研究快报

NEW ISOTHERMAL MODEL FOR GRAIN GROWTH IN NANOCRYSTALLITES

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INTRODUCTION

Nanocrystallites with an average grain size of less than 100 nm have attracted considerable scientific interest because of the improvements in a variety of properties resulted from grain-size refinement in the nanometer scale. The investigation of the thermal stability or grain growth behavior is therefore important from the technological point of view as well as for the purpose of scientific study.

For conventional polycrystalline or coarse grain materials, the driving force for grain growth arising from the decrease of the system energy caused by the reduction of total grain boundary energy. The rate of grain growth is proportional to the radius of curvature of the grain and the kinetic equation of grain growth is as folows[1]

$$D^n - D_0^n = kt \tag{1}$$

where D is the average grain size after annealing, D_0 is the initial average grain size, t is the annealing time and k is a temperature (T) dependent rate constant reflecting the diffusion effect. The constant k can be expressed in an Arrhenius type equation, $k \propto \exp(-Q/RT)$ with Q being the activation energy for isothermal growth and R the gas constant. The index n in Eq. (1) is called the grain growth exponent.

In fact, the dynamics of grain growth and their mechanism for nanocrystallite formation are not clear entirely. Usually, Eq. (1) has been used for characterization of nanocrystallites. But, Eq. (1) can not describe the behavior of nanocrystallite very well.

RESULTS AND DISCUSSION

A new isothermal model for grain growth in nanocrystallites was proposed by considering that k is affected by not only the factor of diffusion but also by the factor of reactivity

$$\frac{1}{k} = \frac{\lambda}{k_D} + \frac{1-\lambda}{k_A} = \frac{\lambda}{\exp(-Q_D/RT)} + \frac{1-\lambda}{\exp(-Q_A/RT)}$$
$$= \lambda\exp(Q_D/RT) + (1-\lambda)\exp(Q_A/RT) \tag{2}$$

where λ is an coefficient of diffusion effect, D and A are the diffusion effect and reactivity effect, respectively, k_D and k_A are constants of diffusion effect and reactivity effect, respectively, Q_D and Q_A are the activation energy for isothermal growth of diffusion and reactivity, respectively. Usually, $D_0 \ll D$, so Eq. (1) becomes

$$1/D = k^{-1/n}t^{-1/n}$$
$$= [\lambda\exp(Q_D/RT) + (1-\lambda)\exp(Q_A/RT)]^{1/n}t^{-1/n} \tag{3}$$

Because of

$$\exp(x) = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \cdots \tag{4}$$

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Table 1　Some regression results of our proposed model and conventional model

System	Author's model			Conventional model			Temp. /K	Data points	Ref.
	R	*SD*	*P*	*R*	*SD*	*P*			
Perovskite	0.9705	0.0063	0.0295	0.8817	0.6018	0.1183	773—1273	4	[3]
Ceria	0.9985	0.0032	<0.0001	0.9699	0.1786	0.0014	300—1173	8	[4]
(Pb,Ca,La)TiO_3	0.9997	0.0006	<0.0001	0.9725	0.1520	0.0055	823—12123	5	[5]
$LaCrO_3$	0.9959	0.0009	0.0003	0.9693	0.2273	0.0064	871—1482	5	[6]
TiO_2	0.9986	0.0023	<0.0001	0.9753	0.1472	0.0046	623—1023	5	[7]

R—correlation coefficient;
P—value-probability (where *R* is zero);
SD—standard deviation of the fit.

Then Eq. (3) becomes

$$1/D=\{1+[\lambda Q_D+(1-\lambda)Q_A]/RT+[\lambda Q_D^2+(1-\lambda)Q_A^2]/2(RT)^2+\cdots\}^{1/n}t^{-1/n} \quad (5)$$

$$[\lambda Q_D^2+(1-\lambda)Q_A^2]/2(RT)^2\ll 1$$

so Eq. (5) becomes

$$1/D\approx\{1+[\lambda Q_D+(1-\lambda)Q_A]/RT\}^{1/n}t^{-1/n}$$
$$=\{1+[\lambda Q_D+(1-\lambda)Q_A]/nRT\}t^{-1/n}$$
$$=t^{-1/n}+t^{-1/n}[\lambda Q_D+(1-\lambda)Q_A]/nRT=A_1+B_1/T \quad (6)$$

Comparatively, as the conventional model, Eq. (1) becomes

$$\ln D=A_2+B_2/T \quad (7)$$

Table 1 lists some regression results of our proposed model, Eq. (6) and the conventional model, Eq. (7). It is shown from Table 1 and Fig. 1 that author's model is better than the conventional one.

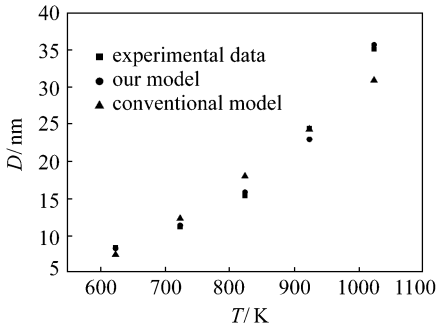

Fig. 1　Comparison of experimental data in Ref. 7 and correlation points of two models

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