NANO-GLASS CERAMICS

Processing, Properties and Applications

Vahak Marghussian

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VAHAK MARGHUSSIAN

School of Metallurgy and Materials Engineering
Iran University of Science and Technology (IUST)
Tehran, Iran

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NANO-GLASS CERAMICS

PREFACE

The nano-structured materials today are the cutting edge of modern advanced materials development. Among these materials, nano-structured glass ceramics, or **nano-glass ceramics**, possessing uniformly dispersed crystals <100 nm in size, have become established in various technical and domestic applications and also offer great promise for many potential new applications. These applications are widely varied, including thermally resistant cookware and radiant stove tops, telescope mirror blanks, radoms, and biomedical materials. They are also very promising candidates for many optical, optoelectronic, and electromagnetic applications, such as lasers, optical amplifiers, solar cells, information storage systems, and ferrofluid technology.

It seems that despite the great potential of the nano-glass ceramics, the importance of these materials has not appreciated enough. No book has been published yet, dealing with these materials.

Hence, this book has been written to fill this gap. It provides detailed coverage of the synthesis and processing methods of nano-glass ceramic materials, their selected properties, and the present and future applications.

In writing this book, while both the theoretical and practical aspects of the subject have been considered, the emphasis has been placed upon the experimental and practical aspects of the subject. The methods of investigation adopted in various stages of synthesis and processing of glass ceramics by researchers and the current state of art in developing nano-structured glass ceramics have been discussed in detail.

Throughout the discussions, wherever possible, the material scientist's point of view regarding the relationship between properties and the parameters of synthesis as well as the microstructure and properties of the resulting glass ceramics has been adopted.

In the discussion of the application of nano-glass ceramics, considerations were given to both the fields of application in which the materials are firmly established as well as the fields where great promise exists for their future exploitation.

While it has been tried to avoid deep scientific discussions, the basic principles of glass science, especially the subject of nucleation and crystallization in glass, have been utilized in

many discussions. Hence, prior knowledge of the glass science, at an introductory level, would help better understanding the subjects discussed here. For the readers with little or no prior knowledge in glass science, the existing textbooks in glass science may be useful in providing the necessary background of the subject.

This book appeals to the graduate students of materials science and engineering, ceramics, and nano-science and nano-technology courses. The application-oriented perspective of the book also makes it suitable for engineers and especially younger researchers who are interested in nano-structured materials. The newcomers of the research field of nano-glass ceramics may find the numerous practical examples and the details of experimental methods represented in the book useful in entering the new field.

INTRODUCTION

By definition, glass ceramics are engineering materials that are first prepared as glass and then are subjected to a carefully controlled heat-treatment procedure in order to convert them to fully or partially crystalline materials. With selecting appropriate glass compositions and controlling crystal nucleation and growth processes in the glass, glass ceramics with tailor-made properties can be fabricated. The development of practical glass ceramics is relatively recent. As far as we know, Re'aumur, a French chemist, was the first person to produce practical glass ceramics. He showed that if glass bottles were heat-treated in a bed of gypsum and sand mixture for several days, they would be converted to a porcelain-like opaque object. Although Re'aumur succeeded in converting glass to a "glass ceramic" material, unfortunately the low strength and deformation of the new product was frustrating for him. Some 200 years after Re'aumur's experiment, S.D. Stookey of Corning Glass Works (Corning, NY) in the United States made an important discovery when one of his photosensitive glass specimens, that was to be opacified by irradiation, was accidentally subjected to a higher than usual temperature during heat treatment; it was converted to an opaque ceramic material, the first true glass ceramic, exhibiting much higher mechanical strength than the original glass, with no distortion. This experiment opened the way for the development of other types of nucleation agents that did not require irradiation of the glass and eventually led to the commercialization of the first glass ceramic product "pyroceram" by Corning Glass Works.

Tremendous developments have occurred in the field of glass-ceramic research and technology since Stookey's pioneering work five decades ago. Today glass ceramics have become established in a wide variety of technical and domestic applications ranging from thermally resistant cookware and radiant stove tops to telescope mirror blanks and radoms and from tiles and artificial stones to biomedical materials and, more recently, as quite interesting potential candidates in some electromagnetic and optoelectronic applications. This can be explained by the nature of the glass ceramic production route that is based on the easier, faster, and less expensive technology of glass manufacturing method. In addition to the ease of fabrication process and higher automation, glass ceramics also possess a uniformity of microstructure and subsequent reproducibility of

properties that result from the homogeneity of the starting glass. Usually the conversion of glass into glass ceramic involves only minor overall volume changes with zero or little porosity which is essential for some applications. Furthermore, glass ceramics provide a wide range of physical and chemical properties that often are not readily obtained in glasses or ceramics. The method of glass ceramic fabrication has its own limitations. It is limited to the materials that relatively easily and at reasonable temperatures can be melted and formed as glass and in subsequent heat treatment in a controllable manner converted into glass ceramics.

Among various types of glass ceramics, **nano-glass ceramics**, containing tiny crystals of <100 nm, are currently utilized in many products and offer great promise for many potential new applications.

Some nano-structured transparent glass ceramics possessing high thermal stability and thermal shock resistance are currently used in high optical applications, such as telescope mirror blanks, cookware, radiant stove tops, and fire doors. Other types of transparent glass ceramics, based on mullite, are considered as host media for luminescent transition metal ions, especially Cr^{3+}, for potential uses in certain fields, such as solar concentrators and tunable lasers. Applications have also been anticipated for nano-structured spinel glass ceramics as optical amplifiers and passive Q-switchers in lasers.

Oxyfluoride glass ceramics have potential applications in the field of up-conversion lasers, fiber amplifiers, and the optical devices for three-dimensional displays.

Nano-structured, transparent glass ceramics containing alkali niobate ferroelectric crystalline phases, because of their large electro-optic effect and strong second harmonic generating ability have great promise in many applications in the fabrication of optical waveguides, modulators, switches, and optical circuits.

Nano-crystalline glass ceramics with high elastic modulus and moderate strength and toughness, based on spinel and enstatite phase assemblages, have been developed for potential use as magnetic disk substrates in computer hard drives. The preparation of nano-crystalline glass ceramics for biomedical application has also attracted considerable attention in recent years as coatings, orthopedic devices, dentistry, as well as magnetic nano-glass ceramics for therapeutic (e.g., hyperthermia and drug-targeting) and diagnostic (e.g., magnetic resonance imaging) applications.

This book covers the details of processing, properties, and application of the most important types of nano-glass ceramics, as known at the present time.

CONTENTS

GLASS CRYSTALLIZATION

Glass ceramics are materials composed of one or more glass and crystal phases. By preparing base glasses with appropriate compositions and by controlling crystal nucleation and growth in these glasses, glass ceramics with tailor-made properties can be fabricated. The key to preparing these types of materials, especially nano-glass ceramics, is the control of the nucleation process. Nucleation is followed by one or more higher-temperature treatments, usually called growth process, to promote crystallization of

the primary phase or phases and development of the desired microstructure. As stated above, the first step in the glass crystallization process which is critical in preparing nano-glass ceramics is the nucleation process.

1.1   Nucleation in Glass

Although it is not the intention in the present book to cover comprehensively the details of all aspects of crystal nucleation in glass systems; however considering the importance of the nucleation process in nano-glass ceramics fabrication and properties, it is felt that the presentation of a brief discussion on nucleation is essential here.

In the last three decades or so, numerous publications including many excellent books, review papers, and proceedings of international conferences on crystallization of glass, in general, and nucleation, in particular, have appeared in the literature. Some of the most important ones that can be recommended for further reading are: McMillan (1979), Strnad (1986), Höland and Beall (2002), James (1982, 1985, 1989), Beall (1993), Zanotto (1994), and Uhlmann and Uhlmann (1993).

In a homogeneous liquid or glass, crystallization starts with nucleation, i.e., the formation of crystal-like fluctuations/ clusters that are able to grow further. Owing to the excess free energy of the crystal/liquid interfacial layer, the free energy of the smallest fluctuations is positive and has a maximum as a function of size. The clusters, smaller than the corresponding critical size, decay with a greater probability than the larger ones, which grow and reach a macroscopic size. The free-energy maximum represents the thermodynamic barrier the system has to pass before forming the crystalline phase.

The appearance of crystalline fluctuations may be catalyzed by foreign particles, container walls, and oxide layers on a surface, a process known as "heterogeneous nucleation."

In the preparation of glass articles, where the formation of nuclei and their subsequent growth to crystals must be avoided, knowing the nucleation rate of crystalline solid phases in glass-forming melts at different temperatures has great practical importance. On the other hand, in preparation of glass ceramics, and especially nano-glass ceramics, which is to be fabricated with tailor-made properties, only achievable by the strict control of microstructure, the knowledge on nucleation mechanism and kinetics is even more critical.

1.1.1 Homogeneous Nucleation

1.1.1.1 Theoretical Background

Homogeneous nucleation supposes the same probability of critical nucleus formation in any given volume or surface element of the system under study.

Tammann (1925) in his classical studies on the crystallization of supercooled liquids showed that below the equilibrium melting temperature, there exists a metastable temperature interval in which nuclei do not form at a detectable rate. In this zone, however, crystals can grow if nuclei are provided, i.e., if the melt is seeded.

At temperatures below this region, the crystallization process is controlled by the rate of formation of nuclei and the crystal growth rate. Melts exhibiting rapid increase in viscosity during cooling show maxima in nucleation and crystal growth rates. This is because of the fact that at the lower temperatures, the high viscosity hinders the atomic rearrangements and diffusion processes which are necessary for nucleation and crystal growth (McMillan, 1979). These melts normally show high glass-forming tendencies. Curves representing nucleation and crystal growth rates for viscous melts have the forms shown in Figure 1.1.
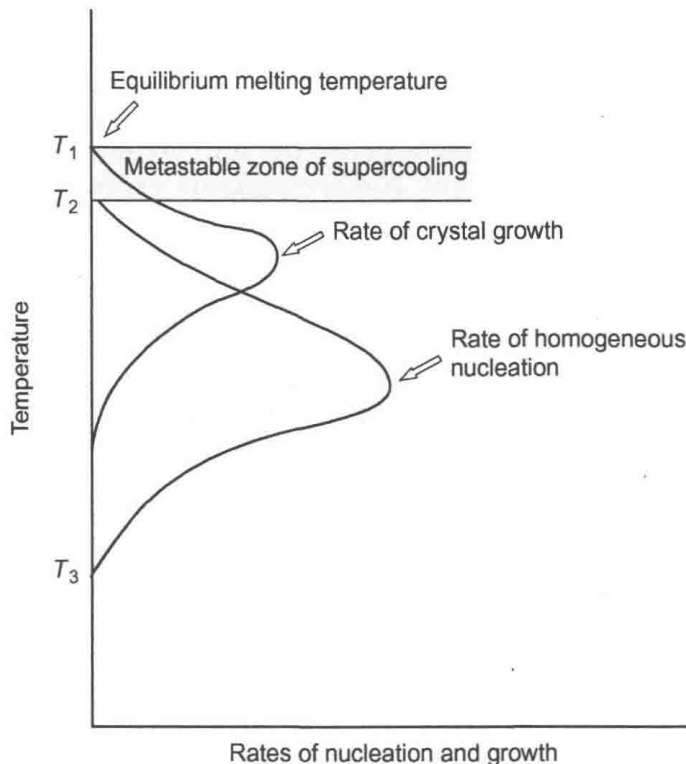

Figure 1.1 Rates of homogeneous nucleation and crystal growth in a viscous liquid.

According to this figure, in order to produce the largest possible number of small crystals, e.g., in nano-glass ceramics, nucleation should occur at or near to the temperature at which the maximum nucleation rate occurs.

It could be noted that there is also a temperature, T_3, below which the homogeneous nucleation rate is zero due to the high viscosity of the melt (Figure 1.1).

In the "classical nucleation theory" (CNT), which is the oldest and the best-studied theory used for calculation of the nucleation kinetics, it is assumed that the nuclei formation and growth take place via single molecule attachment/detachment.

According to the above theory, the rate of homogenous steady-state nucleation (I) at an absolute temperature (T) in a one-component supercooled liquid can be expressed by Eq. (1.1) (Christian, 1975).

$$I = A \exp\left[-\frac{W^* + \Delta G_D}{kT}\right] \qquad (1.1)$$

where W^* is the thermodynamic free-energy barrier to nucleation and ΔG_D is the kinetic barrier, k is the Boltzmann constant, and A is a preexponential factor, given to a good approximation by:

$$A = n_v\left(\frac{kT}{h}\right) \qquad (1.2)$$

where n_v is the number of atoms or, strictly, "formula units" of the crystallizing component phase per unit volume of the liquid and h is Planck's constant. A more accurate expression for A is given by Christian (1975). It is typically $10^{41}-10^{42}/m^3/s$ and may be taken as effectively constant over the temperature range of nucleation measurements.

The thermodynamic barrier to nucleation, W^* (or ΔG^*), can be calculated in the following way.

The net change in energy, W, for the formation of a spherical nucleus of radius r is given by:

$$W = 4/3\pi r^3 \Delta G_v + 4\pi r^2 \sigma \qquad (1.3)$$

In the first energy term ($4/3\pi r^3 \Delta G_v$), ΔG_v, is the change in the free energy in transforming a unit volume of the liquid to a unit volume of the crystal, known as the free energy of crystallization (which is negative below T_m, providing the driving force for crystallization). The second term is given by $4\pi r^2 \sigma$, where σ is the surface energy of the interface per unit area. This term is positive and acts as an obstacle for crystallization. Obviously, W is a function of r and the maximum value of

it, W^* (thermodynamic barrier to nucleation) can be obtained from the W versus r plot.

The radius of the nucleus at the maximum point, r^*, defined as the critical-sized nucleus, can be determined by differentiating W with respect to r and setting equal to zero:

$$dW/dr = 4\pi r^2 \cdot \Delta G_v + 8\pi r\sigma = 0 \quad \text{when} \quad r = r^*$$

Hence,

$$r^* = -2\sigma/\Delta G_v \tag{1.4}$$

Substituting Eq. (1.4) into Eq. (1.3) yields the maximum value, W^* as

$$W^* = 16\pi\sigma^3/3(\Delta G_v)^2 \tag{1.5}$$

Crystal embryos below the critical radius (r^*) are unstable and will tend to dissolve. Embryos with radii exceeding r^* become stable nuclei and continue to grow.

The critical radius increases with rise in temperature, becoming infinite at the melting point.

The free-energy driving force ΔG (per mole) can be calculated if accurate thermodynamic data, including ΔC_p, the difference in specific heats at constant pressure between the crystal and liquid phases, are available as a function of temperature (James, 1985). An approximate expression, only applicable for small undercoolings below the melting point T_m and in which ΔC_p is taken as zero, is

$$\Delta G = -\frac{\Delta H_f(T_m - T)}{T_m} \tag{1.6}$$

where ΔH_f is the heat of fusion per mole and $\Delta G = \Delta G/v_m$ (v_m is the molar volume).

On the other hand, the kinetic barrier to nucleation, ΔG_D, can be expressed in terms of an effective diffusion coefficient D given by

$$D = \left(\frac{kT\lambda^2}{h}\right)\exp\left(-\frac{-\Delta G_D}{kT}\right) \tag{1.7}$$

where λ is a quantity of the order of atomic dimensions ("jump distance"). Various authors have related D to the viscosity of the liquid η by the Stokes–Einstein relation

$$D = \frac{kT}{3\pi\lambda\eta} \tag{1.8}$$

Alternatively, ΔG_D can be obtained from crystal growth measurements at similar temperatures, assuming the kinetic

barriers for nucleation and for growth are the same (Höland and Beal, 2002).

The steady-state nucleation rate, as discussed above, is concerned with the linear part of the curve relating the number of nuclei at a fixed temperature with time (shown schematically in Figure 1.2).

Obviously, there is an initial period during which the nucleation rate is either zero or very small and after prolonged nucleation a saturation effect is reached after which no further nucleation occurs. Before the occurrence of saturation, the nucleation rate can be expressed by

$$I = I_o \exp\left(\frac{\tau}{t}\right) \tag{1.9}$$

where τ is the incubation time and I_o is the steady-state nucleation rate.

The calculation of nucleation rates in glasses using the above equations would require accurate values as a function of temperature for ΔG, ΔG_D, and σ.

Unfortunately, at present accurate data for the aforementioned values exist only for a limited number of glasses. However, even in these cases, the theoretical values should be evaluated by comparing them with experimentally obtained values. Fortunately during the last three to four decades, many experimental methods have been developed for determination of crystal nucleation rates in glasses. The most important methods will be discussed later.

1.1.1.2 Experimental Studies of Homogeneous Nucleation

James (1989), Zanotto (1987), and Zanotto and Weinberg (1989) based on numerous experimental nucleation rate data for several
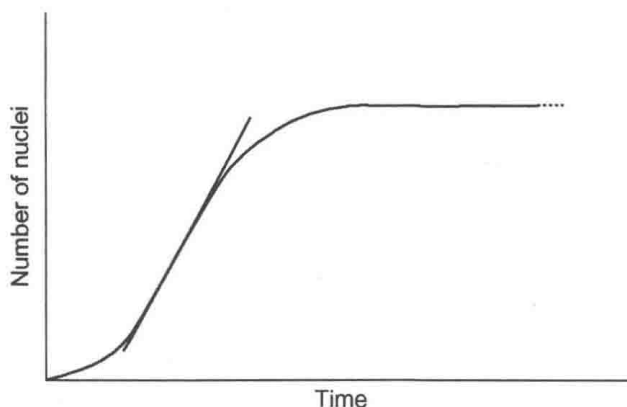
Figure 1.2 Number of nuclei per unit volume versus time at a fixed temperature.

silicate glasses, suggested that glasses having a reduced glass transition temperature, $T_{gr} = T_g/T_m$, higher than $\sim 0.58-0.60$, display only surface crystallization; while glasses possessing values $T_{gr} < 0.58-0.60$, show volume (homogeneous) nucleation. However, since at temperatures $T < T_m$, the nucleation rate is always positive, the absence of volume nucleation for glasses having $T_{gr} > 0.60$ merely indicates undetectable nucleation on laboratory time/size scales. When the glass transition range is reached at relatively high temperatures, $T_{gr} > 0.60$, the work of critical cluster formation is still too large to allow the occurrence of measurable internal crystallization (since the critical cluster size and the work of critical cluster formation decreases with the difference $[T_m - T]$).

Since the work of critical cluster formation and the viscosity may be lower than bulk values on or close to interfaces, the surface crystallization is more commonly observed than internal crystallization (Fokin et al., 2003).

The transition from glasses demonstrating only surface crystallization ($T_{gr} > 0.60$) to glasses exhibiting volume nucleation ($T_{gr} < 0.58$) may be qualitatively explained by an increase in nucleation rate with decreasing T_{gr}.

The increase of the nucleation rate with decreasing T_{gr} was in fact demonstrated by Deubener (2000) for eight silicate glass systems: Li_2O-SiO_2, Na_2O-SiO_2, $BaO-SiO_2$, $CaO-SiO_2$, $Li_2O-Na_2O-SiO_2$, $Na_2O-CaO-SiO_2$, $Li_2O-BaO-SiO_2$, and $MgO-Al_2O_3-SiO_2$ and comprise both stoichiometric and non-stoichiometric compositions. For nonstoichiometric compositions, the liquidus temperatures, T_l, were used to calculate the reduced glass transition temperature.

In compositions belonging to the above silicate systems, in a relatively narrow range of T_{gr} (ranging from 0.47 to 0.58), the nucleation rate drops typically by about ~ 17 orders of magnitude!

Fokin et al. (2003) collected the available data for a number of silicate glasses that exhibit internal nucleation, extending the above list published by Deubener. Their work provided additional experimental evidence for the above-mentioned correlation between nucleation rate and T_{gr}. The existence of an analogous correlation between the temperature of maximum nucleation rate (T_{max}), the induction time at T_{max}, and the reduced glass transition temperature were also demonstrated.

The experimental results on internal homogeneous crystal nucleation in silicate glasses obtained in the last four decades were also reviewed (Fokin et al., 2006).

In this study, particular attention was paid to the analysis of the critical nuclei properties because of its decisive role in the determination of nucleation kinetics.