USE OF A MATHEMATICAL MODEL FOR PORE VOLUME SHRINKAGE OVER A WIDE TEMPERATURE RANGE

V. A. Ivensen

On the basis of experimental data for the sintering of nickel powder under a regime of alternate isothermal and non-isothermal periods, it is shown that a mathematical model of pore volume decrease is capable of describing the process over the temperature range 550-900°C. It appears that in all cases both the time and temperature dependence of pore volume shrinkage are determined by parameter-constants which depend on the method of production of the initial powder.

A mathematical model was created to describe the process of pore volume shrinkage (PVS) under various sintering conditions. It includes, in addition, the initial prerequisites for analyzing the kinetic features of the elementary processes which together determine the time and temperature dependence of PVS. In earlier publications it was shown that the function $W(\tau)$ ($W = -(\dot{v}/v)$ is the relative rate of PVS and τ = time) calculated with the aid of this model for various sintering conditions, including alternating isothermal and nonisothermal periods, is in good agreement with experimental data [1]. Since these experiments were carried out over a relatively narrow temperature range, it seemed necessary to test the model over a wider range of temperatures in order to confirm its utility.

Experimental data on this function for the sintering of powder bodies under a regime of equal time intervals of heating between two isothermal periods have been obtained over a relatively broad temperature range (550-900°C). Use of these data made it possible to determine the kinetic parameters of the elementary processes much more accurately, and to confirm the utility of the model under the selected conditions. It was determined that a substantially more accurate choice of kinetic parameters for the elementary processes, particularly of the activation energies, is needed in order to describe the investigated relationships over a wide temperature range.

The basic parameters of the model are the activation energies for annihilation of initial imperfections E_x, generation of active imperfections $E_x + E_\rho$, disappearance of active imperfections E_{yx}, creep ("flow") of the crystalline substance under the influence of active imperfections E_{yw}, (kJ/g-atom), and also the kinetic properties of the concentration of initial x and active y imperfections (h^{-1}), more thoroughly described in [1].

The mathematical model of PVS includes the following equations:

$$\dot{y} = \omega \exp\left(-\frac{E_x + E_\rho}{RT}\right) x^2 \left(1 + \xi \dot{T}\right) - \Omega \exp\left(-\frac{E_{yx}}{RT}\right) xy, \tag{1}$$

describing the difference between the rate of generation and rate of disappearance of active imperfections, and

$$W = \beta \exp\left(-\frac{E_{yw}}{RT}\right) y, \tag{2}$$

connecting the rate of PVS with the concentration of active imperfections y. In addition, the following equation is used to determine the time dependence of x

$$x = \cfrac{x_0}{x_0 \exp\left(-\cfrac{E_x}{RT}\right)\tau + 1}, \tag{3}$$

in accordance with the assumed kinetics of disappearance of initial (biographical) imperfections

$$\dot{x} = \exp\left(-\frac{E_x}{RT}\right)x^2.$$

Here, the dimensionless constants Ω and ω are preexponential multipliers; β is a parameter which depends on the powder dispersion; and the quantity ξ will be considered below.

Simultaneous solution of Eqs. (1)-(3) with allowance for the function $\dot{T}(\tau)$ leads to a description of the function $W(\tau)$ for the given sintering conditions. The calculation procedure was simplified with the aid of of the following devices. First, instead of the "triangular" plot of $\dot{T}(\tau)$ employed previously to describe the temperature variation, an "idealized" temperature plot was chosen, successfully applied earlier to describe PVS in the early stage of sintering ([2], p. 191). In this case, the plot of heating rate $\dot{T}(\tau)$ is represented by inclined and horizontal lines, the first of which corresponds to a constant rate of temperature increase (T = const), and the second to a pseudo-isothermal period ($\dot{T}$ = 0). In calculations, the time of the pseudo-isothermal is included in that of the truly isothermal period (is added to it). The relationship between the inclined and horizontal lines in the "idealized" plot is chosen so that the heat effect on the process is the same as that for the actual plot $\dot{T}(\tau)$. The "idealized" plot differs more from the actual than the "triangular" plot used in earlier publications [1]. Nevertheless, it enables a quite realistic appraisal of the general nature of change of PVS in the period of rising temperature. Second, in order to describe the subsequent isothermal period, in which the rate of PVS decreases to a quasi-equilibrium level, the equation derived by V. Z. Belen'kim [3] from a mathematical analsis of the model was used:

$$K = \frac{\ln\left[(W_0 - U_0) / (W_\tau - U_\tau)\right]}{\ln(U_0 / U_\tau)}. \tag{4}$$

From this equation, in turn, in light of (3) it follows that

$$W(\tau) = \frac{U_0}{U_0 m\tau + 1} + \frac{W_0 - U_0}{(U_0 m\tau + 1)^k} \tag{5}$$

— the time dependence of W in the period of return to a quasi-equilibrium value after a rise in temperature. Here

$$K = \Omega\exp\left(-\frac{E_{yx} - E_x}{RT}\right), \quad m = \frac{1}{\Theta}\exp\frac{E_{xW} - E_x}{RT}, \quad U = \Theta\exp\left(-\frac{E_{xW}}{RT}\right)x.$$

As in earlier publications, the combined parameters $E_{xW} = E_x + E_\rho - E_{yx} + E_{yW}$ and $\Theta = \beta\omega/\Omega$ are used in the auxiliary equations.

These simplifying assumptions made it possible to perform all calculations using a microcalculator with programmable memory and automatic calculation (Élektronika MK61 type). The function $W(\tau)$ in the period of rising temperature is obtained by integrating Eqs. (1)-(3) of the model, taking into account the temperature plot $\dot{T}(\tau)$, and using a cycle of calculations repeated in steps of 0.02 min. The change of W within the limits of the quasi-isothermal period in the idealized plot does not require separate calculation, since the time of this period is added to the time of the second isothermal period.

The calculation of W in the isothermal period (including the quasi-isothermal) was carried out using Eq. (5), whose constants were computed from the kinetic parameters of the powder. The parameters for a given powder may be called parameter—constants, since a single set provides for calculating the function $W(\tau)$ at all temperatures (within the limits of the experiments carried out). The only exceptions are the quantities x_0 and ξ, which decrease with increasing temperature for well known reasons, and will be considered below.

TABLE 1. Parameter—Constants of the Nickel Powders

Nickel powder	Activation energy, kJ					Preexponential multipliers			
	E_τ	E_ρ	E_π	$E_{\gamma w}$	$E_{\sigma w}$	Ω	●	β	Θ
Oxide	170	188	190	70	238	64,0	7629,0	2,5	298,0
Carbonyl	42	10	52	70	70	19,6	88,6	2,5	11,3

TABLE 2. Rate of Pore Volume Shrinkage in Oxide Nickel Powder Under Conditions of Increasing and Constant Temperature

Time, min	$T=600-700$ °C $(x_0=8,18 \cdot 10^9$ h^{-1} $\zeta=1,33 \cdot 10^{-2}$ h/deg)	$T=650-750$ °C $(x_0=2,48 \cdot 10^9$ h^{-1} $\zeta=7,03 \cdot 10^{-3}$ h/deg	$T=700-800$ °C $(x_0=6,94 \cdot 10^8$ h^{-1} $\zeta=5,52 \cdot 10^{-3}$ h/deg)	$T=750-850$ °C $(x_0=3,19 \cdot 10^8$ h^{-1} $\zeta=3,22 \cdot 10^{-3}$ h/deg)	$T=800-900$ °C $(x_0=2,72 \cdot 10^8$ h-1 $\zeta=1,47 \cdot 10^{-3}$ h/deg)
			Increasing temperature		
0	0,014/0,006	0,02/0,02	0,09/0,004	0,07/0,11	0,204/0,08
0,5	0,072/0,31	0,09/0,46	0,14/0,43	0,13/0,36	0,394/0,16
1,0	0,530/1,00	0,47/1,68	0,46/1,03	0,33/0,65	0,856/1,82
1,5	3,18/3,18	2,36/2,54	1,74/2,00	0,68/1,25	1,92/3,60
2,0	2,54/2,59	1,94/1,78	1,48/1;51	1,19/1,67	4,234/4,70
2,5	↓/↓	↓/↓	1,28/1,14	1,87/1,89	3,27/3,57
			Constant temperature		
0	2,06/1,93	1,61/1,40	1,12/1,08	1,75/1,76	2,64/2,24
1	1,41/1,20	1,11/1,04	0,88/0,88	1,44/1,45	1,96/1,69
3	0,76/0,81	0,72/0,71	0,62/0,71	1,15/1,17	1,35/1,31
6	0,40/0,47	0,43/0,44	0,43/0,44	0,60/0,56	1,09/1,06
10	0,24/0,24	0,29/0,25	0,32/0,32	0,47/0,46	0,83/0,76
15	0,17/0,18	0,21/0,19	0,26/0,25	0,38/0,39	0,66/0,64

Notes. Here and in Table 3 the calculated values of W are given before the slash, and those determined experimentally after the slash. The maximum values of a given parameter are underlined. Values of T in the period of increasing temperature are not indicated, since they are different for each interval. The temperature can be easily calculated from the temperature interval, and also from the current time and that corresponding to maximum W. The values of W at $\tau = 0$ relate to both the beginning of the isothermal period and the end of the period of increasing temperature. For a short time of temperature increase, the transition from the penultimate to the final value is designated by a vertical arrow. In this case the transition time amounts to 0.5 min

The universal parameter—constants of nickel powder from oxide and from carbonyl differed noticeably from those used earlier for a narrower temperature range [1], and, as previously, they were substantially different for powders of different origin (Table 1). It is noted, in passing, that the new parameters could be used to describe the function $W(\tau)$ for all of the sintering cases considered in [1].

The temperature dependent parameters were chosen such that when used, together with the constants for the powder, they would provide values of W which coincided with experimental values at selected points on the $W(\tau)$ curve. The values of x_0 were chosen such that the final values of W after 15 min of isothermal sintering and at the start of the temperature rise coincided, when possible, and the selection of ξ was based on the coincidence of the calculated and experimental maxima of W at the moment of time corresponding to the actual maximum.

The great difference between parameters for powders of the same metal from different sources are astonishing. Neverthless, these differences are confirmed by satisfactory, and sometimes good, agreement of calculated data with the results of experiment. Tables 2 and 3 present values of $W(h^{-1})$ for increasing sintering time in the periods of increasing and constant temperature.

Comparison of the values of W in Tables 2 and 3 show, most importantly, that in the isothermal period following a temperature rise there is satisfactory, and sometimes even good, agreement between calculated and experimental values, but between zero and the maximum value of τ they agree only in the direction of change of W. The latter is a consequence of

divergence of the temperature increase plot assumed in the calculations from the actual plot. Extrapolation of W to smaller times must inevitably lead to intersection of the isothermal curve with the curve representing the increase of W in the period of rising temperature, and the occurrence of a maximum in the method of calculation used is not unexpected. Essential was that the calculated and experimental values of the maximum be reached at equal times of heating. In six cases out of ten the calculated and experimental values differed by less than 0.05 units of W, and consequently, the maxima of W coincided in both value and time (for the case of W calculated at 0.5-min intervals). When the temperature was increased at the rate of 100 degrees per every 2-3 minutes, all phenomena — the increase and decrease of W — occurred so rapidly that the measurement of this parameter at moments of time which were multiples of 0.5 min gave only a general idea of the changes. If at some moment of time the actually observed maximum in W did not agree with the calculated, it was only necessary to prolong extrapolation of the calculated pseudo-isothermal curve by 0.1-0.3 minutes for the rate of PVS to reach a maximum. So, for example, in order to attain the actually observed value of $W = 4.7$ h^{-1} in the temperature range 800-900°C, it is necessary to prolong the calculated curve $W(\tau)$ for the powder from nickel oxide about 0.2 min in the direction of smaller times. When this is done, only an insignificant difference between the calculated and experimental values of the time to reach maximum W are observed.

On the whole, calculation of $W(\tau)$ employing the simplifying assumptions described yielded, in our opinion, completely satisfactory results. Furthermore, the calculation showed that the function $W(\tau)$ is determined over a wide range of temperatures by a single set of parameters — constants for the powder.

The dependence of x and ξ on temperature comes directly out of the initial assumptions of the model: x_0 decreases regularly with increase in the temperature of preliminary sintering before the period of temperature increase (in all cases the sintering time was 30 min). This is a direct consequence of an increased rate of annihilation of the initial genetic imperfections with increasing temperature. The enormous difference (about 5-6 orders) between the values of x for nickel powders from the oxide and from carbonyl by no means indicates that there is such a large difference in the concentrations of imperfections in their crystal structures. There is relatively little difference in the rates W for these powders (less than one order), and in the calculations this is due to a larger value of x for the nickel from oxide, which compensates for a very small exponent at large E_x. Change in x relates to change in the concentration of biographical defects only in powders of like origin, for example when they are heated. Pronounced differences in x values are more probably associated with the qualitative rather than quantitative properties of biographical defects, which depend on the method of powder preparation. Decrease in the value of ξ with decreasing temperature is in agreement with a recent version of the model which allows for the possibility of an intermediate step — the generation and annihilation of vacancies in a chain of reactions connecting the flow of a "defective" crystal with the concentration of initial imperfections [4]. This model assumes the formation of active imperfections by the coagulation (combination) of a portion of the vacancies generated by the disappearance of initial (biographical) imperfections. The time of travel between source and sink, and with this the number of migrating vacancies, increases with decreasing temperature. In this case the number, and, evidently, the fraction of coagulating vacancies increases.

Mathematical analysis of the three-element model $x - U - y$ [4] leads to the equation connecting the parameter ξ with the activation energy of vacancy migration E_U:

$$\xi = \frac{E_x + E_\rho + E_U}{\gamma \cdot RT^2} \exp \frac{E_U}{RT},$$

(6)

where γ (h^{-1}) is the preexponential multiplier of Eq. (7) in [4]. Equation (6) also clarifies the dimensionality of ξ (h/deg) in Eq. (1).

According to Eq. (6) the value of ξ should decrease with increasing temperature, as observed experimentally. We note, in passing, that with the use of a computer it is not necessary to separate the calculation of $W(\tau)$ into two parts. Placing the given temperature plot $\dot{T}(\tau)$ into the program together with the model equations provides for the transition to the isothermal period after $\dot{T}$ has decreased to zero. With this, it is possible to also insert the function $\xi(T)$, given by Eq. (6), into the program, and put the calculation into a more finished form.

In comparing parameters, attention is drawn first of all to the significant differences in the activation energy values E_x, E_ρ, and E_{yx} for powders of different origin. This is a consequence of the substantially different "quality" of biographical defects in crystalline powders obtained in different ways, as discussed a number of times previously. Furthermore, the mechanism by which "active" imperfections affect the flow of a crystalline substance, and also the PVD rate, apparently does not depend on the conditions of formation and "quality" of the biographical defects. This conclusion is indicated by equality

TABLE 3. Rate of Pore Volume Shrinkage in Carbonyl Nickel Powder Under Conditions of Increasing and Constant Temperature.

Time, min	T=550—650 °C (x_0=556 h⁻¹ ζ=1,29·10⁻³ h/deg)	T=600—700 °C (x_0=447 h⁻¹ ζ=7,51·10⁻⁴ h/deg)	T=650—750 °C (x_0=323 h⁻¹ ζ=6,17·10⁻⁴ h/deg)	T=700—800 °C (x_0=253 h⁻¹ ζ=2,74·10⁻⁴ h/deg)	T=750—850 °C (x_0=223 h⁻¹ ζ=2,64·10⁻⁴ h/deg)
			Increasing temperature		
0	0,23/0,27	0,32/0,36	0,40/0,43	0,50/0,50	0,69/0,70
0,5	0,33/0,64	0,46/0,56	0,53/0,58	0,66/0,57	0,82/0,98
1,0	0,48/0,81	0,65/0,91	0,69/0,72	0,78/0,90	1,21/1,35
1,5	0,67/0,90	0,90/1,28	0,89/0,92	1,12/1,17	1,47/1,72
2,0	0,93/1,06	1,20/1,34	1,13/1,17	1,44/1,43	1,85/1,85
2,5	1,26/1,25	1,36/1,35	1,43/1,48	1,30/1,26	↓/↓
			Constant temperature		
0	1,19/1,20	1,29/1,31	1,38/1,40	1,24/1,16	1,77/1,76
1	1,06/1,12	1,16/1,15	1,25/1,18	1,24/1,15	1,62/1,64
3	0,88/0,87	0,98/1,01	1,06/0,94	1,02/1,09	1,40/1,40
6	0,71/0,76	0,81/0,80	0,87/0,86	0,95/0,98	1,17/1,20
10	0,58/0,65	0,68/0,66	0,72/0,69	0,83/0,85	0,98/0,98
15	0,48/0,49	0,57/0,56	0,59/0,61	0,72/0,73	0,83/0,84

of the parameters β and E_{yw} in Eq. (6) for powders obtained under different conditions. These conclusions are based on the results of experiments on the sintering of nickel powders of differing origin. In earlier experiments with copper, silver, iron, cobalt, molybdenum, and tungsten carbide powders (see [5] for details concerning the last two) substantially different, but in all cases significantly increased rates of PVS in the period of temperature increase were observed, as for nickel. This permits us to assume that the sintering of these powders also follows the general laws of behavior predicted by the mathematical model.

The powders were obtained by chemical methods with the formation, under certain conditions, of crystalline particles which exhibit a large concentration of (biographical) defects. The kinetic laws obeyed by these powders remain unchanged up to a sintering temperature close to the melting point (as exemplified by the copper and silver powders [2]). Whether similar behavior is observed during the sintering of powders obtained by spraying molten metal, or by mechanical attrition of solid metal, is not yet clear. It is not excluded that biographical defects which have a noticeable effect on the sintering process are also formed when a melt is solidified. If the effect of biographical (genetic) imperfections is not dominant, then, obviously, the appearance of a different sintering mechanism (high-temperature creep), more probable in the sintering of crystals with a small concentration of defects at high temperatures, may be observed.

From what has been stated here, and the discussion of the problem in the concluding section of [4], it follows that much in the theory of sintering remains unclear. The totality of completed work indicates that analysis of the function $W(\tau)$, or (one and the same) $\dot{v}/v(\tau)$, for various sintering conditions is an important source of information on the processes occurring in heated imperfect crystals. The use of new equipment which is able to continuously record temperature and shrinkage, and, consequently, decrease in pore volume, together with the latest methods for investigating the substructure of crystals, may yield new, and, it is to be assumed, unexpected results.

The author hopes that these possibilities will not be overlooked, and that the studies initiated by him will be continued by those who believe that the "magic crystal" conceals many more mysteries.

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