

# EVOLUTION OF DIFFUSIONAL PHASE TRANSFORMATION WITH VARYING TEMPERATURE

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We suggest an approach for modeling of diffusional phase transformation in a solid state. Our approach is based on the microcarrier nucleation and growth consideration. The known Johnson-Mehl-Avrami (JMA) or Leblond equations can be obtained as special cases of the general modeling frame worked out. The simulation of a dilatometric experiments of the austenite-pearlite phase transformation is presented with a simplified form of our model. The model proved itself to be in a good agreement with experiments for a wide range of cooling rates.

## 1. INTRODUCTION

During heat treatment (or more general, thermoplastic processes) of metal alloys and some other materials different solid-solid phase changes may occur. They cause changes of mechanical properties and some additional (micro-) deformations of material due to rearrangements in crystal lattice. This deformations are affected by (macro-) stresses and yield to macro-deformations. This effect is called sometimes transformation induced plasticity (TRIP) which is in general influenced by stress. Hence, manufacturing articles requiring high accuracy it is of grate importance to take the phase transformation into account. There are different approaches to model TRIP in frame of small and large deformation formalism. Some of them have need of kinetic equations describing phase transformation, see [6], [19] for example. In this paper we consider only the diffusion phase transformation kinetic.

It is commonly accepted that the diffusion phase transformation processes are controlled by nucleation and growth of nuclei, where impingements should be taken into account. First equations based on the analysis of these two effects were obtained in the pioneering papers for the isothermal case. The result of Johnson and Mehl [10], derived originally for the pearlite formation from austenite, reads as follows

$$p(t) = 1 - e^{-\frac{\pi}{3}N_\nu G^3 t^4}, \quad (1)$$

where  $p(t)$  is the volume fraction transformed up to the moment  $t$ .  $N_\nu$  is the rate of nucleation and  $G$  is the rate of the radial growth, both supposed to be constant throughout the reaction.

Criticizing the assumption of the rate of nucleation constance Avrami [2] starts with the asser-tion that the new phase is nucleated by tiny germ nuclei which exist already in the parent phase, whose effective number  $\bar{N}$  depends on the temperature and duration of the superheating, generally decreasing with increase of either. Denoting by  $G$  the averaged rate of growth of the linear dimension of a nucleus Avraimi gets the following kinetic equation for the polyhedral growth

$$p(t) = 1 - e^{-\sigma G^3 \bar{N} t^3}, \quad (2)$$

where  $\sigma$  is a shape factor (equal to  $\frac{4\pi}{3}$  for a sphere, e.g.). We would like to emphasize that in these equations the parameters  $G$  and  $N_\nu$  (or  $\bar{N}$ ) reflect two different effects, namely growth and nucleation respectively. However in the isothermal case one can write

$$p(t) = 1 - e^{-Kt^4} \quad (3)$$

with  $K = \frac{\pi}{3}N_\nu$  instead of (1) or

$$p(t) = 1 - e^{-Kt^3}, \quad (4)$$

with  $K = \sigma G^3 \bar{N}$  instead of (2). Later, paved by Avrami, who stated that the power of  $t$  in (4) varies from 3 to 4 (for the polyhedral growth), it led to the generalized Johnson-Mehl-Avrami (JMA) equation

$$p(t) = \bar{p}(1 - e^{-Kt^n}) \quad (5)$$

which proved itself to be in a good agreement with most of isothermal experiments. Here  $\bar{p}$  is the equilibrium fraction reached at constant temperature  $\theta$  after an infinitely long time. The parameters  $K$  and  $n$  depend on temperature and can be determined from the isothermal time-temperature transformation diagram. We also refer to [4] and [5] for further details and explanations.

In practice it is impossible to reach the prescribed temperature instantaneously. If transformation starts already in the beginning of quenching and goes fast, the equation (5) can not be used at least for the early stage of reaction. To describe the incubation period at the start of transformation the additivity rule was proposed by Scheil [17]. Later it was used for the entire transformation in the nonisothermal case, see e.g. [9]. Let  $\tau(p, \theta)$  be the time needed to reach the  $p$  fraction in the isothermal transformation process at temperature  $\theta$ , then by the additive rule in an anisothermal process  $\theta(t)$  the fraction  $p$  is reached at the moment  $t$  such that

$$\int_0^t \frac{ds}{\tau(p, \theta)} = 1. \quad (6)$$

For the experimental investigation of this rule we refer to the paper of Wever and Krisement [18], for some theoretical investigation of its applicability see, e.g., [8]. Some generalizations can be proposed. As it is known from experiments that the rate of transformation varies essentially in course of reaction even at constant temperature being much higher at the middle stage as at the beginning or at the end. Hence different  $\tau$ -s should be weighted for different stages:

$$\int_0^t \frac{ds}{\tau(p, \theta) f(s, \theta)} = 1, \quad (7)$$

where  $f$  is a nonnegative weighting function. See also [16] for other modifications.

In order to treat non-isothermal transformations the differential form of the JMA equation

$$\frac{dp}{dt} = \bar{p}nKt^{n-1}e^{-Kt^n} \quad (8)$$

obtained from (5) taking time derivative is often used, or sometimes written in an autonomous form:

$$\frac{dp}{dt} = nK^{\frac{1}{n}} \left( -\ln \left( 1 - \frac{p}{\bar{p}} \right) \right)^{1-\frac{1}{n}} (\bar{p} - p), \quad (9)$$

where the factor  $(\bar{p} - p)$  may be regarded as a retardation factor due to impingements. Austin and Ricketts [1] have got a better agreement with experiment with retardation factor  $(\bar{p} - p)^2$ . Trying to get some higher accuracy, there are numerous generalizations of this equation, also combined with Scheil's rule, have been proposed. We refer to the papers [16], [3], [7] where different equations and iteration procedures of such type are discussed and compared on the base of experiments (in the last two papers) performed on the the 100Cr6 steel. It seems that one can always find an appropriate modification of (8) or (9) for a given steel which is in a good agreement with experiment for a certain class of temperature variations, but another equation should be taken if temperature

changes in a different way, say, if the temperature rate is essentially different. We believe that this imperfectness is caused by the fact that the coefficient  $K$  appearing in (5) can not reflect both temperature dependent processes of nucleation and growth, whereas variation of  $n$  brings not so much improvement of the model. Indeed, in (1) and (2) the corresponding parameters appear as a product in  $K$ , hence instead of these two (of nucleation and growth) we have only one parameter  $K$ .

The manufacturing processes in industry are often non-isothermal and the temperature rate may vary drastically. Some essentially new models for the phase evolution are needed which could embrace a wide range of temperature variations. This is the motivation of the investigations presented here. We believe that some parameters controlling the nucleation and growth should be used explicitly. It is also recognized that the history of temperature variation should be taken into account (see [13], [11], [7], e.g.), since the transformed fraction does not depend on time and temperature as their function. For example in [13], [14] a path dependent parameter  $\beta$  is introduced and the product fraction is assumed to be a function of  $\beta$ . In the following we introduce functionals of temperature path.

## 2. MODELING OF KINETIKS BASED ON THE NUCLATION AND GROWTH EFFECTS

In this paper for simplicity we consider only a stress free transformation with only one product phase. Basically we follow the ideas of A. Movchan and S. Kazarina [15] extending their approach to our situation. The stress effected transformation will be treated elsewhere.

Let the temperature  $\theta(t)$  be a given function of time. Let us consider  $V_{t_0}$  the (micro-)volume of the nucleus of the product phase that appeared just at the moment  $t_0$  in a macrovolume  $V$ . We introduce a microparameter  $\rho = \frac{V_{t_0}}{V}$ , which is nothing but the contribution to the volume fraction  $p$  of the new phase transformed. After the overcoming of the energetic barrier this volume  $V_{t_0}$  will grow depending on time  $t$  and current temperature  $\theta(t)$ . To take into account the history of this process we assume that the value of  $\rho$  is a functional of temperature:

$$\rho = \mathcal{F}_\theta(t_0, t). \quad (10)$$

The sum over all such microvolumes appeared up to the current moment  $t$  yields the volume fraction

$$p = \sum_{t_0} \rho(t_0, t) \quad (11)$$

of the product phase in the macrovolume  $V$ . By  $N$  we denote the number of nuclei in the volume  $V$ . We assume that the nucleation rate  $\dot{N}$  depends on time, temperature and current value of the fraction of the new phase

$$\dot{N} = v(t, \theta(t), p). \quad (12)$$

Writing the sum in (11) as an integral over the moments of birth of each nucleus we have the following expression for the volume fraction

$$p = \int_0^t \mathcal{F}_\theta(t_0, t) v(t_0, \theta(t_0), p) dt_0. \quad (13)$$

We assume further that the growth of the microparameter  $\rho$  can be described by the following differential equation

$$\frac{d\rho}{dt} = \mathcal{G}_\theta(t_0, t, \rho, p) \quad (14)$$

with the initial condition

$$\rho(t_0) = \rho^0, \quad (15)$$

where  $\mathcal{G}_\theta$  is some functional of  $\theta(t)$  and  $\rho^0$  is the critical value of microparameter  $\rho$  characterized by the critical radius of the appeared volume needed to overcome the energy barrier. Let us differentiate (13) by the time

$$\frac{dp}{dt} = \rho^0 v(t, \theta, p) + \int_0^t \mathcal{G}_\theta(t_0, t, \rho, p) v(t_0, \theta, p) dt_0, \quad (16)$$

where we have used (14) and (15). The first term of the right side is the contribution to the fraction rate of the new critical volumes appearing at the moment  $t$  with the rate  $v(t, \theta(t), p(t))$ , whereas the second corresponds to the growing process of already existing ones.

Assuming that  $\mathcal{G}_\theta$  is linear with respect to  $\rho$

$$\mathcal{G}_\theta(t_0, t, \rho, p) = \mathcal{A}_\theta(t, p)\rho(t_0, t) + \mathcal{B}_\theta(t, p) \quad (17)$$

and substituting it into equation (16) we obtain the following system of differential equations describing the phase evolution

$$\frac{dp}{dt} = \rho^0 v(t, \theta, p) + \mathcal{A}_\theta(t, p)p + \mathcal{B}_\theta(t, p)N, \quad (18)$$

$$\frac{dN}{dt} = v(t, \theta, p). \quad (19)$$

We emphasize that  $\rho^0, p, N$  and  $v$  have a clear physical meaning. Some concrete expressions for  $\rho_0$  and  $v$  can be deduced from some deeper physical considerations or experiments. For example for the austenitisation in [11] the nucleation rate was taken as Arrhenius term

$$v = N_0 e^{-\frac{Q_N}{R\theta}}, \quad (20)$$

with  $N_0$  as temperature independent rate,  $Q_N$  as the temperature independent activation energy for nucleation and  $R$  as the gas constant.

The system (18-19) can be simplified in some particular cases applying some further assumptions.

## 2. PARTICULAR CASES

### 2.1. Leblond's equation

If the current rate of growth of individual nucleus does not depend on the temperature history and  $\mathcal{B}_\theta$  can be taken as zero, then the system yields to the single equation

$$\frac{dp}{dt} = \rho^0 v(t, \theta, p) + A(t, \theta, p)p, \quad (21)$$

where  $A$  is no more a functional but a function of  $\theta$ .

In simplest case we can take the nucleation rate proportional to the undercooling  $\theta_s - \theta$ , where  $\theta_s$  is the start temperature of the transformation. The nucleation rate should decrease as the fraction of the product phase approaches unity, since there is less place where nucleation can appear. Hence we multiply this term by the retardation factor  $1 - p$  and set

$$v(t, \theta, p) = (\theta_s - \theta)(1 - p). \quad (22)$$

Further, for the rate of  $\rho$  we assume, that it is proportional to the temperature  $\theta$ , since the growth is due to diffusion and the rate of latter can be taken as linearly dependent on  $\theta$ . Then we assume that it decreases with  $p$  approaching unity due to impingements of nuclei and has a singular point at the start of transformation  $p = 0$ . Hence let

$$A(t, \theta, p) = a\theta \frac{1}{p}(1 - p), \quad (23)$$

where  $a$  is a coefficient of proportionality. Substituting the last two equations in (21) we have

$$\frac{dp}{dt} = (\rho^0(\theta_s - \theta) + a\theta)(1 - p), \quad (24)$$

where  $\rho^0$  and  $a$  should be regarded as material parameters reflecting the processes of nucleation and growth respectively. This coincides with the model of Leblond and Devaux (see [12]) with the following characteristic time of transformation

$$\tau(\theta) = \frac{1}{\rho^0(\theta_s - \theta) + a\theta}.$$

## 2.2. Isokinetic equation

Let us consider another heuristic approach. For the formation (or activation) of nuclei on the corner boundaries less energy is needed. So one can assume that the nucleation happens only on the boundaries. If we take into account that boundaries have the Lebesgue measure (3D volume) zero and assume that the value of critical radius is small in comparison with corn size (critical radius  $\ll$  average corn volume), i.e. the measure of all critical volumes is infinitely small in comparison with  $V$  even if they would appear simultaneously at all possible points on the corner boundaries, then we can neglect the first term in (18). Taking  $\mathcal{B}_\theta = 0$  and  $\mathcal{A}_\theta$  as a factorized function  $\mathcal{A}_\theta = f(\theta) \frac{g(p)}{p}$  we arrive to the additive equation for the transformation,

$$\frac{dp}{dt} = f(\theta)g(p), \quad (25)$$

for which the additivity rule (6) always holds.

## 2.3. JMA-equation

Under the above assumptions, taking  $\mathcal{A}_\theta$  in form of the following function

$$\mathcal{A}_\theta = \bar{p}K(\theta)n(\theta)t^{n(\theta)-1} \frac{1}{p}(\bar{p} - p), \quad (26)$$

then we arrive to the differential form of the generalized JMA equation.

We see that one has here a wide framework for application of different assumptions. In general  $\mathcal{B}_\theta(q, p)$  is nonzero and the evolution equation of nucleus is needed. For specification of  $\mathcal{A}_\theta$  and  $\mathcal{B}_\theta$  one should consider the rate functional  $\mathcal{G}_\theta$  closer. We suggest here the following.

## 3. TRANSFORMATION CONTROLLED BY JMA-EQUATION ACCOUNTING FOR THE NUMBER OF NUCLEI

Neglecting the first term in (18) let us consider  $\mathcal{B}_\theta(t, p)N$  as small correcting term and chose (26) for  $\mathcal{A}_\theta$ . It was observed in [7] that in case of JMA-equation the simulated transformation time was shorter as in experiment. Thus we multiply the right side of (26) with a weighting coefficient  $0 < \varepsilon < 1$ . Motivated by (20) we take

$$v = N_0 e^{-\frac{b}{\theta(t)}} \quad (27)$$

for the pearlite transformation. Then integrating we have

$$N = N_0 \int_0^t e^{-\frac{b}{\theta(s)}} ds. \quad (28)$$

For simplicity we consider  $\mathcal{B}_\theta$  as a constant operator  $\mathcal{B}_\theta = \frac{a}{N_0}$ . In experiments we will consider below the full transformation always takes place, thus we can set  $\bar{p} = 1$ . Now we have the following

$$\frac{dp}{dt} = \varepsilon K n t^{n-1} (1-p) + a \int_0^t e^{-\frac{b}{\theta(s)}} ds, \quad (29)$$

where  $\varepsilon$ ,  $a$  and  $b$  have to be fitted.

#### 4. DILATOMETER EXPERIMENTS

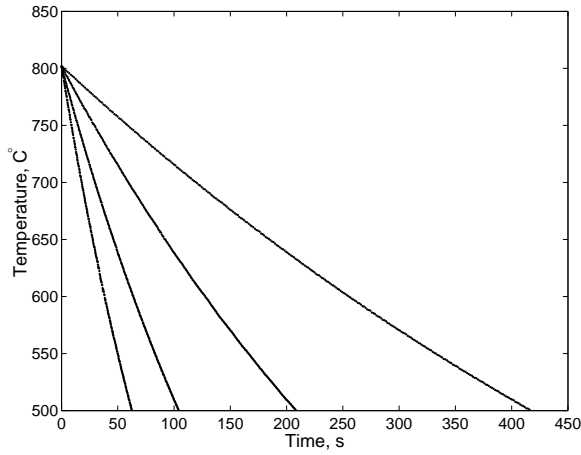


FIGURE 1: Temperature versus time

The cooling of 100Cr6 samples with different rates have been performed on the (Gleeble 3500 Thermal System) dilatometer thermal-mechanical testing machine. Exponential cooling from austenitized samples  $850^\circ\text{C}$  to  $100^\circ\text{C}$  in respectively  $2000\text{s}$ ,  $1000\text{s}$ ,  $500\text{s}$  and  $300\text{s}$ , see Fig. 1. The full transformation from austenite to pearlite was observed ( $\bar{p} = 1$ ). The pearlite fraction was calculated from the following relation (assuming the linear mixture rule for the thermal expansion for pure austenite and pearlite):

$$L(\theta) = pL_p(\theta) + (1-p)L_a(\theta), \quad (30)$$

where  $L(\theta)$  is the current sample length,  $L_a(\theta)$ ,  $L_p(\theta)$  are the corresponding lengths of pure austenite or pearlite sample at temperature  $\theta$ .

We use here the same set of experimental data as in [3] and [7] (papers are available on-line) where different kinetic equations were compared. The temperature dependent parameters  $n$  and  $K$  were obtained from isothermal experiments and approximated as follows

$$\frac{1}{K(\theta)} = \tau_0 e^{\frac{Q}{\theta}} e^{\frac{P}{\theta(\theta_P - \theta)^2}}, \quad n(\theta) = n_0 + n_1\theta.$$

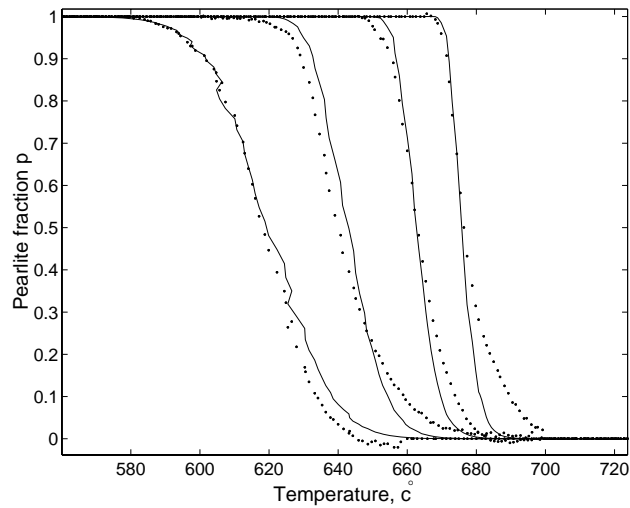


FIGURE 2: Pearlite fraction versus Temperature. Dotted line – calculated from experiment, solid line – Equation (29)

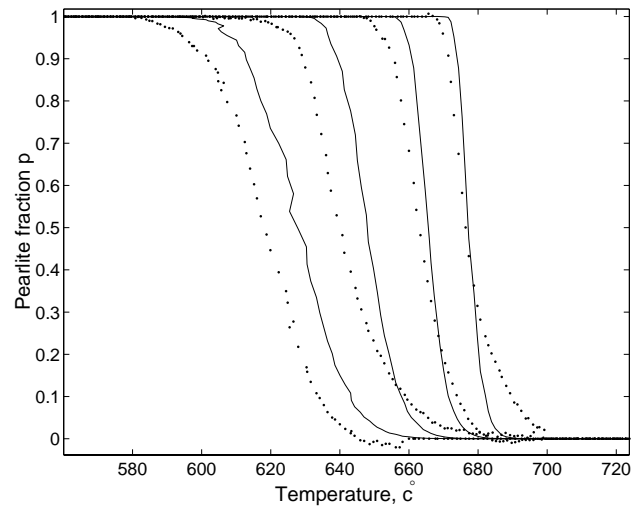


FIGURE 3: Pearlite fraction versus Temperature. Dotted line – calculated from experiment, solid line – JMA-equation

We refer to [3], [7] for further details. Here we took  $\varepsilon = \frac{5}{6}$  in (29) and only  $a$  and  $b$  were fitted to minimize the  $L_2$ -norm of the deviation  $\left(\frac{1}{k} \sum_{j=1}^k \delta_j^2\right)^{\frac{1}{2}}$  (averaged over  $k = 4$  experiments) of the simulation curves from experimental ones. With this criterion  $a = 0.005 \frac{1}{s}$  and  $b = 0.3^\circ C$  have been found.

Simulation results are presented on the Fig. 2. For comparison with JMA-equation we quote the simulation result from [3] and [7] as Fig. 3. On both pictures the left curve corresponds to the slowest cooling scenario, the right one to the fastest scenario.

## CONCLUSIONS

Our intention was to obtain an equation embracing possibly large scale of cooling rates, remaining accurate for different rates. We see that deviations of the JMA-curves from experiments become larger for slower cooling. The accuracy can be improved introducing more parameters (see [3]), but the deviation remains not uniform. From the simulation results performed by equation (29), see Fig. 2, we can conclude first, that deviations are smaller as for JMA-equation and second, that the deviations is rather uniform for different cooling rates. So our aim is achieved, however we have simplified the system (18-19) drastically. We believe that (18-19) can be used for a wider range of temperature variation, even non necessarily monotone scenarios.

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