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Parameters that determine the kinetics of glass formation in the presence of perturbing nanoparticles [1]

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Abstract

The hindering of crystallization upon the addition to metal alloys of perturbing nanoparticles is theoretically analyzed. It is shown that the effect of the particles is to add a surface energy term to the Gibbs energy of formation of the crystalline nucleus. This change in the Gibbs free energy slightly modifies the effective fusion temperature, but significantly changes the nucleation frequency. Besides this surface interaction, the particles introduce an additional effect, the reduction of the volume fraction occupied by the crystallizing phase. The effect of the perturbing particles is characterized by two independent parameters, the volume fraction of particles and another parameter that depends on the particle size, the interfacial energies between the particles and supercooled liquid, and the heat of fusion of the alloy.

Keywords: Fusion temperature; Glass formation kinetics; Hindrance of crystallization; Metal alloys; Nanoparticles; Nucleation frequency

1. Introduction

It is well known that the addition of a third element to a binary melt changes the glass-forming ability upon rapid cooling. This is because of the change in the Gibbs free energy arising from the interaction of the added element with the alloy and the resulting change in the liquidus temperature. It is the purpose of this paper to analyze the particular case in which there is a strong tendency to associate between the added

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element and one of the components of the binary alloy. In this case clusters appear already in the melt and the system can be described as a pseudobinary. A distinct situation appears as compared to complete or partial solutions, the clusters form nanoparticles that change the kinetics of crystallization of the remaining matrix.

In a recent paper [1] this situation was theoretically analyzed and it was shown that these clusters act as perturbing particles that affect the kinetics of crystallization due to an effective change in the melting temperature. This is not a change in the equilibrium melting temperature, it is a kinetic effect arising because the rapid cooling does not alow the nanoparticles to grow and segregate. Hence the particles must be embedded by the phase that is nucleating, introducing an additonal term in the Gibbs free energy that changes the melting temperature. This effective reduction in the melting temperature (for the rapid cooling condition) significantly modifies the nucleation frequency, and only slightly changes the crystal growth velocity. It was shown that even a small reduction of a few percent in the melting temperature can decrease the critical cooling rate for glass formation by orders of magnitude. The melting temperature shift was found to be proportional to the inverse of the size of the perturbing particles.

The model helped understanding the experimental results persented in references [2–5]. In the experiments the nanoparticles were formed by the addition of Sn or Pb to a glass-forming alloy containing Mg (Mg–Zn).

In this paper it will be shown that the perturbing particles not only modify the melting temperature, but also modify the critical nuclei size, thus having an even greater effect on the nucleation frequency. This increase in the size of the critical nuclei is due to the change in the Gibbs free energy of the undercooled nuclei when nanoparticles must be embedded. The hindering of the crystallization due to the effect of the perturbing particles is characterized by two independent parameters: the volume fraction of particles "f" and a coefficient "α" that depends on the particle size and the surface energy.

It is not the aim of our work to obtain precise numerical agreement but to present the simplest possible model in order to determine the dominant qualitative features controlling the critical cooling rate for glass formation. In this manner we expect to determine to which other alloys the scheme already used can be extended, and how to search for suitable elements that would act as perturbing nanoparticles. Many corrections to the model (for example transient nucleation) can be added at the expense of increasing complexity, but such corrections would be meaningless unless a precise description of the particle shape and size distribution is also added, a description that is not available at this stage.

2. Assumptions and approximations

We model the interaction of the added element with the melt by assuming all clusters are spheres of equal size and interact with the matrix through a surface energy term, as in our previous work [1]. This assumption is based on the following arguments that apply for the alloys used in the previously published experiments [2–5].

It is well established [6-10] that the tendency of Sn and Pb to associate with Mg is so strong that clusters of Mg_2Sn or Mg_2Pb already exist in binary and ternary melts. In the ternary as cast samples the Sn is detected only in the Mg_2Sn phase and in the rapidly cooled samples; from the Mössbauer spectra it was established that the Sn was located in a Mg_2Sn-type environment, even in the samples where the phase was not identified by X-ray diffraction [2,3]. Upon rapid cooling such clusters are retained without growing and conform to the perturbing nanoparticles only if Sn or Pb of the proper density is added. It was shown [4] that the optimum amount to be added is related to the fact that if the volume density of the clusters is so high they tend to touch each other, the Mg_2Sn or Mg_2Pb phases segregate as crystalline phases. The optimum was estimated to be a volume fraction $f = 0.05$ of particles that do not touch each other (obtained when the total volume of particles is $F = 1/8$), according to the model presented in Ref. [4].

In the previous theoretical work [1] it was determined that the clusters do not have a strong effect as grain growth barriers. In order for the nanoparticles to modify the nucleation frequency, the density should be large enough and the particles small enough that critical nuclei have a large probability of embedding one particle.

The average number of particles N of radius r_0 per critical nucleus volume of radius r_c is $N = f(r_c/r_0)^3$. With a volume fraction of nanoparticles $f = 0.05$, and for $r_c = 2r_0$ an average $N = 0.4$ results. The critical nucleus radius for the Mg_7Zn_3 phase is larger than 1.6 nm, estimated from known thermodynamic parameters [11] and using the approximation given by Hoffman [12] for the Gibbs free energy.

Although we could not measure the size of the Mg_2Sn clusters, a boundary can be estimated from the Mössbauer spectra that shows the Sn located in a Mg_2Sn-type environment with a broad peak indicating a disordered environment [2,3]. At the cooling rates employed the Mg_2Sn cannot be obtained in an amorphous state and the broadening of the Mössbauer peak must be due to Sn atoms located near the cluster surface. This fact would indicate the presence of a large fraction of atoms at the surface, consistent with the assumption that the clusters are 1.6 nm in diameter (clusters of about 80 atoms), i.e., about one half of the critical radius for the nucleation of the Mg–Zn phase.

Hence we will keep the approximations made in the previous work [1] where the particles were assumed identical and spherical of radius r_0 and only interact with the matrix through the surface energy σ_{cp} with the crystalline phase and σ_{1p} with the liquid. Hence the number of particles embedded by a nucleus is proportional to its volume. Under these conditions the particles introduce an additional surface to a nucleus with an area that increase linearly with the volume of the nucleus, as illustrated in Fig. 1. The free energy added appears then as volume free energy density that changes the melting temperature T_m to a new value T_{mn} given by [1],

$$T_{mn} \simeq T_m \left[1 - \frac{b'f}{r_0} \frac{1}{4/3\pi \Delta H_m (1-f)} \right] \tag{1}$$

where f is the volume fraction occupied by the particles, ΔH_m is the enthalpy of fusion (per unit volume of the crystal phase) of the matrix and $b' = 4\pi(\sigma_{cp} - \sigma_{1p})$ is determined

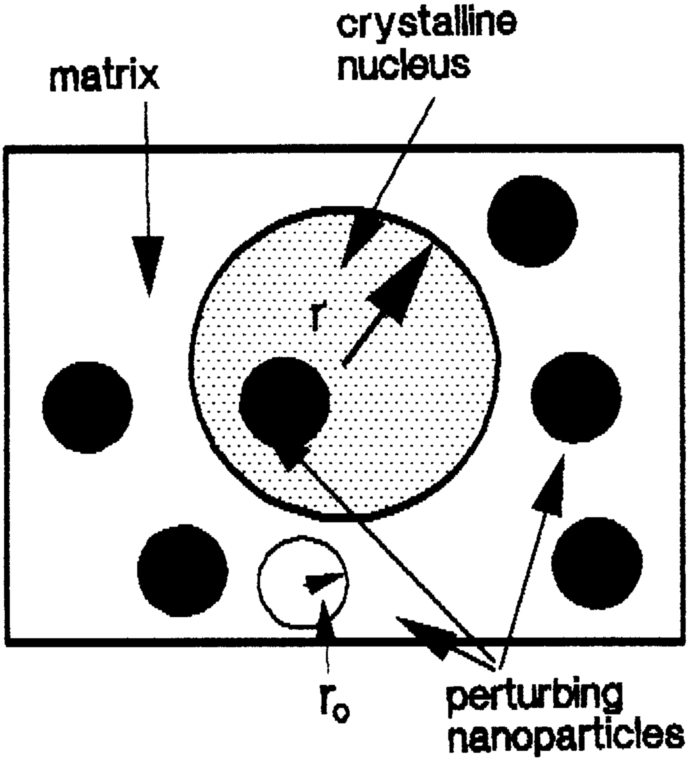

Fig. 1. Schematic drawing showing the hypothesis used in this work. The melted alloy consists of uniformly distributed clusters that act as perturbing particles modifying the crystallization kinetics of the matrix. All particles are assumed the same size. If the crystalline nucleus of radius r embeds a nanoparticle an additional Gibbs free energy term appears due to the surface interaction between the particle and the nucleus.

by the change in the free energy upon crystallization due to the distinct interaction between the particles and the crystalline and liquid phases. It is convenient to define a new parameter that characterizes the shift in the melting temperature of the alloy due to the addition of perturbing nanoparticles:

$$\theta_r = \frac{T_m - T_{mn}}{T_m} \tag{2}$$

From Eqs. (1) and (2) and the definition of b'

$$\theta_r = \alpha \frac{f}{(1-f)} \tag{3}$$

is obtained, where

$$\alpha = \frac{3p}{2r_0} \frac{(2\sigma_{1c})}{\Delta H_m} = \frac{3p}{2r_0} R_0 \tag{4}$$

R_0 is a parameter that depends on the alloy, and for metals is of the order of the mean atomic radius [13–15]. The parameter p is defined by:

$$p = \frac{\sigma_{cp} - \sigma_{1p}}{\sigma_{1c}} \tag{5}$$

The perturbing particles not only change the effective melting temperature but also increase the change in the Gibbs free energy of the crystalline nucleus as [1]:

$$\Delta G = [a(1-f) + b'f/r_0]r^3 + br^2 \equiv Ar^3 + br^2 \tag{6}$$

where the parameter a accounts for the volume energy of the crystalline phase of the remaining matrix; the term $(1-f)$ appears because that phase does not occupy the entire volume of the nucleus. The parameter b accounts for the surface energy from the interaction between the crystal and the liquid. The new critical nucleus will have a radius $r_{cn} = -2b/3A$, that in terms of the radius r_c in the absence of particles is:

$$r^+ = \frac{r_{cn}}{r_c} = \frac{1}{(1-f)\left[1 - \frac{\alpha f}{(1-f)} \frac{1}{\Delta T_r T_r}\right]} \tag{7}$$

where $T_r = T/T_m$ and $\Delta T_r = 1 - T_r$ and the approximation given by Hoffman [12] has been used for the temperature-dependence of the volume free energy:

$$\Delta G_v = \Delta H_m \Delta T_r T_r \tag{8}$$

From Eq. (7) is results that for $\alpha > 0$ ($\theta_r > 0$) then $r^+ > 1$. Hence the critical radius increases with the addition of perturbing particles, reducing the nucleation rate.

In order to compute the nucleation rate, the change in the Gibbs free energy upon the formation of a critical nucleus must be recalculated. Replacing Eq. (7) in (6) gives:

$$\Delta G_{cn} = \Delta G_c (r^+)^2 \tag{9}$$

and using the expression given by Davies [16] for ΔG_c (as used in [1]):

$$\frac{\Delta G_{cn}}{RT} = \frac{1.07}{(T_r)^3 (1-f)^2 [\Delta T_r - \theta_r/T_r]^2} \tag{10}$$

In order to compute the crystal growth rate the temperature-dependence of the volume free enegy must be computed; combination of Eqs. (2) and (6) gives:

$$\frac{-\Delta G_{vn}}{RT} = -\frac{\Delta H_m (1-f)}{R T_m} \left[\Delta T_r - \frac{\theta_r}{T_r}\right] \tag{11}$$

3. Results

The new expressions for the Gibbs free energy can be used in the usual manner [16] to compute the time, t, required in order to crystallize a given fraction X of the material with a nucleation frequency I and a growth rate u (TTT curves) as:

$$t \simeq \left[\frac{X}{Iu^3}\right]^{1/4} = \frac{K_0\eta}{T}\left[\frac{\exp\left[\frac{\Delta G_{cn}}{RT}\right]}{\{1-\exp[-\Delta G_{vn}/(RT)]\}^3}\right]^{1/4} \tag{12}$$

where η is the viscosity, computed using the Vogel–Fulcher approximation [1], and K_0 is a constant that depends on the material and is irrelevant to the computation of the relative changes in the critical cooling rates due to the addition of nanoparticles.

Using Eqs. (10)–(12) gives:

$$t = \frac{K_0\eta}{T}\left[\frac{\exp\left[\frac{1.07}{T_r^3(1-f)^2[\Delta T_r - \theta_r/T_r]^2}\right]}{1-\exp\left[-\frac{\Delta H_m(1-f)}{RT_m}\left(\Delta T_r - \frac{\theta_r}{T_r}\right)\right]^3}\right]^{1/4} \tag{13}$$

The curves of t vs. T (TTT curves) have a nose with a minimum time t_n at a temperature T_n that are used to compute the critical cooling rate as $R_0 = (T_{mn} - T_n)/t_n$. This is the minimum cooling rate such that the cooling curve does not touch the TTT curve. In Figure 2 an example is shown of the shift of the TTT curves as the volume fraction f is increased for a fixed value of the parameter α defined in Eq. (4).

The change in the critical cooling rate with the addition of particles is controlled by two independent parameters, the volume fraction of particles f and the parameter

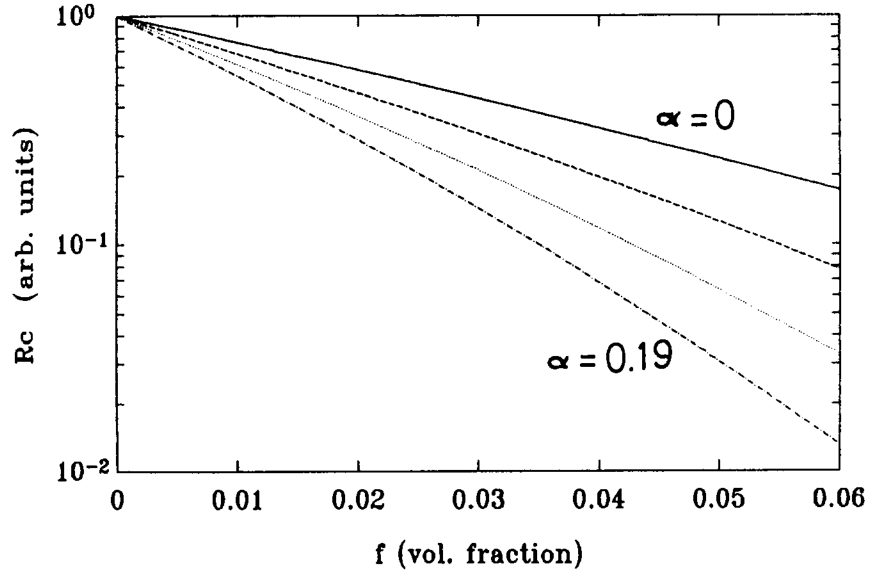

Fig. 2. TTT (time-temperature-transformation) curves obtained from Eq. (13) showing the shift in the position of the nose as the volume fraction of perturbing particles is increased. From left to right f increases in equal steps from $f = 0$ to $f = 0.125$. The parameter $\alpha = 0.07$ was kept constant for all curves. As only the relative change in the critical cooling rate is computed, arbitrary units can be used for time.

α defined by Eq. (3). These two parameters determine the reduced melting temperature T_r and the new critical radius of the nuclei r_{cn}. The parameter f depends on the amount of particles added, and can be controlled experimentally in a continuous manner, while the parameter α depends on the size and type of particle Eqs. (3) and (4). The size cannot be controlled experimentally with the production technique described in Refs. [2–4]. An order of magnitude estimate for α can be made using the relationship $\sigma_{1c}/\Delta H_m = 0.45\,\Omega^{1/3}$ [14,17] where Ω is the atomic volume. Assuming $p = 0.2$ as discussed in Ref. [1], and for $\Omega = 0.02\,\text{nm}^3$ [11], $\alpha = 0.09$ is obtained for a particle radius of $r_0 = 0.8\,\text{nm}$.

From the TTT curves the critical cooling rates (R_c) for the production of glass were computed. The results are shown in Fig. 3, where the cooling rate is given in units of the cooling rate in absence of particles (R_c for $f = 0$). The critical cooling rate was computed as a function of the fraction f for different values of the parameter α between 0 and 0.19. This last value is chosen such that a melting temperature shift of 1% is obtained when $f = 0.05$. The fraction $f = 0.05$ corresponds to the maximum volume fraction of particles that do not touch each other (obtained when the total volume of particles is 1/8), according to the model presented in Ref. [4]. In this figure it can be seen that even with small changes in the fusion temperature, large changes in the critical cooling rate can be achieved. The curves were computed using for the thermodynamic magnitudes ΔH_m and T_g the values that correspond to the phase Mg_7Zn_3 [11] that corresponds to the alloy used in the experiments described in Ref. [2–4].

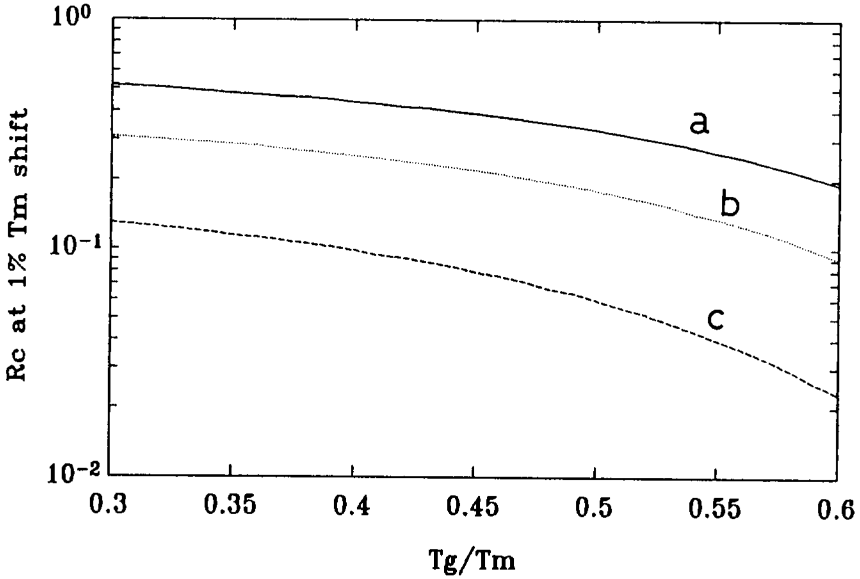

Fig. 3. Critical cooling rate for glass formation as a function of the volume fraction of perturbing particles. The cooling rate is relative to the critical cooling rate when no particles are added. The curves correspond to values for the parameter α (that depends on the interaction between particles and melt) equally spaced increasing from top to bottom, ranging from $\alpha = 0$ to $\alpha = 0.19$.

Fig. 3 shows that the two parameters f and α are relevant to the hindering of the crystallization, while in Ref. [1] only one parameter was used, i.e. the relative melting temperature shift θ_r. As θ_r depends on a particular combination of the two parameters α and f (Eq. (3)), in Fig. 4 a new set of curves were computed in order to show that besides the change in the effective fusion temperature, other factors determine the change in the critical cooling rate. The change in the critical cooling rate was computed as a function of the relative glass transition temperature T_g/T_m keeping constant the other thermodynamic magnitudes that characterize the alloy. This is a simple way to model the hindering action of the particles for alloys with different glass-forming ability (recall that easy glass-formers have larger T_g/T_m). The three curves correspond to the same melting temperature shift $\theta_r = 0.01$, for two values of f (0.01 and 0.05) and the curve obained for the model presented in Ref. [1] where only one parameter (θ_r) appears.

4. Discussion

The results presented in Fig. 3 show that the critical cooling rate decreases uniformly with increasing volume fraction f and the parameter α. The volume fraction cannot be

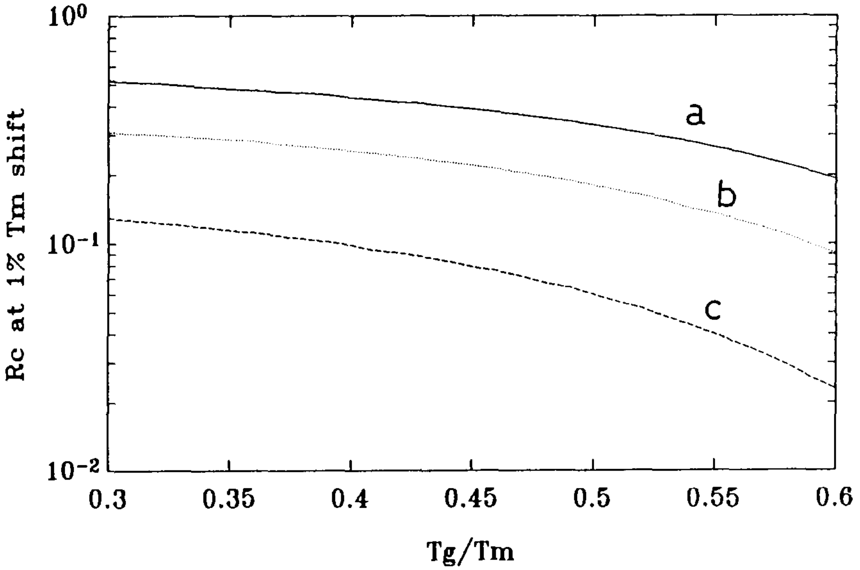

Fig. 4. Relative critical cooling rate as a function of the ratio between the glass transition temperature T_g and the melting temperature T_m. All curves correspond to a relative shift in the melting temperature $\theta_r = 0.01$; (a) obtained with the model of Ref. [1]; (b) model of this work with a volume fraction of particles $f = 0.01$. (c) as for (b) but with $f = 0.05$.

increased indefinitely with the experimental technique proposed in previous work [2–4]. Above a certain value the perturbing particles touch each other and the corresponding phase segregates [4]. A simple model [4] shows that the volume fraction that maximizes the number of particles that do not touch any other is 1/8, and then the maximum volume fraction of those particles that do not touch others is $f = 0.05$. This sets a limit on the parameter f, assuming that, because the hindering action of the particles is very sensitive to the particle size, the particles that touch others grow and can be neglected. The parameter α can be increased by reducing the particle size, as well as the type of particles, but the range that can be covered is probably relatively narrow. No experimental results have been reported in this direction.

The fact that the change in the fusion temperature (θ_r) is not the only relevant parameter is evident (see Fig. 3) from the fact that for $\alpha = 0$ ($\theta_r = 0$) a significant reduction of the critical cooling rate is obtained. If the same temperature shift (Eq. (3)) is obtained with a larger volume fraction, the reduction in the critical cooling rate is larger, as can be seen in Fig. 4 (notice the logarithmic scale). This fact can be understood by inspecting Eq. (10), where the change in the critical nucleus size given by Eq. (7) has been included in the nucleation free energy. The change in the critical size has two contributions, one of them arises from the extra surface energy from the interaction of the particles with the matrix and determined by θ_r. But even in the case in which $\alpha = 0$ (hence $\theta_r = 0$) there is an increase in the critical nucleus not arising from the interaction with the particles but because the matrix that crystallizes occupies only $(1 - f)$ of the nucleus volume. This reduces the change in the volume free energy upon crystallization and this effect is described by the term $(1 - f)$ in Eq. (7) that appears as $(1 - f)^2$ in Eq. (10).

Taking into account both parameters, the dependence of the hindering action on the glass transition temperature is qualitatively similar to that reported in Ref. [1], i.e. easy glass-formers are more sensitive to the addition of particles.

5. Conclusions

The effect of the perturbing particles is to add a surface energy term to the nucleation free energy. Such a term is proportional to the volume fraction of particles and to the inverse of the particle radius, and increases with the surface energy between the perturbing particles and the crystalline phase being hindered. This change in the Gibbs free energy slightly modifies the effective fusion temperature, but has a large effect on the nucleation frequency. A small reduction of only 1% in the fusion temperature can change the critical cooling rate for the glass formation by orders of magnitude.

It has been shown that this additional surface energy is not the only effect determining a change in the critical cooling rate. Even in the extreme of inert particles with no surface interaction, a change in the critical cooling rate appears as a result of the reduction in the volume fraction that the crystallizing matrix occupies. Hence the effect of the perturbing particles can be described by two parameters, the volume fraction "f" and the coefficient "α" defined in Eq. (3). The particle size and the surface energy appear only in the parameter α, which must be made as large as possible.

As a last comment we wish to mention that if instead of the approximation given by Hoffman [12] one uses other approximations for the temperature-dependence of the Gibbs free energy [18–20] somewhat smaller changes in the critical cooling rates are obtained but the orders of magnitude and the conclusions drawn do not change.

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