SOLUBILITY LIMIT OF MN AND SI IN AL-MN-SI AT 550°C

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Abstract

The mutual solid solubility of Mn and Si in aluminum has been measured at 550°C in Al-Mn-Si ternary alloys using the thermo-electrical power (TEP) and the butanol dissolution (SIBUT) techniques. The results are compared to published data. They will be used to optimize the free energies of the COST 507 phase diagram database for light alloy development.

Introduction

Phase diagrams are a very useful tool to solve some of the metallurgical problems arising during the transformation schedule of industrial alloys. They allow, for example, the analysis of solidification paths during casting and/or the optimization of thermal treatments [1,2].

An industrial alloy contains, in general, at least four principal solute elements. The computer aided assessment of the related quinary phase diagram builds on the previous assessment of five unary, ten binary, ten ternary and five quaternary systems. Such an assessment represents a formidable task which is too expensive for a single company or country. However, it becomes feasible on a European scale. Consequently, the major European aluminum companies, together with universities, have joined the European COST 507 (COoperation in Science & Technology) action on light alloy phase diagrams. The objective is to calculate the phase diagram of Al-Mg-Mn-Fe-Si alloys which, today, represent about 90% of the aluminum production.

In this context, Pechiney CRV and SINTEF have launched a collaboration to carry out quantitative characterization of equilibrium microstructures. In this paper, we will present measurements of the Al-Mn and Al-Mn-Si solvus at 550°C.

Material Preparation Procedure

Ternary Al-Mn-Si alloys were prepared from 99.99 purity aluminum and cast in cylindrical steel moulds (diameter: 40mm, height: 150mm). After cooling, two rectangular 15x30x100mm samples were taken from the center of the cast material and then cold rolled from 15mm to 4mm. A TEP (thermo-electric power) sample (4x4x100 mm) was taken out of the cold-rolled alloy and placed, together with the two rolled samples, in a furnace at 550°C±1°C. The TEP sample was removed from the furnace at intervals and a TEP measurement was taken. When the TEP reading reached a stable value (i.e. equilibrium was reached), the sample were characterized.

Experimental Techniques

Two different experimental techniques have been employed to determine the solubility of Mn and Si in the Al-Mn-Si system. These two techniques are discussed below.

TEP Method

The TEP technique [3,4] consists of measuring, at room temperature, the thermo-electric power (TEP) of samples relative to pure aluminum. The TEP measurement, ΔS, is defined by the relation:

$$\Delta S = \frac{\Delta V}{\Delta T} \quad (10^{-8}\ V/K) \tag{1}$$

where ΔV is the voltage generated by the Seebeck effect and ΔT is the temperature difference maintained between the two ends of a flat sample. Typically, ΔT is of the order of 10-20°C. The TEP method provides similar information to that of resistivity measurements; however TEP requires neither a specific sample geometry nor a very clean sample surface and is thus a more convenient technique.

For alloys which do not contain G.P. zones, TEP measurements depend on the matrix composition of solute atoms. If the phonon-drag contribution is neglected, the relation between ΔS and the matrix composition of solute atoms can be described by the Gorter and Nordheim rule [4]:

$$\Delta S = \frac{\sum_i \Delta S_i\, \rho_i\, c_i}{\rho_o + \sum_i \rho_i\, c_i} \tag{2}$$

where ρ_0 is the resistivity of pure aluminum (2.65 $\mu\Omega$.cm), ρ_i and ΔS_i are the specific contribution of solute "i" to, respectively, the resistivity and the thermo-electric power and c_i is the matrix concentration of solute "i" (in wt %). Values of ρ_i and ΔS_i can be taken from Ref[4]. Qualitatively, manganese has a strong negative effect on ΔS, iron has a strong negative effect but has a very limited solubility in aluminum and silicon has a very small negative effect.

In this study, TEP measurements have been used to deduce the manganese matrix concentration. This requires an estimate of the iron and silicon matrix concentrations which are not known a priori. We therefore assume that the iron and silicon levels lie between zero and the solubility limit of the binary alloy at the temperature of interest (this gives a confidence interval for the manganese concentration).

SIBUT Method

The second technique, the SIBUT dissolution method, has been developed by C. J. Simensen and co-workers [5, 6]. The principle of this technique is that butanol reacts with aluminum forming butoxide. When the technique is correctly executed, the result is the dissolution of the aluminum matrix while the intermetallic particles lodged in the matrix remain unaffected. The resulting slurry is then filtered leaving the particles on the filter and the butanol which now contains all the atoms which were previously in solid solution. An important limitation, at this stage, is the pore size of the filters used. Commonly a pore size of 0.2μm is used, meaning that any solvus determinations using this technique demand homogenization of the sample for a period sufficient to eliminate small dispersoids (<0.2 μm) by particle coarsening.

Experiments, however, are underway to develop equipment with nanofilters. Furthermore, small dispersoids can be analyzed by using the related butanol extraction method [7].

Another strength of this technique is the size of the sample. In this investigation samples of 500mg were dissolved. Local variations in matrix composition do not therefore affect the measurements as opposed to, for example, microprobe studies. Also the technique is very useful for the analysis of trace elements in aluminum alloys. The instrument described by Simensen and Spjelkavik[6] gives excellent results. However, a more modern version has been developed which dissolves the sample much more rapidly.

After dissolution the particles may be analyzed using TEM, X-ray diffraction or fluorescence, microprobe etc., without the interference from the matrix observed using conventional methods. The butanol solution may be analyzed using Inductive Coupled Plasma-Atomic Emission Spectrometry (ICP) or Atomic Absorption Spectrometry (AAS), giving a standard deviation of typically 4% in relative terms using our equipment.

Al-Mn Solvus at 550°C

A large scatter between measurements can be found in the literature concerning the solubility limit of manganese in aluminum (see for example the literature review of A.J. McAlister and J.L. Murray [8]). At 550°C, the measurements range from 0.2 to 0.65 wt %. There are two main causes having opposite effects that explain the experimental scatter. Firstly the iron impurity level has a strong effect on the manganese solubility; the concentration of Fe must consequently be maintained as low as possible. Secondly, the kinetics of manganese precipitation are very slow [9]; it is therefore necessary to check that the equilibrium state has been reached. The experimental procedure described above has been applied at 550°C to a binary Al-1wt% Mn alloy (with 30 ppm Fe and less than 50 ppm Si). The approach towards equilibrium is illustrated in Fig.1. As already mentioned, the precipitation kinetics are very slow: after 6000 hours (8 months) the alloy has barely reached equilibrium. At present, our best estimate of the manganese solubility limit at 550°C is 0.43± 0.02 wt %. As will be seen in the next section, the results obtained at 550°C for Al-Mn-Si indicate that this value is reasonable.

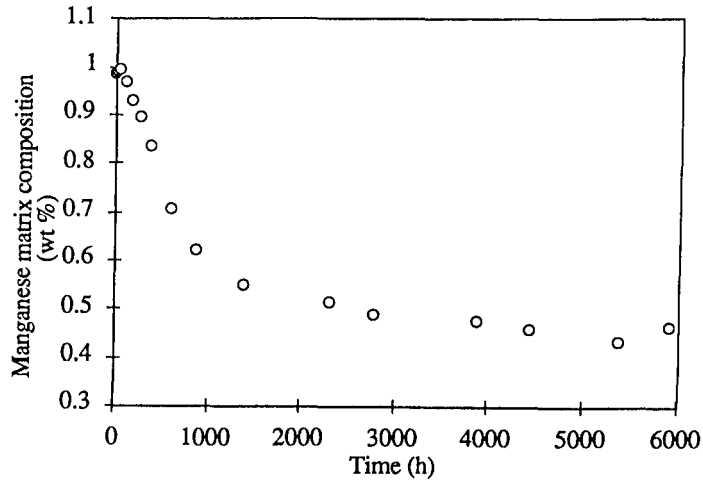

Figure 1: Evolution of the manganese matrix composition of Al -1wt% Mn at 550°C (accuracy of the measurements ±0.02 wt %).

Al-Mn-Si Solvus at 550°C

Ternary Al-Mn-Si alloys have been held at 550°C for up to 650 hours. The silicon strongly accelerates the manganese precipitation and TEP measurements indicate that equilibrium has been reached for all samples. The results are presented in Table I. A good overall agreement is obtained between TEP and SIBUT measurements of the manganese solubility. The experimental solvus has been obtained by using the TEP manganese solubility and the corresponding SIBUT silicon solubility; it is illustrated in Fig.2 together with the phase diagram from Phillips [10].

Table I: The Al-Mn-Si solvus at 550°C: results of the TEP and SIBUT method

Chemical Analysis Composition of the Alloy			Elements in Solid Solution			Phases in equilibrium
			TEP	SIBUT		
Mn (wt%) ±2% relative	Si (wt%) ±6% relative	Fe (ppm) ±2ppm absolute	Mn (wt%) ±0.02wt% absolute	Mn (wt%) ±4% relative	Si (wt%) ±4% relative	
1.00	0.98	25	0.10	0.10	0.40	(Al)+α-AlMnSi
1.00	3.97	28	0.05	-	(1.36)*	(Al)+α-AlMnSi+Si
1.00	5.90	41	0.05	-	-	(Al)+α-AlMnSi+Si
1.98	0.18	24	0.43	0.41	0.04	(Al)+α-AlMnSi+Al_6Mn
1.99	0.75	19	0.25	0.19	0.10	(Al)+α-AlMnSi
1.99	0.96	22	0.16	0.14	0.20	(Al)+α-AlMnSi
2.46	0.49	20	0.43	-	-	(Al)+α-AlMnSi+Al_6Mn

*: Some experimental problems have been encountered with this sample; the silicon solubility has been assumed to be that of the binary Al-Si system at 550°C [10,11].

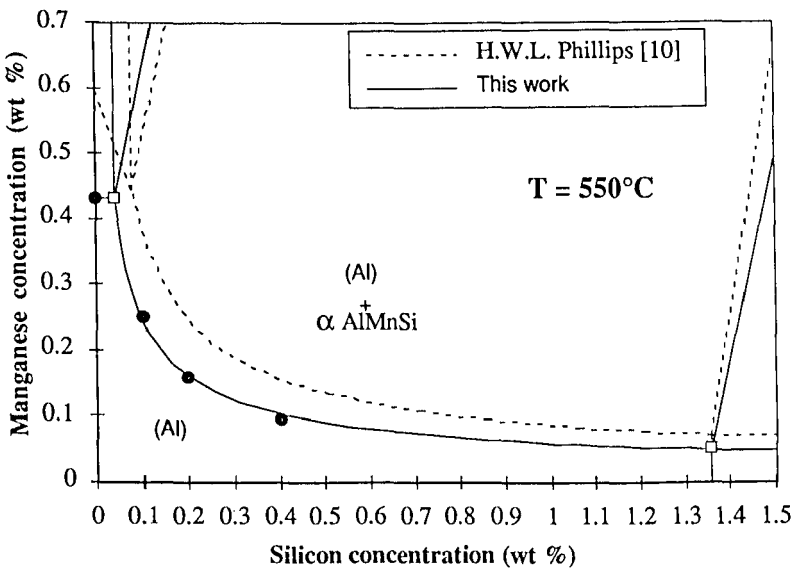

Figure 2: Comparison between the solvus from Phillips[10] and the present work.

Discussion of the Experimental Results

The Al_6Mn phase is known to dissolve a negligible amount of Silicon [10,12]. Thermodynamic calculations show that, in such a case, the manganese matrix concentration of the (Al)+Al_6Mn solvus should be approximately equal to the matrix concentration of the binary Al-Mn alloy (i.e. the solvus should be horizontal in Fig.2). In this respect, the ternary Al-Mn-Si phase diagram from Ref[10] is not compatible with the binary Al-Mn diagram from the same reference. The solubility limits measured in this work for the binary Al-Mn and the ternary Al-Mn-Si alloys are compatible. On the whole, our results indicate a lower solubility limit than that of Phillips [10].

Conclusions

This study presents a revised isothermal section of the Al-Mn-Si phase diagram at 550°C in the Al-rich corner. A new manganese solubility has been measured at 550°C in the binary Al-Mn system (0.43±0.02 wt%) which is compatible with the ternary solubility limits.

At present, similar investigations are underway in the Al-Mn-Fe system using the same experimental techniques.

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