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PHASE COMPOSITION, STRUCTURE AND MANUFACTURABILITY OF NEW EUTECTIC ALLOYS BASED ON THE Al-Ca-Zn-Mg SYSTEM

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ABSTRACT

Using the calculated (Thermo-Calc software) and experimental methods (SEM, TEM, EMPA, DSC, XRD, etc.) the phase composition, structure and hardening of aluminium alloys of the Al-Ca-Zn-Mg system were studied in the following range: 2. 5%Mg, up to 10% Ca, and up to 14% Zn (wt%). Fragments of this quaternary phase diagram in the aluminium corner were constructed, including the liquidus surface, as well as some vertical sections. It was shown that the relatively large amount of zinc enters in the Ca-containing phase, which formula can be described as $(Al,Zn)_4Ca$. An increase of Zn content leads to formation of Al_4Ca primary crystals at lower concentrations of calcium. The eutectic $(Al)+(Al,Zn)_4Ca$ has a fine structure and aluminide particles are capable to spheroidization during the heat treatment at temperature 500 C. The maximal level of hardness observed on calcium containing alloys was higher than 200 HV, what gives the reason to expect good strength properties. With an example of an Al-9% Zn-2,5%Mg-3,5% Ca model experimental alloy based on the $(Al)+(Al,Zn)_4Ca$ eutectic, a principal possibility of manufacturing thin rolled sheets was demonstrated.

KEYWORDS

Aluminium-calcium eutectic, Hardening, Dispersoids, Phase composition

INTRODUCTION

Aluminum alloyed with calcium was first studied in 1970-80s by such authors as Piatti (1976), Moore (1978, 1980), Il'enko (1985), Swaminathan (1990), and Perez-Prado (1997) as superplastic materials. In particular, the alloy systems Al-Ca-Zn were studied (Il'enko, 1985, Swaminathan, 1990, Perez-Prado, 1997). For some time there was no new published works concerning the aluminum-calcium alloys. During the last years many works were published dedicated to the calcium alloying of magnesium alloys (Kim, 2011; Xu, 2011; Aljarrah, 2008; Bakhsheshi, 2014). This urged the authors (Belov, Naumova & Akopyan, 2016) to start studying cast and wrought aluminum-calcium alloys for construction (2008–2014). There is almost no information in the literature concerning triple and more complex diagrams of the aluminum-based system states with calcium and other elements. In recent work, parts of the state diagrams are plotted for the aluminum angle zone: Al-Ca-Mg-Sc (Belov, Naumova & Bazlova, 2016), Al-Ca-Ni-Sc (Belov, Naumova & Bazlova, 2017), Al-Ca-Si-Sc (Belov, Naumova & Akopyan, 2017) and others. Special attention was paid to the study of the system Al-Ca-Zn-Mg (Naumova, 2017). Based on this system creation of advanced extra-high tensile alloys is planned. Wrought extra-high tensile alloys series 7xxx based on the system Al-Zn-Mg-Cu are well studied.

Zinc and magnesium are the traditional reinforcing elements of the solid aluminum solution. The disadvantage of this alloy series is low casting properties. Calcium-alloyed systems contain large amounts of eutectics (Al)+Al_4Ca (where (Al) - solid aluminum-based solution), so their cast properties are much better. That is why the study of the phase equilibriums in the system Al-Ca-Zn-Mg is of great interest. Besides, the works (Kono, 1985, Petzow, 1990) demonstrate that zinc is dissolved in Al_4Ca, forming intermetallic $(Al,Zn)_4Ca$. To detect the alloys with optimum tensile and processing properties, one needs to know how zinc is distributed between the solid aluminum solution and the phase $(Al,Zn)_4Ca$, and what are the properties of the intermetallic Al_4Ca and $(Al,Zn)_4Ca$. All these ideas defined the objectives of the present research, which are:

- Specify the structure of state diagram for Al-Ca-Zn-Mg within the aluminum-rich zone;
- Study the composition and measure the hardness of the intermetallic Al_4Ca and $(Al,Zn)_4Ca$;
- Choose the alloys with optimum composition for the further study of their properties;
- Estimate the alloy workability in casting and rolling as well as some mechanical and physical properties of the semi-products made of them.

EXPERIMENTAL METHODS

The objects of the experimental research included alloys containing 2.5% Mg, 4-10%Ca, and 1-14%Zn. Melting was performed in induction furnace manufactured by RELTEK. The alloys were prepared based on aluminum A99. Under the temperature of aluminum melt of about 780°C metallic calcium was imbedded in aluminum foil in four parts. Then under the melt temperature of 730–740°C zinc and magnesium was imbedded in two parts wrapped with aluminum foil. After complete dissolution of the burden matters the melt remained for 5–10 min under 740°C for alloy composition homogenization. Then under the temperature of 720–740°C the slag was removed. After that the metal was tapped into steel mold under 710–720°C to make slabs with dimensions 15×30×180 mm.

Microstructure of the cast and heat-treated samples was examined using optical microscope Olympus GX51 (OM) and scanning electron microscope TESCAN VEGA 3 (SEM). TESCAN microscope equipped with energy-dispersive unit – micro-analyzer manufactured by Oxford Instruments and AZtec software, was also used for electron microprobe analysis (EMPA). To prepare cross-sections both mechanical and electrolytic grinding were used preformed under voltage of 12 V in the electrolyte containing 75% C_2H_5OH, 12.5% $HClO_4$ and 12.5 % glycerin.

To calculate the phase composition of the system Al–Ca–Mg–Zn the software Thermo-Calc was applied (database TTAL5) (http://www.thermocalc.com, 2017).

Heat treatment of the castings was carried out in a SNOL 8,2/1100 muffle electric furnace at 500°C for 3 h followed by quenching in water and ageing under the temperatures from 100 to 250°C with the interval of 25°C and exposure time at each stage of 3 h (T6 temper). The specific electrical conductivity (σ) was measured by eddy-current testing using a VE-26NP device with high purity Al (99.99%) as an additional standard. Vickers hardness (HV) was used to evaluate the hardness of the castings (Wilson Wolpert 930 N, load 50 N).

RESULTS AND DISCUSSION

Diagram Al-Ca-Zn-Mg

In Belov, Naumova and Akopyan (2016) and Naumova (2015), the authors specified the data (Mondolfo, 1976; Kevorkov & Schmid-Fetzer, 2001; Kevorkov, Schmid-Fetzer & Pisch, 2001), stating the within the system Al-Ca the double eutectics L→(Al)+Al_4Ca (where (Al) – solid aluminum solution) is formed at 7.6%Ca concentration and the temperature of 617°C. The research of the triple systems Al-Ca-Mg (Belov, Naumova & Bazlova, 2016) and Al-Ca-Zn (Naumova, 2015) demonstrated that both magnesium and zinc reduce calcium concentration, under which the primary crystals of the phase Al_4Ca first appear. Under 3%Mg eutectics concentration is about 6.5%Ca. For this research we have chosen the constant concentration of magnesium of 2.5% for all alloys, calcium concentration was changed from 0 to 10%, while zinc concentration was changed from 0 to 14%. Using the Thermo-Calc software the projection of the liquidus surface for system Al-Ca-Zn-Mg was calculated for the aluminum-rich zone under 2.5%Mg (Figure 1). The dashed line is the border of the primary crystal formation, which was plotted based on the experimental data. Under 4%Ca pre-eutectic structure remains in the alloys containing up to 10%Zn, and under 6%Ca the primary crystals appear in the alloys with zinc concentration above 4%.

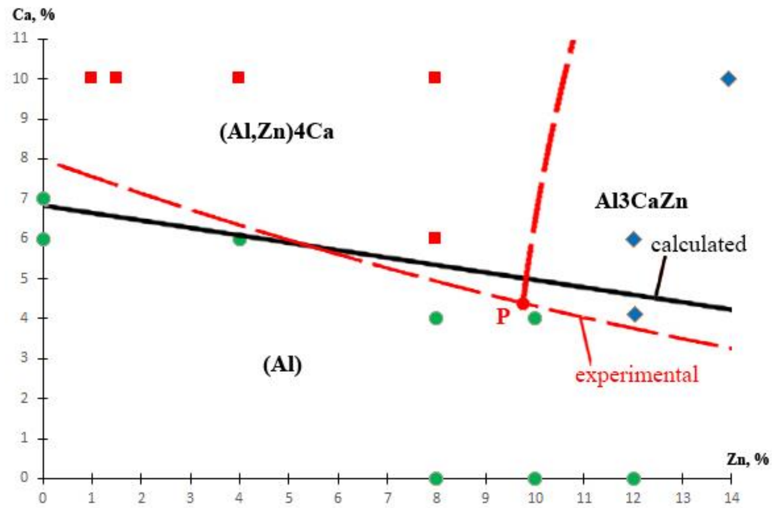


Figure 1. Liquidus projection of Al-Ca-Zn-Mg system at 2.5 wt.%Mg. The dashed line shows the border of the primary crystal appearance obtained through the experiment.

Cast structure of the alloys without calcium consists of dendrites of aluminum solid solution surrounded by the streaks of phases $MgZn_2$ and T ($Al_2Mg_3Zn_3$) (Figure 2a). In alloys without zinc (Figure 2b) the eutectics looks somewhat coarser than in the quaternary alloys (Figures 2c and 2d). In the alloys with hyper-eutectic composition the primary crystals of the phase $(Al,Zn)_4Ca$ are present. In case of increase of zinc concentration is the alloys the amount of the primary crystals grows considerably (Figures 2e and 2f).

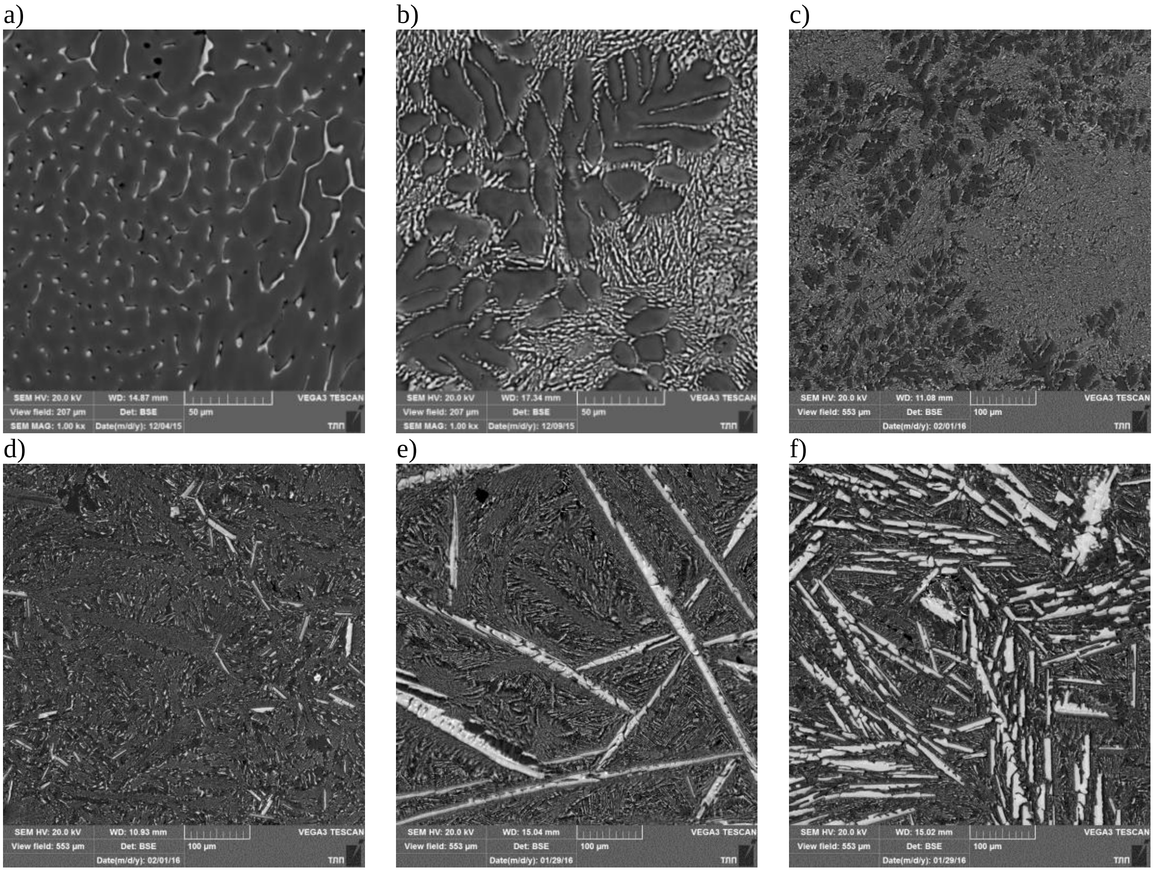
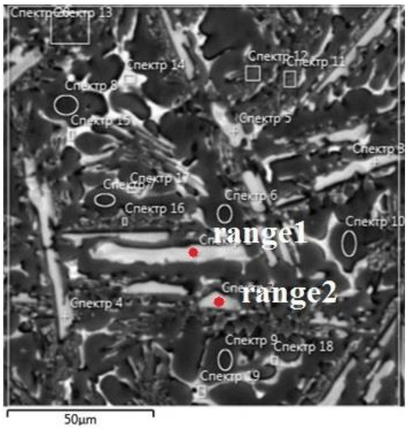


Figure 2. Alloy microstructure in cast state, SEM: a) Al-2.5Mg-8Zn, ×1000; b) Al-2.5Mg-6Ca, ×1000; c) Al-2.5Mg-6Ca-4Zn, ×500; d) Al-2.5Mg-6Ca-8Zn, ×500; e) Al-2.5Mg-10Ca-1Zn, ×500; f) Al-2.5Mg-10Ca-8Zn, ×500.

As the database TTAL5 does not contain the information on the triple phases, the state diagram type should be corrected based on the experimental data. According to EMPA data, the percent concentration of zinc in the primary crystals varies depending on its concentration in the alloy from 5.7wt% (Al-2.5Mg-10Ca-1Zn) to 23wt% (Al-2.5Mg-10Ca-8Zn). In the alloys Al-2.5Mg-4Ca-12Zn, Al-2.5Mg-6Ca-12Zn and Al-2.5Mg-10Ca-14Zn the primary crystal composition corresponds with the phase Al_3CaZn (Figure 3). Based on these data, the dash line is plotted on the liquidus surface projection which divides the zones of primary crystallizing of the phases $(Al,Zn)_4Ca$ and Al_3CaZn (Figure 1).



Spectrum name	Mg wt/at%	Al wt/at%	Ca wt/at%	Zn wt/at%	Sum	Phase
Range 1	0.07/0.10	45.01/61.15	22.45/20.53	32.47/18.21	100	Al_3CaZn
Range 2	0.07/0.11	44.83/61.13	21.80/20.02	33.30/18.74	100	Al_3CaZn

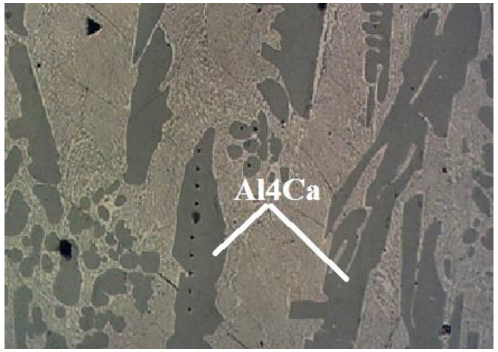
Figure 3. The primary crystal composition in the alloy Al-2.5Mg-6Ca-12Zn (EMPA data).

Nano-Levels of Hardness and Young's Modulus of the Intermetallic (Al,Zn)4Ca

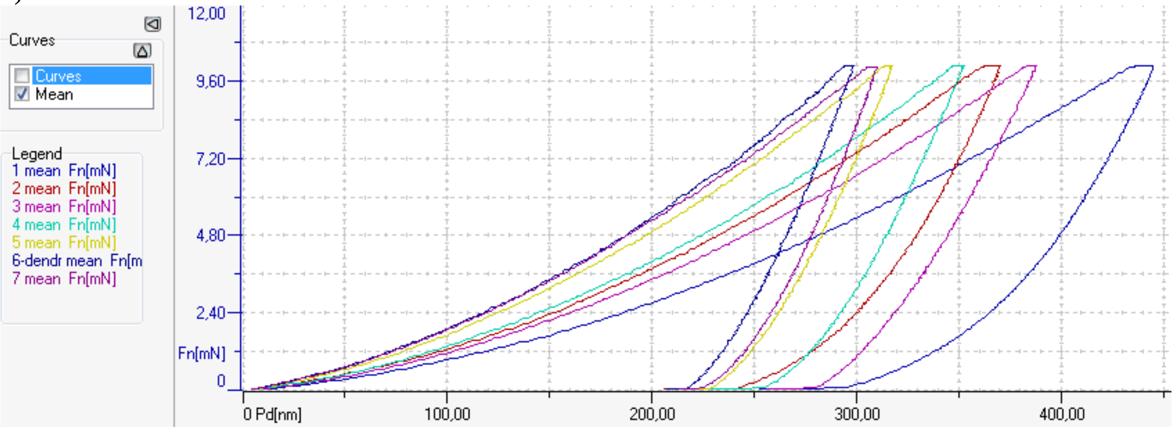
Measurement of the hardness and the elasticity modulus of the primary crystals $(Al,Zn)_4Ca$ in alloys Al-2.5Mg-10Ca-(0-14)Zn was carried out by means of the instrumented indentation method in accordance with the Instruction for hardness measurement using «Nano-Hardness Tester» manufactured by CSM Instruments under the following conditions: applied load 10 mN, contact force hold time 5 s. The results were processed using the Indentation 3.83 computer program (CSM Instruments, Switzerland).

Study of the primary crystals of the phase $(Al,Zn)_4Ca$ in hyper-eutectic alloys demonstrated that their hardness and elasticity modulus grow together with the increase of zinc concentration (Figure 4).

a)



b)



%Zn in the alloy phase	0 Al_4Ca	1 $(Al,Zn)_4Ca$	2 $(Al,Zn)_4Ca$	4 $(Al,Zn)_4Ca$	8 $(Al,Zn)_4Ca$	14 Al_3CaZn
Nano-levels of hardness (H), GPa	2.3 ± 0.1	3.2 ± 0.1	3.0 ± 0.2	3.5 ± 0.1	4.3 ± 0.2	4.8 ±0.3
Young's modulus (E), GPa	53 ± 6	71 ± 1	62 ± 1	80 ± 2	104 ± 6	107 ± 7

Figure 4. Values of the hardness and elasticity modulus for the primary crystals in the alloys Al-2.5Mg-10Ca-(0-14)Zn. a) Microstructure of the Al-2,5Mg-10Ca alloy (The distance between the prints on the vertical is 15 µm); b) Experimental indentation curves (vertical - load, horizontal - depth of indentation).

Effect of Heat Treatment on the Hardness and Electrical Conductivity of Experimental Alloys

Alloys of the optimum composition should be technologically efficient during casting and be significantly hardened after heat treatment. For the selection of such alloys, the degree of decomposition (Al) after aging was measured by measuring hardness and electrical conductivity. The alloys were subjected to thermal treatment in the T6 mode: quenching 450°C, 3 h + 500°C, 3 h, then cooling in water, aging from 100 to 250°C with an interval of 25°C and holding at each stage for 3 h. At 450°C, the excess phases of $MgZn_2$ and T ($Al_2Mg_3Zn_3$) dissolve. As seen in Figure 2, the eutectic (Al) + (Al, Zn) 4Ca has a very fine structure, therefore when heated at 500°C, the Al_4Ca and (Al, Zn) $_4$Ca intermetals are fragmented and rounded. This ensures high plasticity during deformation (Belov, Naumova & Akopyan, 2016).

During annealing the electric conductivity increases as well. For all alloys the temperature of the maximum hardening resulting from precipitation of dispersoids $MgZn_2$ and T ($Al_2Mg_3Zn_3$) from (Al) is 150–175°C. In Figure 5a the diagrams of dependence of hardness on the alloy ageing temperature are shown for the alloys containing different concentration of calcium and 10% of zinc. It is obvious that the more calcium there is, the lower the hardness is and the less is the precipitation strengthening effect. This is due to reduction of the solid solution share in the alloy. So, from the point of view of good combination of mechanical and processing properties the calcium concentration of 3–4% is preferable. Figure 5b demonstrates the increase of hardening during ageing with the increase of zinc concentration in the alloys with 4%Ca. Even though part of the present zinc is dissolved in the eutectic crystals of the phase $(Al,Zn)_4Ca$, its concentration in the solid aluminum solution grows. So, we believe the compositions Al-2.5Mg-4Ca-(8-10)Zn to be the optimum.

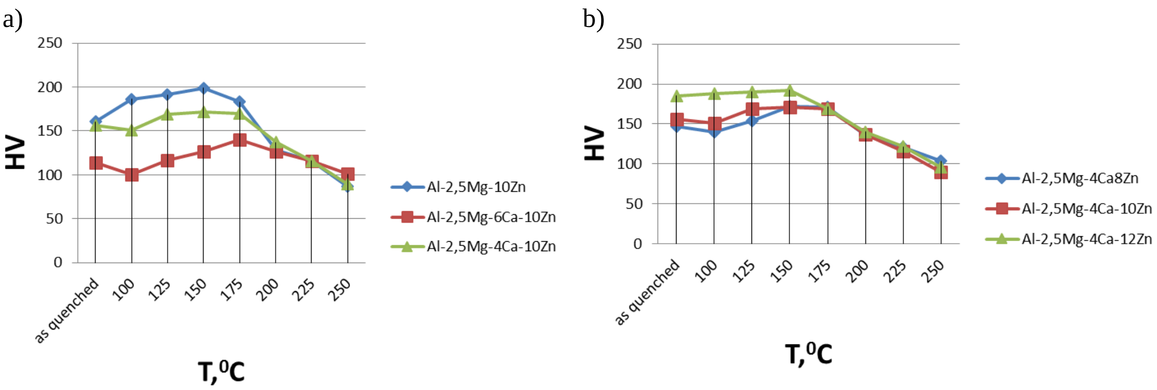


Figure 5. Dependence of the hardness of experimental alloys on the aging temperature.

Figure 6 shows the dependences of the electric conductivity growth (difference between the conductivity of the samples of annealed and chilled states) during annealing (ageing) process on the calcium and zinc concentration in the alloys. The lower the share of the solid aluminum solution in the alloy is and the lower the zinc concentration is, the less change is demonstrated by the electric conductivity of the alloy. The conductivity of eutectic and hyper-eutectic alloys almost does not change during annealing process. In over-aged state (after 3 h of annealing under 250°C) the conductivity of the calcium-free alloys, alloys with 4%Ca and 6%Ca averages at 25, 19 and 17 µS/m, correspondingly. As the electric conductivity is directly related to the thermal conductivity, the alloy Al-6Ca-(up to 7)Zn can be used as advanced alloy with low thermal conductivity.

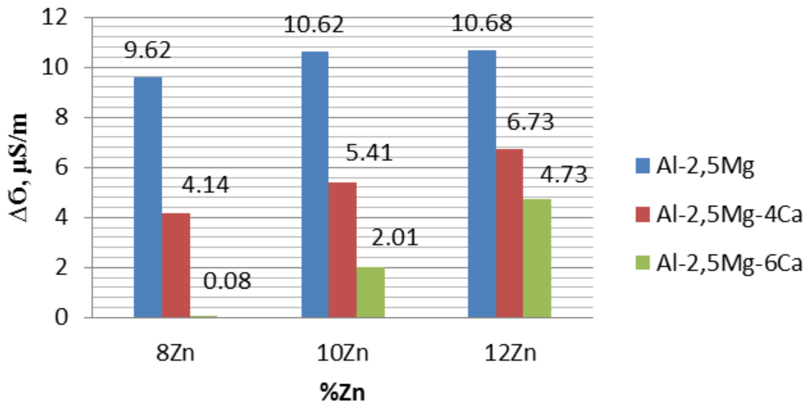


Figure 6. Growth of electric conductivity during the annealing of chilled samples depending on the calcium and zinc concentration in the alloys.

Workability of Alloys in Casting and Rolling

All studies pre-eutectic alloys possess good cast properties, they also can be hot-rolled and cold-rolled up to wrought state of over 80%. The plotted poly-thermal cross-section for 4% concentration of zinc (Figure 7a) shows that the interval of the alloys crystallization is small which results in the opportunity to make mold castings of the 'harp' type without hot tears (Figure 7b). Figure 7c shows hot-rolled and cold-rolled sheets of alloy Al-3.5Ca-2.5Mg-9Zn. Thus we demonstrated, that on the basis of the system Al-Zn-Mg-Ca one can produce advanced aluminum alloys of eutectic type with high values of hardness and probably high strength properties.

a) b) c)

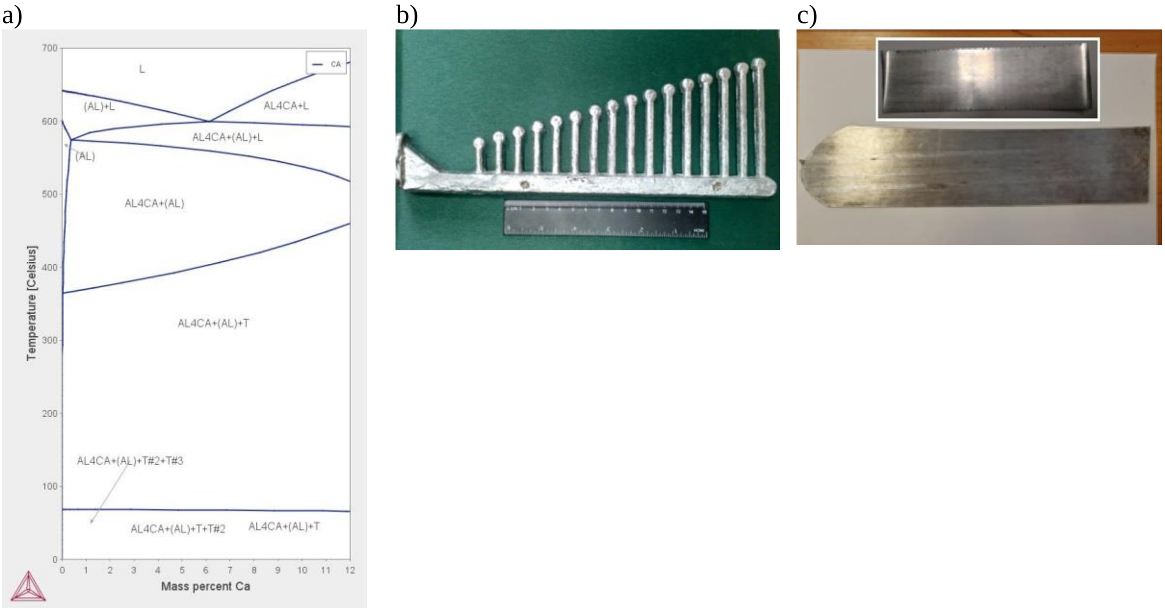


Figure 7 a) The poly-thermal cross-section for the system Al-Ca-Zn-Mg: a- under 2.5%Mg and 4Zn; b) the 'harp' type casting of alloy Al-3.5Ca-2.5Mg-9Zn; c) cold-rolled and hot-rolled sheets of alloy Al-3.5Ca-2.5Mg-9Zn.

CONCLUSIONS

1) By means of calculation (Thermo-Calc) and experimental methods (OM, SEM, EMPA) a liquidus surface of the Al-Ca-Zn-Mg system in the area rich with aluminum has constructed, borders of primary crystallization of phases (Al), $(Al,Zn)_4Ca$ and Al_3CaZn are defined.

2) Properties (hardness and the modulus of elasticity) of the phases Al_4Ca, $(Al, Zn)_4Ca$ and Al_3CaZn are investigated. These characteristics monotonously increase at the increase of Zinc content in the phase.

3) Hardness of alloys depends on the content of Zinc which is distributed between phases $(Al, Zn)_4Ca$ and (Al). The effect of hardening when processing T6 is more, than there is more (Al) and Zn in alloys, but technological and special physical properties are higher in alloys with a bigger proportion of eutectic.

4) Optimum compositions of alloys for different designation are defined: for receiving a combination of good mechanical and technological properties the composition of Al-2,5Mg-4Ca-(8-10)Zn is optimum, and alloys with the lowered heat conductivity and increased foundry properties may contain up to 6%Ca.

5) Shaped castings, hot-rolled and cold-rolled sheets were received from hypo eutectic experimental alloy Al-3,5Ca-2,5Mg-9Zn.

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