Association of Metallurgical Engineers of Serbia
AMES

Scientific paper
UDC: 669.55'71.018.9

COMPARISON OF RHEOLOGICAL BEHAVIOR BETWEEN SEMI-SOLID MIXTURES OF ZA27 ALLOY AND ZA27-Al_2O_3 COMPOSITES

Biljana Bobić[1], Miroslav Babić[2], Slobodan Mitrović[2], Milan T. Jovanović[3*], Ilija Bobić[3]

[1]Research & Development Center IHIS Techno-experts, Belgrade, Serbia
[2]Faculty of Mechanical Engineering, Kragujevac, Serbia
[3]Institute of Nuclear Sciences "Vinča", Belgrade, Serbia

Received 14.07.2009
Accepted 17.09.2009.

Abstract

The rheology of semi-solid mixtures (SSMs) of ZA27 composite strengthened by Al_2O_3 particles with different size and weight fraction has been investigated and compared to that of the matrix ZA27 alloy. The influence of processing variables on the rheological behavior of 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 and paddle stirrers, while SSMs of composites were mixed using paddle stirrer only. On the basis of experimental measurements applying "electrictric method" the values of apparent viscosity were calculated. The values of apparent viscosity for SSMs of composites are lower than those for the matrix ZA27 alloy SSM in the whole range of examined temperatures. 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.

Key words: ZA27 alloy, semi-solid mixtures, particles-strengthened composites, rheological behavior, "electric method"

Introduction

Zinc alloy containing 25 to 27 wt.% Al, 2 to 3 wt.% Cu and about 0,02 wt % Mg is well known as the ZA27 alloy. This alloy has a 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

* Corresponding author: Milan T. Jovanović miljov@vin.bg.ac.rs

of mechanical, chemical (e.g. high corrosion resistance) and technological characteristics (good castability, high wear resistance, machinability).

The main shortcomings of this alloy are porosity [1,2] and generally known fact that mechanical characteristics are deteriorating at higher temperatures (>70˚C). This caused the necessity of the alloy processing in the semi-solid state, e.g. by the thixocasting process, in order to obtain castings with significantly lower porosity. Using the compocasting process that includes addition of strengthening ceramic particles (Al_2O_3, SiC, ZrO_2, TiC) into a semi-solid mixture (SSM) of the matrix 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 SSMs [4], whereas there are 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 rheological characteristics of SSMs. The SSMs are exposed to shear 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 and according to this fact it is possible to control values of shear rate. Thus, the calculation of rheological parameters can be performed with a relatively great accuracy.

In order to obtain composites (by compocasting process) with favorable distribution of strengthening particles in the matrix alloy, it is necessary to perform additional mixing after particles infiltration. During mixing the shear stress stability cannot be achieved because the values of shear stress decrease moving from the stirrer to the wall 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 wall 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 than previously described. The main goal of this paper was to establish the rheological behavior close to real mixing conditions of SSM of ZA27 alloy and to compare them with those of ZA27 composites strengthened by different size and weight fraction of Al_2O_3 particles. 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 evaluation of rheological characteristics.

Experimental

Materials and apparatus

Samples used in this investigations were prepared from thixocastings 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 wt.% Al_2O_3 (12 μm particles size) and 3, 8 and 16 wt.% Al_2O_3 (250 μm particles size) into SSM of matrix ZA27 alloy.

Rheological investigations, thixocasting and compocasting process were performed using the apparatus schematically shown in Fig. 1. The apparatus consists of three sections: for processing (A), for temperature measuring, control and regulation (B) and for measuring and control of the stirrer electric parameters (C).

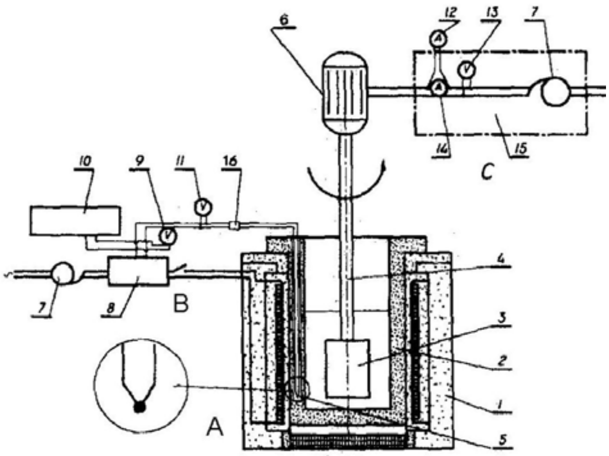

Fig. 1. Schematic view of apparatus for rheological investigations. A. Process section; B. Control and regulation temperature section; C. section for measuring and control of electric parameters, 1. Electro resistance furnace, 2. Alumina crucible, 3. Stirrer, 4. Shaft, 5. Thermocouple.

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 temperature measurement (Figure 1) (5). The laboratory designed stirrer (6) was connected to a monophase electric motor with 250 W maximum power at the maximum rotation number of 2000 rpm and at 220 V. The stirrer was equipped with a built-in potentiometer with manual selection of rotating frequency. A cylinder and a paddle were used as the active part of the stirrer. The cylinder (d=0,04 m) was made of Al_2O_3, while the steel paddle (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 to monitor the changes of mixing power of ZA27 alloy SSMs. In fact, changes of total electric current intensity during mixing at stabilized and constant voltage have been measured.

Applied method

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 was performed gradually. The selected rotation frequency of 450 rpm was achieved when the SSM was cooled at 479°C, it was the starting temperature of controlled mixing process. In the temperature range from 479 to 440°C the change of electric current intensity during mixing at spontaneous cooling (5°C/min) has been measured at every 3°C of lowering temperature. Because of current variations at selected temperature each value of electric current intensity was calculated as an average of 7 to 10 measured values.

Parameters of thixocasting were as follows:

- mixing at 461ºC for 10 min at 450 rpm
- pouring into steel mold preheated at 300 ºC
- pressing at 230 ºC under the pressure of 150 MPa.

Parameters of compocasting were as follows:

- mixing between 461 do 485º C (depending on the weight fraction of strengthener) for 10 min at 450 rpm
- pouring into steel mold preheated at 300 ºC
- pressing at 230 ºC under the pressure of 250 MPa.

Dimensions of pressed castings were: 36 mm diameter and 120 mm height. The aim of pressing was to reduce porosity that cannot be avoided during processes of thixocasting and compocasting.

Microstructural investigations

Microstructural characterization was carried out on either polished or etched samples (etching was performed in 9% nital, i.e. a mixture of 9% nitric acid and alcohol). After usual metallographic preparation microstructure was examined by optical (OM) „Zeiss Axiovert“ microscope and scanning electron microscope (SEM) “Philips XL30“.

Results

Calculation of rheological parameters

The change of solid fraction with temperature in the range from 479 to 440°C is presented in Fig. 2. The dependence is obtained on the basis of Zn-Al equilibrium diagram [2] using the rule of lever. The change of solid fraction increases with decrease of solidification temperature and this increase becomes steep at 455^{o}C.

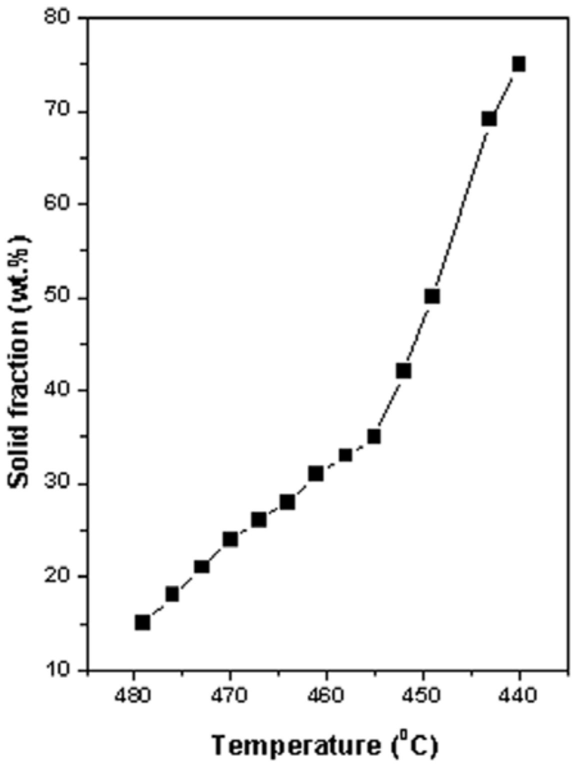

Fig. 2. Solid fraction – temperature dependence of ZA27 alloy during isothermal solidification.

To calculate the apparent viscosity , η, the equation (1) was used:

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

where: ΔM - change of rotation momentum during mixing (Nm), k=0.53, i.e. the relationship between diameters of the mixer and the crucible where mixing is performed, r – radius of stirrer (m), L - length of stirrer immersed in the SSM (m), ω - angular velocity of stirrer (s^{-2}).

Change of rotation momentum ΔM with electric parameters (voltage, electric current) originates from:

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

where: P - power (W), U - voltage (V), cosφ - power parameter, I - electric current intensity (A), then:

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

where: ΔP - change of power (W), Δl - change of current during mixing of SSM (A).

Since:

$M = \frac{P}{\omega}$, then ΔM becomes:

$$\Delta M = \frac{\Delta P}{\omega}$$

where: $\omega = 2 \cdot \pi \cdot n$; n - stirrer frequency (s^{-1}).

Replacing ΔM into equation (1) the expression for apparent viscosity calculation is obtained:

$$\eta = \frac{U \cdot \Delta I \cdot \cos\varphi \cdot \left(1 - k^2\right)}{4 \cdot \pi^3 \cdot n^2 \cdot d^2 \cdot L} \qquad (2)$$

where: d – diameter of stirrer (d=2r).

Because the voltage from the network and geometric parameters during mixing were kept constant, it is possible to express the apparent viscosity as a function of the current intensity change:

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

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 measured during mixing of SSM. Namely, the value of ΔI for mixing of SSM was 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 ΔI for mixing were then used for rheological calculations.

Change of apparent viscosity as a function of temperature during cooling from 479 to 440ºC is presented in Fig. 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 SSM. The change of apparent viscosity values is visible at temperatures above 470ºC, when solid fraction exceeds 24 wt.% (see Fig. 2). Comparing the values of apparent viscosity as dependence 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 region of working temperatures.

The results of rheological behavior of ZA27 alloy SSM and SSMs of composites are presented in Figs. 4 and 5, respectively.

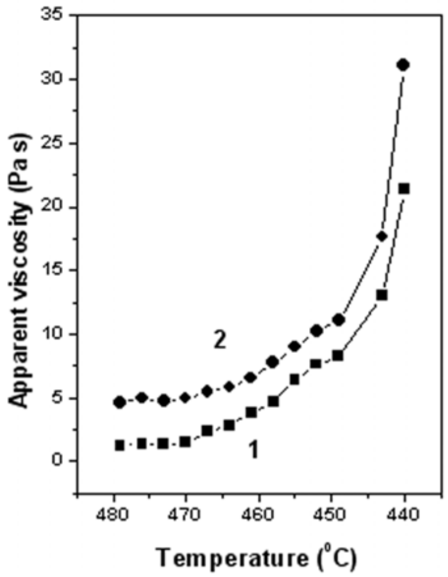

Fig. 3. Apparent viscosity – temperature dependence of ZA27 alloy for different stirrer type. Shear rate 132 s^{-1}., 1-Cylindrical stirrer, 2. Paddle stirrer.

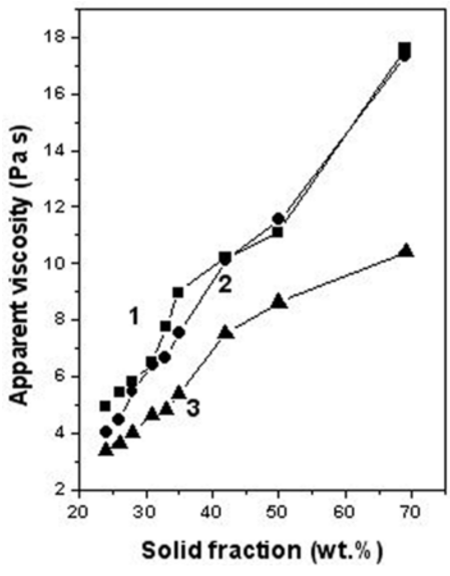

Fig. 4. Apparent viscosity – solid fraction dependence for different reinforcing particle size. Shear rate 132 s^{-1} 1. ZA27; 2. ZA27+3 wt.% Al_2O_3 12 μm; 3. ZA27+3 wt.% Al_2O_3, 250 μm.

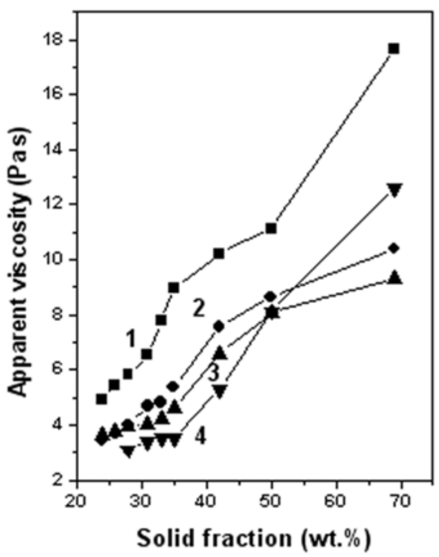

Fig. 5. Apparent viscosity – solid fraction dependence for different mass fraction of reinforcing particles (same size). Shear rate 132 s^{-1}. 1. ZA27, 2. ZA27+3 wt.% Al_2O_3 250 μm; 3. ZA27+8 wt.% Al_2O_3, 250 μm; 4. ZA27+16 wt.% Al_2O_3, 250 μm.

The influence of ceramic particles size on the values of apparent viscosity for SSMs of composites was determined and the results are shown in Fig. 4. It can be seen that the values of apparent viscosity of composites SSMs decrease as the size of Al_2O_3 increases.

The influence of strengthening particles weight fraction on apparent viscosity values is shown in Fig. 5, for the SSMs of composites containing 3, 8 and 16 wt.% Al_2O_3 particles. It can be noticed that until 50 wt.% of solid fraction, values of apparent viscosity decrease as the weight fraction of strengthening particles increases. The values of apparent viscosity for SSMs of composites are lower than those for the matrix ZA27 alloy SSM in the whole temperature range. This fact is extremely important for the further processing of composites.

Metallography

The results of metallographic investigations of ZA27 alloy and its composites before rheological process are presented in Figs. 6 and 7. The microstructure of gravity die cast ZA27 alloy (in preheated steel mold) is shown in Figs. 6a and b.

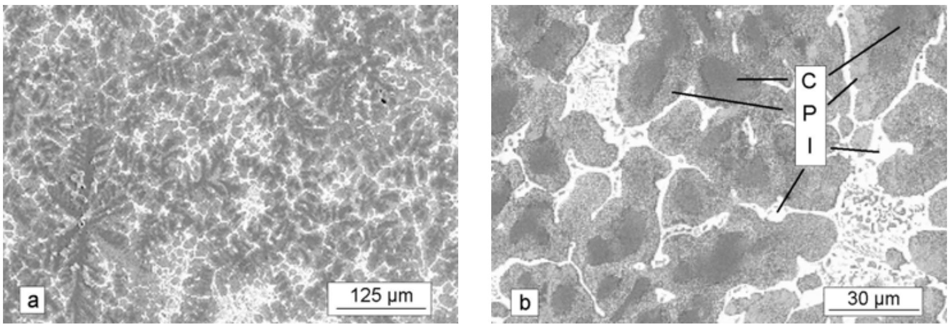

Fig. 6. SEM micrographs of ZA27 as-cast microstructure. Polished. a. Lower magnification showing the general charateristics of microstructure. b. Higher magnification showing details of microstructure, such as: C-dendrite core, P-dendrite periphery, I-interdendritic phase.

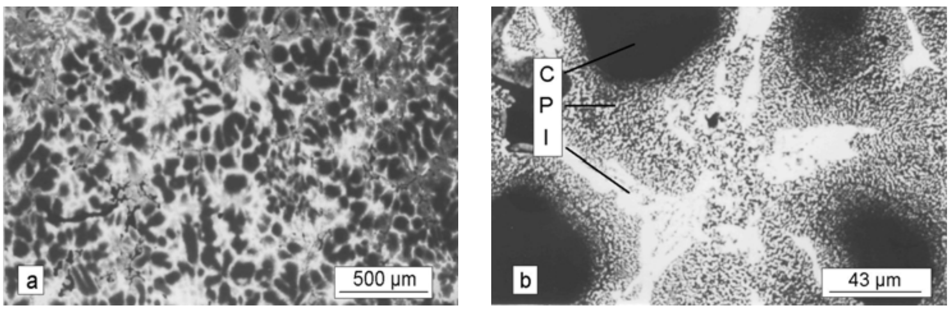

Fig. 7. SEM micrographs of ZA27 thixocast microstructure. Polished. a. Lower magnification showing the general charateristics of microstructure. b. Higher magnification showing details of microstructure, such as: C-dendrite core, P-dendrite periphery, I-interdendritic phase, PP– primary particles.

The structure is typically dendritic. Transformation of the dendritic structure into a non-dendritic took place during the thixocasting process. The microstructure consists of coarse, elliptic primary particles (Figs. 7a and b).

Transformation of the dendritic to non-dendritic structure also occurred during the compocasting process (Figs. 8a and b), i.e. after rheological process and applied pressing.

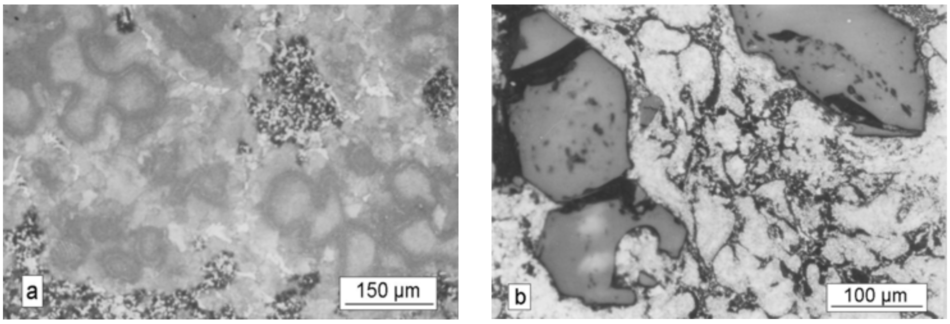

Fig. 8. Micrographs of ZA27-based composites. a. SEM. Polished. ZA27 + 3 wt.% Al_2O_3, 12 μm, SEM; b. OM. Etched, ZA27 + 3 wt.% Al_2O_3, 250 μm.

The morphology and distribution of Al_2O_3 strengthening particles in the matrix of ZA27 alloy are shown in Fig. 9a and b. It can be noticed that small reinforcing particles show a tendency to agglomerate (Fig. 9a), whereas large particles do not show this tendency (Fig. 9b). Due to a significant difference in Al_2O_3 particle size the different magnification of micrographs was chosen in order to illustrate the tendency of small Al_2O_3 particles to agglomeration.

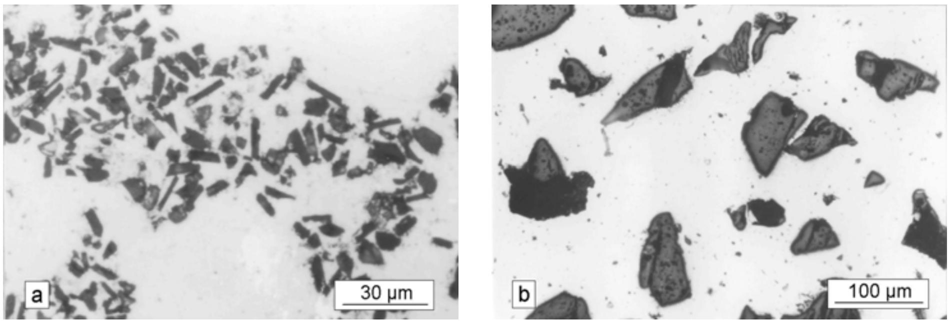

Fig. 9. OM micrographs of ZA27-based composites. Polished. a. ZA27 + 3 wt.% Al_2O_3, 12 μm; b. ZA27+8 wt.% Al_2O_3, 250 μm.

Discussion

The "electric method" enables acquisition 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 Mada et al. [7] it is difficult to obtain precise values of rheological parameters by this method. However, the method can be very useful for the rheological behavior evaluation of SSMs of composites. During rheological investigations carried out in this work quite good reproducibility of results in the series of experiments of SSMs of composites has been achieved.

Results of rheological behavior of base ZA27 alloy in the temperature range from 479 to 440ºC showed 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 when the cylindrical stirrer was used. The possible explanation is as follows: during mixing cylindrical stirrer 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 [4] (Figure 10), who used the Brookfield viscosimeter.

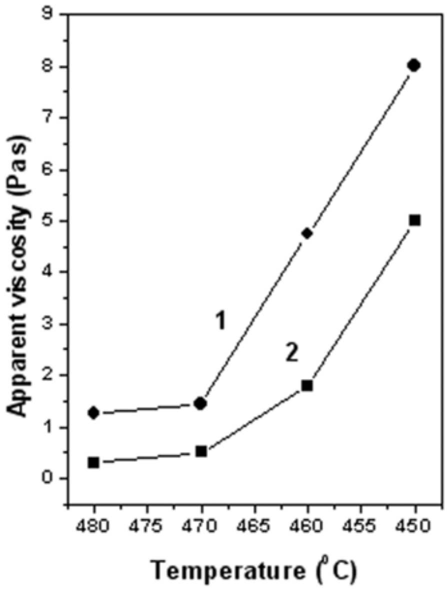

Fig. 10- Comparison between Lehuy`s results and the results obtained in this work, at similar shear rate value. 1. Electrical method, cylindrical stirrer (γ = 132 s^{-1}), 2. Lehuy, Brookfield viscometer, (γ = 125 s^{-1})

For the similar values of shear rate (132s^{-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 weight fraction exceeds 30 wt.%, a certain difference in shear rate can be noticed. In general, the results of this paper explicitly showed that “the electric method” proved to be a reliable and accurate method in determining rheological characteristics of thixocast and compocast SSMs.

The experimental results presented in Figures 3 - 5 clearly demonstrate 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 SSM 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 SSM is lower. This approach is confirmed in this work by the results of metallographic investigations.

Typical microstructure of as-cast ZA27 alloy, presented in Fig. 6a and b, is obtained by gravity die casting. The structure is typically dendritic. (Fig. 6a). The resulting microstructure of peritectic transformation ($L+\alpha=\beta$; L is the liquid phase) with later eutectoid decomposition ($\beta=\alpha+\eta$ at 275ºC). The microconstituents are clearly visible in Fig. 6b at higher magnification. Dendites consist of the dendritic core, C, (α phase rich in aluminum) and a periphery, P, (a mixture of α phase and hexagonal η phase rich in zinc). The η phase is located into interdendritic regions, I.

During thixocasting process the dendritic structure has been transformed into a non-dendritic structure (Fig. 7a and b). At mixing conditions applied in this work, the coarse primary elliptic particles of α phase have appeared. This morphology is in agreement with results of Lehuy et al. [4] and fits into the scheme of structure transformation influenced by shear stress [10]. Micrograph at higher magnification shows details of non-dendritic structure, i.e. dark primary α phase, C, surrounded by gray periphery mixture, P, of α and η phase. Particles of η phase are positioned into elongated interdendritic regions, I.

The same coarse-grained structure has developed in the composites (Fig. 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 (Fig. 9a) incline to agglomeration because of their mutual affinity. The motion of these small-sized particles during mixing is not individual but is in the form of clusters. This means that their influence on breaking up of coarse primary particles of α phase of the matrix alloy is less effective than large Al_2O_3 particles (250 μm). These large Al_2O_3 particles behave as independent particles due to their lower affinity to mutual agglomeration (Fig. 9b).

From the diagram in Fig. 4 it can be seen that SSMs apparent viscosities of ZA27 and the composite (3 wt.% Al_2O_3, 12 μm) are higher than viscosity of composite with larger Al_2O_3 particles (3 wt.% Al_2O_3, 250 μm). In accordance with the assumption previously stated it may be also assumed that the number of interactions between primary α phase particles and large Al_2O_3, particles will increase when the weight fraction of these particles increases (Fig. 5). 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 thermodynamically prevented to a great extent. As a result, the apparent viscosity increases as for the composite containing 16 wt.% Al_2O_3 (particle size - 250 μm).

Conclusions

1. The "electric method" enables calculation of basic rheological parameters with the significant level of accuracy. This method can also be applied to monitor the process of mixing of semi-solid mixture after infiltration of strengthening 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. This fact is of great importance for the further processing of composites. Larger reinforcing particles demonstrate more significant effect in lowering the viscosity.
3. The apparent viscosity of semi-solid mixtures of composites decreases as the weight fraction of strengthening particles increases. This finding is not valid for the composite containing 16 wt.% Al_2O_3 (particle size - 250 μm) when solid fraction is above 50 wt.%.

Acknowledgement

The results of this paper were realized through the projets Nos 14005 i 142027B finacially supported by the Ministry of Science and Technological Development of the Republic of Serbia.

References

[1] R.J. Barnhurst, D. Jacob, AFS Trans. 88-98 (1984)321-328.
[2] H. Lehuy,. J. Mat. Sci. 23 (1988) 2943-2950.
[3] Z. Zhu, Proceedings of the 2nd International Conference, ASM, Materials Park, OH (1988) 93.
[4] H. Lehuy, J. Masounave, J. Blain, J. Mat. Sci. 20 (1985) 105-113.
[5] D. Brabzon, D. J. Browne, A. J. Carr, Mat. Sci. Eng. A356 (2003) 69-80.
[6] H.K Moon, J. Cornie, M. Flemings, ibid. A144 (1991)253-265.
[7] M. Mada, F. Ajersch, ibid. A212 (1996) 157-170.
[8] K. Ichikawa, S. Ishizuka, Trans. Japan Inst. Met. 28 (1987) 434-444.
[9] S. Nagata, Mixing-Principles and Applications, John Wiley & Sons, New York, 1975.
[10] M. Flemings, Met. Trans. 22A (1991) 957-981.