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Activation energy for crystal growth using isothermal and continuous heating processes

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The kinetics of crystallization of plasma-sprayed amorphous cordierite and forsterite have been studied using both the isothermal Johnson–Mehl–Avrami and the continuous-heating Kissinger approaches. The activation energies for crystal growth obtained from the two processes are essentially equivalent: 1600 ± 400 and 1600 ± 300 kJ mol^{-1} for cordierite and 340 ± 88 and 410 ± 45 kJ mol^{-1} for forsterite, using isothermal and continuous heating, respectively. A correlation between the isothermal and non-isothermal crystallization processes is established.

1. Introduction

The kinetics of crystallization and activation energies are frequently studied by two different thermal analysis methods: isothermal and continuous heating. An isothermal process can be described by the Johnson–Mehl–Avrami equation [1]

$$X(t) = 1 - \exp(-kt^m) \tag{1}$$

where $X(t)$ is the volume fraction of the crystalline phase at time t, m is a morphology index and k is a rate constant which is expressed as

$$k(T) = k_0 \exp(-E/RT) \tag{2}$$

where R is the gas constant and E is the activation energy associated with the process. The volume fraction of the crystalline phase can be experimentally determined for a given system using, for example, differential scanning calorimetry (DSC) [2], transmission electron microscopy (TEM) [3], electrical conductivity for a metallic glass [4], as well as other methods.

Conversely, for continuous heating, the kinetics of a phase transformation has been described by Kissinger using DSC or differential thermal analysis (DTA) at different heating rates [5]. The Kissinger equation is expressed as

$$\ln(\alpha/T_m^2) = -E/RT_m + \text{constant} \tag{3}$$

where α is the heating rate and T_m is the temperature at which the maximum rate of conversion occurs. Thus, the activation energy for a phase transition can be obtained from the Kissinger plot, $\ln(\alpha/T_m^2)$ against $1/T_m$.

The Kissinger equation has been directly used to examine the activation energy for the crystallization of amorphous materials [6–9]. However, crystallization is controlled principally by nucleation-and-growth and not by an nth order reaction, as originally derived by Kissinger. Therefore, modified equations were developed for crystallization by taking the crystallization mechanism into consideration [10, 11].

To our knowledge, no study has been carried out on the correlation between isothermal and continuous heating methods for crystallization. The present study is aimed at obtaining the activation energies for crystal growth of plasma-sprayed cordierite and forsterite using both the isothermal Johnson–Mehl–Avrami and continuous-heating Kissinger approaches. We have sought to understand the relationship between the activation energies for crystal growth obtained using these two processes.

2. Theoretical analysis

A calculation of the activation energy associated with the kinetics of crystallization via isothermal and continuous heating processes can be based on two assumptions [11]:

1. The number of nuclei, N, formed per unit volume is inversely proportional to the heating rate

$$N = C/\alpha \tag{4}$$

2. The linear growth of the crystalline phase is related to the activation energy through

$$U = U_0 \exp(-E_l/RT) \tag{5}$$

where E_l is the activation energy for linear growth of the crystalline phase, C and U_0 are constants.

For an isothermal process, the volume of a spherical crystalline phase, V_t, at an annealing time, t, is expressed by [1]

$$V_t = \frac{4\pi}{3}(Ut)^3 N V_0 \tag{6}$$

where V_0 is the initial volume of amorphous material. Based on Equation 4, the number of nuclei reaches a maximum value, N_{max} (mathematically infinite, but physically a large, constant number), in the isothermal process when the heating rate is zero. Substituting N from Equation 4 and U from Equation 5 into Equation 6, the fraction of crystalline phase, X, can be

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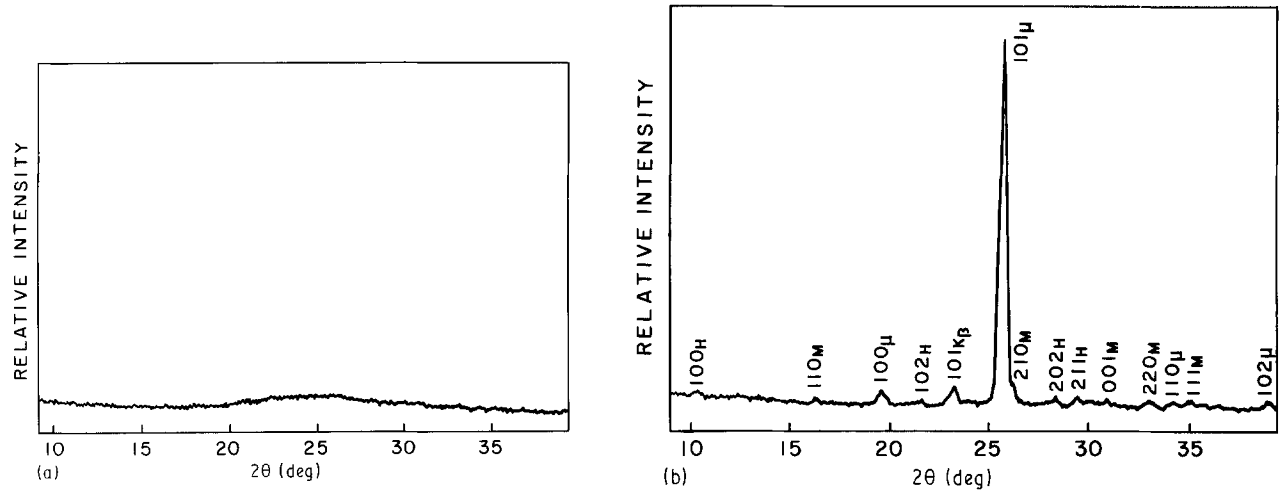

Figure 1 X-ray diffraction patterns of plasma-sprayed cordierite: (a) as-sprayed condition; (b) annealed at 900° C for 4 h. hkl_μ = μ-cordierite, hkl_H = high cordierite, hkl_M = mullite.

expressed as

$$X = \frac{V_t}{V_0} = \frac{4\pi}{3} U_0^3 N_{\max} \exp\left(-\frac{3E_I}{RT}\right) t^3 \qquad (7)$$

or more generally,

$$X = qU_0^m N_{\max} \exp\left(-\frac{mE_I}{RT}\right) t^m \qquad (8)$$

where q is a shape factor and m is a constant which is related to the growth mechanism. Let a constant $K_0 = qU_0^m N_{\max}$, and consider the activation energy for volume crystal growth, E, to be equal to mE_I [12]. Equation 8 becomes

$$X = k_0 \exp\left(-\frac{E}{RT}\right) t^m \qquad (9)$$

Differentiating Equation 9 with respect to t, and considering a depletion correction factor, $(1 - X)$, for the reduction of amorphous phase, the following is obtained

$$\frac{dX}{dt} = mk_0 \exp\left(-\frac{E}{RT}\right) t^{m-1}(1 - X) \qquad (10)$$

Integrating Equation 10 yields the following results

$$X = 1 - \exp(-kt^m) \qquad (11)$$

$$k = k_0 \exp(-E/RT) \qquad (12)$$

For continuous heating at a constant heating rate, α, the radius of a spherical crystal particle, r, can be obtained by integrating Equation 5, $dr/dt = U = U_0 \exp(-E_I/RT)$

$$r = \int_0^t U_0 \exp\left(-\frac{E_I}{RT}\right) dt = \frac{U_0}{\alpha} \int_{T_r}^{T} \exp\left(-\frac{E_I}{RT}\right) dT \qquad (13)$$

This integral can be expressed by Doyle's p-function and solved numerically, if $E_I/RT > 20$ [13].

$$r = \frac{C'}{\alpha} \exp\left(-1.052 \frac{E_I}{RT}\right) \qquad (14)$$

where C' is a constant.

For three-dimensional crystal growth, the variation of crystal volume fraction is expressed as

$$\frac{dX}{dt} = 4\pi r^2 N(1 - X) \frac{dr}{dt} \qquad (15)$$

where $(1 - X)$ is the same depletion correction factor as that for the isothermal process.

Substituting Equations 4, 5 and 14 into Equation 15, gives

$$\frac{dX}{dt} = \frac{4\pi C U_0 C'^2}{\alpha^3}(1 - X) \exp\left(-1.052 \frac{3E_I}{RT}\right) \qquad (16)$$

or more generally

$$\frac{dX}{dt} = \frac{C''}{\alpha^m}(1 - X) \exp\left(-1.052 \frac{mE_I}{RT}\right) \qquad (17)$$

where C'' is a constant.

The rate of increase of X reaches a maximum at a temperature T_m by setting $d/dt(dX/dt) = 0$, leading to

$$\ln\left(\frac{\alpha^n}{T_m^2}\right) = -1.052 \frac{E}{RT_m} + \text{constant} \qquad (18)$$

where $n = m + 1$ is for crystallization process involving nucleation and crystal growth; and $n = m$ is for a system containing a sufficiently large number of nuclei, i.e. crystallization is mainly composed of crystal growth.

3. Experimental procedure

The materials used in this study were cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and forsterite ($2MgO \cdot SiO_2$). The powders were produced by fusing, mechanical reduction and sizing by Muscle Shoals Minerals, yielding 80 wt % of particles in the range between 37 and 74 μm. The deposits were plasma sprayed using an automated Plasma Technics system. In the spray process, the powders are introduced into a high-temperature effluent, heated to a molten state, and rapidly quenched upon impact on a salt-coated steel substrate. After plasma spraying, deposits were removed from the substrate by submersion in water. The plasma-spray parameters as well as the microstructural study of the as-sprayed deposits are given elsewhere [14].

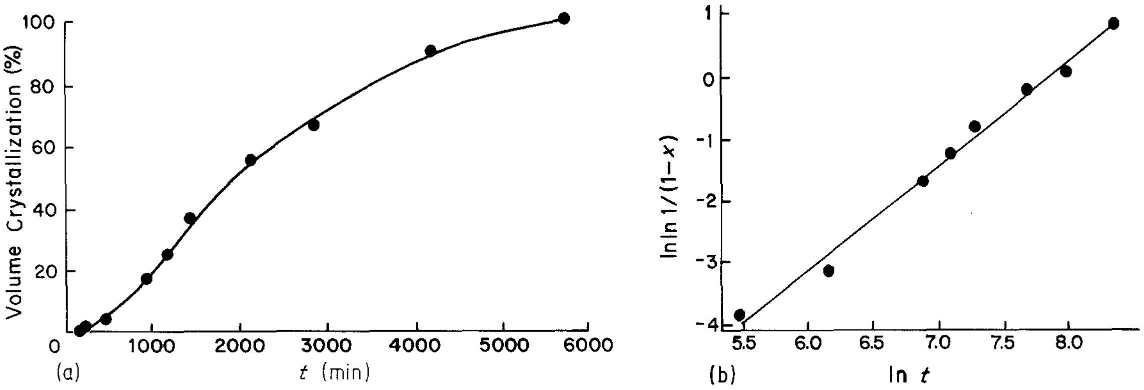

Figure 2 (a) Isothermal crystallization of cordierite at 870° C. (b) Plot of lnln $(1 - X)^{-1}$ against ln (t).

Isothermal crystallization of plasma-sprayed cordierite was studied using a conventional X-ray diffractometer. The samples were heated at 870 and 900° C for different times followed by air cooling. Isothermal crystallization of forsterite was studied using a high-temperature X-ray diffractometer where the sample holder, a platinum strip, could be heated in air to the desired temperature in about 2 min. Data were collected at three isothermal conditions, 670, 700 and 730° C for different times, using Cu$K\alpha$ radiation with a scan rate of $1° \text{min}^{-1}$. The quantitative analysis of crystallinity for a partially devitrified glass is based on the principle that the volume percentage of crystallinity is proportional to the integrated intensity of X-ray diffraction peaks for the partly devitrified glass [15].

For continuous heating, all samples were examined with a Perkin–Elmer 1700 DTA system. The pulverized coating, with particle size less than 60 μm, was placed into the sample holder, and compared with the reference material of alumina powder. The heating rates were selected as 1, 2, 4, 10, 25 and $40° \text{min}^{-1}$.

4. Results and discussion

Figure 1a is an X-ray diffraction pattern of as-sprayed cordierite, indicating that an amorphous structure is obtained by plasma spraying. On annealing at 900° C for 4 h, crystallization to μ-cordierite occurs, as shown in Fig. 1b. The volume fraction of the crystalline cordierite was determined by the relative intensity of the (1 0 1) diffraction peak of the μ-cordierite. Using Equation 11, the growth rates of the crystalline phase are plotted in Fig. 2a for an annealing temperature of 870° C and in Fig. 3a for a temperature of 900° C. Linear regression analyses of the plot, lnln $[1/(1 - X)]$ plotted against ln (t) gives correlation coefficients of 0.995 and 0.978 as well as morphology indexes of 1.70 and 1.53 for the temperatures 870 and 900° C, respectively, as shown in Figs 2b and 3b. Using Equation 12, the activation energy obtained from the isothermal treatments is found to be $1600 \pm 400 \text{kJ mol}^{-1}$.

Fig. 4 is a continuous heating Kissinger plot for cordierite using Equation 18, where m is chosen to be an average value of 1.6. As noted from the X-ray diffraction pattern (Fig. 1a), the as-sprayed cordierite is amorphous, and thus the crystallization process is composed of nucleation and crystal growth, therefore, $n = m + 1$. The activation energy evaluated from the slope of the plot gives a value of $1600 \pm 300 \text{kJ mol}^{-1}$, which agrees well with the value obtained from the isothermal process.

Figs 5a and b are the X-ray diffraction patterns of forsterite in the as-sprayed deposit and the deposit annealed at 700° C for 6 h, respectively. As noted from the X-ray diffraction pattern, the as-sprayed forsterite is composed of amorphous and crystalline phases, and therefore the crystallization process is mainly crystal growth. The isothermal processes were examined by X-ray diffraction of the two stronger peaks (d-spacing 0.388 and 0.246 nm). Linear regression analyses of lnln $[1/(1 - X)]$ plotted against ln (t) gave correlation coefficients of 0.984, 0.985 and 0.985, as well as the morphology indexes of 1.60, 1.62 and 1.67 for the temperatures 670, 700 and 730° C, respectively. The slope in Fig. 6 is used to determine the activation energy from Equation 12, which is found to be $340 \pm 88 \text{kJ mol}^{-1}$.

Fig. 7 is a Kissinger plot for forsterite using Equation 18 where m is 1.6 and n is assumed equal to

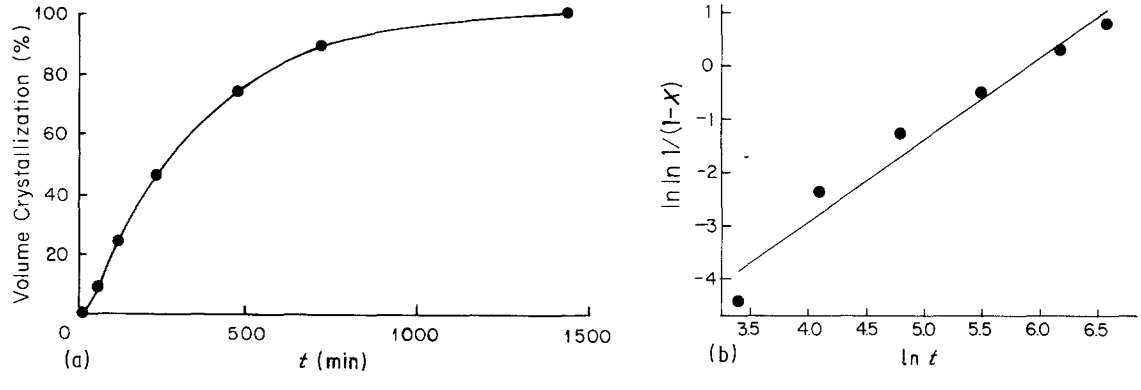

Figure 3 (a) Isothermal crystallization of cordierite at 900° C. (b) Plot of lnln $(1 - X)^{-1}$ against ln (t).

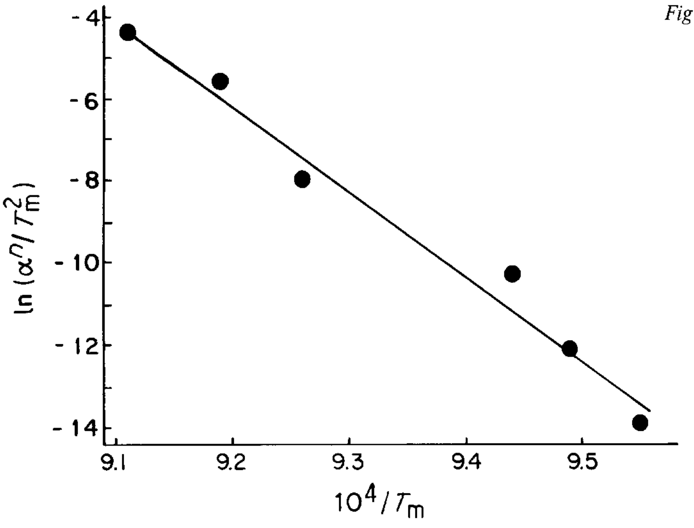

Figure 4 Kissinger-type plot for cordierite using continuous heating.

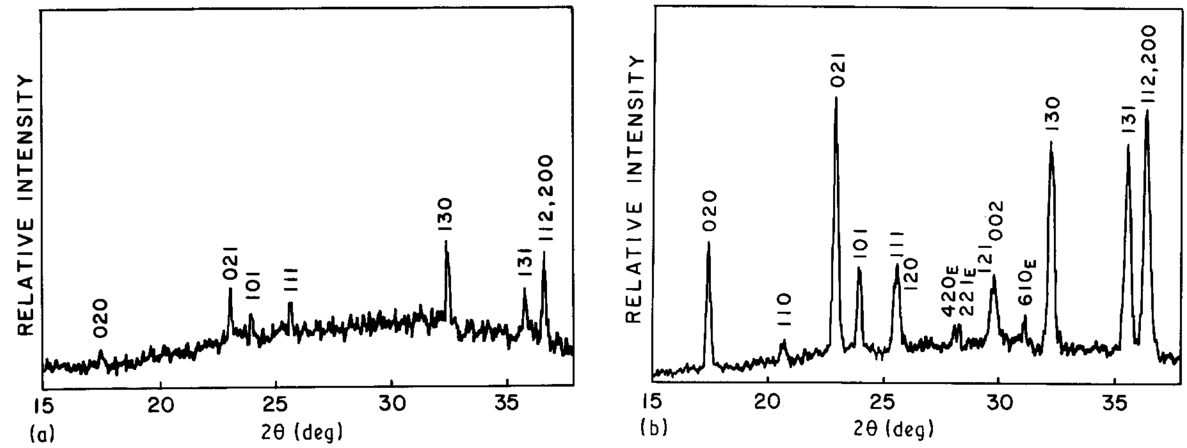

Figure 5 X-ray diffraction patterns of plasma-sprayed forsterite: (a) as-sprayed condition; (b) annealed at 700° C for 6 h. hkl = forsterite, hkl_E = enstatite.

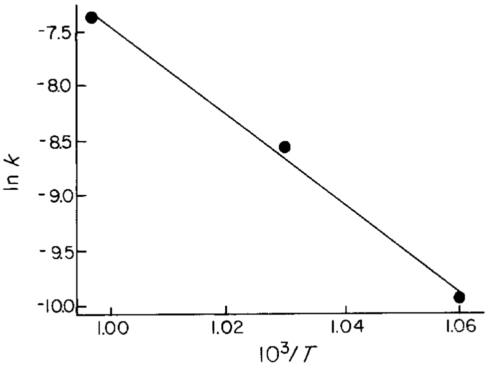

Figure 6 Plot of ln (k) against $1/T$ for isothermal crystal growth of forsterite.

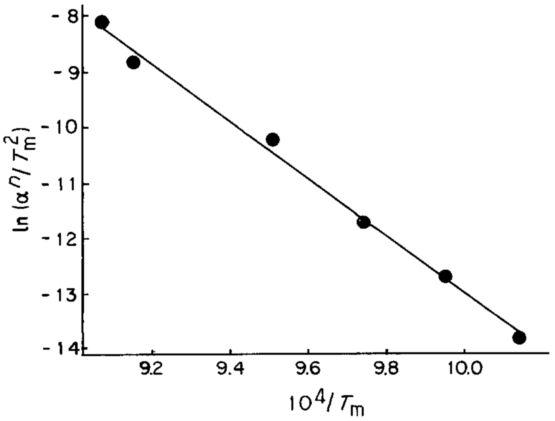

Figure 7 Kissinger-type plot for forsterite using continuous heating.

m for crystal growth. As a result, the activation energy obtained from this continuous heating process is found to be 410 ± 45 kJ mol^{-1}. It can be noted that the activation energies of forsterite obtained from the isothermal and continuous heating methods differ by only 17%.

5. Conclusion

The crystallization kinetics of plasma-sprayed cordierite and forsterite oxides have been studied using isothermal and continuous heating processes. The theoretical development and the experimental results show good agreement between the activation energies for crystal growth obtained from the isothermal and continuous heating methods for both plasma-sprayed cordierite and forsterite.

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