

INFLUENCE OF ZnO SPECIFIC SURFACE AREA ON ITS SINTERING KINETICS

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The aim of this work is an investigation of isothermal sintering kinetics by observing the reduction of the specific surface area of ZnO. Zinc oxide powder is sintered isothermally in air for 5 to 120 min at temperatures from 400 to 900 °C. The decrease in the specific surface area is observed as a function of temperature and sintering time. Models of Ristic–Jovanovic and German are applied in order to define the appropriate parameters. Information on the activation energy of sintering is obtained by the Arrhenius equation. The least square estimation (LSE) method was applied for determining optimum parameter values.

Keywords: sintering, kinetics, specific surface area, zinc oxide powder.

INTRODUCTION

Zinc oxide is a stable compound with a wurtzite-type hexagonal structure. Zinc oxide with a wide band gap of 3.37 eV is one of the most important multifunctional materials, which can be used in many fields, such as optoelectronic devices, gas sensors, solar cells, and varistors [1–4]. The physical properties of ZnO depend strongly on the size and orientation of the crystals as well as the way they interact with each other [5].

It is well known that the sintering process is a widely used method, which causes the specific surface area and porosity decrease and density increase [6]. German [7] proposed a model of the interparticle neck shape during sintering. An important result of this approach is that the kinetic dependence for the rate of surface area reduction on the sintering mechanism has been established. Moreover, Ristic [8] proposed a model, where sintering kinetics is a function of effective surfaces at the beginning and in the end of process.

In the related literature, no results were found regarding the influence of specific surface area on sintering kinetics. Therefore, the sintering kinetics of ZnO powder was investigated, and the models proposed enable us to correlate relation between characteristic parameters for the observed system such as specific surface area and time and sintering temperature as well.

EXPERIMENTAL PROCEDURE

Commercially available ZnO powder (99% p. a. Merck) was used for our experiment. The powder was compacted using a uniaxial double-action pressing process in a 6-mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). The compaction pressure was 49 MPa.

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The isothermal sintering was performed in a tube furnace (Lenton Thermal Design Type 1600). Compacts obtained after pressing were sintered in the temperature range from 400 to 900°C for 5, 15, 30, 60, 90, and 120 min in air. Specific surface area was measured using the BET method.

RESULTS AND DISCUSSION

The average initial value of specific surface area of green samples was $S_0 = 3.95 \text{ m}^2 \cdot \text{g}^{-1}$. Table 1 contains values of the specific surface area of sintered ZnO samples.

During analyses of experimentally obtained results, two methods were employed in order to describe changes in the specific surface area with sintering time. According to German model [7]:

$$\frac{\Delta S}{S_0} = (K \cdot t)^{1/n}, \quad (1)$$

where ΔS is change in the specific surface area during the sintering process; S_0 is the specific surface area of specimens before sintering process; K is particle size characteristic; n is constant that determines the sintering mechanism; t is sintering time. Figure 1 represents the results of sintering analyses of ZnO according to Eq. (1).

Table 2 shows the calculated values of corresponding parameters using German's equation.

Figure 2 shows the $\ln k$ dependence on $1/T$. Inclination modification at approximately 625°C implies a possible change in the sintering mechanism at that temperature. At lower temperatures, the constant rate is higher due to a larger specific surface area, so there is a greater possibility of atomic movement on the surface. This implies that at lower temperatures the surface diffusion sintering mechanism takes place and that, starting from ~625°C, volume diffusion has the major role during the sintering process.

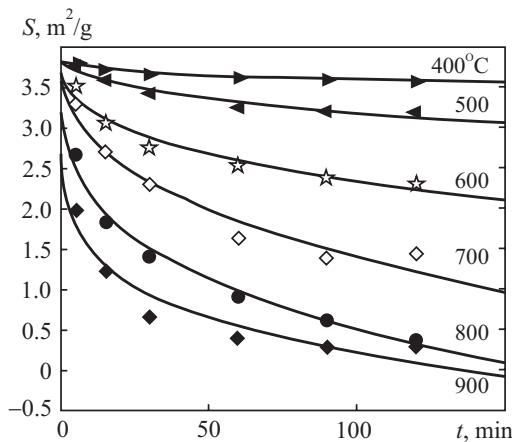


Fig. 1. Reduction of specific surface area according to Eq. (1)

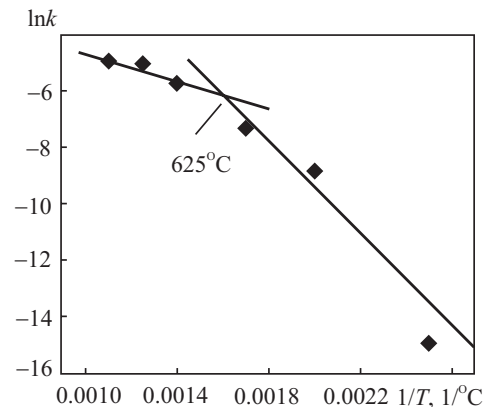


Fig. 2. Diagram of $\ln k$ as a function of $1/T$

TABLE 1. Specific Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$) of Sintered ZnO Samples

$T, ^\circ\text{C}$	t, min					
	5	15	30	60	90	120
400	3.81	3.69	3.65	3.62	3.60	3.59
500	3.78	3.60	3.41	3.26	3.20	3.19
600	3.52	3.06	2.75	2.54	2.39	2.34
700	3.30	2.71	2.31	1.65	1.40	1.43
800	2.68	1.83	1.40	0.92	0.62	0.39
900	2.01	1.22	0.67	0.39	0.30	0.29

TABLE 2. Value of Parameters K , n , and L_{\min} Using Eq. (1)

Parameter	$T, ^\circ\text{C}$					
	400	500	600	700	800	900
K	$3.26 \cdot 10^{-7}$	$1.45 \cdot 10^{-4}$	$6.65 \cdot 10^{-4}$	$3.20 \cdot 10^{-3}$	$6.20 \cdot 10^{-3}$	$7.40 \cdot 10^{-3}$
n	4.33	2.58	3.01	2.62	3.50	5.60
L_{\min}	0.0035	0.0166	0.0556	0.1238	0.0703	0.1996

The activation energy of sintering was calculated assuming the two above-described mechanisms using the Arrhenius equation [6]:

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}, \quad (2)$$

where k is the rate constant; k_0 is the preexponential constant; E_a is the activation energy; R is the universal gas constant ($8.314 \text{ J/K} \cdot \text{mole}$); T is the sintering temperature. The values obtained using Eq. (2) are $E_a = 20.56 \text{ kJ/mole}$ for surface diffusion and $E_a = 67.98 \text{ kJ/mole}$ for volume diffusion.

These values confirm the assumption that surface diffusion is a dominant mechanism during the sintering process at lower temperatures and volume diffusion mechanism is a dominant one at higher temperatures, which demands higher energy consumption. As we mentioned before, a greater possibility of atomic movement is on the grain surface rather than within atoms that are placed inside the grain. Accordingly, lower energy is required for atomic movement on the surface than within the grains.

The second model used in our research was the equation proposed by Ristic [8]:

$$\frac{\Delta S}{S_0} = K \left(1 - B \cdot e^{-s \cdot t} \right) \cdot (s \cdot t)^{\exp \left[-\frac{1}{2} (p^2 \cdot t^2 - 1) \right]}, \quad (3)$$

$$K = k_0 \cdot \exp \left(-\frac{E}{R \cdot T} \right), \quad (4)$$

where ΔS is change in the specific surface area during the sintering process; S_0 is the specific surface area of specimens before the sintering process; B , s , p , and k_0 are parameters of the process.

Figure 3 shows results of sintering analyses of ZnO according to Eq. (3). Table 3 shows the calculated values of corresponding parameters using Ristic's equation. Figure 4 shows $\ln k$ as a function of $1/T$. We can notice similar behavior as in the case of German's equation, and a change in inclination at approximately 640°C .

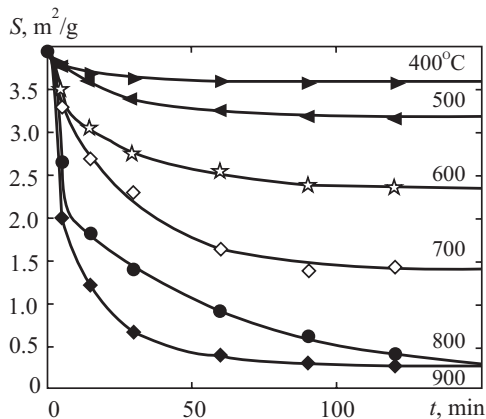


Fig. 3. Reduction of the specific surface area of ZnO according to Eq. (3)

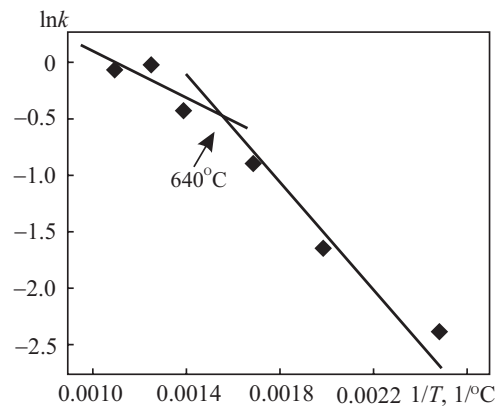


Fig. 4. Diagram $\ln k$ as a function of $1/T$

TABLE 3. Value of Parameters K , B , s , and p Using Eq. (3)

Parameter	$T, ^\circ\text{C}$					
	400	500	600	700	800	900
L_{\min}	$1.289 \cdot 10^{-4}$	$3.686 \cdot 10^{-4}$	0.035	0.025	0.002	0.002
K	0.090	0.195	0.410	0.650	0.970	0.930
B	0.500	0.900	0.700	0.900	0.570	0.570
s	0.039	0.036	0.031	0.035	0.017	0.054
p	0.385	0.485	0.385	0.590	0.440	0.527

Calculated activation energies for these two sintering mechanisms are: $E_a = 8.95$ kJ/mole for surface diffusion and $E_a = 19.73$ kJ/mole for volume diffusion.

Values of calculated activation energies for the above-mentioned sintering mechanisms differ significantly from those calculated using the first model, although both models confirm the assumption that the sintering process includes two different mechanisms: surface and volume diffusion. Also, the results obtained within this paper are in great agreement with the results obtained during our previous experiment [9]. We studied the sintering kinetics of ZnO powder through specific surface reduction applying two models: Nicholson's and Hartman's. A change in the sintering mechanism from surface to volume diffusion occurs within a temperature range from 630 to 680°C.

CONCLUSION

This paper examines the possible use of phenomenological equations in analyses of ZnO sintering kinetics by observing the reduction of the specific surface area according to German and Ristic models. We concluded that the Ristic model fits experimental data better probably due to its complexity and involvement of four different parameters. A change in sintering mechanism from surface diffusion to volume diffusion was noticed at about 620 to 640°C. According to our previous and current analyses, we suggest the use of the Ristic equation to determine the sintering kinetics and sintering mechanisms of other systems as well.

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