Formation of hydrogen blisters during the solution treatment for aluminum alloys

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Abstract

The solution treatment of aluminum alloys can be restricted by the presence of porosity defects caused by the moisture present in the process or by the hydrated front on the material surface. Hydrogen blisters cause deleterious effects on mechanical properties and surface finish. However, the formation of bubbles in solid aluminum is not caused only by the known reaction: \(2\text{Al} + 3\text{H}_2\text{O} = 3\text{H}_2 + \text{Al}_2\text{O}_3\), as it does not explain the interaction of the aluminum oxide layer with the formation mechanisms. In addition, literature approaches show that there is more than one mechanism for the formation of these defects, but no work has made an association between them. Thus, the objective of this work is to carry out extensive research on the state of the art of hydrogen blister formation in aluminum alloys during the solubilization heat treatment. Contemplating different proposed mechanisms of bubble formation on the surface and structure, the analysis of this association of approaches indicated that the mechanisms depend on both permeability, where the hydrated oxide front creates passage for the formation of blister in the sublayer, as well as diffusion and hydrogen solubility in the microstructure.

Keywords: Aluminum alloys; Heat treatment; Hydrogen; Oxidation; Blister.

1 Introduction

Almost all metals contain small amounts of oxygen, hydrogen and nitrogen in their composition, which are often referred to as gases in metals [1,2], whether or not they exist as oxides, hydrides and nitrides [3-5]. The deleterious effects of hydrogen on mechanical properties of metals are well known and have been extensively studied [5-9].

Hydrogen is easily absorbed by reaction of aluminum with water, which comes from sources such as atmospheric moisture, flow of microscopic materials, wet casting tools or organic substances, thus supplying aluminum oxide and dissolved atomic hydrogen [10-12]. In addition, hydrogen absorption mechanisms in solution heat treatment start in surface reactions of aluminum with oxide layer [13-16], cathodic regions can favor hydrogen absorption reactions [17]. Despite this, hydrogen has a low solubility in molten aluminum and, in solid form, and at solution temperature, it has a solubility twenty times lower [12,18].

The complexity of hydrogen blister formation in high temperature heat treatment processes for aluminum alloys is not well-formulated [12]. Figure 1 shows the characteristic defect caused by hydrogen blisters, this defect representing by Hu et al. [19] and MacKenzie [20].

Therefore, understanding the formation of hydrogen blister during heat treatment of aluminum, as well as mechanisms that act in formation of this defect, is essential for reducing production costs of Al alloys, increasing its quality and enhancing its potential mechanical performance. Thus, this work aims to survey and review literature about mechanisms that explain introduction of hydrogen in aluminum alloys during heat treatment operations. This work comprehends analysis in literature of heat treatments of aluminum alloys with temperature within 465 °C and 530 °C.

2 Hydrogen in high temperature solid aluminum alloys

One of the characteristics of heat treatment of aluminum [21] is rapid formation of a thin layer of passive oxide of \(\text{Al}_2\text{O}_3\) [22-24]. The hydrogen bubbles formed in the aluminum microstructure during heat treatment depend on many aspects, such as water vapor pressure [25], solubility [26,27], permeability, diffusivity [28] and activity [28,29]. Some of these aspects can be verified by mass spectrometric analyzer [11] or a thermal desorption spectroscopy system [30]. These factors influence the appearance and growth of blisters. The techniques for measuring hydrogen gas trapped inside micropores can be done using analytical methods such as electric energy loss spectroscopy (EELS) and ultraviolet absorption spectroscopy.
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-6.9 \lg D, and later found a diffusivity between -7 to 9.5 for temperature range mentioned above. The behavior of diffusivity as a function of variation of content of some elements in aluminum alloy is shown in Figure 2. However, studies cover a wide range of conditions, including the effects of temperature, oxide, grain size, aluminum sample purity, sample surface condition and fabricated sample shape [32].

Furthermore, the correlation between distribution of slip and hydrogen sensitivity suggests possibility that moving displacement facilitates transportation of hydrogen material.

2.3 Solubility and activity

The low solubility of hydrogen in aluminum during its heat treatment makes it particularly difficult to quantify
the hydrogen concentrations in lattice [18] which, according to Steward, causes a great dispersion in results found in literature on this topic. Ulanovskiy [1] analyzed some of these data, which also showed discrepancies in hydrogen diffusion coefficients and activation energy values, which can be caused by differences in materials used, in addition to the fact that ‘surface’ hydrogen is not taken into account and that is captured by other mechanisms.

Anyalebechi [33] shows at what heat treatment temperature aluminum can adsorb free hydrogen H+ from H2 dissociation. Hydrogen solubility and activity are significantly influenced by chemical composition of alloy [33,34]. In other works [35,36] it is also shown that the microstructure affects permeability of aluminum alloys. The influence of solubility and hydrogen activity as a function of the content of some elements of alloy present in aluminum at a solution temperature of 500 °C is shown in Figure 3.

The work by He et al. [34] shows that for an alloy Al-Cu-Ga-In-Sn increasing the copper content to up to 8% decreases the hydrogen solubility, while its production of blisters has become more intensified with higher concentrations of copper [34], as also shown in Figure 2 [32]. This increase is justified by increase in hydrogen activity in alloy with higher copper content. The activation energy values of hydrogen solubility in aluminum found by other authors [35,37-39] are relatively close, being between 30 and 80 kJ.mol⁻¹.

2.4 Blister formation mechanism through oxide film

For the formation of hydrogen blisters, aluminum corrosion must occur [40,41]. This requires the presence of water and, thus, the metal to oxidize [42,43]. The use of the relationship between aluminum oxide and water can be made from possible electrochemical situations, analyzing the cathodic and anodic potentials [44]. The oxide film is not a barrier to hydrogen permeation [30]. The heat treatment steps of solubilization influence the reactivity of the Al2O3 layer with atmospheric H2O [45]. According to previous work [26,38,46], the chemical reactions that explain formation of hydrogen gas from atmospheric H2O are those shown in Equations 1, 2 and 3, which concern the mechanism of formation of subsurface hydrogen blisters.

\[
\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 \\
(1)
\]

\[
\text{Al(OH)}_3 + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2 \uparrow \\
(2)
\]

\[
2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \uparrow \\
(3)
\]

In Figure 4a it is shown that the compound Al2O3, which constitutes an amorphous oxide film called alumina (α-Al2O3), reacts with water, producing the compound Al(OH)3, which is a hydrated oxide front in its recrystallized [45]. Thus, the surface alumina oxide can be transformed into a hydrated oxide by absorbing moisture [47], as shown in Equation 1. The solubilization treatment range between 450 °C and 500 °C without atmospheric control favors the transformation of amorphous aluminum oxide film into hydrated oxide on the surface due to its activity [42,47].

In this temperature range, the formation of gibbsite and bayerite is also promoted, as shown in Figure 5, which shows Gibbs free energy graph by temperature of aluminum alloy. Then, Figure 4b shows that the hydrated oxide front Al(OH)3 in contact with Al produces subsurface H2 as Equation 2. The hydrated oxide film formed on sample surface thus creates additional resistance to transfer of formed gas, causing it to form blisters.
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Mackenzie [20] charge hydrogen blisters formed during heat treatment by transition to Al2O3 hydration AIOOH (boehmite) shows in Figure 6a, although this is not formed in solution temperature, although heating does not prevent this compound from being formed [48] shows that the formation of blisters that transform surface oxide into boehmite occurs at temperatures lower than that of solution. In Figure 6b, the oxide transition creates a hydrated front which is the precursor to formation of hydrogen blisters in aluminum surface sublayer, as shown in Equations 4, 5 and 6.

\[
\begin{align*}
\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AIOOH} & \quad (4) \\
\text{Al} + \text{AIOOH} \rightarrow \text{H}_2 + \text{Al}_2\text{O}_3 & \quad (5) \\
\text{Al} + 2\text{H}_2\text{O} \rightarrow \text{AIOOH} + 3\text{H}_{\text{interstitial}} & \quad (6)
\end{align*}
\]

It is necessary for water to contact Al directly or through oxide layer to reaction of Equations 3 and 6 to occur. The authors [46,47] mention two ways to explain contact of aluminum with water. One way explains that water may have permeated the surface layer of hydrated oxide and other way explain that it may have been formed within microstructure by other mechanisms [40]. The first is explained by micro cavities [8] in oxide layer, as shown in Figure 6c. Li [8] estimates that such micro cavities evolve rapidly to cavities when alloy is exposed to temperatures above 150°C.

2.5 Nucleation and growth of microporosities

Toda et al. [49] show that heterogeneous nucleation sites are necessary for hydrogen to form micropores and thus, if these sites are not present, microporosity formation is effectively suppressed. The analyzes of these authors show that a pure aluminum did not form micropores at heat treatment temperature of 550 °C in a time of 90 h. However, the hydrogen was trapped in its microstructure. Su et al. [14] and Toda et al. [49] identified that hydrogen gets stuck in vacancies, making it impossible to move vacancies. For a sample of Al-Zn-Mg alloy, Su et al. [15] indicated distribution of hydrogen in favorable regions and its atomic concentration in regions, as shown in Figure 7.

The work by Su et al. [14] indicates that nucleated hydrogen micropores in particles show premature growth when under loading, revealing such research also that between 7 to 28% of fractures originate from hydrogen micropores. Often, in Al-Mg alloys, about half of hydrogen atoms are trapped in such micropores. The supersaturated hydrogen atoms in aluminum alloys migrate to places such as interstitial positions, vacancies, disagreements, solute atoms, precipitates, intermetallic particles and high-angle grain outlines. After the nucleation of a hydrogen micropore in aluminum alloy it becomes one of the preferred places for its growth in aluminum alloys.

According to Zhang et al. [50] hydrogen micropores are formed from hydrogen vacancy groups. Other studies [11,14] however, show that hydrogen micropores are heterogeneously

Figure 4. Formation and advancement of hydrated front of Al(OH)₃ in (a), Formation of hydrogen blisters at interface Al(OH)₃ and Al in (b).

Figure 5. Gibbs free energy of aluminum hydroxide compared to aluminum oxide as a function of temperature [42].
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Initiated, generally in regions of intermetallic particles in aluminum alloys containing zinc, magnesium and copper.

The displacement of H from an octahedral void in aluminum grid to a vacancy is accompanied by an energy gain of 1.23 eV. Vacancies are stable regions for the formation of H₂, as well as contours and disagreements. The total amount of dissolved hydrogen is determined by pressure of hydrogen and high pressures by its volatility [8,14,15,41]. Hydrogen ions will be present in a significant amount at interstitial lattice locations, grain boundaries and vacancies [21,24].

Another mechanism for formation of micropores in internal regions is the formation of hydrides with elements present in aluminum alloys, such as Mg, Li and Ti, which due to their high affinity increase solubility of hydrogen [1,39]. Despite this, newly formed hydrides are easily displaced to regions of high free energy in microstructure, such as grain outlines and discrepancies, places in which release of hydrogen favors formation of H₂ [26]. Part of origin of the blisters may be related to these hydrides [47, 51, 52,53]. For example, the segregation of magnesium is responsible for part of hydrogen concentration inside the microstructure, given permeation of this metal to grain boundaries, but it is only when a certain level of precipitation occurs in grain boundaries that cracks, due to hydrogen embrittlement, can be nucleated and microstructure becomes susceptible to stress corrosion and fatigue corrosion [54]. It may be that formation of hydrides occurs selectively in incoherent interfaces of precipitates and in contours of grains, thus facilitating nucleation of cracks.

In recent years, images obtained from microtomography by X-ray analysis have been used to observe sites of hydrogen nucleation in aluminum alloys that have undergone thermal treatment of solubilization. Suppose observed micropores are thermal equilibrium, where surface tension γ is balanced by an opposite gas pressure within a micropore P [49], follows that P=4γ/d₂₀₆, where d is the radius of micropore. Two possible growth mechanisms under this thermal equilibrium would be the migration and coalescence of micropores. For the first mechanism to work, micropores must migrate via atom transport through surface diffusion, vacancy volume diffusion, or vapor transport [49]. The focus of this study is limited to treatment solution time, which in turn is based on literature and industry recommendations, and is generally stipulated within 3h [20]. Therefore, the formation of blister until this time interval is considered in this study.

Through the analysis of microtomography in an aluminum alloy at a temperature of 500 °C, Sue et al. [14] showed that intermetallic Mg₃Si (green) and second phase particles (blue) form nucleation sites, and pore A growth, shows Figure 8a. When blister formation mechanisms are activated, blister concentration increases rapidly, Figure 8b shows increase in blister concentration in 0.5 h of treatment. However, in Figure 8c at 1.25 h, low growth and nucleation of hydrogen blisters were observed. The average diameter of hydrogen micropores increases with increasing time of exposure to heat treatment. In long times, such as 7.16 h (Figure 8d), intermetallic particles dissolve and micropores coalesce soon. Sue et al. [14] also observed that growth in spherical particles is greater than in angular particles.

Toda et al. [49] analyzed four samples of aluminum alloys LH, MH, HH and 5N-Al (99.99% Al) submitted to times longer than indicated for their heat treatment and observed that rapid growth of blisters occurs after 5 h, as shown Figure 8.

This growth, however, can be activated within time specified for the solution treatment if conditions are favorable. The decrease in hydrogen diffusivity and the increase in its
solubility are attributable to presence of molecular hydrogen in pores [10,49]. It can be concluded that we can control the formation of hydrogen bubbles during heat treatment at high temperature if we know the mechanisms of these formations, as well as external factors or how the condition of the material favors the formation.

3 Conclusion

Many authors have addressed the mechanisms of hydrogen blister formation in aluminum alloys. In this article it was possible to analyze blister formation models on the surface and structure of aluminum alloys. It was indicated that, at high temperatures during thermal treatment of solubilization, the reaction of hydrogen formation is not a simple and direct reaction of \( 2\text{Al} + 3\text{H}_2\text{O} = 3\text{H}_2 + \text{Al}_2\text{O}_3 \), the mechanisms depend both on permeability, where hydrated oxide front creates passage for formation of blisters in sublayer, and on diffusion and solubility of hydrogen in microstructure. That is, as microporosity is growing, it affects diffusivity and solubility and vice versa. The formation of microporosities that originate hydrogen blisters, however, can be limited by absence of intermetallic.

In pure aluminum there was no blister growth, and it was observed that vacancies were equipped with hydrogen, which limited its displacement.

References


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