Interpretation of Frenkel’s Theory of Sintering Considering Evolution of Activated Pores: II. Model and Reliability

School of Materials Science and Engineering, Shaanxi University of Science & Technology, Xi’an 710021, P. R. China

Abstract:
Frenkel's liquid-phase sintering mechanism has essential influence on the sintering of materials, however, by which only the initial 10% during isothermal sintering can be well explained. To overcome this shortage, Nikolić et al. introduced a mathematical model of shrinkage vs. sintering time concerning the activated volume evolution. This article compares the model established by Nikolić et al. with that of the Frenkel's liquid-phase sintering mechanism. The model is verified reliable via training the height and diameter data of cordierite glass by Giess et al. and the first-order partial differential equation. It is verified that the higher the temperature, the more quickly the value of the first-order partial differential equation with time and the relative initial effective activated volume to that in the final equilibrium state increases to zero, and the more reliable the model is.

Keywords: Frenkel's liquid-phase sintering mechanism; Activated pores; Reliability of the model; The first-order partial differential equation

1. Introduction

Frenkel's liquid-phase sintering mechanism has essential influence on the liquid-phase sintering of materials, by which the sintering of glass powders can be successfully interpreted typically. One significant reason is that the shrinkage vs. sintering time is a simple linear relation, which provides the accurate verification for the experimental results[1, 2]. For the ideal glass system, the relation between sintering time and the interfacial radius of two spheric particles was simple linear, verified by Kingery in the 1950s[3]. Kuczynski and Zaplatynskyj also verified the model was accurate by investigation of the sintering of capillary glass tubes[4].

Experimental researches show that Frenkel's liquid-phase sintering mechanism can only be applied to explain the initial 10% of isothermal sintering process for the mass transport governed by viscous flow. For this shortage, Nikolić et al. introduced the activated volume during sintering of materials, considering that the shrinkage was based on the decrease of the activated volume, and established the model of linear shrinkage vs. sintering time during the isothermal sintering process[5]. Nikolić et al. and Yu et al. validated the accuracy of the model via the sintering of iron powders[2] and the integrated liquid-phase sintering of glass-alumina functionally graded materials[6], respectively. However, there are no published references confirming whether the model is theoretically reliable or not for the interpretation of Frenkel's liquid-phase sintering mechanism. This article validates the reliability of the model by the first-order partial differential equation via comparing the model...
2. Interpretation of Frenkel’s liquid-phase sintering theory

Nikolić et al. introduced the concept of activated volume, and considered that the shrinkage was based on the decrease of the activated volume. According to reference[7], the effective activated volume of a system can be defined as:

\[ V = -RT \left( \frac{\partial \ln D}{\partial P} \right) \]  

(1)

Where the diffusion coefficient D is defined as:

\[ D = \gamma a^2 \nu \exp \left( -\frac{\Delta G}{RT} \right) \]  

(2)

where R is the gas constant, T is the sintering temperature, \( \Delta G \) is the change in free energy, P is the pressure, \( \gamma \) is the geometric factor, a is a crystal lattice constant, and \( \nu \) is the Debye frequency.

From the viewpoint of processes occurring during the sintering, the process can be described as gravitation of the electronic system towards an equilibrium state. As the process proceeds, the effective activated volume of a system - \( V \) at any moment during the sintering process is a parameter that with the increase of sintering time gravitates towards the value of equilibrium-activated volume \( V^+ \). The equilibrium state of a system can be characterized by an equilibrium activated volume - \( V^+ \).

From a physical viewpoint, the effective activated volume of a system can be described as:

\[ V = \frac{N_0}{N_r} V^+ \]  

(3)

Where \( N_0 \) represents the concentration of all defects at any given moment and \( N_r \) the equilibrium concentration of defects in the analyzed system.

According to reference[9], reduction of the effective activated volume can be simply defined as:

\[ \frac{V}{V^+} = 1 + \left( \frac{V^0}{V^+} - 1 \right) \exp \left( -\frac{t}{\tau} \right) \]  

(4)

Where \( \tau \) is the time constant, and usually is with minutes as the unit.

In the most general sense, kinetics of the sintering process can be expressed in terms of the dependence of linear shrinkage during isothermal sintering on the sintering time as[5]:

\[ \frac{\Delta L}{L_0} = K' \left( \frac{t}{\tau} \right)^n \]  

(5)

Where \( K' \) - the sintering rate constant, which depends on sintering temperature and time; \( n \) - a constant, which depends on the sintering mechanism; \( t \) - the sintering time.

The sintering rate constant is defined as:

\[ K' = K_0 \exp \left( -\frac{E}{RT} \right) \cdot \phi \left( \frac{t}{\tau} \right) \]  

(6)

Where \( K_0 \) is a constant, R is the gas constant, E is the activation energy, and T is the sintering temperature. The parameter \( \phi \left( \frac{t}{\tau} \right) \) represents a measure of the degree of sintering.

Provided that sintering is the consequence of the transport of activated volume, then the
degree of sintering can be defined as the ratio between the equilibrium activated volume and the effective activated volume:

\[ \varphi\left(\frac{t}{\tau}\right) = \frac{V^+}{V} \]  

(7)

Then taking eq. (7) into eq. (4), we obtain:

\[ \varphi\left(\frac{t}{\tau}\right) = \frac{1}{1 + \left(\frac{V^0}{V^+} - 1\right) \exp\left(-\frac{t}{\tau}\right)} \]  

(8)

Thus the expression of relative linear shrinkage vs. time is given by:

\[ \frac{\Delta L}{L_0} = \frac{K}{1 + \left(\frac{V^0}{V^+} - 1\right) \exp\left(-\frac{t}{\tau}\right)} \left(\frac{t}{\tau}\right)^n \]  

(9)

3. Reliability of the model

According to Frenkel's theory, the linear shrinkage vs. time can be defined as:

\[ \frac{d\Delta L/L_0}{dt} = \frac{3\gamma(T)}{8r\eta(T)} \]  

(10)

Where \( \gamma(T) \) is the surface tension, \( r \) is the radius of the particles, \( \eta(T) \) is the viscosity at fixed temperature. By simple modification, the equation can be changed into:

\[ \frac{\Delta L}{L_0} = \frac{3\gamma \tau}{8r\eta(T)} \cdot \frac{t}{\tau} \]  

(11)

Suppose \( K_F = \frac{3\gamma \tau}{8r\eta(T)} \), which is a constant at definite temperature, thus:

\[ \frac{\Delta L}{L_0} = K_F \left(\frac{t}{\tau}\right) \]  

(12)

Based on the fact that the linear shrinkage vs. time is unique during the whole sintering process at the definite temperature, thus we obtain:

\[ \frac{K}{1 + \left(\frac{V^0}{V^+} - 1\right) \exp\left(-\frac{t}{\tau}\right)} \left(\frac{t}{\tau}\right)^n = K_F \left(\frac{t}{\tau}\right) \]  

(13)

After simple modification, we obtain:

\[ \frac{\left(\frac{t}{\tau}\right)^{n-1}}{1 + \left(\frac{V^0}{V^+} - 1\right) \exp\left(-\frac{t}{\tau}\right)} = \frac{K_F}{K} = \text{constant} \]  

(14)
Define the function
\[
f\left(\frac{t}{\tau}, n, \frac{v^0}{v}\right) = \left(\frac{t}{\tau}\right)^{n-1} \left[1 + \left(\frac{v^0}{v} - 1\right)\exp\left(-\frac{t}{\tau}\right)\right]
\]
and for the whole sintering process, \(\left.\frac{\partial f}{\partial \left(\frac{t}{\tau}\right)}\right|_{n, \frac{v^0}{v}} = 0\), then:

\[
(15)
\]
Taking into account of eq. (15) for a real sintering process, if the value of \(\partial \psi / \partial (t/\tau)\) is near 0, then the model given in eq. (9) is valid.

The relation between \(\partial \psi / \partial (t/\tau)\) and \(t/\tau, v^0/v - 1\) at 800°C, 820°C, 840°C, 860°C of the height and diameter research data of cordierite glass by Giess et al.[10] are as shown in Fig. 1, Fig. 2, Fig. 3 and Fig. 4, respectively. The detail preparation parameters and other parameters are given in reference [10]. The data are given in our recent submitted article [11]. From Figs. 1 to 4, it is obvious that \(\partial \psi / \partial (t/\tau)\) tends to 0 when \(t/\tau\) is greater than 0.15. It should be
addressed that $\frac{\partial f}{\partial (t/\tau)}$ has large values in the very initial stage of sintering because the value of $(t/\tau)^{n-2}$ is rather large when $t/\tau$ is within a small range. The rate of $\frac{\partial f}{\partial (t/\tau)}$ tends to 0 more quickly with $t/\tau$ and $V_0/V^+/1$ increasing when the temperature increases. In general, the model is reliable according to the value of $\frac{\partial f}{\partial (t/\tau)}$ near 0 in the whole sintering process.

Fig. 3. Effect of $t/\tau$ and $V_0/V^+/1$ on the value of $\frac{\partial f}{\partial (t/\tau)}$ at 840°C.

Fig. 4. Effect of $t/\tau$ and $V_0/V^+/1$ on the value of $\frac{\partial f}{\partial (t/\tau)}$ at 860°C.

4. Conclusion

This article compares the model established by Nikolić et al. with that of Frenkel's theory by the phenomenal interpretation taking into account of the activated volume. The training of the height and diameter research data of cordierite glass by Giess et al. is taken as a case, and the first-order partial differential equation which gives the difference between the two models is defined to verify the reliability of the model. We obtained that $\frac{\partial f}{\partial (t/\tau)}$ of the model tends to zero with $t/\tau$ and $V_0/V^+/1$ increasing during the isothermal sintering process in the case that $n$ is a definite value, which verifies that the model is reliable. On the other hand, it is verified that the higher the temperature, the more quickly the value of the first-order partial differential equation with $t/\tau$ and $V_0/V^+/1$ increases to zero, and the more reliable the model is.
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5. References