha} \right)$$

(1)

where the pure elements in the fcc structure are taken as reference and where the following notations have been used:

- $x_i^{\alpha}$ atomic concentration of element $i$ in the aluminum solid solution,
- $T$ temperature (in Kelvin),
- $R$ gas constant,
- $\Omega_{ij}(T)$ fcc solution interaction parameter between elements $i$ and $j$; it may be written as $\Omega_{ij}(T) = A_{ij} + B_{ij} T$ with $A_{ij}$ and $B_{ij}$ constant.

The chemical potentials of elements are calculated using the general equation:
\[
\mu_i^\alpha = \frac{\partial G^\alpha}{\partial x_i^\alpha} + G^\alpha - \sum_j x_j^\alpha \frac{\partial G^\alpha}{\partial x_j^\alpha}
\]  \hspace{1cm} (2)

For the solid solution, Eq.2 becomes:

\[
\mu_i^\alpha = RT \ln(x_i^\alpha) + \sum \Omega_{ij}(T)x_j^\alpha - \sum \sum \Omega_{jk}(T)x_j^\alpha x_k^\alpha
\]  \hspace{1cm} (3)

The Gibbs free energy for a compound P is expressed by the simple equation in terms of its formation enthalpy, \( \Delta H_f^P \), and its formation entropy, \( \Delta S_f^P \):

\[
G_r = \sum_i x_i^P \mu_i^P = \Delta H_f^P - T \Delta S_f^P
\]  \hspace{1cm} (4)

The aluminum solid solution is in equilibrium with a stoichiometric compound P when the chemical potentials of each element in the solid solution and in the compound are equal. The following expression is then deduced:

\[
\sum x_i^P \mu_i^P = \sum x_i^P \left( RT \ln(x_i^\alpha) + \sum \Omega_{ij}(T)x_j^\alpha - \sum \sum \Omega_{jk}(T)x_j^\alpha x_k^\alpha \right) = \Delta H_f^P - T \Delta S_f^P
\]  \hspace{1cm} (5.a)

The generalized expression for the solubility product is then obtained:

\[
\prod_{i} \left( x_i^\alpha \right)^{x_i^P} = e^{\left[ \frac{\Delta H_f^P - T \Delta S_f^P - \sum \sum \Omega_{ij}(T)x_j^\alpha x_k^\alpha + \sum \sum \Omega_{jkl}(T)x_j^\alpha x_k^\alpha x_l^\alpha}{RT} \right]}
\]  \hspace{1cm} (5.b)

For an ideal solution, \( \Omega_{ij}(T) = 0 \) and Eq.5.b simplifies to the classical expression of the solubility product, \( K_p^\alpha \):

\[
\prod_i \left( x_i^\alpha \right)^{x_i^P} = K_p(T) = e^{\left[ \frac{\Delta H_f^P - T \Delta S_f^P}{RT} \right]}
\]  \hspace{1cm} (6.a)

For a sufficiently dilute regular solid solution, \( x_i^\alpha \approx 1 \), \( x_i^P \approx 0 \) and Eq 5.b simplifies to:

\[
\prod_i \left( x_i^\alpha \right)^{x_i^P} = K_p(T) = e^{\left[ \frac{\Delta H_f^P - \sum x_i^P \Delta H_{Al}^P - \sum \sum x_i^P \Delta H_{Al}^P}{RT} \right]}
\]  \hspace{1cm} (6.b)

It has been shown that the classical solubility product expression (Eq 6.b) is accurate enough for numerous precipitates in aluminum; furthermore a general algorithm has been proposed to handle phase competition and complex phase equilibria [5]. However, when the solute-aluminum interactions are very strong the classical expression is not accurate enough and the generalized expression (Eq 5.b) must be used.

This applies in particular for titanium, scandium and zirconium. In this paper, the effect for zirconium is illustrated.

### 3. Application of the Generalized Solubility Product Concept to Zirconium

In order to predict the solubility of zirconium, it is necessary to know the formation enthalpy and entropy for Al\(_3\)Zr as well as all interaction parameters \( \Omega_{ij} \) (see equation Eq
5.b). Values for the formation entropy, enthalpy, \( \Omega_{\text{Al-Sc}} \) and \( \Omega_{\text{Al-Zr}} \) are taken from the ab-initio calculations of Clouet et al [4, 6]. The other interaction parameters are evaluated from the sub-regular parameters of the COST 507 database [7] except for \( \Omega_{\text{Zr-Zn}} \) which has not been evaluated in [7] and which is taken from our internal database.

The values of the most important interaction parameters are illustrated in Figure 4. As can be seen, scandium, titanium and zirconium have a very strong attractive interaction with aluminum whereas Mg and Li have a strong repulsive interaction with Zr.

If the major alloying elements are assumed to leave unchanged the free energy of Al\(_3\)Zr (D\(_{023}\) or L\(_{12}\)), it is possible to compute their effect on the metastable zirconium solubility limit (see Table 1). As can be seen, the more positive the solute-zirconium interaction, the lower the zirconium solubility limit. This can be easily understood: while adding Li, Mg, Cu, Zn... to the aluminum solid solution, the strong Al-Zr bonds within the fcc solid solution are replaced by weaker Li-Zr, Mg-Zr... bonds resulting in an increase of the aluminum solid solution free energy and therefore in a reduction of the zirconium solubility (stable or metastable). The silicon-zirconium interaction is larger than the aluminum-zirconium one [7, 8]. We have assumed however that this effect is compensated by the tendency for silicon to go into Al\(_3\)Zr forming (Al, Si)\(_3\)Zr [9]. Obviously, a more detailed study for silicon will be needed; it is beyond the scope of this paper. More generally, the model must be extended when solute elements (such as Si, Li, Sc ..) present substantial solubility in Al\(_3\)Zr.

![Figure 4: Most important interaction parameters (at 480°) used to predict the solubility of zirconium in aluminum alloys.](image-url)
Table 1: Effect of a 2wt% addition of Zn or Mg or Li or Cu on the metastable zirconium solubility limit.

<table>
<thead>
<tr>
<th>Case considered</th>
<th>Metastable Zr solubility limit at 480°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary Al-Zr</td>
<td>0.147</td>
</tr>
<tr>
<td>+ 2 wt% Zn</td>
<td>0.134</td>
</tr>
<tr>
<td>+ 2 wt% Cu</td>
<td>0.122</td>
</tr>
<tr>
<td>+ 2 wt% Mg</td>
<td>0.087</td>
</tr>
<tr>
<td>+ 2 wt% Li</td>
<td>0.011</td>
</tr>
</tbody>
</table>

The combined effect of solute elements on the metastable Zr solubility is illustrated in Fig.5. A large effect is observed with Li containing alloys where the solubility limit is reduced by a factor 10; a significant effect is also seen with high strength 7xxx alloys.

![Figure 5: Metastable Zr solubility limit for different aluminum alloys.](image)

Table 2: Alloy composition (wt%) in the calculation presented in Fig.5

<table>
<thead>
<tr>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Li</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>AlZr binaire</td>
</tr>
<tr>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
<td>0.7 – 1.4</td>
<td>5.5</td>
<td>0</td>
<td>7108</td>
</tr>
<tr>
<td>&lt; 0.12</td>
<td>&lt; 0.15</td>
<td>2.0 – 2.6</td>
<td>&lt; 0.10</td>
<td>1.9 – 2.6</td>
<td>5.7 – 6.7</td>
<td>0</td>
<td>7050</td>
</tr>
<tr>
<td>&lt; 0.12</td>
<td>&lt; 0.15</td>
<td>1.4 - 2.1</td>
<td>&lt; 0.20</td>
<td>1.8 – 2.7</td>
<td>7.5 - 8.7</td>
<td>0</td>
<td>7449</td>
</tr>
<tr>
<td>&lt; 0.12</td>
<td>&lt; 0.15</td>
<td>3.2 - 3.8</td>
<td>&lt; 0.35</td>
<td>0.25 - 0.8</td>
<td>&lt; 0.35</td>
<td>0.8 - 1.3</td>
<td>2098</td>
</tr>
<tr>
<td>&lt; 0.12</td>
<td>&lt; 0.15</td>
<td>2.5 - 3.3</td>
<td>&lt; 0.35</td>
<td>0.25 - 0.8</td>
<td>&lt; 0.35</td>
<td>1.4 - 2.1</td>
<td>2196</td>
</tr>
</tbody>
</table>

The predictions for 7050 are compared with Murray's predictions reported in [10]; as shown in Figure 6 both sets of predictions agree well.

4. Conclusions and Perspectives

The metastable zirconium solubility limit corresponding to Al₃Zr in the L1₂ structure must be considered in order to evaluate the ability of zirconium to block recrystallization. This metastable solubility limit is strongly influenced by major alloying additions such as Zn, Cu, Mg, Li.... We can rank the elements with respect to their effect as (increasing effect): Zn<Cu<Mg<Li. The effect of Si still remains to be evaluated in detail; in addition the model must be extended to non-stoichiometric precipitates. The same phenomenon, i.e. a large variation of solubility with major alloying element content, is occurring for Sc, Cr and Ti and can be treated with the same formalism.
Figure 6: Metastable Zr solubility limit for at 7050 alloy: comparison between present work and the prediction of Murray as reported by Robson [10].

References