

SCANNING PHOTOELECTRON MICROSCOPY STUDY OF MICROSTRUCTURE AND CHEMICAL COMPOSITION EFFECTS ON HYDROGEN BEHAVIOUR IN RAPIDLY SOLIDIFIED Al ALLOYS

Structure and chemical composition of rapidly solidified (RS) Al-Cr alloys has been investigated for the first time by means of scanning photoelectron microscopy (SPEM). This study suggests that the revealed nonuniform Cr depth distribution, as far as the high density of quenched-in vacancies is concerned, can be directly related to the reduction of vacancies concentration compared with RS pure Al and affects H behaviour in RS Al-Cr alloys.

Introduction. Aluminium-based alloys have been regarded as lightweight liner materials for efficient storage of compressed hydrogen gas. Meanwhile, one critical assumption is that a major safety problem within the automotive and aerospace sectors concerns the containment of H and is related to the phenomenon of hydrogen embrittlement (HE) of high strength metallic alloys. Although a remarkable international effort has been deployed in recent years to develop a universal mechanism for HE in Al materials (see [1] and references therein), the HE mechanisms still remain controversial concerning Al alloys of commercial interest. At the same time, our recent results show promises in modification of hydrogen behaviour in RS Al alloys prepared at exceptionally high cooling rates in comparison with traditionally processed Al samples [2]. However along with the continued advances in microstructure analysis, experimental data about interactions between lattice defects and solute atoms, both interstitial and substitutional, are scarce regarding Al materials. Therefore study of H/microstructure interactions in RS Al-based alloys accompanied by nanoscale microstructure evaluations presents a crucial task for investigations aimed to manage HE of high strength Al alloys in energy technologies.

The aim of the present work was to examine evolution of microstructure and chemical composition in RS Al-Cr alloys foils influenced by the interaction of lattice defects with the solute atoms. In this paper, we demonstrate the recent progress in the nanoscale and sub-micrometer analysis of RS Al-Cr alloys performed by SPEM using synchrotron radiation. The SPEM was operated in imaging mode and spectroscopic mode with a standard X-ray photoelectron spectroscopy (XPS) from the submicrospot.

Experimental. The RS Al-1.0; 3.0 Cr alloys (at %) 50-100 μm thick and 5-10 mm wide were prepared by using a centrifugal melt quenching technique [2]. The cooling rate was of the order of 10^5 - 10^6 $^\circ\text{C/s}$ [2]. Materials with the following purities: 99.99% Al and 99.9% Cr, were used. Pure Al foil and Cr sample (99.5%) were tested for comparison. For the cross-section view, sample of Al-3.0 Cr alloy was fractured after immersing in liquid nitrogen.

The SPEM measurements were carried out at the ESCA microscopy beamline at the Elettra Synchrotron Light Source. Prior experiments, samples were sputter cleaned in 3 steps of 10 min by Ar^+ bombardment at an ion energy of 2 keV. Chemical and morphological alloys characterization was performed for an air-side surface of the samples with a photon energy of 665 eV, energy resolution of 0.2 eV, and spatial resolution of less than 0.1 μm . The depth of the sample probing was limited to few nm.

Results and discussion. The XPS spectra collected from pure Al and Al-Cr alloys indicate complex compositional structure of the surface of as-cast foils and are shown in Fig. 1. Apart from expected presence both of metallic Al(0) and oxidized Al (Al_2O_3) chemical states in the near-surface region, XPS analysis of RS pure Al revealed some hydration of its surface, see a broadened line shape toward the lower kinetic energy side of the Al 2p spectrum in

Fig. 1a. This can be attributed to the fact RS Al materials [2] contain a high density of lattice defects (quenched-in vacancies, dislocations, and voids). Therefore, while H associated with defects tends to form Al-H bonds during non-equilibrium processing, such as mechanical alloying, ion implantation, etc., we can infer that alumina hydroxide $\text{Al}(\text{OH})_3$ and other hydrides (such as AlH_3 or AlH) are supposed to be additional species in RS Al prepared at high cooling rates. This assignment was signified by obtained O 1s spectra from the foils (not shown here) and also consistent with XPS results for RS Al-rich metallic glasses [3] indicated the presence of Al_2O_3 accompanied by $\text{Al}(\text{OH})_3$ at foils surface.

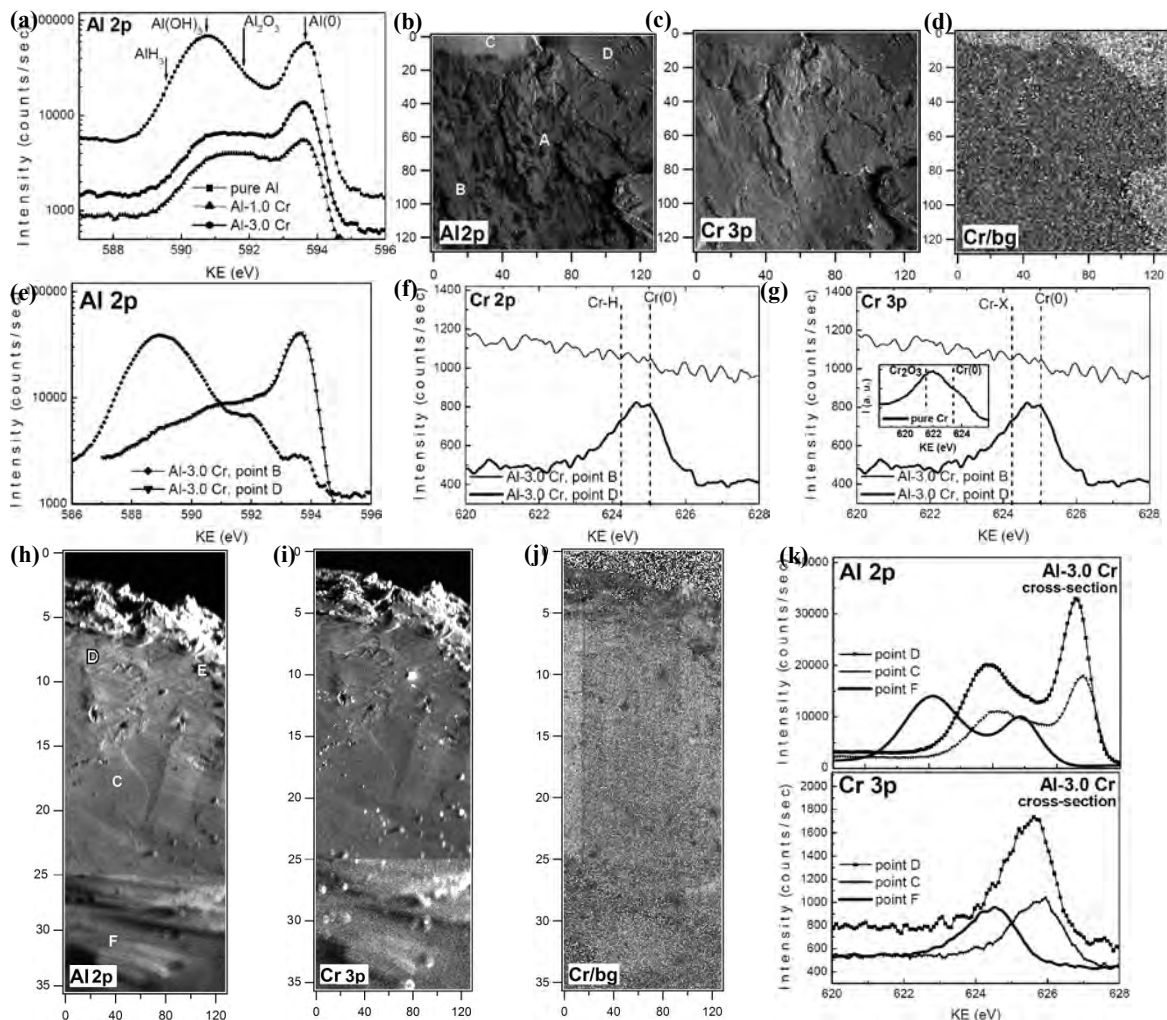


Figure 1: Structure and chemical analysis of RS pure Al and Al-Cr alloys. (a), (e), (f) and (g) XPS spectra of Al and Al-Cr alloys surface. (b)-(d) $(128 \times 128) \mu\text{m}^2$ Al 2p and Cr 3p maps with Cr/background for Al-3.0 Cr alloy surface, respectively. (h)-(j) $(128 \times 356) \mu\text{m}^2$ Al 2p, Cr 3p maps and Cr/background for a transverse cross-section of Al-3.0 Cr alloy foil, respectively; (k) XPS spectra obtained for the cross-section survey of (h)-(j). Wheel-side of the Al-3.0 Cr alloy foil is on the bottom of (h)-(j).

The SPEM images of Al-3.0 Cr alloy revealed the nonhomogeneous distribution of elements at the surface of the foils, which results in formation of Cr-rich and Cr-depleted surface regions, see maps in Figs. 1b and c and Cr/background map in Fig. 1d. It was also found that amount of Cr is considerably reduced in the outermost surface layer compared with a subsurface layer of the foils. In fact, intensity of spectrum signals is very low in Fig. 1f of Cr 2p core level that represents the features of the topmost specimen layer. Similar microstructures were also observed for Al-1.0 Cr alloy foils.

The Cr 3p XPS spectra demonstrate that chromium exists mainly in metallic state $\text{Cr}(0)$ at the subsurface layer in foils, as compared to the oxidized pure Cr reference sample in Fig. 1g. Moreover, these observations indicate that Cr in RS alloys tends to be protected from

oxidation by preferential undersurface segregation and additionally by oxidation of Al. It is also noticeable that Al is found to be selectively oxidized at the foil surface and its oxidation is affected by Cr. The Al 2p curve for Cr-rich grains (regions C and D in Fig. 1b) exhibits a high metallic component Al(0) showing a reduced amount of the aluminum oxides and hydroxides at the foils surface, while Cr-depleted areas (regions A and B in Fig. 1b) exhibit aluminum almost entirely in the oxidized state with only a slight shoulder indicating some metallic Al(0), see Fig. 1e. This can be related to the composition of RS Al-Cr alloys [2] where Al phase is a supersaturated solid solution containing chromium.

The cross-sectional images of Al-3.0 Cr alloy showed the distribution of chromium species through the foil depth up to several hundred micrometers, see Fig. 1h-j. The Cr is assumed to be segregated beneath discussed above narrow air-side region of specimen with followed decrease of its content toward the wheel-side of the samples. Figure 1k illustrates the evolution of Al 2p and Cr 3p signals with the foil depth. The general features of these profiles are quite similar to those of Fig. 1a, e and g and also indicate that intensity and fraction of the metallic Al(0) component depend on Cr segregation. More to the point, the deficit of Cr at the near-surface region found here is in agreement with our recent ion-beam study of Al-Cr alloys by means of Rutherford backscattering spectroscopy [2].

Conclusions. Present work exhibits that SPEM enables investigate how solute atoms interact with lattice defects at microscopic scale to clarify 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 segregation based on the latest atomic level and electronic structure calculations as follows. The solute depletion of the foil surface as a \square sink (\square =vacancy) is caused by the fact that Cr atoms are strongly repelled from vacancies in Al due to a very low Cr- \square binding energy [4] and the Cr atoms flow occurs in the opposite direction of \square flow. Meanwhile, Cr atoms interact sufficiently with dislocations [5], thereby moving dislocation loops are 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 in comparison with pure RS Al. Concerning the above-shown results, found effect of nonuniform Cr depth distribution attributed to reduction the concentration of vacancies can account for detected significant decrease of H amount trapped by vacancies in the presence of Cr compared with the H behaviour in RS pure Al [2]. It follows that further work 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 aluminum alloys.

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