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Characterization of magnesium alloys for semi solid processing

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1 Introduction

Within the last years several casting processes like Thixomolding, Thixocasting, New Rheo Casting, Rheo Die Casting etc. for manufacturing light metal parts in the semi-solid state were investigated. Due to the higher viscosity of a semi-solid melt mold filling can change considerably, compared to conventional die casting [1-2]. In addition effects like thixotropy and shear thinning have to be taken into account [3]. For optimization of a semi-solid casting process, and therefore the quality of the cast part, a fundamental understanding of the rheology is required.

Basic work concerning the rheology of semi-solid melts was started by Flemings and coworkers in the seventies [4]. Since then several studies were done on the alloy Sn-15Pb because of its low reactivity and melting range [5-6]. In addition measurements for various aluminium alloys were carried out [7-8]. Only few investigations on magnesium alloys have been accomplished [9-11]. The published data seem to be inconsistent which might be explained by the high susceptibility of magnesium to oxidation.

The experimental investigations showed that the viscosity of semi-solid melts strongly depends on shear rate and solid fraction. For mathematical description the simple “power-law” model invented by Ostwald and de Waele [12-13] is often used which seems to be suitable for moderate shear rates [9-10, 14-15].

$$\eta = K \cdot \dot{\gamma}^{\,n-1} \tag{1}$$

For constant fraction solid the dynamic viscosity η is correlated to the shear rate to the power of the power law exponent (n-1). The coefficient K and the power law exponent n can be determined from experiments. The power law exponent n can be interpreted as an indicator for the shear rate dependency. Newtonian Fluids, e.g. totally liquid metals, are not dependent on shear rate, the power law exponent is n=1.

For very low and very high shear rates the viscosity approaches a limit asymptotically. This sigmoidal curve was found to be approximated by more complex empirical models from Cross [16] or Carreau-Yasuda [17]

In this paper the rheological behaviour of the magnesium alloy AZ91 is discussed. Shear rate and processing temperature have been varied over a wide range. It was found that the data are in good agreement with an enhanced power-law model from Sisko [18]. An attempt to correlate the model constants with the solid fraction was carried out. Therefore special attention was paid to determine the solid phase content as a function of temperature. Besides databank calculations with the CompuTherm-Modul of the ProCast-software, basing on the

CALPHAD-Method invented by Schmid-Fetzer et al. [19], the correlation of temperature and fraction solid was determined by DSC-analyses.

2 Experimental

For examination of the correlation between temperature and solid fraction for AZ91 experimental investigations with differential scanning calorimetry (DSC) and microscopy were supplemented by databank calculations. A differential scanning calorimeter 409C from Netzsch at WTM, University of Erlangen, was used. In order to avoid reactions the magnesium sample was placed in a tantalum crucible which was covered air-tight under Argon inert gas atmosphere with a spot welder. Data analysis was made with the Netzsch software Proteus. Furthermore measurements with pure aluminium for calibrating the data correction module have been carried out.

For analysis of the microstructure a reflected-light microscope at NMF and a microprobe analyzer type JX1-8100 by Joel at WTM, University of Erlangen, was utilized. An acceleration voltage of 15 kV was used. In addition calculations with CompuTherm-module of the ProCast-software were carried out. This databank allows calculating the solid fraction in thermodynamic equilibrium.

In order to enable a correlation to the alloy used in the rheological experiments the major alloying elements (Al, Mn, Zn) of the magnesium alloy were determined by Glow Discharge Optical Emission Spectroscopy using a Jobin Yvon GD-Profiler located at NMF, with a focus spot of 4 mm. To verify the determined relationship, analyses of the solid phase content of micrographs have been carried out.

For rheological investigations, a high temperature viscometer (Searl-type) at NMF was established. The inserted rotor / crucible – setup according to DIN 53019 is shown in Figure 1 (r_a = 15 mm, r_i = 13-14 mm, L = 39 mm). The cylindrical melting furnace contains four independent heating zones which allow isothermal experiments with temperatures up to 850 °C and a measuring accuracy of less than 0.5 °C. For operation with magnesium alloys, the furnace was evacuated to a vacuum pressure below 10^{-3} mbar and subsequently flushed with Argon 5.0. After repeating this cycle three times, to establish an inert gas atmosphere extensively free from oxygen, the sample was heated up 20 °C above the melting point of the investigated alloy and then cooled down at the desired operation temperature. The steady state viscosity was calculated as the average of the viscosity between 1500 and 1800 seconds. At that time no substantial change of the viscosity was observed. More details concerning the rheological measurements can be found in [20].

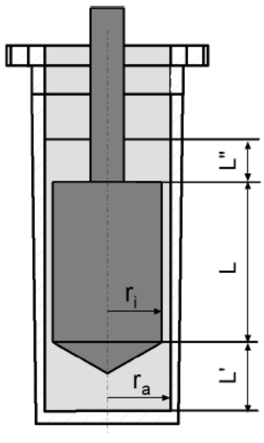

Figure 1: Rotor and crucible of the viscometer at NMF, ref. DIN 53019

3 Results and discussion

Control and determination of the solid fraction is of particular relevance for rheological investigations of semi-solid melts, especially for alloys with small solidification range, where

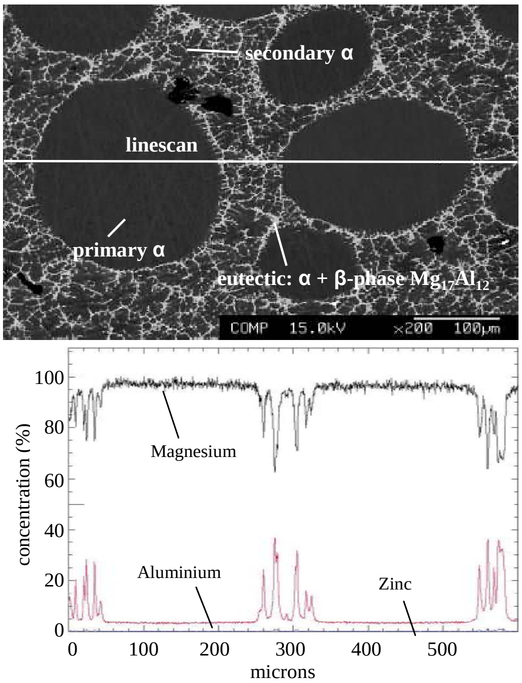

Figure 2: Microstructure of quenched semi-solid AZ91 sheared in the viscometer 400 s at 583 °C at a shear rate of 80 s^{-1} (top) and result of the microprobe linescan (bottom). The diagram shows no gradient of the main alloying elements mangesium, aluminium and zinc in primary α, indicating thermodynamic equilibrium during shearing.

small variations of the temperature can cause considerable changes in solid fraction. Depending on the process the rate of cooling or heating as well as melt flow conditions may lead to differences in microstructure. For example segregation of alloying elements in solid solution might occur, which has to be taken into account in terms of the phase calculations. In the viscometer the slurry is sheared under isothermal conditions.

Figure 2 shows the quenched microstructure of AZ91 after shearing for 400 s at 583 °C at a shear rate of 80 s^{-1} (top) and a microprobe linescan for the major elements Mg, Al and Zn (bottom). The microstructure shows globulitic primary α with a diameter of approximately 200 µm which is formed in the viscometer. It is surrounded by the residual melt solidified during quenching to fine grained secondary α and the eutectic which consists of tertiary α and the intermetallic phase $Mg_{17}Al_{12}$. While within the residual melt distinctive peaks for all elements are observed, no concentration gradient is found in the primary α-phase indicating thermodynamic equilibrium. Therefore all CompuTherm-calculations were done using lever rule.

The influence of the alloy composition on the correlation of solid fraction and temperature is demonstrated in Figure 3. Four curves calculated with CompuTherm are plotted, that represent the lower and upper limit of Al- and Zn-content specified for AZ91 (Al: 8.5 – 9.5 %; Zn: 0.45 – 0.9 %). Higher Al or Zn-contents result in a decrease of the liquidus temperature. The solid phase content at the same temperature is reduced. At a temperature of 590 °C the maximum variation is 18 %, for instance.

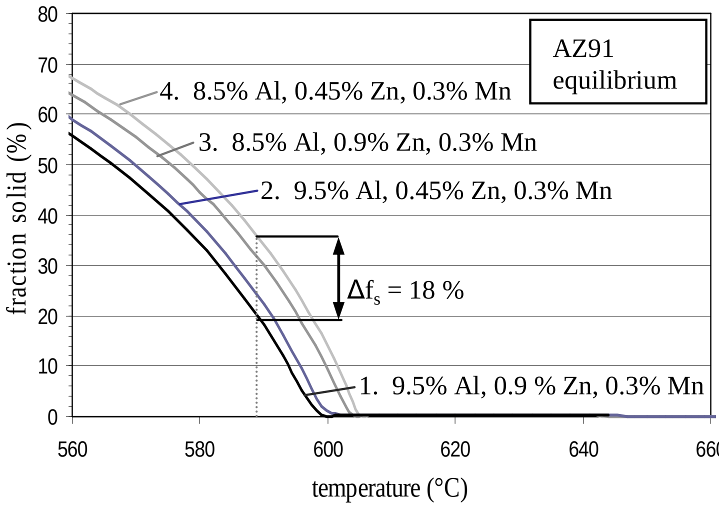

Figure 3: Characteristics of AZ91 in thermodynamic balance. The upper (1) and lower (4) limits of the alloy specification show a distinctive difference in solid fraction, e. g. at 590 °C there is a difference of 18 % in solid fraction content.

In Figure 4 different methods that seem to be applicable for determining the solid phase content as a function of temperature are compared for the alloy composition used in the rheological experiments. In addition to the CompuTherm calculations, results derived by differential scanning analysis and optical microscopy are presented. There is a difference evident between DSC-measurements and the calculations while the results of the microscopic analysis are in good agreement with the calculations. Therefore for correlation to the rheological investigations the CompuTherm calculations were used.

The viscosity measurements for AZ91 show the typical characteristics of a semi-solid metal. For constant shear rate a thixotropic behaviour becomes apparent. The flow resistance shows a distinct decrease over time, converging asymptotic to an equilibrium state, called steady state viscosity (see figure 5). This effect is clearly associated to a change of the morphology of primary α from dendritic to globulitic shape [20].

With increasing shear rate the steady state viscosity decreases. That behaviour, which is called shear thinning, is probably linked to a change of the particle's short range order. According to Bernoulli's equation the pressure near a solid boundary is higher than in the bulk flow. In semi-solid processing, e.g. during mold filling, due to this pressure gradient the particles are pushed to the middle of the filled cross section leading to the formation of a boundary layer without particles [21]. For higher shear rates the pressure gradient increases and the phenomenon becomes more distinct. As a result of the liquid boundary layer the apparent viscosity is decreased.

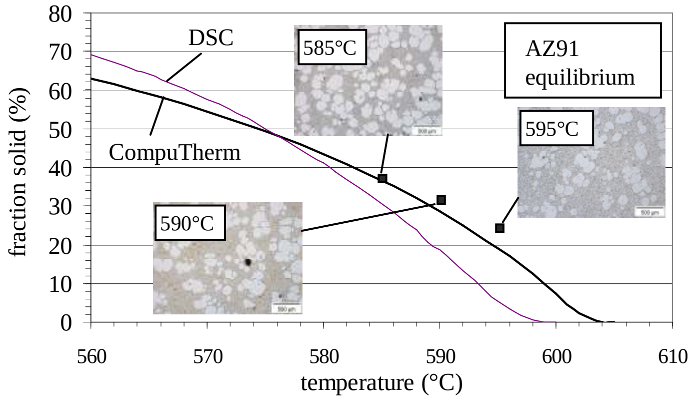

Figure 4: Determination of the solid phase content by DSC, CompuTherm calculation and micrographs for AZ91 with 8.7% Al, 0.9% Zn and 0.19% Mn.

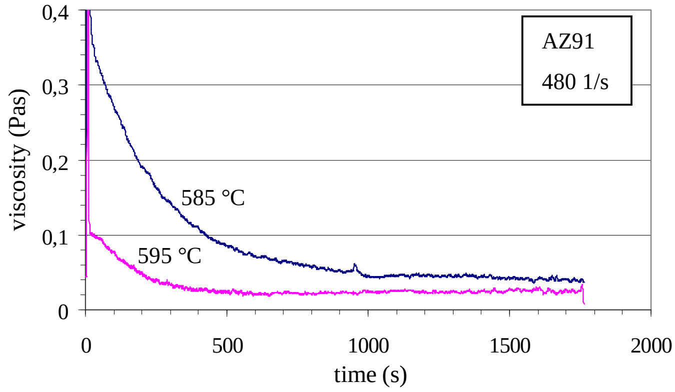

Figure 5: Thixotropic behaviour of AZ91. For constant shear rate the viscosity converges asymptotic to a steady state viscosity. Higher solid fractions lead to higher viscosities.

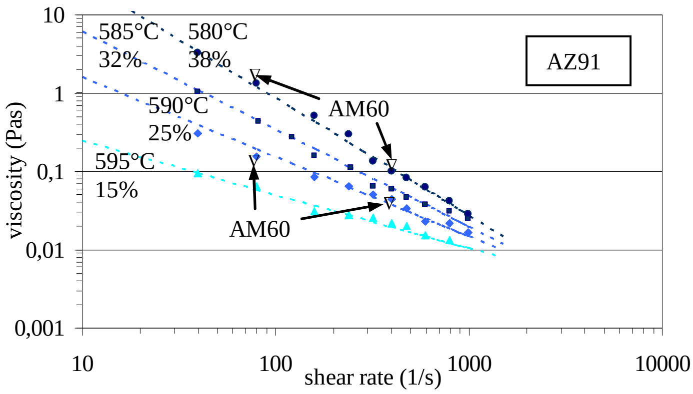

Figure 6: Shear rate dependency of the steady state viscosity of semi-solid AZ91. The power law exponent increases with decreasing solid fraction content.

In Figure 6 the steady state viscosity of AZ91 as a function of shear rate in a log-log plot representing shear thinning behaviour is shown. Solid fractions are ranging from 15 % to 38 % and shear rates are varying between 40 s^{-1} and 1000 s^{-1}. In addition some data points for AM60 are included. For comparable solid fractions the viscosity at a certain shear rate seems to be more or less identical for both alloys. The dotted lines approximate the measuring points according to the power-law model. It is obvious that the power law exponent n changes with solid fraction.

In comparison to the studies for AM50, AM60 and AZ91 published by Fan, Gosh and Van Schilt [9-10] several distinctions appear. Firstly the power-law exponent determined by Fan et al. seems to be almost constant for each alloy. However, most of their measurements were done for solid fractions higher than the maximum of 38 % in this study. It seems to be comprehensible that the power-law exponent has to converge continuously to n=1 for a Newtonian fluid when the solid fraction is reduced to zero. Secondly the viscosities for AZ91 determined by Gosh et al [9] at high shear rates for low fraction solid are almost one order of magnitude higher. However the experimental procedure of Gosh et al is not described in detail. Therefore dissimilarity of the microstructures has to be considered. In addition in [9] higher viscosities for AZ91 and AM50 are mentioned than in [10] for AM50 and AM60.

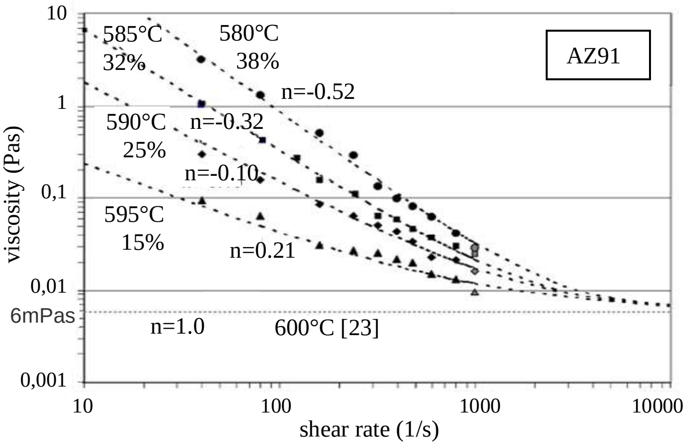

Figure 7: Shear rate dependency of semi-solid AZ91. The critical limit of Newtonian behaviour (n=1) is represented by the viscosity of totally liquid AZ91 according to Park et al [23]. The power law exponent increases with decreasing fraction solid.

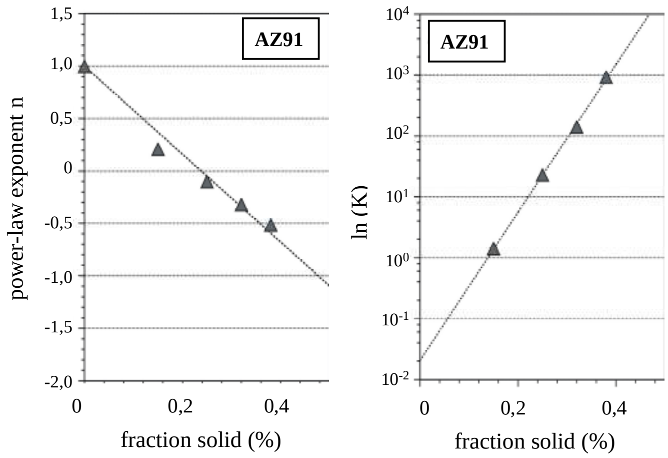

Figure 8: The power law exponent n increases with decreasing fraction solid until Newtonian behaviour (n=1) is reached (left) while the logarithm of constant K is directly proportional to the fraction solid.

For high shear rates > 1000 s^{-1} approximation by the power-law model evidently is not reasonable, because the approximation fits seem to cross. Furthermore the viscosity for the totally liquid alloy is limiting. Park et al [23] published data for AZ91. The value for 600 °C is drawn as a horizontal line in Figure 7 representing the critical limiting value η_∞. For approximating the data points a modified power law model by Sisko [18] was used:

$$\eta = \eta_\infty + K \cdot \dot{\gamma}^{n-1} \tag{2}$$

For η_∞ the viscosity of liquid AZ91 [23] was set. The model fits the data points for the entire range of shear rates quite well. The power-law exponent increases when the solid fraction decreases. For high solid fractions and low shear the models of Sisko and Ostwald-de Waele are almost equivalent. At high shear rates the additional term effects asymptotic behaviour.

In Figure 8 (left) the power-law exponent n is plotted as a function of solid phase content. It seems to depend almost linear on the solid phase content in the considered measuring range:

$$n = 1 - c_1 \cdot f_S \tag{3}$$

The constant K is an exponential function of the solid fraction, which is presented in Figure 8 (right):

$$\ln(K) = \ln(K_0) + c_2 \cdot f_S \tag{4}$$

4 Conclusions

The solid fraction content f_s has significant impact in semi-solid processing. It was shown that databank calculation using the lever rule is an appropriate method for correlating f_s to the processing temperature. The rheological behaviour of the magnesium alloy AZ91 has been determined over a wide range of the solid fraction and shear rate.

Thixotropic behaviour and shear thinning were observed. For approximation of the data an enhanced power-law model by Sisko was successfully used. It was verified that the constant K and the power-law exponent n vary with the solid phase content. For both a mathematic correlation has been proposed. Moreover it was shown that for high shear rates the viscosity converges to the value for the totally liquid alloy.

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