

KINETICS OF HARDNESS CHANGES DURING AGE-HARDENING OF SILUMIN

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Resume

Simple phenomenological description of age-hardening kinetics of supersaturated solid solution is presented using the sum of exponential functions with negative arguments containing rate constants, for whose temperature dependence the Arrhenius equation is used. The number of exponentials in the sum is discussed considering sufficiently accurate description as well as the number of distinguishable processes occurred during hardening. Also the limits of this approach are presented. Hardness changes of silumin during age-hardening are used for demonstration of this procedure.

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1. Introduction

Phase transformation is quite complicated process consisting of several different stages (nucleation of germs of new phase, their free growth, growth after the areas of new phase reach one another, conversion of the residues of old phase) and, therefore, also the description of its kinetics is not simple. Nevertheless the Avrami equation [1] is successfully used in this case, sometimes connected with the names of Johnson and Mehl [2] or also Kolmogorov [3]. At age-hardening of supersaturated solid solutions not only one but several phase or structural changes take place and the kinetics is usually described only graphically. The author tried to use kinetic equations of simple chemical reactions in this case. As the hardening processes take place one after another, the equations of consecutive reactions were used with success for beryllium bronze hardening [4] and for exposure of bearing steels at elevated temperatures [5]. Further studies [6] of steels used for rolling bearings showed that the consecutive reactions can be replaced by concurrent (parallel) reactions with substantially

simpler form of kinetic equations if rate constants differ in orders. In the simplest case of the first order reactions the kinetic equation consists of the sum of exponential functions. This sum was used in this paper for the description of hardness changes of silumin during age-hardening.

All structural changes in supersaturated solution are of physical nature (based on diffusion), therefore the application of the equations of chemical reactions can be found rather unusual. However, both the changes – physical as well as chemical – have two basic common features:

a) in both cases the driving force of processes is determined by the decrease of total energy of structure or system towards its minimum characterising the equilibrium state,

b) structural changes in materials as well as chemical reactions are the processes when certain barrier has to be overcome.

Item a) in the simplest approach (driving force is proportional to the distance from equilibrium state) leads to the kinetic equations

of exponential type, the barrier processes mentioned in b) lead to the description of temperature dependence of rate constants by the Arrhenius equation – without any difference if structural changes or chemical reactions are considered.

2. Basic precondition of the description

Presented procedure is based on very natural precondition: all processes taking place in studied temperature range are qualitatively the same and differ only quantitatively in their rates (described by the Arrhenius equation). This precondition seems to be in contrary with usual approach when different temperature ranges are connected with certain processes (see e.g. four stages of martensite annealing). Nevertheless, the contrary is only apparent: for chosen narrow temperature interval only one of the processes predominates in usual time dwells and the exhibition of all others is small or negligible (either they took place intensively in very short times before considered temporal interval, or they will be considerable in times substantially longer than the interval covers). This is direct consequence of the order difference of rate constants of individual processes, which appear in arguments of exponential functions.

3. Experimental material

Presentation of supposed procedure was made using experimental results from book [7] for 356.0 silumin (signed by the Aluminium Association Casting Alloy Designation System) (see p. 185, Fig. D.2.28) delivered in T4 state (solution treated and aged). This silumin with nominal chemical composition 7.0 wt.% Si and 0.32 wt.% Mg corresponds to EN AC-42100 (EN AC-AlSi7Mg0.3) silumin [8] according to current Czech standards. Solution heat treatment was made at 527 °C during 12 hours, finished by boiling water quench. Age-hardening of cylinder rods with 28.575 mm in diameter and 304.8 mm in length was made at temperatures 149, 177,

204, 227, 260 and 343 °C (300, 350, 400, 440, 500 and 650 °F in the original [7]). The results of HB hardness and *growth* (relative length increase) are available. For the presentation of supposed procedure the hardness was chosen, which is more suitable for this reason in this individual case. From experimental results two the most distant ones were excluded (dwells 500 and 1000 hour at the lowest temperature).

4. Regression calculations

As mentioned above, the kinetic equations of concurrent chemical reactions (the simplest, i.e. of first order), which describe also consecutive reactions if their rate constants differ in orders, were used. Concentration c of newly created reactant changes in time according to equation

$$c(t) = c_f [1 - \exp(-kt)] \quad (1)$$

where c_f is final concentration of newly created reactant and k is rate constant of the reaction. The sum of such equations is used for the description of property change

$$\Delta p(t, T) = \sum_{i=1}^n a_i \{1 - \exp[-k_i(T) \cdot t]\} \quad (2)$$

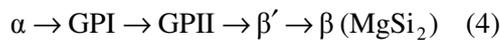
where k_i are rate constants depending on temperature and a_i are coefficients with the same dimension as the property p whose changes are studied (if not only change but *total* value of the property is considered, additional constant a_0 is added in Eq. (2)). These coefficients a_i for $i = 1, \dots, n$ represent maximum changes which can arise in connection with the i -th addend in Eq. (1) (in *correct* case corresponding to the i -th process taking place in material). Temperature dependence of rate constants is described by the Arrhenius equation, which was used in the form

$$k_i(T) = k_i(T_0) \exp \left[-\frac{\varepsilon_i}{\kappa} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (3)$$

more suitable for regression calculations. T_0 represents firmly chosen suitable *reference*

temperature, here it is $T_0 = 500 \text{ K} \approx 227 \text{ }^\circ\text{C}$ representing approximately the midpoint of interval of ageing temperatures, and ε_i are activation energies of individual processes. The Boltzmann constant κ can be replaced by the universal gas constant R if the activation energies of moles are considered.

Description of kinetics using regression function (2) stops to be phenomenological if individual addends in (2) can be assigned to individual processes taking place in materials during structural changes. For studied silumin the scheme of decomposition



is valid, although some authors (e.g. [7]) do not distinguish stages GPI and GPII. It means that number n in Eq. (2) should be equal to 4 but also lower as well as higher integers were tested.

All regression calculations with $n \leq 4$ were done using MS Excel together with its supplement *Solver* [9]. In the cases $n \geq 5$ extremely high interrelations between some pairs of regression parameters appeared and better results were obtained using special regression procedure written in *Pascal* [10].

5. Results of regression calculations

Results of regression calculations using regression function (2) with $n = 4$ are presented in Fig. 1 and Table 1.

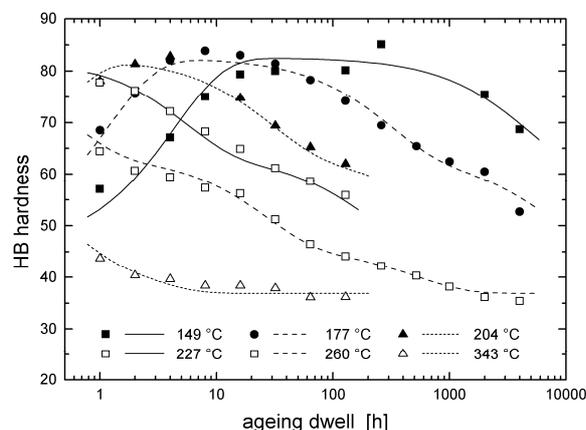


Fig. 1. Regression with regression function (2) for $n = 4$

Table 1
Parameters a_i , rate constants for temperature 500 K (227 °C) and activation energies (parameters of regression function (2) for $n = 4$)

i	a_i (1)	k_i (h^{-1})	ε_i (kJ/mol)
1	37.0	6.56	76
2	-19.2	0.190	150
3	-17.6	0.00529	133
4	-9.0	0.000135	177

Regressions for $n < 4$ are not sufficient:

- for $n = 1$ only the decrease of hardness can be described,
- for $n = 2$ also the increase for lowest temperatures is included but the description is only qualitative,
- for $n = 3$ two highest temperatures are described insufficiently.

Up to $n = 4$ the nonlinear regression calculations were done without problems:

- minimum of sum of squares was reached after relatively low number of iterations,
- for all initial values of regression parameters which were tested, the same final values of regression parameters and also the same minimum of squares were reached (i.e. evidently the global minimum was reached).

Also regression for $n = 5$ was done and the level of fit increased in comparison with $n = 4$, see Fig. 2, but following problems appeared:

- regression calculations stopped at several different minima in the dependence on different choices of initial values of regression parameters (only local minima were reached, the lowest of them needs not be the global minimum),
- calculations needed sometimes many thousands of iterations,
- in some cases calculations using MS Excel finished prematurely and other tool had to be used,

- final values of some regression parameters were nonsensical (e.g. negative value of activation energy),
- standard deviations of some parameters were in many orders higher than their average values (typical for the cases when very close interrelation between parameters exists, i.e. corresponding covariance coefficient is extremely close to 1).

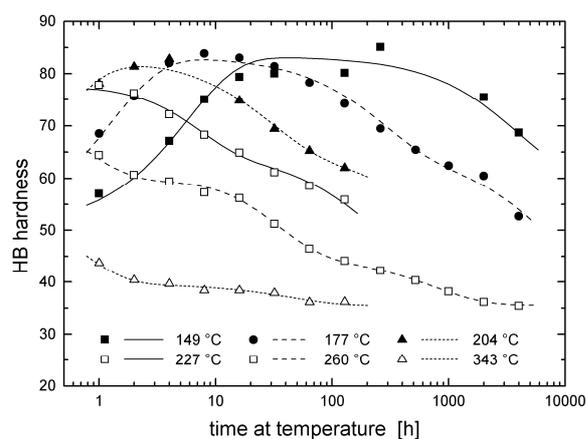


Fig. 2. One of regressions with regression function (2) for $n = 5$

Comparing the results of regression calculations for $n = 4$ and $n = 5$, two different situations appeared:

- one addend in Eq. (2) split into two addends with the values of rate constants and activation energies close to the values of these quantities corresponding to the original addend,
- addend with the values of rate constant and activation energy substantially different from the values of these quantities corresponding to all other addends appeared; mostly extremely low or extremely high values of rate constant were obtained (i.e. in fact only small part of the curve for the lowest or the highest temperature is influenced).

6. Discussion of regression results

In the scheme (4) of decomposition of the studied silumin four processes are considered

and also using of regression function (2) containing four addends leads to quite good fit of experimental results. It probably means that to each of addends one of processes taking place in silumin during age-hardening can be assigned but for reliable assignation deep study of microstructure during the whole decomposition is necessary which is not possible in the case of using results from literature. Other possibility consists in comparison of calculated values of activation energies with published values but the author did not find suitable ones. Also rate constants k_i related to suitable reference temperature and parameters a_i describing the contribution of individual processes to the whole hardness change could be useful for this reason (especially their signs).

Already assuming 5 processes, i.e. using 5 addends in regression function (2) leads to substantial problems in regression calculations. It can mean that 5 processes in age-hardening cannot be distinguished but, on the other hand, it can be connected also with calculation problems of nonlinear regression, above all due to *unsuitable* experimental data (results with too large dispersion, results not covering sufficiently wide ranges of temperatures and times at these temperatures or not covering them sufficiently densely etc.). With the *quality* of results also the number of parameters of regression function is connected: their number can be too high. Generally said, the data for regression calculations of presented type should fulfil following requirements:

- low dispersion (deviations from fitted curve for certain temperature should be lower than or comparable with the differences between different temperatures),
- at least for two lowest temperatures the results for the shortest time should be close to starting value (otherwise the process(es) with highest rate constant cannot be detected),
- at least for two highest temperatures the results for longest times should foreshadow

common horizontal asymptote (otherwise the process(es) with lowest rate constant cannot be detected).

The requirements for detecting initial and final processes at least at two temperatures are connected with the fact that only in this case activation energies determining temperature dependence of rate constants can be calculated. Summarizing mentioned requirements, accurate results covering dwells from very low to very high values at sufficient number of precisely regulated and measured pertinent temperatures are necessary. Used results [7] fulfil these requirements only partially.

On the other hand, obtaining suitable results is quite expansive and time consuming. Short-term heating with precisely defined dwell when quick temperatures change and moreover simultaneously homogeneous distribution of temperature are asked, is experimentally very complicated, long-term heating during several thousands of hours (1 year represents less than 9000 hours) needs one oven for each of temperatures. This is the reason why published data were used in spite of not being ideal for the presented procedure.

Without deep and systematic study of microstructure of decomposing supersaturated solution, any assignation between processes in scheme (1) and processes $i = 1$ to 4 determined by regression calculations can be only speculative but when the numbers in both cases are the same ($n = 4$), this speculation can be done. The higher rate constant is, the sooner the corresponding process takes place. Also so-called characteristic times $t_0 = 1/b$ can be used for such comparison: for t_0 already 63.2 % of conversion passed and when logarithmic temporal scale is used, the change of conversion is for t_0 maximal (as function of $1 - \exp(-bt)$ type in diagram with logarithmic temporal scale has sigmoid form with point of inflexion in t_0). Characteristic times of all four processes for all six experimental temperatures are presented in Table 2. As the sequences of characteristic times

t_{01} to t_{04} are for all experimental temperatures the same (increasing), it is very probable, that sequences in Table 2 corresponds to the sequence of processes in scheme (4).

Table 2

Characteristic times t_{0i} (corresponding to i -th process) for all experimental temperatures T

T (°C)	t_{01} (h)	t_{02} (h)	t_{03} (h)	t_{04} (h)
149	4.37	4 162	68 826	<i>19 × 10⁶</i>
177	1.16	296	6 657	<i>8 × 10⁵</i>
204	0.36	28.6	845	<i>54 377</i>
227	0.15	5.32	191	<i>7 501</i>
260	<i>0.05</i>	<i>0.56</i>	<i>26.0</i>	<i>524</i>
343	<i>5 × 10⁻³</i>	<i>6 × 10⁻³</i>	<i>0.45</i>	<i>2.38</i>

Times at temperatures cover the interval from 1 to 4 000 hours (see both figures). Expanding this interval by one order to $0.1 \div 40\,000$ hours, it can be told that the processes out of this expanded interval play nearly no roles (see characteristic times in Table 2 written in *italics*). It means that e.g. at lowest temperature 149 °C only the 1st and 2nd process are important, while at highest temperature 343 °C only the 3rd and 4th process play significant role (at this temperature the 1st and 2nd process took place at extremely short times and they were completed far before the first hardness measurement was made).

Requirement dealing with the difference of rate constants in orders, which allows using concurrent reactions scheme instead of consecutive one, is fulfilled for reference temperature, see Table 1. It is also fulfilled for all other temperatures with exception of the highest one, see Table 2 presenting reciprocal values of rate constants. Therefore, careful comparison of using consecutive versus concurrent reactions scheme is planned for near future.

Many doubts in assignation of *calculated* processes and processes according to decomposition scheme can be removed when more properties of tested materials are studied

simultaneously. Then also some regression parameters (namely rate constants and activation energies which are common for both or more simultaneously studied properties) can be determined with lower standard deviations. For the studied silumin also the values of growth (relative length increase) are available. Their regression is now in progress. The link with corresponding parameters in regression of hardness changes and common regression of hardness and growth are planned for near future.

7. Conclusions

The sum of exponential functions with negative arguments containing rate constants, for whose temperature dependence the Arrhenius equation is used, proves to be very good tool for the description of age-hardening kinetics of supersaturated solid solutions. This phenomenological procedure is very useful above all in the cases when assignation between addends in sum and processes taking place in studied material can be made (preferably by continuous study of material microstructure, but also regression parameters as rate constants and activation energies can support or confirm the assignation). The procedure was demonstrated here using hardness changes of silumin during age-hardening.

All regression calculations can be usually made using supplement *Solver* in MS Excel. Only in the cases when standard deviations of regression parameters are needed, regression task is very ill-conditioned or very high number of regression parameters is calculated, other software has to be used.

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