

Concurrent Sintering and Crystallization of Glass Spheres

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Abstract

Glass sintering is a subject of both scientific and practical interest. While the kinetics of viscous sintering of monodispersed, spherical, glass particles are well described by the classical models (Frenkel, Mackenzie-Shuttleworth, etc.), the behavior of real glasses, having wide size distributions of irregular particles that show concurrent crystallization, is much more complex and not fully understood. In this article we develop a model that includes all these complicating factors and test it with a commercial glass.

We studied the sintering kinetics of spherical soda-lime-silica glass particles (SiO_2 72.5wt%, MgO 3.3%, CaO 9.8%, Na_2O 13.7%, Al_2O_3 0.4%, Fe_2O_3 0.2%, K_2O 0.1%), which devitrify on sintering into three crystalline phases (Cristobalite, Devitrite and Wollastonite). We performed computer simulations and experimental measurements corresponding to three size distributions (D1, D2 and D3- see Fig.1). We carried out isothermal sintering experiments for the three types of sphere distributions at different temperatures, in order to allow the development of different degrees of crystallization on sintering. Crystallization initiated from a fixed number of sites on the sphere surfaces and developed towards their interior. Figure 2 shows the results for isothermal treatments at a series of temperatures above the glass transition.

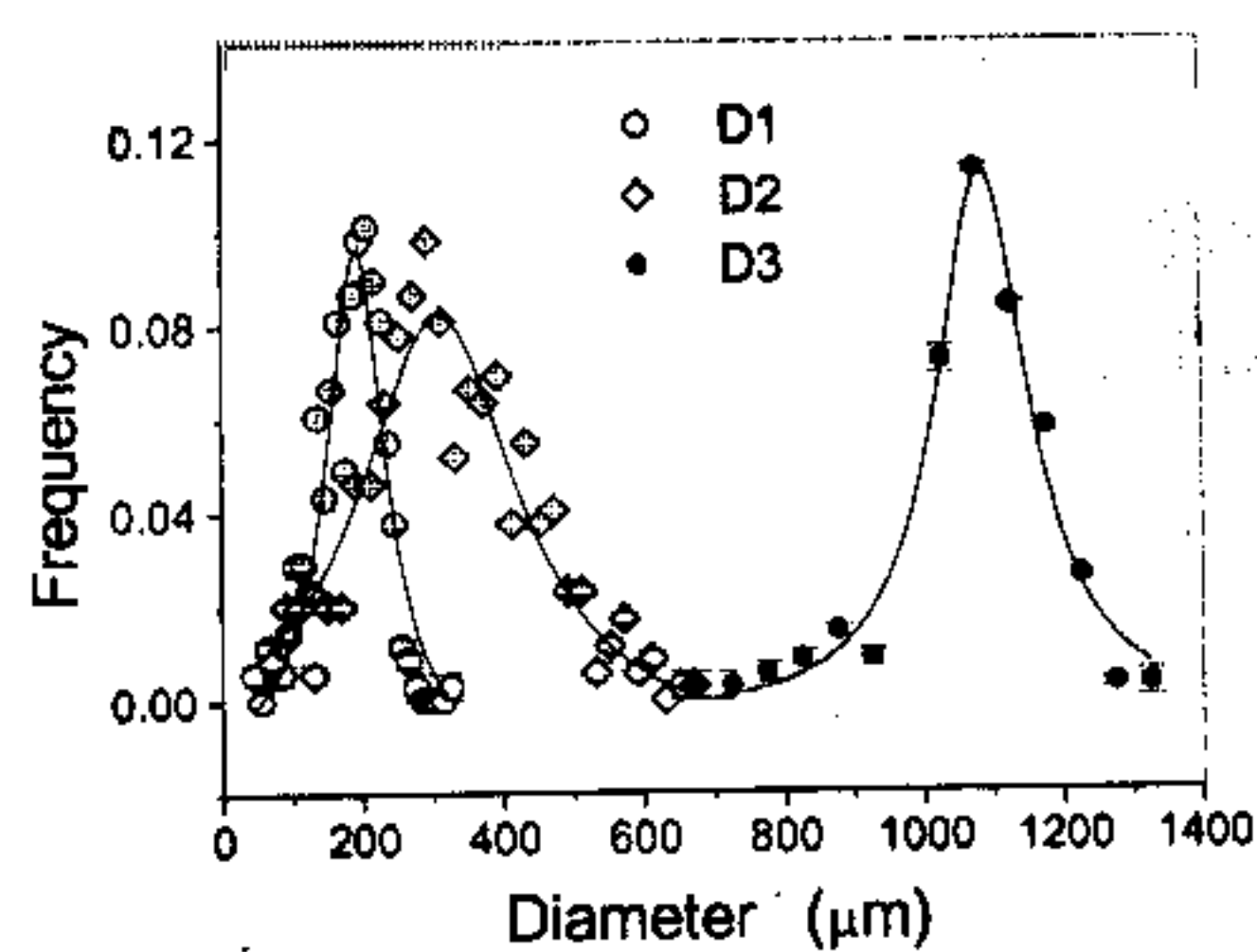


Fig.1: Size distributions of glass spheres D1, D2 and D3.

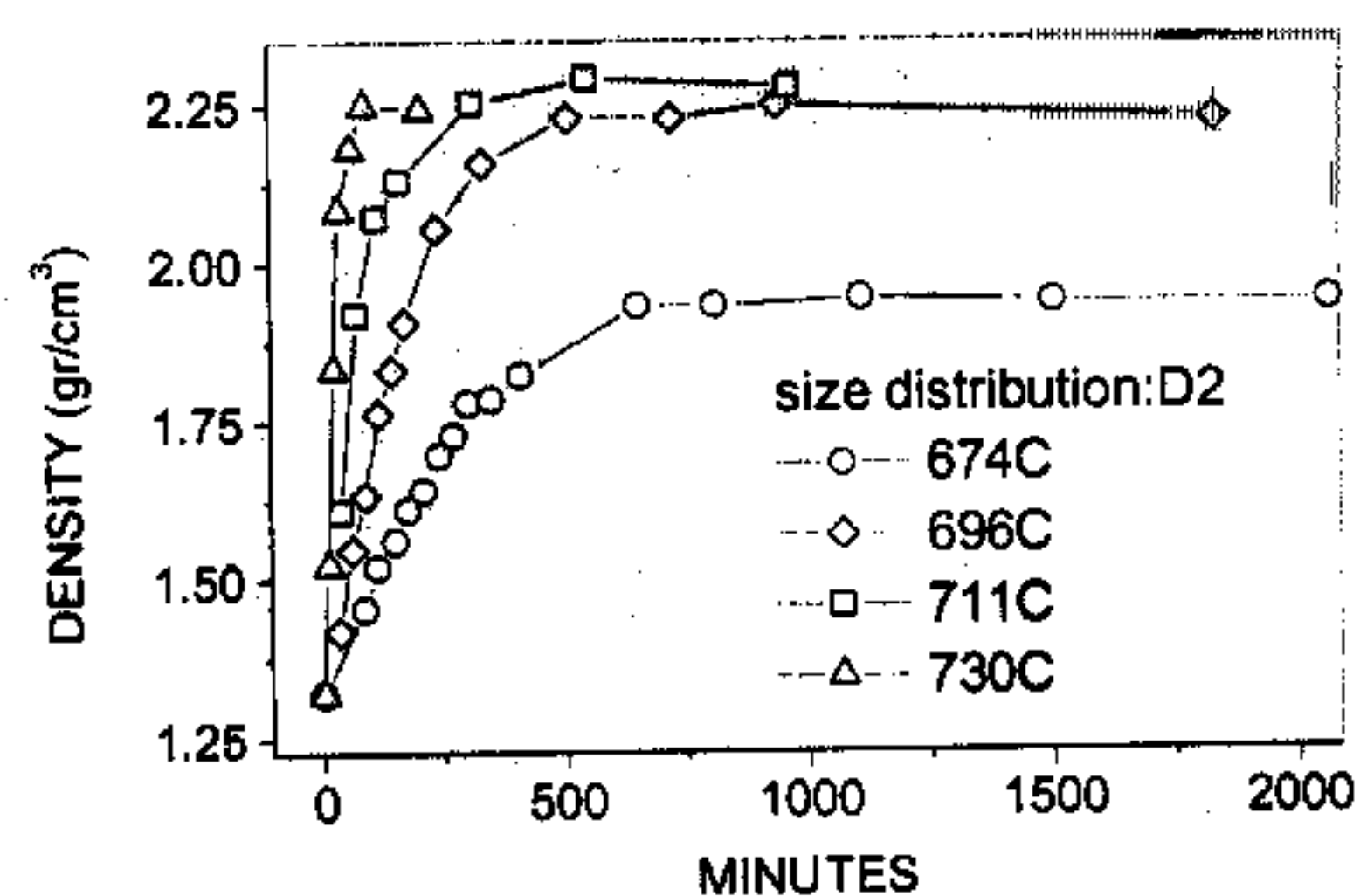


Fig.2: The effect of crystallization on viscous sintering. (experimental data).

We used the "cluster model" [1], previously developed to describe the sintering kinetics of polydispersed, non-crystallizing, glass powders to analyze the sintering kinetics. However, in this paper we extend that model to include the effects of concurrent surface crystallization (proposed by Müller [2]) and volume crystallization originating at the sphere surfaces (proposed by Gutzow [3]). Higher temperatures privileged sintering over crystallization (Fig. 2).

Figure 3 shows densification data of the D3 spheres and calculated curves at 674 °C: a) expected curve if all spheres had identical (smallest) radius of the distribution, without including crystallization effects, b) ibid. but for identical spheres having the largest radius, c) ibid. but considering that all particles have an average radius, d) prediction of the "cluster model", taking into account the real size distribution of spheres but no crystallization, e) prediction of the "extended cluster model", taking into account size distribution and surface crystallization (of two main phases: Cristobalite and Devitrite), f) prediction of the "extended cluster model", taking into account size distribution and both surface and volume crystallization.

The decrease in density for long sintering times, shown by curve f), is due to crystallization of Cristobalite (density=2.33gr/cm³) in the glass interior prevailing over the density change due to crystallization of Devitrite (density=2.72 gr/cm³). The density of the glass is 2.5 gr/cm³.

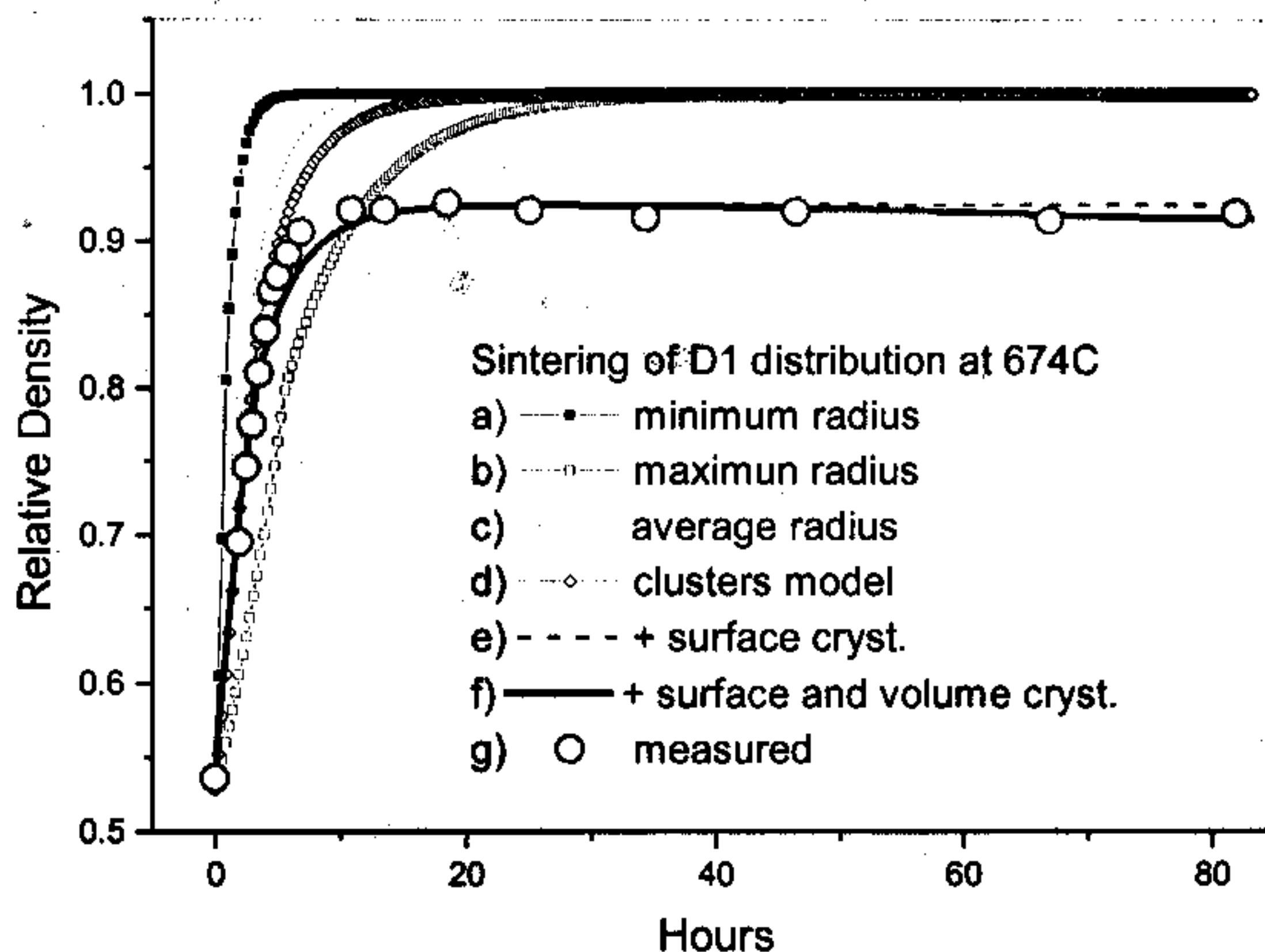


Figure 3: Measured and calculated sintering kinetics of a D3 distribution of glass spheres sintering and crystallizing at 674 °C.

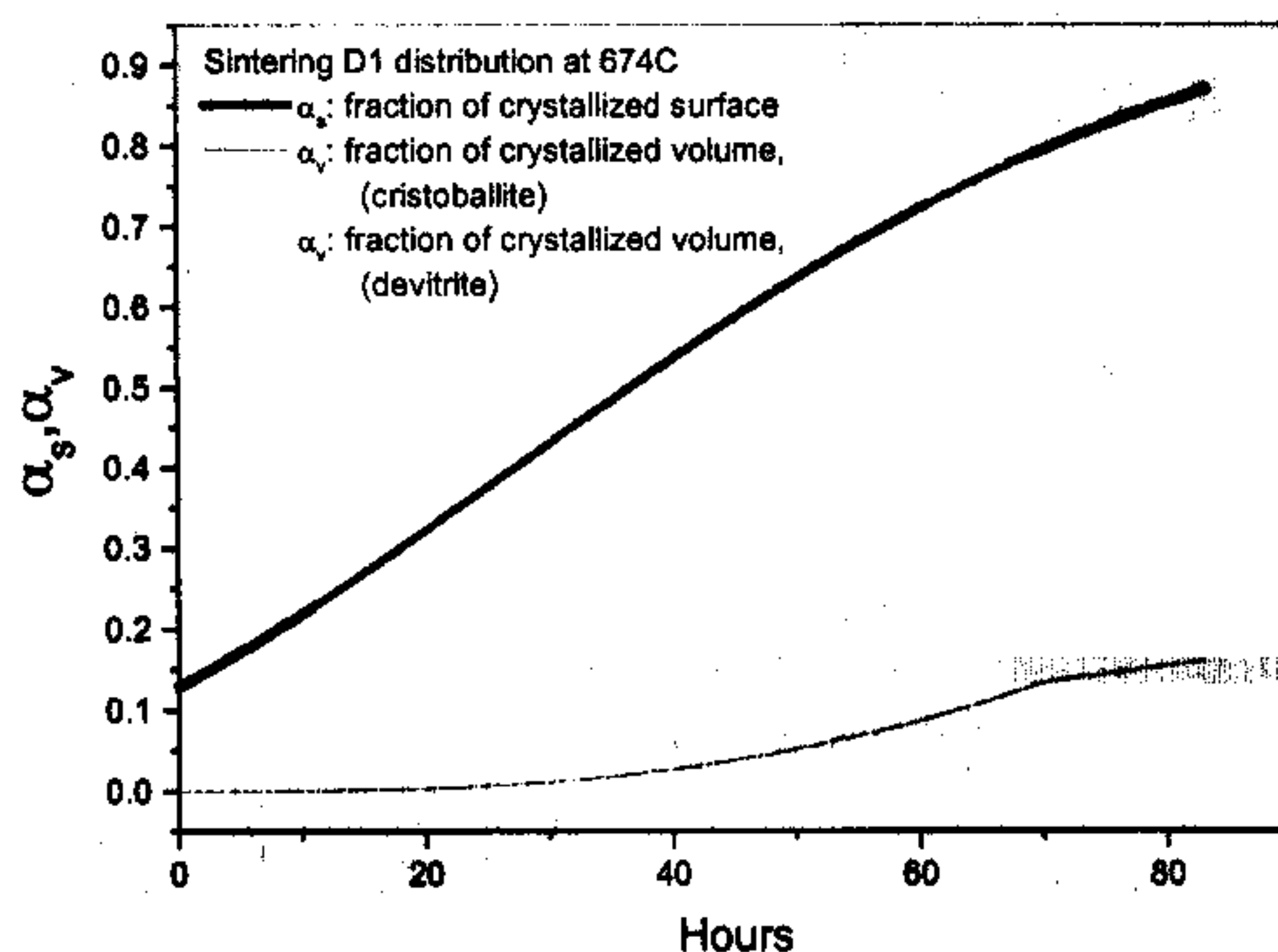


Figure 4: Calculated surface and volume crystallized fractions .

Fig. 4 shows that some crystallized surface fraction exists at time zero. This fact was checked with XRD, which revealed the presence of a small volume fraction of Quartz, which covered about 13% of the sphere surfaces. That figure also shows that the volume fraction devitrified of Cristobalite is larger than that of Devitrite, which agrees with the density decrease observed at higher sintering times.

Temperature, time, iso-density and iso-crystallized fraction plots (T-t-p- α) were computed which allow to specify the physical characteristics of the sinter-crystallized sample for any thermal treatment.

In summary, the "extended cluster model" describes well the experimental results for a series of sintering temperatures and for the three particle size distributions used. Higher temperatures privileged sintering over crystallization. From the computer simulations and experimental results we conclude that:

- there is no critical crystallized surface fraction to stop sintering, but instead a soft modulation of the sintering velocity occurs due to surface crystallization;*
- pre-existing surface crystals have a strong effect on the sintering kinetics;*
- surface crystallization limits the maximum achievable density, favoring porosity;*
- volume crystallization produces density changes that have to be taken into account to describe the sintering kinetics.*

Acknowledgements

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References

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