

Modelling of changes in properties of alloys at elevated temperatures

Jan Kohout*

Department of Mathematics and Physics, Military Technology Faculty, University of Defence, Kounicova St 65, CZ 612 00 Brno, Czech Republic

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Abstract

Long-term exposures of heat-treated metals at sufficiently elevated temperatures (e.g. tempering of quenched steels or age-hardening of supersaturated solid solutions) cause substantial changes in their structures and, consequently, substantial changes in their physical and materials properties. These processes are different in principle but their temporal development as well as their temperature dependence can be modelled by similar types of equations. Their kinetics is generally described by the Johnson–Mehl–Avrami–Kolmogorov equation, the Arrhenius equation expresses their temperature dependence. The paper presents another way more deeply respecting the scheme of processes proceeding in studied materials, which leads to more precise description. The modelling is presented for two cases: for the tempering of quenched bearing steels and for the age-hardening of beryllium bronze.

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1. Introduction

The Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [1–3] describing the temporal dependence of a conversion variable (e.g. the relative amount of newly formed structure) during a transformation

$$x(t) = 1 - \exp[-(kt)^n] \quad (1)$$

has been used as a most general tool for the description of transformations of all kinds. The dependence on temperature is described by the Arrhenius equation for the rate constant

$$k(T) = k_\infty \exp\left(-\frac{\varepsilon}{\kappa T}\right) = k(T_0) \exp\left[-\frac{\varepsilon}{\kappa} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (2)$$

where ε is activation enthalpy, κ the Boltzmann constant and T_0 is a suitably chosen reference temperature (usually from the region of test temperatures). The Avrami exponent n is often considered to be a constant (integer or fraction) not greater than 4 corresponding to the mechanism of the described transformation.

Deeper studies with highly accurate measurements and advanced regression calculations have shown, mainly in last 10 years (e.g. [4,5]), that using the JMAK equation quite inaccurate or even invalid results can be obtained. Therefore this equation

is combined, compared or substituted with other methods, e.g. the Monte Carlo simulations [4,6] or the first-principles studies [7,8]. Also different extensions and modifications of the JMAK model have been made [9–11]. Unfortunately, very gadget and promising equation of Starink [10]

$$x(t) = 1 - \left[\frac{(kt)^n}{\eta} + 1\right]^{-\eta} \quad (3)$$

introducing the impingement parameter η brings substantial problems with the accuracy in determination of just this parameter.

Materials studies using high-resolution electron microscopy (e.g. [12]) prove very convincingly the previously known fact that most microstructural changes can be divided in several simpler processes. In many cases, the failure of the JMAK approach can consist in the attempt to describe a few single processes by a single relation. The presented approach is based on the differentiation of single processes and on the strict determination of their sequence. Then an excellent description of the whole transformation can be obtained even if the equations for temporal development of single processes are quite simple. The approach is presented for two cases, whose complexity is very well known: in detail for the dimensional changes during the tempering of rolling-bearing steels and very briefly for the changes of hardness and resistivity during the age-hardening of beryllium bronze.

* Tel.: +420 973443283; fax: +420 973442888.
E-mail address: jan.kohout@unob.cz.

2. General

Tempering of quenched steels and age-hardening of supersaturated solutions are in principle different processes. In spite of that their temporal development can be modelled by similar types of equations because their driving force is the same: the decrease of total energy of material structure towards its minimum, which characterizes the equilibrium state. The modelling is based on the following presumptions:

- (1) All the processes in the whole studied temperature range are qualitatively the same and they differ only quantitatively in their rates.
- (2) Rate constants depend on temperature according to the Arrhenius equation (2).
- (3) Considering the principle of main link (i.e. only the crucial process in studied stage is considered), complicated temporal dependence of microstructural composition changes can be modelled by the kinetic equations of relatively simple chemical reactions even when physical changes are studied.
- (4) The changes in materials properties can be described by simple functions (often the direct proportionality is sufficient) of the changes in microstructural composition.

3. Processes proceeding during tempering of steels

After quenching of steels tetragonal martensite (TM) with retained austenite (RA) is obtained. During tempering martensite loses supersaturated carbon when ε -carbide (ε) is formed and then martensite is called cubic martensite (CM) because its tetragonality substantially decreased. Continuing treatment leads to the decomposition of retained austenite accompanied by decreasing internal stress. Final equilibrium state of quenched steels can be reached only at higher temperatures or after extremely long periods. It is sometime called sorbite and consists of ferrite (F) and cementite (Cem). As this final stage was not fully finished for the studied steels, its result is written in brackets. In all the stages, the specific volume decreases, only during retained austenite decomposition there is increase of volume. The tempering can be represented by the scheme of consecutive changes

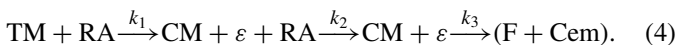


Table 1
Chemical composition of studied bearing steels in wt.%

Steel	C	Mn	Si	Cr	Ni	Cu	P	S
14 109	1.08	0.31	0.30	1.50	0.12	0.14	0.009	0.012
BPS	0.67	0.76	0.23	1.44	0.10	0.16	0.012	0.012

Table 2
Sample dimensions, heat treatment and exposure conditions

Steel	Samples [mm]	Quenching	(Pre)tempering	Exposure conditions
14 109	Dia. 14 × 100	840 °C, 35 min → oil	100 °C, 1–10 h	150 and 180 °C, 2–4000 h
BPS	Dia. 15 × 100	830 °C, 30 min → oil	210 °C, 4 h	120 and 200 °C, 1–2000 h

This scheme of consecutive *reactions* leads to a kinetic equation for the change $\Delta p(t, T)$ of a chosen property $p(t, T)$

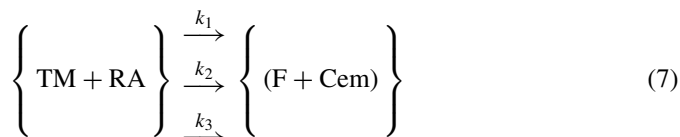
$$\Delta p(t, T) = b[1 - \exp(-k_1 t)] + c \left[1 - \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_1 - k_2} \right] + d[1 - g(t, T)] \quad (5)$$

where

$$g(t, T) = \frac{k_2 k_3 \exp(-k_1 t)}{(k_1 - k_2)(k_1 - k_3)} + \frac{k_1 k_3 \exp(-k_2 t)}{(k_2 - k_1)(k_2 - k_3)} + \frac{k_1 k_2 \exp(-k_3 t)}{(k_3 - k_1)(k_3 - k_2)}. \quad (6)$$

The constants b , c and d multiplying the conversion variables of newly formed components (see the terms in square brackets) express the influences of these components on the change of studied property. If the changes in more properties are studied simultaneously, then these factors are connected with each individual property while the constants ε_i and $k_i(T_0)$ are common for all studied properties.

If inequality $k_1 \gg k_2 \gg k_3$ is strictly fulfilled (difference of two orders is necessary) the rather complicated scheme of consecutive changes can be replaced by simpler scheme of parallel (i.e. independent) changes



with very simple kinetic equation

$$\Delta p(t, T) = b[1 - \exp(-k_1 t)] + c[1 - \exp(-k_2 t)] + d[1 - \exp(-k_3 t)]. \quad (8)$$

Temperature dependence in Eqs. (5), (6) and (8) consists in temperature dependence of rate constants k_i according to the Arrhenius Eq. (2).

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