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PECULIARITIES OF FORMATION AND GROWTH OF NANODISPERSED INTERMETALLIC STRENGTHENING INCLUSIONS IN RAPIDLY-SOLIDIFIED ALLOYS OF Al–Mg–Zr–X-SYSTEM

Dmitrii I. BUDELOVSKIJ¹, Sergei Yu. PETROVICH², Vadim A. LIPIN³

¹ OJSC «Virial», Saint-Petersburg, Russia

² Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg, Russia

³ Higher School of Technology and Energy of Saint Petersburg State University of Industrial Technologies and Design, Saint-Petersburg, Russia

The paper is devoted to the influence of the fourth element on the microstructure of the rapidly-solidified alloys of the Al–Mg–Zr-system. Alloys were additionally doped with high-melting-point metals Ti, Hf, W, and Nb. In the structure of all samples in the immediate area of the cooled surface, uniformly distributed intermetallic inclusions of several nanometers in size were detected. Such a structure can be represented as a dispersion-strengthened composite. A quantitative metallographic analysis was carried out to quantitatively describe the structure of the obtained particles of the cooled melt. The obtained rapidly-solidified alloys can be described as dispersion-strengthened composite materials with the aluminum-magnesium alloy matrix and the intermetallic particles strengthener. Depending on the alloying component, these particles differ in shape (spheres, plates, agglomerates) and in size (from 200 nm when alloying with Hf and W up to 1.2-1.5 μm with Ti and Nb alloying). The X-ray phase analysis (XPA) showed that in the studied alloys of the Al–5Mg–1.2Zr–(0.5–2.0)X-system, high cooling rates of melts lead to the formation of new intermetallic compounds that are absent in equilibrium systems. The example of an alloy with hafnium additive shows that an increase in the content of the alloying component (from 0.5 to 2 % by mass) leads to an increase in the volume ratio of intermetallic inclusions (from 5 to 12.8 %). At the same time, their shape and average size remain unchanged. The additional alloying component will improve the mechanical characteristics of aluminum alloys by increasing the recrystallization threshold of a rapidly-solidified alloy.

Key words: rapidly-solidified alloys, intermetallic compounds, aluminum, magnesium, zirconium, alloying, high-melting-point metals

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Introduction. Aluminum alloys with good strength properties are in high demand and have been successfully used in the manufacture of parts in the fields of engineering requiring durability and relative lightness of products [6].

Alloys obtained by supercooling the melt can in some cases freeze without crystallization, when this occurs the atoms remain «frozen» near the positions they occupied in the liquid state. Thus, the structure has the short-range ordering of atoms without any long-range ordering [12]. By varying the rate of melt cooling, it is possible to control the crystalline structure of the solid state and to obtain the same alloy in the form of coarse, fine or nanocrystalline aggregates, as well as in a composite amorphous-crystalline structure or in an amorphous state [2].

Dispersed particles from 1 μm or less inhibit plastic deformation and material destruction [4]. Rapid solidification of aluminum-magnesium alloys produces small crystalline formations with sizes up to 3-4 nm [7], which means that rapidly solidified aluminum alloys should have significantly higher mechanical characteristics [10].

When zirconium is added to the alloys of the Al–Mg-system, the crystalline grain is noticeably refined, which leads to an increase in the recrystallization threshold [6]. Both phenomena play an important role in the synthesis of nanodispersed inclusions. Reduction of the characteristic size of crystalline grains in the equilibrium system suggests a similar decrease in grain size in metastable fast quenched structures [9]. Zirconium additives slightly increase the mechanical properties of aluminum-magnesium alloys [7].

The improvement of mechanical characteristics of the material and obtainment of finer nano-scale structure can be done by selecting the fourth element of the system functioning as alloying one. The most significant characteristics of this alloying element appear with an increase in the alloy recrystallization threshold. With an increase in the recrystallization threshold, it is possible to preserve the resulting metastable fast quenched structure at higher temperatures than in the alloy

having the original composition. In the process of doping, a decrease in the dimensions of the crystalline grain in the equilibrium system should be achieved, which leads to the formation of an even more dispersed structure during quenching of the melt.

The purpose of this paper is to determine the compounds and nature of their distribution during introduction of the alloying higher-melting-point element into the Al–Mg–Zr-system.

When the melt is cooled, the atoms of the alloying higher-melting-point components become the centers of aluminum crystallization. Thus, with an increase in the content of the additive, the concentration of crystalline phase nuclei of the melt unit volume increases, which in turn leads to a refinement of grain sizes at the same cooling rates. However, the addition of high-melting-point elements to aluminum-magnesium alloys promotes a significant increase in the melting point, so their content in the alloy should be limited [5, 7, 8].

Methods of research. In this work Ti, Hf, W and Nb were used as alloying components of high-melting-point elements. Aluminum alloys of Al–5Mg–1.2Zr–(0.5÷2.0)X-composition were prepared. Cooling of the melt droplets was carried out on a metal rotating disc [8].

A quantitative metallographic analysis was carried out to quantitatively describe the structure of the obtained particles of the cooled melt. For this purpose, new thin sections were cut and their SEM images were obtained. The structure of the obtained granules was studied by scanning electron microscopy using a Supra 40 VP device [11].

The main studied parameters of the structure were the volume ratio of the alloy intermetallic phase and the average size of intermetallic particles. According to the first basic stereometric relation, the proportion of the phase in the alloy volume and in the area of the section is equal to each other. Thus, the volume ratio of the phase was determined by measuring the relative area on the section surface. Processing of SEM images and measurement of structure parameters were performed using the Gwyddion 2.47 package.

A qualitative X-ray phase analysis of the samples was carried out using a Bruker D8 advance diffractometer. The radiation was a copper ($\text{Cu}_{K\alpha}$) one, it uses a database of organic and inorganic compounds PDF-2.

A component corresponding to metallic aluminum was found for all samples, which indicates a presence of sufficiently thin layer of surface oxide, its thickness does not exceed 20 nm.

In the structure of all samples in the immediate area of the cooled surface, uniformly distributed intermetallic inclusions of several nanometers in size were detected. Such a structure can be represented as a dispersion-strengthened composite material.

When adding W, the structure of the material can be described as being non-oriented with intermetallic microparticles of predominantly irregular shape. There are a number of lamellar dispersoids. Intermetallic compounds are evenly distributed in the matrix and slightly differ in size (Fig.1, a).

The structure of the alloy doped with Nb is dominated by lamellar dispersoids of various sizes. A large number of irregularly shaped agglomerates are observed, consisting of three or four differently oriented plates. The distribution of dispersoids in the matrix and their size range are uneven. In the metallic matrix there are intergranular gaps, probably formed during crystallization of the alloy and the decay of the su-

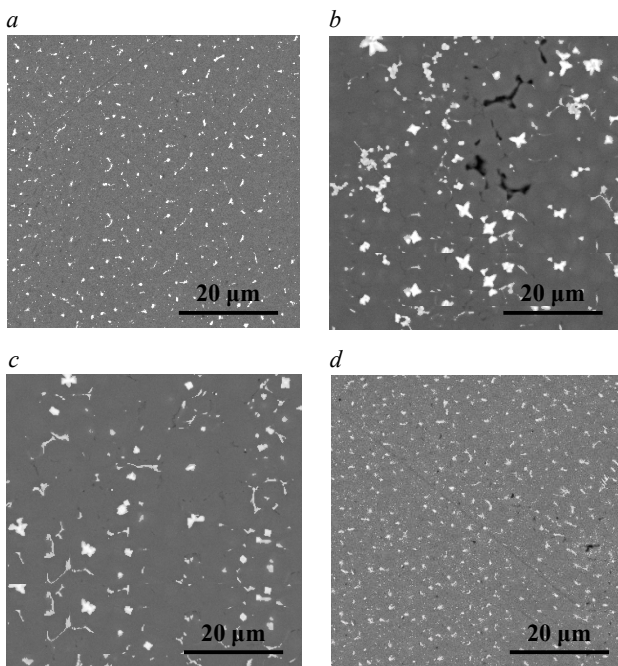


Fig.1. Microstructure of sample sections containing 0.5 % by weight: a – W; b –Nb; c –Ti; d –Hf

persaturated solid solution followed by diffusion of the alloying high-melting-point component (Fig. 1, *b*).

When Ti is added, lamellar particles with different orientations their agglomerates of various shapes are observed. The distribution of intermetallic compounds in the matrix is more uniform than with the addition of Nb. Intergranular gaps are not observed (Fig. 1, *c*).

The structure of the alloy doped with Hf is similar to the alloy with the addition of W: there are dispersions that are close in size and uniformly distributed in the matrix. The shape of inclusions is predominantly lamellar (Fig. 1, *d*).

With an increase in the hafnium content from 0.5 to 1 % by mass, more lamellar inclusions are formed. Their size does not visually change, however, formation of large agglomerates of differently oriented inclusions is noticeable (Fig. 1, *d* and 2, *a*).

With Hf content of 2 % by weight the development of greater amount of lamellar dispersoids is noted. There is formation of intergranular gaps, which is probably caused by the decay of the supersaturated solid solution, as in the niobium-containing sample (Fig. 2, *b*).

The results of a quantitative evaluation of the parameters of the cooled melts sections structure are presented in Table 1.

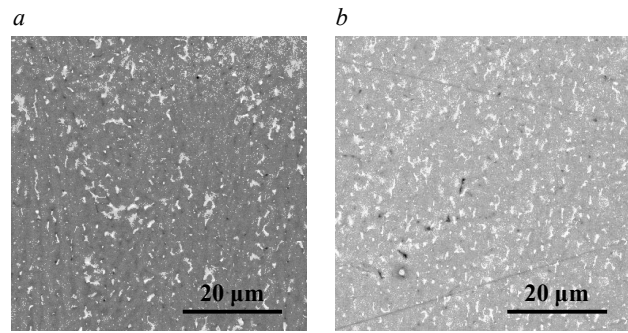


Fig. 2. Microstructure of sample sections containing Hf 1 % (*a*) and 2 % (*b*) by weight

Table 1

Compositions of the studied melts and characteristics of intermetallic inclusions after their ultrafast cooling

Composition, % by weight				Characteristics of intermetallic inclusions		
Al	Mg	Zr	X	Total amount per unit area, units.	Volume ratio, %	Estimated average size, nm
93.3	5.0	1.2	0.5 W	3097	2.31	224
93.3	5.0	1.2	0.5 Nb	1094	5.89	1196
93.3	5.0	1.2	0.5 Ti	1505	4.74	1491
93.3	5.0	1.2	0.5 Hf	9952	5.05	198
92.8	5.0	1.2	1 Hf	14220	9.33	203
91.8	5.0	1.2	2 Hf	21522	12.81	204

Thus, the alloy samples obtained as a result of the experiments can be described as dispersion-strengthened composite materials, in which the matrix is an aluminum alloy, the strengthener is intermetallic particles. Depending on the alloying component, these particles differ in shape (spheres, plates, agglomerates) and in size (from 200 nm when alloying with Hf and W up to 1.2-1.5 μm with Ti and Nb alloying).

When the content of the alloying element is increased as it is shown in the example of hafnium, it is seen that when the content of the high-melting-point component increases, the number and, correspondingly, the volume ratio of dispersoids in the material increase. At the same time, their shape and size remain unchanged.

According to X-ray phase analysis, the alloy with the addition of W is a system based on aluminum. The remaining elements are represented as intermetallic compounds with aluminum, such as: Al₃Zr, AlZr, Al₁₃Mg₇ (Al_{0.65}Mg_{0.35}), Al₁₂Mg₁₇, Al₅W. In addition, characteristic peaks of binary and ternary tungsten-containing intermetallic compounds appear: Al₄W, W₃Mg, Al₁₈Mg₃W₂, AlW₄Zr (Al_{0.17}W_{0.66}Zr_{0.17}) (Fig. 3, *a*).

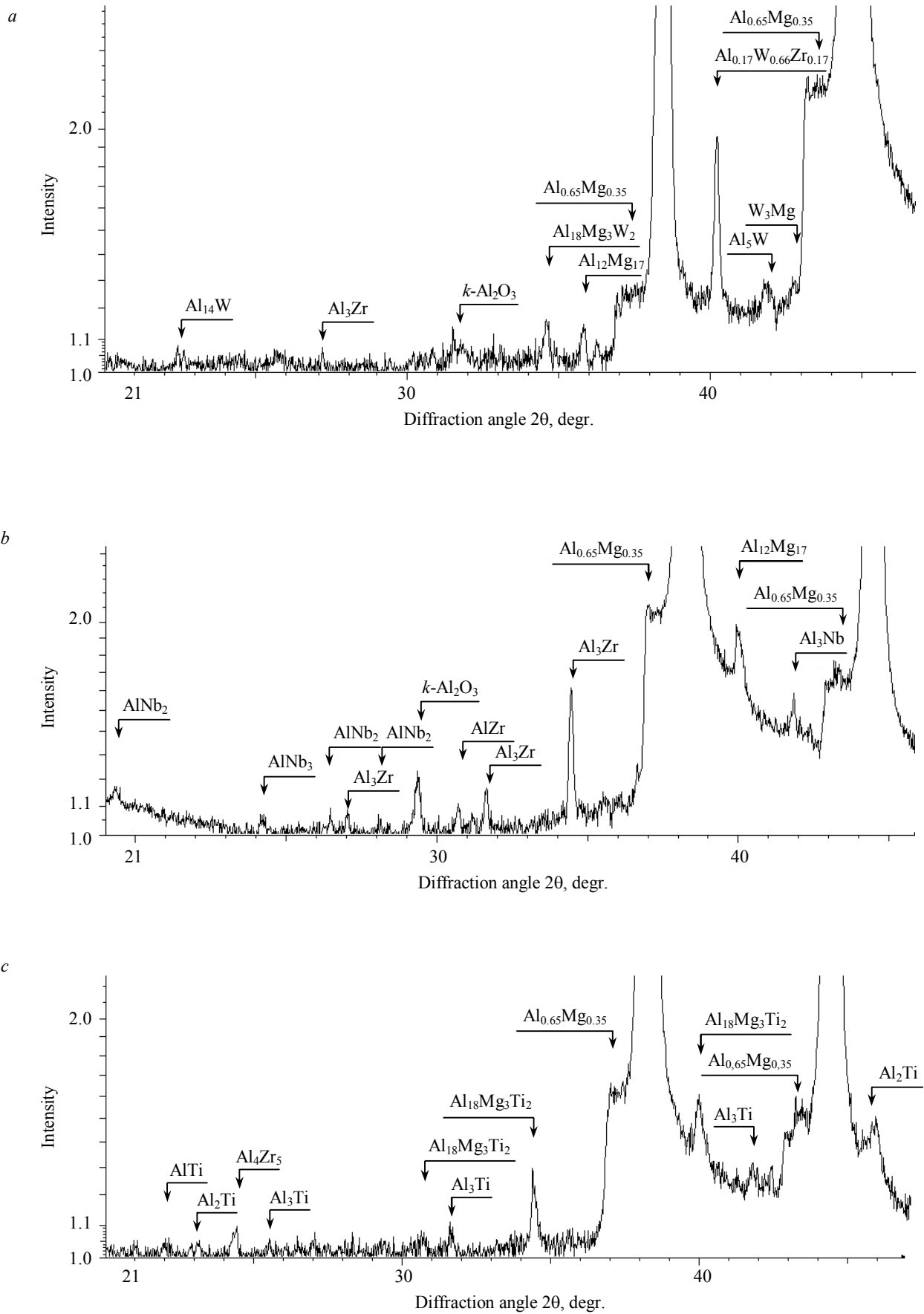


Fig.3. XRD pattern of composition sample: *a* – Al–5Mg–1.2Zr–0.5W; *b* – Al–5Mg–1.2Zr–0.5Nb; *c* – Al–5Mg–1.2Zr–0.5Ti; *d* – Al–5Mg–1.2Zr–0.5Hf; *e* – Al–5Mg–1.2Zr–1Hf; *f* – Al–5Mg–1.2Zr–2Hf

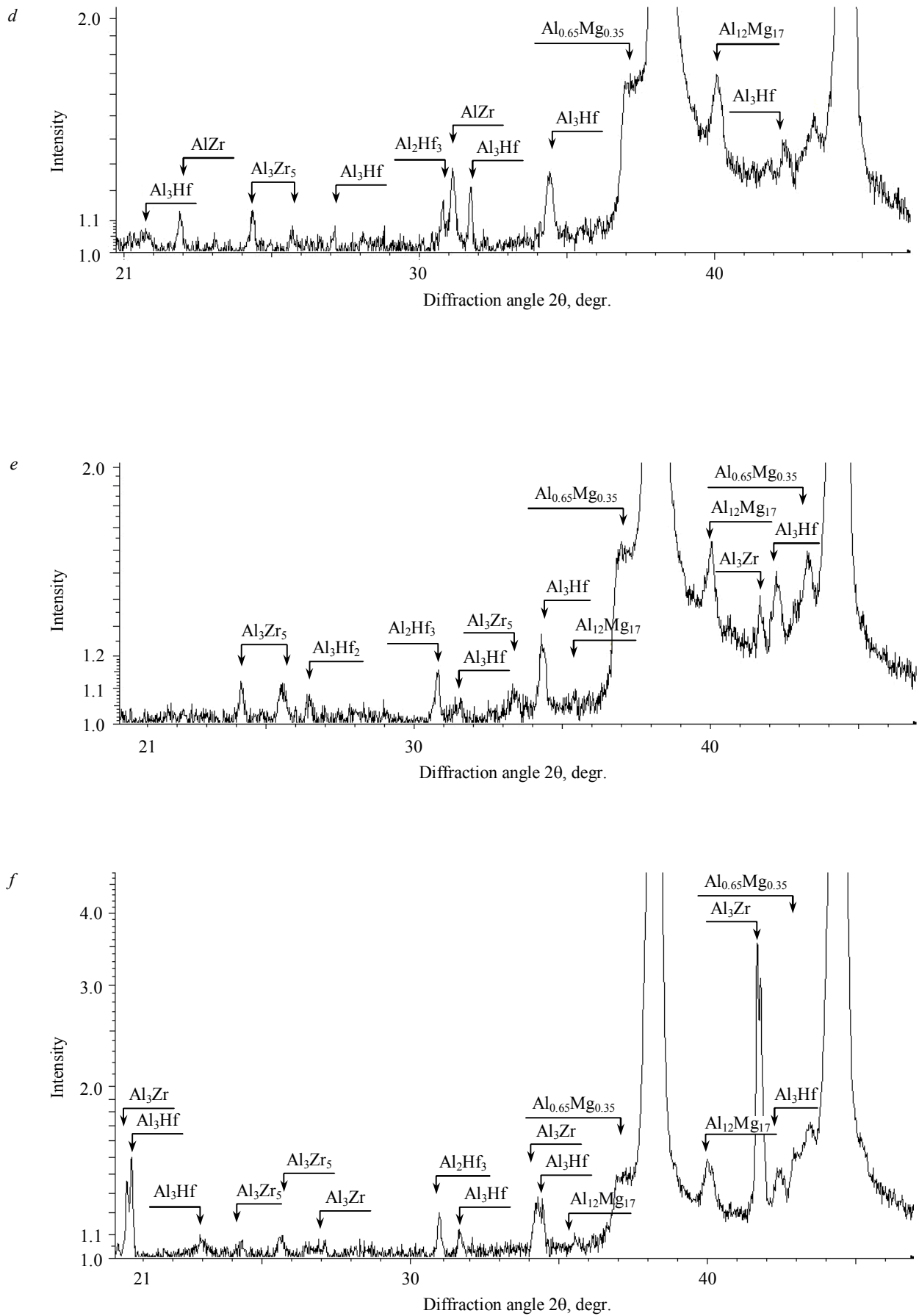


Fig.3. End of XRD pattern



Similar to the previous sample, intermetallic components Al_3Zr , $AlZr$, $Al_{13}Mg_7$ ($Al_{0.65}Mg_{0.35}$), $Al_{12}Mg_{17}$ are present in the alloy when adding Nb. Niobium is part of the compound Al_3Nb , as well as the intermetallic compound $AlNb_2$ (Fig. 3, *b*).

In a system with Ti addition, there are compounds $Al_{13}Mg_7$ ($Al_{0.65}Mg_{0.35}$), Al_4Zr_5 , Al_3Ti , $Al_{18}Mg_3Ti_2$. Unlike other alloys, there is no $Al_{12}Mg_{17}$ compound in this system, as well as intermetallic compositions Al_2Ti and $AlTi$ (Fig.3, *c*).

Hafnium is a part of the intermetallic compounds Al_3Hf and Al_3Hf_2 , as well as the compound Al_2Hf_3 (Fig. 3, *d-e*). Thus, for a sample with 2% by mass of Hf, the matrix is an alloy of the Al-Mg system, and the intermetallic compound has the chemical composition $Al_{20}Zr_6Hf$. According to the results of XPA, this compound is a mixture of intermetallic compounds Al_3Zr_5 , Al_3Hf , Al_3Hf_2 , Al_2Hf_3 and Al_3Zr .

The results of qualitative X-ray phase analysis for all the studied alloys are summarized in Table 2. It follows from the table that during fast cooling of the melt the intermetallic compounds are formed, which are absent in an equilibrium system of the same composition.

Table 2

Results of X-ray phase analysis of alloys

Composition,% by weight				Discovered intermetallic compounds		
Al	Mg	Zr	X	Formed independently of the cooling conditions [10]		Formed only with fast cooling
93.3	5.0	1.2	0.5 W	Al ₁₃ Mg ₇ , Al ₁₂ Mg ₁₇	Al ₃ Zr, Al ₅ W	Al ₄ W, W ₃ Mg, Al ₁₈ Mg ₃ W ₂ , AlW ₄ Zr
93.3	5.0	1.2	0.5 Nb		AlZr, Al ₃ Zr, Al ₃ Nb	AlNb ₂
93.3	5.0	1.2	0.5 Ti		Al ₄ Zr ₅ , Al ₃ Ti, Al ₁₈ Mg ₂ Ti ₃	AlTi, Al ₂ Ti
93.3	5.0	1.2	0.5 Hf		Al ₃ Zr ₅ , Al ₃ Hf, AlZr	Al ₂ Hf ₃
92.8	5.0	1.2	1 Hf		Al ₃ Zr ₅ , Al ₃ Hf, Al ₃ Hf ₂	Al ₂ Hf ₃
91.8	5.0	1.2	2 Hf		Al ₃ Zr ₅ , Al ₃ Hf, Al ₃ Hf ₂	Al ₂ Hf ₃ , Al ₃ Zr

Conclusions. Crystallization of alloys of the Al–Mg–Zr–X-system with high cooling rates leads to a change in the phase composition and structure of the material. As a result of this study, the influence of fast cooling on the structure of the Al–Mg–Zr–X-system alloys has been studied. It has been established that fast cooling of the melts of the Al–Mg–Zr–X-system leads to the formation of new intermetallic phases absent in the equilibrium system.

Samples obtained with fast cooling of the melt can be described as dispersion-strengthened materials, in which the matrix is an aluminum alloy, the strenghtener is uniformly distributed intermetallic particles. Depending on the alloying component, the size of these particles varies (from 200 nm when alloying with Hf and W up to 1.2-1.5 μm with Ti and Nb alloying). The volume ratio of intermetallic compounds varies from 2.3 % for the alloy with 0.5 % by weight to 12.8 % for the alloy with 2 % by mass of Hf.

Using the example of hafnium alloy, it was shown that with increasing content of the alloying component (from 0.5 to 2 % by mass), the volume ratio of intermetallic inclusions increases (from 5 to 12.8 %). At the same time, their shape and average size remain unchanged.

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Authors: **Dmitrii I. Budelovskij**, *Engineer, Impa2010-new@mail.ru (OJSC «Virial», Saint-Petersburg, Russia)*, **Sergei Yu. Petrovich**, *Head of Laboratory, Impa2010-new@mail.ru (Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg, Russia)*, **Vadim A. Lipin**, *Doctor of Engineering Sciences, Head of Department, vadim.lipin@km.ru (Higher School of Technology and Energy of Saint Petersburg State University of Industrial Technologies and Design, Saint-Petersburg, Russia)*.

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