

Effect of topography on wettability of rapidly solidified Al-In alloys

Abstract. The wettability of rapidly solidified foils of Al-In alloys containing up to 4.7 at.% of In was investigated by means of sessile-drop method and atomic force microscopy. It was found that In significantly changes wetting properties of pure Al from a hydrophobic behaviour to a hydrophilic one. The effect of topography on the wetting properties of nano-rough foils demonstrates that an increase in In content up to 0.7 at.% resulted in a transition from a homogeneous to a heterogeneous wetting behaviour when decreasing the roughness of the surface makes it more hydrophilic.

Streszczenie. Zwilżalność szybko skryształizowanych folii stopu Al-In zawierających In do 4,7 at.% została zbadana za pomocą metody „siedzącej kropli” oraz mikroskopii sił atomowych. Określono, że dodatek In znacząco zmienia właściwości zwilżające czystego Al z hydrofobowych na hydrofilowe. Wpływ topografii na właściwości zwilżające nano-chropowatych folii przedstawia, że wzrost zawartości In do 0,7 at.% skutkuje w zmianie właściwości zwilżających z homogenicznych na heterogeniczne oraz zwiększająca się chropowatość powierzchni powoduje, że stają się one hydrofilowe. (Wpływ topografii powierzchni na zwilżalność szybko skryształizowanego stopu Al-In).

Keywords: Wetting, rapid solidification, Al-In alloy, AFM.

Słowa kluczowe: Zwilżalność, szybka krystalizacja, stop Al-In, AFM.

Introduction

Surface microstructure and its wetting characteristics have been the subject of extensive study of metals in a wide range of industrial applications (spray quenching, soldering etc.) and microelectronics. In particular, a lot of attention has been paid to wettability behaviour of aluminium-based alloys [1-3] due to its high thermal and electrical conductivity, low specific weight, low contact resistance as well as non-toxicity and beneficial effects of small amounts of alloying elements on electrochemical properties. Therefore, both from the scientific point of view and the technical side an in-depth understanding of mechanisms which affect the wettability of solid surfaces is of great importance to tailor such properties of engineering and electronic aluminium materials as adhesion, anticorrosion, catalysis, to name a few.

In the case of aluminium, there are a number of experimental approaches which can be classified as roughening methods to modify the surface morphology and vary wetting properties. While pioneering works [4, 5] demonstrated promises in wettability tuning of shallow surface regions of Al-doped materials by means of pulsed laser treatment, our recent studies revealed that the surface roughness can be also controlled by alloying elements in rapidly solidified (RS) aluminium alloys produced using centrifugal quenching method from the melt [6]. By now, rapid solidification processing (RSP) has advanced significantly as a promising process for production of novel materials with beneficial microstructural changes both in laboratory scale studies and industrial sectors [7] because of refinement of grains, extension of solid solubility and formation of metastable phases at extremely high cooling rates. In RS foils of Al alloys, it should be highlighted, the chemical composition and microstructure at the surface was found to differ from the bulk of the foils [8-10] due to a steep temperature gradient which results in solidification of a strongly inhomogeneous melt at RSP. This fact suggests that chemical heterogeneities of RS foil surface, its roughness and local defects may have a strong influence on its wetting properties, emphasizing the need for exploratory research of wettability behaviour of RS Al alloys which is still not addressed to date.

In this work, we investigate effect of surface topography on the wettability of RS foils of Al-In alloys containing up to 4.7 at % of In. Indium is reported to be considered as an alloying element in Al-based alloys for interconnect

applications in electronic devices [11] and is one of the promising additives in lead-free Zn-Al based solders [12] to lower the melting temperature because electronic devices and substrates cannot endure high reflow temperatures. In order to reveal a water contact angle (CA) dependence on the surface topography, a morphology of foils surfaces was studied by means of atomic force microscopy (AFM) prior CA measurements (sessile-drop method).

Experimental

The foils of pure Al (99.98%) and Al-In alloys with a nominal composition ranging from 0.35 to 4.7 at % indium were rapidly solidified in the air by means of the centrifugal melt quenching method on the inner surface of a copper wheel, rotating at 16 m/s liner velocity. Resulted RS foils were typically 5-10 mm in width. The thickness of the foils was 50-100 μm . The cooling rate was of the order of 10^6 K/s [13].

The AFM analysis of foils surface microstructure reported in the present work was performed at the air-facing side to eliminate any effects from topography of the substrate on morphology of the wheel-facing foil surface. The AFM images were obtained by a NT-206 instrument using cantilevers CSC21 and analyzed using the SurfaceXplorer software [14]. Roughness values referred to the average surface roughness values, R_a , were calculated from 7 scans ($20 \times 20 \mu\text{m}^2$ area) for each foil composition. The relative error of R_a definition did not exceed 3.5%.

The sessile-drop method was used for CA measurements of doubly distilled water droplets of 5 μl under ambient conditions. The CA was calculated automatically after stabilization for 60 s of the deposited drop on the foil surface using a specially designed program “Angle” [15]. The results of water CA tests were determined as averages of the values measured at 5 different spots for each foil composition. The relative error of CA measurements was 1%.

Results and discussion

Figure 1 demonstrates that RS foils of pure Al and Al-In alloys are rough on a sub-micron and nanometer scale. Observed surface microgeometry characteristics for pure Al and Al-In alloys include ridge-rich surface regions and microvoids, see a typical AFM height mode scan in Fig. 1a taken from the air-facing surface of RS Al-1.4 at % In alloy foil. As an example, in Fig. 1b, it is clearly seen that the

height of some "waves" and peaks on the foil surface of Al-1.4 at % In alloy reaches 150 nm.

The effect of alloying element concentration on surface roughness of RS Al-In alloys is presented in Fig. 1c. In the case of pure Al, revealed surface undulations are not pronounced and an average roughness R_a value is calculated to be 25.7 nm. However, it was obtained that the roughness of Al-0.35 at % In alloy foils is almost 4 times higher than the roughness of pure Al foils. Figure 1c shows that the surface roughness of alloys is decreased with increase of In concentration up to 4.7 at %. Foils of Al-4.7 at % In alloy exhibit a R_a value of 17 nm, which is the smallest one compared to all other compositions.

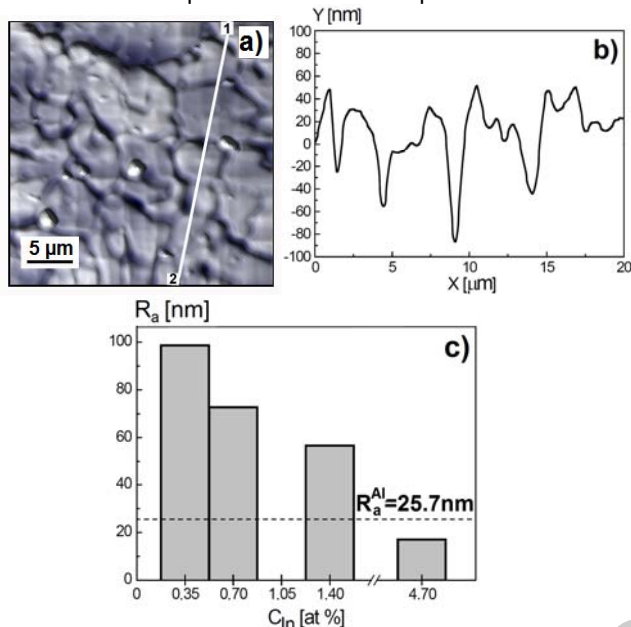


Fig.1. The AFM analysis of RS Al-In alloys: (a) typical 2D image of the foil surface of Al-1.4 at % In alloy, (b) topography profile along the line marked in image (a), (c) average surface roughness of alloys plotted as a function of In concentration

Figure 2 represents shapes of water droplets placed on RS foils of pure Al and Al-In alloys. For the first time, it was found that indium significantly changes wetting properties of pure Al foils which exhibit hydrophobic behaviour with a large CA of 87.7°. The Al-In alloys demonstrated hydrophilic properties when droplet spreading depends on alloying element concentration. The minimum of CA was measured for Al-4.7 at % In alloy with a mean value of 35.8°.

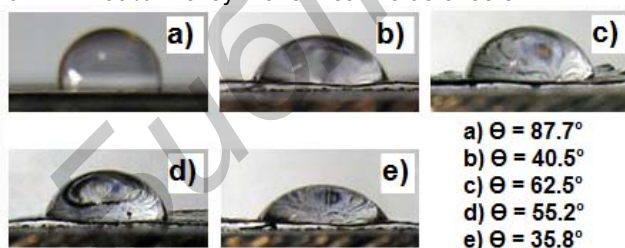


Fig.2. Shape of water droplets on the air-facing surface side of RS foils: (a) pure Al (99.8%), (b) Al-0.35 at % In alloy, (c) Al-0.7 at % In alloy, (d) Al-1.4 at % In alloy, (e) Al-4.7 at % In alloy

To reveal the effect of topography on the wetting properties of RS foils of Al-In alloys, the dependence of water CAs on the foils roughness is depicted in Fig. 3. Here, it is seen that there are two opposite tendencies of wetting behaviour of the alloys. The CA is observed to be 40.5° on the Al-0.35 at % In alloy surface with the highest value of roughness of 98.6 nm and reaches a maximum value of 62.5° when the surface roughness is decreased to 72.8 nm

in case of Al-0.7 at % In alloy. However, it appears that further decrease of R_a results in a noticeable decrease of CAs and a hydrophilic foils surface becomes more hydrophilic.

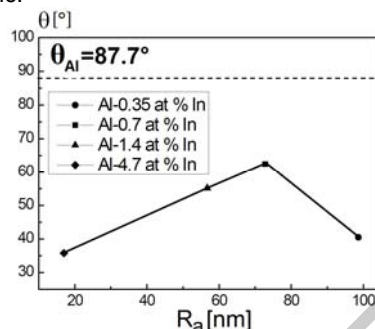


Fig.3. Dependence of the water contact angle on the roughness of RS Al-In alloys

The wetting transition phenomena between hydrophilic and hydrophobic states of solids have been studied extensively to manage spreading of liquid on solid substrates and produce materials with controllable wetting properties. Promising applications of hydrophilic and hydrophobic metal surfaces are related to vital needs to protect materials from the harmful effects of water in a number of industries. The surface is considered to be hydrophilic when the wetting CA is less than 90° and the material possesses beneficial adsorption properties when water drops disperse easily on its surface. On the other side, hydrophobic surface is characterized by the wetting CA of 90° and larger and such material has anticorrosion, defogging and antifouling properties since the water is repelled from its surface.

In this paper, the wettability behaviour has been investigated for nano-rough surfaces of RS Al and Al-In alloys. Without any additional treatments (either roughening or polymer coating) the RS samples of Al was found to exhibit hydrophobic behaviour. Large CA value measured on pure Al foils, as high as 87.7°, attracts a vast interest because water preferably spreads on surfaces with a high free energy [16] and, therefore, aluminium as a high surface-energy metallic material is expected to be hydrophilic. Indeed, only scarce literature data [17, 18] contradict numerous experimental studies [1, 4, 5] where samples of Al and its alloys are reported to exhibit small CAs values, despite different preparation methods. At first glance, the large CAs values observed here on pure Al could be attributed to a presence of hydrophobic organic contaminants [19] or aluminium oxides and hydroxides [20] at its surface after an exposure to atmosphere. But these assumptions fail to explain why RS Al-In alloys was found to possess opposite wetting properties to those of RS pure Al, see Fig. 2. Moreover, as it was argued in [18] where reported CAs on aluminium samples were about 70°, also, these assumptions do not explain a giant contact angle hysteresis observed on polished and degreased metals. Therefore, we suppose that revealed hydrophobic character of pure Al foils can be explained by considering the surface energy gradient. It has been reported that a competition between surface energy gradient along with horizontal and perpendicular directions results in a hydrophilic-hydrophobic-hydrophilic transition on Al-Mg based alloy scratched by sandpaper with varying grits [21]. According to the proposed model [21], a hydrophobic surface on Al-based sample can be obtained by variation of altitude difference H and peak width W between neighbouring sawtooth profiles of the surface, resulting in $H/W > 1$.

The present work demonstrates a strong effect of the topography and composition on the wettability behaviour of RS Al-In alloys. Impact of topography on wetting properties of rough surfaces can be rationalized in terms of either the Wenzel model [21, 22] (the Derjaguin theory [23]) or the Cassie-Baxter model [24]. These models consider two opposite wetting regimes: the homogeneous (Wenzel state) and the heterogeneous (Cassie-Baxter state) regimes. According to the Wenzel model, the wetting behaviour of the rough surface – either hydrophilic or hydrophobic – is enhanced by its roughness when the liquid wets the surface homogeneously and enters the cavities and microvoids. Therefore, a facile approach to fabricate a superhydrophilic surface on Al alloys is to change the morphology of a hydrophilic surface enhancing its roughness [1, 5, 17]. On the other hand, in respect to the Cassie-Baxter model, heterogeneous wetting of the rough surface results in a mixed wetting state when air is trapped on a rough surface below the water droplet. Since air is a hydrophobic material ($\theta=180^\circ$), the air trapping beneath the droplet amplifies surface hydrophobicity. Hence, a suitable technique to attain a superhydrophobicity of Al alloys is to modify a chemical composition of the rough surface and lower the surface energy compared to bare Al materials [1, 2, 5, 17]. It can be also concluded from the Cassie-Baxter model that an increase in the air fraction and a reduction in the solid fraction would enhance the water repellency of a surface regardless of whether the surface is hydrophilic or hydrophobic [2, 21]. Therefore, the Cassie-Baxter model is a more general model which accounts in particular for conditions when a surface shifts from hydrophilic to hydrophobic.

Thus, contact angle measurements indicate that droplets deposited on foils were in the stable Wenzel state when concentration of indium was in the range of 0.35-0.7 at % and in the metastable Cassie-Baxter state on alloys containing higher indium concentration due to the change in surface roughness. These results suggest a wetting transition from a homogeneous to a heterogeneous regime on Al-In alloys with an increase of In content since Al-0.35; 0.7 at % In alloys follow the Wenzel model and exhibit larger CAs and lower wettability when R_a is decreased, i.e. hydrophobicity of hydrophilic alloys is improved with the increase in surface roughness. On the contrary, further decrease of the roughness when alloys contain more than 0.7 at % In leads to a decrease in the contact angle values and a surface becomes more hydrophilic due to a reduction in the air fraction in accordance with the Cassie-Baxter model, see Figs. 1 and 3.

Revealed in the present study hydrophobic-hydrophilic transition occurred when pure Al is doped by indium as well as the transition from a homogeneous to a heterogeneous wetting behaviour of Al-In alloys when In content reaches 0.7 at % imply that not only the topography but also the elemental composition at the foil surface should be taken into account to understand the wettability changes in RS Al-In alloys. From the values of the water CAs as a function of indium concentration in alloys, it can be inferred that the surface segregation phenomenon can account for the changes in both topography and chemical composition in the near-surface region of foils due to the nonuniform dope depth distribution found in RS Al-based alloys when surface is enriched/impoverished with alloying element [6, 8-10, 25, 26]. Apart from structure and phase composition, investigation of the In depth distribution in RS Al-In alloys foils is outside of the scope of this work, but it is currently studied by authors and will be published shortly. Considering the factors which result in the change of

wetting behaviour from the wetted Wenzel state to the composite Cassie-Baxter state on nano-rough foils, it should be additionally emphasized that this phenomenon can be also influenced by a competition between an energy barrier and external forces, particularly Laplace pressure, because of changes in interfacial energies at liquid/vapour, solid/vapour and solid/liquid interfaces during the wetting transition in the vertical direction [27].

This work sheds light onto the structure-wetting properties relationships for RS Al-based alloys. Up to now, complicated process control, complex chemical treatments, poor durability and rather high cost severely limit an application range of many fabrication methods developed to tailor hydrophilic or hydrophobic properties of Al and its alloys. Considering that centrifugal melt quenching is a facile method beneficial to produce microcrystalline Al alloys with improved properties, the present work demonstrates major directions for future research, aimed to develop a present understanding of the physical mechanisms which control the wettability behaviour of aluminium materials on nanometer length scale.

Conclusions

The effect of topography on the wettability of nano-rough rapidly solidified foils of Al-In alloys has been studied by analyzing the roughness and water contact angle values. For the first time, it was found that indium significantly changes wetting properties of pure Al foils which have an average surface roughness of 25.7 nm and exhibit hydrophobic behaviour with a contact angle of 87.7° . The Al-In alloys demonstrated hydrophilic properties, thereby the water contact angle was decreased with the addition of In to pure Al. The minimum of CAs was measured for Al-4.7 at % In alloy with a mean value of 35.8° .

It was obtained that varying degrees of wettability can be achieved by changing In concentration. The surface roughness is decreased in the range of 98.6-17.0 nm as indium concentration rises from 0.35 to 4.7 at %, respectively. An increase in In content up to 0.7 at % resulted in a transition from a homogeneous to a heterogeneous wetting behaviour when decreasing the roughness of the surface makes it more hydrophilic for Al-1.4 at % In and Al-4.7 at % In alloys. Obtained original results expand the current knowledge of mechanisms affecting wettability of nano-rough surfaces of Al alloys.

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REFERENCES

- [1] Liu W., Sun L., Luo Y., Wu R., Jiang H., Chen Y., Zeng G., Liu Y. Facile transition from hydrophilicity to superhydrophilicity and superhydrophobicity on aluminum alloy surface by simple acidetching and polymer coating, *Appl. Surf. Sci.*, 280 (2013), 193-200
- [2] Mohamed A.M.A., Abdullah A.M., Younan N.A. Corrosion behavior of superhydrophobic surfaces: A review, *Arabian Journal of Chemistry*, (2014) doi:10.1016/j.arabj.2014.03.006
- [3] Sommers A.D., Jacobi A.M. Creating micro-scale surface topology to achieve anisotropic wettability on an aluminum surface, *J. Micromech. Microeng.*, 16 (2006) 1571-1578

- [4] Bizi-Bandoki P., Benayoun S., Valette S., Beaugiraud B., Audouard E. Modifications of roughness and wettability properties of metals induced by femtosecond laser treatment, *Appl. Surf. Sci.*, 257 (2011) 5213-5218
- [5] Lee C., Cho H., Kim D., Hwang W. Fabrication of patterned surfaces that exhibit variable wettability ranging from superhydrophobicity to high hydrophilicity by laser irradiation, *Appl. Surf. Sci.*, 288 (2014) 619-624
- [6] Tashlykova-Bushkevich I.I., Change of surface structure (morphology and roughness) of rapidly solidified foils of aluminium through Fe alloying, *J. Surf. Invest. X-Ray, Synchrotron and Neutron Tech.*, 7 (2010) 105-112 (in Russian)
- [7] Herlach D.M., Galenko P., Holland-Moritz D. Metastable Solids from Undercooled Melts, in Pergamon Materials Series, edited by R. Cahn, Elsevier, Amsterdam, 2007, 432 p.
- [8] Tashlykova-Bushkevich I.I., Patterns of concentration-depth profiles in melt-substrate quenched aluminium alloys, *Proc. 12th Int. Conf. on Aluminium alloys*, edited by S. Kumai, O. Umezawa, Y. Takayama, T. Tsuchida and T. Sato (The Japan Inst. Light Metals, Yokohama, Japan, 2010) 1800-1805
- [9] Tashlykova-Bushkevich I.I. Effects of thermal treatment on microstructure of rapidly solidified Al-2.1 at % Mn alloy studied by RBS technique, *J. Alloys Compd.*, 478 (2009) 229-231
- [10] Tashlykova-Bushkevich I.I., Shepelevich V.G. Dope depth distribution in rapidly solidified Al-Ge and Al-Me (Me = Fe, Cu, Sb) alloys, *J. Alloys and Compd.*, 299 (2000) 205-207
- [11] Kailasam S.K., Murarka S.P., Glicksman M.E. Investigation of Aluminum-Indium Alloys for Interconnect Applications, *J. Electrochem. Soc.*, 147 (2000) 4318-4323
- [12] Gancarz T., Pstruś J., Fima P., Mosińska S. Thermal properties and wetting behavior of high temperature Zn-Al-In solders, *J. Mater. Eng. Perform.*, 21 (2012) 599-605
- [13] Miroshnichenko S.I. Quenching from the Liquid State, *Metallurgiya*, Moscow, 1982, 168 p. (in Russian)
- [14] SurfaceXplorer (Microtestmachines, 2012), <http://microtm.com>
- [15] Tashlykov I., Turavets A., Zukowski P., *Acta Phys. Pol. A* 123, (2013) 840-842
- [16] Gennes P.-G., Brochard-Wyart F., Quere D. Capillarity and Wetting Phenomena: drops, bubbles, pearles, waves, Springer, New York, 2004, 287 p.
- [17] Rahimi M., Fojan P., Gurevich L., Afshari A. Effects of aluminium surface morphology and chemical modification on wettability, *Appl. Surf. Sci.* 296 (2014) 124-132
- [18] Lu B., Li N. Versatile aluminium alloy surface with various wettability, *Appl. Surf. Sci.* 326 (2015) 168-173
- [19] Bewig K.W., Zisman W.A. The wetting of gold and platinum by water, *J. Phys. Chem.* 69 (1965) 4238-4242
- [20] Gajewski A. Contact angle and sessile drop diameter hysteresis on metal surfaces, *Intern. J. Heat and Mass Transfer.* 51 (2008) 4628-2636
- [21] Wenzel R.N. Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem. Res.* 28 (1936) 988-994
- [22] Wenzel R.N. Surface roughness and contact angle, *J. Phys. Chem.* 53 (1949) 1466-1467
- [23] Derjaguin B.V. On the dependence of the contact angle on the microrelief or roughness of a wetted solid surface, *Dokl. Akad. Nauk USSR* 51 (1946) 361-364 (in Russian)
- [24] Cassie A.B.D., Baxter S. Wettability of porous surfaces, *Trans. Faraday Soc.* 40 (1944) 546-551
- [25] Tashlykova-Bushkevich I., Amati M., Ryabuhin O., Aleman B., Gregoratti L., Kiskinova M., Shepelevich V.G. Surface segregation of chromium in rapidly solidified Al studied by RBS and SPEM, *Proc. 10th Int. Conf. Interaction Radiation with Solids*, edited by S.V. Ablameyko (Belarusian State Univ., Minsk, Belarus, 2013) 333-335
- [26] Tashlykova-Bushkevich I.I., Amati M., Aleman B., Gregoratti L., Kiskinova M., Shepelevich V.G. Scanning photoelectron microscopy study of microstructure and chemical composition effects on hydrogen behaviour in rapidly solidified Al alloys. *Proc. 2nd Intern. Conf. Applied problems of optics, informatics, radiophysics and condensed matter physics*, edited by V.I. Popenchits and Yu.I. Dudchik (Ministry of Education of the Republic of Belarus, Minsk, Belarus, 2013) 242-245
- [27] Murakami D., Jinnai H., Takahara A. Wetting transition from the Cassie-Baxter state to the Wenzel state on textured polymer surfaces, *Langmuir* 30 (2014) 2061-2067