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Highlighting a rheological behavior of glass melt at high temperature

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1. Introduction

Flow behavior of glass melts and their characterization have attracted remarkable attention in recent years because of their industrial applications and academic interests as a lubricant at high temperature [1–4]. As an example, glass lubricant at high temperature is currently widely used in hot tube extrusion [1–4] and continuous casting process of steel [5–14]. Especially, metallurgists have extensively explored a rheological behavior of glass melts for a continuous casting process of steel industry. Fig. 1 represents a typical mold region of caster where glass melt is actually used for lubricant at high temperature. For their ideal casting condition, the glass melts at casting temperature (1623 K) have to exhibit dual viscos function to reduce slab surface defects. At mold top region with shear rate ranges between 10 and 40 1/s, viscosity glass melt must be high enough to minimize glass melts' entrapment, whereas at mold wall region with sear rate ranges between 100 and 1000 1/s, viscosity of glass melts must be low enough to increase its lubrication ability [5–7].

Such ideal viscous function of the glass melts could easily be accomplished by increasing shear thinning behavior of glass melts [5–7]. The previous researches have proposed two different ingredients which are effective in increasing shear thinning behavior of glass melts. They are relatively large amount of borate and small amount silicon nitride [5–7]. In those researches, it had been interestingly discovered that silicon nitride and borate are effective to enhance shear thinning behavior of glass melt with a very different manner. Borate addition leads to decreasing viscosity at higher shear rates without remarkable viscosity changes at lower shear rates. On the other hands, silicon nitride addition results in increasing viscosity at lower shear rates without remarkable viscosity changes at higher shear rates [6]. In spite of considerable progress in appreciating structural and rheological property of glass melts for academic purpose and developing shear thinning behavior modifier of glass melts applicable to continuous casting process for industrial purpose, identifying advanced rheological parameters of glass melts which will lead to a deeper understanding of nature of glass melt's shear thinning behavior and its modifier's role still remain elusive.

Here, we successfully accomplished CaO-SiO2-CaF2 based glass melts exhibiting the strongest shear thinning behavior ever reported with the modification of structure. The key strategy of such accomplishment is to simultaneously incorporate two shear thinning behavior modifiers; silicon nitride and borate. Moreover, our dynamic viscosity measurement leads to an in-depth understanding of structure – rheological property of glass melts by considering crossover point, $G'' = G'$, together with structural modification caused by each associative additive.

2. Experimental

2.1. Sample preparation

For the glass melts preparation, the reagent-grade chemicals including $CaCO_3$, SiO_2, CaF_2, Al_2O_3, MgO and Na_2CO_3 were melted in a platinum crucible at 1573 K for 30 mins to complete homogeneous state of mixtures. Subsequently, the prepared melts were quenched by applying glass melts into a cold water cooled steel plate. The prepared glass melts have basicity (CaO/SiO_2 ratio) of 0.94 and used for the precursor of glass melts with associative additive. For the preparation glass melts with associative additives, each additive: reagent grade borate and silicon nitride were added to the precursor with an appropriate amount and melted for half an hour to achieve homogeneous state and followed by quenching process on a cold steel plate. Before conducing viscosity measurement, all prepared samples were premelted to achieve chemically stable state. In doing so, it is feasible to avoid a significant chemical composition change before and after the viscosity measurement.

2.2. Rheological measurement

Rheological study was carried out on rotational type rheometer equipped with high temperature furnace (Ravenfield Modle FG MkIV; Ravenfield Designs Ltd., Heywood, UK) under controlled oxygen fugacity. The schematic drawings, specific dimensions and procedures performed are described in Fig. 2 and Table 1. Dynamic viscosity measurement had been conducted for deeper understanding of rheological behavior of glass forming liquid (molten mold flux) and

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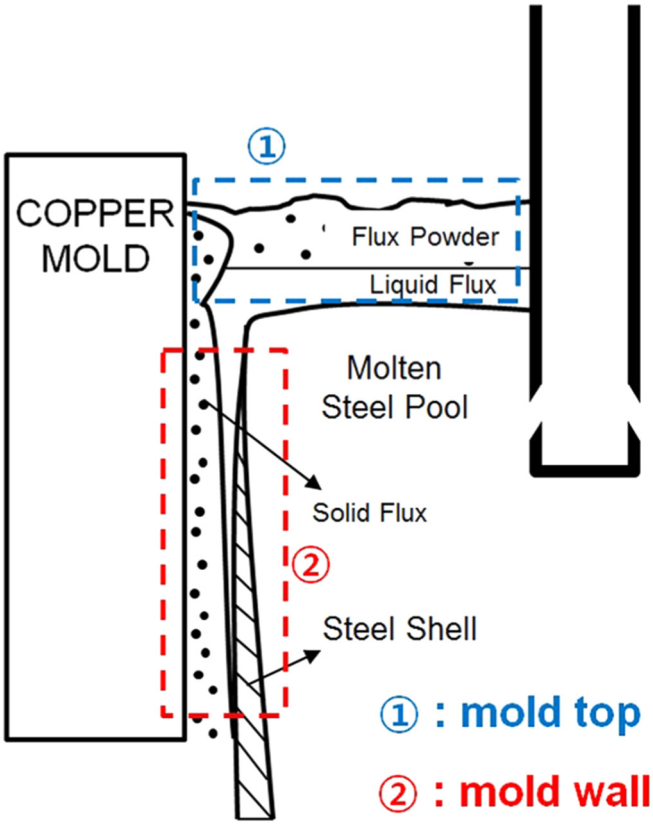

Fig. 1. A schematic diagram of mold area for continuous caster.

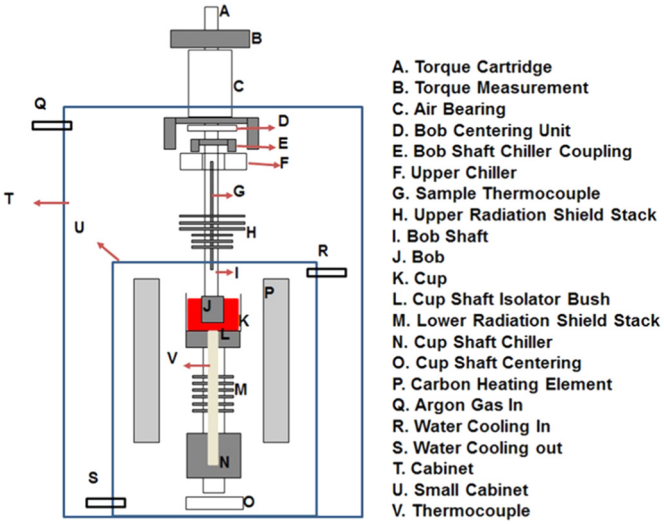

Fig. 2. Schematic depiction of rheometer equipped with high temperature furnace. (Ravenfield Modle FG MkIV; Ravenfield Designs Ltd., Heywood, UK).

Table 1
Specific dimensions of crucible and spindle for viscosity measurement.

Crucible (molybdenum)	Dimension (mm)	Spindle (molybdenum)	Dimension (mm)
Inner radius (R_2)	6.25	Bob radius(R_1)	5
Inner depth	31.6	Total length	240
Height	52.6	Submerged length (h)	10

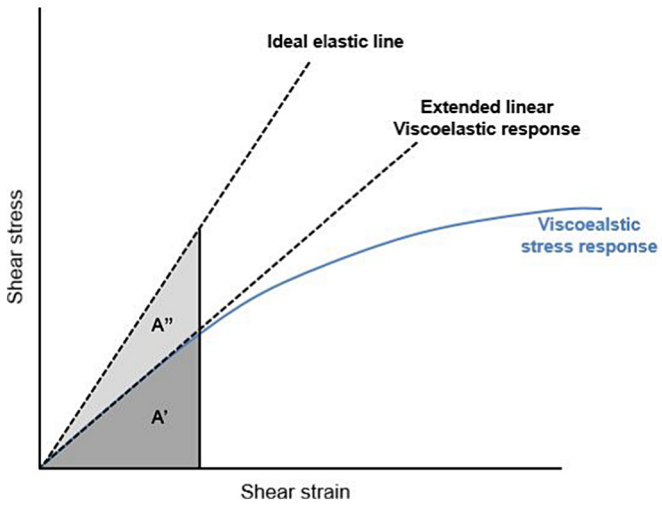

Fig. 3. Area showing viscos and elastic effect of material in shear stress vs shear rate graph.

followed by its analysis with deformation zone estimation.

2.3. Deformation zone estimation

Fig. 3 represents basic concept of Deformation Zone Estimation approach in which phase angle is estimated by the ratio between area beneath ideal elastic line and extended linear viscoelastic line.

An elastic response of viscoelastic material would have a certain degree of elasticity and can be quantified by the extended viscoelastic line in this study. The first linear part of viscoelastic region is extended into a straight line, titled as the extended viscoelastic response. The region beneath extended linear viscoelastic response, highlighted as A′ represents elastic response of viscoelastic material meaning an amount of energy stored. On the other hands, any variation from the ideal elastic line, maximum spring windup, can be contributed to viscose response existed in viscoelastic material. Thus, the region between the ideal elastic line and extended liner viscoelastic response highlighted as A″ represents viscose response of viscoelastic material which means an amount of energy dissipated.

Generally, the phase angle is calculated by using a ratio of storage modulus (G′) to the loss modulus (G″) in oscillatory dynamic measurement. However, in this study, the phase angle is estimated by the proportion between the energy dissipated and the energy stored through Eq. (1).

$$\delta = \tan^{-1}\left(\frac{A''}{A'}\right) \tag{1}$$

Therefore, the phase angle of the viscoelastic material could be determined using the stress-rate response shown by the material when tested on the viscometer. In this case, the shear modulus of the material is equal to the complex modulus of the material.

$$G^* = G \tag{2}$$

Storage (G′) and loss modulus (G″) could be computed as a function of complex modulus and phase angle according to the flowing equations.

$$G' = G^*(\cos\ \delta) = \frac{\sigma_a}{\gamma_a}(\cos\ \delta) \tag{3}$$

$$G'' = G^*(\sin\ \delta) = \frac{\sigma_a}{\gamma_a}(\sin\ \delta) \tag{4}$$

Hence, the viscoelastic properties of the material could be acquired by replacing the shear modulus (G) in place of the complex (G*) according to the Eq. (2).