The role of Cr in H desorption kinetics in rapidly solidified Al

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Abstract. Hydrogen desorption kinetics for rapidly solidified high purity Al and Al-Cr alloy foils containing 1.0, 1.5 and 3.0 at % Cr were investigated by means of thermal desorption analysis (TDA) at a heating rate of 3.3°C/min. For the first time, it was found that oxide inclusions of Al_2O_3 are dominant high-temperature hydrogen traps compared with pores and secondary phase precipitates resulted in rapid solidification of Al and its alloys. The correspondent high-temperature evolution rate peak was identified to be positioned at 600°C for high purity Al and shifted to 630°C for Al-Cr alloys. Amount of hydrogen trapped by dislocations increases in the alloys depending on Cr content. Microstructural hydrogen trapping behaviour in low- and intermediate temperature regions observed here was in coincidence with previous data obtained for RS materials using thermal desorption spectroscopy (TDS). The present results on hydrogen thermal desorption evolution indicate that the effect of oxide surface layers becomes remarkable in TDA measurements and show advantages in combinations of both desorption analysis methods to investigate hydrogen desorption kinetics in materials.

Introduction

In recent years, aluminum alloys have opened up new opportunities as liner materials [1] for efficient storage of compressed gaseous hydrogen. Remarkable international effort has been deployed for experimental assessment of what microstructural features and H-microstructure interactions control mechanical properties of the materials for service in hydrogen gas. Issues on hydrogen trapping are considered to be subjects of practical and scientific interest to manage the problem of environmental hydrogen embrittlement (HE) in high strength Al-based materials. However, HE mechanisms remain controversial concerning Al alloys of commercial interest. The information on H interactions with defects is often limited to high purity aluminum while most mechanical property data have been obtained for Al engineering alloys with transition alloying elements. Therefore, a large number of investigations consider microstructural origin of observed hydrogen traps in the alloys tentatively. A few notable often quoted references are cited here [2-6].

The present study is aimed to investigate the effect of chromium content on hydrogen behaviour in rapidly solidified (RS) Al-Cr alloys with emphasis on desorption of hydrogen at elevated temperatures. We focus here on the analysis of hydrogen trapping by strong trapping sites because they can have deleterious influence on H-related mechanical properties. For instance, micropores in conventionally processed Al alloys were identified to be the major hydrogen trapping site inducing ductile fracture [7]. At the same time, our recent works presented the first detailed investigation on microstructural hydrogen trapping in RS Al studied by means of thermal desorption spectroscopy (TDS) and revealed some promises in modification of hydrogen behaviour. Particularly, it was found that the role of pores in hydrogen trapping is decreased in RS samples compared with pure Al processed by casting at slow rates of solidification. In this work, a hydrogen evolution rate has been measured in air using thermal desorption analysis (TDA) under controlled temperature ramping conditions. This technique applied to study H desorption kinetics at elevated temperatures close to

the sample melting is beneficial in an analyzing of H trapping phenomena over TDS method which requires ultrahigh vacuum.

Experimental Procedure

Rapidly solidified high purity Al (99.9999% purity) and Al-1.0; 1.5; 3.0 Cr alloys (at %) were produced by the centrifugal melt quenching method using a copper wheel in conditions described in details previously [8]. The obtained foils were typically 5-10 mm wide and 50-100 μm thick. The cooling rate was of the order of 10^6 K/s [8]. Prior to TDA tests, samples were rinsed with acetone, dried, weighed, and immediately tested. The TDA measurements were performed using gas chromatography when the degassing hydrogen was transport for analysis by an argon carrier gas (99.999% purity) at a flow rate of 20 ml/min. Foils were tested in a temperature range from room temperature to 800°C at a heating rate of 3.3°C/min. The total concentrations of H evolved from the specimens were calculated by integrating intensities of the TDA spectra with measuring time.

Results and Discussion

Typical profile of hydrogen desorption rate as a function of annealing temperature for RS foils of high purity Al is presented in Fig. 1. The insert in the left upper corner shows enlarged spectra at low- and intermediate-temperatures. In the figure, a prominent egress of H was observed at about 600°C. In addition, TDA spectrum of RS Al suggests overlapping of several small peaks merged into the lower temperature shoulder of the main H desorption peak. The total H content of the sample was equal to 0.012 mass ppt.

Fig. 1 TDA spectra of as-cast RS pure Al and Al-Cr alloys, taken at a heating rate of 3.3°C·min⁻¹

The TDA spectra from RS foils of Al-Cr alloys indicate multiple microstructural trap states appeared as H evolution rate maxima in Fig. 1. It was found that positions of peaks are shifted to higher temperatures when aluminum is doped by chromium. Observed hydrogen desorption peaks labeled as 1a, 2a and 3a were centered at 400, 510 and 630°C, respectively. All spectra also show a burst of H release in the temperature range 700 – 800°C that occurs close to the sample melting in the TDA tests. A small peak detected at 250°C only in the TDA profile from Al-1.0 Cr alloy is not denoted in the figure. Note, the profile from Al-3.0 Cr alloy demonstrates that peaks 1a and 2a manifested as subtle perturbations in the lower temperature shoulder of peak 3a observed for Al-1.0 Cr and Al-1.5 Cr alloys become well defined, while the TDA intensities of signals located at higher temperature side do not change significantly. Measured total concentrations of hydrogen evolved from Al-Cr alloys with 1.0, 1.5 and 3.0 at % Cr were 0.013, 0.114 and 0.159 mass ppt, respectively.

Since the multi peaked structure of hydrogen evolution profiles was indistinct for high purity Al and Al-1.0 Cr alloy, to interpret these new results TDS spectra obtained previously for the same RS samples are shown in Fig. 2 [9], comparing with the TDA spectra from Fig. 1. The conspicuous feature of TDS plots in Fig. 2 is dominant H desorption for the low-temperature region of the spectra (heating rate of 20.0°C·min⁻¹). Three H evolution peaks are clearly seen at 270, 390 and 490°C in TDS spectrum from RS high purity Al and are labeled as 1, 2 and 3 in Fig. 2a [10]. For RS Al-Cr alloys, a broad evolution peak observed with the onset temperature at 190°C was found to be a superposition of above-indicated peak 1 and an additional low-temperature peak positioned at 210°C and detected exceptionally in the alloys, see peak 0 in Fig. 2b [9,11].
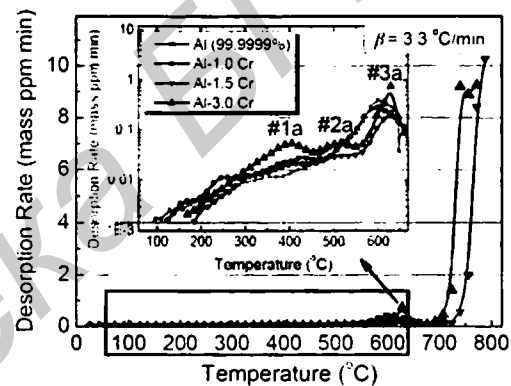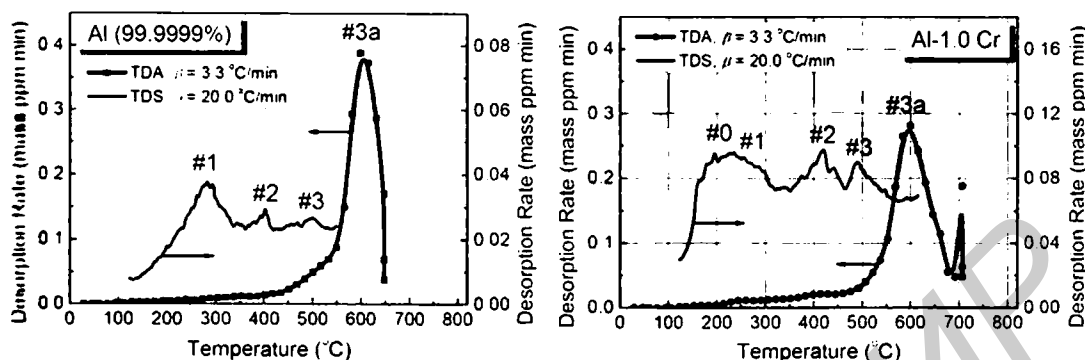
Fig. 2 Comparison of H desorption rates profiles from as-cast RS pure Al and Al-Cr alloys, obtained by TDA and TDS techniques at heating rates of 3.3 and 20.0°C min⁻¹, respectively. The TDS profiles have been taken from our recent work [9]

In this study, the detected hydrogen was an immanency impurity mixed in the material during melting and rapid solidification processing. It is known that hydrogen evolution from metallic materials is affected by microstructural morphology, phase transformations during the thermal analysis and the presence of potential trapping sites. Therefore, as-cast RS foils present the advantage in investigations of H-microstructure interactions, particularly in Al and its alloys, to avoid a surface damage that can occur at hydrogen charging and affect H desorption evolution from pre-charged specimens [12-14]. Our previous works have demonstrated that although the total amount of hydrogen can be varied from specimen to specimen under the similar experimental conditions, a nearly perfect fit of H desorption maxima positions was observed in all RS samples [9-11, 15, 16].

Obtained TDA results of the microstructural hydrogen trapping behaviour reveal new original data on H desorption kinetics at elevated temperatures in RS high purity Al and Al-Cr alloys. Based on the evaluation of the above results, trap-state assignments for low- and intermediate temperature region in TDA spectra are considered to be consistent with patterns of H evolution from the RS materials previously determined by means of TDS. According to our previous work [9], desorption peaks of H located in the comparatively low temperature region are attributed to the trapping sites of Cr atoms in substitutional sites as well as vacancies and dislocations whose binding energies of H are relatively small compared to other trapping sites in the alloys, see in Fig. 2 correspondent peaks 0, 1 and 2 (heating rate of 20.0°C·min⁻¹). However, it is noteworthy to mention that height and position of H desorption peaks are dependent on the heating rates in thermally controlled and activated desorption processes [17]. The spectra display more prominent peaks shifting to higher temperatures with an increasing heating rate. In Fig. 1, this fact provides a possible reason for a lack in TDS measurements of the low-temperature peaks 0 and 1 with expected positions in the lowest temperature range because the peaks are evidently weak and overlapped showing only the shoulder part in the TDA curves (heating rate of 3.3°C·min⁻¹). The possible reason for observed significant reduction of low-temperature desorption peak yields in TDA profiles is discussed later.

On top of that, broad peak 1a is likely to be attributed to peak 2 overlapped with an adjacent peak 3 representing H trapped by pores [9,18]. The fact that peak 1a appears to become more distinct with increase in Cr concentration can be inferred to be related to increase of H amount associated with dislocations and is in line with our previous experiments [9]. In addition, it is assumed that followed peak 2a can be associated with release of hydrogen trapped by Al₇Cr precipitates at a temperature coinciding with coalescence of secondary phase precipitates in RS Al-Cr alloys [15]. Note that peak 2a has not appeared over the explored temperature range in previous TDS spectra from Al-Cr alloys probably because it occurs close to the melting point in case of thermal desorption testing at high heating rates. Concerning unindexed small peak below peak 1a, its origin is not well understood due to a lack of experimental data for Al-Cr alloys and will not be discussed further in the present paper.

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Finally, new high-temperature peak 3a found in the TDA profiles for RS high purity Al and its alloys with chromium cannot be correlated with all the above discussed hydrogen microstructural traps and is lacking, as far as we are concerned, in numerous experimental reports available in the literature on hydrogen behaviour in conventionally processed Al and its alloys [2, 18-20]. Overall, TDS is one of the most frequently employed thermal analysis techniques in identifying different types of H trapping states in Al materials and classifies hydrogen traps into weak and strong trapping sites. However, there are no reports about any high-temperature peaks in experiments on high purity Al performed up to 630°C in a vacuum condition by TDS at heating rates between 8.0 and 10.0°C·min^{-1} [2, 18, 20]. Note that obvious temperature limitations in TDS spectra did not enable detection of high-temperature trap states by outgassing due to high desorption energies to avoid any excessive contamination of the vacuum chamber in case of sample melting.

To understand an origin of the high-temperature peak 3a, one must take into account a related phenomenon observed in some b.c.c. and f.c.c. -structured metals by Lee and Lee [21, 22] who showed that interfaces of oxides and other non-metallic inclusions are dominant strong H trapping sites with high desorption energies while the lattice defects and pores are considered to be shallow traps in iron and nickel. In addition to the work of [22], other authors [23, 24] in experiments on steels have also pointed to a significant role of H-oxide inclusion interactions amplifying that they play an important role in the initiation and in the propagation of cracks under fatigue stresses. Lee and Kim [23] proved that hydrogen evolution rate peak at 630°C (heating rate of 3.3°C·min^{-1}) refers to the interaction of hydrogen with Al_2O_3 inclusions in spring steels. In addition, we should note a peak associated with hydrogen trapped by oxide layers of Al_2O_3 and centered at about 630°C (heating rate of 20.0°C·min^{-1}) in H desorption flux from oxidized Ti-45.0; 50.0 Al alloys [14]. Consequently, based on these discussed above observations, we can argue that oxide inclusions of Al_2O_3 are likely be responsible for the high-temperature peak 3a found in the present work and thus are one of the most energetically favored traps in Al and Al-Cr alloys produced by means of rapid solidification in comparison with conventionally processed counterparts. This assumption is also supported by our results about non-metallic oxide inclusions of Al_2O_3 in RS Al and Al-Cr alloys which were found to be dominant at the foil surfaces through scanning photoelectron microscopy using synchrotron radiation [25]. In fact, integrated intensity of H desorption rate corresponding to oxide inclusions of Al_2O_3 (630°C) in TDA spectra remains almost the same with increasing Cr concentration. Concerning the followed burst of H release detected here during the annealing above 700°C in Al-Cr alloys, its origin, that is likely corresponding to kinetic effects of H release when the sample is melting, should be clarified and is a subject of further investigations.

Another key issue addressed by the present study is that for the first time we performed a comparison of TDA spectra with TDS profiles obtained from the same specimens to get a new insight on the microstructural and composition dependence of hydrogen evolution kinetics in RS high purity Al and its alloys. Obtained contribution should be highlighted as follows. Unexpectedly revealed above uncertainty in identifying the individual desorption rate peaks in the region of low- and intermediate temperatures in TDA profiles discloses the suppression of H evolution over this temperature range affected by oxide layers at the foil surface of the Al-based materials. It is well known that surface layers of aluminum oxide (Al_2O_3) always cover Al and its alloys in the presence of oxygen. Note, instead of TDS data acquired by a quadrupole mass spectrometer in ultrahigh vacuum condition, TDA measurements are carried out in the atmosphere that contains oxygen. Thus, received results obviously show that aluminum oxide surface layer can significantly reduce low-temperature hydrogen desorption observed by means of TDA. It is noteworthy to mention that Takasaki et al. [14] showed that presence of Al_2O_3 oxide layers on the surface Ti-Al alloys strongly decreases the hydrogen evolution rate. It was also verified for oxidized sample that a shift of H desorption peaks is observed at a higher temperature side because of oxide layers at alloy surface.

Summary

In this work, TDA measurements have been conducted in atmosphere containing oxygen to evaluate microstructural hydrogen trapping behaviour in RS foils of high purity Al and Al-1.0; 1.5 and 3.0

Cr alloys. Hydrogen evolution rate peaks were explored over a wide temperature range from room temperature to 800°C. Analysis of TDA results was built on a previous investigation of hydrogen behaviour in the materials studied at a low- and intermediate temperature region by means of TDS using ultrahigh vacuum. It was revealed for the first time that hydrogen Al_2O_3 inclusions can be very strong traps of hydrogen in RS Al and Al-Cr alloys. In the alloys, oxide inclusions were found to be dominant traps while the lattice defects and pores are shallow traps. Position of the high-temperature H desorption maxima associated with the oxide inclusions was identified to dependent weakly on Cr content changing from 600°C for high purity Al to 630°C for Al-3.0 Cr alloy. The amount of hydrogen resided with dislocations tends to be increased when chromium concentration rises. Our results demonstrate that TDA approach is a surface sensitive technique which is preferential in investigations of hydrogen trapping at high-temperature trap states to study the effects of rapid solidification on H trapping and diffusion in Al alloys.

Acknowledgements

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