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ELECTRON BEAM STIMULATED CHEMICAL REACTION IN SOLIDS

N. Z. Lyakhov, V. V. Boldyrev, A. P. Voronin, O. S. Gribkov, I. G. Bochkarev, S. V. Rusakov and V. L. Auslender

Institute of Solid State Chemistry, Siberian Branch of Russian Academy of Science, 630128
Novosibirsk, Kutateladze str. 18, Russia

Abstract

Use of electron beams allows to obtain new effects in high temperature chemistry of solid state. A stimulated influence of irradiation at comparable temperature conditions may be a subject of technological interest taking into account that increase of reaction rate can reach significant values.

Keywords: complex oxides, high temperature chemistry, use of electron beams

Introduction

High power electron beams are available now in many laboratories. This makes possible to create new conditions for solid state reactions when usual heating is associated with high energy irradiation. As a result two samples one of which is heated by usual way and another one by electron beam will have different concentrations of defects at the same temperature and different reactivity. This possibility of comparative studies may be very interesting from the viewpoint of better understanding of reaction mechanisms.

It is to be noted that the process of conversion of beam energy into heat in solids is very fast when electrons are accelerated up to 1÷2 MeV, and appearance of more or less significant concentration of radiation defects for relatively high temperature chemical reactions is rather problematic because of intensive annealing of any defects. Nevertheless, in a number of research works [1, 2] it has been found that heating by electron beams resulted in an appreciable increase of reaction rate in comparison with thermal heating at the same conditions, even for high temperature solid+solid synthesis.

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Reaction of a solid+solid type

Our investigations were based on synthesis of complex oxides. As in example in Fig. 1 the results of kinetic experiments for synthesis of $2CaO:SiO_2$, at the system $CaO–SiO_2$ are presented both for radiation and for thermal conditions. It can be seen that acceleration of synthesis by electron irradiation (and a heating as well) is much higher at relatively low temperatures and tends to zero when reaction temperature increas.

A similar tendency was detected for numerous systems summarized in Table 1. The effect of electron beam irradiation/heating may be characterised by an equivalent temperature of about 100÷200 K lower than for thermal heating at equal reaction rates.

Table 1 System where RT effect was detected

System	Product
$Na_2CO_3 + Fe_2O_3$	$2NaFeO_2$
$Na_2CO_3 + Al_2O_3$	$NaAlO_2$
$CaO + NaAlSiO_4$	Ca_2SiO_4, $NaAlO_2$
$CaO + Al_2O_3 + Fe_2O_3 + SiO_2$	cement
$CaO + Fe_2O_3$	$CaFe_{12}O_{19}$
$Li_2CO_3 + Fe_2O_3$	$LiFe_5O_8$
$BaO + TiO_2$	$BaTiO_3$
$K_2CO_3 + Al_2O_3$	$2KAlO_2$
$MgO + Fe_2O_3$	$MgFe_2O_4$
$NiO + Fe_2O_3$	$NiFe_2O_4$
$MnO + Fe_2O_3$	$MnFe_2O_4$
$CaCO_3$	$CaO + CO_2\uparrow$
$MgCO_3$	$MgO + CO_2\uparrow$
Eu_2O_3	sintering
$LiFeTiO_4$	sintering

To eliminate possible effect of heat transfer within the sample due to non uniform distribution of heat sources on the surface for thermal experiments and in the bulk for radiation treatment the comparative kinetic experiments were made for 'sandwich' samples of NiO and Al_2O_3, as it is shown in Fig. 2. This geometry of radiation zone allows to make measures of the thickness of radiation product layer and to obtain finely values of parabolic rate constants and their temperature dependences for the reaction:

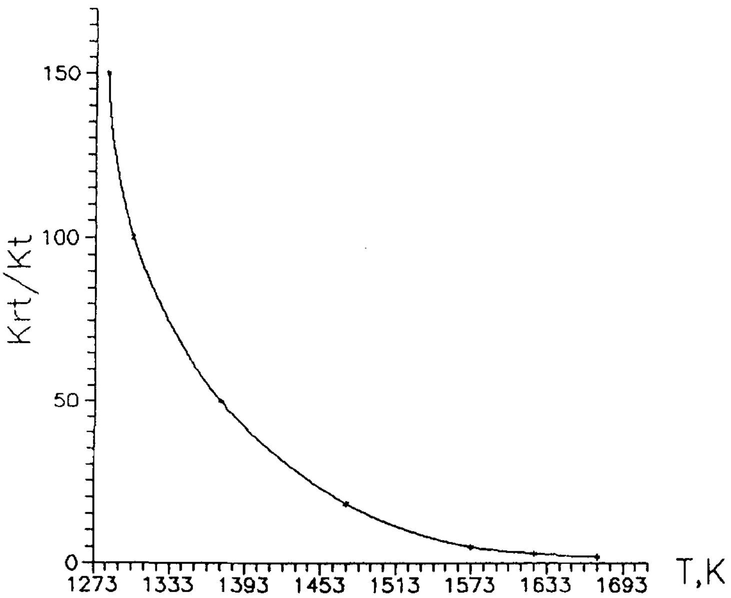

Fig. 1 Dependence of rate constants ratio on temperature of radiation–thermal (Krt) and thermal (Kt) synthesis of calcium disilicate

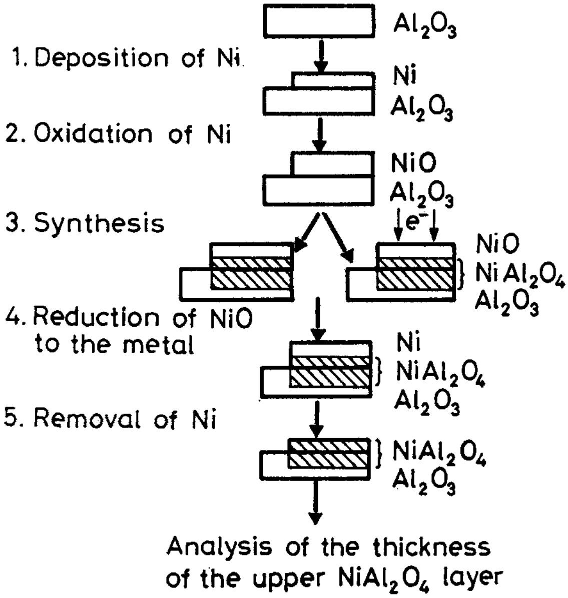

Fig. 2 Schematic representation of the experiments with $NiAl_2O_4$

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \qquad (1)$$

The results can be seen from Fig. 3. Temperature dependence of the reaction rate constants are expressed as follows:

$$K_{el} = 33.8 \cdot 10^4 \exp(-4.87 \text{ eV/kT}), \text{ cm}^2/\text{s} \qquad (2)$$

and

$$K_{therm} = 11.0 \cdot 10^4 \exp(-4.95 \text{ eV/kT}), \text{ cm}^2/\text{s} \qquad (3)$$

where K_{el} is reaction rate constant for electron beam irradiation and K_{therm} is the usual thermal rate constant. The parabolic law for thickness of product layer $x^2 = k\tau$ was always in good agreement with experimental data. Moreover, the results of thermal experiments expressed by Eq. (3) are practically the same as published earlier [3].

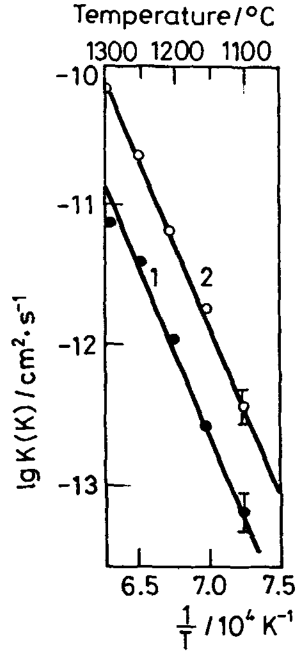

Fig. 3 Dependence lg$K$–f(1/T) for the synthesis of $NiAl_2O_4$. 1- treatment in a furnace; 2 - treatment in electron beam

From this data one should inevitably conclude that the electron beam is the powerful intensifying factor for solid state reactions, at least, when they are diffusion controlled.

A similar result was obtained for the reaction

$$ZnO+Fe_2O_3 \rightarrow ZnFe_2O_4 \quad (4)$$

which is controlled by diffusion of Zn^{2+}-ions.

In this case the rate constant was 4 times higher for radiation synthesis than for thermal one

$$K_{el} = (2.5\pm0.5)\cdot10^{-9}, \text{ cm}^2/\text{s}$$

$$\text{and } K_{therm} = (6.2\pm1.2)\cdot10^{-10}, \text{ cm}^2/\text{s}$$

both at the temperature 1623 K.

Reduction of metal oxides by hydrogen

Reduction of metal oxides is a pure topochemical reaction. Processes of nucleation and at interface between oxide and metal are much more importance in this case than for solid-solid synthesis. That is why these reactions were chosen for comparative studies. All kinetic experiments were made in comparable conditions (temperature, hydrogen pressure, etc.) using special chemical reactor described elsewhere [4].

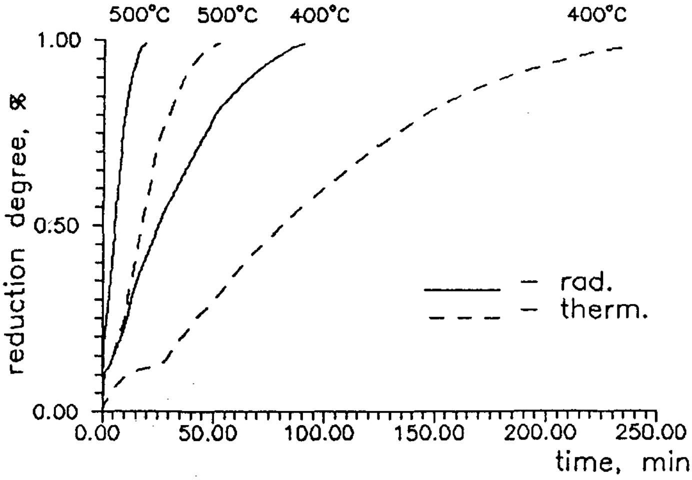

Fig. 4 Kinetics of Fe_2O_3 reduction

In Fig. 4 the conversion degree *vs.* time (*t*) is presented for the reduction of Fe_2O_3 by hydrogen. A pronounced effect of electron beam irradiation is evident.

A two stage reduction $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$ can be described by the first order kinetic equation both at thermal and at radiation conditions. The ratio of the first order constants does not depend on temperature in the range 350–450°C being equal 2.5 for Fe_2O_3 (first stage) and 2.0 for Fe_3O_4 (Table 2).

Table 2 Reduction of oxides by means of hydrogen. The magnitude of radiation effect - $k_{rad.}/k_{therm}$

Oxides	Temp. region/ °C	Ratio $k_{rad.}/k_{therm.}$
Fe_2O_3	350–750	2.5
Fe_3O_4	450–600	2.0
NiO	260–350	3.2–4.0
NiO (1000°C,4h)	280	1.5
WO_3	650–700	1.6
WO_3 (1000°C,4h)	700	4.0

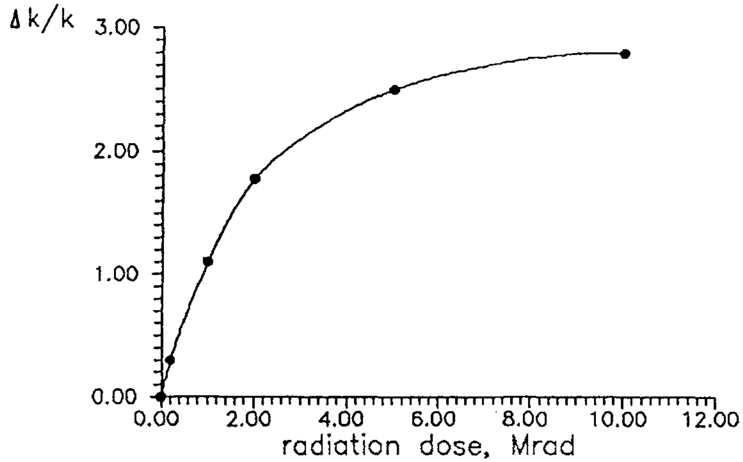

Fig. 5 Dependence of relative growth of reaction rate constant of Fe_2O_3 reduction on preliminary irradiation dose. The stage Fe_2O_3–Fe_3O_4

The other oxides studied in our experiments show similar behaviour as it can be seen from Table 2. For the first stage of the Fe_2O_3 reduction the effect of preliminary irradiation without heating of samples was studied. The dose dependence of the $\Delta k/k$ for thermal reduction at 340°C is shown in Fig. 5. It can be seen that preliminary irradiation really accelerates the reaction rate testifies that radiation defects obtained at room temperature survive at higher temperature when reduction becomes possible. The pity is that we can not identify radiation defects to correlate them with accepted mechanism of oxides reduction. Nevertheless, the fact that formation of radiation defects in a bulk of oxides can influence processes on surface (nucleation) or interface (propagation) is very interesting. Different mechanisms could be suggested one of which and the most simple is participation of these defects in nuclei formation, perhaps, also through diffusion. At least, this suggestion is in agreement with observable first order kinetics of reduction.

Influence of electron beam heating on diffusion

In order to better understand the nature of joint action of heating by high energy electron irradiation the measurements of diffusion coefficients and their temperature dependences were undertaken. We have measured the diffusion coefficients in pure metals Cu and Ag (self-diffusion), in intermetallic systems Ag–Cu and Cu–Al (diffusion of Ag and Cu in the course of formation of solid solutions), and finely Al^{3+} in KBr single crystal.

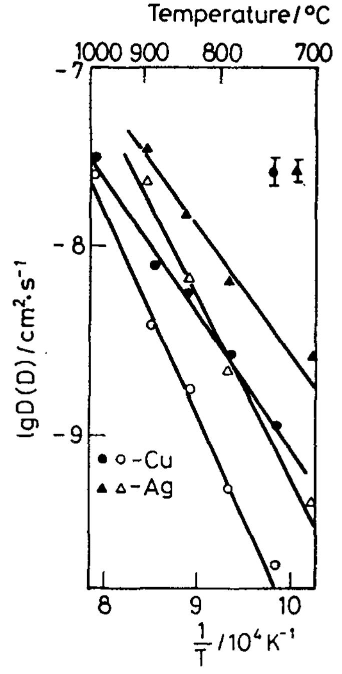

Fig. 6 Temperature dependence of self-diffusion of Cu and Ag o, Δ - furnace; •, ▲ - electrons

Temperature dependence of self-diffusion coefficients are presented in Fig. 6 in comparison with usual thermal experiments. The corresponding equations are as follows:

$$\text{for Cu: } D_{el} = 1.8\cdot10^{-2}\exp(-1.46\ \text{eV/kT}),\ \text{cm}^2/\text{s} \qquad (5)$$

$$D_{\mathrm{therm}} = 7.1 \cdot 10^{-2} \exp(-1.47 \text{ eV/kT}), \text{ cm}^2\text{/s} \qquad (6)$$

$$\text{for Ag: } D_{\mathrm{el}} = 1.78 \exp(-2.22 \text{ eV/kT}), \text{ cm}^2\text{/s} \qquad (7)$$

$$D_{\mathrm{therm}} = 2.7 \exp(-1.90 \text{ eV/kT}), \text{ cm}^2\text{/s} \qquad (8)$$

What is of importance to underline is a difference in activation energy between thermal and electron beam sets of data. This fact differs the results for self-diffusion from those obtained for solid state synthesis or for reduction. Moreover, it is difficult to understand how additional concentration of defects can change activation barriers for elementary steps of self-diffusion in crystalline solids. The possible explanation of this phenomenon will be done below, and before we proceed we consider another experiment. The case in point is the diffusion of Al^{3+} into KBr single crystals measured not only as a function of temperature but also as a function of modulation parameters of electron beam.

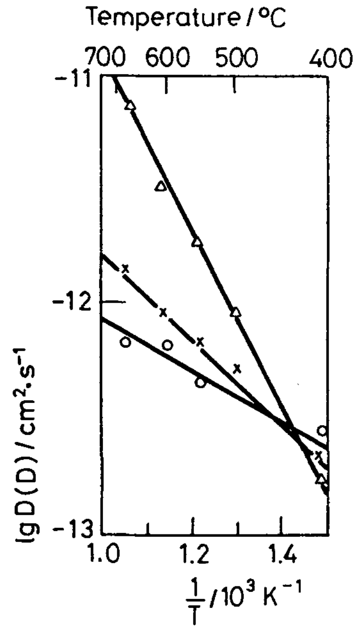

Fig. 7 Dependence lg$D$–f(1/T) o - furnace, x - pulsed electron beam, Δ - stationary electron beam

For this experiments the accelerators of two types were used one of which was pulsed and another one with continuous mode of operation. The results are presented in Fig. 7 and they show that the slope of Arrhenius plots is essentially dependent on parameters of irradiation. This observation transforms the problem of electron beam heating to a quite another one: how the result of irradiation may be connected with modulation parameters of electron beams.

An attempt of explanation

To give more or less general explanation of all results obtained in our experiments we suggested that every pulse of electron irradiation produces an abrupt increase of defect concentration which is additional and over equilibrium to that existing in any solid and providing for diffusion. This additional concentration relaxes then during a pause between pulses to its equilibrium level. Taking into account this relaxation concentration follows the usual first order kinetics.

$$\mathrm{d}N = \mathrm{d}N_o \exp(-k_1 t), \tag{9}$$

where k_1, in turn, is also dependent on temperature according to Arrhenius law

$$k_1 = k_{o1} \exp(-E_1/RT). \tag{10}$$

We can write for the concentration of defects taking part in diffusion (vacancies, for example):

$$N(t) = N_e(T) + \mathrm{d}N(t) \tag{11}$$

or else:

$$N(t) = N_o \exp(-\mathrm{d}H_f/RT) + \mathrm{d}N_o \exp(-k_1 t). \tag{12}$$

From this expression it is easy to pass to diffusion coefficient D_v (for vacancy diffusion):

$$D_v = a^2 \exp(-E_m/RT) \cdot N(T, t)/N_o =$$

$$= a^2 \exp(-E_m/RT) \cdot \exp(-\mathrm{d}H_f/RT) + \mathrm{d}N_o/N_o \exp(-k_1 t). \tag{13}$$

The average value $\langle D_v \rangle$ over a period of pulse repetition τ_o should be compared with an experimental value. But we do not know the real value of D_o so we can compare only the relative value of $\langle D_v/D_o \rangle$. Calculated results are presented in Fig. 8 in the form of Arrhenius plots for different modulation frequencies. It can be seen that according to activation parameters summarized in Table 3 one can obtain dependences practically of all types shown in Figs 3 and 6 for the experimental systems.

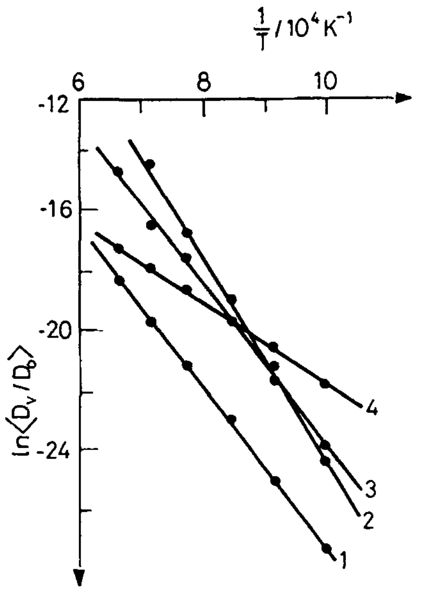

Fig. 8 Results of computer calculations for the model given in coordinate system $\ln D_v/D_o$–$1/T$. Parameters for realization of temperature conditions are given in Table 3

Table 3 Calculated data for a model

N	E_m/kJ·mole^{-1}	dH_f/ kJ·mole^{-1}	T/K	dN_o	τ/s
1.	105.0	125.0	1000÷1500		
2.	105.0	125.0	1000	$1\cdot10^{-5}$	0.2
			1100	$5\cdot10^{-5}$	0.1
			1200	$2\cdot10^{-4}$	0.01
			1300	$2\cdot10^{-4}$	0.005
			1400	$7\cdot10^{-4}$	0.005
3.	105.0	125.0	1000	$1\cdot10^{-5}$	0.1
			1100	$5\cdot10^{-5}$	0.1
			1200	$1\cdot10^{-4}$	0.1
			1300	$5\cdot10^{-4}$	0.1
			1400	$1\cdot10^{-3}$	0.1
			1500	$5\cdot10^{-3}$	0.1
4.	105.0	125.0	1000	$1\cdot10^{-4}$	0.2
			1100	$1\cdot10^{-4}$	0.02
			1200	$1\cdot10^{-4}$	0.01
			1300	$1\cdot10^{-4}$	0.001

This qualitative agreement can be taken as an argument for the non-steady-state mechanism of stimulation of solid state processes controlled by diffusion.

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Zusammenfassung — Der Einsatz von Elektronenstrahlen ermöglicht neue Effekte in der Hochtemperaturchemie des festen Zustandes. Ein durch Strahlung hervorgerufener Effekt bei vergleichbaren Temperaturbedingungen kann hinsichtlich der Tatsache, daß die Erhöhung der Reaktionsgeschwindigkeit signifikante Werte erreichen kann, von verfahrenstechnischem Interesse sein.