Zirconium Solubility in Aluminum Alloys

C. Sigli

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

Keywords: Al3Zr, solubility, solvus, phase diagram, zirconium, 7050, 7108, 7449, 2196, 2098

Abstract

It has been reported in the literature that major alloying elements can have a very strong effect on the precipitation behavior of AI_3Zr . 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 Al_3Zr chemistry but different structure: $D0_{23}$ and $L1_2$ (see Figure 1). The stable structure is $D0_{23}$; it forms semi coherent or incoherent precipitates in the aluminum matrix. The metastable $L1_2$ 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 $L1_2$ phase is responsible for the effectiveness of Zr to control recrystallization in aluminum alloys.

The solubility limits of the stable $D0_{23}$ phase and of the metastable $L1_2$ 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 $L1_2$ 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.



Figure 1: DO_{23} (left) and $L1_2$ (right) structures for AI_3Zr .

Figure 2: Stable [1] and metastable [4] Al-Zr binary phase diagram.



Figure 3: Predicted concentration gradient within dendrites in an as-cast binary alloy containing 0.1 wt% Zr (1D model) compared with the metastable zirconium solubility

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:

$$G^{\alpha} = \sum_{i} \sum_{j,j>i} x_{i}^{\alpha} x_{j}^{\alpha} \Omega_{ij}(T) + RT \sum_{i} x_{i}^{\alpha} \ln\left(x_{i}^{\alpha}\right)$$
(1)

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

 x_i^{α} 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 $\Omega_{ii}(T)=A_{ii}+B_{ii}T$ with Aij and Bij constant.

The chemical potentials of elements are calculated using the general equation:

$$\mu_i^{\alpha} = \frac{\partial G^{\alpha}}{\partial x_i^{\alpha}} + G^{\alpha} - \sum_j x_j^{\alpha} \frac{\partial G^{\alpha}}{\partial x_j^{\alpha}}$$
(2)

For the solid solution, Eq.2 becomes:

$$\mu_i^{\alpha} = RT \ln\left(x_i^{\alpha}\right) + \sum_{j, j \neq i} \Omega_{ij}(T) x_j^{\alpha} - \sum_j \sum_{k>j} \Omega_{jk}(T) x_j^{\alpha} x_k^{\alpha}$$
(3)

The Gibbs free energy for a compound P is expressed by the simple equation in terms of its formation enthalpy, ΔH_f^P , and its formation entropy, ΔS_f^P :

$$G_{p} = \sum_{i} x_{i}^{p} \mu_{i}^{p} = \Delta H_{f}^{p} - T \Delta S_{f}^{p}$$
(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:

$$\sum_{i} x_{i}^{P} \mu_{i}^{P} = \sum_{i} x_{i}^{P} \left\{ RT \ln\left(x_{i}^{\alpha}\right) + \sum_{j, j \neq i} \Omega_{ij}(T) x_{j}^{\alpha} - \sum_{j} \sum_{k>j} \Omega_{jk}(T) x_{j}^{\alpha} x_{k}^{\alpha} \right\} = \Delta H_{f}^{P} - T \Delta S_{f}^{P}$$
(5.a)

The generalized expression for the solubility product is then obtained:

$$\prod_{i} \left(x_{i}^{\alpha} \right)^{x_{i}^{p}} = e^{\left\{ \frac{\Delta H_{f}^{p} - T\Delta S_{f}^{p} - \sum_{i \ j, j \neq i} \Omega_{ij}(T) x_{j}^{\alpha} x_{i}^{p} + \sum_{j \ k > j} \Omega_{jk}(T) x_{j}^{\alpha} x_{k}^{\alpha} \right\}}{RT} \right\}}$$
(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:

$$\prod_{i} \left(x_{i}^{\alpha} \right)^{x_{i}^{p}} = K_{p}(T) = e^{\left\{ \frac{\Delta H_{f}^{p} - T \Delta S_{f}^{p}}{RT} \right\}}$$
(6.a)

For a sufficiently dilute regular solid solution, $x_{Al}^{\alpha} \approx 1, x_{i,i\neq Al}^{\alpha} \approx 0$ and Eq 5.b simplifies to:

$$\prod_{i} \left(x_{i}^{\alpha} \right)^{x_{i}^{p}} = K_{p}(T) = e^{\left\{ \underbrace{\left(\Delta H_{f}^{p} - \sum_{i \neq Al} x_{i}^{p} A_{Al-i} \right) - T\left(\Delta S_{f}^{p} + \sum_{i \neq Al} x_{i}^{p} B_{Al-i} \right) \right\}}_{RT}$$
(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 Al₃Zr as well as all interaction parameters Ω_{ij} (see equation Eq

5.b). Values for the formation entropy, enthalpy, Ω_{AI-Sc} and Ω_{AI-Zr} are taken from the abinitio 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 Ω_{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.



Figure 4: Most important interaction parameters (at 480°) used to predict the solubility of zirconium in aluminum alloys.

If the major alloying elements are assumed to leave unchanged the free energy of Al_3Zr (DO_{23} or $L1_2$), 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_3Zr forming (Al,Si)₃Zr [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_3Zr .

Table 1: Effect of a 2wt% addition of Zn or Mg or Li or Cu on the metastable zirconium solubility limit.

Case considered	Metastable Zr solubility limit at 480°C (wt%)
Binary Al-Zr	0.147
+ 2 wt% Zn	0.134
+ 2 wt% Cu	0.122
+ 2 wt% Mg	0.087
+ 2 wt% Li	0.011

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.

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

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

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

- H. W. L. Phillips, Annotated Equilibrium Diagrams of Some Aluminium Alloy Systems, vol. 25: Institute of Metals, 1959. [1]
- [2] N. Saunders, "Calculated Stable and Metastable Phase Equilibria in Al-Li-Zr Alloys," Z. Metallkd., vol. 80, pp. 894, 1989.
- J. Murray, A. Peruzzi, and J. P. Abriata, "The Al-Zr (Aluminum-Zirconium) System," Journal of Phase [3] *Equilibria*, vol. 13, pp. 277, 1992. E. Clouet, M. Nastar, C. Sigli, and J. M. Sanchez, "First Principle Study of the Solubility of Zr in Al,"
- [4] Phys. Rev. B, vol. 65, 2002.
- C. Sigli, L. Maenner, C. Sztur, and R. Shahani, "Phase Diagram, Solidification and Heat Treatment [5] of Aluminum Alloys," presented at Aluminum Alloys: Their Physical and Mechanical Properties (ICAA6), Toyohashi, Japan, 1998. E. Clouet, M. Nastar, and C. Sigli, "Nucleation of Al₃Zr and Al₃Sc in aluminum alloys: from kinetic Monte Carlo simulations to classical nucleation theory," *To be published in Phys. Rev. B*, 2004. I. Ansara, A. T. Dinsdale, and M. H. Rand, *Thermochemical database for light metal alloys*, vol. 1-3:
- [6]
- [7] COST 507, European Commission, 1998.
- H. Bakker, Enthalpies in Alloys, Miedema's Semi-Empirical Model: Trans Tech Publications LTD, [8] 1998.
- [9] T. Sato, A. Kamio, and G. W. Lorimer, "Effects of Si and Ti additions on the Nucleation and Phase Stability of the L1₂ type Al₃Zr Phase in Al-Zr alloys," presented at Aluminum Alloys: Their Physical and Mechanical Properties (ICAA5), Grenoble, France, 1996. J. D. Robson and P. B. Prangnell, "Al₃Zr Dispersoid Precipitation in Multicomponent Aluminum
- [10] Alloys," Mat. Science and Eng., vol. A352, pp. 240, 2003.