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Rheological behavior of semi-solid TiB_2 reinforced Al composite

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Abstract: The rheological behavior of the semi-solid TiB_2 reinforced Al−Mg alloy composite slurry was investigated, which is required for the mould filling simulations during the semi-solid processing. TiB_2 reinforced in-situ Al−Mg alloy composite samples were remelted and subsequently brought to the semi-solid temperature regime within the heating chamber of a Searle type rheometer. In order to understand the rheological behavior of composites, three different types of experiment were carried out, namely, steady state test, continuous cooling test and isothermal test. Apart from that, the thixotropic nature of the slurry was confirmed from the obtained hysteresis loops during the experimentation. The results indicate that when isothermally held, the composite slurry exhibits pseudo-plasticity and shows shear-thinning behavior up to the shear rate of 1300 s^{-1}, and at higher shear rates (>1300 s^{-1}), it shows a shear thickening tendency, which is probably due to the agglomeration of non-deformable nano-TiB_2 particles. The pseudo-plastic behavior of the slurry was also estimated employing intermittent step changes of shear rate (shear jump test).

Key words: rheology; shear thinning; in-situ nano-TiB_2; thixotropy; shear thickening

1 Introduction

Rheocasting and thixocasting of metallic alloys and composites utilize semi-solid slurries in which non-dendritic (spheroidal) solid particles are dispersed in a liquid melt [1−4]. The rheological characterization of these metallic alloys and composites in semi-solid state is highly important in the die-casting stage for analyzing their distinctive flow behaviour (rheology). The rheological responses under the rapid changes in shear rate, form the basis of modelling the die filling and die design processes. The reduction in viscosity of semi-solid slurry under application of shear (Thixotropy) leads to complete filling of the mould sections during the casting process. Usually semi-solid slurries exhibit the following complex rheological behaviours, pseudo-plasticity and thixotropy. Owing to the ubiquity of Al alloys in mechanical construction and automotive industries, the rheological characterization of Al alloys (A356, A380) have already been carried out [2,5,6]. However, there is limited information related to the rheological behaviour of Al composites [7−9]. In this study, the rheological characterisation of Al-based in-situ composite reinforced with TiB_2 particles (Al−4Mg−0.15Sc−0.075Zr−2TiB_2) was performed to investigate its capability to fill the die cavity of engineering components under the application of shear at semi-solid state. The present class of composites are popular due to their excellent mechanical and tribological properties, and high stiffness and hardness of submicron size particles. The particles produced by the reaction are rapidly dispersed in the liquid Al alloy and refine the grain structure during the solidification. A uniform dispersion of reinforcement particle in the matrix in a composite is one of the factors for getting improved mechanical properties [10]. Sc and Zr are added within the melt during the composite development to obtain modified microstructural features in the cast parts [11]. Earlier investigation has shown marked improvement in mechanical properties of the present class of composite owing to the presence of nano-TiB_2 particles at the grain boundaries. The formation of such nano-TiB_2 was attributed to the presence of Sc in the melt [10].

In the present study, the remelting and subsequent cooling of the composite was performed within the heating chamber of high temperature rheometer to perform rheological investigations at semi-solid state. At

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semi-solid state, the whole system becomes one having three components: primary solid phase of the matrix (α(Al)), liquid alloy matrix and reinforced particles (TiB_2). It is therefore interesting to consider the effect of the presence of small reinforced particles (TiB_2) on the rheological behavior of the total system. The understanding of the rheological behavior would therefore be beneficial for semi-solid metal processing of this class of composites.

2 Experimental

The Al−4Mg−0.15Sc−0.075Zr−2TiB_2 composite was cast by diluting Al−2Sc, Al−10Zr and 99.9% Mg master alloys along with commercially pure Al in a resistance heating furnace. TiB_2 was allowed to form by in-situ reaction of K_2TiF_6 and KBF_4 salt mixture at 800 °C for 60 min. The TiB_2 particles produced by the reaction were rapidly dispersed in the liquid Al alloy and refined the grain structure during the solidification. The composite melt was stirred for 2 min with a graphite blade followed by the addition of Mg to form the required Al−Mg−Sc−Zr composite reinforced with TiB_2 particles. Finally, the casting was made by pouring the molten composite into the permanent mould. The chemical composition of the alloy obtained is shown in Table 1.

Table 1 Chemical composition of TiB_2 reinforced Al composite (mass fraction, %)

Mg	Sc	Fe	Si	Zr	Al
0.34	0.16	0.20	0.40	0.065	Bal.

The rheological experiments were performed with a high-temperature Searle type rheometer. Searle type rheometer has a rotating inner bob and a stationary outer cup, as shown in Fig. 1. The detailed working principle of Searle type rheometer was explained elsewhere [6]. Though the solidus and liquidus temperatures of the base Al−Mg alloy are available in Ref. [12], however, in order to carry out the rheological study, the digital scanning calorimetry (DSC) analysis of the in-situ composite was performed and the temperature regimes of rheological investigations were selected based on the DSC findings. The DSC findings reveal the solidus and liquidus temperatures of the composite which are approximately 580 and 650 °C, respectively (Fig. 2).

The steady state test was performed to determine the change in the viscosity of semi-solid slurry with fixed shear rate. The time dependent nature of slurry was generally observed from the steady state test. During an isothermal holding (615 °C) and at a shear rate of 600 s^{-1}, the apparent viscosity of slurry was recorded for a period of 60 min. The test was terminated at 60 min to nullify

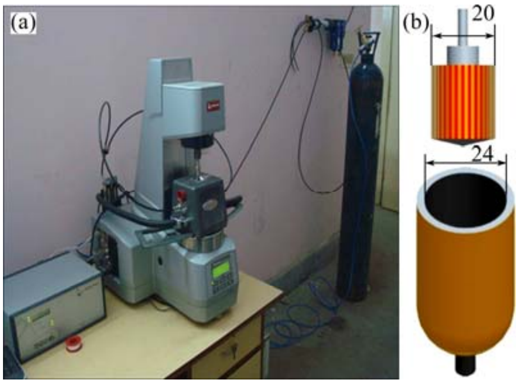

Fig. 1 Searle type rheometer (a) and schematic view of bob and cup arrangement (b) (unit: mm)

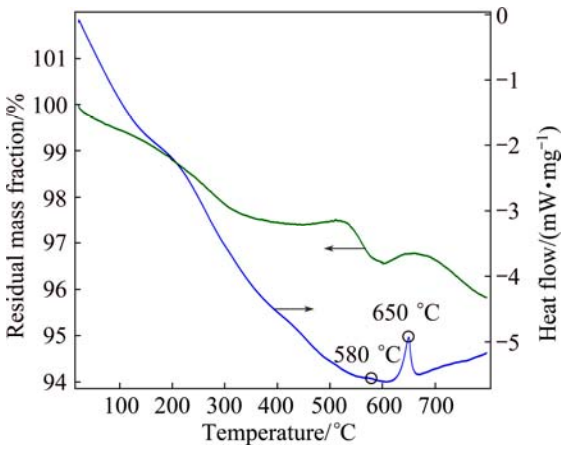

Fig. 2 DSC curve of composite

the dominance of Ostwald ripening over the globularization of primary Al grains [13].

During the continuous cooling test, the superheated melt was cooled from 660 °C at a cooling rate of 5 °C/min down to the semi-solid temperature of 605 °C while the shear rate is fixed at 700 s^{-1}. Whereas for the isothermal test, the shear rate varied from 10 to 1500 s^{-1} at the selected temperatures. The shear rate jump test was also performed following an earlier investigation on A356 Al alloy [6,14] in order to simulate the real life situations, where sudden increase and decrease in shear rate were inevitable. It is well known that semi-solid slurries exhibit time-dependence, non-Newtonian flow known as thixotropy, therefore, the thixotropic nature of the slurry is confirmed from the hysteresis loops obtained during the experimentation. The thixotropic test for the Al−4Mg−0.15Sc−0.075Zr−2TiB_2 composite slurry was performed at a temperature of 615 °C. Firstly, a steady state viscosity value of the slurry was obtained at a shear rate of 400 s^{-1}. The shear rate was then ramped down to zero and kept at this level for a rest period of 10 min. The shear rate was then immediately ramped back to 400 s^{-1} and immediately ramped back to zero by setting the ramp up and ramp down period of 5 s each.

The thixotropic viscosity loops were generated for the composite slurry from this cyclic shear rate profile.

3 Results and discussion

3.1 Steady state test

It is observed from the steady state test that the viscosity continuously decreases due to the structural breakdown of primary phase (primary Al) clusters, which occurs during shear with more spheroidal shape of the independent primary phases. However, the steady state value of viscosity depends on the shear rate and solid fraction [15]. Similar behavior was reported earlier for A356 Al alloy by DAS et al [6]. Figure 3 shows the change in viscosity with time at a fixed shear rate of 600 s^{-1}.

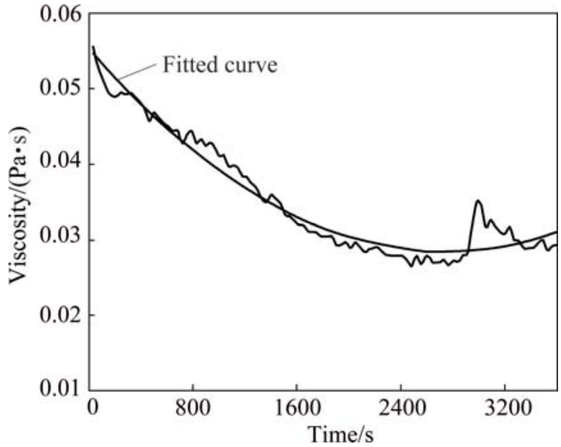

Fig. 3 Variation of viscosity with time at fixed shear rate of 600 s^{-1}

3.2 Continuous cooling test

The continuous cooling test highlights the effect of temperature on the viscosity of semi-solid melt. A continuous increase of viscosity is seen due to the increase of solid fraction within the composite slurry with decreasing the temperature (Fig. 4). The application of a constant shear rate and continuous decrease of temperature results in the primary Al particle agglomeration, coagulation, sintering and ripening [16−19] and in turn decreases their sphericity [20] (more dendritic) and thereby contributing towards increased viscosity. In addition, the increase of the amount of reinforced particles (TiB_2) with decreasing the temperature also leads to an increase of the viscosity. A similar behavior was observed for semi-solid Mg_2Si/AM60 Mg matrix composites by HU et al [9].

3.3 Isothermal test

The isothermal test was carried out to investigate the effect of change in shear rate on the change in viscosity of the semi-solid melt at fixed temperatures. Figure 5 shows the variation of viscosity with increasing the shear rate from 10 to 1500 s^{-1} at fixed temperatures. The relationship of the primary Al content within the slurry and the corresponding temperature for the rheological investigation can be estimated from the Scheil equation given below:

$$f_s = \frac{1}{1-k_p}\left[\frac{t-t_l}{t-t_m}\right] \tag{1}$$

where f_s is the mass fraction of primary Al phase, t is the temperature of the melt during the rheological investigation, t_l is the liquidus temperature of the selected composite (650 °C), t_m is the melting temperature of pure Al (665 °C) and k_p is the participation coefficient, which is normally considered as 0.13 for Al alloys [3,4].

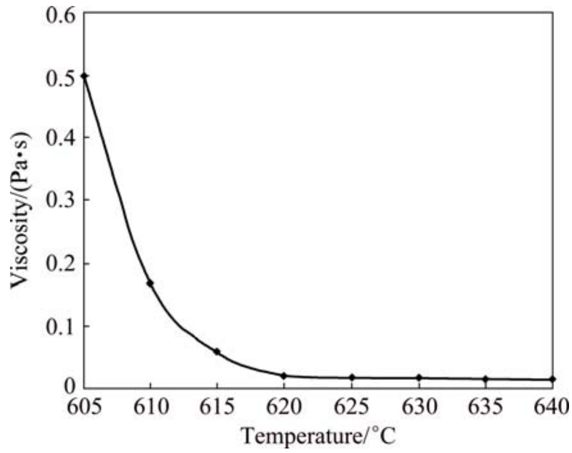

Fig. 4 Variation of viscosity with temperature at fixed shear rate of 700 s^{-1}

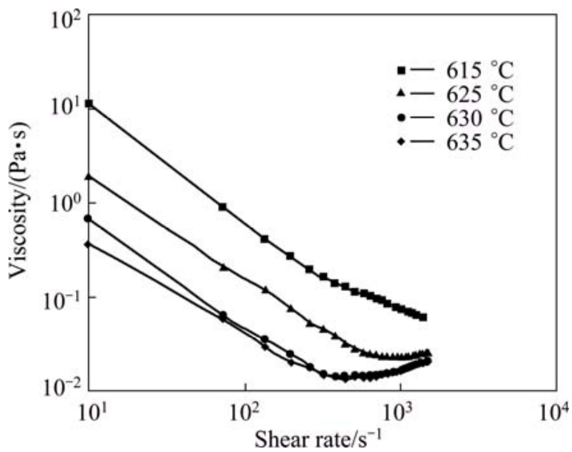

Fig. 5 Variation of viscosity with shear rate at different temperatures

The decrease of viscosity is observed in the shear rate range of 10−1300 s^{-1} due to the breakdown of agglomerated primary spheroid particles which are present in the semi-solid composite melt. It is observed that at higher shear rates (1300−1500 s^{-1}), the melt exhibits the tendency of shear thickening. As the shear forces increase, the aggregates break up and release entrapped liquid. The shear thickening behavior at higher shear rates of the semi-solid melt is due to the presence of non-deformable TiB_2 particles (a majority of which are 30−50 nm in size), which are present in the composite slurry, come out of the grain boundaries and agglomerates, thereby remaining as solid suspension in the slurry. This probably contributes to the increase of viscosity with increasing the shear rate. Nano TiB_2 particles are generally deposited at the grain boundaries of the composite, as shown in Fig. 6, which come out of the matrix at semi-solid state. The presence of nano-TiB_2 particles is shown in Fig. 6 and their XRD spectra may be seen from the earlier published work of similar class of composites [10]. This tendency of shear thickening behavior is found to be more predominant at higher temperature (635 °C) compared with that at lower temperature (615 °C). This is due to the fact that at higher temperature, the solid fraction is less and the non-deformable TiB_2 particles play a major role in controlling the viscosity.

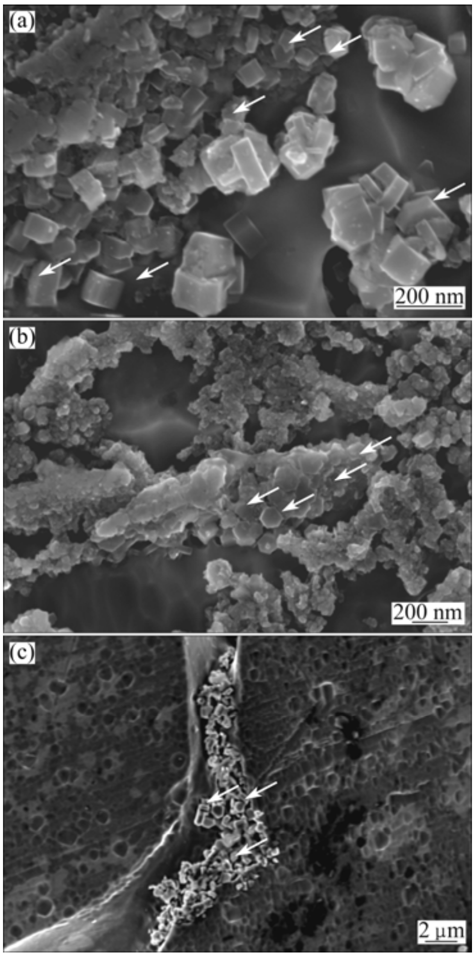

Fig. 6 Distribution of non-deformable TiB_2 particles (hexagonal in shape marked by arrows) deposited at two different locations along grain boundaries in semi-solid processed sample (a, b) and in as-cast sample (c)

3.4 Shear jump test

The effect of shear jump on the slurry viscosity is shown in Fig. 7. The experiment was performed by dropping the shear rate in steps from 1500 to 10 s^{-1} at 615 °C. After attaining a steady state at the initial shear rate of 1500 s^{-1}, the shear rate suddenly drops to a lower value. The value of the down peak viscosity just after the new shearing is taken as the new viscosity level corresponding to the new shear rate, while the original microstructure is considered to be unchanged. The measured shear stress (τ) values decreases with the step down of shear rate ($\dot{\gamma}$) up to 500 s^{-1} due to the decrease of shear rate, which dominates the increase of viscosity values. However, after the shear rate drops below 500 s^{-1}, the shear stress immediately shows steep increase due to the catastrophic increase of viscosity (η) values (Fig. 7), which enhances the product of shear rate and viscosity, i.e., $\tau=\eta\times\dot{\gamma}$. Also it can be seen that the shear stress increases with the time following a step-decrease of shear rate. This is because at relatively higher shear rates, the degree of agglomeration is very low and the reduced agglomeration signifies a smaller contribution to the measured shear stress. But at lower shear rates, the semi-solid slurry is highly agglomerated, thereby resulting in large particles with entrapped liquid, hence high viscosity or shear stress measured. When a step change in shear rate is imposed, the shear stress will drop immediately and then gradually increase until it reaches an equilibrium value for the shear rate over the time. A finite time is usually required to establish a new steady-state value of shear stress/viscosity corresponding to the change in shear rate. The test results therefore confirm pseudo-plastic behavior of the semi-solid composite slurry.

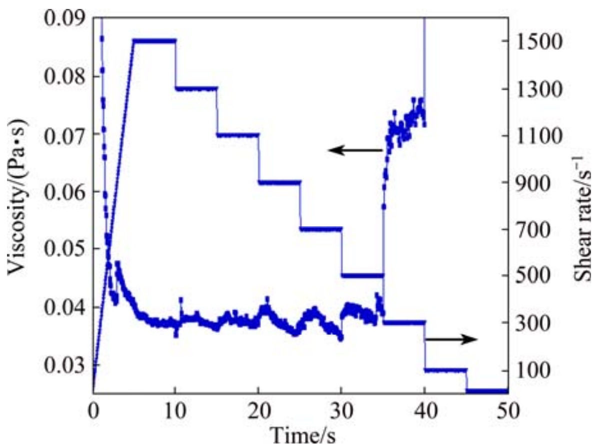

Fig. 7 Variation of viscosity with time jumps in shear rate

3.5 Steady state and isostructural flow curve

The isostructural behavior is a result of spontaneous change in the flow behavior due to a sudden change in the shear rate, i.e., shear jump [6,14]. It is analyzed that the microstructural morphology of the semi-solid slurry remains unchanged under the steady state of the previous shear rate, in the first instance of shear jump. The steady state and isostructural shear stress and their corresponding flow curves were evaluated from the above shear rate jump experiment (Fig. 8). The shear stress values which are recorded at the first instance of shear jump are termed as isostructural shear stress. The isostructural shear stress values for all the shear rates under consideration constitute the isostructural flow curve. After the shear jump, the shear stress values approach towards equilibrium after finite time (approximately 5 min, as evidenced in this study). The equilibrium shear stress values are recorded for the corresponding new shear rate and the steady state flow curve is obtained out of it. The steady state and isostructural flow curves indicate the degree of flowability of the composite slurry in the case of sudden change in the shear rate, and occur during the real life situations such as high pressure die casting, squeeze casting, rheo-moulding, thixo-moulding, etc.

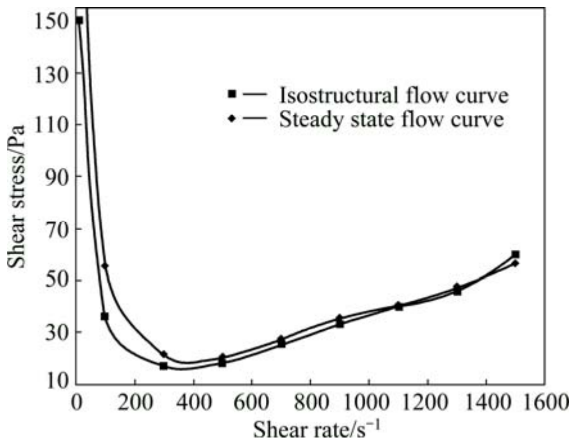

Fig. 8 Isostructural and steady state flow curves

3.6 Thixotropic hysteresis loop

The thixotropic behavior of semi-solid slurry has been demonstrated by JOLY and MEHRABIAN [21] on Sn−15Pb alloy by measuring the hysteresis loops during a cyclic shear deformation. The obtained thixotropic viscosity loops for the composite are shown in Fig. 9. During the rest period, the microstructure changes as the solid particles agglomerate to form larger particles. When the shearing is resumed, the agglomerated microstructure proceeds to give a peak value of shear stress, which subsequently reduces and then gradually attains steady state with time. Similar observation has been made by KOKE and MODIGELL [22]. The enclosed area within the shear stress loops recorded during the thixotropy tests indicates the degree of thixotropy of the alloy. Longer rest time will result in larger enclosed areas within the loops (increased thixotropy) due to an increased amount of primary phase agglomeration or clustering.

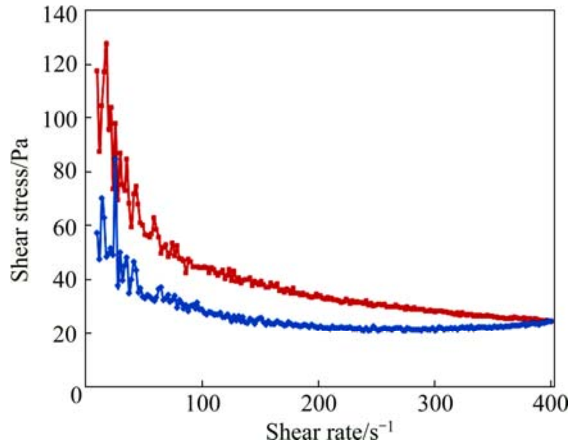

Fig. 9 Hysteresis loops generated during thixotropic tests

4 Conclusions

1) When isothermally held, the composite slurry exhibits non-Newtonian shear-thinning (pseudo-plasticity) behavior up to the shear rate of 1300 s^{-1}. At higher shear rates (>1300 s^{-1}), it exhibits a shear thickening tendency probably due to the agglomeration of non-deformable TiB_2 particles.

2) During continuous cooling experiment, the viscosity values of the composite slurry depend on the shear rate, cooling rate, volume fraction of primary Al phase and presence of TiB_2 particles.

3) The pseudo-plastic behavior of the composite slurry is assessed by the shear jump test, and subsequently the steady state and isostructural flow curves are derived out of the test results, which points towards the flow behavior of composite slurry in the case of sudden drop or increase of shear rate, occurs in practice.

4) When semi-solid slurry is sheared after a period of rest, it displays a characteristic transient stage, thereby confirming the thixotropic nature of the composites.

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半固态 TiB_2 增强铝基复合材料的流变性能

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摘　要：研究半固态 TiB_2 增强 Al−Mg 合金复合材料浆料的流变性能，对半固态加工过程中的充型模拟是必需的。在一台 Searle 型流变仪的加热室内，将 TiB_2 增强原位 Al−Mg 合金复合材料样品再熔化，随后将温度降低到半固态温度范围。为了复合材料的流变性能，进行三种不同的实验：稳态实验、连续冷却实验和等温实验。此外，从实验得到的滞回曲线证实了浆料的触变性。结果表明：当等温保持时，复合材料浆料显示假塑性和剪切变稀行为直到剪切速率达到 1300 s^{-1}；在更高剪切速率(>1300 s^{-1})下，它显示出剪切增稠趋势，这可能是由于不可变形的纳米 TiB_2 颗粒的团聚引起的。通过剪切速率的间歇阶跃变化(剪切突变实验)也证实了浆料的假塑性行为。

关键词：流变学；剪切变稀；原位纳米 TiB_2；触变性；剪切增稠

(Edited by Mu-lan QIN)