

An Analytical Model for the Isothermal and Isochronal Kinetics of Phase and Structural Transformations in Nano structured Materials

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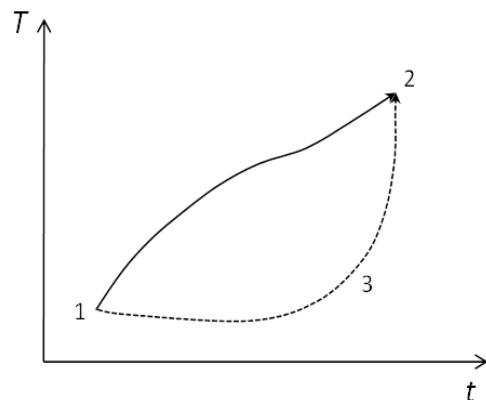
Abstract— Nanoparticles are widely used to design novel materials with new physical properties nowadays. A lot of technologies comprise the nanoscale materials thermal processing. This processing is possible at lower temperatures and over shorter durations than for the corresponding regular materials. A novel theoretical method is developed in present article to compute the necessary conditions of the nanoscale materials processing. The method is relevant for the different kinds of nanomaterials processing, both isothermal and non-isothermal. It is found that if the diffusion mechanism is the same at any different temperatures, then the thermal processing durations, which give the same structural transformation at these temperatures, can be calculated in the framework of this method. The calculated results on the nanopowders sintering are consistent with the available experimental values. The method is also applied to nucleation and growth transformations.

Index Terms—Activation enthalpy, diffusion, equivalent processing duration, nanopowder sintering, nanoscale materials.

I. INTRODUCTION

A lot of processes in metallurgy are controlled by diffusion. The diffusion rate depends on the way of diffusion, processing temperature and the characteristic size of nanoparticles forming nanoscale materials. For many technologies dealing with macroscopic substances, there exists an experience which facilitates the determination of the optimal processing conditions. In turn, some computation methods have been developed for these purposes. For example, the computation of isothermal and non-isothermal phase transitions in steel is widely carried out by processing of TTT-diagrams data [1]–[3]. The phase-field method is also used to describe structural transformations in steel [4], [5]. As well other approaches to this problem exist (e.g. [6], [7]). Among them, one can use Sheil’s additive rule to compute the way of diffusion-controlled transformations in a non-isothermal annealing (see e.g. [8]–[11]). According to the additive rule, the following relationship is valid:

$$\int_0^{t_\xi} \frac{dt}{\tau_\xi(T)} = 1, \quad (1)$$



where T is the absolute temperature, $T = T(t)$, t is the duration of the non-isothermal transformation, τ_ξ denotes the time required for the isothermal transformation of the fraction ξ at the temperature T . However, it was reported in [12]–[14] that, for some steels, serious discrepancies exist between the experimental results and the non-isothermal numerical calculations in terms of (1). For the sake of simplicity, it is assumed that the kinetic coefficients are constant with respect to transformation duration and temperature. The dimensionless time variable β has been introduced by the following way [9], [14]. Let us assume that the transformation mechanism is the same in a region of the T - t diagram (Fig. 1) and that β is proportional to the number of atomic jumps. T determines the atomic mobility and t defines the duration of the transformation. Under these conditions, the variable β obeys the following relation:

$$\beta(t) = \int_0^t k(T(z)) dz, \quad (2)$$

which can be considered as dimensionless time of the transformation [9]. Here $k(T)$ is the rate constant for which the Arrhenius equation is usually used:

$$k = k_0 \exp\left[-\frac{Q_a}{RT}\right], \quad (3)$$

where Q_a is the activation energy, k_0 is the pre-exponential factor, R is the universal gas constant. In general case, the thermal paths 132 and 12 lead to the different final states at the point 2. It was assumed in [9] that β is a state variable. Hence, the fraction transformed is fully determined by β . In the framework of this assumption, the only case, which gives the same state at the point 2 is following. If both the thermal paths are of the equal values of β , they also are of the same final state at the point 2 (see Fig.1). It will be shown below that this assumption is invalid in general case. In present article we shall develop a model to connect the diffusion in nanoscale materials with that in regular materials. We shall also evaluate the relevance of (1) to isochronal annealing (annealing with the constant rate of heating or cooling).

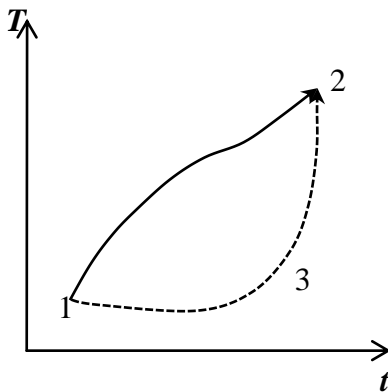


Fig. 1 Temperature – time diagram ($T-t$ diagram) for non-isothermal annealing. A thermally activated phase transformation follows two different thermal paths from the point 1 to the point 2. In general, different thermal paths give different values of the transformation stages ξ in the same final point of the $T-t$ diagram

II. MODEL

A. General consideration

Let phase and structural transformations proceed in a homogeneous closed system. It will be assumed that the variables T , p and ξ fully determine the state of the system [15]. They are time-dependent functions during the transformation. But the nature of their time dependency is different. In general, the functions $T(t)$ and $p(t)$ can be defined arbitrary. On the contrary, $\xi(t)$ is not an arbitrary function, because it obeys the differential equation

$$\frac{d\xi}{dt} = \mathbf{v}(p, T, \xi), \quad (4)$$

where \mathbf{v} is the transformation rate. Evidently, \mathbf{v} is a state function. If the functions $T(t)$ and $p(t)$ are chosen on the basis of, for example, technological conditions, we can rewrite (4) as

$$\frac{d\xi}{dt} = \mathbf{v}(t, \xi(t)). \quad (5)$$

Usually, the initial value of ξ is known. It means that there exists a unique solution of (5). Thus, we have the unique solution after defining $T(t)$ and $p(t)$. In the most cases, $p = \text{const}$, hence the solution $\xi = \xi(t)$ is only determined by the initial condition $\xi(0) = \xi_0$ and the function $T(t)$. The latter function can be shown as a curve in the $T-t$ diagram. The thermal path is the name of this curve. Arbitrary two points in this diagram can be connected each other by different thermal paths. In general, the different thermal paths give different values of ξ in the final point. Therefore, one has to use a state function to compute $\xi(t)$. Equation (5) is appropriate for this purpose, because \mathbf{v} is a state function. Otherwise, the function ξ is not a state function, thus it is inappropriate to use the isothermal function $\xi(T_i, t)$ to compute the non-isothermal transformation kinetics. Here T_i is the temperature of the isothermal transformation. Hence, in order to compute $\xi(t)$ under non-isothermal conditions, it is necessary to solve (5). Firstly, we shall consider a simple diffusion transformation, which goes without a new phase nucleation. It may be, for example, crystal grain growth, powder sintering and so on. In such a case, diffusion controls all physical processes under this transformation. It is assumed that \mathbf{v} can depend on ξ only implicitly. Thus, the variables t and T uniquely determine the thermodynamic state of the transforming system. For non-isothermal annealing, it means that $\mathbf{v} = \mathbf{v}(t)$ and $T = T(t)$, and that the introduction of the dimensionless time β is possible via (2). Thus, the kinetics of this kind of structural transformations meets Sheil's equation. A problem encountered in practice is to compare the isothermal annealing with the non-isothermal that for the same material. For this purpose, let isothermal and non-isothermal infinitesimal transformations be equal to each other, i.e.

$$\mathbf{v}(T_i) d\tau = \mathbf{v}(t) dt. \quad (6)$$

Here it is assumed that the detailed functional form of $T(t)$ is known, and T_i and τ are temperature and duration of the isothermal annealing. The solutions of (6) will be considered below for the most familiar structural transformations.

B. Transformations without nucleation of a new phase

Choosing the Arrhenius law of thermally-activated transformation rates (see (3)) gives the evident relation

$$\tau = \exp\left[\frac{Q_a}{RT_i}\right] \int_0^t \exp\left[-\frac{Q_a}{RT(z)}\right] dz. \quad (7)$$

The integrand in (7) depends on the function $T(t)$. A way of heating (cooling) determines the result of the integration. In the simplest case, one can adopt that $T(t) = T_0 \pm \omega t$ (isochronal annealing). Here T_0 is an initial temperature, $\pm\omega$ is a constant rate of heating (+) or that of cooling (-). The analytical solution of (7) in the case of the isochronal annealing was obtained elsewhere [9], [14]. It is of the form

$$\tau = e^x \frac{Q_a}{\pm \omega R} \left[\frac{E_2(x_1)}{x_1} - \frac{E_2(x_0)}{x_0} \right]. \quad (8)$$

Here $x = Q_a / (RT_i)$; $E_2(x_j)$ is the exponential integral [16]; $x_j = Q_a / (RT_j)$, $j = 0, 1$; T_0 and T_1 denote the initial and final temperatures of the non-isothermal transformation respectively.

The diffusivity depends on the nanoparticle characteristic size at the nanoscale. Thus, one can assume that there exists temperature T_{eq} at which the diffusivity of a nanoscale material is the same as the diffusivity of a related macroscopic material at a given temperature T_i . The relation for the nanoscale diffusivity $D(T, \chi)$ was derived previously [17] and meets the relation

$$D(T, \chi) = D_0 \exp(-\Delta H_a(\chi) / (RT)), \quad (9)$$

where ΔH_a is the size-dependent activation enthalpy, $\chi = r/r_0$ is the dimensionless characteristic size of nanoparticles, r denotes the characteristic size of nano-objects. For a nanorod and a nanoparticle, r is their radius. For a thin film, r means its half thickness. Here r_0 is determined by the relation $r_0 = (3-d)h$, where d the dimension of nano-object that equals 0, 1, and 2 for nanoparticles, nanorods and thin films respectively. Here h is the atomic diameter. In this notation, $D(T, \infty)$ is the diffusivity at the macroscopic scale (in the limit $r \rightarrow \infty$). It is assumed that the pre-exponential factor D_0 depends on χ very weakly in comparison with the exponential in (9) and, therefore, can be considered as size-independent. The activation enthalpy is of the form

$$\Delta H_a(\chi) = \Delta H_a(\infty) \left(1 - (\chi - 1)^{-1} \right) \exp[-(\alpha - 1) / (\chi - 1)]. \quad (10)$$

Here $\Delta H_a(\infty)$ is the activation enthalpy of self-diffusion in the related regular materials, $\alpha = \sigma_s^2 / \sigma_v^2$, σ_s^2 and σ_v^2 are the mean square displacement of surface and bulk atoms of nanoparticles respectively. If the nanoparticles are not embedded in matrix, then $\alpha = (2S_{vib} / 3R) + 1$. Here S_{vib} is the vibrational component of the bulk melting entropy [17]. In order to derive an explicit relation for T_{eq} , one can equate the regular material diffusivity, at this temperature, to the related nanostructured material diffusivity. Let us adopt that in the both cases the pre-exponential factors in (9) are equal. Then the equality of these diffusivities leads to the equality of the corresponding exponents. Thus, equating $\Delta H_a(\infty) / (RT_i)$ to $\Delta H_a(\chi) / (RT_{eq})$ and accounting for (10), we have

$$T_{eq} = T_i \left[1 - (\chi - 1)^{-1} \right] \exp[-(\alpha - 1) / (\chi - 1)]. \quad (11)$$

It is evident that χ may be time-dependent, because nanoparticles may change, in general, their mean size and form during transformation. In such a case, it is necessary to

consider (11) with the additional condition $\chi = \chi(\tau)$. Let us assume below that the change in χ is negligible over all transformation. In the opposite case, it is necessary to obtain the function $\chi(\tau)$ previously to solve this problem by (6).

Two problems arise from the non-isothermal annealing of nanostructured materials. The first problem is to compare the isothermal annealing with the non-isothermal one for the same nanostructured material. Equation (8) allows solving this problem if χ does not change drastically during the transformation. The second problem is to establish a relationship between the isothermal annealing of regular materials with the non-isothermal one of related nanostructured materials. In order to solve this problem, we can write, analogous to (6), the relation

$$D(T_i, \infty) d\tau = D(T(t), \chi) dt, \quad (12)$$

where T_i denotes a temperature of the isothermal transformation, τ is the isothermal transformation duration. After integrating both sides of (12), one has

$$\tau = \exp \left[\frac{\Delta H_a(\infty)}{RT_i} \right] \int_0^t \exp \left[-\frac{\Delta H_a(\chi)}{RT(z)} \right] dz. \quad (13)$$

In general, χ may be a function of t . The integrand in this equation depends on the function $T(t)$. Thus, a way of heating (cooling) determines the result of the integration. Equation (8) is an analytical solution for this case under the following notation: $Q_a = \Delta H_a(\infty)$, $x = \Delta H_a(\infty) / (RT_i)$, $x_j = \Delta H_a(\zeta) / (RT_j)$, $j = 0, 1$. In practice, $x_j \gg 1$. Therefore, the exponential integral $E_2(x)$ can be expanded as a power series of x^{-1} [9], [16]. Note that we have followed the convention that χ is time-independent to derive (7).

C. Phase transformations with nucleation and growth of a new phase

Now let us consider a non-isothermal transformation accompanied by nucleation and growth of a new phase. The kinetics of phase transformations is often described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation. We shall consider (5) in terms of the extended volume concept (see e.g. [18]). In general, one can write (5) as it was supposed in [19]:

$$\frac{d\xi}{dt} = (1 - \xi)^\lambda \frac{d\xi_{ex}}{dt}, \quad (14)$$

where $\lambda = 1$ for Avrami-type equations, $\xi = V/V_{eq}$ and $\xi_{ex} = V_{ex}/V_{eq}$, V_{eq} and V_{ex} are the equilibrium and extended volume of the new phase respectively. It follows immediately that

$$\xi_{ex} = \frac{1}{\lambda - 1} \left[(1 - \xi)^{1 - \lambda} - 1 \right]. \quad (15)$$

It is evident that equations (14) and (15) are valid in the non-isothermal conditions too. It is assumed here, similar to the JMAK model, that the transformed volume, V_p , around a single nucleus grows according to

$$V_p = \mathfrak{Z} [G(\tau - \theta)]^m, \quad (16)$$

where G is the growth rate, \mathfrak{Z} is a geometrical factor, θ is the time at which the nucleus is formed, whilst m is a constant related to the dimensionality of the growth and the mode of transformation. The extended volume is defined as

$$V_{ex}(\tau) = \mathfrak{Z} \int_0^\tau I(\theta) V_p(\tau, \theta) d\theta. \quad (17)$$

Here $I(\theta)$ is the nucleation rate. The integral in the right-side of (17) has been considered for different nucleation ways (e.g., in [18], [20], and [21]). Usually, taking the integral in (17) gives the extended volume in the following simple form:

$$V_{ex} = A(T) \tau^n. \quad (18)$$

Here n is a constant. In order to adjust (16) and (17) to the non-isothermal transformation, one must write the former equation in the integral form:

$$V_p = \mathfrak{Z} \left(\int_\theta^t G(z) dz \right)^m. \quad (19)$$

Substituting this equation into (17) gives that

$$V_{ex} = \mathfrak{Z} \int_0^t I(\vartheta) \left(\int_\vartheta^t G(z) dz \right)^m d\vartheta. \quad (20)$$

Here $V_{ex} = V_{eq} \xi_{ex}$, ϑ is the time at which the nucleus is formed in the non-isothermal transformation.

Let us consider an isothermal phase transformation and a non-isothermal one which both give the same transformed fraction ξ . It is assumed that both the thermal paths correspond to the same transformation mode. According to (8), these transformation ways lead to the same value of ξ if the corresponding values of ξ_{ex} are equal to each other. Using this conclusion, we can derive an analogue of Sheil's equation. In order to obtain this new relationship, we divide (20) by its isothermal analogue (17). It gives the following equation:

$$\frac{\int_0^{\xi_{ex}} I(\vartheta) \left(\int_\vartheta^{\xi_{ex}} G(z) dz \right)^m d\vartheta}{\int_0^{\tau_{\xi}} I(\theta) \left(\int_\theta^{\tau_{\xi}} G(\zeta) d\zeta \right)^m d\theta} = 1. \quad (21)$$

If the functions $I(t)$ and $G(t)$ depend on t only implicitly via the dependency $T = T(t)$, then the denominator in (21) takes the form of (17) with $n = m + 1$ and $A(T) = I(T)G(T)/(m+1)$. Replacing the denominator by the right-hand side of (18) and equating θ to ϑ yields

$$(m+1) \int_0^{\xi_{ex}} [G(\theta)]^m [\tau_{\xi}(\theta)]^{-(m+1)} \left(\int_\theta^{\xi_{ex}} G(z) dz \right)^m d\theta = 1. \quad (22)$$

Now it is evident that a further simplification of (22) is necessary to derive the analogue of Sheil's additive rule. For this purpose we shall consider the inner integral. First, it will be assumed that G is an Arrhenius-type function:

$$G(T) = G_0 \exp[-Q_G/(RT)]. \quad (23)$$

Second, we shall adopt the convention that the rate of cooling (or heating) ω is constant. Hence, the transition temperature meets the relation $T = T_0 \pm \omega t$. Under these severe conditions, we have that

$$\int_\theta^t G(z) dz = \frac{Q_G G_0}{R\omega} \left[\frac{E_2(x_1)}{x_1} - \frac{E_2(x_\theta)}{x_\theta} \right] = G(\theta) \tau(\theta), \quad (24)$$

where $E_k(x)$ is the generalized exponential integral, $k = 0, 1, 2, \dots$; $x_1 = Q_G/(RT(t))$, $x_\theta = Q_G/(RT(\theta))$. $G(\theta)$ meets (23) at $T = T(\theta)$, $\tau(\theta)$ defines by (8) at $x_i = x_\theta$. Substituting (24) into (22) gives

$$(m+1) \int_0^{\xi_{ex}} \left(\frac{\tau(\theta)}{\tau_{\xi}(\theta)} \right)^m \frac{d\theta}{\tau_{\xi}(\theta)} = 1. \quad (25)$$

Now it is evident that Sheil's equation corresponds to this equation if $m = 0$. The physical meaning of $\tau(\theta)$ and $\tau_{\xi}(\theta)$ are different. $\tau(\theta)$ is the duration of the isothermal annealing at $T(\theta)$, which is equivalent to the non-isothermal annealing within the temperature interval from $T(\theta)$ to $T(\xi)$. Their equivalence means that both these annealing conditions give the same growth of a nucleus formed at θ . Otherwise, $\tau_{\xi}(\theta)$ is the isothermal transformation duration at $T(\theta)$ which is necessary to obtain the transformed fraction ξ . In the latter case, the transformation occurs by the nucleation and growth mechanisms. Therefore, if the transformation occurs in nanostructured materials, equation (13) is relevant to compute $\tau(\theta)$. The new phase growth in regular materials can be considered in two limits, i.e. the interface controlled growth and the diffusion controlled growth [18]. Processes at the particle/matrix interface govern the growth of the new phase particle in the first limit. The matrix atoms, which transfer into the new phase particle, have to overcome an energy barrier Q_a formed by the interface. The reverse atom flux is usually negligible because of the phase transformation driving force. For example, the activation energy Q_a to move an atom across the austenite-ferrite interface may, to a first approximation, can be estimated by the experimental activation energy for self-diffusion of iron atoms in the parent phase [21], [22]. In the second limit, the long distance diffusion in the matrix governs the growth of the new phase particles. Evidently, a phase transformation in nanostructured materials does not imply the long-distance diffusion usually. Therefore, the transformation occurs by the new phase nucleation and its interface controlled growth. It implies that $Q_G = Q_a$ and that Q_G , thus, meets the same size dependency as ΔH_a (see (10)).

For the sake of simplicity, let us consider the JMAK equation

$$\xi(T, t) = 1 - \exp[-A(T) \tau^n], \quad (26)$$

here $A(T) = B \exp[-Q/(RT)]$, B is a constant. In the

interface controlled growth mode, the effective activation energy Q obeys the following relation [20]:

$$Q = \frac{m}{p} Q_G + \left(n - \frac{m}{p} \right) Q_N, \quad (27)$$

where Q_N is the activation energies of nucleation, $n = m$ in the case of site saturation and $n = m/p + 1$ in the case of continuous nucleation, m is the number of dimensions in which the particle grows. Here the term site saturation means that the number of (supercritical) nuclei does not change during the transformation because all nuclei are already present at $\tau = 0$. The coefficient p equals 1 or 2 if the interface controlled growth mode or the bulk controlled one, respectively, takes place.

In regular polycrystalline materials the formation of a nucleus of the new phase creates the interfaces between the new phase and the parent phase. The transformation driving force $\Delta G_v = V_N (\mu_2 - \mu_1)$ partly compensates the interfacial Gibbs energy $\Delta G_s = C \sigma_{12} V_N^{2/3}$. Here V_N is the critical nucleus volume, μ_1 and μ_2 are the chemical potentials of the parent and the new phases, correspondingly; C is a constant depending on the nucleus form, σ_{12} is the interface surface tension. The positive difference $\Delta G_s - \Delta G_v$ gives an energy barrier for nucleation W . It was noticed in [22] that when the new phase nuclei are formed at the grain boundaries, they adsorb a part of these boundaries. It causes a release of the grain boundary energy that decreases or completely removes the energy barrier in the case of regular materials. Now consider the phase transition in nanostructured materials. In these materials there is a high density of the grain boundaries. Therefore, the new phase nucleus formation releases the grain boundary in sufficient amount to remove the nucleation energy barrier. It implies that $Q_N = 0$ for nanostructured materials. Substituting this result in (27) gives $Q = mQ_G$ that corresponds to the site saturated mode. It was shown above that Q_G meets the same temperature dependency as ΔH_a (see (10)). Thus we have that

$$Q(\chi) = Q(\infty) \left[1 - (\chi - 1)^{-1} \right] \exp \left[-(\alpha - 1) / (\chi - 1) \right], \quad (28)$$

where $Q(\chi)$ and $Q(\infty)$ are the effective activation energy of the phase transition in nanostructured materials and in regular ones respectively.

III. RESULTS AND DISCUSSION

A. The sintering onset temperature

If sintering of nanopowders allows producing innovative materials. Numerous nanopowders indicates depressed sintering onset temperatures ($0.2-0.3T_m$) as compared to conventional powders ($0.5-0.8T_m$) [23]. For designing new materials, it is important to predict the sintering onset temperature of nanopowders (T_{sn}) and to choose an appropriate temperature interval to deplete the grain growth during sintering. It is known that the sintering activation

energy Q_a depends on the characteristic size of powder nanoparticles (see e.g. [23], [24]). Equation (11) is appropriate to estimate the nanopowder sintering onset temperature on the basis of the known one of the relative regular material (T_s). For this purpose, it is sufficient to replace T_{eq} and T_i by T_{sn} and T_s respectively. Let us consider the sintering of the Sm, Co and Mo nanopowders as an example. The necessary parameters for the calculation are presented in Table 1. It was shown in [25] that the Sm nanoparticles with a mean diameter of 75 nm start to sinter at 593 K. This value of T_{sn} gives us that the corresponding value of T_s equals 626 K. It was also shown in [26] that the critical temperature for the destabilization of the Co nanograin structure with the characteristic grain size about 40 nm is above 803 K. It follows from [27] that regular Co powders start to sinter at 883 K approximately.

Table 1. The necessary parameters for the T_{sn} calculations. T_m is the melting temperature [28], h is the atomic diameter [29], α is the parameter of (10), T_s is the sintering onset temperature

Material	T_m [28] K	h [29] nm	α	T_s K	T_s/T_m
Co	1767	0.2766	1.63	883 [26]	0.5
Mo	2893	0.3100	1.895	1373 [27]	0.47
Sm	1345	0.3988	1.63	626 [25]	0.47

The direct calculation via (11) gives that $T_{sn} = 822$ K for the Co nanopowder with the average size of 40 nm. This value of T_{sn} is in close agreement with the experimental result mentioned above. In order to evaluate T_s of a regular Mo powder, one can consider the shrinkage dependency on temperature, which is represented in [30]. It gives that T_s is about 1373 K. Note, however, that the average size of nanoparticles is appropriate to determine T_{sn} in the only case if the nanoparticles size distribution is sharp. This is because T_{sn} decreases with decrease in the nanoparticles characteristic size (see (11)). Therefore, the sintering is activated by the smallest nanoparticles if there is a sufficient amount of them in a nanopowder. In general, using the average nanoparticles size in Eq. 11 gives an inflated estimate of T_{sn} . For example, let us consider Fig. 2. The dependency T_{sn} on r is very weak if $r > 20$ nm (see Fig. 2). For nanoparticles with characteristic size more than 50 nm, this dependency is negligible. However, if $r < 15$ nm approximately, the sintering onset temperature changes abruptly. For example, T_{sn} of the Co nanoparticles with the characteristic sizes 15, 10 and 5 nm equals 801, 758 and 624 K correspondingly. It means that Co nanopowders which are of the same average nanoparticles size sinter, in general, at different T_{sn} if their nanoparticle size distributions strongly differ from one another in the region of small r ($r < 15$ nm).

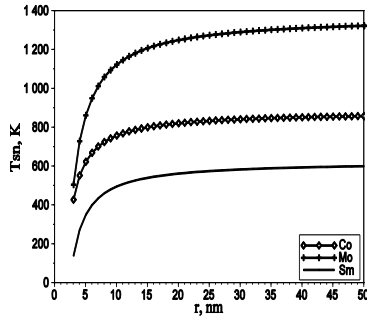


Fig. 2: Dependency of the sintering onset temperature T_{sn} on the nanoparticles characteristic radius r

Thus, the nanoparticles size distribution has an influence on T_{sn} .

B. A relationship between regular and nanoscale kinetics of sintering

The master sintering curve (MSC) is one of useful methods to predict and to control sintering during a non-isothermal annealing [31], [32]. According to [33] and [34], changes in length, L , that occur during sintering can be described by a linearly additive sum of the following form:

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{k_bT} \left(\frac{\Gamma_b D_b}{a_p^3} + \frac{\Gamma_s D_s \delta}{a_p^4} \right), \quad (29)$$

where γ is the surface energy, Ω is the atomic volume, and a_p is the mean grain diameter, Γ_j is the dimensionless parameter, D_j is the diffusivity, δ is the average width of a grain boundary. The first and the second terms in the brackets correspond to bulk and surface diffusion respectively. If one assumes that the quantities a_p , Γ_b and Γ_s are independent of microstructure or relative density ρ , then we can rearrange (29) so that one side, $\Phi(\rho)$, contains all the properties dependent on density whereas the other side, $\Theta[T(t)]$, depends only on the thermal path and activation energy. Let a single mechanism dominates during sintering, the volume or grain boundary diffusion, then the arrangement of (29) in this manner leads to:

$$\Phi(\rho) = \Theta[T(t)], \quad (30)$$

with

$$\Theta[T(t)] = \int_0^t \exp[-Q/(RT)] T^{-1} dt = \omega^{-1} [E_1(x_1) - E_1(x_0)]. \quad (31)$$

Here it is assumed that $T = T_0 + \omega t$ in the right-hand side of this equation, i.e. the isochronal heating is implied. The functional relationship between ρ and $\Phi(\rho)$ is the MSC, which is unique for each powder and green forming method, including a fixed green density [33]. Generally, sintering of most materials is combination of different diffusion mechanisms (volume, surface and grain boundary diffusion) [34]. At these conditions, the value of activation energy which determined by the MSC differs from the known values of the activation energy (activation energy for grain boundary or volume diffusion). At the nanoscale, it is impossible to

separate the grain boundary diffusive transfer from the volume one, because they are completely mixed during nanopowder sintering. In this case, the activation energy meets (10) and depends on the nanoparticles characteristic size.

In the framework of the present theory, equations (5) and (31) are of the similar form. Moreover, usually $x \gg 1$ so that the series

$E_k = x^{-1} e^{-x} (1 - kx^{-1} + k(k+1)x^{-2} - k(k+1)(k+2)x^{-3} + \dots)$ is valid [35]. Here $k = 0, 1, 2, \dots$. Taking the first term of this series gives that $E_1(x) \approx x^{-1} e^{-x}$. Using this in (31) gives

$$\Phi(\rho) = \omega^{-1} \left(\frac{e^{-x_1}}{x_1} - \frac{e^{-x_0}}{x_0} \right). \quad (32)$$

The MSC activation energy can be found by the different ways [31], [32], [36]. Equation (32) is also appropriate for this purpose even if an explicit form of $\Phi(\rho)$ is unknown. In order to determine the sintering activation energy, one can perform two sintering annealing with different heating rates to obtain two different dependencies, $\rho(T(t), \omega_1)$ and $\rho(T(t), \omega_2)$. Evidently, there exist values of temperature, T_1 and T_2 , at which the density is the same, i.e. $\rho(T_1, \omega_1) = \rho(T_2, \omega_2)$. According to (32), its right-hand sides are also equal in value. In this case, equating the right-hand sides of (32) with T_1, ω_1 and T_2, ω_2 gives a new equation which allows computing the sintering activation energy in the ordinary way. In practice, this problem is often solved by graphical method (see e.g. [30] and [36]). The MSC is obviously a particular case of the model developed above. Let us associate the sintering duration of a nanopowder (τ_n) with the one of its corresponding regular powder (τ_r). For this purpose, one can equate the right-hand sides of (32), associated with the nanopowder MSC, to the one, associated with the regular powder MSC, and to solve for $T_s = T_1(\tau_n, \omega_n)$ or $T_s = T_1(\tau_r, \omega_r)$. This equation is of the form

$$\omega_r^{-1} \left(\frac{e^{-x_{r1}}}{x_{r1}} - \frac{e^{-x_{r0}}}{x_{r0}} \right) = \omega_n^{-1} \left(\frac{e^{-x_{n1}}}{x_{n1}} - \frac{e^{-x_{n0}}}{x_{n0}} \right), \quad (33)$$

where the notation is the same as in (8) but indexes r and n which correspond to the regular powder and the nanopowder respectively. Note, that equation (33) is valid if the physical process controlling the sintering is the same for both powders. We assume that the sintering kinetics is the same in both cases at the initial stage of sintering. It means that (33) is applicable for this sintering stage. The activation energy of sintering is also necessary to use this equation. As an example, we have computed the sintering onset temperature of ZnO microcrystalline powder on the basis of the known sintering onset temperatures of the nanopowder (see Table 2). Both temperatures can be determined from the densification curves shown in [37] and, thus, the value of T_s obtained from (33) can be compared with that extracted from the experimental data. It was revealed that T_s computed by this way is equal to 961 K

that is in good agreement with the microcrystalline powder onset temperature estimated from the isochronal densification curves (see Table 2). Therefore, this method is appropriate to calculate the sintering onset temperature of powders with different particles characteristic size. Sheil's equation, as we have already noted, is also applicable to this kind of structural transformations.

Table 2. Physical characteristics of ZnO powder [37]

ZnO powder	Average particle size (nm)	Q_a , kJ/mol	T_s , K
microcrystalline	790	296±21	960
nanocrystalline	48	268±25	870

C. Sheil's equation

If a diffusion-controlled transformation proceeds through the new phase nucleation and growth, Sheil's equation (see (1)) is often used to compute the volume fraction of a new phase produced during a non-isothermal phase transformation in steel [1], [2]. Let us estimate an error which is caused by using this equation instead of (26). For this purpose, we introduce a new function defined by

$$R(\xi) = (t_\xi - t_\xi^*) / t_\xi, \quad (34)$$

where ξ is the transformed fraction, t_ξ and t_ξ^* are the transformation durations computed via (26) and 1 respectively. Thus $R(\xi)$ shows the relative deviation of t_ξ^* from t_ξ . In order to obtain the dependency $R = R(\omega)$, let us create a model of a diffusive phase transformation of steel. The dependency $\tau_\xi = \tau_\xi(T)$ is necessary to compute function $R(\xi)$ for a given material. It is appropriate to obtain $\tau_\xi(T)$ for this computation to use a model isothermal diagram for pearlitic steel from [8]:

$$\tau_\xi = K_\xi \left(\frac{T_{eq}}{T_{eq} - T} \right)^3 \exp \left(\frac{Q_\tau}{RT} \right), \quad (35)$$

where $K_\xi = 3 \cdot 10^{-8}$ s for $\xi = 0.01$, $T_{eq} = 1000$ K, $Q_\tau = 83.7$ kJ/mol. We also use the value $n = 4$, which was obtained for the pearlite transformation in eutectoid steel in [2]. Let us assume that the new phase nucleation occurs by the continuous nucleation way and that $m = 3$ in our model. As a result, we have the estimation that $Q_G = 112$ kJ/mol and $Q = 336$ kJ/mol, which follows from (27), (28) and (35). In the following computation of $R(\omega)$, we also adopt that Q_N is negligible in comparison with Q_G , i.e. $Q_N \approx 0$. According to [38], the activation energy of the pearlite growth Q_G is equal to 148 kJ/mol. Hence, the parameters of our model are close to the experimental ones. The results of the computation are shown in Fig. 3. The value of R increases with the cooling rate and approaches the value of 0.11 at the cooling rate of 100 K/s (see Fig. 3).

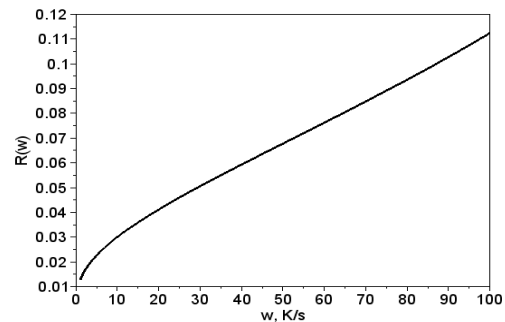


Fig. 3 the results of the $R(w)$ computation. Here w is the cooling rate

During a solid state phase transformation in a polycrystalline material, the new phase forms preferentially at the grain boundaries of the parent phase. After the nucleation sites depletion, only the grain growth occurs. According to Cahn's theory [18], the JMAK equation with $m = 3$ (see (27)), describes the first transformation stage. At the second transformation stage, m approaches zero in the limit $\tau \rightarrow \infty$. In nano crystalline materials, the number of the grain boundary atoms is comparable with the number of the bulk atoms. Hence, the most part of the transformation is completed at the first stage. The onset of transformation occurs when the first growing nucleus of the new phase appears in the parent phase. The time interval which is necessary to produce the new phase nucleus is called the incubation time τ_{in} [18], [39]. Evidently, the incubation time of isothermal phase transformation strongly depends on the isothermal annealing temperature. Firstly, Eq. 1 was applied to calculate the incubation time of non-isothermal phase transition. Then the use of this equation was extended from the incubation time to the whole range of the phase transformation [39], [40]. The incubation time is the appropriate parameter to estimate the material stability against the phase transformation, because the more this stability, the more the incubation time. One can control the material stability by the different ways, e.g. by the thermal and mechanical pretreatment of the material. The rolling of steel before transformation can create additional nucleation centers which facilitate the following phase transformation, and therefore decreases the incubation time. In alloy steel, the inhomogeneity of the alloying elements concentration can play the similar role [29]. It means that, in general, the lower limits of integration in (1) and (26) must be replaced by τ_{in} . Nevertheless, we shall limit our considerations exclusively to the nanostructured materials. In this case the incubation time is very short or absent at all, because of the high structure inhomogeneity. Thus, the approximation $\tau_{in} = 0$ is usually appropriate for phase transformations in nanostructured materials.

IV. CONCLUSION

The developed new method allows comparing the phase and structural transformations in nanostructured materials

with corresponding ones in regular materials. Moreover, this method is applicable to both isothermal and non-isothermal conditions. It gives a unique possibility to describe the isothermal and non-isothermal physical properties of nanostructured materials on the base of the known physical properties of related regular ones and, to a great extent, facilitates the development of novel nanostructured materials. The analytical relationship was deduced for the first time to compute the sintering onset temperatures of nanostructured materials on the basis of those known for the relative regular materials or vice versa. The average size of nanoparticles is not a good characteristic of nanopowders if one considers their sintering. The nanoparticles with the smaller characteristic size can activate sintering because the nanoparticles activation energy of diffusion is reduced with decrease in their characteristic size. Therefore, the size distribution has an effect on the process of sintering, even if the nano powders are of the same average characteristic size. It gives an additional way to control the nanopowder sintering. It was shown that the additivity rule is invalid in the case if it is used to describe the phase transformation accompanied by nucleation and growth of a new phase. The new equation was derived to describe this kind of phase transformations during the non-isothermal annealing. Only at the low rate of heating or cooling (approximately less than 5 K/s), Sheil's equation becomes a good approximation of this new adequate equation. Note, however, that under severe physical restrictions, one can derive Sheil's equation in terms of the extended volume approximation. Nevertheless, the additivity rule can be valid in the case of phase and structural transformations which do not proceed by the nucleation and growth mechanism.

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