Exploration of the viscosity temperature dependences and microstructure of magnesium-based commercial alloy AZ91D with small additions of calcium

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Abstract. The technique of rotating oscillation damping of a crucible filled in with the melt under investigation was used for measurement of viscosity of the Mg-based AZ91D commercial alloy with various additions of calcium. The viscosity was measured in liquid state in temperature interval from 600 up to 840 °C. The comparative metallographic investigation of the structure of samples with calcium content of 0.0, 0.4, 0.6 and 0.8 wt.% which were crystallized just after re-melting at the temperature of 640 °C and after heating in liquid state up to 850 °C were made. It was shown that the thermal treatment of samples in liquid state is accompanied by considerable changes in the cast structure that forms after the crystallization of the samples.

1. Introduction

Alloys of the Mg-Al-Zn system and, in particular, the most popular of them AZ91 and its analogs, are widely used in modern technology, mainly owing to their high castability, good mechanical properties and corrosion resistance [1]. Their properties have been intensively studied lately, first of all in connection with their use in automotive industry as alloys for die casting [2,3]. The structure and properties of these alloys can be improved by introducing small amounts of various elements, including calcium.

It is well known that calcium reduces the tendency of Mg-Al-Zn alloys to oxidation in the process of melting, improves their tightness, thermal-treatment susceptibility, heat resistance, but at the same time the presence of more than 0.2% Ca in these alloys (here and in the subsequent discussion the concentration is given in mass percentage) results in their embrittlement [4].

The mechanism of the effect of calcium additions on the structure and properties of magnesium alloys is for the time being poorly understood. The authors [5] connect it with the limitation of the growth of the β-phase of Mg₁₇Al₁₂ under the action of the first portions of calcium and with the appearance of a new phase of Al₃Ca at a further increase of Ca contend. It seems probable to us that
additional information on the peculiarities of effect of different amounts of calcium on the structure of the AZ91D alloy might be obtained from the results of investigating the properties of the initial melts, in particular, their viscosity.

To proof this hypothesis we studied viscosity temperature dependences of liquid AZ91D alloy without any additions of Ca and with 0.3%, 0.4%, 0.6%, 0.8% and 1% wt.% Ca in the temperature interval between 600 and 840°C, in helium atmosphere. The comparative metallographic investigation of the structure of samples with calcium content of 0.0, 0.4, 0.6 and 0.8 wt.% which were crystallized after re-melting at the temperature of 640°C and after heating in liquid state up to 850°C were made also.

2. Experimental Procedure
The paper investigates the same samples as in [5]. They were prepared on the basis of the commercial alloy AZ91D containing 90.01% Mg, 9.00% Al, 0.73% Zn, 0.19% Mn, 0.058% Si, 0.0037% Cl, <0.0003% Be, 0.007% Fe, 0.0036% Cu and 0.0019% Ni, into which the required quantity of the master alloy Mg-30% Ca was introdused at 730 °C. The melting was realized in an electric resistance furnace in protective atmosphere of CO₂ – 0.5 % SF₆. After stirring for 2 min at the indicated temperature the melt was allowed to stand for 10 min and then poured into steel cylindrical moulds 30mm in diameter and 65 mm in height heated previously up to 280-300 °C.

To prevent the evaporation of magnesium from the crucible graphite crucibles placed in steel container with a screw cover were used. The crucibles were placed into the container under the stream of pure helium.

The viscosity was measured by the method of damping torsion oscillations of a crusible with a melt on the setup whose scheme is presented in [6]. The values of kinematic viscosity for a melt were calculated by the procedure of Shvidkovsky for low-viscous liquids [6]. Before every measurement the melt was allowed to stand at given temperature for not less than 12 minutes.

Metallographic investigations of the structure of samples of the base alloy and those containing 0.4, 0.6 and 0.8% Ca before and after the mentioned thermal treatment in the liquid state were made on optical microscope “Neopt-32” with a computer attachment for a quantitative phase analysis and photographing of the objects.

3. Results and Discussion
In the Figure 1 one can see the structures of the initial samples. They consist of grains of magnesium-based solid solution and intermetallic phases inside and at the boundaries of the matrix grains (figure 1a). In samples with a high content of calcium dark crystals of Mg₅Ca of rounded form appear additionally (Figure 1b).

![Figure 1a. Structure of initial sample AZ91d alloy + 0.4% Ca.](image1a)

![Figure 1b. Structure of initial sample AZ91d alloy + 0.8% Ca.](image1b)
Figure 2. Temperature dependences of kinematic viscosity of the base alloy AZ91D and samples with 0.3, 0.4, 0.6, 0.8, and 1.0% Ca obtained in the course of heating from 600 to 840 °C and subsequent cooling.
Viscosity vs temperature dependences of the samples are shown in Figure 2. Within the limits of the declared measurement error the curves $\nu(T)$ of the base alloy and that with 0.3% Ca obtained in heating and cooling coincide. In a sample with 0.4% Ca the ramification of the heating and the cooling curves manifests conspicuously in the whole investigated temperature range (viscosity hysteresis).

With a further increase in the calcium concentration the ramification of the dependences $\nu(T)$ becomes less pronounced, at high temperatures there appears their coinciding segment, and ramification point decreases to 700$^\circ$C at 0.6% Ca and disappears altogether in a sample with 0.8% Ca. With calcium content of 1% hysteresis of viscosity with a ramification point of about 775$^\circ$C is again registered distinctly.

The present paper studies the effect of superheating the alloy AZ91D and AZ91D with additions of 0.4, 0.6 and 0.8% Ca above the ramification point of temperature dependences of the viscosity on the structure of a cast metal. For each composition of alloy two samples were studied: the first one was overheated up to 850 $^\circ$C and the second was heated up to 640 $^\circ$C only.

After superheating the melts up to 850$^\circ$C, i.e. above the ramification point of $\nu(T)$ dependences of samples containing calcium one could note a further grows of grains of the base alloy and partial dissolution of the compound Mg$_{17}$Al$_{12}$. In samples containing calcium a superheat in the liquid state above the ramification point of the curves $\nu(T)$ is also accompanied by the roughening of the structure. Besides, one can note the dispersion of intermetallic phases at the boundaries of grains and a decrease in the volume fraction of eutectics. The modifying effect of calcium is also retained after a superheat, but, as in the case of samples that have not been heat treated in the liquid state an increase in content of Ca above 0.4% is not accompanied by an amplification of this effect. For AZ91D+0.6% Ca with heating the melt up to 850$^\circ$C the content of intermetallic phases has increased not slightly. For AZ91D+0.8% Ca the heating causes crushing of phases on the grain boundaries.

The authors believe that the most original result of the presented work is ramification of temperature dependences of the viscosity of Ca-containing melts, which manifests itself more or less distinctly depending on the concentration of Ca. In the base melt no viscosity hysteresis was observed. It could means that in the AZ91D melts containing Ca one can observe an irreversible rearrangement of structure while heating. The temperature of this rearrangement depends on the concentration of calcium. To confirm or to refuse this, it is necessary to make additional investigations of the binary and ternary systems which are the basis for the melt AZ91D.

### 4. Conclusion

Thus, in the process of doing the present work the authors managed to solve some serious methodical problems connected with the high volatility of magnesium and its alloys in the liquid state. As a result, well-reproduced temperature dependences of the viscosity of melts AZ91D and AZ91D with various Ca content have been obtained. Indications of the irreversible structural changes that are observed in this melts at temperatures depending on the Ca content have been discovered for the first time. It is shown that the thermal treatment of samples in the liquid state, which includes their heating to temperatures exceeding that of irreversible rearrangements, is accompanied by considerable changes in the cast structure that forms after the crystallization of the samples.

### References

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