

## Microstructure, elemental and phase composition and their influence on hydrophilic properties of rapidly solidified Al-In alloys

**Abstract.** The microstructure, elemental and phase composition of rapidly solidified foils of Al-In alloys were investigated using SEM with EDX, XRD and RBS. It was found that thin surface layers of foils are enriched with indium that results in hydrophilization of alloys. Wetting transition from the homogeneous Wenzel state to the heterogeneous Cassie-Baxter state observed when indium content increases at the foil surface of hydrophilic Al-In alloys is discussed in terms of the penetration of water into the micro/nanostructures of foil surfaces.

**Streszczenie.** Na podstawie pomiarów SEM z EDX, XRD i RBS przeprowadzono badania składu pierwiastkowego, fazy i mikrostruktury szybko zestalonych powłok stopów Al-In. Stwierdzono, że cienkie warstwy powierzchniowe powłok wzbogacają się w ind, co powoduje hydrofilizację stopów. Przejście zawilgocenia z jednolitego stanu Wenzel do heterogenicznego stanu Cassie-Baxter, obserwowanego gdy następuje wzrost zawartości indu na powierzchni powłoki hydrofilowych stopów Al-In, zostało przeanalizowane pod kątem wnikania wody do powierzchniowych mikro i nano struktur powłoki. (Mikrostruktura, skład pierwiastkowy i fazy oraz ich wpływ na hydrofilowe właściwości szybko zestalonych stopów Al-In).

**Keywords:** Rapid solidification, wetting, Al-In alloys, elemental chemical analysis.

**Słowa kluczowe:** Szybkie zestalanie, zwilżanie, stopy Al-In, elementarna analiza chemiczna

### Introduction

Recently, wetting behaviour of aluminum alloys has drawn considerable attention because hydrophilic and hydrophobic metal surfaces exhibit promising applications in energetics, electronics and radio engineering. Since chemical composition and topography play a key role in the control of surface wettability [1], surface sensitive methods for elemental depth profiling analysis are required to understand the influence of different alloying elements on wetting state of aluminium materials in order to develop multicomponent alloys with tailored properties.

The technology of rapid solidification processing (RSP) is one of perspective methods for manufacturing aluminum alloys with improved physical properties. Scientific research data show that RSP allows to increase solubility of alloying elements and get alloys with fine-grained structure that considerably improves physical and mechanical characteristics of materials [2]. Our studies have demonstrated for the first time the possibility of production of rapidly solidified (RS) aluminum alloys with controlled wettability to protect materials from the harmful effects of water. Earlier we revealed that nature of water wetting of both foil surfaces of pure Al received by high-speed crystallization from melt is hydrophobic [3-5]. Addition of low-melting In additive to Al, which forms monotectic system with aluminum, significantly changes the nature of water wettability of foil surfaces. It was established that Al-In alloys possess hydrophilic properties [3, 5]. Therefore, for the purpose of structure modifying and wettability control of surfaces of aluminum materials this work presents a continuation of the research carried out on RS Al-In alloys and it is aimed to reveal how surface chemistry affects wetting properties of alloys.

### Experimental

Binary Al-In alloys which contain 0.1; 0.2; 0.35; 0.4; 0.7; 1.2; 1.4; 2.4; 4.7 and 6.4 at.% of In were rapidly solidified in the air by means of the centrifugal melt quenching method on the inner surface of a rotating copper wheel. Foils of 30-80  $\mu\text{m}$  thick were selected for investigations. Cooling rate made about  $10^6$  K/c [6].

For studying of microstructure and phase composition of received foils, the scanning electron microscope of LEO 1455 VP type equipped with "HKL CHANNEL 5" add-on device for energy-dispersive X-ray spectroscopy (EDX) was used. The analysis was conducted at the accelerating voltage of 20 kV with magnification from 2000 to 60000. Determination of phase composition was also carried out by X-ray diffraction (XRD) analysis on a DRON-3.0 diffractometer using monochromatized Co K $\alpha$  radiation (a doublet  $\lambda_{\alpha 1} = 1.78892$  Å and  $\lambda_{\alpha 2} = 1.79278$  Å).

The element layer-by-layer analysis of RS foils of Al-In alloys was made using Rutherford backscattering spectrometry (RBS) using 1.7 MeV helium ions, scattering geometry was  $\theta_1 = 0^\circ$ ,  $\theta_2 = 20^\circ$ ,  $\theta = 160^\circ$ . Processing of received RBS spectra was carried out by the known technique [7] and with the use of computer modeling by means of RUMP software. Energy resolution of the detecting system was ~ 20 keV that provided the layer-by-layer analysis of alloys with an accuracy of 0.03  $\mu\text{m}$ . The error of determination of In content by RBS method made about 3-6 % [7].

Studying of sample surface topography and definition of its roughness was performed by means of atomic force microscopy (AFM) on an atomic-force microscope NT-206 with use of CSC-38 probes. Average roughness (arithmetical mean height)  $R_a$  was determined by the averaging of data obtained from 7 scans ( $20 \times 20$  of  $\mu\text{m}^2$  area), chosen at random. For typical 2D-AFM foils images, scanning of a surface profile along 10 horizontal lines located at distance of 2  $\mu\text{m}$  from each other was performed, using Surface Explorer [8] program, and 10 corresponding histograms of surface topography elements distribution on height were plotted. By results of averaging, then for each 2D-AFM image the resulting histogram of structural surface elements distribution on height was constructed and average total roughness  $R_z$  of profiles was calculated as the sum of average maximum profile peak heights and average maximum profile valley depths [9].

## Results and discussion

Studying of a surface morphology of RS foils of Al-In alloys by AFM demonstrated micro- and nanosized structural elements present on foil surfaces, Fig. 1. The average size of grains in foils of pure aluminum makes about 9  $\mu\text{m}$ . The alloying of aluminum with indium leads to reduction of grain size. For instance, for RS foils containing 0.8 at % In the average size of grains decreases to 5  $\mu\text{m}$ . With increase of indium concentration a tendency of grain size reduction remains the same, and the average size of grains makes less than 1  $\mu\text{m}$  in foils with indium content exceeding monotectic composition. The data obtained by means of SEM showed the cellular structure formed in foils, which localization and sizes of structural elements depend on a surface of the analysis. Cellular structure on the wheel-side surface (A) is observed mainly in cavities of the micron size formed because of rupture of a melt drop at contact with a crystallizer surface – the copper wheel [10, 11]. On A side of foils, depending on concentration of In, the size of cells varies from small to larger (from 1 to 20  $\mu\text{m}$ ), and on the air-facing surface (B) of foils the cells are distributed on dimensional groups more homogeneously (from 1 to 5  $\mu\text{m}$ ).

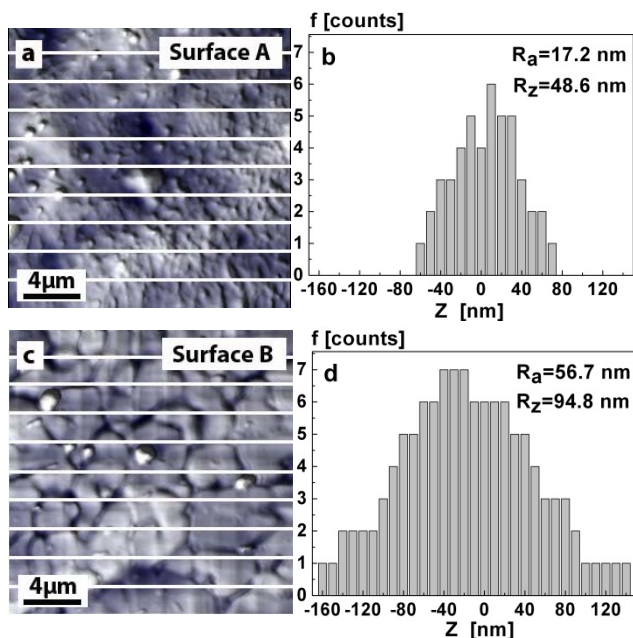


Fig.1. Typical 2D-AFM images of A and B foil surfaces of Al-1.4 at.% In alloy (a, c) with profile lines marked in images and corresponding histograms (b, d) derived from surface height distributions obtained over all profiles.

Roughness parameters of RS foil surfaces depend on a surface of the analysis and concentration of In in alloys. Figures 1b and 1d clearly demonstrate distribution on dimensional groups of the average measured values of peak heights and valley depths of a surface topography on the opposite sides of a sample of Al-1.4 at.% In alloy foil. The topography of A surface of samples significantly differs from the topography of their B surface, Fig. 1a, c. The last is caused by presence of different features on the surface of RS foils, for instance cavities, flat plateaus, conical shaped sharp and obtuse tips. As it is possible to see in Fig. 1, the  $R_z$  value defined for B surface of Al-1.4 at.% In alloy foil exceeds the value measured for A surface twice. For RS alloys containing 0.35, 0.7, 1.7 and 4.7 at.% In, the average  $R_z$  value measured for A surface depending on indium contents changes in the range from 48.6 to 116.0 nm, and for B surface ranges from 46.3 to 212.4 nm. The tendency that B surface is characterized by the greatest values of

roughness parameters ( $R_a$ ,  $R_z$ ) in comparison with A surface remains the same for all RS Al-In alloys except for Al-4.7 at.% In alloy.

The typical XRD pattern taken from RS Al-1.2 at.% in alloy is presented in Fig. 2a. The diffraction peaks belong to Al and In only and no other peaks were detected. All diffraction patterns of RS foils of Al-In alloys are similar and differ only in the intensity of the diffraction peaks related to indium which rises at increase in its concentration in samples. The EDX analysis demonstrates that white inclusions distributed in a dark matrix of SEM-images of foil surfaces of Al-In alloys (Fig. 2b) are indium particles which segregate to the grain boundaries. Note, that In precipitates located in grains have smaller sizes. The XRD peaks of indium observed in XRD patterns of samples (Fig. 2a) and white inclusions of SEM-images of RS foils of Al-In alloys (Fig. 2b) demonstrate that when obtaining foils of Al-In alloys by RSP method there does not occur full dissolution of indium in aluminum. Thus, studying the phase composition of foils by EDX and XRD methods showed that RS foils of Al-In alloys represent the two-phase system consisting of supersaturated Al-based solid solution and fine-dispersed particles of indium.

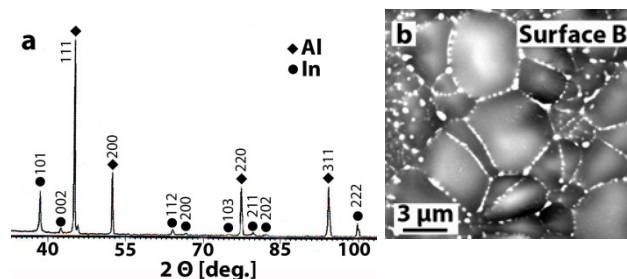


Fig.2. Characterization of indium precipitates in Al-In alloy foils: XRD diffraction pattern of Al-1.2 at.% In alloy (a) and SEM image of B surface of Al-0.4 at.% In alloy (b).

Typical SEM micrographs of a transverse cross-section of RS Al-1.2 at.% In alloy are given in Fig. 3. In the area close to A side of foils of Al-In alloys more than a half of observed In particles have the size to 0.2  $\mu\text{m}$ . The area close to B side of foils is characterized by precipitates larger by size, as the melt starts cooling down and solidifies from the wheel-side. During rapid solidification the cooling rate is decreased across the foil thickness and indium precipitates manage to merge and form larger inclusions on B side.

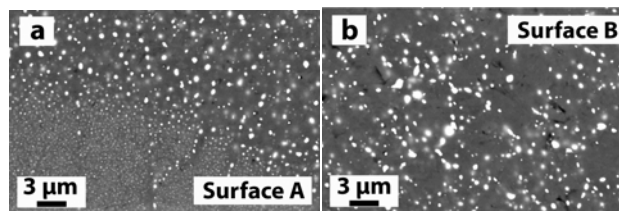


Fig.3. Typical SEM-images showing microstructure variation through the foil thickness near A (a) and B (b) surfaces of Al-1.2 at.% In alloy foil.

At increase of indium concentration in alloys from 1.2 to 6.4 at.% it is observed linear enlargement of d size of the precipitated particles on both A and B sides (Fig. 4a). Figure 4b clearly demonstrates dependence of number n of particles in volume unit in RS Al-In alloys on concentration of In. It was found that with the increase of In concentration the number of particles in volume unit of foil decreases. At the same time the quantity of indium particles on A side is higher, than on B side. Observed dependence of number of particles on elemental composition of RS foils of Al-In alloys

is explained by the increase in the average size and volume of particles (Fig. 4a) caused by the increase of In concentration in alloy. Different degrees of an inclination for A and B surfaces of  $d$  and  $n$  curves as functions of calculated contents of In in alloys, apparently, are connected with the fact that due to intensive heat removal and, respectively, the larger cooling rate, solubility of In near the wheel-side surface is higher than near the air-side surface (Fig. 4).

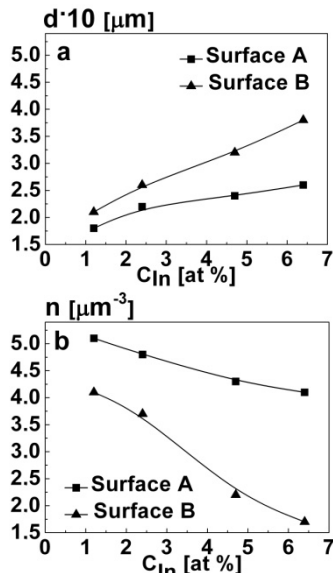


Fig.4. Dependence of the average amount of precipitates  $d$  (a) and average number of indium  $n$  particles in volume unit (b) on indium concentration in foils of Al-In alloys.

The effect of non-uniform distribution of In along depth of foils was found for all studied RS Al-In alloys, Fig.5. For example, for a lightly doped Al-0.2 at % In alloy it was obtained by RBS that thin near-surface layers ( $\sim 0.03 \mu\text{m}$  thick) are enriched with indium: concentration of In reaches 2.6 at %. The average measured In concentration in the near-surface region from 0.2 to  $2.0 \mu\text{m}$  thick makes about 0.5 at % that by 2.5 times exceeds the indium concentration in this alloy. At a depth of  $2.0 \mu\text{m}$  of the analyzed layer at further increase in the depth of RBS analysis the increase of In concentration is observed. The found enrichment by indium of thin near-surface layers of foil can be explained by diffusion of alloying element atom-vacancy complexes to the foil surface which acts as a sink for defects [12].

Analyzing the ratio of In concentration on foil surface  $C_{\text{In}}^{\text{max}}$  to its content in an alloy  $C_{\text{In}}^{\text{calc}}$  calculated by means of RBS for A and B surfaces, we found the tendency common for all RS Al-In alloys: the extent of a surface enrichment is the greatest at low concentration of alloying element (to 0.36 at % In), Fig. 5 a, b. For example, for A and B surfaces of foil of Al - 0.2 at % In alloy the extent of enrichment makes 11.2 and 15.3 times respectively. In addition, for lightly doped Al-In alloys it is found there is a tendency at the foil surface to increased indium content on B surface in comparison with A surface (Fig. 6a, b). This dependence is well correlated with similar results received for RS foils of Al-Fe and Al-Sb alloys [13,14] and can be explained by the revealed in this work change of microstructure through the foil depth because of reduction of cooling rate during rapid solidification.

Recently, we measured the equilibrium water contact angle (CA) of RS foils of pure aluminum and Al-In alloys by means of sessile drop method and studied dependence of CA  $\theta^{\text{CA}}$  on foil surface roughness [3,5]. It was found that RS

foils of Al-In alloys exhibit hydrophilic properties and have low CAs of distilled water droplets on surfaces. The transition from homogeneous regime of wetting, observed for lightly doped Al-In alloys, to heterogeneous regime was revealed when the value of  $\theta^{\text{CA}}$  decreases with a decrease of foil surface roughness. Application of RBS in this work allowed to establish the fact that wetting is more pronounced when the indium concentration in a near-surface layer is increased that leads to decreasing CAs [5], Fig. 6. Character of hydrophilic behavior of Al-In alloy foils as a function of indium content in samples is identical for both A and B surfaces and it confirms the above conclusion (Fig. 6).

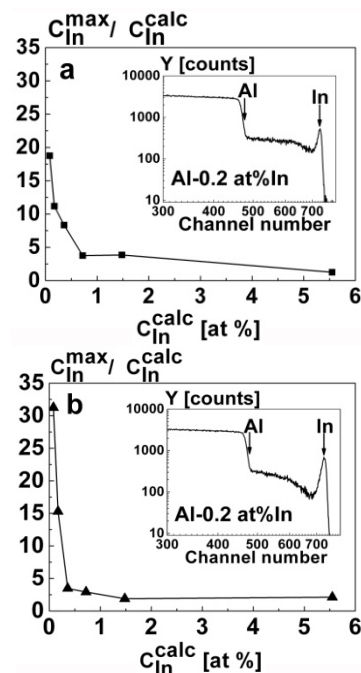


Fig.5. Dependence of indium enrichment ratio of thin near-surface layer ( $0.03 \mu\text{m}$ ) of Al-In alloys on its concentration in alloys measured by RBS for A (a) and B (b) surfaces.

The observed micro- and nano-scale features of microstructure found at foil surfaces of Al-In alloys mean that the water droplet is larger than the roughness scale and the Wenzel and Cassie-Baxter models can be applied to describe surface wettability of RS samples. In fact, as it was reported recently, equations of Wenzel and Cassie-Baxter are fair only if the line of contact of solid and liquid phases allows to consider the contact angle of wetting invariable along the line of contact [15,16]. At the same time, instead of Wenzel wettability model [17,18] which considers the homogeneous regime of wetting when the liquid penetrates into the roughness micro-grooves, the model Cassie-Baxter [19] describes heterogeneous regime of wetting when air is trapped below a droplet and there is no penetration of the liquid inside the grooves.

Wetting of surfaces of solid materials with organic liquids, aqueous solutions plays an important and sometimes defining role in many technology and natural processes. Depending on industrial tasks wetting can render both positive and negative influence on properties of materials [20]. Therefore, when speak about wetting as about the surface phenomenon, the researches which are aimed to separate the contributions to wetting behavior given by micro/nanostructures and elemental composition of surface layers of hydrophobic/hydrophilic materials are of special interest.

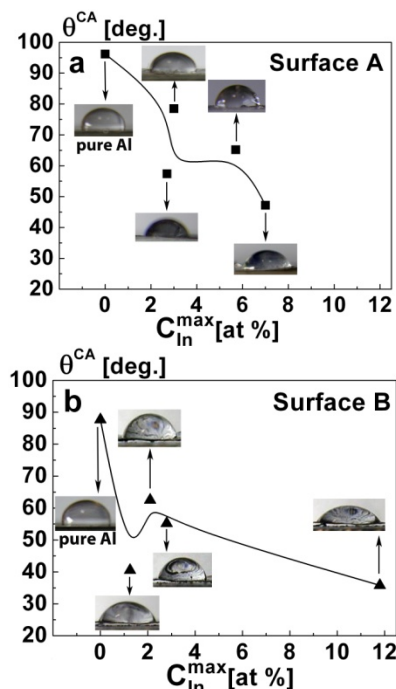


Fig.6. Effect of In content at A (a) and B (b) foil surfaces of Al-In alloys on the CAs.

## Conclusions

The influence of microstructure, elemental and phase composition of RS Al-In alloys on their water wettability is studied. It was defined that foils of aluminum alloys containing from 0.2 to 6.6 at% In have microcrystalline structure and consist of supersaturated  $\alpha$ -Al solid solution and dispersed particles of In, which density and size depend on concentration of indium in an alloy. Experimentally established indium enrichment of surfaces of RS Al-In alloys results in hydrophilization of Al-based foils. This leads to a conclusion about a possibility to control wettability behavior of aluminum materials received by rapid solidification processing by addition of different alloying elements to aluminum.

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