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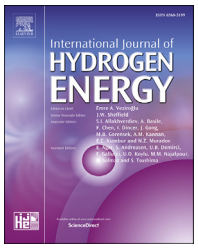

Study of the ternary system Al–H–*RE* (*RE* = Er, La and Y) in liquid state

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ABSTRACT

Hydrogen is the only gas able to dissolve in aluminum. The solubility **S** of hydrogen in Al obeys the Sieverts' law and **S** is much larger in the liquid phase (above 660.4 °C) than in the solid one. This might lead to the formation of porosity during aluminum casting. In the present work, the ternary system Al–H–*RE* (*RE* = Er, La, Y) is investigated. The equilibria between the different phases are determined in the presence of liquid Al, *RE* and H_2 gas by both experimental measurements and phase diagram calculations. The possible formation of metallic hydrides and the change in the hydrogen solubility **S** are discussed regarding pressure and temperature determining the thermodynamics of the system.

Introduction

Aluminum is a metal widely used in metallurgy for various applications in transportation, packaging or building. Aluminum alone exhibits rather poor mechanical properties but they can be significantly improved by alloying Al with other elements like Li, Cu, Mn, Mg or Si.

Hydrogen is the only gas soluble in aluminum and its alloys. The quantity of hydrogen absorbed by solubilization in the liquid phase in an aluminum alloy remains low, of the order of 10^{-4} at.% H. It can dissolve in both the solid and the liquid phase following the Sieverts' law. The solubility in the solid phase is systematically lower than in the liquid phase. Therefore, upon solidification, a large fraction of the atomic hydrogen dissolved in the liquid phase recombines in gaseous form in the solid, generating bubbles in the alloys. The presence of alloying elements affects the solubility and favors the presence of structural defects, which increases the solubility. In the liquid phase, it is noted that elements which have a strong affinity with hydrogen (Mg, Ti, Li, etc.) tend to increase the solubility [1]. On the contrary alloying elements such as Si, Cu or Fe which form unstable hydrides decrease the solubility of hydrogen in the alloy [1].

Rare Earths (*RE*) are known to form very stable hydrides in the range 2–3 H per metal [2,3]. A study of the binary diagrams and enthalpies of formation shows that several rare earths like Er, La or Y form solid hydrides at temperatures above 660 °C, *i.e.* the temperature of aluminum solidification. The addition of a 4*f* element in aluminum might therefore have two effects: a change in the hydrogen solubility **S** in the aluminum-hydrogen solution and/or the precipitation of rare earth hydride in the liquid phase. Such phenomenon has been already reported by Chiotti and Woerner [4] for magnesium and Mg-Zn alloys for which they observed precipitation of hydrides in the temperature range 500–900 °C from the following added solutes Ca, Y and Th. Similarly, Smithells [5] reported precipitation of ZrH_2 in liquid magnesium.

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In the present work, aluminum alloyed with small quantities of Rare Earths (*RE* = Er, La, Y) is investigated in liquid state in the presence of hydrogen gas. Solubility measurements are made and compared to ternary phase diagram calculations. Effects of the *RE* addition on the Al sorption properties are discussed.

Experimental

The alloys were obtained by induction melting of the pure elements (Al, La 5N; Y 3N; Er 4N purities) under vacuum in a water-cooled copper crucible under secondary vacuum (10^{-6} mbar). The ingots were used as-cast without any further thermal treatment. Composition were chosen according to the known binary Al–*RE* phase diagrams for *RE* = Er, La and Y [6] in the range 1–2% mol., *i.e.* in the aluminum-rich part of the diagram.

Structural analysis was made at room temperature by X-ray powder diffraction using a Bruker D8 Advance diffractometer with Cu-K_α radiation, flat plate, Bragg–Brentano geometry and backscattered rear graphite monochromator. Experimental data were refined with the Rietveld method using the Fullprof program [7]. Chemical analysis was performed by electron probe micro-analysis (EPMA) using a Cameca SX-100 to check the composition of the alloys. Sample observation was made with a Zeiss LEO Scanning Electron Microscope (SEM) equipped with a field emission gun and an energy dispersive X-ray detector (EDX).

Hydrogen solubility **S** was determined with a high temperature hydrogen rig by manometric measurements using the Sieverts' method. The sample holder was heated at two temperatures 675 and 725 °C (*i.e.* above T_{liq} = 660.4 °C for pure Al) and the working hydrogen pressure was set to 50 kPa (0.5 bar). The sample holder was made of a boron nitride bed filled with Al and introduced in a quartz tube to limit hydrogen permeation out of the rig. The metal to dead-volume ratio was optimized to accurately detect small fraction of sorbed hydrogen. Strong temperature gradient between the thermostated bath of the rig and the heated sample holder leads to cautious measurements. Therefore, the mass of the samples (7–8 g) and the amount of introduced dihydrogen were adjusted so that there was much less gas than the quantity necessary to form the *RE* hydride in order to improve the detection level.

The Al–Er–H ternary phase diagrams have been assessed with the Calphad method using the Thermo-Calc software [8]. This technique consists in describing the Gibbs energies of all the phases present in the system as a function of temperature and composition. The thermodynamic description of the constitutive binary systems have been taken from published assessments: Er–H [9], Al–Er [10], Al–H [11]. The phases taken into account in the present work are: gas, liquid, *bcc*, *fcc*, *hcp*, Al_2Er_3, Al_2Er, Al_3Er, AlEr, $AlEr_2$, α-AlH_3, γ-AlH_3, β-AlH_3, ErH_3, and ErH_2. The gas phase contains Al, H and H_2 species. The solid and liquid solutions contain the three elements. No hydrogen solubility is considered in the binary Al-Er compounds and no Al solubility in considered in the erbium hydrides. Calculations are made by combining the three databases and performing ternary extrapolations considering that no ternary phase is formed and that the ternary interaction parameters are negligible.

Results

Sample characterizations

All samples have been characterized by X-ray diffraction. Results are given in Table 1. All patterns can be indexed with cubic aluminum and various binary phases when rare earths are added. For La and Er, the first Al-richest intermetallic phases reported in the phase diagrams ($Al_{11}La_3$ and Al_3Er respectively [6]) are observed. A typical powder diffraction pattern is shown in Fig. 1 for the composition $Al_{98}La_2$ that exhibits the two-phase coexistence. However, this is not the case for Y for which some phases are observed but cannot be indexed correctly with the known binary phases of the Al-Y binary phase diagram. Further investigations, as described in the next section, have shown that those phases are metastable occurring in the as cast sample but not present any more after thermal treatment. All crystallographic data for the identified phases are in agreement with literature data.

Table 1 – XRD characterizations of as cast samples for different amounts of added rare earths.

Rare earth	Nominal composition (%. mol)	As cast observed phases (XRD)	Expected mass fraction	Obs. mass fraction (XRD)	Space group	Cell parameters (Å)
None	0	Al	100%	100%	$Fm\bar{3}m$	a = 4.0486(1)
Y	1.00	Al	–	–	$Fm\bar{3}m$	a = 4.0492(3)
		1 unidentified phase				
Y	2.00	Al	–	–	$Fm\bar{3}m$	a = 4.0489(9)
		2 unidentified phases				
La	1.00	Al	95.6	92.3	$Fm\bar{3}m$	a = 4.0484(1)
		$Al_{11}La_3$	4.4	7.7	$Immm$	a = 4.4341(5); b = 10.125(1); c = 13.149(2)
La	2.00	Al	90.9	85.4	$Fm\bar{3}m$	a = 4.0487(1)
		$Al_{11}La_3$	9.1	14.6	$Immm$	a = 4.4349(4); b = 10.1261(9); c = 13.149(1)
Er	1.98	Al	96.2	92.8	$Fm\bar{3}mPm\bar{3}m$	a = 4.0495(1)
		$ErAl_3$	3.8	7.2		a = 4.2116(2)