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PHYSICOCHEMICAL AND STRUCTURAL INVESTIGATIONS OF MATERIALS

PHASE EQUILIBRIA IN THE Mg – Al – Ca SYSTEM (REGION 50-100 MASS% Mg)

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Phase equilibria in the ternary system Mg – Al – Ca in the composition range 50-100 mass% Mg were studied by the methods of differential thermal, x-ray diffraction, electron-probe and microscopic analysis. The projection of the liquidus surface on the concentration triangle, isothermal section at 150°C and polythermal sections at 4.5, 8.5, and 16 mass% Al were constructed. It was determined that additions of Al and Ca decrease the liquidus temperature of magnesium alloys (from 650 to 438°C). It is shown that the three-phase region <Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> *exists at 150°C with the corresponding two-phase fields. The temperature dependence of the homogeneity range of the Mg-based solid solution was determined, and also the temperatures of the phase transformations which occur in the investigated range of compositions in the system.*

Keywords: *phase equilibrum, liquidus, polythermal section, phase region, phase transformation.*

INTRODUCTION

Alloys of the ternary system Mg – Al – Ca have stimulated the interest of investigators as a potential matrix for alloys of multicomponent systems and composite materials. Special attention is paid to alloys in the Mg-rich range of compositions because they serve as the base for light and strong structural materials and are cheaper than magnesium alloys containing Sc, Y, and rare-earth metals (REM).

The state diagrams of the binary systems which adjoin the Mg – Al – Ca system are given in [1]. Data on the structure of the ternary system are collected in [2]. A quasibinary section Mg – Al_2Ca with a eutectic point close to 79 at.% Mg exists in this system, and also a ternary eutectic at approximately 9 at.% Al and 79 at.% Mg [3]. The temperature of the quasibinary eutectic is 535°C [4]. Isothermal sections of the system at 450, 370, and 290°C are given in [5]. It is shown that the three-phase equilibria <Mg> + Al_2Ca + Mg_2Ca and <Mg> + Al_2Ca + $Mg_{17}Al_{12}$ exist in the system, and the solubility of aluminum in magnesium decreases with increasing calcium concentration in the alloys.

The objective of this investigation was to construct the isothermal section at 150°C and the polythermal sections at 4.5, 8.5, and 16 mass% Al, and also the projection of the liquidus surface on the concentration triangle at the magnesium corner of the ternary system Mg – Al – Ca.

METHODS OF INVESTIGATION

We have investigated alloys in the magnesium-rich region of the Mg – Al – Ca system. They were prepared from highly pure components by induction melting followed by slow cooling in the furnace, and also by quenching from the melt with minimum loss of material. The methods of differential thermal analysis (DTA), x-ray diffraction (XRD),

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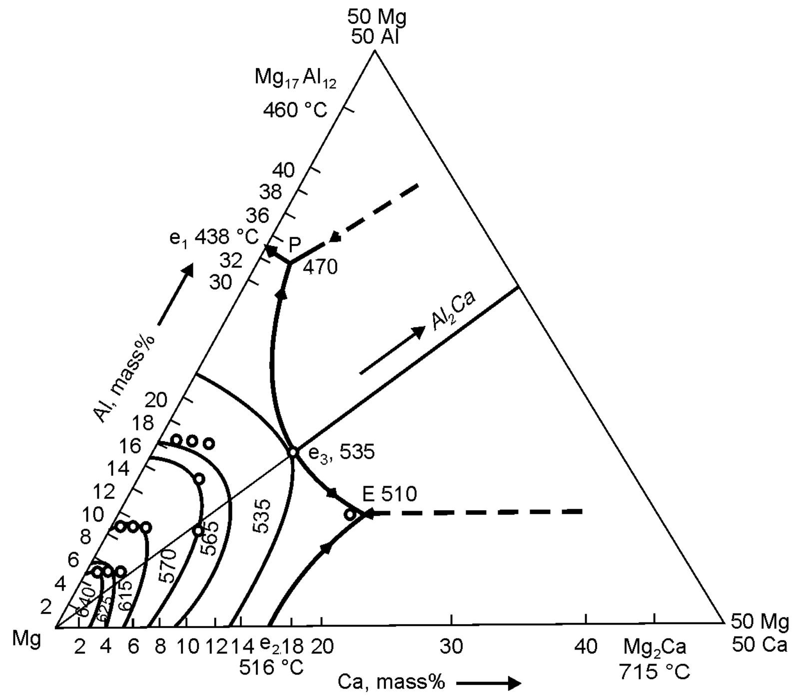

Fig. 1. Projection of the liquidus surface of the magnesium-rich region of the Mg – Al – Ca system.

electron-probe microanalysis (EPMA) and microstructural analysis were used. Differential thermal analysis was carried out in the unit VDTA-8M with a wire thermocouple in an atmosphere of grade VCh helium: temperature was measured with a tungsten – tungsten-rhenium thermocouple VR-20. The thermocouple was calibrated with standards of Rh, Pt, Fe, Cu, Au, and Al. The specimens were heated and cooled at the rate of 80 deg/min. Reproducibility of the temperature scale in the range 0-1000°C was 3°C. X-ray diffraction analysis of the specimens was carried out in monochromatic CuK_α radiation on the diffractometer DRON-UM1: the monochromater was a graphite monocrystal installed in the diffracted beam. The lattice constants of the registered phases were determined by least squares analysis. Electron-probe microanalysis of the investigated alloys was carried out on the instrument CAMEBAX of the firm "Cameka", microstructural on the optical microscope MIM-7. For construction of the isothermal section the alloys were homogenized at 400°C for 20 h in the furnace SShVL in an argon atmosphere, then annealed at 150°C for 95 h. The phase composition of the annealed alloys was determined with the aid of the above-described methods.

RESULTS OF THE INVESTIGATION AND DISCUSSION

Liquidus Surface. In order to construct isotherms on the projection of the liquidus surface (Fig. 1) DTA data concerning the liquidus temperature of alloys in which a magnesium solid solution first crystallized out was used (Table 1), and also data in the literature concerning the position of liquidus curves corresponding to the crystallization of a magnesium solid solution, as well as the invariant points in the adjoining binary systems Mg – Al and Mg – Ca [2]. The direction of monovariant curves was determined from data on the melting temperature of alloys (Table 1) whose compositions correspond, according to [3], to the compositions of the ternary eutectic $L_E \Leftrightarrow$ <Mg> + Mg_2Ca + Al_2Ca and the quasibinary eutectic $e_3 \Leftrightarrow$ <Mg> + Al_2Ca. Thus, the melting temperature of the ternary eutectic is ~510°C and the quasibinary ~535°C, which agrees with the data of [4]. We have determined the position and temperature of one more invariant point existing in the investigated range of compositions in the given system. This point corresponds to the composition of liquid participating in the peritectic transformation L_P + $Al_2Ca \Leftrightarrow$ <Mg> + $Mg_{17}Al_{12}$ which occurs at 470°C. The liquidus surface of the solid solution based on Mg goes down from the melting temperature of Mg (650°C) to the temperatures of the eutectics in the adjoining binary systems Mg – Al and Mg – Ca: $e_1 \Leftrightarrow$ <Mg> + $Mg_{17}Al_{12}$ (438°C) and $e_2 \Leftrightarrow$ <Mg> + Mg_2Ca (516°C) and also to the temperature of the quasibinary eutectic $e_3 \Leftrightarrow$ <Mg> + Al_2Ca

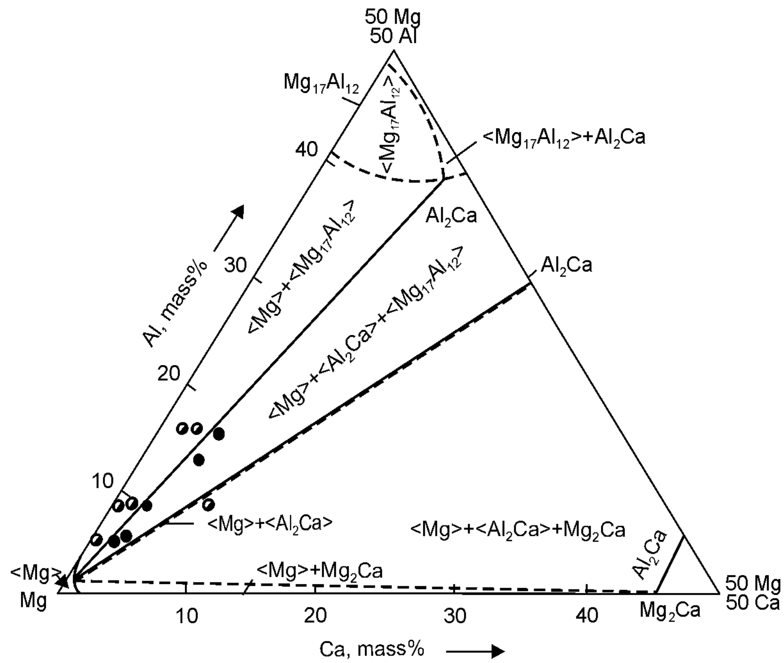

Fig. 2. Isothermal section of the Mg – Al – Ca system at 150°C. Composition range 50-100 mass% Mg.

TABLE 1. Composition of Mg – Al – Ca Alloys and Their Liquidus Temperatures

Composition No.	Alloy composition, mass%			Liquidus temperature, °C
	Mg	Al	Ca	
1	94.7	4.5	0.8	640
2	93.5	4.5	2.0	625
3	92.5	4.5	3.0	625
4	90.5	8.5	1.0	620
5	89.5	8.5	2.0	615
6	88.5	8.5	3.0	605
7	83.6	8.6	7.8	570
8	82.4	13.2	4.4	570
9	82.0	16.0	2.0	565
10	81.0	16.0	3.0	560
11	80.0	16.0	4.0	555
12	74.0	14.6	11.0	535
13	72.6	9.2	18.2	510

(535°C) (Fig. 1). The point e_3 on the liquidus surface represents a saddle point from which, along the monovariant curves e_3P and e_3E, further temperature decrease occurs and, correspondingly, lowering of the liquidus surface to 510°C at point E and 470°C at point P. From point P, as a consequence of a reaction along the monovariant curve Pe_1 following the peritectic $L_P + Al_2Ca \Leftrightarrow$ <Mg> + $Mg_{17}Al_{12}$, an additional temperature decrease occurs down to 438°C, the temperature of the eutectic reaction $e_1 \Leftrightarrow$ <Mg> + $Mg_{17}Al_{12}$ in the binary system Mg – Al.

Thus, the liquidus temperature decreases with increase in the aluminum as well as calcium concentration relative to the composition of the quasibinary eutectic in Mg-based alloys. The lowest liquidus temperatures, 470-438°C, appear in the ternary alloys containing no more than 3 mass% Ca and approximately 32 mass% Al (Fig. 1). The

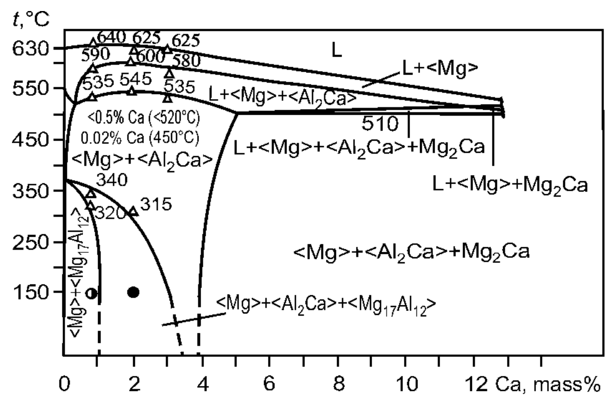

Fig. 3. Polythermal section of the Mg – Al – Ca system at 4.5 mass% Al.

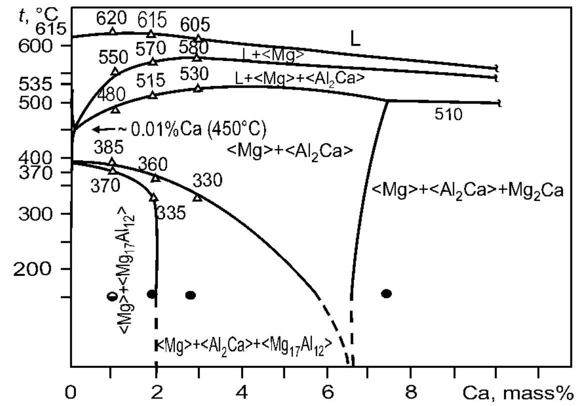

Fig. 4. Polythermal section of the Mg – Al – Ca system at 8.5 mass% Al.

liquidus surfaces of the phases $MgCa_2$, Al_2Ca, and $Mg_{17}Al_{12}$ adjoin the liquidus surface of the Mg-based solid solution along the monovariant curves e_2E, EP, and Pe_1, respectively.

Isothermal Section at 150°C. It follows from data on the phase composition of alloys annealed at 150°C that in the Mg – Al – Ca system a three-phase region <Mg> + $Mg_{17}Al_{12}$ + Al_2Ca exists at 150°C (Fig. 2, Table 2). According to data in the literature [1] the solubilities of aluminum and calcium in magnesium in the binary systems Al – Mg and Ca – Mg at 150°C are 2.37, and 0.15 mass%, respectively. Extrapolating the curve of joint solubility of aluminum and calcium in magnesium from 450, 370, and 290°C in the Mg – Al – C system [3, 5] to 150°C, we determined the location of the homogeneity range of the magnesium solid solution at 150°C.

EPMA of the alloy containing, according to XRD, <Mg> + $Mg_{17}Al_{12}$ showed that in the Mg-based solid solution in the vicinity of the ray Mg – Al_2Ca the solubility of Ca is 0.10 mass%, and in the phase $Mg_{17}Al_{12}$ approximately 10 mass%. The solubility of Al in magnesium with a HCP lattice at 150°C on the ray <Mg> – Al_2Ca is substantial compared to that at higher temperatures: 0.1 mass%.

Polythermal Sections of the System at the Concentrations 4.5, 8.5, and 16 mass% Al. Polythermal sections corresponding to 4.5, 8.5 and 16 mass% Al with calcium concentration no greater than 15 mass% were constructed from DTA data on the temperatures of the phase transformations which occur in these alloys (Table 2), the phase state of the alloys at 150°C, and literature data on the solubility of calcium and aluminum in the magnesium solid solution at 450, 370 and 290°C.

At 4.5 mass% Al the maximum solubility of calcium reaches 0.5 mass% at a temperature slightly below 520°C (Fig. 3). It sharply decreases with decreasing temperature and at 450°C is only about 0.02 mass%. Further temperature decrease produces a monotonic decrease in the homogeneity range of the magnesium solid solution, depending on the concentration of calcium in the alloys. The boundary positions of phase transformations occurring in the given alloys were determined from thermal effects on the heating and cooling curves of the alloys. The boundaries of phase fields were determined by XRD analysis of specimens annealed at 150°C (Table 2). The phase composition of two-phase alloys <Mg> + <Al_2Ca> changes at 450°C and lower temperatures. Thus, two phase transformations were observed in the alloy containing 0.8 mass% Ca for the following boundaries: <Mg> + <Al_2Ca>/<Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> at 340°C and <Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$>/<Mg> + <$Mg_{17}Al_{12}$> at 320°C. In alloys containing 2 mass% Ca a phase transformation in the solid state only was found at the boundary: <Mg> + <Al_2Ca>/<Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> at 315°C, but in the alloy with 3 mass% Ca corresponding effects at these temperatures were not observed. This might be a consequence of the steepness of the boundary of the phase transformation <Mg> + <Al_2Ca>/<Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$>. Extrapolation of the position of the given boundaries to 150°C and the phase composition of the alloys at 150°C (Table 2) established the concentration and temperature regions of phase transformations in specimens

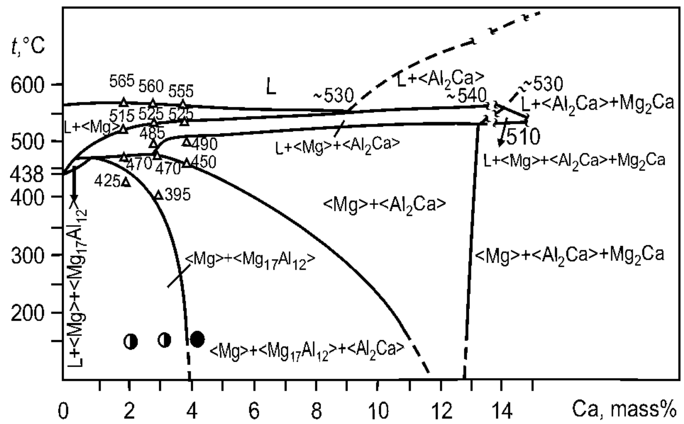

Fig. 5. Polythermal section of the Mg – Al – Ca system at 16 mass% Al.

TABLE 2. Phase Compositions and Lattice Parameters of Phases in the Magnesium-Rich Region of the Mg – Al – Ca System at 150°C*

Composition No.	Phase composition	Lattice parameters, nm			
		<Mg>		<$Mg_{17}Al_{12}$>	<Al_2Ca>
		a	*c*	*a*	*a*
1	<Mg> + (<$Mg_{17}Al_{12}$>)**	0.3194(1)	0.5188(1)	-	-
2	<Mg> + <Al_2Ca> + (<$Mg_{17}Al_{12}$>)	0.3204(1)	0.5202(1)	-	0.8047(1)
3	<Mg> + <Al_2Ca>	0.3205(1)	0.5205(1)	-	0.8050(1)
4	<Mg> + (<$Mg_{17}Al_{12}$>)	0.3180(1)	0.5171(1)	-	-
5	<Mg> + <Al_2Ca> + (<$Mg_{17}Al_{12}$>)	0.3185(1)	0.5179(1)	-	0.7984(2)
6	<Mg> + <Al_2Ca> + (<$Mg_{17}Al_{12}$>)	0.3193(1)	0.5187(1)	-	0.8010(1)
7	<Mg> + <Al_2Ca>	0.3205(1)	0.5208(1)	-	0.8058(1)
8	<Mg> + <Al_2Ca> + < $Mg_{17}Al_{12}$>	0.3183(1)	0.5178(1)	1.0662(3)	0.7982(2)
9	<Mg> + <$Mg_{17}Al_{12}$>	0.3183(1)	0.5172(1)	1.0657(1)	-

*Furnace cooled. **Parentheses indicate a small quantity of the phase; angular brackets indicate a solid solution based on the phase.

containing 4.5 mass% Al with additions of calcium up to 4 mass%. At 150°C the three-phase region <Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> is found between 1 and 3 mass% Ca (Fig. 3).

In the polythermal section 8.5 mass% Al (Fig. 4) a tendency for the solubility of calcium in the magnesium solid solution to decrease was observed. Thus, its maximum solubility is 0.01 mass% at approximately 450°C. This decreases with decreasing temperature and at approximately 370°C is practically zero, which agrees with the data of [5]. Alloys of the compositions studied by us (Table 1) at subsolidus temperatures are located in the two-phase region <Mg> + <Al_2Ca>. However, at lower temperatures thermal effects on the heating and cooling curves of the alloys were observed corresponding to phase transformations at the boundaries of the phase fields <Mg> + <Al_2Ca>/<Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> and <Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$>/<Mg> + <$Mg_{17}Al_{12}$>. Extrapolation of the positions of the given boundaries to 150°C and the phase compositions of the investigated alloys annealed at 150°C (Table 2) establishes the extent of the three-phase region <Mg> + <Al_2Ca> + <$Mg_{17}Al_{12}$> in the given section at 150°C as from 2 to 6 mass% Ca.

In distinction from the sections considered above, on the section at 16 mass% Al (Fig. 5.) there is no single-phase region of solid solution of aluminum and calcium in magnesium. The boundaries of the phase fields constructed from DTA data on phase transformation temperatures and XRD data on the phase composition of alloys annealed at 150°C show a displacement of the three-phase field <Mg> + <$Mg_{17}Al_{12}$> + <Al_2Ca> with decreasing temperature toward the region of Ca-rich alloys. At 150°C it is located between 4 and 11 mass% Ca (Fig. 2).

Conclusions

Based on experimental results the projection of the liquidus surface of the <Mg> + <Al_2Ca> system on the concentration triangle, polythermal sections at the constant aluminum concentrations 4.5, 8.5, and 16 mass%, and the isothermal section at 150°C were constructed. The joint solubility of aluminum and calcium in magnesium at 150°C was determined. This is 0.1 mass% for each of these elements in the vicinity of the ray <Mg> + <Al_2Ca>.

The solubility limit of calcium in the Mg-based solid solution changes with the concentration of aluminum in the alloys, sharply decreasing from 0.5 mass% at 4.5 mass% Al and 520°C to 0.01 mass% at 8.5 mass% Al and 450°C.

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