



KINETICS OF THE CHANGES IN PHYSICAL AND MECHANICAL PROPERTIES OF STRUCTURAL MATERIALS AS A RESULT OF THE CHANGES IN THEIR STRUCTURE

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ABSTRACT

Long-term exposures of various structural materials at sufficiently elevated temperatures cause substantial changes in materials structures and, consequently, substantial changes in materials properties, regardless metals or polymers are considered. Even when very different processes take place in those materials (tempering of steels, age-hardening of alloys, degradation of polymers), their temporal and temperature dependence is very similar and, therefore, their kinetics can be described using similar equations. The temporal dependence can be approximately described using kinetic equations of simple chemical reactions even when purely physical processes are studied. The temperature dependence of the processes is described as a rule with temperature dependence of rate constants of the kinetic equations according to the Arrhenius equation. Due to a close relationship between the changes in materials properties and the changes in resulting structure, both these changes can be described with the equations of the same type. Then the study of the changes in materials properties allows to determine the parameters of the processes taking place in studied materials and the determined parameters enable to construct predictive curves describing the changes in materials properties in the conditions in which the materials have not been tested.

KEYWORDS

Tempering of steels, age-hardening of alloys, degradation of polymers.

INTRODUCTION

Substantial changes in most of properties of structural materials (metals as well as polymers) due to substantial microstructural or chemical changes during long-term exposures at elevated temperatures are a consequence of decreasing total energy of considered materials (or the materials together with surrounding medium) which tends nearer towards its equilibrium state. The groups of processes taking place in the materials are called according to the main of the processes or according to the most important changing property. Consequently tempering of steels, age-hardening of solid solutions or degradation of polymers are spoken about.

The substance of the processes is different: physical (phase transformations based on diffusion) or chemical (oxidation or thermodegradation). In spite of this, their temporal

dependence can be described by similar types of equations: kinetic equations of relatively simple chemical reactions and/or the Avrami equation. This equation describes both purely chemical reactions in solid phase and structural changes of physical nature, above all in metals. The kinetic equation of diffusion is not very suitable for this reason because neither its solution can be expressed by simple function nor diffusion coefficient is independent on concentration as assumed in its simple form. No other than the Arrhenius equation is usually used for the expression of temperature dependence of studied processes: it describes temperature dependence of rate constants in kinetic equations.

A close dependence of the changes in materials properties on the changes in resulting (micro)structure (very often the direct proportion or another simple rule is sufficient to consider) enables the description of the properties using equations analogous with the equations describing the processes which take place in studied materials. In this way the study of the changes in materials properties allows to distinguish successive stages of the processes and to determine their parameters. On the other hand, on the basis of determined parameters predictive curves (mean values as well as tolerance limits) can be constructed describing the changes in materials properties in the conditions in which the materials were not tested. Various examples of mechanical and physical properties of metals and polymers varying during the exposures at elevated temperatures are presented below.

BASIC PRESUMPTIONS

Studies of the changes in materials properties at elevated temperatures are usually based on following presumptions concerning the processes taking place in the materials:

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

$$k_i(T) = k_{i\infty} \exp\left(-\frac{\varepsilon_i}{\kappa T}\right) \quad \text{or better} \quad k_i(T) = k_i(T_0) \exp\left[-\frac{\varepsilon_i}{\kappa} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (1)$$

where k_i is rate constant of i -th process, ε_i is its activation enthalpy, κ is the Boltzmann constant, and T_0 is a suitably chosen reference temperature.

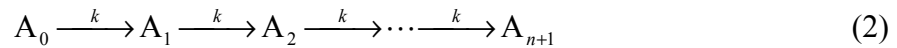
Besides presumptions concerning the relation between the changes in materials composition and materials properties are needed:

1. Considering principle of main link, complicated temporal dependence of microstructural and chemical composition changes can be approximately described by kinetic equations of relatively simple chemical reactions.
2. The changes in materials properties can be described by simple functions (mostly the direct proportionality is sufficient) of the changes in microstructural and chemical composition.

DEGRADATION OF POLYMERS

Degradation of polymers consists in a decomposition of their macromolecular chains. Simple kinetic equation of this process can be based on following considerations [1]: The original

chain A_0 dissociates into two chains A_1 with the same chemical properties, then chains A_1 dissociate into chains A_2 etc. The process can be described by scheme



and by kinetic equation for conversion variable x depending on time t

$$x(t) = 1 - e^{-kt} \left[1 + \sum_{i=1}^n \frac{(kt)^i}{i!} \right]. \quad (3)$$

Besides degradation which decreases the strength of polymer, some other processes appear which increase the polymer strength (above all cross-linking and crystallinity fraction increase – but not drying which was made before the exposures started). Usually they cannot be distinguished and, therefore, they are described commonly as one process. As a rule, the simplest kinetic equation (equation of first order chemical reaction) is sufficient for this reason. It can be expressed by simple exponential function.

The results of tensile tests of bearing cages made from polyamide composite and exposed in dry air (for more details see [2]) are presented in Fig. 1.

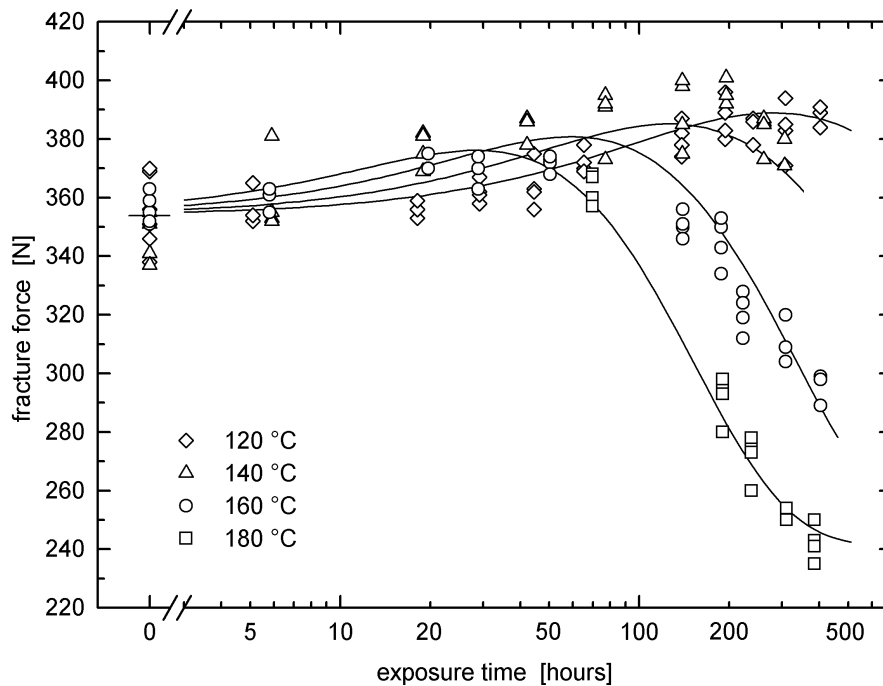


Fig. 1: Temporal dependence of fracture force of bearing cages made from polyamide composite and exposed in dry air at presented temperatures.

Regression calculations showed that the optimum value of n (number of dissociations) is 1 (i.e. polyamide was really very well stabilized against thermooxidation). Then the equation describing temporal dependence of fracture force is

$$F_{fr}(t, T) = a - b \exp(-k_1 t) + c \exp(-k_2 t)(1 + k_2 t) \quad (4)$$

where a is parameter describing the final value of fracture force (for $t \rightarrow \infty$), b is parameter describing the maximum influence of cross-linking (and/or crystallinity change), and c is parameter describing the maximum influence of degradation. Temperature dependence of fracture force consists in temperature dependence of rate constants, see Eq. (1).

Regression calculations give the values of all regression parameters (mean values as well as standard deviations). Using them, predictive curves can be constructed describing the changes in fracture force in the conditions in which the materials have not been tested. An example of predictive curves is presented in Fig. 2 for possible service conditions (lower temperatures and longer times than at test exposures). Besides mean values also lower tolerance limits 0.9/0.9 are drawn (i.e. with probability of 90 % can be said that the part of 90 % of future test results will not lie below the tolerance limit curve).

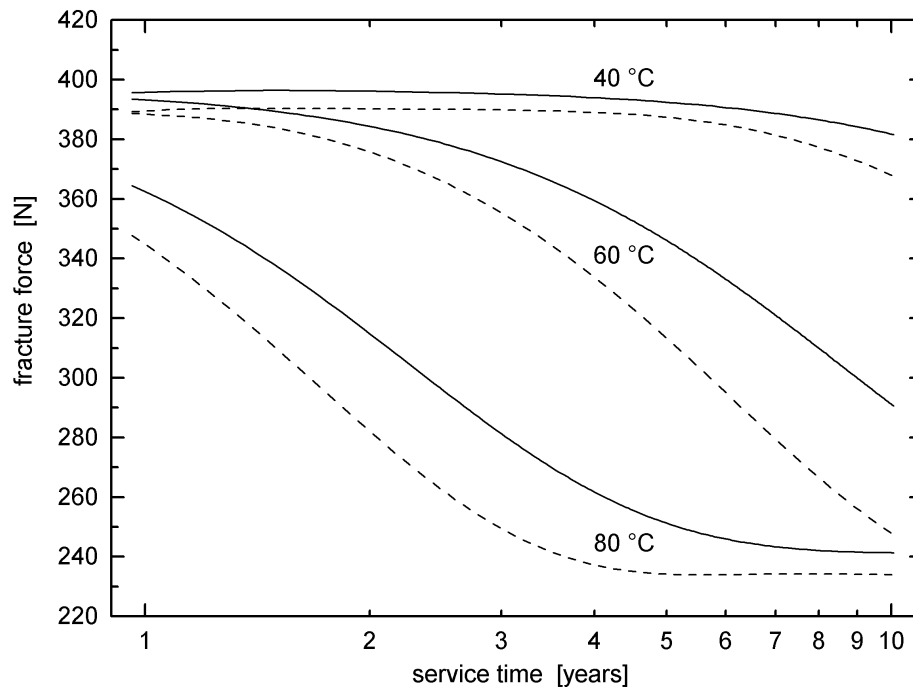


Fig. 2: Predictive curves of fracture force of bearing cages at untested temperatures for long service times (full lines: mean values, dashed lines: lower tolerance limits 0.9/0.9).

During a study of degradation of the same polyamide cages exposed in a gear oil, not only fracture force but also fracture deformation were measured [2, 3], see Fig. 3. In this case the influence of oil had to be included among the other influences. Theoretical analysis (the influence of oil should depend on its diffusion in cages) together with the best fit of the results led to the Avrami equation with exponent value of $n = \frac{1}{2}$ which coincides with kinetic equation of diffusion, especially for not very long times,

$$x(t) = 1 - \exp(-\sqrt{kt}) \approx \sqrt{kt} \quad \text{for } t \ll \frac{1}{k} \quad (5)$$

when well-known parabolic relation describing diffusion processes is obtained. Then the equation describing temporal dependence of fracture force as well as of fracture deformation, obtained by extending Eq. (4), is

$$p(t, T) = a - b \exp(-k_1 t) + c \exp(-k_2 t)(1 + k_2 t) + d \exp(-\sqrt{k_3 t}) \quad (6)$$

where d is parameter describing the maximum influence of oil. This equation is valid for both measured quantities (force as well as deformation) with the same values of all parameters except parameters a , b , c , and d which are different for force from those for deformation. Regression calculations really show that the values of parameters k_i and ε_i determined on the

basis of force dependence are relatively close to those obtained from deformation dependence and then a weighted mean of corresponding parameter values can be calculated with lower common standard deviation. Therefore, parallel measuring of two or more quantities leads to more precise study of the group of processes and in this way more accurately determined values of regression parameters lead to narrower tolerance bands of predictive curves.

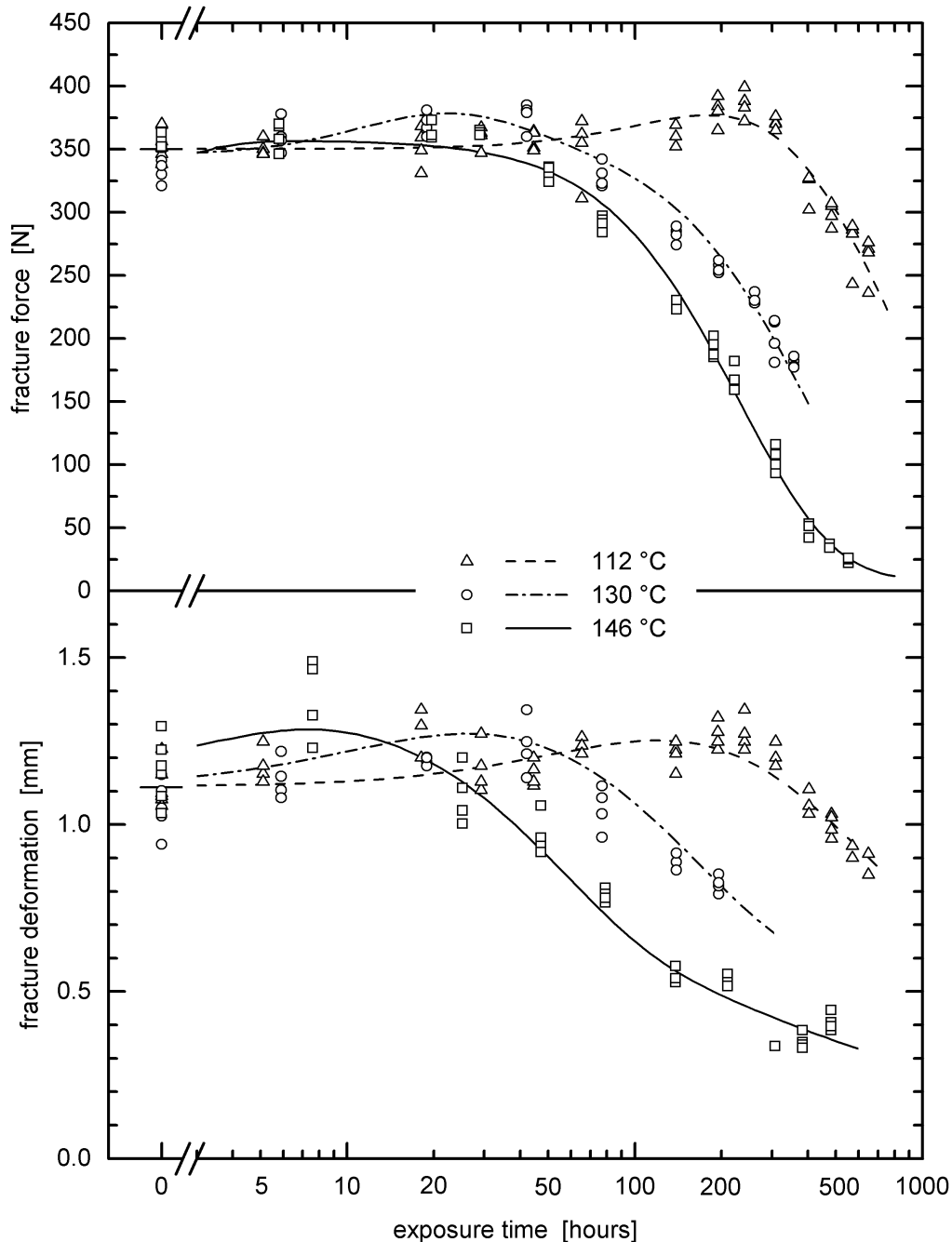


Fig. 5: Temporal dependence of fracture force and fracture deformation of polyamide bearing cages exposed in gear oil at presented temperatures.

AGE-HARDENING OF SOLID SOLUTIONS

Parallel measuring of two quantities was also made during the age-hardening of beryllium bronze: hardness HV 0.3 and resistivity (i.e. specific resistance) were determined, see Fig. 4,

for more details see [4, 5]. While in the previous case fracture force and fracture deformation were closely connected mechanical properties determined on the basis of one test (static tensile test), hardness and resistivity are extremely different properties describing different types of behaviour (mechanical and electrical) and determined on the basis of principally different tests.

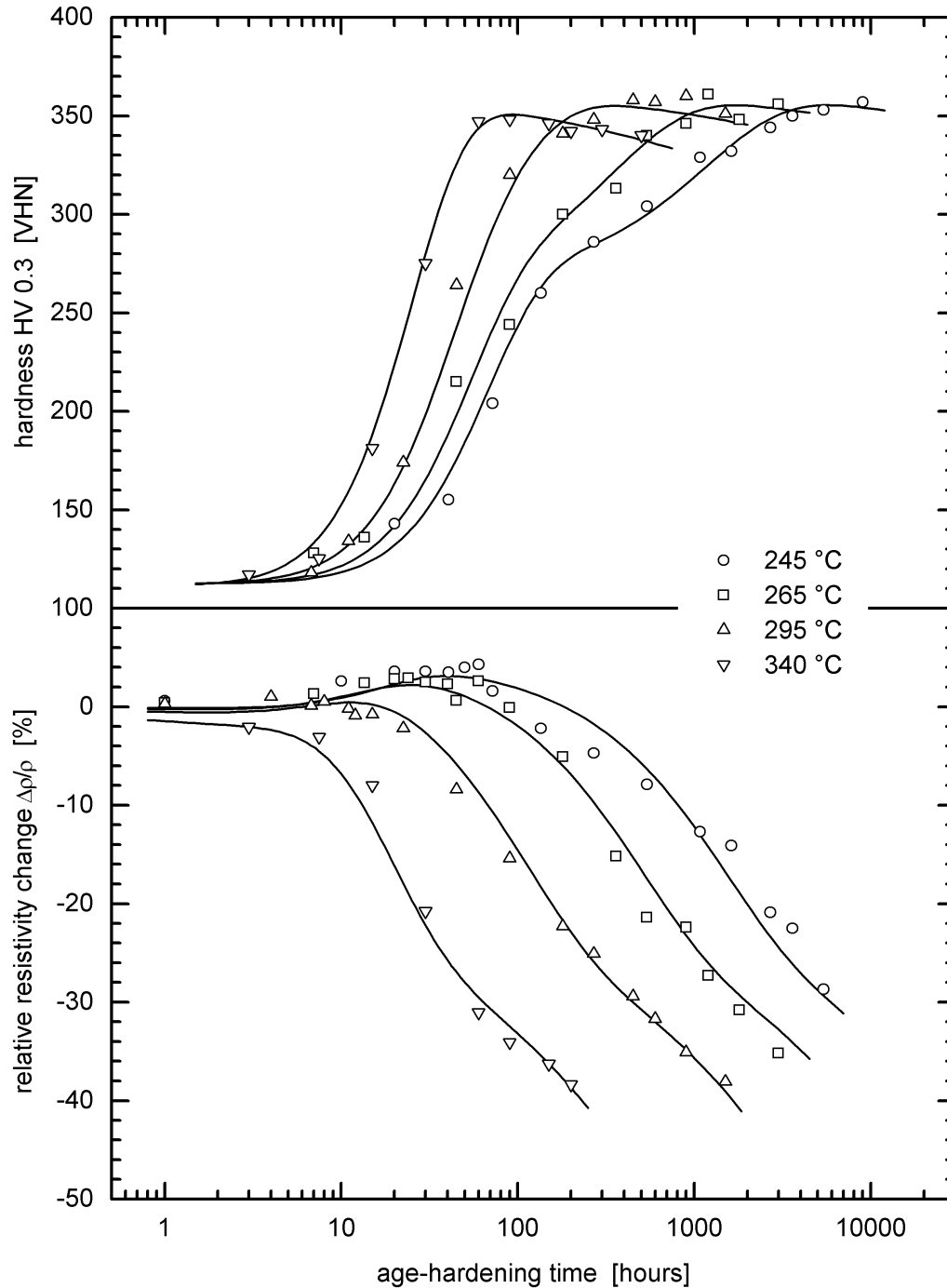
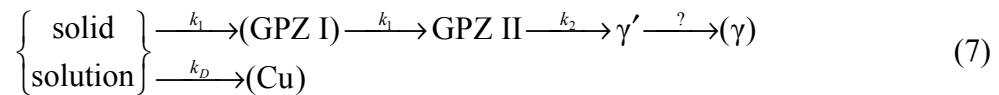


Fig. 4: Temporal dependence of HV 0.3 hardness and relative resistivity changes of beryllium bronze during age-hardening at presented temperatures.

The stages of age-hardening processes in solid solution are described in every book concerning materials science or materials engineering:

1. Monatomic layers of alloying metal called the Guinier-Preston zones of first type (GPZ I)
2. Alternating monatomic layers of basic and alloying metal called the Guinier-Preston zones of second type (GPZ II)
3. Precipitates of metastable γ' phase partially incoherent with solid solution.
4. Precipitates of stable γ phase fully incoherent with solid solution in which the atoms of basic and alloying metal are presented in the ratio of small integers.

It can be expressed by scheme



whose general features are generally known but whose following details were obtained after rather difficult and large regression calculations [6]. The same rate constant k_1 in first and second step means that the GPZ I and GPZ II are created by the same mechanism. GPZ I in brackets means that the considering of GPZ I creation is necessary in kinetic equations but its properties are not substantially different from the structural components adjoining GPZ I in the scheme. Final components in bracket (γ and pure Cu) mean that they were not reached during all the time of exposure. Final forms of kinetic equations of hardness and of relative resistivity change are

$$\text{HV } 0.3(t, T) = 45 + (h - 45) \exp(-\sqrt{k_D} t) + b_1 f_b(t, T) + c_1 f_c(t, T), \quad (8)$$

$$\frac{\Delta\rho(t, T)}{\rho} = 100 \left(\frac{1}{6} - 1 \right) \exp(-\sqrt{k_D} t) + b_2 f_b(t, T) + c_2 f_c(t, T). \quad (9)$$

The properties of pure Cu (HVN = 45 [7] and the ratio of the resistivity of initial solid solution to the resistivity of pure Cu ≈ 6 [7, 8]) had to be taken in Eqs (8) and (9) because the final state was not reached during exposure and, therefore, its properties cannot be determined from obtained results. For common functions f_b and f_c following relations are valid

$$f_b(t, T) = \left(\frac{k_1}{k_1 - k_2} \right)^2 \{ [(k_2 - k_1)t - 1] \exp(-k_1 t) + \exp(-k_2 t) \}, \quad (10)$$

$$f_c(t, T) = 1 - \left\{ 1 + k_1 t + \left(\frac{k_1}{k_1 + k_2} \right)^2 [(k_2 - k_1)t - 1] \right\} \exp(-k_1 t) - \left(\frac{k_1}{k_2 - k_1} \right)^2 \exp(-k_2 t) \quad (11)$$

where (and hereafter) $k_i = k_i(T)$ according to Eq. (1). In this case the calculated values of parameters k_i (not so much ε_i) are quite different for hardness dependence and for resistivity dependence. It may be the consequence of substantially different nature of both properties. The procedure in which the fit of both hardness dependence and resistivity dependence is made simultaneously with common values of parameters k_i and ε_i is developed in this time.

TEMPERING OF HARDENED STEELS

The martensite obtained after quenching is usually called tetragonal martensite (TM) due to its relatively high tetragonality. Usually certain part of austenite retains in the structure after quenching, called retained austenite (RA). During tempering martensite loses a part of carbon and because its tetragonality decreases it is called cubic martensite (CM). Decreasing

internal stress together with continuing exposure leads to the decomposition of retained austenite (RA). Later or at higher temperatures martensite turns into fine globular pearlite (GP), sometimes a structure reached before this final structure is called sorbite (S). The changes during tempering can be represented by scheme of consecutive changes



This scheme of consecutive changes leads to relatively complicated kinetic equation [9]

$$p(t, T) = b[1 - \exp(-k_1 t)] + c \left[1 - \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_1 - k_2} \right] + d[1 - g(t, T)], \quad (13)$$

where

$$g(t, T) = \frac{k_2 k_3 \exp(-k_1 t)}{(k_1 - k_2)(k_1 - k_3)} + \frac{k_1 k_3 \exp(-k_2 t)}{(k_2 - k_1)(k_2 - k_3)} + \frac{k_1 k_2 \exp(-k_3 t)}{(k_3 - k_1)(k_3 - k_2)}. \quad (14)$$

If inequality $k_1 \gg k_2 \gg k_3$ is strictly fulfilled (the difference of two orders is necessary) the scheme of consecutive changes can be replaced by the scheme of parallel changes



with very simple kinetic equation

$$p(t, T) = b[1 - \exp(-k_1 t)] + c[1 - \exp(-k_2 t)] + d[1 - \exp(-k_3 t)]. \quad (16)$$

An example of relative length change of ČSN 41 4109 bearing steel [10] is given in Fig. 5. The fit as well as predictive curves are practically the same when Eq. (13) or Eq. (16) is used.

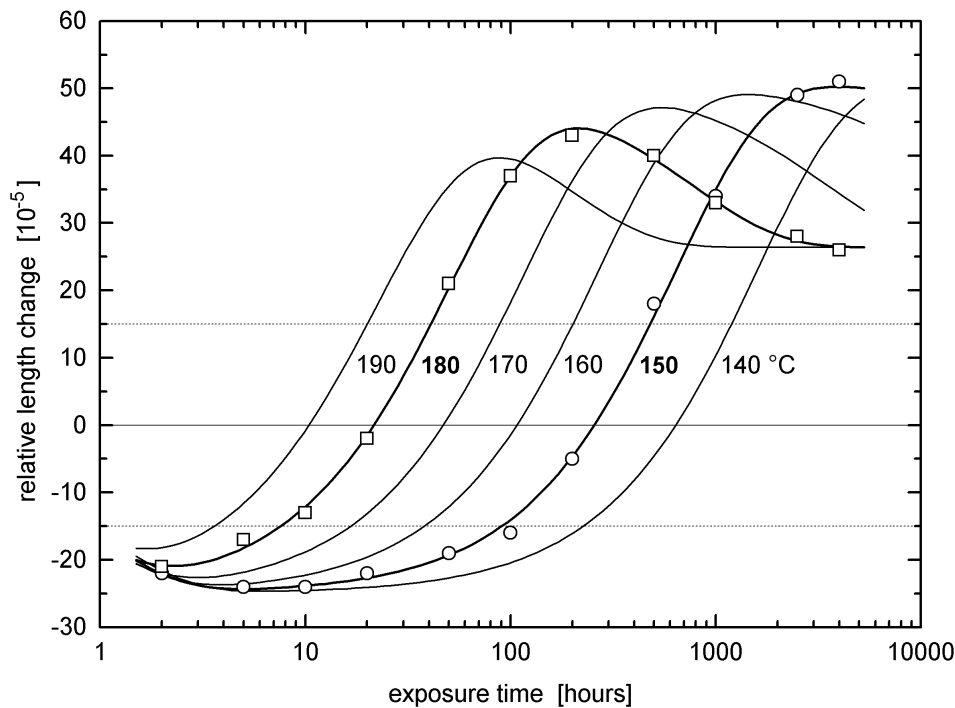


Fig. 5: Temporal dependence of relative length change measured during exposures at 150 and 180 °C after tempering (100 °C, 1 hour). Heavy lines represent fit, light lines mean prediction.

While the results in Fig. 5 were obtained after defined previous tempering (temperature of 100 °C, dwell of 1 hour) a question appears if previous tempering with various parameters (various temperatures and various dwells) can be considered. Fig. 6 is evidence of possibility to do it where the tempering with various dwells preceded the proper exposure.

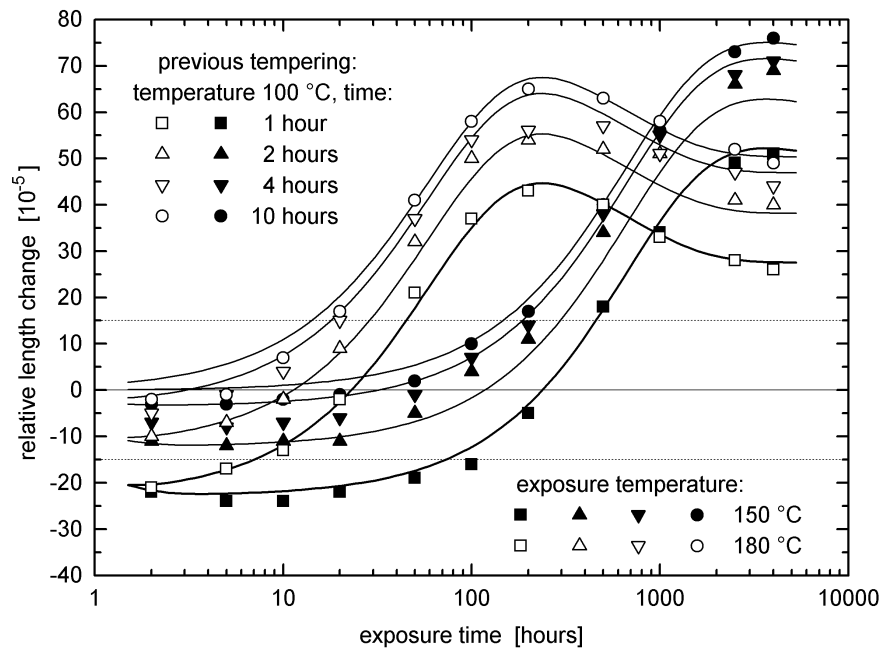


Fig. 6: Temporal dependence of relative length change measured during exposures at 150 and 180 °C after tempering (100 °C, 1 to 10 h). Heavy lines correspond to heavy lines in Fig. 5.

The basis of following considerations consists in the presumption that previous tempering as well as proper exposure represent in fact the same group of processes even if realized at different temperatures and with an interruption. Using the Arrhenius equation, the tempering with the dwell of t_i at the temperature of T_i can be converted to temporal shift $\Delta t_i(T; t_i, T_i)$ which corresponds to i -th process (described by rate constant of k_i and by activation enthalpy of ε_i) and to exposure temperature of T

$$\Delta t_i(T; t_i, T_i) = t_i \exp \left[\frac{\varepsilon_i}{\kappa} \left(\frac{1}{T} - \frac{1}{T_i} \right) \right]. \quad (17)$$

Then the function of two variables (temperature and dwell of exposure) is replaced by the function of four variable (temperature and dwell of exposure + temperature and dwell of previous tempering) according to following scheme

$$p(t, T) = \sum_i f_i(t, T) \Rightarrow p(t, T; t_i, T_i) = \sum_i f_i[t + \Delta t_i(T; t_i, T_i), T]. \quad (18)$$

Also a shift of studied quantity (here relative length change) is necessary in this case because all changes during exposure are usually measured starting from zero, regardless of various conditions of previous tempering. This concept is successful in the case of low tempering temperatures, see Fig. 6. Such low temperatures are not used in practice because then the dimensional changes of bearing steels during service time could be unacceptably large (see allowable limits $\pm 15 \cdot 10^{-5}$ presented in Figs 5 and 6 by dashed lines). For higher tempering temperature an additional temporal shift seems to have to be added for including the influence of rise time of tempering temperature. A suitable estimation of this shift is solved now.

CONCLUSIONS

1. A simplified description of kinetics of the changes in materials properties during exposure at elevated temperatures, based on the Arrhenius equation and kinetic equations of relatively simple chemical reactions, was successfully used for various structural materials: steels, age-hardenable alloys, and polymer composites.
2. The description leads to regression functions used for fitting experimental dependence and for calculation of regression parameters. On their basis the construction of predictive curves can be done which describe the changes in materials properties also at conditions at which the tests have not been performed. Mean values and standard deviations of regression parameters allow to construct mean predictive curves and their tolerance bands.
3. Parallel study of two (or more) materials properties leads to the better identification of processes taking place in materials and the more precise determination of their parameters. Then also predictive curves can be determined more precisely, with narrower tolerance bands.
4. Usually the changes in materials properties can be studied in dependence on the time and temperature of exposure. In the case of hardened steels, the influence of previous tempering can be included by certain temporal shifts explained in the paper.

ACKNOWLEDGEMENT

Financial support of the Ministry of Defence of the Czech Republic within project MO 83171199106 is gratefully acknowledged.

The author is grateful to all authors (see [4, 5, 10]) whose original experimental results were used in his calculations.

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