SURFACE SEGREGATION OF CHROMIUM IN RAPIDLY SOLIDIFIED AL STUDIED BY RBS AND SPEM

I.I. Tashlykova-Bushkevich1), M. Amati2), O.V. Ryabuhin3), B. Aleman2), L. Gregoratti2),
M. Kiskinova2), V.G. Shepelevich4)
1)Belarusian State University of Informatics and Radioelectronics,
P. Brovki Str. 6, 220013 Minsk, Belarus, iya.itb@gmail.com
2)Elettra Synchrotron Light Source,
SS14-km 163.5 in Area Science Park, 34012 Basovizza, Trieste, Italy
3)Ural Federal University named after the first President of Russia B.N.Yeltsin,
Mir Str. 19 , 620002 Yekaterinburg, Russia,
4)Belarusian State University, Av. Independence 4, 220050 Minsk, Belarus

Depth profiling of elemental composition has been examined for rapidly solidified Al-Cr alloy foils containing 1.0 and 3.0 at % Cr by means of Rutherford backscattering spectroscopy (RBS) and scanning photoelectron microscopy (SPEM) using synchrotron radiation. Surface microstructure was monitored using atomic force microscopy (AFM). Analysis of SPEM images and X-ray photoelectron spectroscopy (XPS) spectra from the alloy constituents revealed Cr segregation beneath the foils surface with a corresponding depletion of the outermost surface layer. The deficiency of Cr at the near-surface region found here is in agreement with concentration depth profiles measured by RBS. The investigated segregation behaviour of alloying elements in Al-based foils is discussed concerning the role of lattice defects on solute/microstructure interactions toward hydrogen behaviour in RS materials.

Introduction

The large advances in transportation, storage and use of gaseous hydrogen (H) as a sustainable energy carrier in recent years have opened up new opportunities in Al-based systems, which are regarded as the most promising liner materials [1] for efficient storage of compressed gas. In response, a large number of studies on H-microstructure interactions in traditionally processed Al and its alloys have been performed (e.g. [2-4] and references therein). However, it is known that a major safety problem within the automotive and aerospace sectors concerns the phenomenon of hydrogen embrittlement (HE) of high strength metallic materials exposed to hydrogen at high pressure. The HE mechanisms of commercial Al alloys remain controversial. At the same time, the advanced technique of rapid solidification processing (RSP) results in alloys with significantly beneficial modifications to microstructure and resulting properties compared with conventionally processed counterparts [5]. Our recent results highlighted a lack of information on H behaviour in rapidly solidified (RS) Al materials prepared at exceptionally high cooling rates [6,7]. For the first time, we found promising modifications to the behaviour of hydrogen related to benign traps serving as H sinks in Al materials. Therefore, studies of H-microstructure interactions in RS Al-based alloys accompanied by nanoscale microstructure evaluations present a crucial task for investigations aimed at managing HE of high strength Al alloys in energy technologies.

This paper focuses on microstructural features that affect diffusion and trapping of hydrogen in RS Al-based alloys. In this work, the surface microstructures were evaluated by means of RBS and SPEM in a complementary way to carry out depth profiling of the elemental composition in RS Al-Cr alloys. It is noteworthy here, as far as we are concerned, that no paper has yet reported on SPEM study of microcrystalline RS Al alloys with information on surface segregation of Cr in RS Al-Cr alloy foils to investigate the role of solutes in H/microstructure interactions in the material. Atomic force microscopy (AFM) experiments were performed to monitor surface morphology and topography of the foils.

Experimental

RS foils of Al-1.0; 1.0 Cr (at %) alloys were produced by the centrifugal melt quenching method using a copper wheel in the air on the inner surface of a polished copper drum with a diameter of 20 cm, rotating at 16 m/s linear velocity. The cooling rate was on the order of 10^6 K/s [8]. The obtained foils were typically 5-10 mm wide and 50-100 μm thick.

The surface microstructure of the air-facing side of the foils was examined by AFM employing a NT-206 instrument using a Si probe. Height images were analysed using the SurfaceXplorer and SurfaceView software [9]. Roughness values in the paper refer to the average surface roughness values, R_a, calculated from 20x20μm^2 AFM scans.

The RBS measurements were done in vacuum with a 3.0 MeV He$^+$ ion source (laboratory scattering angle of 170º). The data were then fit with the SIMNRA software analysis package [10]. The relative error of concentration definition of Cr in the alloys did not exceed 5%.

The SPEM measurements were carried out at the ESCA microscopy beamline at the 3rd generation Elettra Synchrotron Light Source. In prior experiments, samples were sputter cleaned in 3 steps of 10 min by Ar$^+$ bombardment with an ion energy of 2 keV to remove carbon on foil surfaces. Structure and chemical alloy characterization was performed for the air-facing surface and the cross-section of the samples with a photon energy of 665 eV, energy resolution of 0.2eV, and spatial resolution of less than 0.1 μm. The SPEM set-up has been described in details elsewhere [11]. Measurements were conducted at room temperature with the pressure lower than 10^{-9} mbar. All XPS spectra were normalized to the incident photon flux. The depth of the sample probing was limited to a few nanometers.

Results and discussion

Figure 1 shows typical height mode scans taken from the air-facing surface of the Al-3.0 Cr alloy foils by means of AFM. Observed surface microgeometry characteristics include ridge-rich surface regions and microvoids. The roughness value R_a is calculated to be 15.1 nm. The height of some ”waves” and peaks on the air-facing surface reaches 200 nm, Fig. 1a.

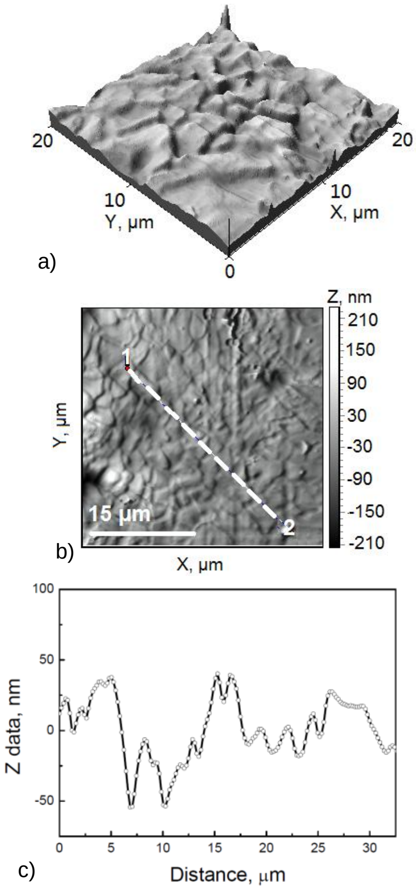

Fig. 1. Microstructure of RS Al-3.0 Cr alloy foil observed by AFM: (a) and (b) 3D and 2D images from as-cast foil, respectively, (c) topography profile along the line marked in image (c)

Typical RBS spectrum, evaluated to determine composition-depth profile in the near-surface region of Al-Cr alloy foils, is represented in Fig. 2. The Cr depth distribution is reflected around the edge signal of Cr because the yield in the RBS spectra is proportional to the elemental concentration, as shown in Fig. 2 for the Al-3.0 Cr alloy.

The Cr depletion was revealed in the thin surface layers (0.03 µm) of the foils when its content was measured to be 0.6 at % in the air-drum region. Fitted Cr depth profiles indicate that the difference between Cr concentration at the foil surface and its nominal concentration makes up 80%.

The SPEM images of Al-Cr alloys exhibited the nonhomogeneous distribution of elements at the surface of the foils. As can be seen in Fig. 3, brightness in the images from Al 2p and Cr 3p core level reflects the change in the surface composition and is proportional to the relative concentration of the corresponding alloying element. Some contrast in Fig. 3a, b can also arise from topography of the foils illustrated in Fig. 1.

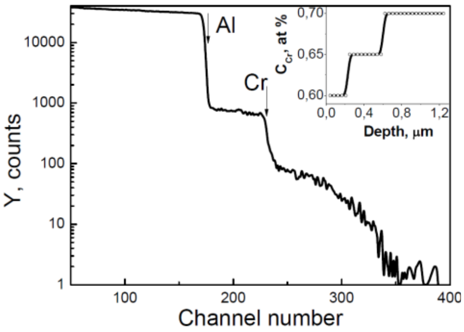

Fig. 2. Typical RBS spectrum and Cr-concentration depth profile for RS Al-3.0 Cr alloy

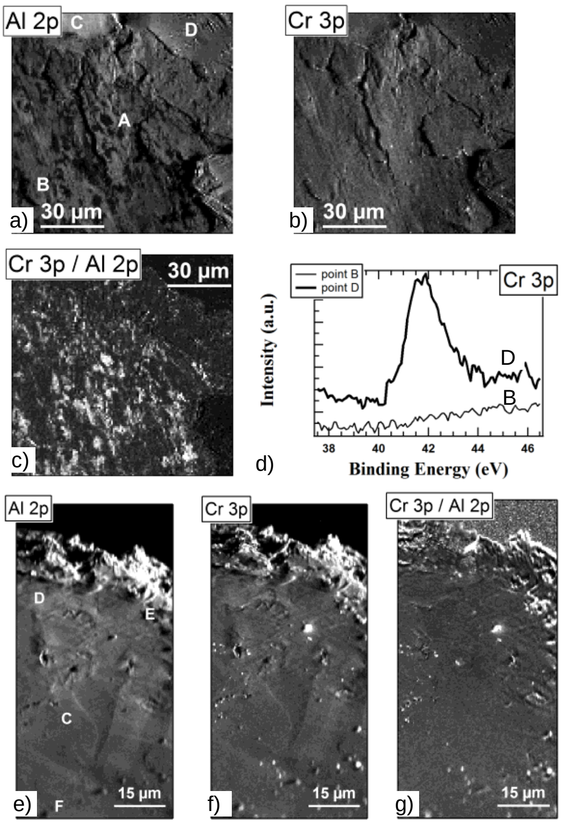

Fig. 3. SPEM analysis of RS Al-3.0 Cr alloy foil: (a)-(c) (128×128) µm^2 images of Al 2p, Cr 3p maps and Cr 3p / Al 2p map for foil surface, respectively, (d) XPS spectra of Cr 3p taken in spots indicated in image (a), (e) – (g) (45×90) µm^2 images of Al 2p, Cr 3p maps and Cr 3p / Al 2p map for transverse cross-section, respectively

It was found that rapid solidification resulted in formation of Cr-rich and Cr-depleted regions at the foils surface, see in Fig. 3a-c regions C and D in comparison with regions A and B for Al-3.0 Cr alloy, respectively. In addition, it should be highlighted that the amount of Cr was considerably reduced in the outermost surface layer when compared with the subsurface layer of the foils. In fact, intensity of spectrum signals was very low for the Cr 2p core level, which represents the features of the topmost specimen layer. Therefore SPEM images from Cr 3p core level can be considered to reveal the bulk features of near surface region of the foils. Note, the Cr is presumed to be present in the foils both as metallic Cr and oxidized Cr. The ESCA chemical analysis of RS Al-Cr alloy foils is discussed in details elsewhere [12].

The cross-sectional images of Al-3.0 Cr alloy shows the distribution of chromium species through the foil depth, see Figs. 3e-g. Analysis of XPS profiles exhibits the deficit of Cr at the near-surface region of the foils. The Cr is assumed to segregate beneath the narrow air-facing region of specimen with a corresponding decrease of its content toward the wheel-side of the samples.

The present work illustrates that both SPEM and the ion beam analysis technique, RBS, are high-resolution techniques that provide high spatial resolution and allied compositional, chemical and structural information in the examination of RS Al alloys. Both methods are considered to be complimentary and enable the evaluation of how solute atoms interact with lattice defects at microscopic scale, clarifying the role of solute in H/microstructure interactions in the materials toward H behaviour in RS Al alloys. Revealed for the first time, Cr segregation phenomenon beneath the foil surface suggests the process of segregation based on the latest atomic level and electronic structure calculations are as follows. The solute depletion of the foil surface – acting as a □ sink (□=vacancy) – is caused by the fact that Cr atoms are strongly repelled from vacancies in Al due to a very low Cr-□ binding energy [13, 14]. Therefore, the flow of Cr atoms occurs in the opposite direction of □ flow. At the same time, Cr atoms interact sufficiently with dislocations [15, 16], thereby the translation of dislocation loops slow down and act as sinks for vacancies. Further elaboration of these results suggests that the total concentration of vacancies is drastically reduced in RS Al-Cr alloys as compared to pure RS Al. Concerning the above-shown results, the found effect of non-uniform Cr depth distribution is attributed to the reduced concentration of vacancies and can account for the recently detected significant decrease of H content trapped by vacancies in the presence of Cr compared with RS pure Al [6]. This phenomenon is suggested to be a result of Cr segregation processes.

This work is a first step of the systematic study on microstructure evolution and chemical state changes toward H behaviour in RS Al alloys. Further investigations of microstructure evolution at sub-μm scale and alloying element segregation in RS Al alloys will develop mechanistic understandings of H interactions with microstructure aimed to control hydrogen embrittlement in high strength Al based materials.

Conclusions

The present study demonstrates the advances of using scanning photoelectron microscopy and imaging accomplished by RBS and AFM to investigate the surface segregation of alloying elements in RS aluminum. Depth profiling of elemental composition indicates that RS microstructure evolution is influenced by solute-nanostructured defect interactions in Al-Cr alloys. It was found that Cr 2p and 3p core level photoemission spectra exhibits foil surface impoverishment of chromium. In agreement with dope depth profiling as carried out by RBS, the revealed phenomenon can be attributed to the fact that Cr drastically reduces the concentration of vacancies compared with RS pure Al, and affects H behaviour in RS Al-Cr alloys. Obtained results indicate that the surface microstructure of the Al alloy foils at the submicrometer scale, as far as the high density of quenched-in vacancies is concerned, is essential to elucidate how the microstructural morphology resulting from rapid solidification affects hydrogen trapping at lattice defects.

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