

## Hydrogen profiling in rapidly solidified Al-Fe alloy foils

**Abstract.** Elemental composition of rapidly solidified Al-0.2 at.% Fe alloy has been examined using elastic recoil detection technique and Rutherford backscattering spectroscopy to investigate the changes in hydrogen depth distribution under heat treatment. It was found that hydrogen was limited to near-surface region (400 nm) of as-cast foils. Most detected hydrogen was localized in the subsurface regions and estimated to be 3.6 at.%. Strong hydrogen segregation on air-side surface was observed in alloy annealed at 500°C and showed increase in its content up to 9.6 at.%.

**Streszczenie.** Zbadano skład pierwiastkowy szybko zestalonego stopu Al. 0.2 at.%-Fe przy użyciu metod elastycznego odrzutu (ERD) oraz rozpraszania wstecznego Rutherforda (RBS) w celu zanalizowania zmian rozkładu głębokościowego wodoru zachodzących w trakcie obróbki termicznej. Stwierdzono, że koncentracja wodoru była ograniczona do obszaru przypowierzchniowego (400nm) nowowytworzonych powłok. Większość zawartości wykrytego wodoru była umiejscowiona w obszarach podpowierzchniowych i została oszacowana na 3.6 at.%. Dla stopu wygrzewanego w temperaturze 500°C zaobserwowano silną segregację wodoru na zewnętrznej stronie powierzchni oraz wzrost jego zawartości do 9.6 at.%. (**Profilowanie wodoru w szybko zestalonych foliach ze stopu Al-Fe**).

**Keywords:** Rapid solidification, IBA techniques, Al-Fe alloy, hydrogen.

**Słowa kluczowe:** szybkie zestalanie, techniki analizy wiązki jonowej (IBA), stop Al-Fe, wodór.

### Introduction

Rapid solidification processing (RSP) is an advanced technique that results in alloys with beneficial modifications of microstructure and properties compared with conventionally processed counterparts [1]. Therefore Al based alloys modified through RSP have attracted attention as structural materials as well as versatile materials for electrical engineering. In spite of extensive studies of surface segregation phenomena of alloying elements in rapidly solidified (RS) Al alloys [2-4], information about hydrogen content and its segregation in the subsurface regions is lacking. Nevertheless, hydrogen has drastic effects on physical and electrical properties of materials. One critical assumption is that the hydrogen depth-profiling in RS Al alloys foils is of current practical and fundamental interests to promote understanding of H/microstructure interactions and effect of microstructural features on hydrogen segregation and transport in alloys produced at exceptionally high cooling rates. In fact, our recent macroscopic investigations of hydrogen behaviour using thermal desorption spectroscopy (TDS) clearly showed that hydrogen trapping in the RS Al and its alloys [5] is significantly changed in comparison with traditionally processed materials [6, 7].

The present work focuses on depth-profiling of hydrogen in RS Al-Fe alloy foils under heat treatment. A feature of this paper is the application of nondestructive ion beam analysis techniques for surface elemental study with nanoscale precision. The Rutherford backscattering spectroscopy (RBS) was used to monitor elemental composition of the foils. While analysis for hydrogen is a challenge to many conventional approaches including routine RBS technique because of its very low mass, we employed elastic recoil detection (ERD) spectroscopy as a powerful tool to detect and profile impurity concentrations of hydrogen in the near surface regions of the RS foils.

### Experimental

Foils of RS Al-0.2 Fe (at.%) alloy were cast by centrifugal melt quenching in the air on the inner surface of the polished copper drum with a diameter of 20 cm, rotating at 16 m/s liner velocity. Obtained samples were typically up to 8 cm in length, 50-70  $\mu\text{m}$  in thickness and 5-10 mm in width. In order to investigate the early stages as well as the later stages of solidification, the drum-side surface (A) and the air-side surface (B) of the foils were both subjects of this study. The melt cooling rate for surfaces A and B of the foils was estimated from the known cooling rate-sample

thickness relationship for employed method of rapid solidification, as described in [4]. It was of the order of  $10^6$  and  $10^5$  °C/s accordingly.

Elemental composition and structure of RS foils were investigated by means of RBS and ERD in a cyclotron R-7M using 3.0 MeV  $^4\text{He}^+$  ions with an energy resolution of 40 keV. The beam spot had a diameter of 1.8 mm. In the RBS experiments the foils were positioned normal to the incident beam and the backscattered  $^4\text{He}^+$  ions were detected by an energy sensitive detector placed at a scattering angle of  $135^\circ$ ; the details are given elsewhere [5]. On the other hand, ERD spectra were obtained when foils were rotated to  $75^\circ$  from the normal position, see Fig. 1. Recoiled  $^1\text{H}^+$  ions were detected with a detector at  $30^\circ$  scattering angle position. An absorber (21  $\mu\text{m}$  Mylar stopper foil) was used in front of detector to range out forward scattered  $^4\text{He}^+$  primary beam.

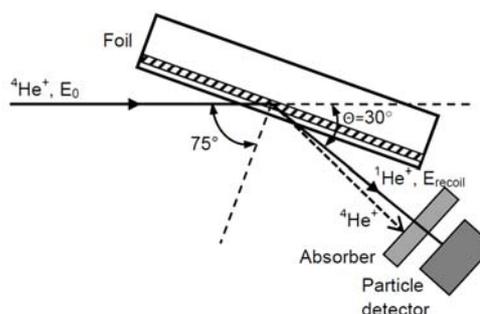


Fig.1. Schematic representation of experimental setup for ERD hydrogen profiling in RS foils. A  $^4\text{He}$ -ion beam of energy  $E_0$  is incident on a foil at a  $15^\circ$  angle with respect to the sample surface

The raw RBS and ERD data were smoothed in order to reduce statistical fluctuations and fitted by computer simulation with SIMNRA code. While the He ERD shows good depth resolution for the near-surface hydrogen [8], quantifying the H content in foils ascribed to rare edge of its signal in the low energy side of spectra was restricted within the depth up to around  $1.0 \mu\text{m}$ . The relative error of concentration definition of hydrogen and iron in the alloys did not exceed 20 and 15%, respectively. Isothermal annealing of the specimens was carried out in the temperature range 150-500°C for 2 h at each temperature.

### Results and discussion

Typical RBS and ERD spectra obtained from both surfaces of as-cast RS Al-0.2 Fe alloy foils are

demonstrated in Fig. 2. The arrows in the figure indicate positions for surface O, Al, Fe and technical impurity Cd atoms in RBS spectra. The presence of impurity Cd in the alloy foils was confirmed by means of X-ray fluorescence analysis described in a previous paper [9]. As can be seen in Fig. 2, RBS experiments show nonuniform iron depth distribution below the foil surface up to a depth of 1.2  $\mu\text{m}$ . The Fe and Cd contents in as-cast samples were measured to be 0.46 and 0.05 at.% at the thin (60 nm) surface A layer. Note that a noticeable surface segregation of Fe is obtained for the surface B. There is 0.60 and 0.03 at.% Fe and Cd, respectively, in the topmost layer of surface B of the Al-Fe alloy. The oxygen concentration at thin layers of both surfaces was estimated to be about 10.0 at.%. Overall, iron measured average bulk concentration exceeds its nominal content in the alloy and makes about 0.60 and 0.43 at.% at 1.2  $\mu\text{m}$  depth of foils surfaces A and B, respectively.

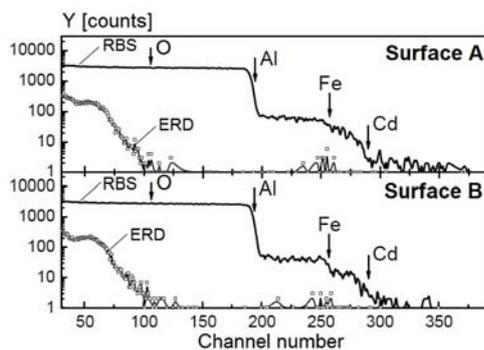


Fig.2. Typical RBS and ERD spectra from 3.0 MeV  $^4\text{He}$ -ion beam of as-cast Al-0.2 Fe alloy foils

It was obtained that the ERD analysis reflects surface hydrogen as well as bulk hydrogen in Al-0.2 Fe alloy. Observed ERD signal at about 67 channel in Fig. 2 shows some accumulation of H at the foils surface. This comes from the fact that as-cast samples were stored in the ambient atmosphere and the signal is related to water adsorbed on the foil surfaces. The next flat background signal from H indicates its uniform distribution in subsurface region of as-cast samples. It was found that H concentration in the 50-nm-thick layer ranges from 1.0 to 2.4 at.% at the surfaces A and B, respectively. Content of H is the same in the depth around 400 nm below both surfaces and makes about 3.6 at.%.

Figure 3 represents the evolution of H depth profiles in foils annealed at different temperatures. The insets show experimental ERD spectra of annealed alloy foils. Since H content at the foil surface increases due to annealing, we can observe that H is uniformly distributed from the top of the surface A up to 400 nm depth in annealed foils. The region near surface A contains 4.0 at.% H in foils annealed at 500°C. On the other hand, a significant feature of Fig. 3 is observed strong segregation of hydrogen in the vicinity of the surface B. Its amount reaches 9.6 at.%. In addition, thickness of the H-containing layer near the surface B is increased up to 800 nm.

At present, investigations of hydrogen migration, trapping and its interactions with microstructure are considered to be of prime importance to various potential applications of Al materials with the exposure to hydrogen (e.g., issues of hydrogen effects on electrical properties of interfaces, hydrogen embrittlement, etc.) [7, 10]. Meanwhile, hydrogen behaviour in high strength alloys is known to be strongly affected by their microstructural changes (structural defects formation) related to fabrication process and material treatments. As far as we are concerned, up to date investigations of H concentration profiles were carried out

on bulk Al samples charged with hydrogen using gas plasma, ion implantation, electrochemical and chemical methods [11]. Isothermal annealing and ramp heating experiments have been shown to elucidate multiple trapping of hydrogen by microstructural heterogeneities that dominate its behaviour and kinetics of desorption in alloys. By constant heating rate desorption technique, we recently found out a prevailing hydrogen desorption over the low temperature range 150-300°C in RS pure Al [5] in contrast to traditionally processed Al specimens exhibited increased hydrogen egress at high temperatures exceeding 350°C [6, 7]. Therefore it should be supposed that direct correspondence in composition-depth profiles of H in Al materials produced by conventional and RSP techniques cannot be expected.

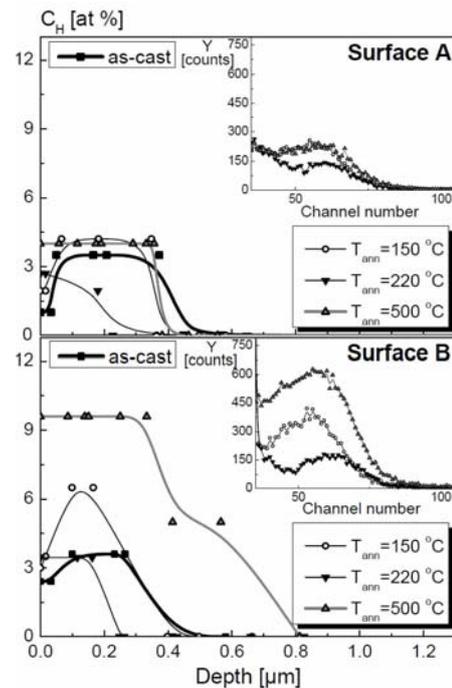


Fig.3. ERD analysis results of hydrogen depth distribution in Al-0.2 Fe alloy foils depending on thermal annealing

This work addresses the near-surface elemental composition of RS Al-Fe alloy to measure depth profiles of immanency impurity hydrogen introduced into alloy during fabrication. This type of hydrogen is in a category of hydrogen already present in the materials prior to the service. As it was investigated in details, the foils of lightly-doped Al-Fe alloys are microcrystalline and composed of metastable  $\alpha$ -solid solution stable up to 250°C [12]. Since ERD technique presented in Fig. 1 is a useful tool for the structural study of hydrogen lateral distribution in alloys, detected clear H signal in Fig. 2 shows the hydrogen segregation within the narrow near-surface region of the foils. In this context it is worth noting, as RBS results obtained here demonstrate in Fig. 2, that RS Al-Fe alloy is structurally heterogeneous, showing pronounced segregation of alloying element, iron, to the foil surface B, which exhibits the finest grains in comparison with opposite side A [13]. Similar nonuniform dope depth distribution was previously revealed in RS Al alloys with Si, Fe, Co, Ni, Cu, Ge, and Sb [4]. This solute enrichment phenomenon is believed to be attributed to the formation of vacancy-solute atom complexes that diffuse to the foil surfaces at RSP.

Our experimental findings on H dope depth distribution are consistent with demonstrated in atomistic simulations tendency for hydrogen to diffuse out and remains on the

surface of pure aluminum bulk [14]. As it was emphasized in [14], the presence of an oxide on the surface completely alters the thermodynamic balance, making it possible to H atoms to retain in the bulk. The fact of decreased H content in the topmost layers of as-cast foils points out that presence of oxygen has an effect on surface hydrogen in Al-Fe alloy. Therefore it is thought that H resided in the oxide corresponds to alumina hydroxide  $\text{Al}(\text{OH})_3$  observed as a 100 nm thick layer on the surface of electrochemically charged Al [11, 15]. Moreover, formation of hydroxide and other metastable aluminum hydride phases have been reported in Al implanted with hydrogen [16, 17]. Indeed, from ERD spectra, the total concentration of segregated H is much higher than calculated previously amount of atomic H trapped at structural defects in RS Al alloys (for instance, about 5.0 at ppm (0.2 mass ppm) trapped H was estimated in RS Al-1.0 Cr alloy by TDS) [5]. This makes it unlikely that measured here H is trapped by solute atoms or lattice defects. From these results we conclude that segregated hydrogen is a major part of H trapped in Al-Fe alloy and forms hydrides in the near-surface regions of foils.

It is important to mention that a large decrease in the amount of hydrogen moved to a shallower depth could be expected in annealed Al-Fe alloy similar to that observed when electrochemically charged Al is annealed [15]. Nevertheless, the ERD analysis indicates here that there is an increase of H content in the near-surface regions of annealed foils. This fact suggests the crucial role of oxygen present in the annealing atmosphere and points to conclusion about temperature stimulated oxidation of the samples. Indeed, RBS analysis showed increase in the oxygen content up to 35 at.% at the foil surfaces annealed at 500°C [9]. In addition, we obtain that concentration of H at the near-surface region grows four times at the foil side B when annealing temperature rises up to 500°C, see Fig. 3. Therefore it appears to indicate diffusion of H to the foil surfaces during thermal annealing. The comparison of ERD spectra from both surfaces makes one point clear that H depth profiles in annealed foils seem to be dependent on surface microstructure which also plays a significant role in the alloying element behaviour in this alloy system, as stated above. Thus, strong H segregation at the surface B of annealed alloy is a result of decomposition of formed hydride phases and is likely attributed to microstructural differences of both surfaces in macro- and micro-scale.

In the present study, RBS and ERD findings show that direct measurements of the surface segregation behaviour of solute elements on a microstructural length scale provide a new insight into structure evolution of RS Al alloys. To clarify RSP effect on H behaviour in Al alloys a multiscale framework is needed to obtain both structural and chemical information about near-surface multilayered elemental composition including oxide film of RS Al-based alloys.

## Conclusions

The behaviour of solute elements in near-surface regions of rapidly solidified Al-Fe alloy foils has been investigated, focusing on hydrogen depth distribution in the foils under thermal annealing. It was found that H segregation up to 400 nm depth below surface shows a maximum value of 3.6 at.% H, indicating formation of hydride structure. The H egress of 9.6 at.% was evaluated on air-side surface of foils annealed at 500°C and suggests dependence of H coverage on microstructural heterogeneities of foil surfaces. Performed analysis of the H depth profiles will promote understanding of the effect of microstructural features on hydrogen trapping and segregation in rapidly solidified Al-based alloys.

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