

Chapter 15

Comments on DTA/DSC Methods for Estimation of Crystal Nucleation Rates in Glass-Forming Melts

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*Adapted from Journal of Non-Crystalline Solids, vol. 356,
Vladimir M. Fokin, Aluísio A. Cabral, Raphael M.C.V. Reis,
Marcio L.F. Nascimento, Edgar D. Zanotto, Critical assessment
of DTA–DSC methods for the study of nucleation kinetics in
glasses, pp. 358–367, Copyright (2010), with permission from
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15.1 Introduction

Detailed information about crystallization kinetics is important for glass-ceramic (GC) production, which, in most cases, is based on controlled internal crystallization. In this context, kinetic parameters such as crystal nucleation rate and time-lag (or induction period) for nucleation are of great interest because they can be used to define the crystal number density, N (nuclei/m³), which in turn limits the maximal average size, \bar{R}_{\max} , of the crystals in the resulting microstructure. Both quantities determine, to a great extent, the properties and applications of GCs. The traditional method to estimate the number density of nucleated crystals (supercritical nuclei) consists of the development of these nuclei at a relatively high temperature (higher

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J. Šesták and P. Šimon (eds.), *Thermal Analysis of Micro, Nano- and Non-Crystalline Materials*, Hot Topics in Thermal Analysis and Calorimetry 9,
DOI 10.1007/978-90-481-3150-1_15,

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than the previous nucleation temperature) up to a detectable size by optical or electron microscopy [1]. This method, developed by Gustav Tammann (Tammann's method) more than 100 years ago to measure crystal nucleation rate in organic liquids [2], was successfully applied to inorganic glasses for the first time by Ito et al. [3] and Filipovich and Kalinina [4]. It provides an estimation of the number of supercritical nuclei needed for the determination of the steady-state nucleation rate and the time-lag for nucleation. However, Tammann's method is laborious because it includes image analysis of crystallized samples. The foregoing method is valid for the cases of stoichiometric (when crystal and glass have the same composition) and nonstoichiometric crystallization.

Qualitative studies of crystallization kinetics using differential thermal analysis (DTA)/differential scanning calorimetry (DSC) techniques, widely used in laboratory practice, can be quite useful because they provide swift information about characteristic temperatures, such as the glass transition temperature, T_g , the crystallization peak, the *liquidus*, and sometimes the number of crystalline phases.

Beginning in the 1980s, semi-quantitative and quantitative methods based on DTA/DSC experiments have been developed for the study of glass crystallization kinetics ([5–10]). Because DTA/DSC equipments are handy and, as claimed by Ray et al. [9], “*The DTA technique is less tedious, requires a smaller amount of sample, and is at least 10 times faster than the conventional methods,*” DTA/DSC methods have been widely used. In the present chapter we want to bring the researcher's attention to some problems of DTA/DSC methods and to caution them against its “automatic” application. For this purpose, the main assumptions underlying the DSC/DTA methods are experimentally tested, and the values of nucleation rates are estimated by thermal analyses and optical measurements for glasses of the same melt.

15.2 Brief Description of Nonisothermal Methods to Study the Crystallization Kinetics

As opposed to Tammann's method, the nonisothermal (DTA/DSC) methods are concerned with the overall crystallization kinetics and can be divided into two types.

- (I) The first type allows one to plot a curve of similar temperature dependence as the nucleation rate, but not the actual values. This type of nonisothermal method is based on the reasonable assumption that the inverse temperature of the crystallization peak, $1/T_c$, on a DSC/DTA curve, is proportional to the number density of nuclei, N [5], because the higher the N , the faster the overall crystallization kinetics and, hence, the release of the crystallization heat can be detected at lower temperatures. Therefore, a plot of $1/T_c$ versus the temperature of nucleation treatment, T_N , for a given time may reflect the temperature dependence of the nucleation rate or, more exactly, of the crystal number density nucleated in a given period of time. Sometimes the height of

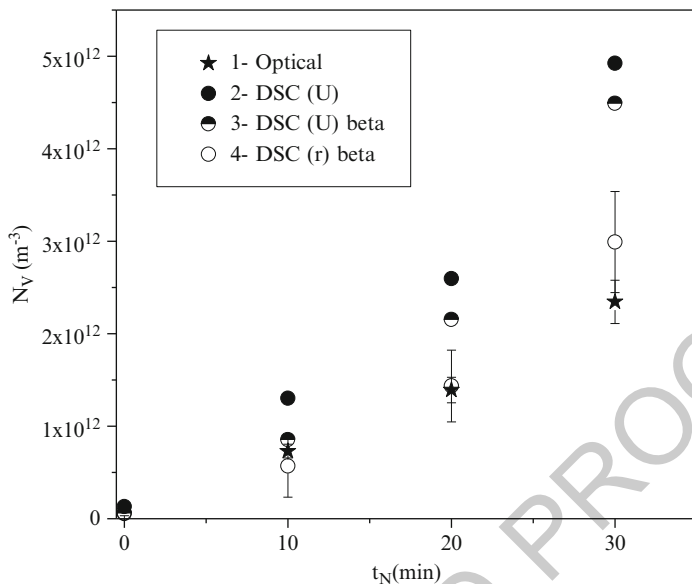


Fig. 15.16 Crystal number density in L_1S_2 glass versus time of nucleation at $T_N = 480^\circ C$ obtained by different methods: 1 optical microscopy, 2 DSC method by Eq. (15.10), 3 Eq. (15.12), 4 Eq. (15.15)

adequate values of t_N and t_G , one needs to have some idea about the nucleation rate 457
to avoid total crystallization of the sample or a too weak change in the crystallization 458
peak area. Moreover, one has to know the value of the crystal growth rate at T_G and 459
the crystal shape. Finally, the preparation of bulk samples with regular shape is quite 460
laborious compared to the preparation of a powder, but the use of powders results in 461
important and unaccountable errors caused by surface crystallization. 462

15.9 Conclusions 463

We tested two DSC/DTA methods against the traditional microscopy method to 464
estimate the temperature range of the nucleation rate maximum and the number of 465
supercritical crystal nuclei. The dependence of the DSC/DTA crystallization peak 466
position on the number of preexisting nuclei is not linear. This fact together with 467
non-steady-state nucleation (which is always significant at some temperature range 468
below or just above the glass transition temperature) distorts the real temperature 469
dependence of the nucleation rate when one employs the shift of crystallization 470
peak method. 471

The ratio between volume and surface crystallization depends not only on the 472
sample size, but also on the number density of internal crystals. The role of surface 473

crystallization is more pronounced when the number of internal crystals is small, for example, in the case of athermal crystals. Hence, particle size alone is not sufficient to account for the relative importance of surface crystallization. Also, crystal growth in the nonisothermal regime can have a significant effect on the calculated crystal number density and nucleation rates. The area of a DTA/DSC crystallization peak can be affected by the formation of nonequilibrium phases or by elastic stresses. All these factors make an accurate analysis of nucleation kinetics by DSC/DTA methods difficult.

Finally, one needs preliminary data on the nucleation and growth rates of the studied glass to take into account all the foregoing effects when employing DTA/DSC methods to determine nucleation kinetics. Only when such nonisothermal methods are properly employed can they give useful kinetic information, which includes the crystal number density and nucleation rates, but they are as laborious as the traditional microscopy methods!

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