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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 of hydrogen in Al obeys the Sieverts' law and 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 H₂ 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.

Keywords: *rare earth hydrides; aluminum; hydrogen solubility; ternary phase diagram; Calphad; Thermodynamic modelling.*

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1. 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 to 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 *4f* 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.

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.

2. 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 to 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 $Cu-K_{\alpha}$ 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 microanalysis (EPMA) using a Cameca SX-100 to check the composition of the alloys. Sample observation were 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 $T_{liq}=660.4^{\circ}C$ 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 , $AlEr$, $AlEr_2$, $\alpha-AlH_3$, $\gamma-AlH_3$, $\beta-AlH_3$, 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 is 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.

3. Results

3.1 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 ($\text{Al}_{11}\text{La}_3$ and Al_3Er respectively [6]) are observed. A typical powder diffraction pattern is shown in Figure 1 for the composition $\text{Al}_{98}\text{La}_2$ 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.

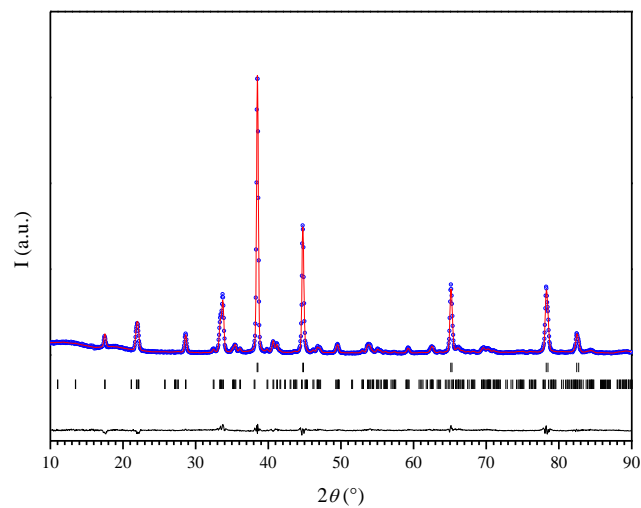


Figure 1 – Refined X-ray powder diffraction pattern for the composition $\text{Al}_{98}\text{La}_2$ showing the coexistence of two phases: pure Al ($Fm\bar{3}m$) and $\text{Al}_{11}\text{La}_3$ ($Immm$). Measured (blue dots), calculated (red solid line), and difference curves (black line below); vertical bars correspond to line positions of the two observed phases from top to bottom; radiation $\text{Cu-K}\alpha$.

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 1 unidentified phase	-	--	$Fm\bar{3}m$	$a=4.0492(3)$
Y	2.00	Al 2 ununidentified phases	--	--	$Fm\bar{3}m$	$a= 4.0489(9)$
La	1.00	Al $Al_{11}La_3$	95.6 4.4	92.3 7.7	$Fm\bar{3}m$ $Immm$	$a = 4.0484(1)$ $a = 4.4341(5);$ $b=10.125(1);$ $c = 13.149(2)$
La	2.00	Al $Al_{11}La_3$	90.9 9.1	85.4 14.6	$Fm\bar{3}m$ $Immm$	$a = 4.0487(1)$ $a = 4.4349(4);$ $b = 10.1261(9);$ $c = 13.149(1)$
Er	1.98	Al $ErAl_3$	96.2 3.8	92.8 7.2	$Fm\bar{3}m$ $Pm\bar{3}m$	$a = 4.0495(1)$ $a = 4.2116(2)$

3.2 Hydrogen absorption in liquid state

Sorption measurements were made for the different samples at two temperatures (675 and 725 °C), *i.e.* above the melting of aluminum. Results are given for all samples in Table 2. Pure aluminum was also measured to assess the accuracy of the equipment. The observed value for pure Al is 0.02 mmol of H dissolved in the tested sample (67 ppm mol), one order of magnitude larger than the value calculated with the Sieverts' law with such a sample of 8g. For binary systems, the quantity of hydrogen absorbed after 1h is in the range 0.02-0.07 mmol H, slightly higher than pure Al indicating some influence of the rare earth addition. However, these values are two orders of magnitude lower than that expected in case of the formation of the dihydrides REH_2 .

Table 2 – Weight, temperature and hydrogen quantities observed for the different sorption measurements. The phases observed by XRD after exposure in liquid state to H₂ gas.

Samples	Weight	T	Total H in the rig	H absorbed after 1h	Global solubility	Expected H absorbed for REH ₂	Phases observed (XRD) after exposure in liquid state to H ₂ gas
	(g)	(°C)	(mmol H)	(mmol H)	(ppmmol)	(mmol H)	
Pure Al	8.0254	675	0.444	0.02	67	-	Al
Al ₉₉ Y ₁	8.1500	675	0.443	0.05	169	5.906	Al, Al ₃ Y
Al ₉₈ Y ₂	7.3654	675	0.526	0.05	192	5.220	Al, Al ₃ Y
Al ₉₈ Y ₂	6.6938	725	0.528	0.04	169	4.744	Al, Al ₃ Y
Al ₉₉ La ₁	8.5655	675	0.522	0.04	131	6.097	Al, Al ₁₁ La ₃
Al ₉₈ La ₂	6.8248	725	0.532	0.07	300	4.672	Al, Al ₁₁ La ₃
Al ₉₉ Er ₁	6.5092	725	0.527	0.02	87	4.717	Al, Al ₃ Er

After solidification at room temperature, the samples were analyzed by XRD to check any hydride formation. The observed phases are all metallic and the same as in the as-cast samples for La and Er. For Y, it is worth to note that the unidentified phases reported for the as-cast samples are no longer present whereas the intermetallic Al₃Y is observed.

3.3 Calphad calculations

For a better understanding of the equilibrium existing in the ternary system Al-H-RE in the Al liquid state (667 °C), Calphad calculations have been carried out at this temperature and at various pressures in the range 1 to 10⁸ Pa for the system Al-Er-H. First calculation at 1 Pa shows that ErH₂ does not form at this low pressure (Figure 2a). The binary hydride appears for 10 Pa in equilibrium with the intermetallic phase AlEr₂ (Figure 2b). This is in agreement with the equilibrium pressure of ErH₂ at this temperature which is calculated at 3.87 Pa. At 100 Pa, a three-phase equilibrium

between ErH_2 and Al-rich intermetallic occurs (Figure 2c). Increasing the pressure up to 10 MPa (Figure 2d) does not allow to obtain an equilibrium between ErH_2 and liquid aluminum. Such an equilibrium is only observed under 100 MPa (Figure 2e). This agrees with the calculated pressure (33.2 MPa) at which equilibrium between liquid Al, ErH_2 and gaseous H_2 is expected to occur. For a better interpretation of our experimental data, the ternary phase diagram has been also calculated at 50 kPa and 667°C (Figure 2f), *i.e.* using the experimental thermodynamic conditions of section 3.2. The equilibrium is found between liquid Al, Al_3Er and H_2 gas only, in fairly good agreement with our data obtained from Sieverts' measurements and XRD analysis.

From the calculation of the phase diagram, it is also possible to estimate the solubility of H in the liquid phase depending on the rare earth composition. The variation of S is shown in Figure 3 at 940K (667°C) and 100 Pa. It is worth to note that the value for pure Al is in relatively good agreement with the Sieverts' law. When adding 2% mol. of erbium, a slight decrease of S from 0.0253 down to $0.0236 \text{ Ncm}^3/100\text{g(Al)}$ (-6.7%) is observed.

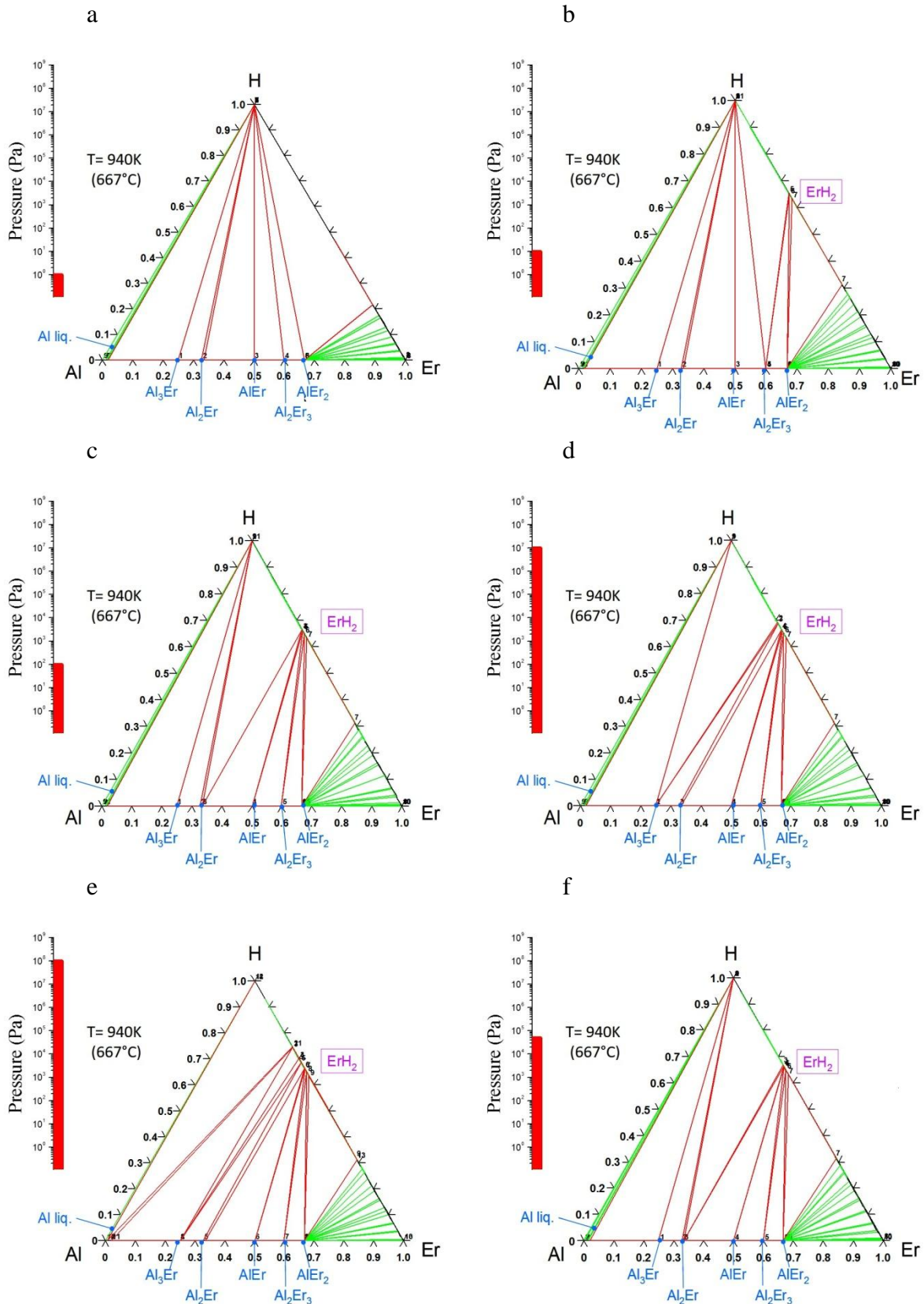


Figure 2 – Ternary phase diagrams calculated at 940K (667°C) for the system Al-Er-H with increasing hydrogen pressures: (a) 1 Pa; (b) 10 Pa; (c) 100 Pa; (d) 10 MPa; (e) 100 MPa; (f) 50 kPa.

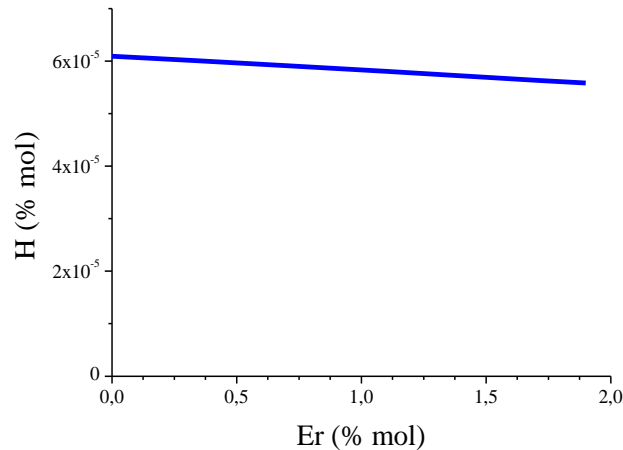


Figure 3 – Variation of the H concentration (% mol) as a function of the Er content (% mol) in the ternary system Al-Er-H at 940K (667°C) and 100 Pa.

4. Discussion

Aluminum can be alloyed with small quantities of rare earths in the range 1~2% mol. After solidification, equilibrium between pure Al and either $Al_{11}La_3$ or Al_3Er is observed. For Y, some unidentified phases are observed but after the thermal treatment done during the sorption experiment, they transform into the expected Al_3Y phase showing that they are not related to contamination but rather to some out-of-equilibrium state. It can then be concluded that for the three rare earths, the obtained phases are in agreement with the Al-rich part of the published phase diagrams[6].

H sorption experiments have been performed in liquid state at two temperatures (675 and 725°C). Though slightly overestimated, the H-sorbed quantities are close to what is expected according to the Sieverts' law for pure Al. When adding small quantities of rare earths, a small increase of the solubility is observed, except for Er. However, the absorbed hydrogen values are well below the quantities expected in the case hydrides would be formed(7th column in Table 2).

There are two orders of magnitude between the measured values (6th column in Table 2) as compared to the calculated ones. Moreover, XRD analysis of the samples made after the experiments confirmed the presence of the Al-rich phases only without any traces of REH_2 . This rules out the possible formation of rare earth hydrides, at least in our thermodynamic conditions, as reported by Chiotti and Woerner for Mg(Al).

At this stage, to determine whether or not precipitation of a solid hydride is possible in these systems, the Al-Er-H phase diagram has been calculated using the Calphad method at a temperature close to the aluminum melting temperature (667 °C) with increasing hydrogen pressure. From these data, it is possible to determine the phase equilibria. We show that at this temperature, ErH_2 does form at low pressure (3.87 Pa) but not in equilibrium with liquid aluminum. Increasing the pressure leads to phase equilibrium between ErH_2 and Al-rich intermetallics but again not liquid Al. Such an equilibrium between liquid Al, ErH_2 and H_2 gas occurs only above 33.2 MPa. This well explained why the hydride precipitation was not observed in our experimental conditions made at lower pressure (50 kPa).

Additionally, Calphad calculations allow to determine the solubility S as a function of the erbium composition. We observed a slight decrease of the solubility from 0.0253 down to 0.0236 $Ncm^3/100g(Al)$ for 2% mol. of added erbium at 940 K (667°C) and 100 Pa. This result does not contradict our experimental measurements for which the solubility does not increase for 2% mol. of added Er (Table 2) showing a positive effect of this rare earth compared to La or Y. At this stage, more calculated data are needed to predict the possible formation of solid hydrides within liquid Al at low pressure but also to determine whether or not element addition can induce significant changes in the H solubility in liquid aluminum. On this basis, other metal forming hydrides might be investigated to propose aluminum alloy composition with lower porosity related

to hydrogen solubility.

5. Conclusion

The system Al-H-RE has been investigated regarding H solubility in the metallic liquid phase using both experimental and calculated data. Our study shows that hydride precipitation in solid state in the liquid phase is possible for these systems only at high pressure (33.2 MPa). However, Calphad calculations show that adding 2% mol. of erbium could slightly decrease the H solubility in liquid aluminum (by approximately 7%).

6. Acknowledgements

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Table caption

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Figure caption

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