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Department of Physics and Astronomy (a) and Mechanical Engineering Department (b), Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque¹⁾ and Los Alamos National Laboratory²⁾ (c)

Remarks on the Thermodynamics of Sintering of Ceramics

By

L. SKALA³⁾ (a), V. M. KENKRE (a), M. W. WEISER (b), and J. D. KATZ (c)

In the microwave sintering of some materials a rapid increase of their density is observed in a relatively small temperature range of about 100 K. This may be viewed as a transition from a metastable low density state to a more stable state with a density close to the maximum theoretical density. A thermodynamic description of this transition similar to the Landau theory of phase transitions is suggested and applied to the sintering of boron carbide and alumina.

Beim Mikrowellensintern wird in einigen Materialien ein schneller Anstieg ihrer Dichte innerhalb eines relativ schmalen Temperaturbereichs von 100 K festgestellt. Dies kann als ein Übergang von einem metastabilen Zustand mit geringer Dichte in einen stabileren Zustand mit einer Dichte nahe der theoretischen Maximaldichte aufgefaßt werden. Es wird eine thermodynamische Beschreibung dieses Übergangs, ähnlich der Landau-Theorie für Phasenübergänge, vorgeschlagen und auf das Sintern von Borkarbid und Tonerde angewandt.

1. Introduction

In comparison with conventional heating, microwave sintering of ceramic materials has been found to have several advantages over conventional heating primarily as a result of the volume absorption of the microwave field energy during heating. When used for the industrially important process of sintering, it has been found to lead to a larger sintering rate, and higher quality of the final product. Such basic and economic advantages have attracted the attention of both fundamental and applied research in the area of the interaction of microwaves with ceramics [1 to 4].

The basic features of the temperature dependence of the sample density during the sintering process are as follows. The density is flat to a certain value of the temperature, undergoes a rapid increase in a small temperature range (about 100 K), and is again temperature-independent after the density approaches 0.95 to 0.99 of the maximum theoretical density. The present analysis is a thermodynamic description of the sintering process based on viewing the rapid increase of the density in the relatively narrow temperature interval as a transition from a metastable low density state existing at low temperatures to a high density stable state at high temperatures. The differences between the metastable state and the stable one depend on a number of characteristics of the sample: density, grain shape, grain size

¹⁾ Albuquerque, New Mexico 87131, USA.

²⁾ Los Alamos, New Mexico 87475, USA.

³⁾ On leave of absence from the Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, CS-12116 Prague 2, Czechoslovakia.

distribution and surface area, agglomerate size, agglomerate density, coordination number of particles, neck size between particles, porosity, and pore locations to list a few. It is obvious that the Gibbs free energy of the metastable state depends not only on the pressure p and temperature T as thermodynamic variables but also on the above-mentioned parameters. However, the most important parameter in this respect is, we suggest, the density of the sample (denoted as s henceforth).

The points of departure of our analysis in this paper are the assumptions that the Gibbs free energy G is a function of p , T , and s , $G = G(p, T, s)$, that the (pre-sintering) metastable state corresponds, not to the absolute minimum of the Gibbs free energy, but to a higher local minimum determined by the value of s , and that the high density (post-sintering) state corresponds to the absolute minimum of G . Our description of the sintering process is, thus, as follows. Before densification, at the lower temperature T_1 , the Gibbs free energy of the metastable state equals $G(p, T_1, s_1)$, where the initial low density s_1 corresponds to a local minimum of G . After densification, at the high temperature T_2 , the Gibbs free energy becomes $G(p, T_2, s_2)$ where the final high density s_2 is closer to the maximum theoretical density. After cooling the sample again to temperature T_1 , the Gibbs free energy equals $G(p, T_1, s_2)$, where $G(p, T_1, s_2) < G(p, T_1, s_1)$. Because of the last condition, the sintering process is irreversible.

Our analysis is derived from arguments presented in the Landau theory of phase transitions [5]. However, there are three important differences between phase transitions and the sintering process we analyze here. First, sintering involves a transition from a metastable state to a stable state. Second, the process of sintering is irreversible. Third, the density parameter s increases in sintering during the passage of the system from the local minimum to the absolute minimum of the Gibbs free energy whereas in phase transitions, the order parameter goes down. Nevertheless, the basic considerations of [5] can be applied to our problem as shown below.

In Section 2, we present the application of the arguments of the Landau approach to sintering, and in Section 3 we carry out a modification of that approach in order to extract a more realistic Gibbs potential (from which further thermodynamic quantities can be obtained more realistically) from existing experiments on boron carbide and alumina.

2. Application of the Landau Approach

As in the Landau theory [5 to 7], we assume that the Gibbs free energy per unit volume equals

$$G = G_0 + A(s - s_1)^2 + C(s - s_1)^4, \quad (1)$$

where s is the relative density of the sample, s_1 the initial density at temperature T_1 , $G_0 = G_0(p, T)$ the Gibbs free energy at the initial density $s = s_1$, C is temperature-independent, and

$$A = -a(T - T_1), \quad (2)$$

where $a > 0$ is a constant. By the relative density we mean the ratio of the actual density to the maximum theoretical density so that $s = 1$ corresponds to the sample being at its maximum theoretical density. Note here that the third difference between phase transition theory and the present analysis referred to at the end of Section 1 above is responsible for the difference in sign in the A coefficient in (2) relative to the case in [5].

Equation (1) assumes the most simple expression for $G(s)$ with two minima. The first minimum is at $s = s_1$. The second minimum exists only for $T > T_1$ and occurs at the value of s given by

$$s = s_1 + [(a/2C)(T - T_1)]^{1/2}. \quad (3)$$

The value of G at this point is smaller than at $s = s_1$. This means that, with increasing temperature ($T > T_1$), the density of the sample increases in agreement with (3). If s is the density of the sample at temperature T we can write, eliminating $(a/2C)$,

$$s = s_1 + (s_2 - s_1) [(T - T_1)/(T_2 - T_1)]^{1/2}. \quad (4)$$

The dependence of G on s is given by

$$G = G_0 + a \{ (T_1 - T)(s - s_1)^2 + (1/2)(s - s_1)^4 [(T_2 - T_1)/(s_2 - s_1)^2] \}. \quad (5)$$

The value of the Gibbs free energy is G_0 at the local minimum s_1 , but is given by

$$G = G_0 - (a/2) [(s_2 - s_1)^2/(T_2 - T_1)] (T - T_1)^2 \quad (6)$$

at the minimum given by (4). We see that, as the temperature increases from T_1 to T_2 , the Gibbs free energy goes down as the system passes from the metastable to the stable state.

Knowledge of the thermodynamic potentials allows us to calculate various other physical quantities and their mutual relations. For example, the entropy of the system is given by

$$S = -(\partial G/\partial T)_p = -(\partial G_0/\partial T)_p + a [(s_2 - s_1)^2/(T_2 - T_1)] (T - T_1) \quad (7)$$

and is seen to increase with temperature. The difference of the entropies at temperatures T_2 and T_1 equals

$$S = a(s_2 - s_1)^2. \quad (8)$$

The specific heat at constant pressure c_p (per unit volume) is given by

$$c_p(T) = T(\partial S/\partial T)_p = c_p(T_1) + Ta(s_2 - s_1)^2/(T_2 - T_1). \quad (9)$$

The difference of the specific heats before and after sintering equals

$$c_p(T_2) - c_p(T_1) = Ta(s_2 - s_1)^2/(T_2 - T_1). \quad (10)$$

According to this equation, the specific heat c_p increases during sintering. This is as expected since the mass of the sample remains constant while its volume decreases due to densification. Equation (10) can be used for determining the unknown constant a from experimental data prior to using it in prediction and description of other derived quantities.

The temperature dependence $s(T)$ given by (4) was obtained from experimental observations on boron carbide and alumina (see dashed lines in Fig. 1a, b). These curves correspond to $s_1 = 0.59$, $T_1 = 1840^\circ\text{C}$, $s_2 = 0.95$, $T_2 = 2005^\circ\text{C}$ for boron carbide and to $s_1 = 0.67$, $T_1 = 900^\circ\text{C}$, $s_2 = 0.98$, $T_2 = 1200^\circ\text{C}$ for alumina. The resulting value of $(s_2 - s_1)^2/(T_2 - T_1)$ is similar in both cases: $0.785 \times 10^{-3} \text{ K}^{-1}$ for boron carbide and $0.32 \times 10^{-3} \text{ K}^{-1}$ for alumina.

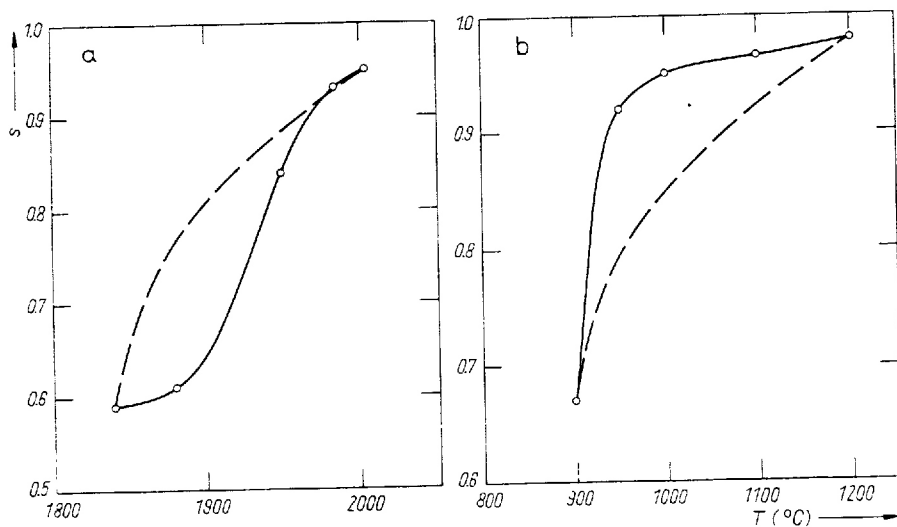


Fig. 1. The relative density s of a) boron carbide and b) alumina as a function of temperature T . Dots are experimental data from [1] and [2], dashed lines correspond to (4), and full lines give the function f , (13)

In Fig. 2 dashed lines show the s -dependence of the Gibbs free energy for three different temperatures. We see that, with increasing temperature, the minimum of G corresponding to (4) shifts to higher densities in agreement with experiment.

3. Modification of the Landau Approach

Although the assumed form of G (see (1)) does not produce striking fits to the data, the agreement is not unreasonable and supports the ideas presented in this paper. In order to get a more accurate description of the $s(T)$ curve than that provided by (4), we have carried out the following modification of the approach of Section 2. We assume the Gibbs free

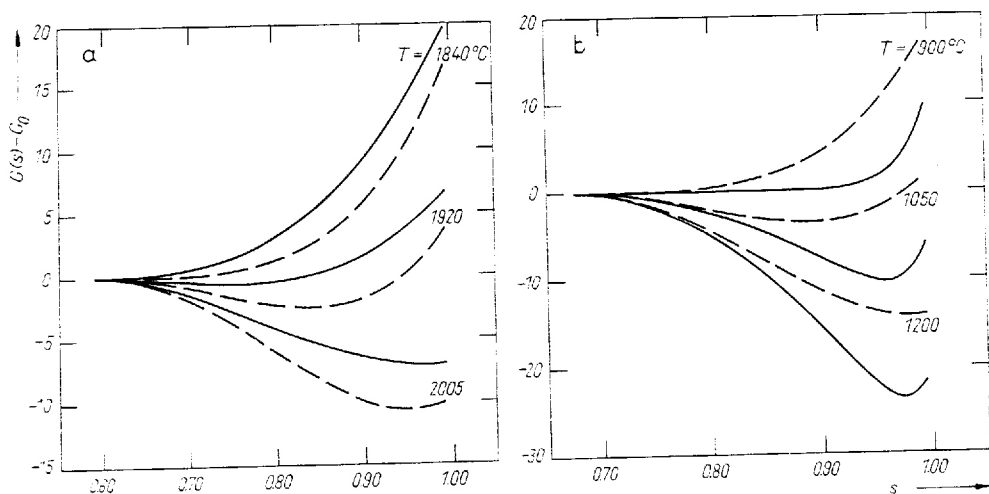


Fig. 2. The Gibbs free energy $G(s) - G_0$ in units of the constant a , for three different temperatures for a) boron carbide and b) alumina. Dashed lines correspond to (5) and full lines to (16)

energy to have the more general form

$$G = G_0 + A(s - s_1)^2 + \int_{s_1}^s ds'(s' - s_1)g(s' - s_1). \quad (11)$$

The second term on the right-hand side of (11) is the same as that in (1), but the third term contains an unknown function $g(s)$ which is to be determined from the experimental dependence $s(T)$. The condition for the minimum of $G(s)$ is $s = s_1$ or

$$g(s - s_1) = -2A = 2a(T - T_1). \quad (12)$$

The form $g(s) = 4Cs^2$ reduces this analysis to that of Section 2 and (12) to (3). Our interest lies, however, in the extraction of $g(s)$ from data rather than in assuming forms for it. To that end, we denote the observed dependence of s on the temperature T as f ,

$$s - s_1 = f(T - T_1), \quad (13)$$

and invert the function numerically to get

$$T - T_1 = f^{-1}(s - s_1). \quad (14)$$

It follows from (12) and (14) that

$$g(s - s_1) = 2af^{-1}(s - s_1). \quad (15)$$

The unknown function g (and thereby the Gibbs free energy and other derived quantities) is thus related directly to the observed behavior of $s(T)$ and can be easily determined from experimental data.

The Gibbs free energy now equals

$$G = G_0 + a \left[(T_1 - T)(s - s_1)^2 + 2 \int_0^{s-s_1} ds' s' f^{-1}(s') \right]. \quad (16)$$

The entropy S and the specific heat $c_p(T)$ are found to be given by

$$S = -(\partial G_0 / \partial T)_p + a[f(T - T_1)]^2, \quad (17)$$

$$c_p(T) = c_p(T_1) + aT(\partial/\partial T)[f(T - T_1)]^2. \quad (18)$$

The Gibbs free energy obtained thus from our modified analysis from (16) is shown in Fig. 2 (solid lines) for boron carbide and alumina. The corresponding $s(T)$ curves are the actually observed ones (solid lines) in Fig. 1. The analysis in the present section provides, thus, a practical recipe for extracting the Gibbs potential from data more realistically than through a straightforward application of Landau arguments and can be used to obtain derived quantities for further verification of the ideas proposed.

4. Conclusions

We have suggested here a simple thermodynamic description of sintering based on the analogy with the Landau theory of phase transitions and its modification. This description is particularly suitable for microwave sintering (although it can be used for conventional sintering as well) because, in the case of microwave sintering, the temperature interval over which the transition takes place (over which the $s(T)$ curve is not flat) is usually much

smaller than that in the case of conventional sintering. The smallness of the interval is important for the justification of the expansion in (1) which neglects the pressure dependence of A and the pressure and temperature dependence of C . The analysis we have presented for the extraction of the Gibbs potential in a more general form than as given by (1) is evidently limited by the form (11) but allows, as Fig. 1 and 2 show, a more accurate description of the data. Among the quantities that can then be calculated for the purposes of prediction and verification are not only entropy and specific heat, as we have shown, but also the difference of specific heats at constant pressure and volume, i.e. $c_p - c_v$, compressibility, and the coefficient of thermal expansion.

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