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An indirect model for sintering thermodynamics

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Abstract: A model was proposed and used to calculate the changes in enthalpy (ΔH°), entropy (ΔS°), and Gibbs energy (ΔG°), as well as equilibrium constant (K) relating to the sintering of alumina compacts. Specific nanopore volume (V) of the compacts was assumed as a thermodynamic variable. A hypothetical equilibrium constant (K_h) and corresponding Gibbs energy (ΔG_h°) were calculated depending on the V value measured after each sintering. The thermodynamic relationships with the SI units were respectively evaluated for the initial-stage (i) sintering between 1000 and 1200 °C and final-stage (f) sintering between 1200 and 1600 °C in the following form: $\Delta G_i^\circ = -RT \ln K_i = \Delta H_i^\circ - T\Delta S_i^\circ = 161,042 - 110.5T$ and $\Delta G_f^\circ = -RT \ln K_f = \Delta H_f^\circ - T\Delta S_f^\circ = 39,000 - 47.5T$.

Key words: Alumina, nanoporosity, sintering, thermodynamics

1. Introduction

Thermodynamics is a powerful tool to determine the direction and equilibrium state of physicochemical processes. Despite this importance, it has been employed only infrequently to changes in solids such as dehydration, dehydroxylation, calcination, transformation, sintering, carbonization, and carburizing processes occurring at elevated temperatures. One of the most important of those is sintering, which is the densification of powder compacts by firing during the last step of ceramic production.^{1–3}

The driving force of mass transfer during sintering is the chemical potential (molar Gibbs energy or molar free enthalpy) difference of several chemical species between various sites in the firing compacts. The chemical potential of a chemical species changes depending on the composition, temperature, and pressure as well as lattice defects and surface curvature of the powder particles located in a compact. Various chemical species are transferred from one path only or more paths depending on the difference in their chemical potentials between various sites in the compact.

The sintering kinetics for several compacts has been intensively investigated.^{4–8} However, since the exact data are not easily available for compacts at elevated temperatures, thermodynamics has been employed only seldom to sintering. Despite several interpretations from various points of view, the studies on sintering thermodynamics are not adequate.^{9–15} To overcome these difficulties, new approaches are required. Therefore, the aim of the present study was to propose and use a hypothetical thermodynamic model for sintering of alumina compacts based on specific nanopore volume as thermodynamic variable.

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2. Proposed thermodynamic model

Since knowledge of the basic thermodynamic quantities for compacts is limited at high temperatures, a hypothetical thermodynamic model was proposed to fill the gap on the basis of the following assumptions.^{16–18}

1. Firing time of ceramic compacts should be sufficient to establish a thermodynamic equilibrium for sintering.
2. Measurable variables such as porosity, bulk density, shrinkage, and hardness used in the kinetic calculations^{4–8} before equilibrium can be also used in the thermodynamic calculations at equilibrium state similar to activity of a component.
3. Change in the selected thermodynamic variable should be negligibly by cooling the compacts from the firing up to measuring temperature.
4. When the sintering is at equilibrium, a hypothetical equilibrium constant (K_h) can be defined depending on the selected thermodynamic variable.
5. The basic thermodynamic relationships between the real enthalpy change (ΔH^o), entropy change (ΔS^o), Gibbs energy (ΔG^o), and equilibrium constant (K) should be valid also for the hypothetical calculations starting from the K_h mentioned above.
6. The slope of the plots pertaining to the hypothetical and real thermodynamic quantities depending on the temperature should be equal whereas their absolute values would be different. In other words, the real and hypothetical thermodynamic plots either would be parallel or overlap each other. For example,

$$d \ln K_h / dT = d \ln K / dT = \Delta H^o / RT^2 \text{ but } K_h \neq K \quad (1)$$

$$d\Delta G_h^o / dT = d\Delta G^o / dT = -\Delta S^o \text{ but } \Delta G_h^o \neq \Delta G^o \quad (2)$$

relations should be valid, where K_h and ΔG_h^o are hypothetical but K , ΔH^o , ΔG^o , and ΔS^o are real.

7. If the $\ln K_h$ vs. $1/T$ and ΔG_h^o vs. T plots are straight lines, the real ΔH^o and ΔS^o are calculated from their slope, respectively. Thus, the equations of the lines are written as follows:

$$\ln K_h = -\Delta H^o / RT + \Delta S_h^o / R \quad (3)$$

$$\Delta G_h^o = -\Delta S^o T + \Delta H_h^o, \quad (4)$$

where ΔH_h^o and ΔS_h^o are the hypothetical enthalpy and entropy changes.

8. Similarly, the real thermodynamic relationships are given as follows:

$$\ln K = -\Delta H^o / RT + \Delta S^o / R \quad (5)$$

$$\Delta G^o = -\Delta S^o T + \Delta H^o \quad (6)$$

3. Results and discussion

The specific nanopore volume (V) of compacts fired at different temperatures is given in the Table. The V quantity was assumed as a thermodynamic variable. Using V , a hypothetical equilibrium constant (K_h), characterizing the sintering was defined as follows:

$$\text{residual nanopore volume } (V) \leftrightarrow \text{closed nanopore volume } (V_i - V)$$

$$K_h = (V_i - V)/V, \quad (7)$$

where V_i is the largest nanopore volume measured before sintering of the compact calcined at 950 °C for 2 h.

Table. Specific nanopore volume (V), hypothetical equilibrium constant (K_h), and hypothetical Gibbs energy (ΔG_h^0) of the alumina compact for each firing temperature.

$T/^\circ\text{C}$	T/K	$(1/T)/10^{-3}\text{K}^{-1}$	$V/\text{cm}^3\text{g}^{-1}$	$K_h = (V_i - V)/V$	$\ln K_h$	$\Delta G_h^0/\text{J mol}^{-1}$
950	1223	0.8177	$V_i = 0.200$	-	-	-
1000	1273	0.7855	0.172	0.163	-1.8153	19,213
1050	1323	0.7559	0.163	0.227	-1.4828	16,310
1100	1373	0.7283	0.132	0.515	-0.6633	7572
1200	1473	0.6789	0.092	1.174	0.1603	-1964
1300	1573	0.6357	0.083	1.410	0.3433	-4490
1400	1673	0.5977	0.060	2.333	0.8473	-11,785
1500	1773	0.5640	0.047	3.255	1.1803	-17,398
1600	1873	0.5339	0.045	3.444	1.2367	-19,259

The K_h value for each sintering was calculated from the last relationship. The corresponding hypothetical Gibbs energies were calculated from the well-known thermodynamic equation

$$\Delta G_h^0 = -RT \ln K_h, \quad (8)$$

where T is the absolute temperature of sintering and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant. The K_h and ΔG_h^0 values as a function of temperature are given in the Table.

The van't Hoff graph of $\ln K_h$ vs. $1/T$ and the graph of ΔG_h^0 vs. T were plotted and given in Figures 1 and 2, respectively. Two straight lines having different slopes located in each graph revealed that the sintering occurs in two steps. The first step between 1000 °C and 1200 °C and the second step between 1200 °C and 1600 °C are called initial-stage sintering (i) and final-stage sintering (f), respectively. The mathematical equation with the high correlation factor (R^2) for each straight line was found and is given in the figures.

The respective values $\Delta H_i^0 = 161,042 \text{ J mol}^{-1}$ and $\Delta S_{hi}^0 = 110.8 \text{ J mol}^{-1} \text{ K}^{-1}$ as well as $\Delta H_f^0 = 39,000 \text{ J mol}^{-1}$ and $\Delta S_{hf}^0 = 31.2 \text{ J mol}^{-1} \text{ K}^{-1}$ were evaluated from the slopes and intercept of the straight lines in Figure 1. Similarly, the values $\Delta S_i^0 = 110.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_{hi}^0 = 16,073 \text{ J mol}^{-1}$ as well as $\Delta S_f^0 = 47.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_{hf}^0 = 68,485 \text{ J mol}^{-1}$ were evaluated from the slope and intercept of the straight lines in Figure 2.

By using the real quantities temperature dependence of the real Gibbs energy (ΔG^0) and real equilibrium constant (K) for initial-and final-stage sintering can be respectively written in SI units as follows:

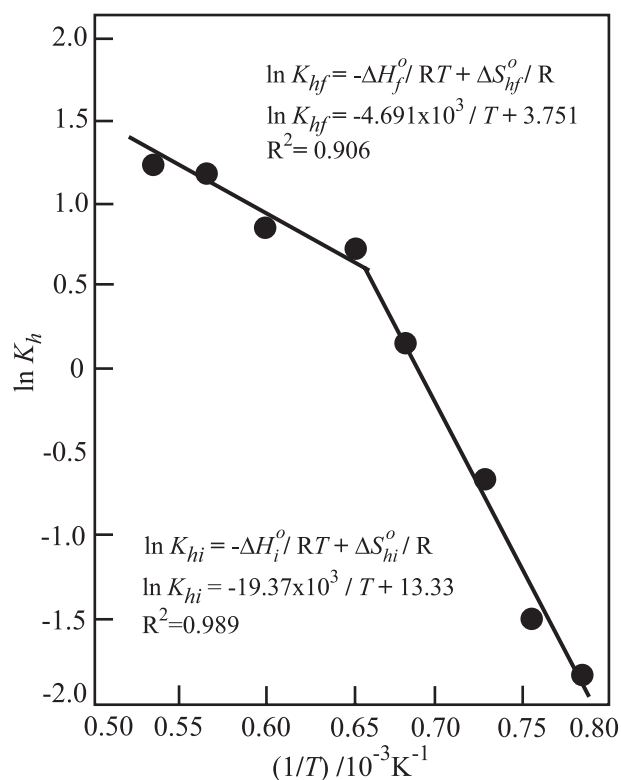


Figure 1. van't Hoff plot of the hypothetical equilibrium constant for the initial and final sinterings.

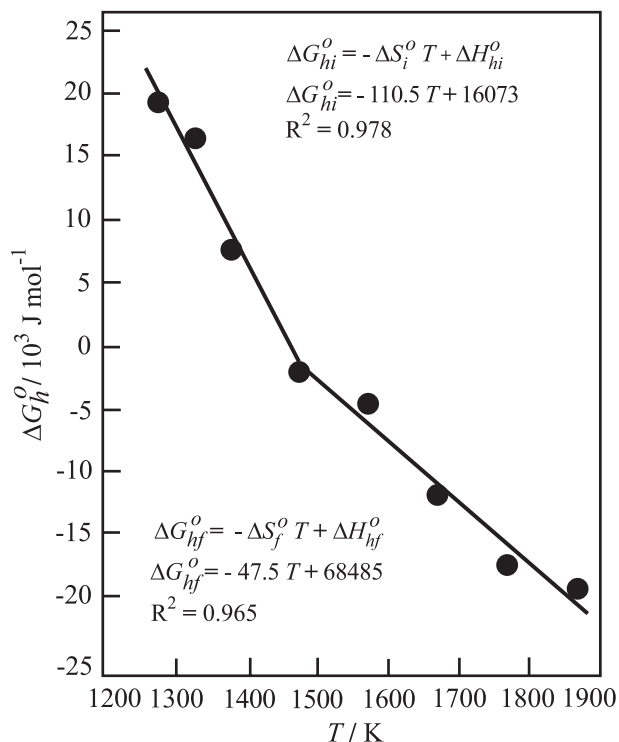


Figure 2. Variation in the hypothetical Gibbs energy vs. temperature for the initial and final sinterings.

$$\Delta G_i^o = -RT \ln K_i = \Delta H_i^o - T\Delta S_i^o = 161,042 - 110.5T \quad (9)$$

$$\Delta G_f^o = -RT \ln K_f = \Delta H_f^o - T\Delta S_f^o = 39,000 - 47.5T \quad (10)$$

According to the last two relationships Gibbs energies would be $\Delta G_i^o > 0$ and $\Delta G_f^o < 0$ before and after 1200 °C, respectively. The positive value of ΔG_i^o indicated that the initial-stage sintering equilibrium cannot be established spontaneously. In contrast, the negative value of ΔG_f^o showed that the final-stage sintering equilibrium was established spontaneously.

4. Conclusions

An indirect thermodynamic method was proposed to examine sintering alumina compacts. Specific nanopore volume was used as a thermodynamic variable. Other measurable variables changing with firing temperature such as bulk density, shrinkage, and microhardness may be used instead of nanoporosity. The most general relation between the real thermodynamic quantities for equilibrium can be obtained from the hypothetical ones. This method may be used to examine the dehydration, dehydroxylation, calcination, recrystallization, carbonization, and carburizing of all amorphous and crystalline solids.

5. Experimental

The alumina powder using in this study was prepared by emulsion evaporation. The calcination, morphology, particle size distribution, thermal behavior, and adsorptive properties of the powder were extensively studied in previous works.^{19–23}

The powder was homogeneously mixed with oleic acid (10% by mass) in a mortar. Previously weighed samples from the mixture were compacted under 32 MPa by a uniaxial press (Graseby/Specac). Compacts with a diameter of 14 mm were heated from room temperature to 950 °C at a heating rate of 10 K min⁻¹ and left at this temperature for 2 h to ensure complete calcination. The calcined compacts were then fired at different temperatures between 1000 and 1600 °C for 2 h. At the end of firing, each compact was cooled to room temperature, without any cooling regime. Specific nanopore volume for calcined and as well as sintered compacts was determined from the nitrogen adsorption/desorption data obtained at liquid nitrogen temperature.^{21,22}

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