Composition and stability of $Al_2(Mg,Ca)$ compound in alloys of Al – Mg – Ca – (Zn) system

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Alloys based on the Al – Mg – Ca – (Zn) system may be attractive as a class of low-density aluminum alloys combining strength, technological effectiveness and lightness. With a minimum proportion of zinc, magnesium plays the main role in strengthening, which should be maximally included in the composition of an aluminum (Al)-based solid solution. Therefore, compounds that pull magnesium from (Al) can lead to a decrease in the strength of the alloy. Such a compound is the phase described by the formula $Al_2(Mg,Ca)$ and previously undetectable in alloys of the Al – Mg – Ca – (Zn) system. The aim of the work was to determine the magnesium concentrations at which this compound was detected, to study its stoichiometric composition, stability during heat treatment and to determine the temperature range of its formation. The solution of these problems was implemented using optical (OM) and scanning microscopy (SEM) techniques, thermal analysis and the CALPHAD computational approach. $Al_2(Mg,Ca)$ was determined to be present in alloys containing 3–6% magnesium and 4% calcium, and changes its stoichiometric composition inversely depending on the magnesium content: with the decrease of magnesium, its share in the compound increases. The classical heat treatment for magnals has no effect on the chemical composition of the phase, and it remains stable. A temperature range was identified in the Al4%Mg8%Ca alloy when the formation of the compound of interest was detected. The alleged nature of its occurrence is described by the eutectic reaction $L \rightarrow (Al) + Al_2(Mg,Ca)$. At the same time, the actual data of the thermal analysis have good convergence with the calculated values.

Key words: aluminium, magnesium, calcium, compounds, microstructure, crystallization.

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Introduction

The development of inexpensive lightweight and durable alloys with excellent corrosion resistance is of great importance due to the need to reduce the weight of vehicles [1, 2]. Alloys based on aluminum doped with magnesium (5xx and 5xxx series) are traditional representatives of this direction. At the same time, practically no new compounds are found in them. The exception is the solubility of magnesium in already known phases [3]. At the same time, in recent years, aluminum alloys with calcium have been studied, including multicomponent alloys, as an alternative to existing alloys and characterized by reduced density. In particular, new technological aspects were studied in order to improve strength properties and improve corrosion resistance [4–6]. Within the researches, new intermetallics were found and confirmed, in particular $Al_{10}CaFe_2$, $Al_{10}CaMn_2$, Al_9CaNi, $Al_{10}CaMn_2$, $Al_{27}Ca_3Cu_7$, Al_8CaCu, $(Al,Cu)_4Ca$, $(Al,Zn)_4Ca$ [7–12]. Among them, alloys doped mainly with magnesium have not been sufficiently studied [13, 14]. As a separate class of lightweight materials, these alloys may be of significant practical interest, especially in the context of trends in increasing energy efficiency of vehicles.

Previously, it was believed that there are no triple compounds in the Al – Mg – Ca system. However, in the works [15, 16], a compound described by the formula $Al_2(Mg,Ca)$ was discovered, the nature of the appearance of which remained unclear. Assumptions have been made about the reasons for the formation of this phase, according to which the $(Al,Zn)_4Ca$ phase was formed earlier and was a substrate for the subsequent crystallization and growth of crystals of the non-equilibrium phase β-Al_3Mg_2 with subsequent transformation into $Al_2(Mg,Ca)$. This may explain the proximity of the Al_3Mg_2 and $Al_2(Mg,Ca)$ phases in the conglomerates.

Understanding the characteristics of the proposed compound is important in terms of ensuring the strength and ductility of the alloy. Indeed, as is known, solid-solution strengthening from magnesium addition without the need for heat treatment is an effective method of improving the mechanical properties of pure aluminum [17]. Additional alloying of aluminum with calcium leads to the formation of calcium-containing eutectics and also contributes to the growth of strength and positively affects the casting characteristics. The presence of the compound $Al_2(Mg,Ca)$ raises the issue of its role in pulling magnesium

from a solid solution, which could potentially reduce strength. Its effect on the plasticity of aluminium-calcium eutectic is also unclear.

Based on the above description, the objectives of the study were:

– identify concentration limits for magnesium content, at which the Al_2(Mg,Ca) phase is fixed;

– determine the stability of the composition of the atomic phase of Al_2(Mg, Ca) depending on the magnesium content;

– determine the stability of the Al_2(Mg,Ca) phase after heat treatment;

– determine the temperature range of Al_2(Mg,Ca) phase formation.

Methods

The objects of study were 7 alloys of the Al – Mg – Ca – (Zn) system, the composition of which is presented in **Table 1**. All alloys were prepared using pure components: aluminum grade A99 (GOST 11069–2019), magnesium grade Mg90 (GOST 804–93), calcium (TU 20.13.23-001-45034953–2022) and zinc grade Ts0 (GOST 3640–94). Melting was carried out in an electric resistance furnace of the GRAFICARBO brand in graphite crucibles with a capacity of 2 kg of gold at a furnace temperature of 750 °C. Aluminum was primarily melted, and then calcium, magnesium, and zinc wrapped in aluminum foil were sequentially introduced. Casting was carried out in a graphite crucible to obtain cast ingots with overall dimensions of 10 × 20 × 180 mm. The cooling rate of the melt in the mold was about 10 °C/s. Further, the bottom and upper parts were cut off from the ingots, and samples for metallographic studies were made from the middle working area.

Table 1
Composition of the studied alloys

Alloy	Marking	The actual content of the element, mass.%				
		Al	Mg	Ca	Zn	Fe
Al6%Mg4%Ca	640	Bal.	6.2	3.7	–	0.1
Al5%Mg4%Ca1%Zn	541	Bal.	5.3	4.0	1.1	<0.1
Al4%Mg4%Ca2%Zn	442	Bal.	4.5	4.2	2.1	<0.1
Al3%Mg4%Ca3%Zn	343	Bal.	3.6	4.2	3.5	<0.1
Al2%Mg4%Ca4%Zn	244	Bal.	2.1	4.2	4.0	<0.1
Al1%Mg4%Ca5%Zn	145	Bal.	1.1	3.7	5.0	<0.1
Al4%Mg8%Ca	480	Bal.	7.6	4.4	–	<0.1

Table 2
Changes in the composition of (Al) and Al_2(Mg,Ca) of the studied alloys obtained after cooling with a furnace. The averaged composition of the phases over several spectra of the MRSA analysis is given

Alloy	640	541	442	343	244	145
The content of Mg in Al_2(Mg,Ca), at.%						
SC	14.7 ± 1.5	17.8 ± 0.6	19.4 ± 0.2	22.2 ± 0.9	–	–
SC+T4	14.4 ± 1.7	17.5 ± 0.4	19.6 ± 1.4	22.0 ± 0.7	–	–
The content of Ca in Al_2(Mg,Ca), at.%						
SC	13.1 ± 1.1	15.5 ± 0.5	14.4 ± 0.4	11.5 ± 0.8	–	–
SC+T4	12.4 ± 4.1	16.3 ± 0.5	13.2 ± 1.2	11.9 ± 0.5	–	–
The content of Zn in Al_2(Mg,Ca), at.%						
SC	–	0.6 ± 0.2	0.8 ± 0.4	1.9 ± 0.8	–	–
SC+T4	–	0.6 ± 0.3	0.7 ± 0.3	1.4 ± 0.6	–	–
Content of Mg in (Al), at.%						
SC	6.9 ± 2.7	6.2 ± 0.6	6.0 ± 0.9	4.8 ± 1.4	2.8 ± 1.2	1.7 ± 0.7
SC+T4	6.5 ± 0.5	6.9 ± 1.1	6.4 ± 1.0	4.6 ± 0.6	2.4 ± 0.6	1.7 ± 0.3

Note: the Al content in the Al_2(Mg,Ca) phase for alloys 541, 442 and 343 remained constant (66.1 ± 0.8 / 65.9 ± 0.5 at.% for SC and SC + T4, respectively), and in alloy 640 it was higher – 72.2 ± 1.2 / 73.0 ± 3.3 at.% for SC and SC+T4, respectively.

The preparation of samples for microstructural studies was carried out by mechanical grinding and polishing using a diamond suspension. After polishing, the samples were etched in 0.5% HF solution for 30 s. The microstructure was examined using a Tescan Vega 3 scanning electron microscope equipped with an attachment with an electronic microprobe analyzer MRSA and Aztec software, as well as a Zeiss Axio Observer.D1m optical microscope. Quantitative structure parameters were evaluated using software tools: ImageJ and Origin Pro 18. Thermodynamic calculations were performed using the Thermo-Calc software package (TCW5 version, TTAL5 database). Direct thermal analysis was performed on an ATT-2006 temperature meter (ACTACOM) with a chromel-alumel (CA) thermocouple in conjunction with ATE Easy Monitor software. The thermocouple readings were calibrated using A99 grade aluminum. The heat treatment was carried out in an electric furnace manufactured by SNOL 8,2/1100. The accuracy of maintaining the temperature was 1 °C. The heat treatment modes are shown in **Table 2**. Cooling with the furnace was performed in a melting furnace by heating to 700 °C, holding for 15 minutes and cooling with the furnace to ambient temperature. Thus, a cooling rate of ~0.6 °C/s was achieved. This mode is hereinafter referred to as SC.

Results

Initially, the area of appearance of the Al_2(Mg,Ca) phase was considered at a variable magnesium content (from 6% to 1%) and constant calcium (4%). The solubility of zinc in this phase was also tested. The choice of alloy compositions was based on previously performed studies [9–11]. The cast microstructure of the investigated group of alloys is shown in **Fig. 1**

In the **Fig. 1, *a*** corresponding to the alloy Al6%Mg4%Ca,

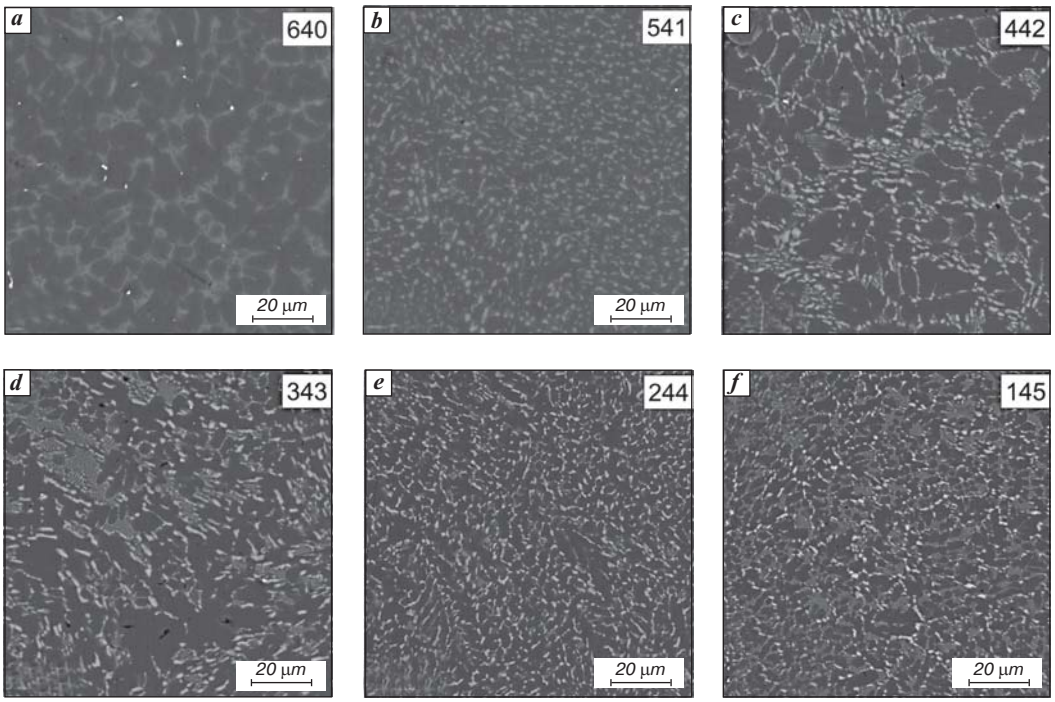

Fig. 1. Images of microstructures of alloys of 6-1% Mg at 4% Ca in the cast state. The alloy markings are indicated on each framed image

4 phases are visible against the background of the aluminum matrix, which differ in shade: light gray, dark gray, dark and light. According to quantitative analysis, they correspondingly relate to: eutectic [(Al) + Al_4Ca], $Al_2(Mg,Ca)$, Al_3Mg_2 and $Al_{10}CaFe_2/Al_3Fe$. According to calculations in Thermo-Calc [18], the volume fraction of the Al_3Mg_2 phase in the cast state should be 18%, which is more than the Al_4Ca phase (16.7%). However, β-phase inclusions are quite rare, which indicates a high proportion of dissolved magnesium in (Al).This also applies to the assumed $Al_2(Mg,Ca)$ phase, which is practically not visually detectable in the SEM and OM images.

With a further decrease in the magnesium content, the shape of eutectic particles changes, against which there are practically no other phases. Only in the alloy Al 5%Mg4%Ca1%Zn **(Fig. 1, *b*)** dark gray inclusions inscribed in eutectic are revealed. For a more detailed identification of the desired phase, cooling with a furnace was performed, during which an increase in the linear dimensions of the crystals occurred, which facilitated the analysis.

In the slowly cooled structure of the Al6%Mg4%Ca alloy **(Fig. 2, *a*)**, the eutectic crystals are visually indistinguishable, however, the data from the element distribution maps (see **Fig. 2, *a1-a3***) show the presence of two types of eutectic structures containing aluminum/calcium and aluminum/magnesium/calcium. According to the results of the MRSA, the formulas of the described compounds are Al_4Ca and $Al_2(Mg,Ca)$. There is no noticeable difference in morphology between them. The visual similarity in the BSE scanning mode is explained by the proximity of the atomic numbers of aluminum and magnesium, as well as the fact that the proportion of calcium in these compounds differs by no more than 7 at.%. Due to such a small difference, even in the secondary electron (SE) regime, it is quite difficult to determine the boundary between phases. With the addition of zinc to the alloy, the Al_4Ca phase, in which zinc is dissolved, acquires a higher atomic weight and looks lighter **(Fig. 2, *b, c*)**, which facilitates identification. It was expected that with a decrease in the magnesium content in the alloy, its concentration in the phase would also decrease, and calcium, on the contrary, would increase. However, the opposite effect is observed **(Table 2)**, which increases with a further decrease in magnesium. At the same time, the proportion of the desired $Al_2(Mg,Ca)$ phase decreases markedly, and it is not fixed in alloys 244 and 145 (see **Table 1**). It is worth noting that in alloys with a magnesium content of 4–6%, non-equilibrium inclusions of the Al_3Mg_2 phase are not detected, and the solubility of zinc in $Al_2(Mg,Ca)$ increases from 0.2 to 0.8 at.%.

Based on the assumption that the compound $Al_2(Mg,Ca)$ is metastable and is formed simultaneously with the compound Al_3Mg_2 [15], the microstructure of slowly cooled samples was studied after quenching in water from a temperature of 440 °C and holding for 3 hours **(Fig. 2, *d–f*)**. The results obtained demonstrate the stability of the studied phase under these parameters, while the stoichiometric composition also does not change. The magnesium content in (Al) remains almost constant, which indicates a minimum proportion of the excess phase of Al_3Mg_2 after cooling with a furnace. To quantify the volume fraction of the $Al_2(Mg,Ca)$ phase, images of alloys 640, 541 and 442 were analyzed (see **Table 1**). Since

this phase is practically absent in the Al3%Mg4%Ca3%Zn alloy, it was not included in the calculation. To do this, the occupied area was first analyzed by (Al) and Al_4Ca/$(Al,Zn)_4Ca$, after which the difference between 100% and the sum of the areas was obtained. As a result, the proportion of the $Al_2(Mg,Ca)$ phase was: $10.2 \pm 0.9\%$, $10.3 \pm 1.5\%$ and $6.1 \pm 1.4\%$ for alloys 640, 541 and 442 (see **Table 1**) accordingly.

To identify the temperature range of the formation of the compound $Al_2(Mg,Ca)$, an eutectic alloy Al4%Mg8%Ca was obtained. During the experiment, the alloy samples were melted at a temperature of 700 °C, held for 15 minutes after melting and sequentially cooled with a furnace to temperatures of 600, 550, 500 and 450 °C. The temperature during the cooling process was fixed with a *X*-thermocouple. When the temperature approached the

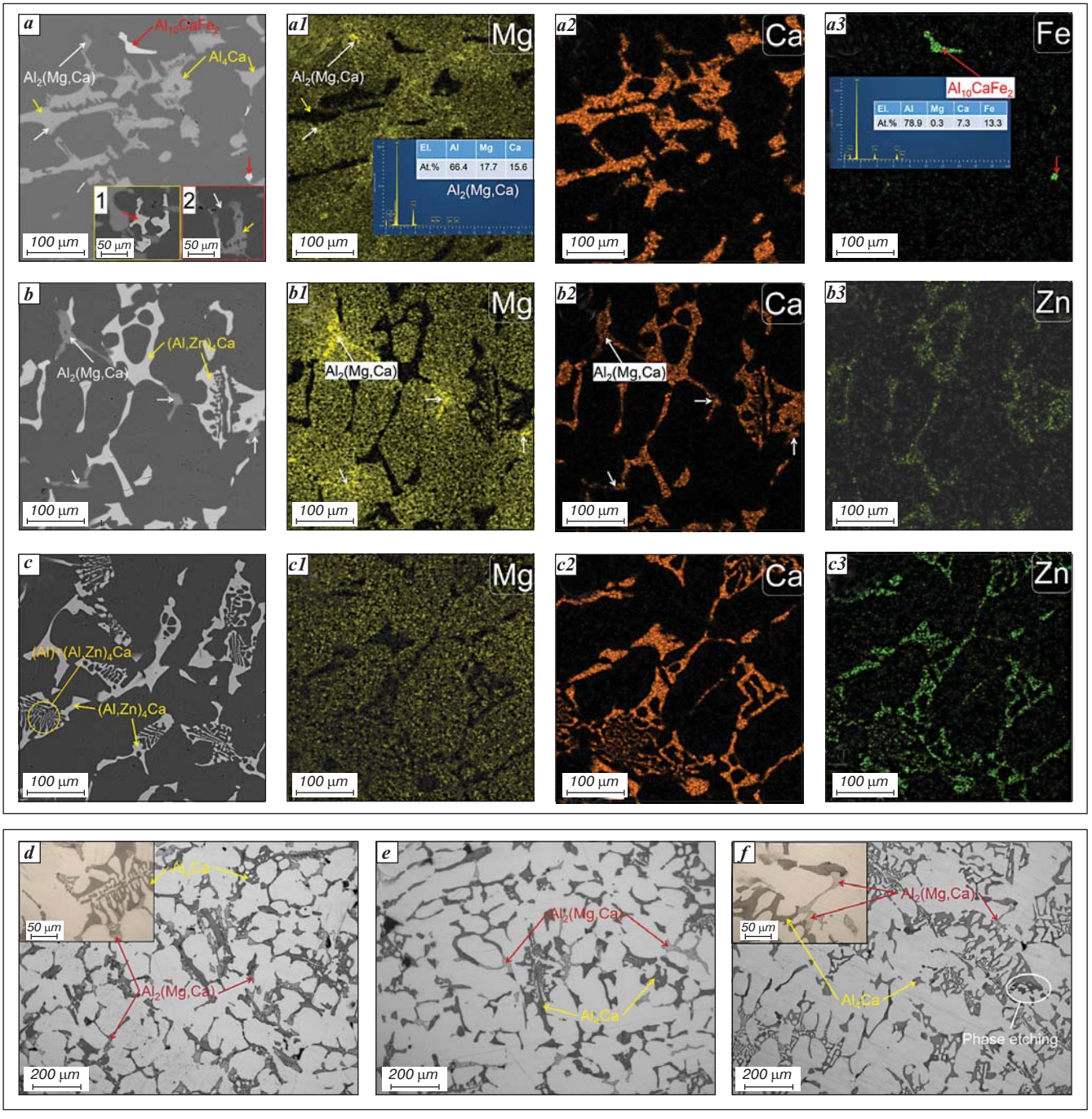

Fig. 2. Images of microstructures of alloys 6–2% Mg at 4% Ca after cooling with a furnace (*a–c3*, SEM) and cooling with a furnace and quenching with 440 °C with an exposure of 3 hours (*d–f*, OM): (*a–a3*, *d*) — Al6%Mg4%Ca; (*b–b3*) — Al4%Mg4%Ca2%Zn; (*c–c3*) — Al2%Mg4%Ca4%Zn; *e* — Al5%Mg4%Ca1%Zn; *f* — Al3%Mg4%Ca3%Zn. Images *a1–a3*, *b1–b3* and *c1–c3* show the MRSA maps of the distribution of elements and individual spectra corresponding to images *a*, *b*, c, respectively

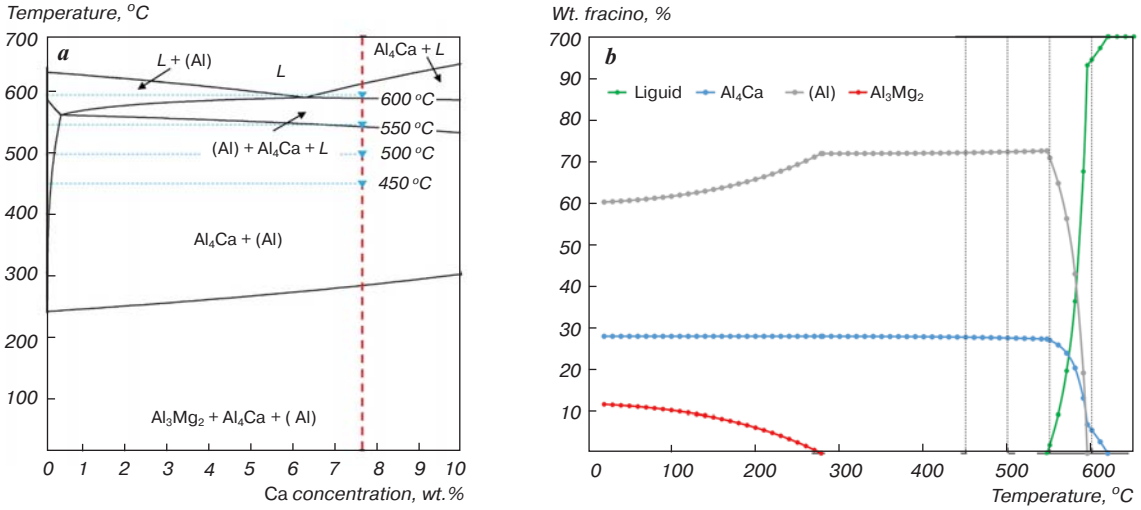

Fig. 3. Thermodynamic calculations of the Al – Mg – Ca system and alloy Al4%Mg8%Ca: *a* – Polythermal cross section of the Al – Mg – Ca diagram at 4.4% Mg; *b* – calculated dependences of the mass fraction of phases on the temperature of the alloy Al4%Mg8%Ca (In Fig. 3, *a* the vertical line indicates the position of the alloy in terms of calcium content, and the horizontal lines indicate the quenching temperature from the solid–liquid state. In Fig. 3, *b*, the vertical lines indicate the quenching temperatures from the solid-liquid state)

set point (3 °C higher), the sample was removed from the furnace and cooled in water. According to the calculation (**Fig. 3, *a***, the calculation is given for the actual composition of the alloy, see **Table. 1**), the alloy begins to crystallize with the formation of primary crystals of the Al_4Ca phase (at 619 °C), and the temperature of the beginning and end of eutectic formation [(Al)+Al_4Ca] is 595 and 547 °C, respectively. At 547 °C, according to the conditions of equilibrium crystallization, the liquid disappears. According to the graphs of the dependence of the mass fraction of phases on temperature **(Fig. 3, *b*)**, it can be seen that the calcium-containing phase shows an active growth up to ~ 545 °C, after which it changes slightly.

In the cast state, the alloy is represented by an almost completely eutectic structure with separate inclusions of primary crystals (PC) of the Al_4Ca phase having a length of up to 100 microns. Needle-like primary crystals and dispersed eutectic are also detected in the sample hardened with 600 °C [(Al)+Al_4Ca] in the composition of a crystallized liquid. The composition of primary crystals is presented in **Table 3** and it is quite close to the previously confirmed data [7–11]. Subsequent cooling and crystallization (550 °C) reveal the formed framework of the lamellar eutectic and the amorphous phase corresponding to the crystallized liquid. The composition of the eutectic crystals has stabilized and corresponds to the composition of the equilibrium Al_4Ca. At the same time, the liquid phase is enriched with magnesium, the concentration of which in it exceeds that in (Al) by 2 times. The presence of calcium in the liquid may be explained by the nonequilibrium nature of crystallization, according to which, below the calculated temperature of disappearance of the liquid phase, a residual liquid of a different composition from the equilibrium may be present.

Table 3

The average phase composition of the alloy Al4%Mg8%Ca after cooling with a furnace and quenching at temperatures of 600, 550, 500 and 450 °C

Temperature, °C	Phase	The content of the element, at.%		
		Al	Mg	Ca
600	Al_4Ca (PC)	80.8 ± 0.3	0.6 ± 0.1	18.6 ± 0.3
	Eut.+liquid	90.9 ± 4.3	5.2 ± 2.9	4.8 ± 3.4
550	(Al)	95.8 ± 1.0	4.2 ± 1.1	0
	Al_4Ca (PC) and Al_4Ca (Eut.)	80.1 ± 0.4	0.5 ± 0.2	19.4 ± 0.6
	Liquid	85.2 ± 0.5	10.4 ± 0.1	4.5 ± 0.4
500	(Al)	93.1 ± 2.3	6.5 ± 1.6	0
	Al_4Ca (PC) and Al_4Ca (Eut.)	79.2 ± 0.4	1.1 ± 0.6	19.7 ± 0.2
	Liquid +Al_3Mg_2	64.9 ± 0.6	34.0 ± 0.6	1.0 ± 0.1
	Al_2(Mg,Ca)	70.7 ± 1.3	14.2 ± 0.7	15.1 ± 0.8
450	(Al)	91.0 ± 4.3	8.2 ± 3.9	0
	Al_4Ca (PC) and Al_4Ca (Eut.)	79.7 ± 1.1	1.0 ± 0.9	19.3 ± 0.8
	Al_3Mg_2	62.6 ± 0.2	36.8 ± 0.3	0.7 ± 0.1
	Al_2(Mg,Ca)	66.9 ± 1.1	20.3 ± 1.9	12.9 ± 2.1

At 500 °C, two changes can be observed in contrast to the previous state. First, the crystallization of a magnesium-enriched liquid corresponding in its composition to the compound Al_3Mg_2. The second change is the identification of a spongy structure resembling the eutectic phase of Al_4Ca. MRSA analysis shows a high content of dissolved magnesium and calcium, in addition to aluminum. The results of the analysis of individual spectra showed that the composition of this compound corresponds to the desired

phase of $Al_2(Mg,Ca)$. Also, the segregation of magnesium atoms to primary crystals of the Al_4Ca phase is visible from the maps of the distribution of elements. The transverse linear analysis shows an increase in the magnesium content along the edges of the crystal and is close to the composition of the surrounding matrix. In the last sample (quenching with 450 °C), the alloy structure is close to the previous state, except for the more pronounced contrast of the phase components. It is worth noting that the MRSA analysis of the regions (Al) located close to the proposed compound $Al_2(Mg,Ca)$ showed an increased proportion of magnesium (up to 14 at.%), while near Al_4Ca crystals its proportion decreases to 6 at.%. This can be seen from the spread of values in **Table 3**, which shows the average data.

The results of the direct thermal analysis and the curve of the first derivative *dT/dt* are shown in **Fig. 4.** The *dT/dt* curve allows you to better see the changes occurring during the crystallization process. In the alloy Al4%Mg8%Ca, the T_1 point corresponds to the beginning of eutectic

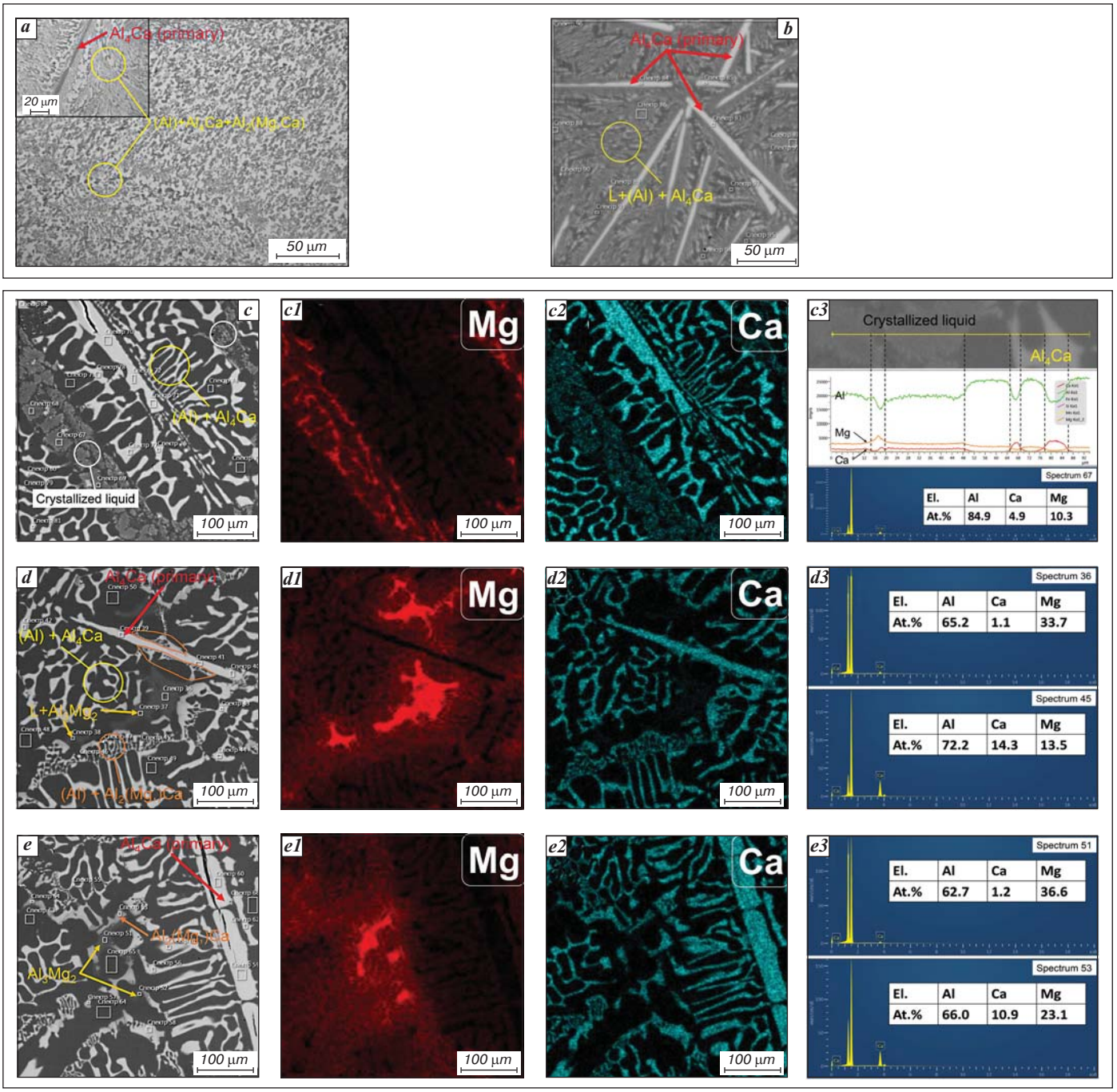

Fig. 4. Images of microstructures of Al4%Mg8%Ca alloy in the cast state (*a*) and after cooling with a furnace and interval quenching (*b–e)*: *b* – from 600 °C; *c–c3* — from 550 °C; *d–d3* — from 500 °C; *e–e3* — with 450 °C. Images *c1–c3*, *d1–d3* and *e1–e3* show MRSA- maps of the distribution of elements and individual spectra corresponding to images *c, d, e*

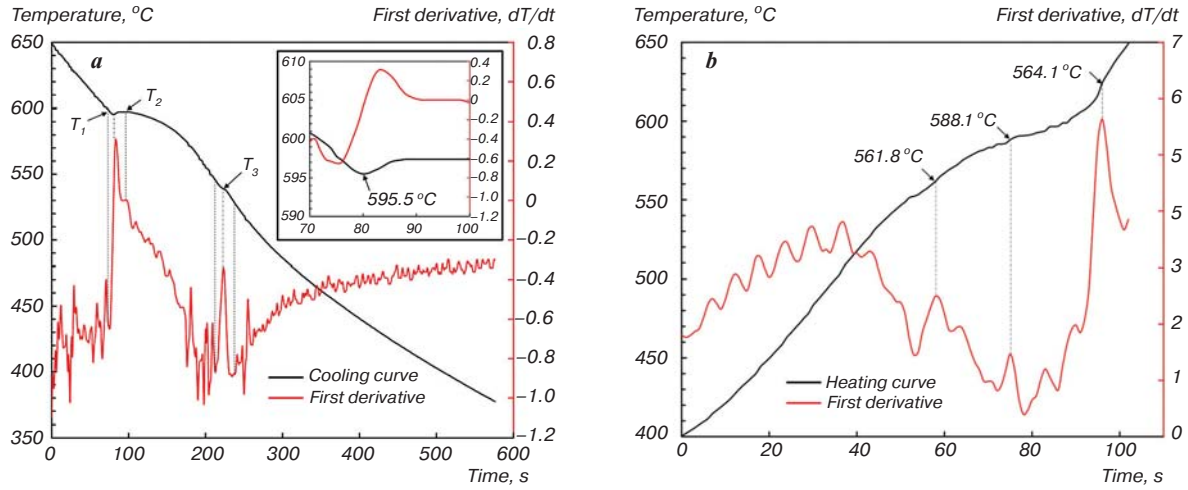

Fig. 5. Cooling (*a*) and heating (*b*) curves and corresponding curves of the first derivative *dT/dt* of the alloy Al4%Mg8%Ca

nucleation (596.7 °C) **(Fig. 4, *a*)**. After a sharp jump, the *dT/dt* curve reaches a plateau, which indicates an increase in the eutectic phase $L \rightarrow$ (Al) + + Al_4Ca. The end of the eutectic growth is marked by the T_2 point (597.4 °C), characterized by an inflection and departure into the negative range of values. In the future, the plateau turns into a smooth curve corresponding to the enlargement of eutectic crystals. During crystallization, several peaks are recorded, which may indicate ongoing transformations. At the same time, an inflection on the cooling curve (T_3 point) is clearly noticeable, corresponding to the most intense peak (539.3 °C). This temperature may indicate an ongoing peritectic or eutectic reaction, in which the Al_2(Mg,Ca) phase appears. The probable formula of the peritectic reaction is as follows: L + + $Al_4Ca \rightarrow$ (Al) + Al_2(Mg,Ca). As a rule, such a reaction does not take place completely and evidence of a diffusion process is revealed in the form of rims of one phase around another [7]. No similar effect was found during the microstructural analysis of this work and previous ones [15, 16]. Therefore, it is possible that this reaction is eutectic: $L \rightarrow$ (Al) + Al_2(Mg,Ca).

No changes were recorded below 450 °C, in particular, the release of Al_3Mg_2 from the (Al) phase. This can be attributed to its small fraction, since, as can be seen from the data in **Table 3**, magnesium is mainly dissolved in (Al). On the heating curves and the corresponding derivative *dT/dt* **(Fig. 4, *b*)**, an inflection corresponding to the liquidus temperature is well detected. These observations are in good agreement with microstructural studies of samples hardened at different temperatures (see **Fig. 4**).

In accordance with the performed studies and observations, **Fig. 5** shows an isothermal section of the Al – Mg – Ca system, showing the distribution of phase regions in the solid state (at 25 °C). Earlier, in [15], a schematic representation of the boundaries of phase regions in the solid state in the Al – Mg – Ca system was given. Since it has been determined that zinc is mainly soluble in (Al) and Al_4Ca, and in the Al_2(Mg,Ca) phase its content

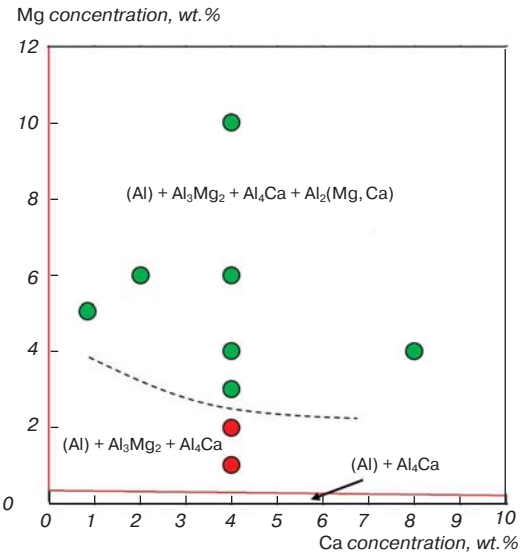

Fig. 6. Distribution of phase regions in the Al – Mg – Ca system in the cast state

is limited to 0.8 at.% (in alloy 442), its effect on the phase composition can be neglected. The green circles indicate alloys in which the compound Al_2(Mg,Ca) was detected explicitly [15] or indirectly [19] by the SEM method, and the red ones — in which it is absent. It is worth mentioning separately that earlier studies [12–14] were carried out, in which the presence of the Al_2(Mg,Ca) phase was assumed, but at the time of the research this was not the subject of a search and the structures of furnace-cooled alloys were not studied. The dashed line indicates the assumed boundary of the region in which the Al_2(Mg,Ca) phase will be absent. In the future, it is planned to clarify the boundaries of the phase regions and to study the triple compound in detail using "thin" research methods.

Conclusions

1. The existence of the triple compound Al_2(Mg,Ca) in alloys of the Al – Mg – Ca – (Zn) system was recorded in the range of concentrations of magnesium 3–6% at

4% calcium. As the magnesium content in the alloy decreased, its content in the composition of the phase increased. At the same time, the volume fraction of the phase decreased markedly.

2. A wide area of homogeneity of the compound $Al_2(Mg,Ca)$ has been revealed, which varies with the content of calcium from 11 to 13 at.% and magnesium from 14 to 22 at.%. The content of aluminum in the phase for alloys containing magnesium is 3–5%, while stable within 66 at%, but higher in alloy Al6%Mg4%Ca (72 at.%). After quenching from 440 °C and holding for 3 hours, the atomic composition of this phase remained stable.

3. By sequential crystallization from the solid-liquid state in a triple alloy of Al4%Mg8%Ca, the temperature range of formation of the compound $Al_2(Mg,Ca)$ was determined. By SEM methods, the compound was detected at 450-500 °C, while with a decrease in temperature its composition changed slightly: the magnesium content increased and the calcium content decreased.

4. The critical temperatures of phase transitions were determined by direct thermal analysis and data processing. They showed good convergence with the obtained theoretical data and microstructural observations during the interval-temperature processing. In the absence of signs of a peritectic reaction, it is assumed that the $Al_2(Mg,Ca)$ phase has a eutectic reaction origin in the $L \rightarrow (Al) + Al_2(Mg,Ca)$.

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