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Cooling history of a wet-granulated blast furnace slag (GBS)

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ABSTRACT

Granulated blast furnace slag (GBS) is a glassy by-product of the steel industry that is formed during quenching of the molten slag after the blast furnace in a water-jet. To elucidate the cooling history of GBS, calorimetric scanning in the glass transition range and viscometric experiments at temperatures above the liquidus were performed. The GBS studied was of industrial origin with a d_{50} = 700 μm and > 99% glassy. It is found that GBS glass is of high potential energy, showing a fictive temperature that is approx. 160 K higher than the glass transition temperature under standard cooling conditions. Using different viscosity models and the relationship between quench rate and shear viscosity at the fictive temperature it is calculated that GBS was formed at a cooling rate of approx. $2.6 \times 10^5\,\mathrm{K\,s^{-1}}$ corresponding to a shear viscosity of $10^{5.9}$ Pa s. Due to the high T_f and high amount of heat that is released during structural relaxation, GBS is assigned to the class of hyperquenched glasses.

1. Introduction

Granulated blast furnace slag (GBS) is a non-metallic by-product of the steel industry (annual GBS production is approx. 280 million tons) that is formed when after leaving the blast furnace the molten slag is quenched using powerful water jets or fast rotating drums in air. GBS is a fine, granular, almost fully glassy material of calcium aluminosilicate composition. GBS material exhibits latent hydraulic (cementitious) properties [1–4] and furthermore as cement constituent or concrete addition it serves advantageous technical, environmental and economic benefits [5–8]. The reactivity of ground GBS (so-called GGBS) in cement is found to be influenced by the slag properties such as the glass content and its chemical composition as well as the mineralogical composition of residual crystal fraction [9, 10]. As the residual crystalline material is unreactive, small crystal fractions can be beneficial for blending cement. Thus, temperature-time-transformation (TTT) and continuous-cooling-transformation (CCT) diagrams have been determined using the hot thermocouple method in which the tips of a thermocouple are welded in a U-type shape to heat and measure the temperature simultaneously [11, 12]. On the one hand TTT and CCT curves show that GBS glass is formed when the cooling rate exceeds 10^0–$10^1\,\mathrm{K\,s^{-1}}$. On the other hand, the cooling rates of industrially manufactured GBS are generally unknown and only estimated to be above $10^2\,\mathrm{K\,s^{-1}}$ [11]. However, variation in operation parameter, such as molten slag temperature, water jet flow and disc rotation speed may cause the formation of GBS glass with different cooling history and therefore different structure and properties [13]. As a consequence of these fluctuations, the performance of GBS from different production campaigns and sites becomes less predictable.

Generally, the cooling history of glasses can be estimated through their fictive temperature T_f. Despite the fact that the dependence of T_f on cooling rate has been established for > 40 years [14–17], it has not been applied to GBS. The present work aims therefore to express the cooling history of GBS by T_f and cooling rate. The former is determined by calorimetric scanning, whereas the latter requires information on the viscosity-temperature curve. To provide viscosity data at temperatures above the liquidus, rotational viscometry of the molten granules was utilized. The implementation of T_f and cooling rate as parameters of the GBS production might allow assessment of samples independently of their composition and simplify the control and modification of the quenching process according to desired properties (e.g. reactivity in cementitious systems).

2. Material and methods

2.1. Material

The wet-granulated blast furnace slag (GBS) under investigation was

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of industrial origin (moisture 10.6 wt%) and of chemical composition 0.03 P_2O_5, 33.4 SiO_2, 1.98 TiO_2, 11.4 Al_2O_3, 44.9 CaO, 5.7 MgO, 0.75 FeO, 0.23 MnO, 0.36 K_2O and 0.17 Na_2O (wt%) as analyzed by X-ray fluorescence (Σ = 98.92%; 100-Σ = 1.08% volatile species). Transmission optical microscopy of the immersed granules revealed a glassy volume fraction > 99%. Granulometry (sieve analysis) revealed a monomodal particle size distribution with a mean size $d_{50} = 700$ µm (not shown). The GBS glass was analyzed as received without any processing prior to analysis.

2.2. Methods

Using logarithmic scales, the cooling rate q_c and the shear viscosity at the fictive temperature $\eta(T_f)$ are related by a dimensionless shift factor K in the form

$$\lg q_c = K - \lg \eta(T_f) \tag{1}$$

with $K = 11.3$ [16] and $K = 11.35$ [18]. In order to determine the cooling history from Eq. (1), knowledge of both T_f and the viscosity-temperature dependence are required. The fictive temperature of a glass of unknown thermal history can be determined from the difference in the heat capacity curves of a first upscan using the heating rate q_{h1} and a second upscan at the same heating rate ($q_{h2} = q_{h1}$) upon cooling the glass with $q_{c1} = q_{h2}$. The second upscan represents the thermally equilibrated glass, whereas the first upscan captures the relaxation (heat release) of the initial glass structure towards the liquid state. A hysteresis is evident between the heating curves of the first and second cycle, if the cooling rate of the as received glass and the cooling rate of the second cycle are different. T_f upon cooling can be graphically computed by matching the areas under the curves for which one has [15, 17]:

$$\int_{T_c}^{T_{eq}} (c_{p2} - c_{p1})dT = \int_{T_g}^{T_f} (c_{pl} - c_{pg})dT \tag{2}$$

where T_c is the onset temperature at which the release of heat starts, T_{eq} is the temperature at which the hysteresis closes ($c_{p2} = c_{p1}$), T_g is the glass transition temperature (i.e. the fictive temperature of the standard cooling rate with $q_{h2} = q_{c1} = 10\,K\,min^{-1}$ [17]) and c_{pg}, c_{pl} are heat capacities of the equilibrated glass and liquid state, respectively.

As T_f of a highly quenched glass can exceed T_g of the standard cooling by > 100 K (e.g., hyperquenched basalt glass fiber: $\Delta T = T_f - T_g = 204$ K; $T_f = 1.22T_g$ [17]), a direct determination of the viscosity at T_f is complicated due to the proneness of GBS to crystallize in this temperature range. For that reason, viscosity data that capture the glass transition range are calculated by Eq. (1) using fictive temperatures which are received from DSC heat flow measurements at different cooling rates. On the other hand, data that capture the range above liquidus temperature T_L, (at $T > T_L$ the melt is stable against crystallization) are gained directly by conducting rheometric experiments. Both sets of data are used to compute the viscosity-temperature curve of GBS. Frequently used equations representing the temperature dependence of viscosity of glass-forming liquids are:

VFTH [19–21]:

$$\lg \eta = A_1 + \frac{B_1}{T - C_1} \tag{3}$$

AG [22]:

$$\lg \eta = A_2 + \frac{B_2}{T \ln(T/C_2)} \tag{4}$$

AM [23]:

$$\lg \eta = A_3 + \left(\frac{B_3}{T}\right)^{C_3} \tag{5}$$

and MYEGA [24]:

$$\lg \eta = A_4 + \frac{B_4}{T} \exp\left(\frac{C_4}{T}\right) \tag{6}$$

where A_n, B_n and C_n ($n = 1, 2, 3$ and 4) are adjustable parameters. It is expected that the predicted viscosity at T_f will vary as the accurateness of the above viscosity models is different [24]. To account for the error that arises from the interpolating viscosities by Eqs. (3)–(6) all four models were used in our data analysis.

3. Experimental

3.1. Calorimetry

To compensate for possible inhomogeneity, three samples of the same lot were used for calorimetry. The first sample was measured in a DSC (404F3 Pegasus; Netzsch, Selb, Germany), whereas for samples 2 and 3 a TGA equipped with DSC sensor (TGA/DSC 3^+, Mettler Toledo, Greifensee, Switzerland) was used. Each measurement was carried out with 20–30 mg GBS granules in a PtRh-crucible in a nitrogen environment. Sample 1 was subjected to the sequence of heating to 1095 K, with subsequent cooling to 313 K followed by reheating to 1273 K. Heating (q_{h1}), cooling (q_{c1}) and reheating (q_{h2}) were performed with $10\,K\,min^{-1}$. For calculation of heat capacities c_{p1} and c_{p2} of the first and second run, the baseline and a sapphire standard were measured as well. Samples 2 and 3 were subjected to a series of down- and upscans with rates 2.5, 5, 10, 20, 25 and $30\,K\,min^{-1}$ with preliminary heating of $10\,K\,min^{-1}$ for relaxation (heat release) and setting a desired cooling history. The cooling rate was always matching with following heating rate. Each experiment was conducted with upscans up to 1095 K (approx. 80 K above T_g) followed by cooling down to 723 K (approx. 290 K below T_g). All the upscans, except for the first, were used to determine the fictive temperatures T_f as extrapolated onset temperatures. These were computed graphically by determining the crossover temperature of two tangents aligned to the base and the decreasing flank of the endotherm, respectively. T_f of the as received GBS (first run) was also graphically computed but using the method of matching areas, which is described in detail elsewhere [15, 17]. To fit the heat capacity values in the glassy field best, a Maier-Kelley curve equation $c_{pg} = a + bT + cT^{-2} + dT^{-0.5}$ [25] was constructed. To obtain the total heat ΔH_{ex} that is released by the GBS, the area covered by c_{p2} and c_{p1} curves was calculated according to the left-hand side of Eq. (2).

3.2. Rheometry

Due to the proneness of GBS to crystallize the viscosity of GBS was measured by a Searle-type rotational rheometer (RV20, RC20, TP 1700, Haake, Karlsruhe, Germany) at temperatures above the liquidus. Approx. 68 g of GBS was placed into a PtRh10-crucible and heated up to 1730 K until the GBS was completely molten. Subsequently, a Pt-spindle was inserted into the molten GBS with the lower end of the rod about 2 mm above the bottom of the crucible. The spindle was then rotated and the shear stress as well as the shear rate were recorded at constant temperature of 1730 K. After the measurement the temperature was set subsequently to lower values and after temperature equilibrium the next measurement started until crystallization of the GBS was detected by strongly increasing values of the shear stress. The rheometer was calibrated by the standard glass G1 of the PTB (Physikalisch-Technische Bundesanstalt) [26]. For homogenous melts (crystal-free) the error in viscosity is ± 0.02 lg units [27].

4. Results

The thermal stability of GBS subjected to a first DSC upscan (heating rate $10\,K\,min^{-1}$) is illustrated in Fig. 1. The DSC curve consists of three well-defined signals (glass transition, crystallization, melting) that are characteristic for a glass that easily crystallizes during heating. After the