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Influence of Fermi energy equalization on crystal nucleation in glass melts

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Abstract: The energy saving produced by the equalization of Fermi energies of a crystal and a melt has been associated to the crystal formation in undercooled melts to determine the new homogeneous-nucleation critical-temperature T_2 and the new nucleation critical barrier as a function of the temperature T . Small unmelted clusters act as nuclei by reducing the critical energy barrier and the nucleation times; the glass transition temperature T_g occurs near $T=T_2$. The temperature dependence of the specific heat difference of the undercooled melt with the

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1- Introduction

Transformations liquid-solid are accompanied by changes of the conduction electron number per volume unit. The equalization of Fermi energies of a solid particle and of its melt produces an unknown energy saving ε_v equal to a fraction ε_{ls} of the fusion heat per volume unit. All crystal nucleation models have been built to describe the crystallization of all types of materials without taking account of ε_v in metallic alloys [1-3]. This contribution has been recently added to the Gibbs free energy change associated to a crystal formation in 38 liquid elements; tiny intrinsic crystals can survive above the melting temperature and act as heterogeneous nuclei for crystallization above a homogeneous-nucleation critical-temperature T_2 ; the thermal variation of ε_{ls} is an even function of θ having a maximum value $\varepsilon_{ls0}=0.217$ for $T=T_m$ in agreement with the thermodynamic equilibrium conditions and a zero value when the free volume of melts disappears [4-6].

The same analysis is applied to metallic glass-forming melts because large values of ε_{ls0} induced by large Fermi energy changes are expected due to weak localization of conduction electrons in the melts [7,9].

2- The crystal nucleation model completed

When the Gibbs free energy change for a crystal formation takes account of the energy saving $-\varepsilon_v$, the relations (1) and (2) are obtained for 38 liquid elements[4-6]:

$$\varepsilon_v = \varepsilon_{ls} \frac{\Delta H_m}{V_m} \quad \text{where} \quad \varepsilon_{ls} = \varepsilon_{ls0} \left(1 - \frac{\theta^2}{\theta_0^2}\right) \quad (1)$$

The new critical energy barrier $\frac{\Delta G_{2ls}^*}{kT}$ and the new critical radius $R_{2ls}(\theta)$ are equal to:

$$\frac{\Delta G_{2ls}^*}{k_B T} = \frac{16\pi\Delta S_m \alpha_{2ls}^3}{3N_A k_B (\theta - \varepsilon_{ls})^2 (1 + \theta)}; \quad R_{2ls} = -2 \frac{\alpha_{2ls}}{\theta - \varepsilon_{ls}} \left(\frac{V_m}{N_A}\right)^{1/3} \quad \text{where} \quad \alpha_{2ls} \Delta S_m^{1/3} = \left(\frac{12R}{432\pi}\right)^{1/3} \times (Ln K_{ls})^{1/3} (1 + \varepsilon_{ls}) \quad (2)$$

ΔS_m being the fusion entropy per mole, V_m the molar volume, N_A the Avogadro number, ΔH_m the fusion enthalpy per mole, $Ln[K_{ls}(T)] \leq 90 \pm 2$ or $(K_{ls} \leq 10^{39 \pm 1} \text{ m}^{-3} \cdot \text{s}^{-1})$, $\theta_0 = (T_0 - T_m)/T_m$, T_0 the disappearance temperature of the free volume and of ε_{ls} ; tiny crystals can survive above T_m up

to $\theta = \varepsilon_{ls}$. Their radius cannot grow because the critical barrier ΔG_{2ls}^* is diverging when θ tends to $\theta = \varepsilon_{ls}$ and is in fact reduced to a value smaller than the critical radius of liquid -droplet homogeneous - nucleation [6]; these nano-size crystals of radius R govern the crystallization for $0 > \theta > \theta_2$ because the homogeneous nucleation energy barrier $\frac{\Delta G_{2ls}^*}{kT}$ is reduced by the free energy saving $\frac{\Delta G_{nm}}{kT}$ due to the previous solidification of these intrinsic crystals of radius R_{nm} .

The contribution $\frac{\Delta G_{nm}}{kT}$ to the effective critical energy barrier is calculated using (3) [10]; its thermal variation is determined by the temperature dependence of the critical radius R_{2ls} ; R_{nm} is temperature independent as long as the nucleation time is not attained:

$$\frac{\Delta G_{nm}}{\Delta G_{2ls}^*(\theta)} = 3\left(\frac{R_{nm}}{R_{2ls}}\right)^2 - 2\left(\frac{R_{nm}}{R_{2ls}}\right)^3 \quad (3)$$

Assuming that the intrinsic nuclei are numerous, the nucleation rate $J \text{ m}^{-3} \text{ s}^{-1}$ is given by (4) [1-3, 17]:

$$\ln(J.v.t_{sn}) = \ln(K_{ls}.v.t_{sn}) - \frac{\Delta G_{2ls}^*}{kT} + \frac{\Delta G_{nm}}{kT} \quad (4)$$

J attains a maximum equal to 1 for $\theta_2 = (\varepsilon_{2ls} - 2)/3$ when the nucleation is homogeneous; θ_2 does not depend on $\ln[K_{ls}(\theta)]$ values. The steady-state nucleation time t_{sn} necessary to observe the first crystallization induced by a heterogeneous nucleation at a temperature T is given by $J.v.t_{sn} = 1$ where $J \gg 1$.

3- The glass transition

The ε_{ls0} values of glass-forming melts are deduced from the measured $\theta_g = (T_g - T_m)/3$ using $\varepsilon_{ls} = 3\theta_2 + 2$ where $\theta_2 = \theta_g$ or $T_2 = T_m[\varepsilon_{ls}(T_2) + 1]/3$ where $T_2 = T_g$. The K_{ls} value is equal to a constant $A\eta_0$ weakly varying with T divided by the viscosity η given by a Vogel-Fulcher Tammann (VFT) equation [10]. It is assumed that the free volume disappears at $T = T_0$ or $\theta = \theta_0$ as a consequence of the Doolittle relation between the viscosity and the free volume [10]; D^* is the glass fragility parameter. $\ln(K_{ls})$ is chosen equal to :

$$\ln(K_{ls}) = \ln\left(\frac{A\eta_0}{\eta}\right) = \ln A - \frac{D^* T_0}{(T - T_0)} \quad (5)$$

$\ln A$ is of the order of 90 and will be slightly varied. The values of T_m , T_g , θ_g , T_0 , θ_0 , D^* and ε_{ls0}^1 of some undercooled melts are given in Table 1.

Table 1

The melting temperature T_m , the glass transition T_g , The VFT temperature T_{0l} of the undercooled melt, the glass fragility D^* , $\theta_g = (T_g - T_m)/T_m$, $\theta_{0l} = (T_{0l} - T_m)/T_m$, the calculated nose temperature T_n , the electronic energy saving coefficient ε_{ls0}^l at $T = T_m$ associated to a crystal formation are given for various melts with references. $N^\circ 1 = Pd_{43}Cu_{27}Ni_{10}P_{20}$ ($A = 84$); $N^\circ 2 = Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ ($A = 84$); $N^\circ 3 = Mg_{65}Y_{10}Cu_{25}$ ($A = 86$); $N^\circ 4 = Nickel$ ($A = 90$).

N°	Ref.	T_m (K)	T_g (K)	T_{0l} (K)	D^*	T_n (K)	ε_{ls0}^l
1	[12,20]	802	585	452.3	9.14	726	1.93
2	[14,21]	937	625	412.5	18.5	800	1.55
3	[22]	739	420	260	22.1	565	1.27
		739	400	260	22.1	563	1.25
4	[15]	1725	425	575	0	575	0.217

The glass transition is accompanied by a free volume freezing and a thermal variation change of ε_v below θ_g as compared to that of the undercooled liquid; $\varepsilon_{ls}^l = \varepsilon_{ls0}^l [1 - (\theta/\theta_{0l})^2]$ will be changed in $\varepsilon_{ls}^g = \varepsilon_{ls0}^g [1 - (\theta/\theta_{0g})^2]$ with $\varepsilon_{ls}^l(\theta_g) = \varepsilon_{ls}^g(\theta_g)$, ε_{ls}^l and ε_{ls}^g respectively being the electronic energy saving coefficients in the undercooled liquid and in the glass; θ_{0l} and θ_{0g} respectively corresponding to the liquid and the glass VFT temperatures. The specific heat jump $\Delta C_p = C_p^l - C_p^g$ per unit volume can be calculated from the derivative of $(\varepsilon_v^l - \varepsilon_v^g)$:

$$\Delta C_p = C_p^l - C_p^g = \frac{d(\varepsilon_v^l - \varepsilon_v^g)}{dT} = \frac{2\Delta H_m \theta}{T_m V_m} [\varepsilon_{ls0}^g \theta_{0g}^{-2} - \varepsilon_{ls0}^l \theta_{0l}^{-2}] \quad (6)$$

it is a linear function of the temperature in agreement with measurements on $Pd_{43}Cu_{27}Ni_{10}P_{20}$ alloys [12].

Figure 1:

The calculated difference $\Delta C_p(T)$ between the glass specific heat C_{pg} and the specific heat C_{pl} of $Pd_{43}Cu_{27}Ni_{10}P_{20}$ undercooled melt extrapolated from $T_g = 585$ K down to $T_{ol} = 452.3$ K.

The parameters $\varepsilon_{ls}^g = 1.726$ and $\theta_{0g} = -0.484$ are determined by using the specific heat jump of 13 J/mole (0.177 J/g) at $T = T_g$ and by assuming that the glass transition does not produce any discontinuity of ε_{ls} . The jump ΔC_p is represented in Figure 1 as a function of θ only for $\theta_{0l} < \theta < 0$ because ε_{ls}^l stays equal to zero below $\theta = \theta_{0l}$. The theoretical thermal variation of ΔC_p given by (7) is in very good agreement with experimental measurements on $Pd_{43}Cu_{27}Ni_{10}P_{20}$ alloys:

$$\Delta C_p (J / g) = C_p^l - C_p^g = 0.644 - 0.000803 * T \quad (7)$$

A residual contribution linearly varying with the temperature below θ_g down to θ_{0l} is reproduced. The model also predicts a change of the VFT temperature of Pd-Ni-Cu-P glass from 452.3 K ($\theta_{0l} = -0.436$) to 413.8 K ($\theta_{0g} = -0.484$). A viscosity weakening below the glass transition has been already observed in some glasses [10, 22].

The glass transition has been defined by $T_g = T_2$ without special validation. The temperature θ_2 could be a little larger or smaller than θ_g instead of being equal. In the first case, the energy barrier increases and then decreases very quickly and could make the crystallization much easier; then, the glass transition has to be very close to θ_2 . In the second case, the VFT temperature T_{0g} is decreased as compared to the initial value corresponding to $\theta_g = \theta_2$ and then, the viscosity weakening is amplified. Measurements of viscosity below the glass transition and of the specific heat jump are necessary to evaluate any difference in this relation. The temperature T_{0g} has not to be too low as compared to T_{0l} because the viscosity would be too much weakened below T_g ; the relation $\theta_2 \cong \theta_g$ seems to be more compatible with few results already known [10, 22].

4- Temperature-Time-Transformation diagrams

The calculation of the nucleation time t of the first crystallization has to take account not only of the steady-state nucleation time t_{sn} but also of the time-lag τ_{ns} in transient nucleation [10] with:

$$t = t_{sn} + \frac{\pi^2}{6} \tau_{ns} \quad \text{when } t \gg \frac{\pi^2}{6} \tau_{ns} \quad (8)$$

$$J \tau^{ns} = \frac{a_0^* N}{2\pi \Gamma(z)} \exp\left(-\frac{\Delta G_{eff}^*}{kT}\right) \quad \text{where} \quad \Gamma(z) = \left(\frac{1}{3\pi kT} \frac{\Delta G_{2ls}^*}{j_c^2}\right)^{1/2}, \quad (9)$$

J is the steady-state nucleation rate equal to $(v \cdot t_{sn})^{-1}$, $\Gamma(z)$ the Zeldovitch-factor, $a_0^* = \pi^2 / 6$, N the atom number per volume unit, j_c the atom number in the critical sphere. The first crystallization occurs when $J = (v \cdot t_{sn})^{-1}$; t_{sn} can be calculated from (4) only when the sample volume v is known. The critical energy barrier is obtained by using (2) and the values of ε_{ls}^1 as a function of θ ; t_{sn} is deduced from (4) with $\ln(K_{ls})$ given by (5). The various parameters used in these calculations are given in Table 1. The time-lag is easily obtained when t_{sn} has been determined. The influence of τ_{ns} is very important near the glass transition. The calculated nose temperatures T_n of $Mg_{65}Y_{10}Cu_{25}$, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Pd_{43}Cu_{27}Ni_{10}P_{20}$ and Nickel melts are given in Table 1 in agreement with measurements.

$Pd_{43}Cu_{27}Ni_{10}P_{20}$

The isothermal- crystallization first-event of several mg samples have been studied by processing in B_2O_3 [13,16,20,23]; it is not reproducible above 700K because the contribution ΔG_{nm} is varying from sample to sample. The calculated TTT curves are reproducible below 700K when the nucleation time at the nose temperature is strongly varying; it is due to the large contribution of the time-lag τ_{ns} at lower temperatures.

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

The TTT diagram has been studied using a containerless electrostatic levitation technique [14]. The nose temperature and the nose time are 800 K and 70 s, respectively. Two TTT curves have been calculated by using the parameters given in Table 1, $A = 86$ and 90. They have respectively nose temperatures of 800 K and 745 K.

$Mg_{65}Y_{10}Cu_{25}$

The experimental TTT diagrams are easily reproduced by using sample volumes varying from $1.2E-9$ to $4E-10$ m³, $A=86$, $400 < T_g < 420$ K. The nose temperature is varying from 563 to 565 K [22].

Nickel

The liquid elements have $\theta_2 = -2/3$ or $T_2 = 0.333T_m$; the nickel glass transition T_g after a cooling rate of $3E+10$ K/s is equal to $0.246 \cdot T_m$ [15]. The glass transition is smaller than $0.33 \cdot T_m$ because the measurement time is too long compared to the cooling time. The TTT diagram calculated with $\ln K_{ls} = 90$ has a nose at $T_n = 0.333T_m$.

5. Conclusion

The glass transition T_g occurs near the new homogeneous-nucleation critical-temperature T_2 equal to $T_2 = T_m[\varepsilon_{ls}(T_2) + 1]/3$; values of ε_{ls0} are larger than 1 in bulk glasses [4-6]. It produces a free volume freezing [10, 18] and an increase of the electronic energy saving ε_v below T_g without step; ε_{ls}^l is continuously changed in ε_{ls}^g , ε_{ls}^l and ε_{ls}^g respectively being the electronic energy saving coefficients in the undercooled liquid and in the glass. The specific heat jump $\Delta C_p = C_p^l - C_p^g$ at $T=T_g$ of the $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ undercooled liquid is used to calculate $(\frac{d(\varepsilon_v^l - \varepsilon_v^g)}{dT})_{T=T_g}$ that is a linear function of T and the parameters involved in ε_{ls}^g . The theoretical thermal variation of ΔC_p is then in very good agreement with the experimental measurements of $\Delta C_p = C_p^l - C_p^g$ [12].

Large values of ε_{ls0} have been used to predict the nose temperature of TTT diagrams of Nickel, $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$, $\text{Mg}_{65}\text{Y}_{10}\text{Cu}_{25}$ [11-15]. They explain the critical cooling and heating rate variations, the magnitude order changes of the crystallization time by the existence of intrinsic heterogeneous nuclei which are not melted. Their presence is known since many years in spite of applying relatively large overheating [24-27].

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