Kinetics of Hydrogen Desorption from Rapidly Solidified Al-Cr Alloys*

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The thermal desorption spectroscopy has been applied to analyse hydrogen desorption from foils of Al-Cr alloys containing up to 3.0 mol% Cr produced by centrifugal melt quenching. Surface morphology of the alloys was monitored using atomic force microscopy and scanning electron microscopy. It was revealed that hydrogen behaviour is strongly affected by microstructural features available due to rapid solidification and represents at least four hydrogen trap sites in Al-Cr alloys. The Cr atoms in lattice sites are identified as predominant trap site. The occupancy of dislocations was estimated to be rather high in contrast to vacancies and pores in alloys. The amount of hydrogen trapped by vacancies is drastically decreased with increase in Cr concentration. These hydrogen/microstructure interactions were discussed regarding rapidly solidified pure aluminum as well as traditionally processed aluminum samples. [doi:10.2320/matertrans.L-MZ201104]

(Received October 2, 2010; Accepted December 29, 2010; Published April 13, 2011)

Keywords: thermal desorption spectroscopy, rapid solidification, aluminum-chromium alloys, hydrogen

1. Introduction

Nowadays development of embrittlement-resistant materials is considered to be one of the most technically challenging aspects of hydrogen storage in innovative fuel cell vehicles. Although considerable effort has been made to explain the phenomenon of hydrogen embrittlement in metals and alloys,¹⁻³⁾ it has been recognised that the mechanisms associated with such degradation in mechanical properties remain incompletely understood from the mechanistic point of view. Since recently aluminium alloys have been regarded as lightweight materials for high pressure gas storage tank^{4,5)} basic research needs related to the problem of their hydrogen embrittlement include such issues as hydrogen behaviour and its interaction with lattice defects (vacancies, pores, solute impurities, grain boundaries, dislocations, etc.). Up to date, numerous investigations are conducted on traditionally processed aluminium materials and highlight the key role of the microstructure in hydrogen trapping and segregation.⁶⁻⁹⁾ What has been lacking, so far, is identification in aluminum based alloys of hydrogen interactions with enhanced microstructure solidified at exceptionally high cooling rates. At the same time, effect of such advanced technique as rapid solidification processing (RSP) on the microstructure of aluminium materials yields desirable improving of properties in comparison with conventionally processed counterparts^{10,11)} and includes extended solid solution range, refinement of as-solidified microstructure, reduced levels of segregation, formation of non-equilibrium phases as well as a high density of defects (vacancies and dislocations) in the metal.¹¹⁾ Therefore analysis of hydrogen behaviour in rapidly solidified (RS) aluminum alloys is of considerable importance because of its potential impact on developing mechanistic understanding of hydrogen/microstructure interactions in order to

control hydrogen embrittlement in high strength aluminum based materials.

This paper focuses on the investigation of hydrogen trapping in RS foils of Al-Cr alloys prepared through centrifugal melt quenching. Note that RS alloys on basis of Al-Cr system are an example of heat-resistant lightweight structural materials because of their high-temperature mechanical properties and enhanced thermal stability.^{12,13)} In the study, thermal desorption spectroscopy (TDS) was applied to detect hydrogen evolution from RS alloys. In fact, hydrogen is the only gas that is appreciably soluble in aluminium and its alloys. Difficulties in detection of hydrogen states in the materials are mainly caused by its high mobility and small quantity. The thermal desorption analysis represents a modern approach to this problem and can be regarded as a superior technique because of its sensitivity and the accuracy of measurements.^{14,15)} To monitor surface morphology of the foils we employed atomic force microscopy (AFM) and scanning electron microscopy (SEM). It should be noticed that initial research^{16,17)} on H desorption processes in RS aluminum and preliminary results obtained for its lightly doped RS binary alloys with Ti, Cr and Zr have clearly demonstrated a great difference between hydrogen behavior in RS aluminum foils and one in traditionally processed aluminum samples.^{7,18)} Therefore the purpose of the present research is to examine hydrogen desorption kinetics in RS Al-Cr alloys in relation to their microstructural features depending on alloy composition. The identification of H/microstructure interactions in the Al-Cr alloys was discussed in contrast to aluminum prepared through RSP as well as traditionally processed samples.

2. Experimental

The Al-Cr alloys with Cr content (mol%) of 1.0, 1.5 and 3.0 were manufactured from 99.99% pure aluminum and 99.9% pure Cr by melting in an induction electric furnace under an argon atmosphere. Specimens of the alloys were

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Fig. 1 Typical AFM and SEM observation of RS Al-Cr alloys. (a) the drum-side of as-cast Al-1.0 Cr alloy foil, (b) the drum-side and (c) air-side of as-cast Al-3.0 Cr alloy foils, (d) the drum-side of TDS tested Al-1.0 Cr alloy foil.

then rapidly solidified by centrifugal melt quenching at a cooling rate of the order of $10^{6^{\circ}\text{C}\cdot\text{s}^{-1}}$ as follows. The droplet of molten alloy was splashed in the air on the inner surface of the polished copper drum with a diameter of 20 cm, rotating at $16\text{ m}\cdot\text{s}^{-1}$ liner velocity. This produced microcrystalline foils, typically up to 8 cm in length, 30–60 μm in thickness and 5–10 mm in width.²⁰⁾ Hydrogen detected in the present work was the immaturity impurity which was mixed in the material during melting and RSP.

As-cast foils of Al-Cr alloys were characterized by means of SEM and AFM techniques. The SEM observations were carried out using a LEO1455 scanning electron microscope operated at 20 kV. The AFM images were acquired through an NT-206 instrument. No special treatment was applied to the surface of the samples prior to inspection in a contact mode in air using a Si probe. Height images ($20 \times 20\text{ }\mu\text{m}^2$ area) were collected simultaneously and analysed using the Surface Xplorer and Surface View software.²¹⁾ Roughness values in this paper refer to the average surface roughness values, R_a , calculated from AFM surface topographic data.

Hydrogen trapping and evolution were evaluated in TDS measurements employing an ESCO EMD-WA1000S/W machine described in detail elsewhere.²²⁾ Generally, TDS curve describes a hydrogen evolution from the sample upon heating by plotting the rate of hydrogen desorption versus temperature. It enables to characterize the types of multiple traps for hydrogen by detecting of temperatures T_m associated with desorption peaks for each trap state. Each observed desorption maximum depends on the activation energy for hydrogen release from the trap as well as the content of trapped hydrogen and the trap density. Before examination, the RS specimens were sectioned. Sample of 6–12 mg from each foil was etched in 10% sodium hydroxide (1 min), 10% nitric acid (1 min), rinsed in water, dried, and immediately tested through TDS technique. During a TDS test, a foil was heated from 120 to 600°C at a constant heating rate

β of $20^{\circ}\text{C}\cdot\text{min}^{-1}$ in a vacuum. To collect background hydrogen spectrum the sample was re-heated under the same conditions when its temperature was reduced to room temperature. Each hydrogen thermal desorption spectrum was plotted with Origin Pro software²³⁾ subtracting the background. The TDS treated samples were further analyzed by using AFM.

3. Results and Discussion

The AFM was utilized to examine surface morphology and roughness of as-cast RS foils of Al-Cr alloys. Representative height mode scans taken from the drum-side surface of the Al-1.0 Cr alloy foils are illustrated in Fig. 1. The gross morphological feature of the foils is wave-like bending of the surface. The roughness value R_a is determined to be 38.5 nm. The height of some “waves” and peaks on the drum-side surface reaches 320 nm, Fig. 1(a). In Fig. 1, SEM micrographs of both surfaces of Al-3.0 Cr alloy show no significant difference in microstructures of the drum-side and air-side surfaces, meaning little difference in quenching effect between both surfaces. The other noticeable microstructural feature is the presence of pores that were not distributed evenly across the foil surface as indicated both by the AFM imaging and SEM imaging in Fig. 1(a), (b) and (c). Figure 1(d) represents that TDS tests resulted in the foil surface smoothing and pores disappearance. The surface roughness value of Al-1.0 Cr alloy is reduced by a factor of ~ 3 after TDS experiments.

Typical TDS spectra from as-cast RS Al-Cr alloys are presented in Fig. 2(a). The data of recognized peak temperatures T_m and trap sites assigned from literature^{7,17,18,24,25)} as discussed later are summarized in Table 1. Note that TDS spectrum from RS foil of pure aluminum¹⁷⁾ shown also in Fig. 2(a) for comparison exhibits three distinct desorption peaks at about 270, 390 and 490°C, denoted 1, 2 and 3.

Fig. 2 TDS analysis of RS aluminum (Al) with different Cr content (mol%). (a) kinetic curves of hydrogen desorption from foils, taken at a heating rate of 20°C·min⁻¹, (b) histogram showing hydrogen content in foils. The TDS plot for 99.99% pure aluminum foil,¹⁷⁾ taken at a heating rate of 20°C·min⁻¹, is also shown in the Fig. 2(a) for comparison (open circle).

Fig. 3 TDS analysis of traditionally processed aluminum samples. (a) kinetic curve of hydrogen desorption from 99.999% pure aluminum sample, taken at a heating rate of 10°C·min⁻¹, after Young and Scully,¹⁸⁾ (b) kinetic curves of hydrogen desorption from 99.99% pure aluminum specimens with different volume fraction of blisters, taken at a heating rate of 8°C·min⁻¹, after Itoh.⁷⁾

Table 1 Trap site identification for hydrogen in RS aluminum (Al) with different Cr content (mol%).

Trap site	Peak temperature for trap site, T_m /°C				Trap site description
	Al	Al-1.0 Cr	Al-1.5 Cr	Al-3.0 Cr	
Peak 0	—	210	210	190	Solute atoms ^{24,25)}
Peak 1	270	270	270	270	Vacancies ^{7,17)}
Peak 2	390	410	410	410	Dislocations ^{7,18)}
Peak 3	490	480	460	470	Pores ^{7,24)}

Additional prominent low-temperature peak detected at 190°C is observed exceptionally in the samples alloyed with Cr and labeled as 0 on TDS curve from Al-3.0 Cr alloy. It was found out, for the temperature range from 350 to 600°C, variation in temperatures T_m of desorption peaks is marginal for RS Al-Cr alloys and RS aluminum foils. Overall, for Al-1.0 Cr and Al-1.5 Cr alloys, it can be assumed that broad desorption peak lying between 150 and 300°C is a superposition of above-indicated peaks 0 and 1. The low-temperature peak 0 overlaps with a separate peak positioned near 270°C in the TDS plot from aluminum. Since desorption rate peaks in TDS spectra have varying breadth and height, it

is well known that overlapped and partially hidden peaks are typical for H trapping at multiple states in a complex microstructure. Therefore it is considered that at least four peaks are identified in the spectra for all Al-Cr alloys, see Table 1. Note that hydrogen thermal desorption curves from RS Al-0.4 Cr alloy¹⁶⁾ exhibit peak temperatures identical with those stated above. A new small peak detected at 340°C only in the TDS profile from Al-3.0 Cr alloy is not denoted in Table 1. Figure 2(b) shows the amount of hydrogen C_H desorbed from the foils within the examined temperature range, obtained by integrating the spectra plotted in Fig. 2(a). As illustrated in Fig. 2(b), it was observed that total H egress changed inversely to increase in Cr content for studied aluminum alloys. Finally, the total concentration of hydrogen C_H evolved upon TDS experiments was measured to be 0.206 mass ppm for Al-3.0 Cr alloy.

In most aluminium alloys, transition metals (Ti, Cr, Fe, Zr, etc.) are known to be employed to increase the thermal stability of conventional alloys because they retard recrystallization.^{13,26)} However, the concentration of these alloying elements are strongly limited and often do not exceed 0.1 mol% due to the formation of intermetallic compounds which reduce plasticity, deformability and strength. In our previous work²⁷⁾ it was reported that alloys containing Cr

under 1.0 mol% produced through centrifugal melt quenching are composed of metastable α -solid solution stable up to 300°C. The presence of intermetallic Al₇Cr phase particles distributed homogeneously in the α -aluminium matrix was reported for RS Al-1.5 Cr alloy.²⁷⁾ The average grain size of the RS foils was in the range of several μm . According to the present analysis, surface microgeometry characteristics include ridge-rich surface regions and pores in RS Al-Cr alloys. In fact, similar surface topography structures have been already observed for as-cast RS aluminum and Al-Fe alloys.^{17,28)} It was obtained that roughness of foil surface depends on both composition of the sample and topography of contact area of the melt and the drum. As for detected pores, hydrogen porosity in aluminium alloys can be attributed both to solidification shrinkage and gas bubbles expelled from the molten material during RSP.²⁹⁾ From Fig. 1, it is apparent that the heat treatment during TDS tests results in the foil surface smoothing and pore disappearance in part. A similar tendency has been also reported recently for RS pure aluminum.¹⁷⁾

In this study, we performed the TDS measurements to reveal the roles of unique microstructural features on the hydrogen desorption and its composition dependence in RS Al-Cr alloys. It should be pointed out that dislocations, vacancies, lattice interstices (hydrogen in solution), pores, precipitates of secondary phases, solute atoms and grain boundaries are potential trap sites for hydrogen in aluminium and its alloys. Meanwhile, hydrogen interactions with dislocations as well as vacancies are considered to contribute mostly to hydrogen embrittlement of aluminium materials.^{3,9,25,30)} The scope of this paper did not allow for a detailed comparison of the hydrogen-desorption-rate curves from RS pure aluminum with those reported for traditionally processed pure aluminum although references to the hydrogen trapping and evolution in conventional aluminium have been alluded to in the text. Figure 3 exemplifies thermal desorption spectra from pure polycrystalline aluminum¹⁸⁾ as well as aluminum produced by a DC cast rolling ingots.⁷⁾ It is clearly shown that similar to bursts of hydrogen egress from RS pure aluminum demonstrated here in Fig. 2(a), traditionally processed aluminum specimens exhibit three desorption peaks in TDS spectra. The temperatures of peaks are consistent with data listed in Table 1. However, there is controversy about identification of hydrogen trapping in high purity aluminum. In Fig. 3(a) shown that Young and Scully¹⁸⁾ have suggested that these trapping sites stated from low to high desorption energy are associated with interstitial lattice sites, dislocations, and vacancies, respectively. Unfortunately, this identification has not helped to clarify results gained by the present authors for RS samples. The fact is that, firstly, this trap identification does not take into account the porosity which is one of the noticeable defects in aluminium alloys. Although RSP reduces porosity of the samples in comparison with casting,²⁹⁾ the pores are easily observed for RS pure aluminum¹⁷⁾ as well as for RS Al-Cr alloys, see Fig. 1. Secondly, it fails to explain our thermal desorption experiments on aluminum foils exposed to humid air after TDS tests.¹⁷⁾ On the other hand, recently Itoh^{7,31)} has revealed that these desorption peaks 1, 2 and 3 are related to the hydrogen in aluminum trapped by vacancies, dislocations

and pores/blisters, respectively, see Fig. 3(b). The vacancy/hydrogen pairs was deduced to migrate sufficient distance to be released from the inside of the specimen at much lower temperature than the 3rd peak temperature. Furthermore, Toda *et al.*^{24,32)} have elucidated presence of hydrogen micropores in pure aluminum and its alloys processed through casting as well as hot and cold rolling. It was pointed out for Al-Mg alloys that micropores filled and pressurized with molecular hydrogen are predominant hydrogen trap site, while the occupancy for dislocation traps is very high both in the alloys and pure aluminum.²⁴⁾

Therefore it is considered that in RS pure aluminum foils hydrogen resides at trapping sites at vacancies, dislocations and pores as listed in Table 1. Whereas outward quantitative resemblance of peak positions in TDS profiles, it should be emphasized that quenched-in vacancies play a dominant role in H trapping in pure aluminum foils produced by means of RSP. Indeed, RS samples exhibit a significant increase of the amount of hydrogen trapped at vacancies instead of pronounced hydrogen trapping at dislocations specified for traditionally processed aluminum specimens,^{7,18,24)} see Figs. 2(a) and 3. Thus, we associate the 270 and 410°C trap states as well as the highest binding energy trap site at 470°C in RS Al-Cr alloys to the same microstructural features as in RS pure aluminum. The trap site having the lowest binding energy (see peak 0 in the TDS spectra) is tentatively attributable to hydrogen in the interstitial lattice sites trapped by Cr atoms from literature.^{24,25)} The shifting of the first desorption peak in case of RS Al-Zr alloys to a lower temperature compared with RS pure aluminum provides further evidence and was determined recently.¹⁶⁾ It should be noticed, apart from above, the peak 3 may correspond to the Al₇Cr phase particle coarsening as well as pore disappearance in the alloys. However, the noticeable peak at 480°C reported for RS Al-0.4 Cr alloy¹⁶⁾ supports identification of peak 3 as a pore trap state. This fact is evident because of absent of the secondary phase precipitates in RS Al-0.4 Cr alloy foils.²⁷⁾ The identification of the small peak in the vicinity of peak 2 cannot be explained due to a lack of experimental data for Al-Cr alloys and is a subject of further investigations.

This work demonstrates that hydrogen behaviour in RS Al-Cr alloys strongly depends on microcrystalline structure and exhibits composition dependence. As seen in Fig. 2, hydrogen desorption kinetics in the foils are qualitatively changed in the presence of alloying element. The Cr atoms in lattice sites are identified as predominant hydrogen trap site. The amount of hydrogen trapped at vacancies in the alloys is obviously decreased with increase in Cr content and with the formation of vacancy-solute atom complexes.³³⁾ In fact, vacancies play an important role in the transport of alloying element atoms even during RSP³⁴⁾ and cause nonuniform dope depth distribution in the near-surface region of RS aluminum alloy foils.³³⁾ It also can be inferred that the amount of H associated with dislocations increases with increasing Cr content in the foils. In contrast, along with increase in Cr-rich precipitates the role of pores in H trapping is decreased in the alloys. Meanwhile, height of the desorption peak related to hydrogen release from pores exceeds the one in case of RS pure aluminum and can be

caused by known fact that aluminium alloys usually show higher porosity than high-purity aluminium.²⁴⁾ The total H egress obtained was changed inversely to Cr content in investigated Al-Cr alloys, as shown in Fig. 2(b), meaning its probable dependence on secondary phase precipitates too.

To conclude this paper we would like to make some comments on the challenging questions from a fundamental point of view and outline future prospects. The TDS technique employed for hydrogen desorption kinetics analysis provides new insight into the hydrogen/microstructure interactions in RS aluminium alloys. It was revealed that hydrogen behaviour in respect to alloy composition is complicated and depends on microstructural features available due to rapid solidification. There appears to be a need for further work that will necessitate a multiscale framework to clarify details of complex hydrogen interactions and evolution in modified RS microstructures related to the topic of hydrogen embrittlement control in high strength aluminium alloys.

4. Conclusion

This study has demonstrated the effect both of RSP and Cr content on hydrogen desorption kinetics from aluminium materials. Based on the above evaluation of the TDS spectra, at least four H desorption rate peaks in the thermal desorption spectra are identified for Al-Cr alloys. It was found out that studied RS Al-Cr alloys represent the release of hydrogen trapped at Cr atoms in lattice sites as well as vacancies, dislocations and pores. The most prominent effect is the dominance of the trap state of Cr atoms in the alloys. The hydrogen amount resided with quenched-in vacancies in RS aluminum is drastically decreases in the presence of Cr. Furthermore, the amount of hydrogen associated with dislocations increases with rise in Cr content in the foils. In contrast, along with increase in Cr-rich precipitates the role of pores in hydrogen trapping is decreased in the alloys.

Acknowledgements

The authors would like to thank Light Metals Education Foundation Inc. and Japan Aluminium Association. This work was supported by Matsumae International Foundation Grant No. 08G11 to I. Tashlykova-Bushkevich.

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