RHEOLOGICAL BEHAVIOR OF ZA27 ALLOY SEMI-SOLID SLURRIES AND Al_2O_3 PARTICULATE / ZA27 COMPOSITE SLURRIES

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ABSTRACT
The rheology of Al_2O_3 particulate/ZA27 composite slurries has been investigated and compared with that of the matrix ZA27 alloy. The influence of processing variables on the rheological behavior of semi-solid mixtures (SSMs) was examined. The mixing power change of SSMs was determined by the "electric method" in the temperature range from 479 to 440˚C, at constant cooling rate. Mixing of ZA27 alloy SSM was carried out using cylindrical stirrer and paddle stirrer, while SSMs of composites were mixed using paddle stirrer only. On the basis of experimental measurements the values of the most important rheological parameters (apparent viscosity and shear rate) were calculated. It was noticed that apparent viscosity of SSMs of composites containing small Al_2O_3 particles is higher comparing to that of composites with large Al_2O_3 particles.

KEYWORDS**:** ZA27 alloy, Semi-solid mixtures, Particulate composites, Rheological characteristics, **"**Electric method**"**

1. INTRODUCTION

A zinc alloy containing 25 to 27 wt.% Al, 2 to 3 wt.% Cu and about 0,02 wt % Mg is well known as the ZA 27 alloy. This alloy has broad commercial use, from small parts obtained by pressure die casting to large sliding bearings produced by sand casting. Broadening of the alloy application field is the result of favorable combination of its mechanical, chemical (e.g high corrosion resistance) and technological characteristics (good castability, high wear resistance, machinability).

The main shortcomings of this alloy are its porosity /1,2/ and generally known fact that mechanical characteristics are getting worse at higher temperatures (>70˚C). This caused the necessity of the alloy processing in the semi-solid state, e.g. by the rheo-casting process, in order to get castings with significantly lower porosity. Using the compocasting process that includes addition of strengthening ceramic particles (Al_2O_3, SiC etc.) into semi solid mixture (SSM) of base ZA27 alloy, it is possible to obtain composites of low porosity. These composites preserve the favorable mechanical characteristics at higher temperatures /3/.

It is usual that rheological investigations accompany the application of a semi-solid processing method. There are a few papers relating to the rheology of ZA27 alloy semi-solid mixtures /4/, while there are practically no published articles concerning the rheological investigations of ZA27 based composites. This is in contrast to numerous published papers referring the rheological investigations of aluminum alloys, as well as aluminum alloy based composites /5-8/.

Viscosimeters have been usually used in testing SSMs rheological characteristics. The SSMs are exposed to shearing stress in extremely narrow gaps between static and rotating parts of the viscosimeter /4-6/. The mixing is carried out at a nearly constant shear stress, with the possibility to control values of shear rate. Thus, the calculation of rheological parameters can be performed with great accuracy.

In order to get composites (by compocasting process) with favorable distribution of strenghtening particles in the base alloy, it is necessary to perform additional mixing after particles infiltration. During this additional mixing the shear stress stability cannot be achieved, because the values of shear stress decrease moving from the stirrer to the walls of the crucible. The shear stress distribution is dependent on processing parameters.

A group of Japanese authors has investigated rheological characteristics of hypereutectic Al-Si alloy in induction vacuum furnace, where a distance from the stirrer to the walls of crucible was significantly larger than in viscosimeters with gaps /8/.

This more realistic approach has been applied in this work as well, but the detection method used to monitor changes during mixing was different. The so called "method of measuring input power for commutator motor" /9/ ("electric method“ in the further text) was performed in this work as the basis for calculation of rheological characteristics.

The main goal of this work was to establish the basic rheological characteristics of ZA27 alloy and its SSMs composites in real mixing conditions.

2. EXPERIMENTAL DETAILS

2.1 Test specimens, apparatus and method

The specimens were made of rheo-castings of ZA27 alloy, as well as of its composites (produced by compocasting process) with Al_2O_3 particles as a strengthener. The composites were obtained by addition of 3, 8 and 16 wt.% Al_2O_3 (250 μm particles size) and 3 wt.% Al_2O_3 (12 μm particles size) into SSM of base ZA27 alloy**.**

Rheological investigations, rheo-casting and compocasting process were performed using apparatus shematically shown in Figure 1. The apparatus consists of three sections: for process-

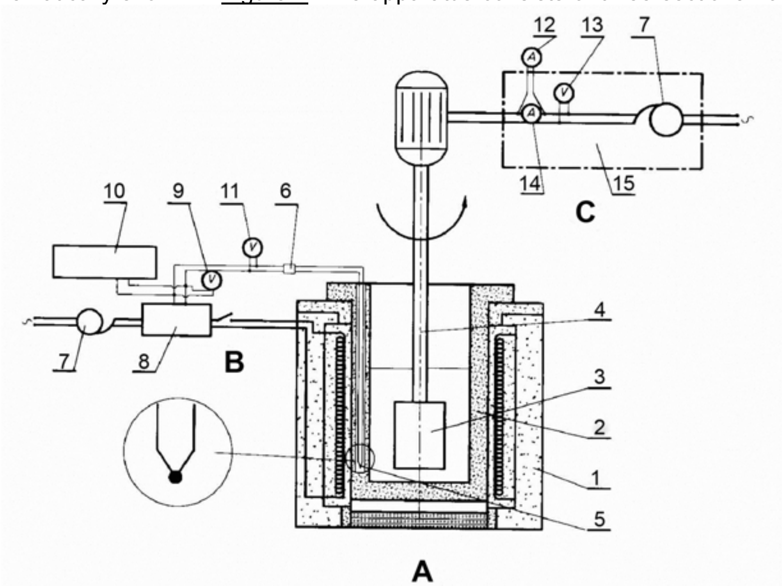

Figure 1: Schematical view of apparatus for rheological investigations. A. Process section**;** B. Control and regulation temperature section; C. section for measuring and control of electric parameters, 1. Electro resistance furnace, 2. Alumina crucible, 3. Stirrer, 4. Shaft, 5. Thermocouple.

ing (A), for temperature measuring, control and regulation (B) and for measuring and control of the stirrer electric parameters (C).

Processing part of the apparatus (A) consists of the laboratory electro resistance furnace of 2,5 kW power and a stirrer. The crucible for rheological investigationis (d = 0,075 m) was made of Al_2O_3, with a vertical hole (like a tube) placed in the wall of the crucible, containing thermocouple for continuous measuring of temperature (Figure 1) /5/. The laboratory stirrer (6) was connected to a monophase electric motor with 250 W maximal power, at maximal rotation number of 2000 rpm, for the 220 V voltage. The stirrer was equipped with a built-in potentiometer with manual selection of rotating frequency. A cylinder and a plate were used as the active part of the stirrer**.** The cylinder (d=0,04 m) was made of Al_2O_3, while the steel plate (0,04 x 0,002 x 0,100 m) was coated with an Al_2O_3 layer. A universal measuring device (12) (″Keithly 177 Microvolt DMM″) with digital display was used for precise measurements of current intensity changes during mixing process. The measuring range was 0 to 2000 mA.

A variation of "electric method” has been applied for monitoring the mixing power changes of ZA27 alloy semi-solid slurries. As a matter of fact, the changes of total electric current intensity during mixing at stabilized**,** i.e. at constant voltage have been measured. The electric method is a comparative one. Namely, the value of actual electric current intensity for SSM mixing is obtained by subtraction of the measured value of electric current intensity (drawn from the electric network by electromotor of stirrer, at any temperature in the working range) from the value of electric current intensity measured when the stirrer rotates in the air. The obtained values of electric current intensity for mixing can be used for rheological calculations.

2.2 Experimental procedure

Mixing of ZA27 alloy SSM, as well as mixing of SSMs of composites (with Al_2O_3 particles) has been performed. Mixing of ZA27 alloy SSM was carried out using both cylindrical and paddle stirrers, while SSMs of composites were mixed using the paddle stirrer only. The mixing was performed in a laminar flow regime at 450 rpm.

The active part of stirrer was immersed into the ZA27 alloy SSM, as well as into the SSMs of composites at 485°C. The rotation of stirrer started at a lower frequency than selected. The increase of rotation number was performed gradually. The selected rotation frequency of 450 rpm was achieved after cooling the semi-solid mixture at 479°C, that was the starting temperature of controlled mixing process. The change of electric current intensity during mixing at spontaneous cooling (5°C/min) has been measured at every 3°C of lowering temperature, in the temperature range from 479 to 440°C. Because of current value variations near the selected temperature, each value of electric current intensity was calculated as an average of 7 to 10 measured values, in mentioned temperature range.

3. EXPERIMENTAL RESULTS

3.1 Calculation of rheological parameters

The change of solid fraction with temperature decrease in the range from 479 to 440°C is presented in Figure 2. The dependence is obtained on the basis of Zn-Al equilibrium diagram /2/ using the rule of lever.

Using the experimental results obtained in this work by the "electric method" and transforming the relation for apparent viscosity calculation /8/, it was possible to connect the changes of apparent viscosity of semi-solid slurries and the changes of electric current intensity, during mixing in the temperature range from 479 to 440ºC:

$$\eta = \frac{\Delta M \cdot (1 - k)^2}{4 \cdot \pi \cdot r^2 \cdot L \cdot \omega} \qquad (1)$$

The meaning of symbols in equations (1) to (3) is given in Appendix 1.

Replacing the change of rotation momentum ΔM in previous equation with electric parameters (voltage, electric current), the expression for apparent viscosity calculation is obtained:

$$\eta = \frac{U \cdot \Delta I \cdot \cos\varphi \cdot \left(1 - k^2\right)}{4 \cdot \pi \cdot n^2 \cdot d^2 \cdot L} \qquad (2)$$

Since the voltage from the network was constant (220 W) and geometric parameters during mixing were held constant, it was possible to express the apparent viscosity as a function of the current intensity change:

$$\eta = f(\Delta I) = 6{,}35\ \frac{\Delta I}{L} \qquad (3)$$

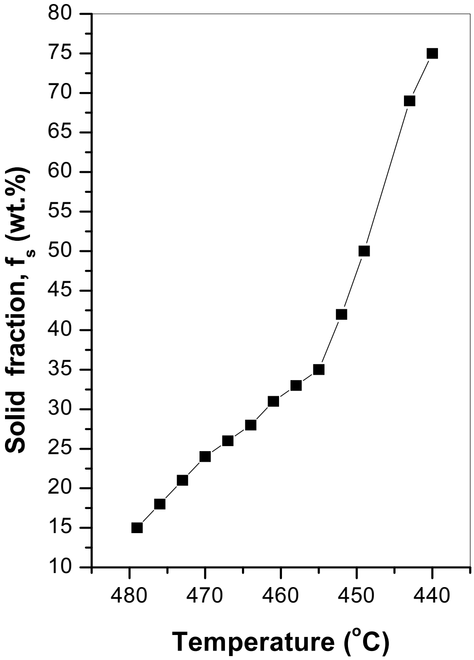

Figure 2: Solid fraction-temperature dependence of ZA27 alloy during isothermal solidification.

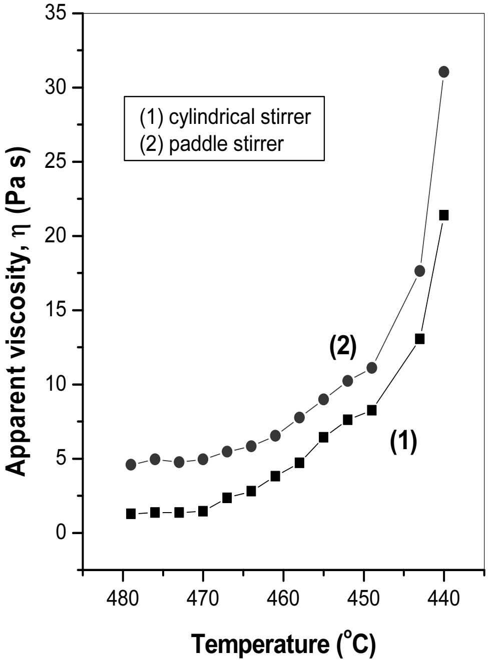

Figure 3: Apparent viscosity-temperature dependence of ZA27 alloy for different stirrer type. Shear rate 132 s^{-1}.

The values of current intensity change ΔI (necessary for the calculation of apparent viscosity according to equation 3) were determined on the basis of the experimental values of electric current intensity that were measured during mixing of semi-solid slurries. The values of electric current intensity measured at a stirrer rotation in air were subtracted from these experimental values, and thus the values of ΔI were obtained.

The changes of apparent viscosity as a function of temperature during cooling from 479 to 440ºC are presented in Figure 3, for the SSM of ZA27 alloy. The curves were obtained using the cylindrical as well as the paddle stirrer, at 450 rpm, i.e. at shear rate of 132 s^{-1}. In both cases, the value of apparent viscosity increases when temperature decreases, i.e. with growth of solid fraction in the semi-solid mixture. The change of apparent viscosity values are visible at temperatures below 470ºC, when solid fraction exceeds 24 wt.%.

Comparing the values of apparent viscosity depending on the stirrer shape (other experimental conditions were kept unchanged) it can be seen that calculated values of apparent viscosity obtained for the paddle stirrer are higher than those for the cylindrical stirrer, in the whole area of working remperatures This is in agreement with the fact that calculated values of shear stress (Appendix 1) are also higher for the paddle stirrer, in the whole working range.

The results of rheological investigations of ZA27 alloy SSMs and SSMs of composites are presented in Figure 4 and Figure 5. The values of apparent viscosity for SSMs of composites are lower than those for the base ZA27 alloy SSMs, in the whole temperature range. This fact is extremely important for the further processing of composites.

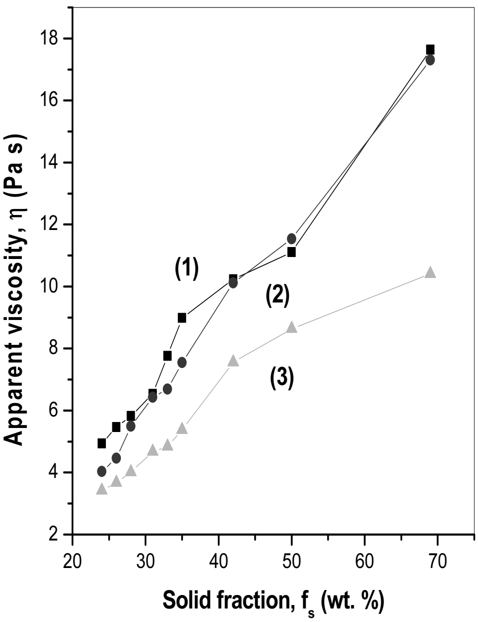

Figure 4: Apparent viscosity – solid fraction dependence for different reinforcing particle size. Shear rate 132 s^{-1}.Legend: 1. ZA27, 2. ZA27+3 wt.% Al_2O_3, 12 µm, 3. ZA27+3 wt.% Al_2O_3, 250 µm.

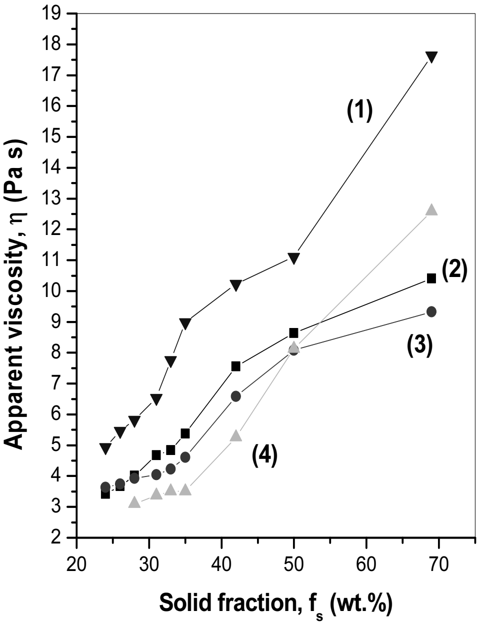

Figure 5: Apparent viscosity – solid fraction dependence for different mass fraction of reinforcing particles (same size). Shear rate 132 s^{-1}. Legend: 1. ZA27, 2. ZA27+3 wt.% Al_2O_3, 250 µm, 3. ZA27+8 wt.% Al_2O_3, 250 µm, 4. ZA27+16 wt.% Al_2O_3, 250 µm.

The influence of ceramic particles size on the values of apparent viscosity for SSMs of composites was determined and the results are shown in Figure 4. It can be seen that the values of apparent viscosity of composites SSMs decrease as the particles size increases.

The influence of strengthening particles mass fraction on apparent viscosity values is shown in Figure 5, for the SSMs of composites containing 3, 8 and 16 wt.% Al_2O_3 particles, respectively. It can be noticed that until 50 wt.% of solid fraction, values of apparent viscosity decrease as the weight fraction of strengthening particles increases.

3.2 Metallography

The results of metallographic investigations of ZA27 alloy and its composites before rheological examinations are presented in Figures 6 - 9. The microstructure of gravity die cast ZA27 alloy (in preheated steel mold) is shown in Figure 6a and b. The structure is typically dendritic (Figure

6a). The complex shape of dendrites is the consequence of the peritectic transformation during solidification of the semi-solid mixture. Dendites consist of the dendritic core (α phase rich in aluminum) and a periphery (a mixture of α phase and hexagonal η phase rich in zinc). The hexagonal η phase is located into interdendritic regions. These microconstituents are more easily visible in Figure 6b (SEM) at higher magnification.

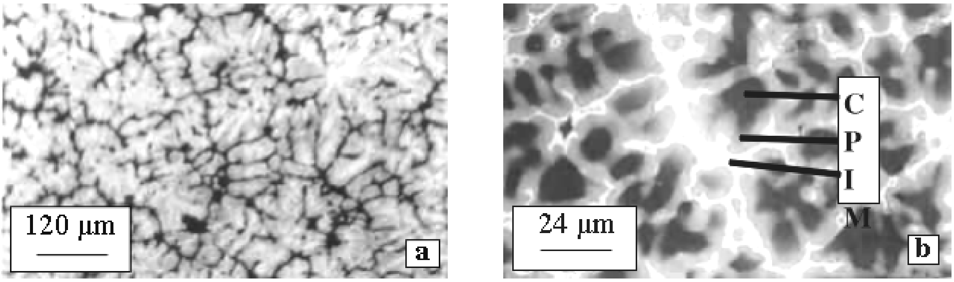

Figure 6: ZA27, as cast, a) OM, b) SEM, C-dendrite core, P-dendrite periphery, I-interdendritic phase.

Transformation of the dendritic structure into a non-dendritic took place during the rheocasting process. The microstructure consists of coarse, elliptic primary particles. The resulting microstructure of peritectic transformation ($L+\alpha=\beta$; L is the liquid phase) with later eutectoid decomposition ($\beta=\alpha+\eta$ at 275ºC) may be seen at higher magnification (Figure 7b) in the form of dark strips around gray primary particles. Transformation of the dendritic to non-dendritic structure also occurred during the compocasting process (Figure 8 a and b).

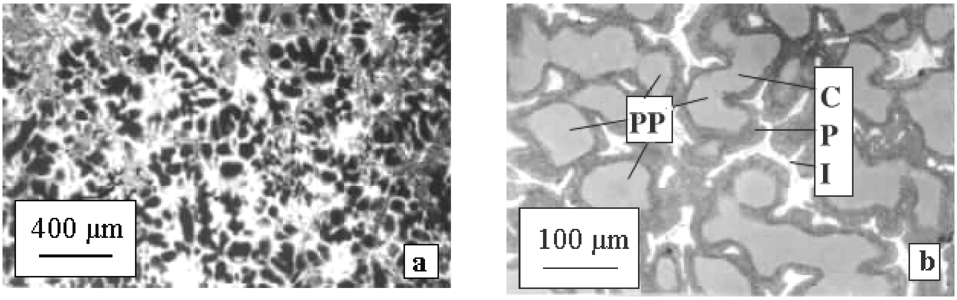

Figure 7: ZA27, rheo-cast, SEM. C-dendrite core, P-dendrite periphery, I-interdendritic phase, PP– primary particles.

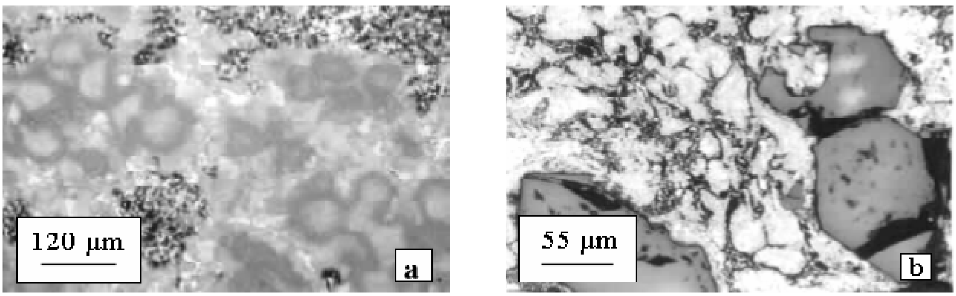

Figure 8: Composites: a) ZA27 + 3 wt.% Al_2O_3, 12 µm, SEM, b) ZA27 + 3 wt.% Al_2O_3, 250 µm, OM.

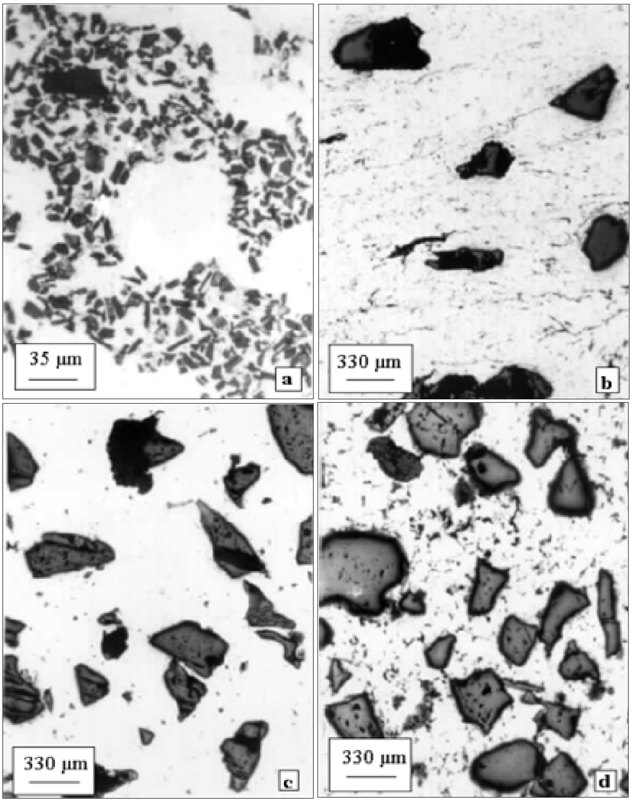

Figure 9: Composites (OM): a) ZA27 + 3 wt.% Al_2O_3, 12 µm, b) ZA27 + 3 wt.% Al_2O_3, 250 µm, c) ZA27+8 wt.% Al_2O_3, 250 µm, d) ZA27+16 wt.% Al_2O_3, 250 µm.

The microstructures of the obtained Al_2O_3/ZA27 composites are shown in Figure 9 (a - d). It can be noticed that small reinforcing particles show a tendency to agglomerate (Figure 9a), whereas large particles do not show the tendency to agglomeration (Figure 9b, c and d).

4. DISCUSSION

The "electric method" enables providing of experimental data for approximate calculation of the most important rheological parameters. Using this method it is possible to determine the consumed mixing power, necessary to overcome the fluid resistance during stirrer rotation. According to /7/, it is difficult to get precise values of rheological parameters by this method. However, the method can be very useful for the rheological behavior evaluation of SSMs of composites. The reproducibility of results in the series of experiments has been achieved in this work during rheological investigations of composites semi-solid slurries.

During rheological investigations of base ZA27 alloy in the temperature range from 479 to 440ºC, it was noticed that the values of apparent viscosities differ depending on the stirrer type. The calculated values of apparent viscosities are higher in the case of paddle stirrer comparing to those obtained by using the cylindrical stirrer. The possible explanation could be as follows: during mixing cylindrical stirrer practically produces only shearing of adjacent layers of fluid, whereas paddle stirrer causes additional fluid flow. In order to keep the constant value of selected rotation frequency, the electric current of higher intensity must be drawn from the electric network, and consequently the mixing power increases.

The calculated values of apparent viscosities obtained in this work (in the case of cylindrical stirrer) are in agreement with the values reported by Lehuy and coworkers /3/ (Figure 10), who used the Brookfield viscosimeter. For the similar values of shear rate ($132 s^{-1}$ in this work and $125 s^{-1}$ in Lehuy's) the agreement is very good in the range of low and medium viscosities (from 24 to 30 wt.% solid fraction). When the solid fraction exceeds 30 wt.%, a certain difference in shear rate can be noticed, being more marked for another type of stirrer.

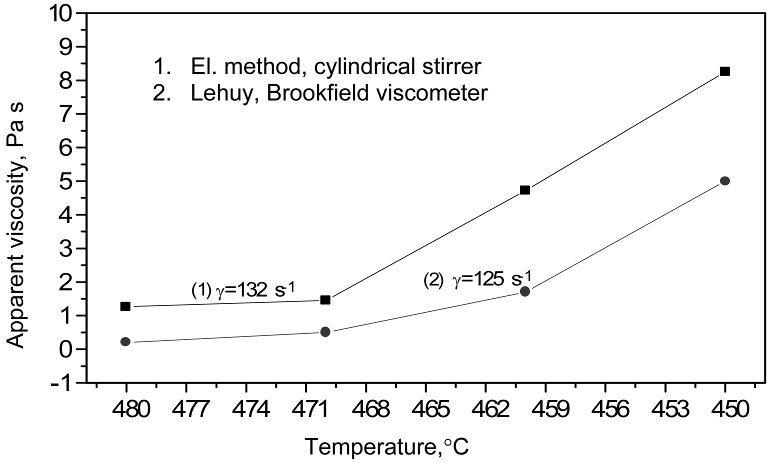

Figure 10: Comparison between Lehuy′s results and the results obtained in this work, at similar shear rate value.

The experimental results presented in Figures 3 - 5 clearly show the effect of stirrer type on the rheological characteristics of base ZA27 alloy SSM, as well as the influence of particles size and particles weight fraction on the rheological characteristics of SSMs of composites. The observed lower viscosity values in the case of base ZA27 alloy SSMs comparing to viscosity values of SSMs of composites has been noticed earlier /6/. The suggested explanation emphasizes the importance of strenghtening particles interaction with primary particles of α phase originating during soldification process. Because of particles collisions the agglomeration is prevented, as well as internal friction, and consequently the viscosity of semi–solid mixture is lower. This approach is confirmed in this work by the results of metallographic investigations.

Typical structure of as cast ZA27 alloy, presented in Figure 6 (a and b), is obtained by gravity die casting. During rheocasting process, the dendritic structure has been transformed into a structure in Figure 7 (a and b). At mixing conditions applied in this work, the coarse primary elliptic particles of α phase have appeared, that is in agreement with /4/ and fits into the scheme of structure transformation influenced by shear stress /10/. The same coarse-grained structure has developed in the composites (Figure 8a and b). These results strongly suggest the necessity of further experimental work in order to find out the appropriate mixing parameters at higher shear rates.

The small size (12 μm) strengthening Al_2O_3 particles (Figure 9a) incline to agglomeration because of their mutual affinity. It can be assumed that their motion during mixing is not individual but is in the form of clusters. This means that their influence on deagglomeration of coarse primary particles of base alloy is smaller than that of large reinforcing particles (250 μm Al_2O_3).

These large Al_2O_3 particles behave as independent particles (Figure 9b-d) because of their lower affinity to mutual agglomeration.

From the diagrams shown in Figure 4 it can be seen that differences between apparent viscosity values for ZA27 alloy SSM and the SSM of composite (3 wt.% Al_2O_3, 12 μm) are significantly smaller than those for semi-solid mixture of ZA27 alloy and the composite with larger Al_2O_3 particles (3 wt.% Al_2O_3, 250 μm). In accordance with the assumption previously stated the number of interactions between primary particles of base alloy and reinforcing particles increases when the weight fraction of large particles (250 μm) increases. Thus, further reducing of apparent viscosity can be observed, until the end of viscosity area with average viscosity values (about 50 wt.% solid fraction). Due to the process of SSM cooling and large weight fraction of added particles, the medium becomes extremely dense after reaching this area. The mixing process takes place with difficulty and consequently the interactions between primary particles of base alloy and reinforcing particles are termodinamically prevented to a great extent. As a result the apparent viscosity increases as it was shown in Figure 5 for the composite containing 16 wt.% Al_2O_3 (particle size - 250 μm).

5. CONCLUSIONS

1. The electric method enables calculation of basic rheological parameters with the significant level of accuracy. This method can be also applied to monitor the mixing process after infiltration of strenghtening particles during compocasting process.
2. The infiltration of Al_2O_3 particles into the semi-solid mixture of ZA27 alloy causes the decrease of apparent viscosity values. Larger reinforcing particles demonstrate more significant effect in lowering the viscosity.
3. The apparent viscosity of SSMs of composites decreases as the weight fraction of strengthening particles increases.
4. Applying rheo-casting and compocasting process and in order to achieve the fine-grained microstructure, as well as to accomplish the favorable distribution of reinforcing particles (in the case of composites), it is necessary to perform further investigations at higher shear rates, i.e. using more intensive mixing.

6. APPENDIX

Calculations and symbols of rheological parameters

a. Power of mixing and rotation momentum of the mixer

$$P = U \cdot I \cdot cos\varphi$$
$$\Delta P = U \cdot \Delta I \cdot cos\varphi$$

$$M = \frac{P}{\omega},$$
$$\omega = 2 \cdot \pi \cdot n$$
$$\Delta M = \frac{\Delta P}{\omega}$$

P-power (W), M-momentum (Nm), U-voltage (V), cosφ-power parameter, I-electric current intensity (A), ω-angular velocity of stirrer (s^{-2}), n-mixer frequency (s^{-1}), ΔI-change of current during mixing (A), ΔM-change of rotation momentum during mixing (Nm).

b. Apparent viscosity

From $\eta = \frac{M \cdot (1-k^2)}{4 \cdot \pi \cdot r^{2\cdot} \cdot L \cdot \omega}$ $\quad \eta = \frac{\Delta M \cdot (1-k^2)}{4 \cdot \pi \cdot r^{2\cdot} \cdot L \cdot \omega}$ $\quad \eta = \frac{U \cdot \Delta I \cdot cos\varphi \cdot (1-k^2)}{4 \cdot \pi \cdot n^2 \cdot d^{2\cdot} \cdot L}$

L- length of stirrer immersed in the SSM (m), ρ-density of semi solid medium (kg/m^3).
r – radius of stirrer (m).

c. Shear stress, shear rate

From $\eta = \dfrac{M \cdot (1-k^2)}{4 \cdot \pi \cdot r^{2} \cdot L \cdot \omega}$

$$\eta = \frac{F \cdot (1-k^2)}{2 \cdot A \cdot \omega}$$

$$\tau = \eta \cdot \frac{2 \cdot \omega}{1-k^2} \qquad \gamma = \frac{4 \cdot \pi \cdot n}{1-k^2}$$

A- surface of contact stirrer-medium (m^2)
τ- shear stress (Pa)
γ- shear rate (s^{-1})

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