Computer prediction system on solid/ solid reaction kinetics [①]

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[**Abstract**] A computer software system of kinetic predication of solid/ solid reaction, KinPreSSR, was developed using Visual C^{++} and FoxPro. It includes two main modules, REACTION and DIFFUSION. KinPreSSR deals with the kinetics on the diffusion in solids as well as solid/ solid reactions. The REACTION module in KinPreSSR was mainly described, which has organized the commonly recognized kinetic models, parameters, and employed both numerical and graphical methods for data analyses. The proper combination between the kinetic contents and the analytical methods enables users to use KinPreSSR for the evaluation and prediction of solid/ solid reactions interested. As an example to show some of functions of KinPreSSR, the kinetics analysis for the reaction between $SrCO_3$ and TiO_2 powders to form $SrTiO_3$ with a series of kinetic data from isothermal measurements was demonstrated.

[**Key words**] solid/ solid reactions; kinetic prediction; software system

[**CLC number**] TB 321　　　　　　　　　　　　　[**Document code**] A

1 INTRODUCTION

Great achievements have been reached in the development of computerized thermochemical or thermodynamics databases since the later 1960s[1]. However, efforts toward the establishment of the relevant kinetics database and software system could be traced back to only a decade ago. In fact, there are only a few reports about kinetics software systems such as KINDAS[2], DICTRA[3] and Intellectualized Database Management System on Kinetics of Metallurgy and Material (IDMSKM) developed by the authors[4]. The previous work of IDMSKM had concentrated on the necessary databases of physical properties of metallurgical melts as well as subsystems on gas/ solid and gas/ liquid reaction kinetics.

Solid/ solid reactions and diffusion in solids are the most important phenomena in materials processing and interaction between materials themselves in the working environment. The materials design, the control and optimization of materials manufacture often necessitate the information regarding the process mechanism analysis and rate predictions. In order to meet such a requirement, kinetics prediction system of solid/ solid reactions (KinPreSSR), as a continuation of IDMSKM, is developed.

KinPreSSR consists of two major modules, REACTION and DIFFUSION dealing with the kinetic analysis and evaluations of solid/ solid reactions and diffusion in solids respectively. In this paper, attention is focused on the description of REACTION module. DIFFUSION module will be presented elsewhere in the near future.

2 STRUCTURE AND MAIN FEATURES

Fig. 1 shows the structure of KinPreSSR. In either module of REACTION or DIFFUSION, there are two sub-modules, DBMS and Evaluation & Prediction. DBMS means database management system.
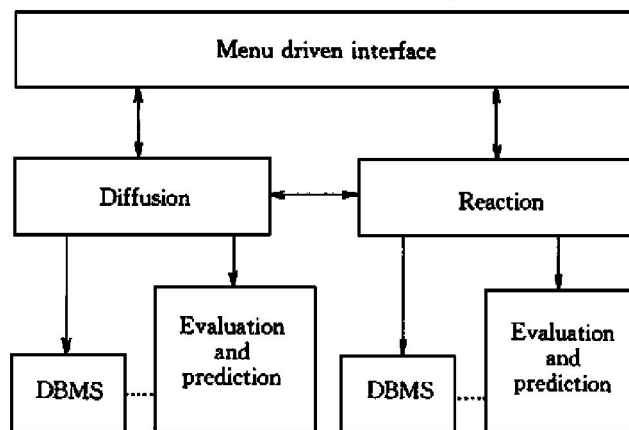

Fig. 1　Structure of KinPreSSR

KinPreSSR possesses main features as: 1) user-friendly and interactive operation mode; 2) a windows application system with graphical display on screen and printed outputs; 3) various file management functions, "save" in user specified type of files, including ASCII files for the convenience of data exchanging and processing.

3 REACTION MODULE IN KinPreSSR

3. 1　Fundamental bases of solid/ solid reaction kinetic evaluation

Since the first kinetic model for solid state reactions between powdered reactants was formulated by Jander[5, 6], a number of rate equations have been proposed and tested[7~ 12] and the total number of kinetics models is nearly 40. Several authors[13~ 17] have reviewed the merits of these equations.

Some models are used only for some special reaction systems, or the mathematical formalism of some models is similar and it is difficult to distinguish the models in the data analysis, so, only commonly recognized models[14] have been selected for the kinetic evaluations in KinPreSSR. These models are symbolized with two letters and listed in Table 1. The reaction mechanism, i. e. the rate controlling steps are included in the second column, while the relevant integral equations for the reaction kinetics are illustrated in the third column.

Generally, the solid/ solid reactions are classified into four categories as:

1) The diffusion-controlled reactions corresponding to models of $D_1 \sim D_5$.

2) The nucleation-controlled reactions corresponding to $N_1 \sim N_5$.

3) The interface-reaction controlling mechanism corresponding to $R_1 \sim R_3$.

4) Diffusion and interface-reaction mixed controlling mechanism corresponding to M_1.

To identify rate models, a given set of observations of fraction transformed α vs time t are usually tested for linearity by plotting $f(\alpha)$ vs t and using linear regression analysis, or graphical analysis. Both of the analysis approaches have been adopted for evaluations in REACTION.

Linear regression analysis is carried out by comparing the models in Table 1 in terms of their correlation coefficients, and the linearity of the $f(\alpha)$ vs t plots.

Graphical analysis was proposed by Sharp[11]. The functions on the left hand side of the kinetic equations listed in Table 1, except N_3, N_4 and M_1, can be converted to an expression in the form as $f(\alpha) = C(t/ t_{0.5})$ by a mathematical treatment. $t_{0.5}$ is the time required to reach a fractional conversion of 0.5, usually called as reduced-time, and C is a constant only depending on the formalism of $f(\alpha)$. For example, the equation D_4 in Table 1 put forward by Ginstling and Brounshtein for a diffusion controlled reaction can be converted to $D_4(\alpha) = 0.036\ 7(t/ t_{0.5})$. The models in Table 1 will be compared by comparing the shapes of α vs reduced-time $t_{0.5}$ plots, so the rate model is identified.

In addition, Arrhenius equation is adopted in KinPreSSR to get the kinetics parameters. The temperature dependence of reaction rate constant is expressed by $k = k_0 \exp\left[-\dfrac{E}{RT}\right]$, where k is reaction rate constant, k_0 is pro-exponential factor, E is activation energy of reaction, R is gas constant and T is temperature in Kelvin.

3. 2　Main functions of REACTION

Multi-order menu and Windows mode have been adopted in KinPreSSR. If Reaction in main menu is clicked, four submenu items, Reaction/ Single model fitting, Reaction/ Multi-model fitting, Reaction/ Prediction and Reaction/ Query will pop-up. The main functions of REACTION are summarized as follows.

Table 1　Models used in kinetics analysis of solid/ solid reaction in KinPreSSR

Symbol	Model	Equation(c is a constant)
R_1	1-D interface reaction	$\alpha = kt$
R_2	2-D interface reaction	$1 - (1-\alpha)^{1/2} = kt$
R_3	3-D interface reaction	$1 - (1-\alpha)^{1/3} = kt$
N_1	Nucleation (Avrami)	$[-\ln(1-\alpha)]^{1/2} = kt$
N_2	Nucleation (Erofe'ev)	$[-\ln(1-\alpha)]^{1/3} = kt$
N_3	Nucleation (Avrami-Erofe'ev)	$\ln\ln(1/(1-\alpha)) = k\ln t + c$
N_4	1-D nucleation and a constant growth rate	$\ln \alpha = kt$
N_5	Random nucleation and rapid growth	$-\ln(1-\alpha) = kt$
M_1	Diffusion and interface-reaction mixed controlling mechanism	$\alpha = k\ln t + c$
D_1	1-D diffusion	$\alpha^2 = kt$
D_2	2-D diffusion	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$
D_3	3-D Diffusion (Jander)	$[1 - (1-\alpha)^{1/3}]^2 = kt$
D_4	3-D Diffusion (Ginstling and Brounshtein)	$1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt$
D_5	3-D Diffusion (Carter) *	$\dfrac{z - (z-1)(1-\alpha)^{2/3} - [1 + (z-1)\alpha]^{2/3}}{z-1} = kt$

* Refers to the volume of the reaction product per unit volume of the initial materials.

1) The reaction mechanism could be estimated by the linear regression analysis of a given series of experimental data of fractional conversion, α, for a solid reactant with the reaction time, t, at a specified temperature.

2) With pre-ascertained rate controlling step, the kinetic model of a reaction could be determined, the corresponding kinetic parameters can be extracted.

3) Two routes are provided for the kinetic evaluation and prediction of a reaction, such as to predict time required to reach a specified fractional conversion at a given reaction temperature or to take the converse task.

4) The kinetic parameters stored in the Database sub-module, DBMS in REACTION for reactions at specified experimental conditions could be retrieved and be used for the evaluation and predictions.

5) With a reasonable amount of experimental data, interpolation or exploration method within a specified conversion fraction and temperature range could be used for the analyses and predictions.

6) Graphical, tabular and simple text modes are comprehensively used and could be selected for the display of results.

4   KINETIC ANALYSIS OF FORMATION SrTiO₃ FROM SrCO₃ AND TiO₂

In this section, an example is given to reveal how KinPreSSR is being used, therefore partially to show functions of the system.

Table 2[18] presents a series of kinetic data of α and t for the reactions between $SrCO_3$ and TiO_2 powders to form $SrTiO_3$ at 5 different temperatures from 788 ℃ to 934 ℃. If the submenu item of Reaction/ multi model fitting is clicked, a dialog window will pop-up. Users may firstly input data of α and t at a certain temperature, then select models to be exam-

ined from R_1 to D_5. From the upper-right side in this window, Linear regression or Graphics can be selected. If Linear regression is selected, KinPreSSR will display the results of linear regression analysis. The displayed contents include listing three models in order of their absolute correlation coefficient values, which would be all greater than those generated from all the other selected models. Fig. 2 is the example of output for data at 788 ℃, the linearity of $f(\alpha)$ vs t plots and correlation coefficients are clearly displayed. With such an approach, it can be determined that the Ginstling-Brounshtein model (D_4) is the most satisfactory rate model at 788 ℃, 866 ℃, 906 ℃ and 934 ℃, while the Jander model (D_3) can be found to give best fitting at 820 ℃. Since either D_4 or D_3, is formulated on the basis of diffusion-controlled reactions, so the diffusion-controlled mechanism can be determined as diffusion-control. If "Graphical analysis" is selected, KinPreSSR could show a direct shape comparison between the standard α-$t/t_{0.5}$ curves of selected models with the experimental data marked on the same plot. Fig. 3 is such a comparison between the data at 866 ℃ in Table 2 with the standard curves while using Graphical analysis mode. For the sake of clarity, the comparison of the data with a single curve selected is also available.

If data for more than two temperatures are available, and the mechanism at each of the temperatures is the same, also the corresponding Arrehenius plot and the apparent reaction activation energy could be given. Fig. 4 is such an output example for data listed in the Table 3 after selecting menu item of Reaction/ Single model fitting. It illustrates that the kinetics of the reaction can be described fairly well by Ginsting-Brounsheein model (D_4) and the apparent activation energy evaluated based on this model is 270 kJ/mol. The mechanical analysis of model D_4 is shown in Table 4.

Table 2   Fraction of $SrTiO_3$ converted from $SrTiO_3$-TiO_2(anatase) mixtures as function of time at various temperatures[18]

788 ℃		820 ℃		866 ℃		906 ℃		934 ℃	
t/h	α	t/h	α	t/h	α	t/h	α	t/min	α
0.25	0.0854	0.25	0.1298	0.25	0.2871	0.25	0.3825	10	0.5076
0.5	0.1287	0.5	0.1752	0.5	0.435	0.5	0.551	20	0.7410
1	0.167	1	0.2684	1	0.6334	1	0.7565	30	0.8606
2	0.2789	2	0.4497	2	0.831	2	0.9438	40	0.9254
4	0.3911	4	0.6887	4	0.9899	–	–	60	0.9908
7	0.4886	7	0.8274	–	–	–	–	–	–
10	0.6303	10	0.8956	–	–	–	–	–	–
15	0.7123	–	–	–	–	–	–	–	–
24	0.8352	–	–	–	–	–	–	–	–

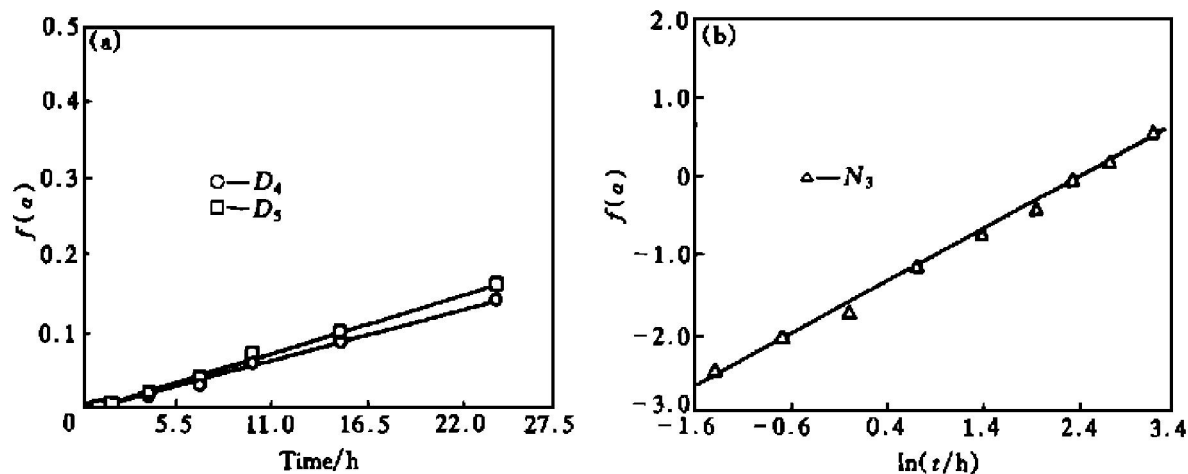**Fig. 2** Graphical display data at 788 ℃ in Table 2 using $f(α)$ for fitting
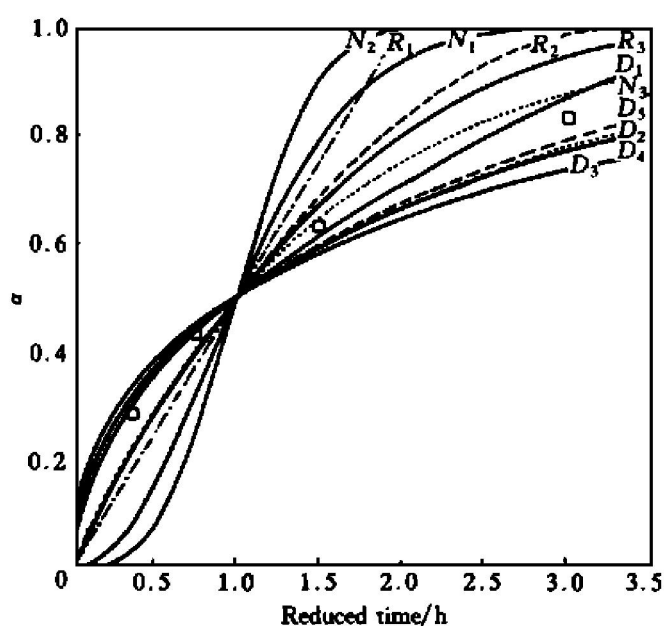(a) $-f(α)= D_4$, D_5; (b) $-f(α)= N_3$

Fig. 3 Graphical display data at 866 ℃
and function $f(α)$ in Table 2 for fitting

5 DISCUSSION

The plot shown in Fig. 3 illustrates that models for D_1, D_2, D_3, D_4 and D_5 are very similar; D_2, D_3 and D_4 can hardly be distinguished below $α = 0.7$. Likewise curves for R_2 and R_3 are close similarly. The situation could also be reflected from the very close correlation coefficient values with the relevant models. This may imply that the extremely accurate data from experimental measurements would be needed to distinguish the reaction mechanism from the various options. If powder reactants are used, particles of uniform size and shape might be desirable, which could seldom be satisfied. Carter[19] has stated that to warrant any conclusions as to the validity of a model, the data must fit the model to 100% reaction. This may be an ideal situation but is difficult to be reached. Some available micro-observations, especial-

ly dynamic measurements, could be helpful approaches to identify the mechanism of the reactions con-
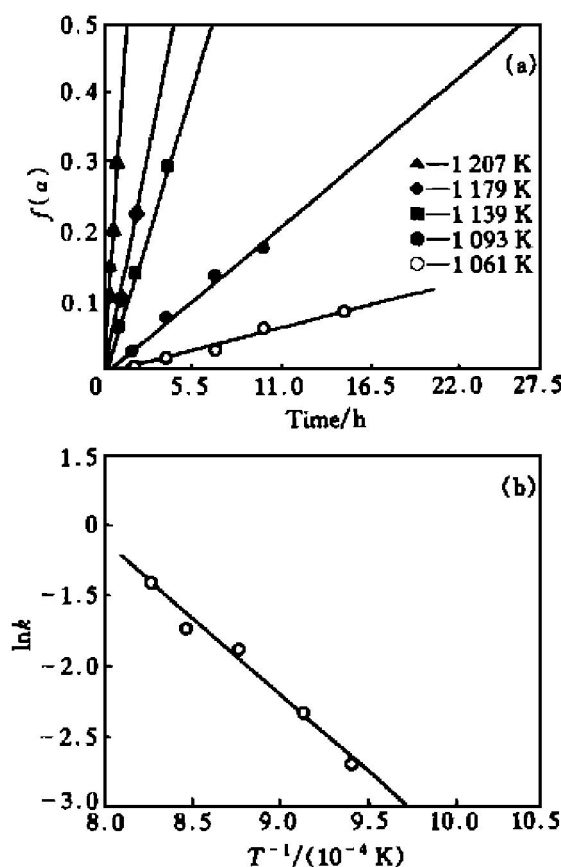

Fig. 4 All graphical display data in Table 2 after submenu item of Reaction/ Single model fitting
(a) $-f(α)= D_4$; (b) $-$Arrhenius plots

Table 3 Mechanism analysis using linear regression

Model symbol	D_4	D_5	N_3
Correlation coeff	0.998 05	0.997 84	0.997 46
Rate constant/ h^{-1}	0.005 93	0.006 79	0.658 60
Standard deviation	0.003 44	0.003 79	0.079 32
Number of points	9	9	9

Table 4　Mechanism analysis of model D_4

Temperature/K	Rate const/h^{-1}	Intercept	$r(k)$	SD	Activation energy
1 061.00	0.005 9	0.000 0	0.998 0	0.003 4	$E = 270\,633.50\,\text{J/mol}$
1 093.00	0.018 6	0.000 0	0.995 9	0.007 5	$k_0 = 1.44 \times 10^{11}$
1 139.00	0.072 0	0.000 0	0.999 9	0.007 6	$r(k) = 0.989\,98$
1 179.00	0.109 6	0.000 0	0.999 9	0.007 5	
1 207.00	0.300 6	0.000 0	0.997 1	0.007 9	

SD is standard deviation, $r(k)$ is the correlation coefficient of linear regression $\ln(k/[k])$ against $1/T$.

cerned.

6　CONCLSTIONS

KinPreSSR is a Windows application dealing with the kinetics of the diffusion in solid state as well as solid/ solid reactions, which are most important phenomena in materials manufacture and interactions with their working environments. KinPreSSR has organized the commonly recognized kinetic models, parameters and employed both numerical and graphical methods for data analyses, evaluation and prediction. The information provided by using KinPreSSR is useful for materials design and optimization of technology processing.

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(Edited by LONG Huai zhong)