The shape of diopside glass particles probed by the non-isothermal crystallization kinetics and Differential Scanning Calorimetry

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A B S T R A C T

The densification rate of glass powder compacts on heating can be calculated by the *Clusters* model of sintering, in which the particle shape is considered as a correction factor and obtained by fitting the model itself to experimental data. The crystallization of a diopside glass particle compact was characterized by Differential Scanning Calorimetry (DSC) and the resulting peak compared with the analytically calculated for particles with distinct regular morphologies and constant volume, aiming to access an effective particle shape parameter independently. The crystallization kinetics was calculated for the diopside composition considering heterogeneous surface nucleation and the phase transformation evolving due to a crystallized surface layer, whose thickness grows inward the particles, contracting the residual glass. The crystallization peaks were compared with the experimental DSC peaks for a diopside glass powder with irregular-shaped particles in a narrow size range. The calculated peaks ranged from the same temperature interval of the experimental one, but their overall shape and maximum temperature were greatly influenced by the different particle geometries. The particle shape must thus be taken into account in the analysis of glass powder crystallization by DSC, which is then a promising technique for the characterization of an effective shape factor for glass particles under crystallization.

1. Introduction

An important problem in modeling the sintering with concurrent crystallization of glasses is taking into account the particle shape effect. The *Clusters* model [1,2], for example, can approximately describe the glass sintering kinetics with concurrent crystallization. However, it must be improved concerning the particle shape. In such model, the particle shape effect is related to the deviation from the ideal spherical shape. An empirical correction factor (K_s) related to the particle shape is considered by fitting the model to the experimental densification kinetics data. Defining $K_s = 1$ for spherical particles, the K_s of irregular particles was reported ranging from 1.8 to 5 [2,3]. So far, regarding the *Clusters* model, there is no simple method to independently evaluate the shape effect of irregular particles, and the particle shape becomes essential to provide accurate information about glass sintering kinetics as well as the adequacy of the *Clusters* model itself.

The particle size is often characterized by indirect techniques, generally attributing to each particle the diameter of a sphere that would produce the same effect measured on such particle subjected to some physical process, such as sedimentation in a viscous liquid, or X-ray or laser diffraction. In the past, the direct imaging was substituted by such techniques due to the long and boring analysis needed to collect significant statistics from a collection of particles. Currently, modern image analysis has been available for particles above ~10 μm diameter, the optical microscopy resolution limit, as a result of new advances in hardware and software for fast and automatic image capturing and analysis. Nevertheless, the precise characterization of the glass particle shape and size during sintering and crystallization is still missing. Image analysis of particles by microscopy (2D) or X-ray tomography (3D) can provide a direct way to access the shape of particles in one powder. In this case, the aspect ratio, defined as the length-to-width ratio [4], is a popular parameter used to describe irregular shapes quantitatively. However, it reflects only the particle elongation, making no distinction between square and circle, for instance. Other shape factors derive from the aspect ratio combining surface texture and roundness [5–8], although the best indicator to evaluate particle shape has been a combination of two or more such factors [9,10]. One of the problems to find a shape factor via digital imaging is its variation under experimental conditions since scale and resolution strongly influence it, and several pictures must be analyzed to suffice the statistics to achieve the desired results. Other attempts to obtain a shape factor derive from particle sedimentation in a fluid [9,11], which have shown that the choice of indirect methods to obtain it is strongly related to the particularity of the problem under analysis, and the development of an

effective shape factor is often necessary.

Surface crystallization strongly affects the sintering of glass particles [12] and may gauge the effective particle shape in a glass-sintering compact. In this sense, the diopside (CaO·MgO·2SiO$_2$) stoichiometric composition is especially suitable for a test glass. It presents only heterogeneous surface crystallization, and depending on the particle size its surface nuclei concentration can be sufficiently high [13] to quickly form a continuous surface layer, enabling the use of a simple volume contraction model to evaluate the phase transformation kinetics.

The main purpose of this work is to probe glass particle shape from the crystallization kinetics detected by Differential Scanning Calorimetric (DSC). The expected crystallization kinetics was evaluated as a function of particle shape, for different regular morphologies, keeping the initial particle volume constant, by using geometric contraction models of transformation kinetics. The calculated results were compared with experimental DSC crystallization peaks of a diopside glass powder with known average particle size.

2. Theoretical proposal

The classical phase transformation kinetics of Johnson & Mehl [14], Avrami [15–17] and Kolmogorov [18] (JMAK) considers the occupation of an infinite surface or volume by nucleation and growth of regions of a new phase. Accordingly, the transformed fraction $\alpha(t)$ at time t can be calculated by

$$\alpha(t) = 1 - e^{(-\alpha'(t))}, \tag{1}$$

where $\alpha'(t)$ is the transformed fraction, known as extended volume, not limited by the overlapping of neighboring crystals. Different expressions for $\alpha'(t)$ can be derived according to the nucleation mechanism (homogeneous or heterogeneous), nucleus distribution (superficial or volumetric) and crystal shape (spherical, squared, etc.).

The crystallization of glass particles represents a more complex case of transformation kinetics to which the JMAK theory does not rigorously apply due to the finite surface and volume [19]. Nevertheless, JMAK expressions for $\alpha(t)$ were developed for spherical glass particles with different crystal morphologies growing from their surface [20–25]. Müller [20] used an alternative approach for semi-cubic crystals on cubic particles.

An alternative particle crystallization kinetics for heterogeneous nucleation and high surface nuclei density is the geometric contraction model, in which crystals grow to form a continuous layer on the particle surface, which subsequently grows inwards with thickness given by the crystal growth rate [26]. Such model is relatively easy to apply to regular-shaped particles. Müller [20], Weinberg [24] and Reis [25] models consistently approach the geometric contraction model in the case of infinite surface nuclei concentration.

The geometric contraction model does not satisfy the real case of a finite surface nuclei density; nevertheless, it can approximately apply to glasses with high surface nuclei concentration and known particle shape. In the case of glasses with low surface nuclei concentration, a surface treatment can be previously applied to particles to promote the required condition. Fest et al. [27] verified that milling by different abrasives inflicts different mechanical damage on the surface of glass particles in one powder. Consequently, one can increase the surface nuclei concentration to make crystals quickly impinge to form a thin crystalline surface layer that then grows inwards in the particle. In this sense, diopside is a suitable testing glass, since it presents fast heterogeneous surface nucleation from a fixed number of active sites [13] to form a crystalline shell, even on non-stoichiometric compositions [28–30]. Lopez-Richard et al. [31] calculated the 3D-to-1D crystallization mode transition in spherical particles of vitreous diopside, showing that the surface layer becomes continuous approximately after 4 h of isothermal heat treatment at 1098 K.

After a continuous crystallized layer forms on the particle surface,

the residual glass crystallization kinetics can be related to the area under the crystallization peak measured by DSC, supposing it proportional to the rate of heat released during the phase transformation. A change of variables time t to temperature T can be readily made in the JMAK model for the temperature changing at a constant rate q, $dT = qdt$. An explicit expression for the non-isothermal JMAK $\alpha(T)$ as a function of T was given by Weinberg & Zanotto [32], supposing time-independent nucleation and crystal growth rates. For a stoichiometric diopside glass, nucleation occurs heterogeneously from a constant (athermal) number of surface nucleation sites and the crystal growth rate can be considered time-independent. Considering fixed the initial sample volume and a peak of unitary area after 100% transformation, a function $DSC(T)$ relative to the crystallization of a stoichiometric glass determined by DSC can thus be defined [31] as

$$DSC(T) = \frac{d[\alpha(T)]}{dT}. \tag{2}$$

The crystallized fraction $\alpha(T)$ as a function of temperature T is given by

$$\alpha(T) = \frac{V_c(T)}{V_T}, \tag{3}$$

where $V_c(T)$ is the transformed volume, which depends on the crystal growth rate $u(T)$ and the particle size, and V_T is the total volume. In the general case of non-isothermal heating at rate q, the crystallized layer thickness growing from the surface is given by

$$h(T) = \int_{T_0}^{T} \frac{u(T)}{q} dT, \tag{4}$$

where T_0 is the initial temperature (set as T_g, the glass transition temperature). It is necessary to know the particle shape to exactly calculate the crystallization kinetics, however, if the crystal growth rate is known and the geometric contraction model is considered, the crystallized fraction of glass particles with different regular geometries can be assessed as a function of temperature. This approach of direct calculation of $V_c(T)$ is an easy way to evaluate how a DSC crystallization peak behaves as a function of particle shape.

2.1. Geometric contraction model applied to solids with different regular geometries

Analytical expressions for cubic, spherical, ellipsoidal and parallelepipedal particles can be easily derived to calculate the transformed volume of a crystallized shell with layer thickness growing from the surface (Fig. 1) as a function of time or temperature. The residual glass is confined to a volume of the same geometry as the starting particle, shrinking towards the particle center. DSC crystallization curves can then be calculated from Eqs. (2) and (3) for glass powders formed by particles having the considered geometries and presenting only surface crystallization. To compare DSC curves calculated for different geometries, the total volume V_T can be held constant and equal to L^3, referent to a cube edge of length L.

In the simplest case of a cubic particle, the transformed volume can be expressed by

$$V_{cube}(LT) = [L^3 - (L - 2 \cdot h(T))^3], \tag{5}$$

and substituting it into Eq. (3), one obtains the transformed fraction as a function of T and L,

$$\alpha_{cube}(LT) = \left[1 - \left(1 - \frac{2 \cdot h(T)}{L} \right)^3 \right]. \tag{6}$$

In the case of a spherical particle, the *equivalent spherical* diameter D can be calculated as a function of the cube side L,