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Extension of Isothermal Time-Temperature Parameters to Non-isothermal Conditions: Application to the Simulation of Rapid Tempering

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A phenomenological method for constructing non-isothermal, generalized time-temperature parameters (GTT parameters) is presented. An analysis of the relationship between the various traditional isothermal time-temperature parameters has verified that the generalized Dorn-parameter is regarded to be the sole non-isothermal complex parameter to which a rigorous, physically well-founded interpretation is attributed. Possible applications of GTT parameters are illustrated by examples concerning the prediction of hardness change in quenched steels during rapid tempering treatments.

Keywords: kinetic function, diffusion, steels, laser cladding, secondary hardening

0 INTRODUCTION

Generalized time-temperature parameters permitting a numerical characterization and prediction of transformation processes occurring at varying temperatures are the natural extensions of the well-known isothermal complex parameters [1] to [5].

In this paper, a general phenomenological model and method for constructing non-isothermal generalized time-temperature parameters (GTT parameters) are described. The main advantage of using GTT parameters is that non-isothermal processes of various types may be described and compared on the basis of numerical criteria. Moreover, it will be verified that the generalized Dorn-parameter is regarded to be the sole non-isothermal complex parameter to which a rigorous, physically well-founded interpretation is attributed. Application of GTT parameters will be demonstrated on examples concerning the prediction of the change of as-quenched hardness in steels during rapid tempering treatments. In practice, a non-isothermal tempering of such type can be performed by induction, electron beam or laser heating.

1 ISOTHERMAL TIME-TEMPERATURE PARAMETERS

Traditional isothermal time-temperature parameters (ITT-parameters) incorporate the combined effect of the time t and the temperature T on the kinetics of micro-structural transformation processes occurring in alloys.

A conventional ITT-parameter denoted by P can be formulated in the following general form:

$$P = P(t,T) = h_0(T)t^{h_1(T)} . \tag{1}$$

In Eq. (1) h_0 and h_1 are appropriately selected strictly monotone and continuous functions, and T is the so-called normalized temperature defined as

$$T = \frac{T_C + e_1}{e_2} . \tag{2}$$

In Eq. (2) T_C is the temperature [°C], e_1 and e_2 are the positive scale factors. (In the majority of cases e_1= 273 and e_2= 1. This implies that T will be identical to the absolute temperature in Kelvin.)

The well-known types of ITT-parameters are the Hollomon-Jaffe [1] and the Dorn parameter [2] and [3]. The Hollomon-Jaffe

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parameter P_H (defined for case of $t > 0$) is formulated as:

$$P_H = T\left(C + \ln t\right) = \ln(t^T e^{CT}) \tag{3}$$

where C is a positive constant, while the Dorn parameter, P_D is:

$$P_D = t \exp\left(-\frac{Q_D}{RT}\right) \tag{4}$$

where Q_D is stands for the apparent activation energy and R is the universal gas constant.

In order to characterize and compare various types of ITT-parameters an equivalence relation by which ITT parameters can unambiguously be classified into disjoint groups is defined. By definition, ITT parameters P_A and P_B are called equivalent, (denoted by $P_A \sim P_B$), if there exists a strictly monotone and continuous function $U = U(x)$ for which:

$$P_B = U\left(P_A\right) \tag{5}$$

is fulfilled. Since the inverse U^{in} of the function U exists, from this it follows that $P_A = U^{in}(P_B)$. This implies that the equation above defines an equivalence relation, which satisfies the following conditions:

$$P_A \sim P_A \quad \text{(identity)} \tag{6.1}$$

$$\text{if } P_A \sim P_B \text{ then } P_B \sim P_A \quad \text{(Symmetry)} \tag{6.2}$$

$$\text{if } P_A \sim P_B \text{ and } P_B \sim P_C \text{ then } P_A \sim P_C \quad \text{(Transitivity).} \tag{6.3}$$

The importance of this equivalence relation lies in the following fact: All ITT parameters belonging to the same equivalence classe are considered as "equivalent parameters" in the sense that they characterize the progress of the transformation process in an identical manner.

For example, ITT parameters denoted by P_R, P_S and P_V in Table 1 are equivalent, because in all three cases it is possible to construct a strictly monotonous function U=U(x) by which the mapping represented by Eq. (5) can be performed. It is worth noting that the Hollomon-Jaffe parameter P_H belongs to another class of equivalence. This means that P_H is not equivalent with parameters P_R, P_S or P_V.

2 THE GENERALIZED TIME-EMPERATURE PARAMETERS

There are several techniques for constructing GTT parameters of various forms [2] to [5]. In order to obtain "well-behaved" non-isothermal parameters, a GTT parameter P_g needs to have the following form:

$$P_g = Z\left\{\int_0^t H(t_u, T(t_u))dt_u\right\} \tag{7}$$

where Z and H are appropriately selected strictly monotone and continuous functions. From this definition it follows that P_g is considered as a functional of temperature function $T = T(t)$ characterizing the thermal history of the process.

As an example, in Table 1, the generalized versions of three equivalent ITT parameters (P_R, P_S and P_V) are also given. It is obvious that under isothermal conditions, GTT parameters denoted by $P_{R,g}$, $P_{S,g}$ and $P_{V,g}$ will be identical to P_R, P_S and P_V, respectively.

Table 1. *Equivalent isothermal time-temperature parameters P_R, P_S, P_V and their generalized non-isothermal versions (B_0, B_1, B_2 and B_3 are selected constants)*

Equivalent time-temperature parameter	Generalized time-temperature parameter
$P_R = t \exp\left[-\frac{B_0}{T}\right] \quad \left(B_0 > 0\right)$	$P_{R,g} = \int_0^t \exp\left[-\frac{B_0}{T}\right] dt_u$
$P_S = \frac{B_1}{T} + B_2 \lg\left(t\right) \quad \left(B_1 * B_2 < 0\right)$	$P_{S,g} = B_2 \lg\left[\int_0^t 10^{\frac{B_1}{B_2 T}} dt_u\right]$
$P_V = \left[\frac{B_3}{T} + \ln\left(t\right)\right]^{-1} \quad \left(B_3 < 0\right)$	$P_{V,g} = \left[\ln \int_0^t \exp\left[\frac{B_3}{T}\right] dt_u\right]^{-1}$

Table 2. *Three different generalizations of the isothermal time-temperature parameter P_L.*

Isothermal time-temperature parameter	Generalized time-temperature parameter
$P_L = 10^{C_1 T} t^{C_2 T}$ where $T = \dfrac{T_C\left[°\mathrm{C}\right] + 273}{1000}$	$P^{(1)}{}_{L,g} = C_2 \int\limits_0^t T 10^{C_1 T} t^{C_2 T - 1} dt$
	$P^{(2)}{}_{L,g} = \left[\dfrac{C_2}{C_1} \int\limits_0^t T 10^T t^{\frac{C_2}{C_1} T - 1} dt \right]^{C_1}$
	$P^{(3)}{}_{L,g} = \left[\int\limits_0^t T 10^{\frac{C_2}{C_1} T} t^{T-1} dt \right]^{C_2}$

3 A SIMPLE METHOD FOR CONSTRUCTING GTT PARAMETERS

As it has been previously mentioned, there are several possibilities for generating GTT parameters from the same ITT parameter. In Table 2, three GTT parameters of different types are included. All of them are constructed from the same ITT parameter denoted by P_L. This implies that at constant temperatures the three GTT parameters in Table 2 will be identical to the isothermal parameter P_L.

Below a simple and general method for generating GTT parameters will be outlined. This technique is based on following concept: Let us assume that the kinetic function describing the isothermal transformation process is known, and given in the form:

$$G(y) - E(T)t^{F(T)} = 0 \tag{8}$$

where $y = y(t)$ is the kinetic variable of the transformation (i.e. the extent of completion of process after laps of time t), G, E and F are properly selected functions, and $y(0) = y_0$ represents the initial value for $t = 0$.

As a first step, from Eq. (8) the isothermal kinetic differential equation of the process is constructed:

$$\frac{dy}{dt} = \frac{E(T)F(T)}{\dfrac{\partial G}{\partial y}} t^{F(T)-1}. \tag{9}$$

As a second step, by solving the differential Eq. (9), the isothermal kinetic function is rewritten in the form:

$$y(t) = G^{in}\left\{ \int\limits_0^t E(T)F(T)t_u^{F(T)-1} dt_u + G(y_0) \right\}. \tag{10}$$

Finally, starting with Eq. (10), the required GTT parameter P_g is defined as follows:

$$P_g = Z\left\{ \int\limits_0^t E(T)F(T)t_u^{F(T)-1}\Big|_{T=T(t_u)} dt_u \right\}. \tag{11}$$

Since in Eqs. (8) to (11), G and Z are strictly monotone continuous functions, this implies that their inverse functions G^{in} and Z^{in} exist.

By introducing GTT parameters, the description of the transformation processes occurring under non-isothermal conditions becomes simpler. This is due to the fact that by means of GTT parameter (11), the corresponding non-isothermal kinetic function can be written in the following general form:

$$y(t) = G^{in}\left\{ Z^{in}(P_g) + G(y_0) \right\}. \tag{12}$$

It is easy to see that if the temperature is constant, Eqs. (12) and (10) will be identical.

4 THE GENERALIZED DORN PARAMETER

Below it is demonstrated that the application of the generalized Dorn parameter has some special advantages. Additionally it will be shown that the generalized Dorn parameter is in fact considered as the sole theoretically well founded GTT parameter.

Let us assume that identity $F(\mathrm{T}) \equiv 1$ is fulfilled for function F in Eq. (8). Hence, the corresponding isothermal kinetic function given by Eq. (8) can be reduced to:

$$G(y) - E(T)t = 0\,. \tag{13}$$

In this case the GTT parameter represented by Eq. (11) is simplified to:

$$P_g = Z\left\{\int_0^t E(T(t_u))dt_u\right\}. \tag{14}$$

In many reactions it is supposed that the Arrhenius-law controls the temperature-dependent rate of the isothermal transformation processes. This implies that $E(T)$ can be written as:

$$E(T) = k_0 \exp\left(-\frac{Q_A}{RT}\right) \tag{15}$$

where k_0 is the pre-exponential factor, and Q_A is the activation energy of the process. Now, by choosing function Z in the form of $Z(x) = x/k_0$, and by substituting formula (15) into Eq. (14), we obtain the generalized Dorn parameter $P_{D,g}$:

$$P_{D,g} = \int_0^t \exp\left(-\frac{Q_A}{RT}\right)dt_u. \tag{16}$$

It can be concluded that there is a strong relationship between the Dorn parameter and the Arrhenius-formula.

One of the most important properties of the Dorn parameter is that its value is completely determined by the temperature spectrum. If temperature is a continuous function of time, the temperature spectrum is characterized by the so-called temperature amplitude density function $g(T)$ [3]. This is defined in a given temperature interval $[T_{\min}, T_{\max}]$ where $T_{\min}$ and $T_{\max}$ stand for the minimum and maximum temperature values, respectively.

From the previous considerations it follows that if the temperature amplitude density function $g(T)$ is known, the generalized Dorn parameter can be transformed into the form

$$P_{D,g} = t\int_{T_{\min}}^{T_{\max}} \exp\left(-\frac{Q_A}{RT}\right)g(T)dT. \tag{17}$$

As an example, in Fig. 1 three different temperature functions and their corresponding temperature amplitude density functions denoted by $g_a(T)$, $g_b(T)$ and $g_c(T)$ are illustrated.

Considering the sinusoidal temperature amplitude density function $g_c(T)$, it can be verified that the generalized Dorn parameter (consequently the predicted progress of non-isothermal transformations) does not depend on the frequency of temperature oscillations. It should be noted that the Dorn parameter represented by Eq. (17) can be simply computed by using numerical integration.

5 CORRESPONDENCE BETWEEN THE GENERALIZED DORN PARAMETER AND THE DIFFUSION BASED TRANSFORMATIONS

It is important to emphasize that there is a strict relationship between the generalized Dorn parameter and the kinetics of non-isothermal diffusion processes (diffusion based transformations). To verify this, let us consider the Fick's second law:

$$\frac{\partial\eta}{\partial t} = \nabla[D\nabla\eta] \tag{18}$$

describing the change of concentration $\eta = \varphi(\mathbf{r}, t)$ of a given alloying element as a function of the coordinates t (time) and $\mathbf{r}$ (location). In Eq. (18) $D = D(T)$ stands for the temperature-dependent diffusion coefficient given as:

$$D(T) = D_0 \exp\left(-\frac{Q_F}{RT}\right) \tag{19}$$

where D_0 is a positive constant and Q_F is the activation energy of the diffusion process.

In certain cases, depending on the choice of the boundary conditions, it can be verified that by using the so-called Kirchoff-transformation, the determination of the non-isothermal solution $\eta = \varphi_2(\mathbf{r}, t)$ of differential Eq. (18) can be reduced to the computation of the isothermal solution $\eta = \varphi_1(\mathbf{r}, t)$ [6]. This is explaned by the fact that, for isothermal case, the solution of Eq. (18) can be written as:

$$\eta = \varphi_1(\mathbf{r}, t) = \Phi(\mathbf{r}, P_F) \tag{20}$$

where Φ is a real function and P_F is identical to:

$$P_F = t\exp\left(\frac{Q_F}{RT}\right). \tag{21}$$

For the non-isothermal case, the corresponding concentration distribution can be calculated as:

$$\eta = \varphi_2(\mathbf{r}, t) = \Phi(\mathbf{r}, P_{F,g}) \tag{22}$$

where:

$$P_{F,g} = \int_0^t \exp\left(\frac{Q_F}{RT(t_u)}\right)dt_u \tag{23}$$

by definition. Hence, provided that the isothermal solution $\eta = \Phi(\mathbf{r}, P_F)$ of Eq. (18) is known in the form of $\eta = \Phi(\mathbf{r}, P_F)$, from this, the solution $\eta = \varphi_2(\mathbf{r}, t)$ (which is valid even for non-isothermal conditions) can be simply obtained by substituting P_F with $P_{F,g}$ in the function $\Phi(\mathbf{r},P_F)$.

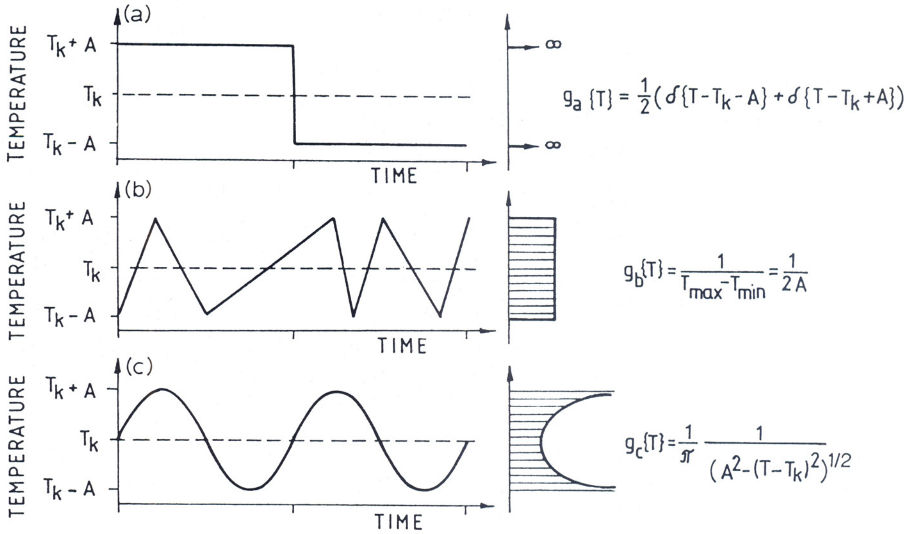


Fig. 1. *Three different time-temperature functions and their temperature amplitude density functions (A is the temperature amplitude, T_k is the mean temperature, δ(x) is the Dirac function)*

In fact, $P_{F,g}$ is a new variable which is generated by the Kirchoff-transformation in order to simplify the solution of the Fick's second law [6] and [7]. It is obvious that variable $P_{F,g}$, (in spite of its unusual dimension of length squared), may be regarded as a GTT parameter which is identical in form to the generalized Dorn parameter (16). From these considerations it follows that the majority of diffusion-based transformation processes can be efficiently predicted by kinetic functions including the generalized Dorn parameter.

6 APPLICATIONS

A practical application of the generalized Dorn parameter is demonstrated by two examples. Both of them concern the prediction of the change of as-quenched hardness as a result of tempering with rapid heating.

6.1 Non-Isothermal Tempering of a Low-Alloy Quenched Steel

For our investigations the low alloy structural steel CMo4 was used. The chemical composition of this steel grade was found to be: 0.41% C, 0.24% Si, 0.68% Mn, 1.00% Cr, and 0.12% Mo.

In order to predict the hardness decrease during tempering with varying temperature we selected a kinetic function defined as

$$\begin{aligned} HV &= HV_{\min} + \\ &(HV_q - HV_{\min})\exp\left\{-\gamma P_{D,g}^{\beta}\right\} = \\ &HV_{\min} + (HV_q - HV_{\min}) \\ &\exp\left\{-\gamma\left(\int_0^t \exp\left(-\frac{Q_M}{R(T_C+273)}\right)dt\right)^{\beta}\right\} \end{aligned} \qquad (24)$$

where $HV_{\min}$ is the minimum Vickers hardness, HV_q is the as-quenched Vickers hardness, Q_M is the apparent activation energy, β and γ are fitting constants. Parameters Q_M, β and γ were estimated using experimental data obtained from isothermal tempering tests (austenitizing followed by quenching, and isothermal tempering at temperatures 350, 450, 550 and 650°C.)

In Eq. (24) the model parameters are: $HV_{\min}$ = 100, HV_q = 718, Q_M = 324173 J/mol, R = 8.314 J/(mol·K), β = 0.04967 and γ = 5.7079. The initial microstructure was fully martensitic, HV_q represents the hardness of martensite after quenching.

In Figs. 2 to 5 some results concerning different tempering processes of steel CMo4 are illustrated. In all cases the total tempering time was t_T = 180 *s*.

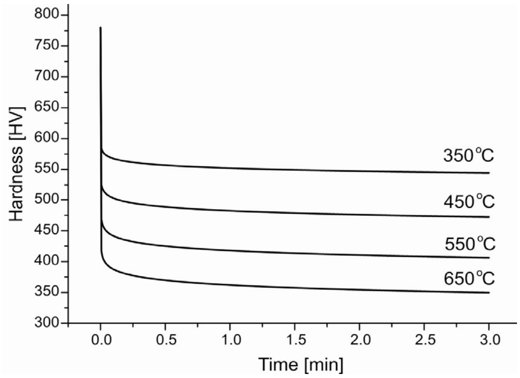
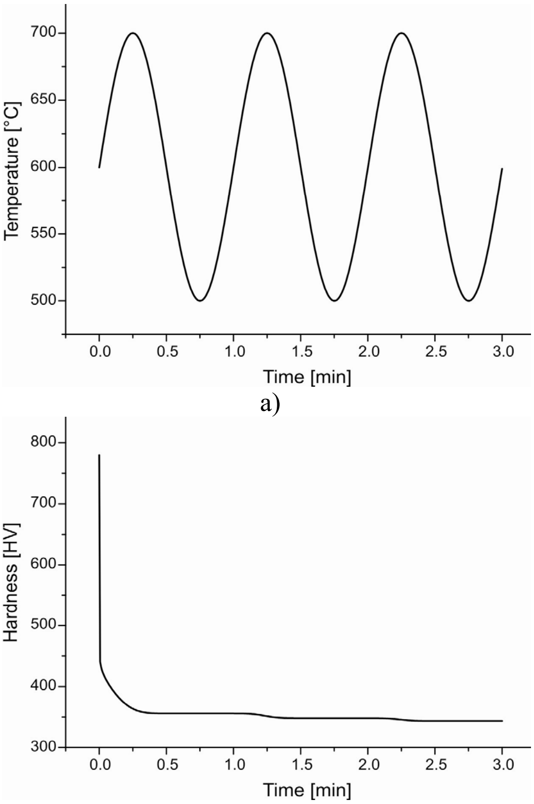


Fig. 2. *Calculated hardness obtained by simulated isothermal tempering*



a)

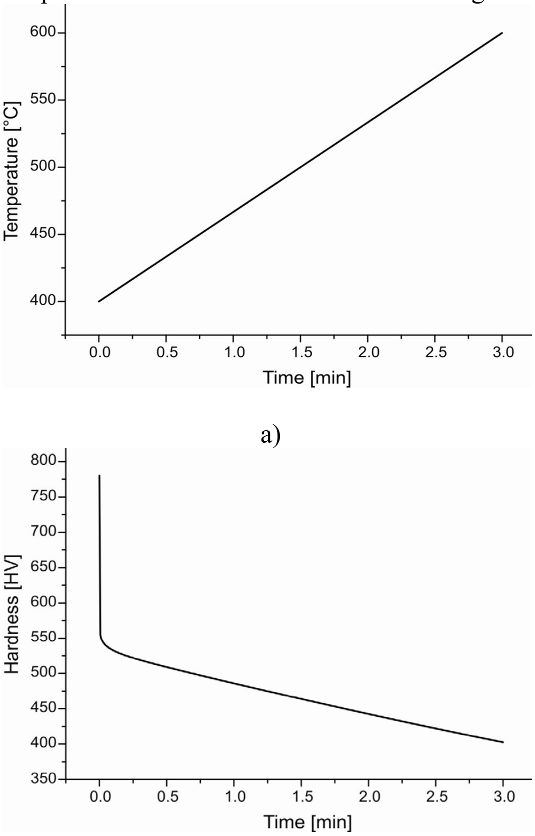
b)

Fig. 3. *Non-isothermal tempering. (a) the sinusoidal temperature function $T_S(t)$ used for computer simulation (b) the predicted hardness decrease as a function of time*

Fig. 2 shows a traditional isothermal tempering diagram. As can be observed, the decrease of initial hardness is rapid as it practically occurs at the beginning within some seconds. Fig. 3 illustrates a simulated tempering process characterized by a sinusoidal temperature function T_S(t):

$$T_S(t) = 600 + 100 * \sin\left(\frac{2\pi}{60}t\right) \quad (25)$$

where *t* is the tempering time in seconds, the time period is 60 seconds, the temperature amplitude is 100°C. As it can be seen the intensive decrease of as-quenched hardness is similar to that in Fig. 2.



a)

b)

Fig. 4. *Non-isothermal tempering. (a) the linearly increasing temperature function T_{LI} (t) used for computer simulation (b) the predicted hardness decrease as a function of time*

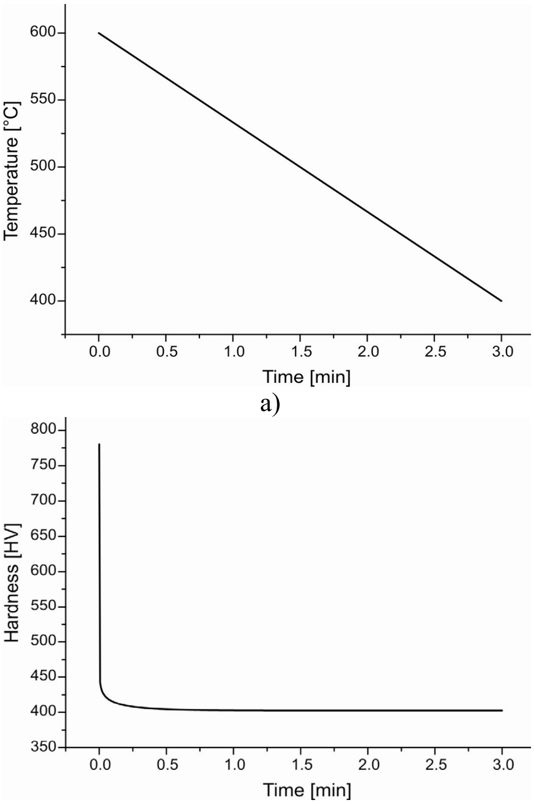
In Figs. 4 and 5, the results for tempering with linearly increasing and decreasing temperature functions T_{LI}(*t*) and T_{LD}(*t*) are depicted. These temperature cycles are defined as:

$$T_{LI}(t) = 400 + \left(\frac{200}{180}\right)t \quad (26)$$

and

$$T_{LD}(t) = 600 - \left(\frac{200}{180}\right)t\,. \quad (27)$$

Comparing the predicted hardness values obtained with time-temperature functions $T_{\mathrm{LI}}(t)$ and $T_{\mathrm{LD}}(t)$ it can be observed that at the end of the tempering process (i.e. at time $t_{\mathrm{T}} = 180$ s) the same hardness of 402 HV is obtained. This can be explained by the fact that in the time interval $[0, t_{\mathrm{T}}]$ temperature functions $T_{\mathrm{LI}}(t)$ and $T_{\mathrm{LD}}(t)$ are characterized by identical temperature amplitude density functions. (See Eq.17)



a)

b)

Fig. 5. *Non-isothermal tempering. (a) The linearly decreasing temperature function T_{LD} (t) used for computer simulation (b) The predicted hardness decrease as a function of time*

6.2 Non-isothermal Tempering of Alloy Steel with Secondary Hardening

The concept of generalized time-temperature parameters can be extended to describe the hardness change in alloy steels exhibiting a secondary hardening. Basically, secondary hardening is a result of precipitation of ultrafine dispersion alloy carbides during tempering. As it is known, tungsten, chromium, molybdenum and vanadium that are strong carbide forming elements are most commonly used to achieve secondary hardening.

The applicability of the generalized Dorn parameter to the prediction of hardness change is demonstrated by the simulation of tempering process in a steel containing 0.5% carbon and 2.1% vanadium.

Data pairs (selected temperatures and corresponding hardness values for 1 hour tempering) obtained from isothermal tempering experiments were used to construct a simple phenomenological kinetic model describing the hardness change during isothermal tempering [8]. The model suggested is represented by the following kinetic function:

$$HV = HV_{\max} - \left\{ A_0 + A_1 P_a^{1/12} + A_2 P_a^{2/12} + A_3 P_a^{3/12} \right\}^2 \qquad (28)$$

where $A_0 = 3.4521$, $A_1 = 537.805$, $A_2 = -7587.326$ and $A_3 = 29418.63$ are fitting constants obtained by regression analysis and $HV_{\max} = 715$ stands for the maximum value of Vickers hardness. In this phenomenological kinetic model it was assumed that $HV_{\max}$ is identical to the as-quenched hardness.

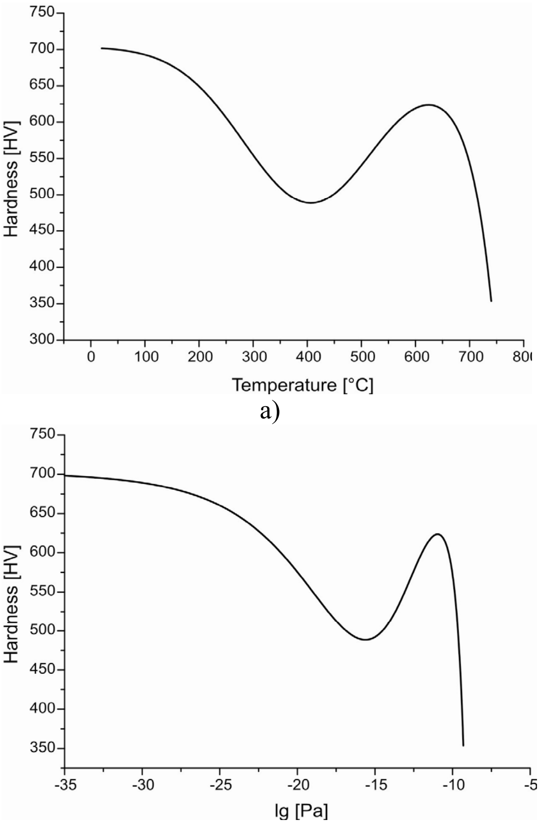
The isothermal Dorn parameter P_{a} in Eq. (28) is given by:

$$P_a = t \exp\left(-\frac{Q_{av}}{R(T_C + 273)} \right) \qquad (29)$$

where t is the time in seconds, and $Q_{\mathrm{av}} = 249420$ J/mol. It should be emphasized that for alloys exhibiting secondary hardening phenomenon the apparent activation energy Q_{av} is considered only as an average (weighted) value. This means that Q_{av} is defined as the weighted linear combination of the activation energies of the individual and overlapping precipitation reactions that occur simultaneously during tempering [9].

Fig. 6a represents a traditional isothermal tempering diagram, that is, hardness versus temperature illustrated for 1 hour tempering time. In Fig. 6b the hardness is given as a function of the logarithmic Dorn parameter.

Prediction results for the non-isothermal tempering of the selected vanadium alloy steel are depicted in Fig. 7. For simulation purposes, a linearly increasing temperature function T_{VA}(t) has been chosen (see Fig. 7a):



a)

b)

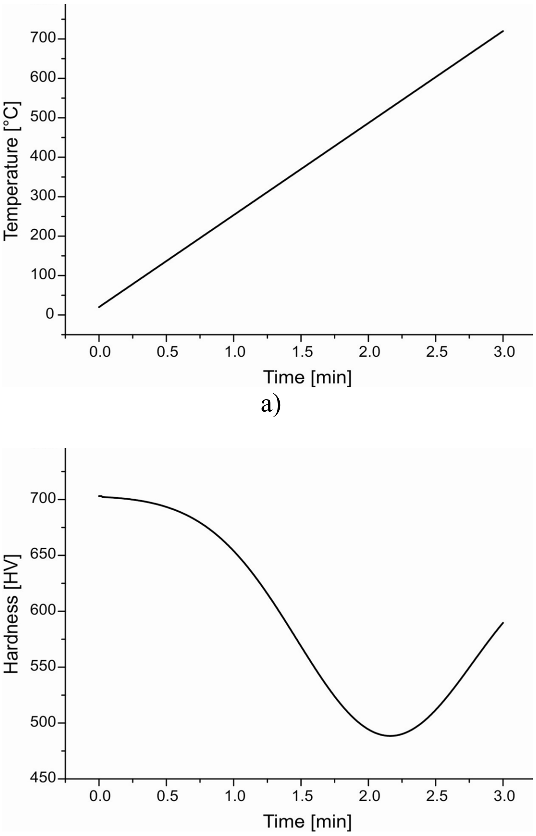
Fig. 6. *Tempering curves obtained for a vanadium alloy steel with secondary hardening (a) Hardness after isothermal tempering for one hour (b) Predicted hardness as a function of the isothermal logarithmic Dorn parameter*

$$T_{VA}(t) = 20 + \left(\frac{700}{180}\right)t \tag{30}$$

where t is the tempering time (seconds). The computed hardness as a function of time during heating up is shown in Fig. 7b. This concept of prediction has been successfully applied to estimate the hardness change as a result of non-isothermal tempering processes taking place during laser cladding [9].

7 SUMMARY

A phenomenological method for constructing generalized time-temperature parameters has been described. It has been verified that the generalized Dorn parameter is regarded to be the sole non-isothermal complex parameter to which a rigorous, physically well-founded interpretation is attributed. Applications of the generalized Dorn parameter are illustrated in the examples concerning the hardness prediction during rapid tempering when the temperature is continually changing.



a)

b)

Fig. 7. *Simulation of non-isothermal tempering of a vanadium alloy steel with secondary hardening (a) The linearly increasing temperature function T_{VA} (t) used for computer simulation (b) The predicted hardness change as a function of tempering time*

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