A FRACTAL MODEL FOR THE CRYSTALLIZATION KINETICS

by

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The Kolmogorov-Johnson-Mehl-Avrami equation is wildly applied in the crystallization kinetics, and Avrami exponent involved in the equation plays an important role in crystallization process. Here we show that the Kolmogorov-Johnson-Mehl-Avrami equation can be obtained by a fractal crystallization model, and the exponent is explained as the fractal dimension in time, which depends upon the chain length and molecule weight.

Key words: *Kolmogorov-Johnson-Mehl-Avrami model, fractal derivative, isothermal crystallization, fractal calculus*

Introduction

The crystallization process plays an important role in material science, a higher crystallization always implies higher permanence of the material, *e. g.*, higher mechanical property [1-3] and higher geometric potential (surface energy) [4-7]. The first-order kinetics for the degree of crystallization, u, can be expressed:

$$\frac{\mathrm{d}u}{\mathrm{d}t} = k(1-u),\ u(0) = 0 \tag{1}$$

where k is the crystallization rate:

$$u(t) = 1 - \mathrm{e}^{-kt} \tag{2}$$

Equation (2) is, however, valid for limited cases, and it is generally modified [8-10]:

$$u(t) = 1 - \exp[-(kt)^{\alpha}] \tag{3}$$

where α is the Avrami exponent. In literature, eq. (3) is called as the Kolmogorov-Johnson-Mehl-Avrami equation (KJMA equation) [11]. This paper will insight into the physical understanding of Avrami exponent, which varies generally from 1-4.

Fractal crystallization model

The crystallization process depends upon the internal structure of the solid body, including the rigid lattice of molecules, the molecule chain, the molecule weight, and atoms or ions. A longer chain or a larger molecule weight always means slower crystallization process [12, 13]. Additionally the nucleation and growth processes will also affect the degree of crystallization.

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We assume that the regularity of each molecule chain or lattice in the internal structure of the studied solid body requires averagely Δt for a crystal growth, when $t > \Delta t$ the first-order kinetic law can be approximately predicted the degree of crystallization, however, when $t < \Delta t$, the degree of crystallization is unpredictable. So we need the two scales of time to describe the degree of crystallization [14, 15], one is the large-scale $t > \Delta t$ for the continuum model, and the other is a smaller scale, Δt, for the fractal model [16].

Generally the degree of crystallization is not differentiable with respect to time, but it is differentiable with respect to t^{α}, where α is the fractal dimension.

According to the aforementioned analysis, the first-order kinetics should be modified:

$$\frac{\mathrm{d}u}{\mathrm{d}t^{\alpha}} = K(1-u),\ u(0) = 0 \tag{4}$$

where K is a constant, $\mathrm{d}u/\mathrm{d}t^{\alpha}$ – the fractal derivative defined [16]:

$$\frac{\mathrm{d}u}{\mathrm{d}t^{\alpha}}(t_0^{\alpha}) = \lim_{\substack{t-t_0\to\Delta t \\ \Delta t\neq 0}} \frac{u(t^{\alpha}) - u(t_0^{\alpha})}{(t-t_0)^{\alpha}} \tag{5}$$

The fractal models using the aforementioned fractal derivative has been widely applied to various complex problems [17-27]. The solution of eq. (4):

$$u = 1 - \exp(-Kt^{\alpha}) \tag{6}$$

When $K = k^{\alpha}$, eq. (6) is the KJMA equation.

Conclusion

Nottale found that time does be discontinuous in microphysics [28], that means that the fractal kinetics takes place on micro time scale. Hereby we explain Avrami exponent as the fractal dimension in time, it depends upon the molecule's chain length and the molecule's weight. A longer chain or a larger molecule weight implies a smaller Avrami exponent.

This paper suggests for the first time ever a fractal crystallization kinetics, which can take into account the molecule's structure and properties, the model leads exactly to the KJMA equation [11], revealing our theory is reliable.

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