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SOLIDIFICATION OF MOLTEN ZINC CHLORIDE
Experimental and theoretical studies

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Solidification of molten zinc chloride was studied both experimentally and theoretically. By isothermal thermal analysis the time needed for the melt to crystallize at a given temperature ranging between 453 and 553 K was determined and the data obtained were compared with those of a calculated TTT curve. The extremum coordinates (temperature T_N, time t_N) of the curve, critical cooling rate v_{CR}, interfacial energy σ, and an additional parameter of kinetics barrier for nucleation ε were determined as T_N=508 K, t_N=7.29 s, v_{CR}=11.38 K s^{-1}, σ=0.11956 J m^{-2} and ε=0.5712. By non-isothermal method the critical cooling rate of glass formation was determined as 1.25 K s^{-1}.

Keywords: *construction of a TTT curve, isothermal and non-isothermal thermal analyses, transformation kinetics, zinc chloride solidification*

Introduction

The melts of some chemical elements and compounds undergo a phase transition and solidify into a crystalline form whereas others do not undergo any phase transition and transform into a glass-like aggregate state. However, there are also compounds that can form both glasses and crystals. The mode of solidification – vitrification or crystallization – depends on conditions of prevailing thermal melt treatment, first of all on the rate of the melt cooling. Glass formation is more probable at higher cooling rates when there is not enough time for bondings rearrangement and nuclei formation and at high melt viscosity when species mobility in the melt is reduced.

Such a compound which is able to form both crystalline and glassy states is zinc chloride – $ZnCl_2$. It is often designated as a strong or typical glass former which vitrifies even at a very low cooling rate [1]. This is supported by the well-known fact that its melt viscosity value is very high, almost 45 P at 593 K [2]. However, zinc chloride also crystallizes with the hexagonal symmetry and its network structure is broken up on melting and further heating with a production of species such as $[ZnCl_4]^-$ tetrahedrons and simple ions. The glassy zinc chloride is also formed by the above mentioned tetrahedrons and their network in comparison to the crystalline material is heavily damaged [2]. Both crystalline and glassy zinc chloride are strongly hygroscopic in air and show high transmittance in the near UV and the mid IR.

Glass forming ability is expressed by means of critical cooling rate v_{CR} [3]. It is the lowest rate at which glass can be formed. If the glass forming ability is higher, the glass formation is easier and the critical cooling rate is lower. This rate can be determined experimentally by methods of thermal analysis or theoretically by construction of the time-temperature-transformation (TTT) curve [3, 4]. TTT curves have been studied not only in inorganic systems but also in systems of polymer compounds [5].

The present paper deals with the study of molten zinc chloride solidification both experimentally by methods of thermal analysis under isothermal and non-isothermal conditions and theoretically by a construction of the TTT curve. The theoretical TTT curve is compared to the experimental data and the values of the interfacial energy σ and the kinetics barrier for nucleation E are searched for to get the best agreement with the experimental data. Moreover, the critical cooling rate, at which the molten zinc chloride is just transformed into a glass-like aggregate state, was determined and discussed within the framework of both experimental and theoretical results.

Theory

Phase transformation occurs by nucleation and growth process. Crystallized volume fraction X is given by

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$$X(t)=\frac{V(t)}{V_0}=1-\exp\left[\int_0^t I(t')v(t-t')\mathrm{d}t'\right] \quad (1)$$

where V_0 is the initial volume of the system, $V(t)$ the volume of the newly formed crystalline phase, I denotes the nucleation rate and $v(t-t')$ is the volume of the crystallization center at time t created at time t'. If one supposes that crystallization fraction is very small, ($X(t)$<<1), the interaction of crystallization centers can be neglected. Using the steady state approach for nucleation rate one gets [4]

$$X(t)=\frac{\pi}{3}Iu^3t^4 \quad (2)$$

where u is the growth rate of nuclei. It has been widely accepted that the border of the lowest detectable fraction $X=10^{-6}$ [4] and thus the product (Iu^3) of the stationary nucleation rate I and the growth rate u can be determined from Eq. (2) if the transformation time at a given temperature is known. According to the Turnbull and Fischer model [6] for the transient frequencies of attachment (detachment) of molecules on (from) the nucleus surface for liquid-solid transition the growth rate u is given by

$$u=N_\mathrm{S}\frac{m_1}{\rho}\left(\frac{k_\mathrm{B}T}{h}\right)\exp\left(-\frac{E}{k_\mathrm{B}T}\right)\left[1-\exp\left(-\frac{\Delta H_\mathrm{F}\,(T_\mathrm{M}-T)}{RT_\mathrm{M}T}\right)\right] \quad (3)$$

where N_S is the surface density of molecules, m_1 the molecular mass, k_B denotes the Boltzmann constant, ρ is the density of the solid phase, h the Planck constant, T the temperature, E denotes the activation energy of diffusion across the phase interface (so-called kinetics barrier of nucleation), ΔH_F is the heat of fusion (J mol^{-1}), T_M the melting temperature, R the gas constant, $N_\mathrm{S}\approx a_0^{-2}$, a_0 being the mean molecular distance in the solid phase.

Stationary nucleation rate can be determined from the following equation

$$I=k^+_{n^*}zF^0_{n^*} \quad (4)$$

where $k^+_{n^*}$ is the attachment frequency of molecules on the critical nucleus surface, z denotes the Zeldovich factor, n^* is the critical number of molecules in nucleus and $F^0_{n^*}$ the equilibrium number of critical nuclei (for details see [7]). Based on the model for transient frequency [6] and self-consistent classical model for equilibrium number of nuclei (SCC) the stationary homogeneous nucleation rate I may be written

$$I=N_0N_\mathrm{S}\frac{m_1}{\rho}\sqrt{\frac{4\sigma k_\mathrm{B}T}{h^2}}\exp\left(-\frac{E}{k_\mathrm{B}T}\right)\exp\left(-\frac{\Delta G_{n^*}}{k_\mathrm{B}T}\right) \quad (5)$$

where

$$N_0=N\exp\left(\frac{-\Delta\mu+\gamma\sigma}{k_\mathrm{B}T}\right) \quad (6)$$

N is the number of molecules in unit volume, σ the interfacial energy, γ denotes the form factor ($\gamma n^{2/3}$ is the surface area of nucleus formed by n molecules). $\Delta\mu$ is the difference of chemical potential of both phases and it is given by

$$\Delta\mu=\frac{\Delta H_\mathrm{F}}{T_\mathrm{M}N_\mathrm{A}}(T_\mathrm{M}-T) \quad (7)$$

where N_A is the Avogadro number. The energy barrier of nucleation ΔG_{n^*} is expressed as

$$\Delta G_{n^*}=\frac{16}{3}\pi\sigma^3\left(\frac{m_1}{\rho}\right)^2\frac{T_\mathrm{M}^2N_\mathrm{A}^2}{\Delta H_\mathrm{F}^2\,(T_\mathrm{M}-T)^2} \quad (8)$$

Experimental

Zinc chloride is strongly hydroscopic and so great attention was paid to the removal of water and other hygroscopic impurities from raw material. They were removed by halogenation of molten chloride by a mixture of halogenating agents and subsequent zone refining [8].

The solidification of molten zinc chloride was examined by a direct temperature measurement of a sample, about 10 g in mass, sealed in a special quartz ampoule. The scheme of the ampoule is shown in Fig. 1. The ampoule was 8 mm in inner diameter and 80 mm in length and during measurement it was placed in a vertical furnace. Temperature in the ampoule was measured by five thermocouples regularly located in a capillary tube along the ampoule axis. This arrangement enables us to scan temperature profile along the whole melt column. Due to temperature

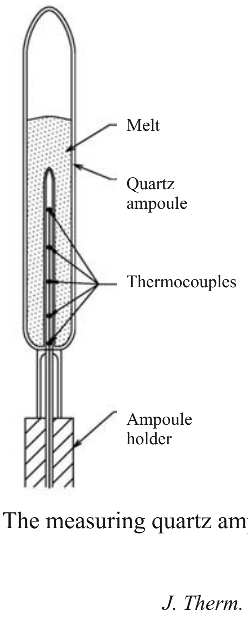

Fig. 1 The measuring quartz ampoule

changes its height moved between 30 and 40 mm. Two types of measurements – non-isothermal and isothermal ones were performed. In all measurements made, first the ampoule with the sample was heated with a heating rate of 40 K min^{-1} up to 916 K, melt overheating was 325 K and then the melt was homogenized at this temperature for 60 min. In the non-isothermal method the melt was cooled down with rates ranged between 0.1 and 6 K s^{-1} below supposed temperature of glass transition.

In the isothermal method the melt was quickly cooled down from the homogenization temperature to a given temperature below the melting point of zinc chloride and tempered at this temperature until the melt crystallized.

Temperature was measured and recorded at intervals of 1 s by a measuring Ahlborn 2290-8 Almemo unit.

Results and discussion

Theoretical construction of TTT curve

Theoretical construction of the TTT curve for zinc chloride solidification was based on computation of the time required to produce a crystallized volume fraction $X=10^{-6}$ at a given temperature according to Eqs (1), (3) and (5) and the aim was to find the best agreement with experimental data.

Problem how to choose unknown interfacial energy σ and kinetic barrier for nucleation E was solved in the following way: firstly, it was supposed that E is approximately equal to the activation energy of viscous flow E_V [9] and its value was calculated based on the relation

$$\exp\left(-\frac{E}{k_B T}\right)=\frac{h}{3\pi a_0^3 \eta} \qquad (9)$$

where η is the melt viscosity. Secondly, we introduced the parameter $\varepsilon=\exp(-E_0/k_B T)$, which is only a multiplying factor of nucleation rate I (Eq. (5)) and growth rate u (Eq. (3)). The justification of this was confirmed by the previous analysis of phase transformation process in the glass forming systems [10]. Temperature dependences of E and E_V are similar and both of energies are only shifted by some additional energy factor E_0, i.e. $E=E_V+E_0$ [10].

In the first step of calculation (no fitting of parameters) TTT curves were determined using approximation Eq. (9) for calculation of E from viscosity data. For the interfacial energy σ the following values 0.10, 0.11, 0.12, 0.13 and 0.14 J m^{-2}, constant in the temperature range in question, were used. For computation the values of the following parameters were chosen: T_M=591 K, ρ=2907 kg m^{-3}, N= $1.28\cdot10^{28}$ m^{-3}, $\Delta H_M=1.25\cdot10^5$ J mol^{-1}, $a_0=4.27\cdot10^{-10}$ m and viscosity data are given by $\log(\eta)=33.465-43872/T+1.5518\cdot10^7/T^2$ according to [11].

The results of the first computation – full lines for the individual σ values – are shown in Fig. 2 together with the experimental data (circles). The shape of the TTT curves strongly depends on the interfacial energy and it is seen that the set of the σ values was chosen quite appropriate [12]. The TTT curve for σ=0.12 J m^{-2} seems to give reasonable agreement with the experimental data.

In the other step a fitting procedure was applied and the additional parameter $\varepsilon=\exp[-E_0/k_B T]$ and σ were fitting parameters. The TTT curve obtained after fitting is shown in Fig. 3. All the obtained parameters (interfacial energy σ, additional parameter ε, coordinates of the extremum of the calculated TTT curve and critical cooling rate v_{CR}) are summarized in Table 1.

The critical cooling rate v_{CR} was calculated from the temperature T_N and the time t_N (coordinates of the

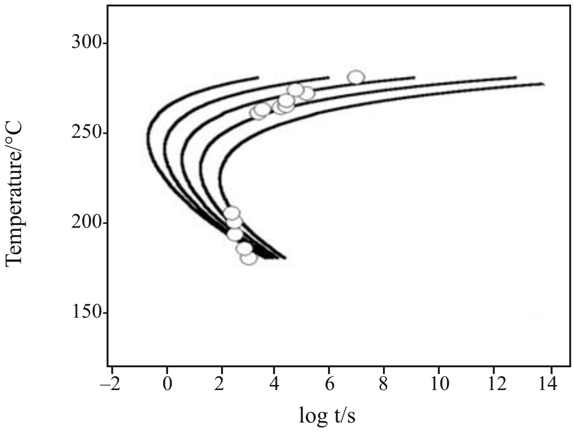

Fig. 2 Temperature *vs.* common logarithm of time (TTT diagram) for interfacial energy σ=0.10, 0.11, 0.12, 0.13 and 0.14 J m^{-2} (full lines from left to right). Circles correspond to the experimental data

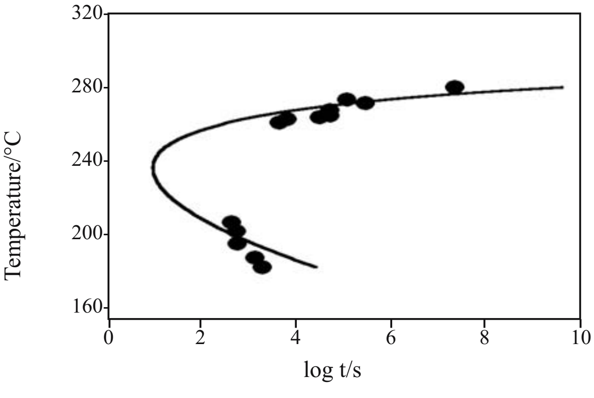

Fig. 3 Temperature *vs.* common logarithm of time for interfacial energy σ=0.11956 J m^{-2} and additional parameter ε=0.5712. Circles correspond to the experimental data

Table 1 Parameters of the $ZnCl_2$ TTT curve

σ interfacial energy/J m^{-2}	ε additional parameter	T_N temperature/K	t_N time/s	v_{CR} critical cooling rate/K s^{-1}
0.11956	0.5712	508	7.29	11.38

extremum of the TTT curve) according to the following formula:

$$v_{CR}=\frac{T_M-T_N}{t_N} \tag{10}$$

Interfacial energy σ depends on temperature due to changing surface structure of nuclei. However, this temperature dependence is unknown and so we decided to use the values of σ constant in the studied temperature range. In our opinion this approach is clearer from the physical point of view.

If one fits σ parameter at various temperature (i.e. temperature dependence of σ is taken into account) coincidence between experimental data and model could be better but such approach is rather disputable due to model limits (e.g. at higher supercoolings the time delay of nucleation increases with increasing viscosity and 'stationary' approximation to nucleation rate is rather problematic).

Experimental determination of TTT curve

In our isothermal study on the solidification of molten zinc chloride the time needed for the melt to crystallize at a given temperature was determined and compared with theoretical predictions. The measured time lags of crystallization *vs.* temperature are shown in Fig. 2 as circles. As the time lag determination at temperatures near to the extremum or nose of the TTT curve was next to impossible, two groups of data were obtained – the first one for the temperatures higher than that at the extremum and the other one for lower temperatures. As temperature decreases (at higher temperature set) the time needed for the melt crystallization shortens. Below the extremum temperature the time lag again increases.

Experimental determination of critical cooling rate

Critical cooling rate was also determined under non-isothermal condition. Figure 4 shows time dependences of temperature for five various cooling rates between 0.6 and 6.15 K s^{-1}, which unambiguously show if the melt crystallizes or vitrifies. The melt crystallizes at lower cooling rates (curves 1, 2 and 3) and there are effects connected with the crystallization heat release on the thermal analysis traces. At higher cooling rates, above 1.2 K s^{-1}, crystallization did not occur and the melt transformed into a glass-like aggregate state without any thermal effect. Based on all the performed measurements a cooling rate of 1.25 K s^{-1} was stated as the critical cooling rate for the formation of glassy zinc chloride. This cooling rate is a little less than that obtained from calculated TTT curve. The main reason is that in the former the data was measured under non-isothermal conditions, while in the later under isothermal ones.

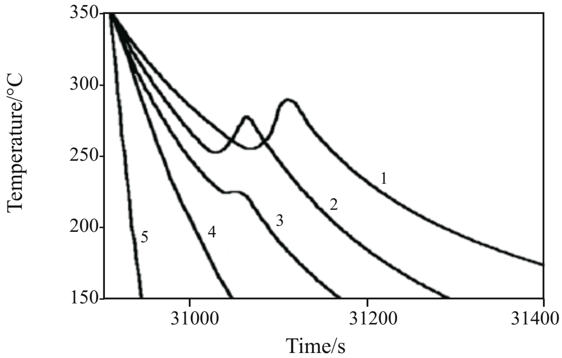

Fig. 4 The cooling curves for the following cooling rates: 1 – 0.6, 2 – 0.92, 3 – 1.17, 4 – 1.85 and 5 – 6.15 K s^{-1}

Conclusions

The mode of molten zinc chloride solidification – vitrification or crystallization – was studied both experimentally by methods of thermal analysis under isothermal and non-isothermal conditions and theoretically by computation of the TTT curve. Time needed for the molten $ZnCl_2$ to crystallize was determined by the isothermal method. Computation of the TTT curve was based on Uhlmann´s assumptions [4]. As some needed material parameters (activation energy for nucleation E and interfacial energy σ) were not known, they were determined by the following way: interfacial energy σ was taken as fitting parameter, which does not depend on temperature, and activation energy for nucleation E was determined from viscosity data. Moreover additional parameter $\varepsilon=\exp[-E_0/k_BT]$, which reduces the kinetic barrier of nucleation, was introduced. First, TTT curves were calculated for σ=0.10, 0.11, 0.12, 0.13 and 0.14 J m^{-2} constant in studied temperature range, without any fitting procedure of parameters. Second, interfacial energy σ and additional parameter ε were fitted to get the best agreement with the experimental data (σ=0.11956 J m^{-2} and ε=0.5712).

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