# Modelling of sintering processes in borosilicate glasses with rigid inclusions

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In the present work, the sintering behaviour of a borosilicate glass ($60SiO_2$-$24B_2O_3$-$16Na_2O$, %mol.) and the composite material formed by the glass and zirconia fibres has been characterised as a function of the particle size of the glass powders, the fibres volume fraction, and the temperature and time of the sintering treatment. The composite material is suitable for sealing the gas manifolds of molten carbonate fuel cells (MCFC), and the sintering temperatures close to the working temperature of the cell (650ºC).

For better understanding the influence of the glass surface crystallisation and of the fibres on the sintering kinetics, the "clustering model" which applies simultaneously the Frenkel and Mackenzie and Shuttleworth (MS) theories was used. New considerations are included to account for the presence of the rigid inclusions. For applying the model, it is necessary to know the particle size distribution of the glass powder, the viscosity and surface tension of the glass, as well as a shape parameter for the geometry of the glass powder and the fibres size. The model also allows to include the effect of surface crystallisation as an inhibitor for densification, but it does not consider the effect of entrapped air and degasification during sintering and crystallisation.

The application of this model allows a greater comprehension of the sintering process and to obtain working conditions through which the porosity and crystallinity can be controlled, thus minimising the number of experiments.

## 1. INTRODUCTION

In a previous work, the sintering behaviour of mixtures of a borosilicate glass and $ZrO_2$ fibres has been studied as a function of the particle size of the glass powder, sintering temperature and time in order to optimise sealing properties[1]. The experimental results were explained by using different sintering models for a glass matrix containing rigid inclusions such as Schere´s model [2, 3, 4] and Raj and Bordia model[5]. In these cases, the sintering results did not fit the theoretical sintering models in presence of rigid inclusions, since these models do not consider the size and geometry of the inclusion as well as possible reactivity with the matrix. These facts together with the glass devitrification during sintering process made these models non-applicable.

In this work we analyse the sintering kinetics of the same system applying the Clusters model as a more realistic approximation. The Clusters model, considers the sintering of a size distribution of particles as the summation of the sintering of each particle size[6]. Sintering with concurrent crystallisation, within the frame of the clusters model was discussed in[7]. In the following we present a new approach for modelling glass powders with rigid inclusions as an extension of Clusters model.

## 2. EXPERIMENTAL

A borosilicate glass with composition $60SiO_2$. $24B_2O_3$. $16Na_2O$, %mol. has been used for this study. The batch was prepared from silica sand, reagent grade $Na_2CO_3$ and vitreous $B_2O_3$, and melted in air in Pt crucible in a electric furnace at 1500°C during one hour. After melting, the glass was milled and sieved to obtain three different particle sizes, fraction A (40-60 μm), B (40-20 μm) and C (<20μm).

A commercial zirconia fibre stabilised with ytria (8% weight) with 1.6 mm of medium length and 3-6 $\mu$m of diameter was employed. Borosilicate glass powders were mixed with the zirconia fibres in different proportions. Cylindrical samples were prepared by isostatic pressing.

The compacts were isothermally treated in electrical furnace in air at temperatures between 600-750°C during different times. The densities of the green and treated samples were measured by Archimedes method employing Hg. The theoretical density was calculated from the rule of mixtures.

Experimental procedure is described in more detail in [1].

## 3. RESULTS

The sintering process between two particles, as described by Frenkel[8], needs the shortening of the distance between the two particle centers and the simultaneous reduction of the total surface. During this process a neck between both particles is formed, where at the first moment there only was a contact between the two glassy surfaces. The driving force for sintering is the surface energy of the particles, the kinematical path being accomplished by viscous flow.

In a mixture of glass particles and rigid inclusions, three types of contacts appear: glass-glass, glass-inclusion, inclusion-inclusion. Glass-glass contacts behave as Frenkel already described, reacting through viscous flow. In a contact glass-inclusion, there is no possibility for the inclusion to change its shape (since it is supposed rigid) and the only possibility for the glass particle is to spheroidize by viscous flow. This type of contact is always present between the crucible (when used) and the sample's particles.

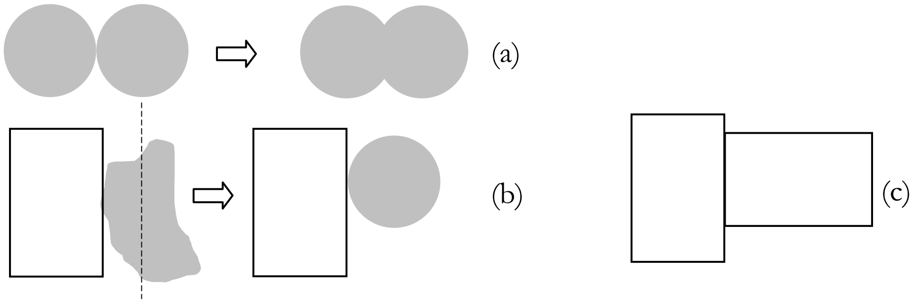

Fig.1: Particle shape evolution during sintering. Solid grey particles are glass particles, white particles represent fibres. (a) glass-glass contacts. (b) inclusion-glass contacts. (c) Inclusion-inclusion contact. There is no evolution of the geometry with time.

The inclusion-inclusion contacts do not evolve, their geometry remaining constant. Thus, the viscous flow that develops necks from the glass-glass contacts provides the major contribution to the sintering kinetics.

Three different volumes can be differentiated inside the sample. Volume V1: only *glass-glass* contacts which densify according to the Clusters model, V2: only including *glass-inclusions* contacts, which can be defined as the volume that surrounds all inclusions with a height approximately equal to a particle radius which maintains the original porosity of the green sample (0.61 in this case), and V3: the volume of inclusions (the volume of the fibres itself), which density is also constant (6.09 in this work).

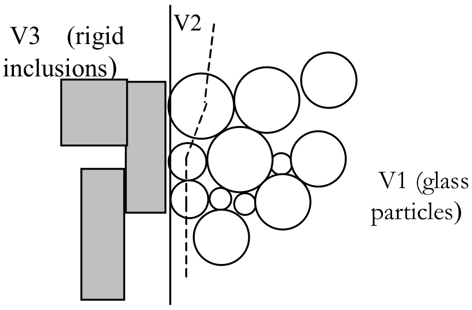

Fig.2: Scheme of the three different volumes (V1, V2 and V3).

The kinetics of sintering is due to shrinkage of volume V1, since V2 and V3 can be considered constant. The value of V1 is calculated with Eq. (1) where VT is the total volume of the sample and *fibresurface* is the surface area of the rigid inclusions in the sample.

$$V1 = VT - V2 - V3 \tag{1a}$$

$$V2 = \sum_{r} \text{fibresurface}.v_r.r \tag{1b}$$

Dividing (1a) by VT

$$v1 = 1 - v2 - v3 \tag{2}$$

where v1, v2 and v3 are volume fractions. The volume V2 is a volume of glass particles that does not participate in the sintering process. Then each particle size volume fraction $v_r$ is reduced by the volume by the fraction of the particles with radius r that belongs to the volume V2 (fibre surface*$v_r$*r/VT).

v1 will decrease with an increase of the fibre content v3. When all the sample be composed by fibres (v3=1), v1=0 and there is no sintering.

But actually, Eq. (2), is a good approximation for fibre fractions in the range 0- 0.2.

In a “diluted” system, fibres do not interact among them and during the sample shrinkage they are pushed by the viscous flow. When the fibre content increases, contacts among fibres also increase. Considering the case of long fibres a fibre network is formed conforming glass regions that sinter almost independently one from the other. Stresses imposed by glass on the fibres during sintering are not sufficient to deform this network. Finally with a fibre volume fraction of about 0.65 no shrinkage was observed [1].

This effect is empirically modelled by introducing a function $\phi(xf)$, which is 1 for fibres contents $0<xf<0.2$ and goes from 1 to 0 for $0.2<xf<0.65$. Then the volume v1 is calculated as

$$v1 = (1 - v2 - v3) * \phi(x) \tag{5}$$

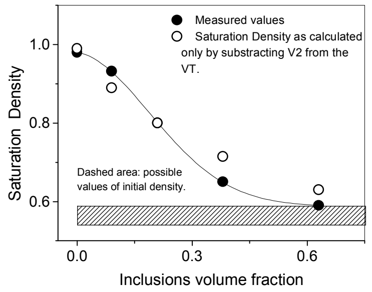

Fig.3: Measured saturation density vs. fibre content and calculated values.

The three size distributions A, B and C used in this work are described in [1].

Since no values were available for the density of nucleation sites Ns and crystal growth rate U for quartz, that is the main phase appearing with devitrification, these values were estimated from experimental saturation density values at 625 °C and 650 °C[9]. The value of $N_s$ used was 3. $10^9$ $m^{-2}$, but in the case of small particles it was always supposed one nucleation site per particle. This means a nucleation site density varying with particle size. Nevertheless, in the systems studied here, crystallization has not a large effect in the experiments. The crystal growth rate was empirically estimated as $10^{-10}$ $ms^{-1}$ at 625°C and $6.10^{-10}$ $ms^{-1}$ at 650°C [9]. The shape factor used was 1.6 for distribution B, and 1 for distributions A and C. The viscosity values that best fitted all measurements were $10^{9.35}$ P.s. at 625°C and $10^{8.35}$ Pa.s. at 650°C [1].

Measurements and calculations corresponding to the sintering kinetics of fraction C with different fibre content at 625ºC and measurements and calculations corresponding to the sintering kinetics of fraction A, B and C at 650ºC are shown in figures 4 and 5.

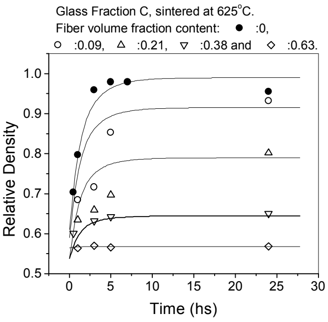

Fig.4: Experimental points and theorical calculations (curves).

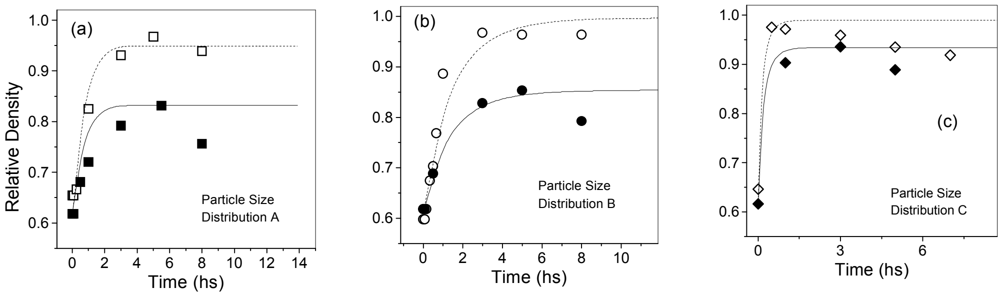

Fig.5: Experimental points (hollow: without fibres, solid: with 0.09 fibre volume fraction) and theoretical calculations (curves).

## 4. DISCUSSION

The clusters model for polydispersed glass particles has been applied for the study of the sintering kinetics of a composite of glass particles and rigid inclusions with concurrent surface crystallisation. This is a complicated system in which many parameters (as Ns and U) are unknown, and even it exhibits bubble formation due to gases originated during the glass crystallization or degassing of the glass particles during sintering. Moreover, the space distribution of the fibres is not always random, since during the sample pressing it is possible that some alignment of the fibres (and also of the particles) can take place.

Due to the complexity of this problem, the model presented here makes use of assumptions that simplify its mathematical treatment. For example the determination of the height of volume V2 as the particle radius or the function $\phi(xf)$ which is empirically introduced. It is also remarkable that when the inclusions are in a high concentration (> 20% vol.) new mechanisms hinder the sintering rate, it becoming negligible for a fibre content of about 65 % vol.

The advantages of the model consist on allowing to predict trends in sintering kinetic and saturation density as a function of particle size distribution, fibre diameter and sintering temperature, even in the presence of glass particles devitrification.

From the model, it is evident that for reducing the porosity of the sample, the volume V2 (the volume which has inclusion-glass contacts) must be reduced. This condition is fulfilled for example decreasing the glass particle size. Other solutions could be the coating of inclusions with a glassy layer, eliminating the inclusion-glass contacts, and decreasing V2 .

Figure 4 and 5 show that a good agreement is generally found between calculations and experiments.

## 5. CONCLUSIONS

The Clusters model for sintering of glasses in presence of rigid inclusions has been successfully applied to the system borosilicate glass/zirconia fibres. These first calculations, show that the model used in this work is an alternative to the well known Scherer´s and Raj and Bordia models. The main advantage of the Clusters model is that it allows to consider particle size distribution, dimensions of inclusions, and concurrent sintering with glass surface crystallisation.

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