

Patterns of Concentration-Depth Profiles in Melt-Substrate Quenched Aluminium Alloys

Iya I. Tashlykova-Bushkevich

Belarusian State University of Informatics and Radioelectronics, P. Brovki Str. 6, Minsk 220013, Belarus

Depth profiling analysis of rapidly solidified (RS) foils of Al alloys provides new insight into microstructure evolution of the materials during non-equilibrium solidification at exceptionally high cooling rates. Original Rutherford backscattering spectroscopy (RBS) investigations of the near-surface region of rapidly solidified binary Al-Ti; V; Mn; Fe; Co; Ni; Cu; Zn; Ge; Sb alloy systems were overviewed to point out features of the discovered nonuniform dope depth distribution profiles within the cooling rates in the range of 10^5 - 10^8 K/s. For the first time it was obtained that the concentration-depth profiles in the Al alloy foils could be classified into three groups with respect to surface segregation. It was clearly demonstrated strong effect both of the system composition and thermal annealing on the revealed patterns of the layer-by-layer composition up to 1.2 μm depth below foil surface. Along with the continued advances in microstructure analysis, it is evident that attention to the surface microstructure of the Al alloy foils is essential in understanding of solidification mechanisms, taking place during rapid solidification.

Keywords: *Liquid quenching; Aluminium alloys; Rutherford backscattering; Microstructure; Depth profile analysis*

1 Introduction

One important trend in manufacturing of Al-based alloys is the usage of rapid solidification processing (RSP), which leads to significant and often potentially beneficial modifications of their microstructure and improved properties compared with the conventional solidification techniques. In fact, RSP defined as cooling from the liquid to the solid at exceptionally high cooling rates exceeding 10^4 K/s is capable of producing grain refinement, increases in the equilibrium solid solubilities of solute elements and inducing one or more of the metastable effects [1-4]. Intense interest in rapidly solidified (RS) Al alloys for their applications in the aerospace and automotive industries, and other structural applications, causes large number of experimental papers in this area.

Microstructural investigations of shallow surface regions of RS Al-base alloys represent an urgent task both from physical and practical points of view because many chemical and physical properties of materials in high-technology applications depend on the composition and structure of their surfaces. Particular interests are to reveal the influence of alloy composition and RSP solidification characteristics on dope depth distribution and to correlate layer-by-layer elemental composition with RS microstructure [3,5-7]. Nevertheless, as far as we are concerned, there are no direct experimental surveys on depth profiling analysis of RS foils of Al alloys. Only few studies have thus far addressed such microscale phenomenon and are scattered in the literature.

The main aim of this review is to present a range of original works that have been undertaken over the ten recent years to carry out detail elemental analysis of foil surface regions of selected RS Al binary alloys. A feature of this paper is the application of high-resolution RBS technique coupled with RUMP software analysis package [8] in providing direct observations of the evolution of the microstructure through the foil depth. In addition, it should be highlighted that this work makes an overview of effect on depth profiles of solute elements having partition coefficient $k_e < 1$ as well as $k_e > 1$. Effects of cooling rate and thermal annealing on layer-by-layer composition are also considered. After summarizing of presented concentration-depth profile patterns in the Al alloy foils,

the paper is concluded with open questions and brief commentary regarding prospects for future developments within the field of this research endeavour.

2 Experimental

Most of the studies reported here were performed on lightly doped binary Al-Ti; Mn; Fe; Co; Cu; Zn; Ge; Sb alloys composed of supersaturated α -solid solution. In addition, some binary Al-V; Fe; Co; Ni; Cu; Zn; Ge; Sb alloys containing secondary phases were also examined. The composition of the alloys used in this study is shown in Table 1. The alloys were prepared from Al and dopes grade of 99.99 and 99.9%, respectively. Ingots of Al-Ti; V; Mn; Fe; Co; Zn; Ge alloys were obtained using melting in an induction electric furnace, which was performed in an argon atmosphere. Meanwhile, ingots of Al-Ni; Cu; Sb alloys as well as some Al-Fe; Ge alloys were manufactured by melting of alloying elements in a quartz tube in a nitrogen atmosphere.

Table 1: Characterization of the RS Al alloys (at %) in the present study.

System	Dope concentration, secondary phase	Treatment, annealing T (°C)	System	Dope concentration, secondary phase	Treatment, annealing T (°C)
Al-Ti	0.4	as-cast	Al-Zn	1.0	as-cast
Al-V	0.4, Al ₁₀ V phase	as-cast		4.0	as-cast, 200, 500
Al-Mn	1.0	as-cast		6.0, Zn-rich phase	as-cast
	2.1	as-cast, 200, 500	Al-Ge	0.4	as-cast
Al-Fe	0.25	as-cast, 140		1.6, γ phases	as-cast
	0.3	as-cast		2.4, γ phases	as-cast
	1.0	as-cast		3.2, γ phases	as-cast
	2.0, Al ₆ Fe	as-cast, 140, 500		5.0, γ phases	as-cast
Al-Co	0.3	as-cast	Al-Sb	0.2	as-cast
	2.4, Al ₉ Co ₂ phase	as-cast		0.8, AlSb phase	as-cast
Al-Ni	0.3, Al ₃ Ni phase	as-cast		1.6, AlSb phase	as-cast
Al-Cu	0.5	as-cast		2.4, AlSb phase	as-cast
	1.2, Al ₂ Cu phase	as-cast		3.2, AlSb phase	as-cast
	2.1, Al ₂ Cu phase	as-cast			
	3.0, Al ₂ Cu phase	as-cast			

Alloys were rapidly solidified by centrifugal melt quenching as follows. The droplet of molten alloy was splashed in the air on the inner surface of the polished copper drum with a diameter of 20 cm, rotating at 16 m/s liner velocity. Resulted foils were typically 5-10 mm in width. The thickness of foil bulk parts and tails was 30-70 and below 0.2 μm , respectively. The melt cooling rate for both bulk parts and tails of the foils was estimated from the known cooling rate-sample thickness relationship for employed method of rapid solidification [9]. It was of the order of 10^6 and 10^8 K/s accordingly. Isothermal annealing of the selected alloys was carried out at constant temperatures for 1 h at each temperature. Initial composition, regimes of annealing and data of phase composition of all Al alloys manufactured for this study are listed in Table 1.

The solute profiles in the near surface region of the samples have been studied by RBS technique. The RBS experiments were carried out using a MeV helium ion beam from a van de Graaff accelerator in a total of four different laboratories: in Russia (*the Research Institute of Nuclear Physics of the Moscow State University*), Germany (*the Fridrich Schiller University (Jena)*) and the *Rosendorf Scientific Research Institute (Dresden)*) and the UK (*the University of Salford*). The

principles and capabilities of this ion beam analysis technique can be found in the specified textbooks [10,11]. It is worth noting that by employing the RUMP software we are able to derive information from the surface layers to a depth of about 1.2 μm which is within the foil grain according to our estimates [12]. Spatial definition depended on the beam spot size ensures that RBS analysis coupled with RUMP code gives an opportunity for simultaneous inspection of the microstructural features above 10^3 grains at the foil surface.

3 Results and Discussion

The Al alloy foils processed through RSP were microcrystalline, Fig. 1a. The average grain size was several microns and depended on alloying composition [12]. In order to investigate the early stages of solidification near the surface of the cooper drum, the drum-side surface (A) both of foil bulk parts and tails has been studied. Additionally, the air-side surface (B) of the foils has been examined to investigate the later studies of solidification. Overall, during RSP the melt starts cooling down and solidifies from the drum-side. Therefore the cooling rate decreases significantly across the foil thickness [13]. This above difference makes up single-order [14]. Thus, we have studied composition depth profiles of the Al alloys solidified at variations of the cooling rate from 10^5 up to 10^8 K/s.

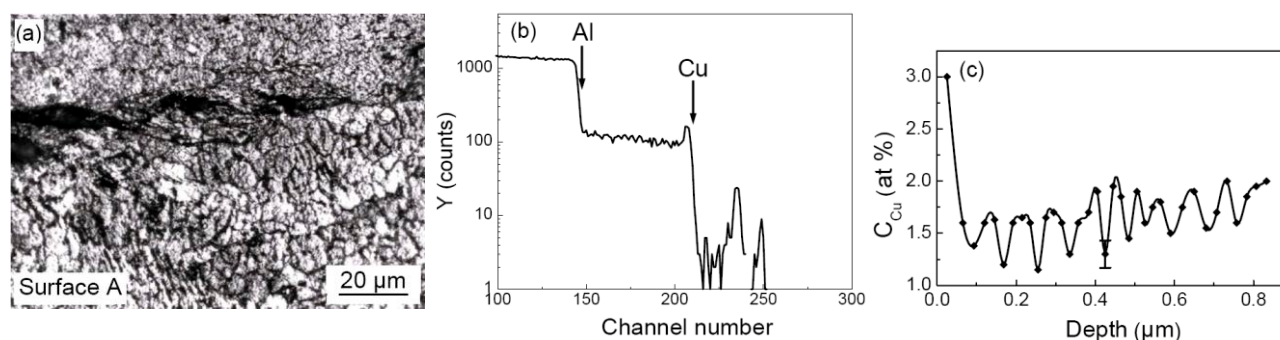


Fig. 1: Microstructure analysis of Al-Cu alloy foils: (a) optical micrograph of transverse cross-section through the thickness of the Al-3.0 Cu alloy [12]; (b) typical RBS spectrum (scattering angle $\theta = 170^\circ$, $E_0 = 2.0$ MeV) from A surface of Al-2.1 Cu alloy [15]; (c) correspondent Cu depth distribution in Al-2.1 Cu alloy [15].

The carried out depth profiling analysis indicates that solute elements are distributed irregularly in a surface region both at near drum-side and air-side of all listed RS Al alloys up to a depth of about 1.2 μm . However, the observed nonuniform concentration depth profiles were found out to have some features which are drastic different. It was obtained that a thin surface layer (0.02-0.03 μm) is enriched with solute in the Al-Fe; Co; Ni; Cu; Ge; Sb alloys [15-17]. The typical alloying element distribution in the enriched near-surface region of the foils is represented in Fig. 1b. The collected RBS spectrum clearly demonstrates a Cu edge peak at the foil surface. Figure 1c shows Cu-concentration depth profile with maximum concentration at the surface derived from the RUMP fitted spectrum. Figures 1b, c also illustrate that the depth profiles exhibit slow increase in the dope content as a function of depth over the entire 0.1-1.2 μm region below the surface. On the other hand, a significantly different behaviour was detected in the Al-Mn; Zn [18,19] alloys, as shown in Fig. 2a. The above responses of collected RBS spectra reflect unexpected reduction of the dope content in the thin surface layer and followed its rapid rise to the next layer of 0.1 μm depth. Overall, it should be pointed out that a strong dependence of dope depth profiles on melt cooling rates in the range 10^5 - 10^8 K/s was not observed unless dope segregation it appears to be the highest at the foil air-side of the Al-Fe; Zn; Ge; Sb alloys. It was also likely that nonuniformity of the profiles is reduced in the presence of secondary phases in the alloys. Notice that in cast bulk samples an irregular dope depth distribution in the near-surface layer is not observed by the RBS technique in the limits of depth resolution [20].

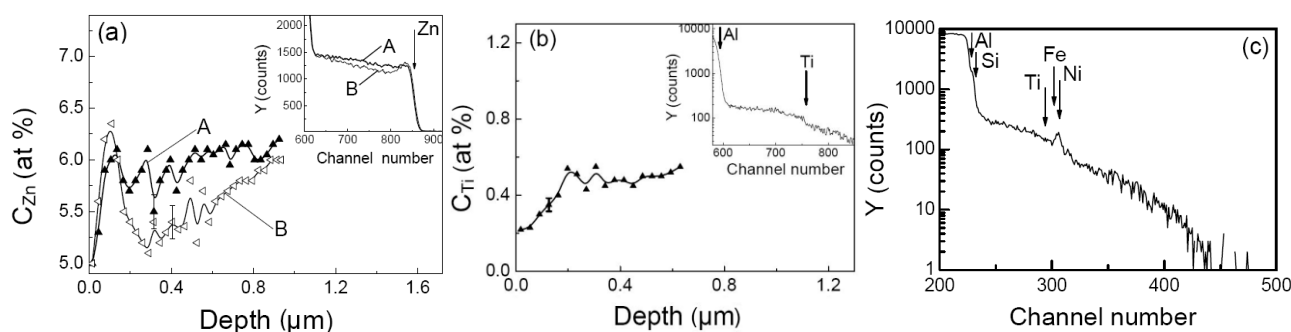


Fig. 2: Microstructure analysis of Al-Zn, Al-Ti and Al-Si-Ti alloy foils: (a) Zn depth distribution through the Al-6.0 Zn alloy near A and B foil surfaces with correspondent RBS spectra ($\theta = 160^\circ$, $E_0 = 2.4$ MeV) in the inset [18]; (b) Ti depth distribution in Al-0.7 Ti alloy near A surface with correspondent RBS spectrum ($\theta = 160^\circ$, $E_0 = 1.9$ MeV) in the inset [21]; (c) typical RBS spectrum ($\theta = 168^\circ$, $E_0 = 2.0$ MeV) from Al-9.6Si-0.8Ti alloy with 0.15 Fe and 0.07 Ni dopes [22].

In contrast to concentration-depth profiles stated above, the important feature of concentration-depth profiles in the Al-Ti; V alloys is the surface deficit of Ti as well as V [21, 23]. In fact, generalized description of the observed profiles is increasing of the dope concentration as a function of depth in the narrow near-surface region, see Fig. 2b. This tendency of Ti and V depth distribution is sharply different from above specified features of the dope profiles in the Al-Fe; Co; Ni; Cu; Ge; Sb alloys and the Al-Mn; Zn alloys.

Overall, the revealed profile differences should be highlighted by collected RBS spectra from microcrystalline RS Al-9.6 Si-0.8 Ti alloy with 0.15 Fe and 0.07 Ni dopes [22]. This alloy is the system attracting interest within the framework of this paper due to the presence of dopes exhibiting different depth distribution behaviour in the binary Al alloys as it was stated above. Moreover, Ti, Fe and Ni are the technologically important elements widely used as modifying dopes in Al-Si alloys.

Figure 2c reflects that separation of the neighbor Al and Si elements as well as Fe and Ni elements is within the limits of the RBS technique. Since the amounts of Si and Al in the alloy are maximum, the use of RUMP code allows determining of Si depth distribution. As regards Fe and Ni, their amount was determined only in total by RBS analysis. Thus, there are two points to note from Fig. 2c. Firstly, the RBS spectrum indicates a Si, Fe and Ni distribution with concentration peaks at the surface those correspond to 24.0 Si and 0.9 at % for Fe and Ni in total. Furthermore, it was found out that the Si concentration oscillates through the foil thickness of the layer up to 0.2 μm. Secondly, the Ti concentration is lowered at the surface and makes 0.3 at % increasing as a function of depth. Hence, the use of RBS in depth profiling of the Al-Si-Ti alloy reveals that observed Si, Ti, Fe and Ni depth distribution appears to be in accordance with those observed in the binary Al alloys.

In this paper, the solute depth redistribution affected by the annealing temperature is analysed for the Al-Fe; Mn; Zn alloys. Thermal annealing of the binary Al alloys show the reversed trend of the dope depth redistribution in the Al-Fe alloy in contrast to the Al-Mn; Zn alloys. It was found that the dope surface segregation is remarkable at 500°C in the Al-Mn; Zn alloys [18,19]. On the contrary, the amount of Fe at the surface decreases with temperature of annealing [16].

Based on presented results, it is shown that the centrifugal melt quenching of the Al alloys presents unexpected examples of dope depth profiles in the near-surface regions of the foils. The binary Al alloy systems that have been explored by RBS technique could be distinguished according to equilibrium partition coefficient of the dope in Al. Alloy systems within the first group having $k_e < 1$ are the Al-Fe; Co; Ni; Cu; Ge; Sb alloys as well as Al-Mn; Zn alloys. The Al-Ti; V alloys belong to the second group of alloy systems having $k_e > 1$. Thus, the general implications of performed examinations of the works aimed at RBS elemental analysis of the RS foils are considered as follows.

The above patterns of layer-by-layer composition found out to be strongly influenced by the composition of the system and by the thermal annealing treatment. Performed depth profiling

analysis show that the segregation of alloying element at the foil surface is probably caused by the diffusion of solute atoms associated with nonequilibrium vacancies. Indeed, rapid solidification of Al alloys is a non-equilibrium processing method that results in high concentration of quenched-in vacancies in the alloys [2]. Furthermore, vacancies are able to form mobile complexes vacancy-solute atom and diffuse to the surface, which is their sink, even at such high rates of cooling and solidification of the melt as during RSP [24,25]. Hence, our observations demonstrate that vacancy play important role in the transport of alloying element atoms and are in a good agreement with studies of vacancy kinetics applied to investigate the morphology of Al-base alloys. The foil air-side RBS spectra indicate the highest dope content at the surface, and this outcome is in accordance with known phenomenon that the crystallization of the drum-side region is accelerated versus that at the opposite air-side. The above interpretation is also supported by the fact that Ti and V have very low diffusion coefficients in solid Al [4]. Taking into consideration clearly visible differences of the grain microstructure of the Al-Zn alloys from that in the Al-Cu; Ge; Sb alloys, we can suppose that detected surface impoverishment by Zn and Mn is related to effect of grain microstructure detailed elsewhere [19] on the dope depth distribution. It is thus likely that decreasing solidification velocity because of recalescence that accompanies rapid growth into an undercooled melt and increasing solid-liquid interface temperature lead to the microstructural variations in macro- and micro-scale. However, the issue of effect of the partition coefficient value on dope depth distribution behaviour in the Al alloys is not clear. Meanwhile, the formation of secondary phases appears to complicate concentration dependence of dope depth distribution. Since we focus on the depth profiling analysis in this study, we have not performed more detailed discussion of the processes occurring during isothermal annealing of the Al-based alloys considered elsewhere [16,19,20]. The correlation of concentration-depth profiles with phase composition of alloys is evidenced by RBS experiments performed both on as-cast alloys composed of supersaturated α -solid solution with precipitates of secondary phases and alloys annealed at different temperatures.

To conclude this paper we would like to make some comments on the challenging questions from a fundamental point of view and outline future prospects. The RBS technique employed for depth profiling analysis provides new critical information on the patterns of dope depth distribution in RS Al alloys. It was revealed that dope depth distribution behaviour is complicated and depends on partition coefficient, phase formation, type of grain structure, concentration of dopes and solidification rate. Carried out investigation of the layer-by-layer elemental composition emphasizes topics worthy of extensive research, aimed to advance present understanding of physical mechanisms which control the final RS microstructures of Al-based alloys. We hope that presented for consideration original experimental results will be contribution to this scientifically important filed.

4 Summary

The RSP are material-processing methods developed to produce Al-based alloys with desirable properties due to microstructure and phase modifications. Original collected RBS spectra shown in this paper point out advances in precise layer-by-layer composition analysis of binary Al-Ti; V; Mn; Fe; Co; Ni; Cu; Zn; Ge; Sb alloys performed by means of RBS technique over the ten recent years. The depth profiles have been investigated in respect to alloy system and temperature of annealing and showed nonuniform dope depth distribution below the foil surface up to a depth of 1.2 μm . The effects of composition and thermal annealing treatment are remarkable. The enrichment of the thin surface layer by the dope was revealed for the Al-Fe; Co; Ni; Cu; Ge; Sb alloys in sharp contrast to its impoverishment in the Al-Mn; Zn alloys. On the other hand, there was surface deficit by dope in the Al-Ti; V alloys. Regarding the thermal annealing of the alloys, the trends of dope redistribution indicate opposite directions of dope atom diffusion in Al-Fe alloys in contrary to Al-Mn; Zn alloys. The revealed features of the dope depth distribution remain the same for cooling rates in the range of 10^5 - 10^8 K/s.

5 Acknowledgements

Initial research on the elemental composition analysis was funded by the Belarus republican fund of basic researches. Dr. V. Kulikauskas (Scientific Research Institute of Nuclear Physics of the Moscow State University, Russia) is gratefully acknowledged for providing RBS facilities to perform examination of most of the samples used in this work. The author would also like to thank Professor G. Carter (the University of Salford (Salford), the UK), Professor W. Wesch (the Friedrich Schiller University (Jena), Germany) and Dr. R. Grötzschel (Rossendorf Scientific Research Institute (Dresden), Germany) for assistance in carrying out the RBS experiments.

6 References

- [1] M. Asta, C. Beckermann, A. Karma, W. Kurz, R. Napolitano, M. Plapp, G. Purdy, M. Rappaz and R. Trivedi: *Acta Mater* 57 (2009) 941-971.
- [2] T. S. Srivatsan, T. S. Sudarshan and E. J. Lavernia: *Prog Mater Sci* 39 (1995) 317-409.
- [3] W. J. Boettinger, S. R. Coriell, A. Karma, W. Kurz, M. Rappaz and R. Trivedi: *Acta Mater* 48 (2000) 43-70.
- [4] *Aluminum: Properties and Physical Metallurgy* (Reference Book), Ed. by J. E Hatch, (American Society for Metals, Metals Park, Ohio, United States, 1984) pp. 40-63.
- [5] J. G. Hoekstra, S. B. Quadri, J. R. Scully and J. M. Fitz-Gerald: *Adv Eng Mater* 7 (2005) 805-809.
- [6] P. M. Smith and M. J. Aziz: *Acta Metall et Mater* 42 (1994) 3515-3525.
- [7] G.-X. Wang, V. Prasad, E. F. Matthys: *Mater Sci and Eng A* (1997) 22547-58.
- [8] RUMP (Rutherford backscattering spectroscopy analysis package) by M. Thompson (Cornell University, USA, 2009), <http://www.genplot.com>.
- [9] S. I. Miroshnichenko: *Quenching from the Liquid State* (Metallurgiya, Moscow, 1982), pp. 1-168 (in Russian).
- [10] F. F. Komarov, M. A. Kumakhov and I. S. Tashlykov: *Non-destructive ion beam analysis of surfaces* (Gordon and Breach Science Publisher, New York, 1990), pp. 61-101.
- [11] G. Foti, J. W. Mayer and E. Rimini: *Ion beam handbook for material analysis*, Ed. by J. W. Mayer and E. Rimini, (Academic Press, New York, 1977), pp. 42-68.
- [12] V. G. Shepelevich, I. I. Tashlykova-Bushkevich and A. G. Anisovich: *Physics and chemistry of materials treatment c/c Fizika i khimiya obrabotki materialov 4* (Riezensky Science Publishing, Great Britain, 1999), pp. 343-348.
- [13] K. Nagashio and K. Kuribayashi: *Acta Mater* 5 (2006) 42353-2360.
- [14] Yu. K. Kovneristy, N. P. Bolotina, A. A. Rovaev, E. K. Osipov and E. A. Trofimova: *Izvestiya Akademii nauk USSR Metalliyi* (1983) 476-79 (in Russian).
- [15] I. I. Tashlykova-Bushkevich and V. G. Shepelevich: *J Alloys Compd* 299 (2000) 205-207.
- [16] I. I. Tashlykova-Bushkevich, E. S. Gut'ko, V. G. Shepelevich and S. M. Baraishuk: *J Surface Investigation X-ray, Synchrotron and Neutron Techniques* (2008) 2310-316 (in Russian).
- [17] I. I. Tashlykova-Bushkevich, V. S. Kulikauskas, W. Wesch, E. Wendler, R. Grötzschel and V. G. Shepelevich: *Physics and Chemistry of Material Treatment 3* (2004) 75-80 (in Russian).
- [18] I. I. Tashlykova-Bushkevich, E. S. Gut'ko and V. G. Shepelevich: *J Adv Mater* (2005) 1254-61.
- [19] I. I. Tashlykova-Bushkevich: *J Alloys Compd* 478 (2009) 229-231.
- [20] V. Shepelevich and I. Tashlykova-Bushkevich: *Mater Sci Forum* 248-249 (1997) 385-388.
- [21] I. I. Tashlykova-Bushkevich, E. Yu. Neumerzhyskaya and V. G. Shepelevich: *Powder Metallurgy: the Republican interdepartmental collection of Proc* 29 (2006) 313-318 (in Russian).
- [22] I. I. Tashlykova-Bushkevich: *Vacuum* 78 (2005) 529-532.
- [23] I. I. Tashlykova-Bushkevich, V. G. Shepelevich and E. Yu. Neumerzhyskaya: *J. Surface Investigation. X-Ray, Synchrotron and Neutron Techniques 4* (2007) 69-72 (in Russian).
- [24] F. Pleiter and C. Hohenemser: *Phys Rev B* 25 (1982) 106-125.
- [25] M. de Haas and J. Th. M. de Hosson: *Scripta Mater* 44 (2001) 281-286.