

EFFECT OF Cr ON HYDROPHOBICITY OF RAPIDLY SOLIDIFIED Al

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The effect of Cr on hydrophobicity of Al has been investigated in rapidly solidified Al-1.0Cr and Al-3.0Cr (at.%) alloys by means of SPEM, AFM and distilled water CA measurements. The results demonstrate the crucial importance of both chemical composition and surface morphology of alloys for the control of their wettability.

1. Introduction

In hydrogen storage technologies, aluminum-based materials are a favorite candidate for hydrogen tanks because of an excellent gas barrier property coupled with their lightness [1]. The progress in commercialization of hydrogen fuel cell vehicles requires a development of high-strength aluminum alloys immune to hydrogen embrittlement (HE) for a use in compressed hydrogen storage systems where maximum filling pressure is increased up to 70–100 MPa. In response, remarkable international efforts have been deployed for an assessment of factors that account for hydrogen-assisted fracture behavior of Al materials. In spite of controversy on HE mechanisms in Al alloys in the literature, a consensus has emerged that H provides the dominant damage mechanism for high strength alloys stressed in moist environments. Particular attention is focused on corrosion effects which can occur at wetted surfaces when atomic H enter and diffuse through the metal.

In our recent work H desorption measurements were successfully accompanied by nanoscale microstructural evaluation of rapidly solidified (RS) Al and an Al-Cr alloy by means of synchrotron-based photoelectron microscopy [2] to gain insight into hydrogen/microstructure interactions developing H embrittlement mechanisms in Al-based alloys. The objective of this paper is to investigate how chemical composition and microstructure affect surface wettability of RS Al-Cr alloys.

2. Experimental

Foils of pure Al, Al-1.0Cr and Al-3.0Cr alloys (at.%) were produced by the centrifugal melt quenching method in air using a Cu wheel. The cooling rate was of the order of 10^6 K/s. The thickness of foil bulk parts was 50–100 μm .

The chemical composition was studied using scanning photoelectron microscopy (SPEM) at the ESCA microscopy beamline at the 3rd generation Elettra Synchrotron Laboratory. In prior experiments, samples were sputter cleaned in 3 steps of 10 min by Ar^+ bombardment with an ion energy of 2 keV to eliminate surface contamination by carbon. Air-facing surface was examined with a photon energy of 665 eV, energy resolution of 0.2 eV, and spatial resolution of less than 0.1 μm . The SPEM set-up has been described in details elsewhere [2]. The foil roughness was characterized by means of atomic force microscopy (AFM) by a NT-206 instrument. Average surface roughness characteristics were calculated using SurfaceXplorer software. The contact angles (CAs) for the air-facing foil side were determined using the sessile-drop technique. The measurements were conducted using a 5 μl droplet of distilled water at room temperature with the relative error of 1 %.

3. Results and discussion

Fig. 1 shows SPEM images of an air-side surface of RS Al-1.0Cr and Al-3.0 Cr alloys. The contrast of the raw images in Figs. 1a and c reflect both the foil surface elemental composition and morphology. Figs. 1b,d present a lateral distribution of elements mapped in SPEM images.

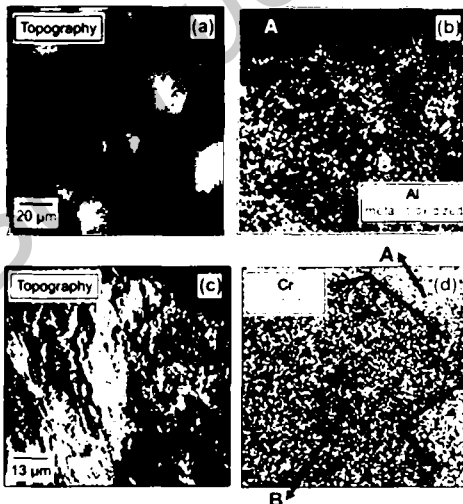


Figure 1. SPEM images for Al 2p (a) and chemical map (b) obtained as the ratio of Al 2p metallic and oxidized species maps from the same area (a) of Al-1.0Cr alloy foil, illustrating the relative local concentration of metallic Al. SPEM images for Cr 2p_{3/2} (c) and Cr/background (d) maps acquired for Al-3.0Cr alloy. The black solid lines in (d) indicate Cr-rich areas at upper and bottom right side corners.

The changes in the elemental composition can be observed as a difference in brightness in the image proportional to the relative concentration of indicated elements, see Figs. 1b and d. Comparing the Cr and Al metal/oxide maps one can see a clear correlation between the regions of higher/lower Cr content and lower/higher Al oxide content. Black solid lines in the map of Fig. 1d mark the boundary between the Cr-rich and Cr-depleted (areas A and B, respectively).

The foil morphology in AFM images shown in Fig. 2 demonstrates that RS Al-1.0Cr and Al-3.0Cr alloys are rough on a sub-micron and nanometer scale and include ridge-rich surface regions and microvoids. The surface roughness is increased from 39.2 nm for Al-1.0Cr alloy to 42.7 nm for Al-3.0Cr alloy. The CA measured at the surface of Al-1.0Cr alloy (86.2 deg) was larger than that measured at the surface of Al-3.0Cr alloy (75.2 deg).

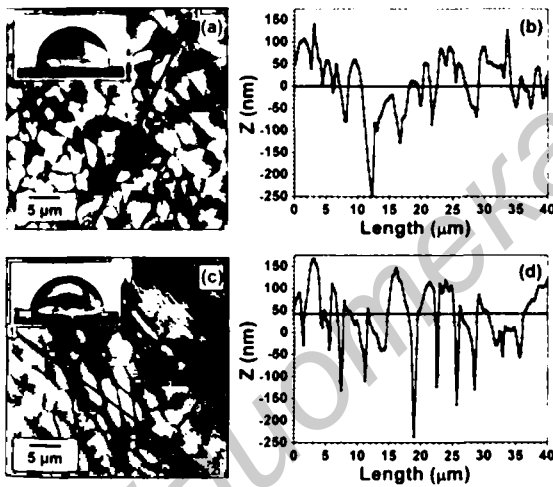


Figure 2. AFM surface images of Al-1.0Cr (a) and Al-3.0Cr (c) alloys and correspondent section analysis (b) and (d) performed along the lines shown in (a) and (c), respectively. The inserts in left upper corner of images (a) and (c) show the shape of distilled water droplets on foil surfaces.

The wettability behavior has been investigated for nano-rough surfaces of RS Al-Cr alloys concerning specific surface properties, such as morphology, roughness, and surface chemistry. The present SPEM results reflect the chemical composition of foil surface, rich in Al oxide species with some scarce contribution of Cr. The Cr-rich areas (regions A in Fig. 1) exhibit a high metallic component of Al at the foil surface, while Cr-free areas (regions B in Fig. 1) indicate Al almost entirely in the oxidized state. Recently, we reported that oxide inclusions of Al_2O_3 as well as $\text{Al}(\text{OH})_3$ and AlOOH are found both on and below the Al and Al-Cr alloy surfaces [2]. As the RS Al materials can contain a high density of lattice defects, we can attribute the presence of aluminum

hydroxides and oxyhydroxides to the formation of Al-H bonds during such non-equilibrium processing as rapid solidification processing.

It was found that Al-1.0Cr alloy exhibits hydrophobic behavior, as its large CA value is in a good agreement with the data which we obtained for RS pure Al (87.7 deg) [3]. One can argue that detected widespread regions with lack of Cr at foil surface of Al-1.0Cr alloy account for it. This fact attracts a vast interest because Al is a high surface-energy metallic material expected to be hydrophilic [4]. At the same time, the decrease of CA measured on Al-3.0Cr alloy, see Figs. 2c,d, shows a wetting transition from hydrophobic to hydrophilic state of the samples with the increase of Cr content when the surface roughness tends to be increased and according to the Wenzel model [4] the water wets the surface homogeneously and enters the cavities and microvoids.

4. Conclusion

The wettability of RS Al- x Cr alloys, $x = 1.0; 3.0$ at.%, has been observed to depend on chemical composition and surface morphology. The wetting transition from hydrophobic to hydrophilic state of the foils was found with the increase of Cr content when stable Wenzel state of water droplet is observed.

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