

ELEMENTAL ANALYSIS OF RAPIDLY SOLIDIFIED Al-Cr ALLOY FOILS BY RBS METHOD

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Rapidly solidified (RS) Al-0.8; 1.0 Cr alloy (at %) foils were produced by the centrifugal melt quenching technique. The alloys were investigated using atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS) and thermal desorption spectroscopy (TDS). It was obtained that the as-cast foils show a wave-like bending of a drum-side surface, the surface roughness value of the Al-1.0 Cr alloy amounts to 38.5 nm. The RBS measurements indicated that rapid solidification processing (RSP) decreases the Cr concentration up to 0.5 at % in a drum-side surface layer extending to a depth of 0.06 μm for the Al-0.8 Cr alloy. Three distinct H-desorption-rate peaks were observed at about 220, 420 and 460°C on TDS spectra. Amount of H for the Al-1.0 Cr alloy was estimated as 5.1 at ppm. The AFM results revealed that the surface roughness value of the foils is reduced by a factor of ~3 after TDS tests.

Introduction

At present RS alloys on basis of Al-Cr system are considered as heat-resistant lightweight structural materials because of their high-temperature mechanical properties and thermal stability. Although the microstructure and properties of Al-Cr alloys has been extensively studied [1,2], there is a lack of information on elemental analysis of the alloys, such as data on surface segregation of Cr and H behaviour in RS Al-Cr alloy foils. Indeed, effects of dopes on the H content in RS Al alloys are studied insufficiently. Meanwhile, it is well known that H can degrade the mechanical properties of alloys, and therefore cause material failure. Experiments on the casting of Al have demonstrated that the strength of castings may be reduced by as much as 90% because of gas entrapment, shrinkage cavities, and hot tears [3]. At the same time, RSP reduces porosity of the samples in comparison with conventionally processed alloys [3], and thus higher mechanical properties can be expected.

The aim of this work was to carry out elemental analysis of RS lightly doped Al-Cr alloys to evaluate microstructural features of the materials into micro-scale of physical processes, taking place during RSP. Scans of RBS were performed for level-by-level study of the elemental composition in the near surface region of the foils. It should be emphasized that the RBS coupled with RUMP software analysis package [4] is a quantitative analytical technique which provides precise investigation of surface composition of specimens. Furthermore, our results [5] also point out preferable combination of surface analysing techniques with AFM to correlate dope depth profiles of samples with morphology and topography of their surface. For a study of H behaviour in Al-Cr alloy foils we employed TDS because of H is invisible to RBS. In fact, due to its superior accuracy of H content measurements TDS can be used to examine H-microstructure interactions and quantify H trap states in metals [6].

Experimental

RS foils of Al-0.8; 1.0 Cr alloys were produced by the centrifugal melt quenching method using a copper wheel. The RSP technique was described in de-

tail elsewhere [7]. Obtained foils were typically 5-10 mm wide and 50-70 μm thick. The cooling rate was of the order of 10^6 K/s [8].

The surface microstructure of the foils was examined by AFM employing a NT-206 instrument. No special treatment was applied to the surface of the samples prior to inspection in a contact mode in air using a Si probe. Height images ($20 \times 20 \mu\text{m}^2$ area) were collected simultaneously and analysed using the SurfaceXplorer and SurfaceView software. Roughness values in this paper refer to the average surface roughness values, R_a , calculated from the AFM surface topographic data. The RBS measurements were done in vacuum with a 2.0 MeV He^+ ion source (laboratory scattering angle of 160°). The data were then fit with the RUMP software analysis package. The relative error of concentration definition of Cr in the alloys did not exceed 5%. TDS tests were executed on ESCO UVH-1200 & HA-200 machine. The samples were heated from 100 to 540°C at a heating rate of 5K/min. Afterwards, when the foil temperature reached 100°C the tests were repeated to measure background spectra. Finally TDS spectra were discussed after eliminating the background. The amount of H was determined from the intensity of the desorption peaks. Selected foils were also analysed after TDS tests by using AFM.

Results and discussion

The AFM was utilized to examine the topography and the roughness of as-cast RS foils. Representative height mode scans taken from the drum-side surface of the Al-1.0 Cr alloy foils are illustrated in Fig. 1. The gross morphological feature of the foils is wave-like bending of the surface. The roughness value R_a is calculated to be 38.5 nm. The height of some "waves" and peaks on the drum-side surface reaches 320 nm, Fig. 1a.

Fig. 2 shows RBS spectrum of He^+ ions from the Al-0.8 Cr alloy foils. The arrows in the figure indicate the positions for surface Cr and Al atoms. The simulation of the Cr concentration-depth profile by RUMP revealed that the Cr content is lowered in the drum-side surface layer (0.06 μm) and makes 0.5 at %. In the next layer Cr is homogeneously distributed over the examined up to 1.0 μm surface layer. Its average

concentration is about 0.7 at % and is lower than the nominal concentration by 13%.

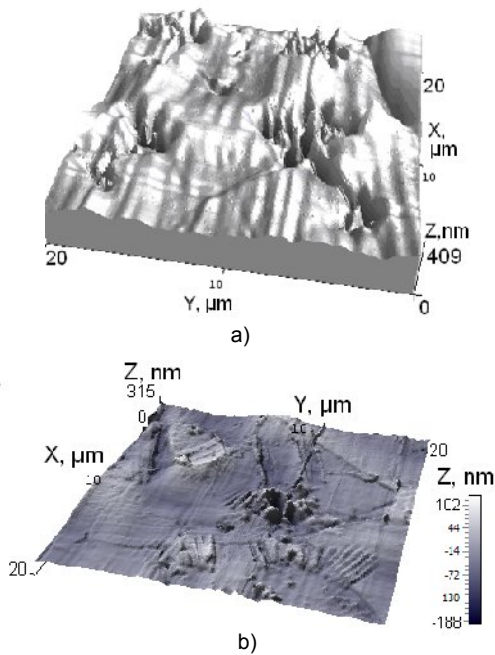


Fig. 1. Atomic force micrographs of the drum-side of Al-1.0 Cr alloy foils: as-cast (a) and examined by TDS (b).

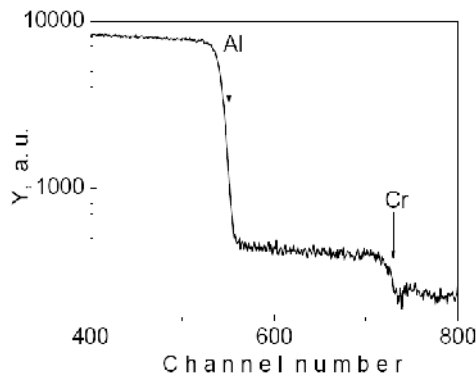


Fig. 2. Typical RBS spectrum ($\Theta = 160^\circ$, $E = 2.0$ MeV) from as-cast Al-0.8 Cr alloy foils.

The desorption process of H from the Al-1.0 Cr alloy foils was examined by TDS. Three peaks were detected at about 220, 420 and 460°C, see Fig. 3. Significant thermal desorption, corresponding to the first peak, has been observed starting at 120°C. Total content of H was estimated as 5.1 at ppm (0.2 mass ppm).

The surface topography of the Al-1.0 Cr alloy was measured by AFM after TDS experiments, in order to observe the topographic changes of the foil surface. The view in Fig. 1b presents that there is a modification of the surface topography occurred after annealing during TDS experiments. The annealed foils showed the smoothed drum-side surface, Fig. 1. The R_a is decreased up to 13.9 nm.

In our previous work [9] it was reported that the RS Al-0.8; 1.0 Cr alloys are microcrystalline and composed of metastable α -Al solid solution. Analysis of the three-dimensional AFM images reveals that surface microgeometry characteristics include ridge-rich surface regions and micro-voids. The micro-

voids can be attributed to the gas bubbles expelled from the molten material during RSP. From the AFM micrographs, it is evident that the heat treatment during TDS tests results in the foil surface smoothing and voids disappearance. It should be noted that similar surface topography structures were already observed for as-cast RS Al-Fe alloys. In fact, examination of RS Al-Fe alloys using AFM [5] showed that the roughness of the drum-side foil surface depends on both composition of the sample and topography of contact area of the melt and the drum.

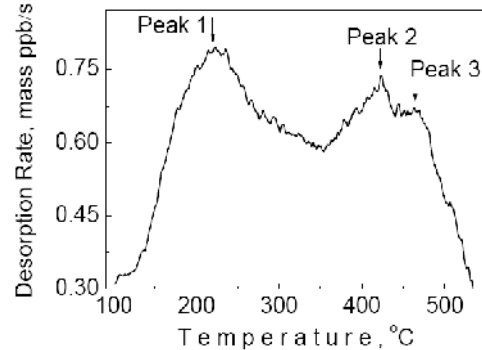


Fig. 3. Typical desorption spectrum for as-cast Al-1.0 Cr alloy foils, tested at 20K/min.

The established distribution character of Cr through the depth of the RS alloy foils in the layer up to 1.0 μm is coordinated to the pattern of the dope composition-depth profiles earlier established by us in the lightly doped binary Al alloys. In fact, as stated in our previous papers [7,10,11], content of solute in the surface layer in binary Al-Ti; V; Mn alloys is decreased. One of the probable reasons of the obtained dope depth distribution regularities in the Al-Cr alloy system may be a value of solute equilibrium partition coefficients k_e in Al. It is known from the equilibrium phase diagrams of the binary Al alloys that $k_e^{Ti, V, Cr, Mn} > 1$ [12]. It has also to be commented that the character of the solute distribution in the foil is radically different in Al alloys with dopes that has $k_e < 1$ [5,13,14]. In cast bulk samples, a nonuniform over the depth distribution of dopes in the near-surface layer is not observed by the RBS method in the limits of depth resolution [13].

Comparison to the AFM images and above-mentioned RBS data leads to the conclusion that the results of the RBS layer-by-layer analysis of the RS Al-based alloy foils are realistic. The question of the effect of the surface roughness of the sample on the shape of the RBS curves is considered in [15,16]. First of all, it is stated that in the case of beam incidence along the normal to the surface (the geometry considered in this work), the effect of roughness on the shape of the RBS spectrum is minimal. Secondly, for samples with a nonuniform surface, due to the presence of hillocks and valleys, the yield of particles in the high-energy region decreases. Due to this, the concentration in the surface layer of the sample is below the actual value. However, this effect is insignificant if the beam size is comparable with the size of inhomogeneities [16].

Within the last decade, research activities dedicated to behavior of H in pure Al and its alloys expe-

rienced considerable amplification [17, 18]. There exists a large potential for the utilization of advanced Al alloys without hydrogen embrittlement in the fuel cell vehicles [19]. Such effects as embrittlement and phase transformations induced by the presence of H have been investigated by considering two aspects: microstructure and microscopic mechanical properties. However, the complete mechanism of H-microstructure interactions has not yet been fully understood. It is known that H in pure Al exists at the interstitial sites and also is trapped by or contained in defects such as vacancies, dislocations, voids and blisters. We can suppose that desorption peaks 1 and 2 are associated with H trapped by Cr atoms in interstitial lattice sites and at dislocations, respectively. Previously, it was established for traditionally processed (rolled and annealed) Al foils that there are two distinct peaks at about 200 and 480°C on TDS spectra tested at 10K/min [20]. It should be noted that the magnitude of that second peak at 480°C correspondent to H trapping at dislocations is less than that of the peak 2 for the RS Al-Cr alloy. It points out the significance of dislocations as trapping state for absorbed H during RSP. Shifting of the peak 2 position in Fig. 3 in comparison with that noted above for rolled Al samples is believed to be caused by microstructural features of the RS foils. As it is known, rise of heating rate and presence of dope atoms increase the temperature of the desorption peak [38, 39]. In agreement with previous published results about microstructural changes during annealing of RS Al-Cr alloys [14] and AFM data (see Fig. 1), the peak 3 possible to attribute to Al₇Cr particles coarsening as well as void disappearance in the Al-Cr alloys. Indeed, decomposition of the supersaturated Al-based solid solution leads to precipitation of the Al₇Cr phase at annealing temperatures above 280°C.

Analysis of dope depth distribution and H desorption processes in RS Al alloys is important both for study of RS microstructures and its thermal stability and creating of H storage materials. Therefore researches are underway on the effects of non-equilibrium solidification on the surface dope segregation and H behaviour in RS Al alloys. Because a few experimental surveys provide such information and also to identify trap states of H in the material, it is necessary to continue the study of microstructure correlation with elemental composition of RS Al alloys.

Conclusions

The present study demonstrated that RSP of Al-0.8; 1.0 Cr alloys results in a formation of the drum-side foil surface that exhibits ridge-rich regions and micro-voids. The surface roughness of the Al-1.0 Cr alloy is estimated as 38.5 nm. Inhomogeneous distribution of Cr in the foil near-surface region was found out in the Al-0.8 Cr alloy. Surface layer (up to 0.06 μm) is depleted of dope elemental, its makes 0.5 Cr. The average concentration experimentally measured in the next layer is lower than the nominal value by 13%. There are three H desorption peaks at about 220, 420 and 460°C in TDS spectra from the Al-1.0 Cr alloy. The surface topography of the foils examined by TDS showed smoothing of the foil surface

and voids disappearance. The comparison of the results with the previous measurements on traditionally processed Al foils points out the effect of dope and RS microstructure on the kinetics of H desorption from the Al-Cr alloy foils.

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References

1. Xiao Y., Zhong J., Li W., Ma Z. // J. Mater. Sci. – 2008. – V.43. – P.324.
2. Inoue A., Kimura H., Masumoto T. // J. Mater. Sci. – 1987. – V.22. – P.1758.
3. Collot J. // Mater. Manuf. Processes. – 2001. – V.16. – P.595.
4. Doolittle L. N. // Nucl. Instr. and Meth. – 1985. – Vol. B9. – P. 344.
5. Tashlykova-Bushkevich I.I., Shepelevich V.G., Gut'ko E.S., Baraishuk S.M. // J. Surface Investigation. X-ray, Synchrotron and Neutron Techniques. – 2008. – V.2. – P.310.
6. Turnbull A., Hutchings R.B., Ferriss D.H. // Mater.Sci. Eng. A. – 1997. – V.238. – P.317.
7. Tashlykova-Bushkevich I.I. // J. Alloys Compd. – 2009. – V.478. – P.229.
8. Miroshnichenko S.I. Quenching from the Liquid State. – Moscow: Metallurgiya, 1982. – 168 p. (in Russian).
9. Neumerzhytskaya E.Yu., Shepelevich V.G. // Adv. Mater. – 2005. – V.4. – P.69 (in Russian).
10. Tashlykova-Bushkevich I.I., Neumerzhytskaya E.Yu., Shepelevich V.G. // Powder Metallurgy: the Republican interdepartmental collection of proc. – 2006. – V.29. – P. 313 (in Russian).
11. Tashlykova-Bushkevich I.I., Shepelevich V.G., Neumerzhytskaya E.Yu. // J. Surface Investigation. X-Ray, Synchrotron and Neutron Techniques. – 2007. – V.4. – P.69 (in Russian).
12. Lyakishev N.P. Condition Diagrams of double metal systems. – Moscow: Mashinostroenie, v. 1, 1996. – 992 p. (in Russian).
13. Shepelevich V., Tashlykova-Bushkevich I. // Mater. Sci. Forum. – 1997. – V.248-249. – P.385.
14. Tashlykova-Bushkevich I.I., Shepelevich V.G. // J. Alloys Compd. – 2000. – V.299. – P.205.
15. Knudson A.R. // Nucl. Instrum. Methods. – 1980. – V.168. – P.163.
16. Klyuchnikov A.A., Pucherov N.N., Chesnokova T.D., Shcherbin V.N. Methods of Charged-Particle Beam Analysis. – Kiev: Naukova Dumka, 1987. – 152 p (in Russian).
17. Scully J.R., Young Jr. G.A., Smith S.W. // Mater. Sci. Forum. – 2000. – V.331-337. – P.1583.
18. Carlson K.D., Lin Z., Beckermann C. // Metall. Trans. B. – 2007. – V.38B. – P.541.
19. Horikawa K., Kobayashi H., Tanigaki K., Yamada H. // ICAA: Proc. 11th Int. Conf. – Aachen, Germany, 2008. – P.1436.
20. Izumi T., Itoh G. // ISCIU: Proc. 3th Int. Conf. – Mito, Japan, 2007. – P.275.
21. Hayashi S. // Jpn. J. Appl. Phys. – 1998. – V.37. – P.930.