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CHANGES OF MATERIAL PROPERTIES OF SILUMIN DURING AGE-HARDENING

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 whose temperature dependence is described by the Arrhenius equation. To determine the number of exponentials in the sum is very important: it should be sufficiently high to obtain accurate description of kinetics and sufficiently low to keep the simplicity and practical applicability of this description. The HB hardness and growth changes (i.e. relative length increase) of silumin during age-hardening are studied separately and then commonly as various manifestations of the same hardening.

Keywords: aluminium alloys; silumin; ageing; hardening; kinetics; hardness; growth

1. Introduction

Description even of simple phase transformation based on diffusion processes is quite complicated because it consists 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. Age-hardening of supersaturated solid solutions represents the sequence of several phase or structural changes; therefore its kinetics is very complicated and it 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 [1] and for exposure of bearing steels at elevated temperatures [2]. Further studies [3] of steels for rolling bearing steels 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 and growth (i.e. relative length increase) during age-hardening of silumin, which is often used also in special technology.

All structural changes in supersaturated solution are the consequence of diffusion, which belongs among physical processes. 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 – regardless 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 contrary to usual approach when different temperature ranges are connected with certain processes (see e.g. four stages of martensite annealing). Nevertheless, the contradiction 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, i.e. 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 [4] for 355.0 silumin (signed by the Alu-

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minium Association Casting Alloy Designation System) (see p. 182, Fig. D.2.19) delivered in T4 state (solution treated and aged). This silumin with nominal chemical composition 5.0 wt.% Si, 1.25 wt.% Cu and 0.5 wt.% Mg corresponds to EN AC-45000 (EN AC-45000 subeutectic silumin [5] according to European 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 [4]). The results of both HB hardness and growth were used in this paper only for times at temperatures 10 000 hours or shorter.

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. 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. If the proportionality among structural changes and property changes is supposed, then the property change can be described by the sum of such equations

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

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 – these coefficients describe supposed proportionality among structural changes and property changes (if not only change but *total* value of the property is considered, additional constant a_0 is added in Eq. (2) – here $a_0 = 0$ is used for growth and $a_0 \neq 0$ is used for HB hardness). 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 $T_0 = 500 \text{ K} \approx 227 \text{ °C}$ 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 only phenomenological if individual addends in (2) can be assigned to individual processes taking place in materials during structural changes. As studied silumin contains besides aluminium and silicon

also copper and magnesium, all following schemes of decomposition should be taken into account during hardening



Although some authors (e.g. [5]) do not distinguish stages GPI and GPII, many different processes are to be considered during age-hardening of studied silumin, i.e. number n in Eq. (2) can reach quite high integers.

All regression calculations were done using MS Excel together with its supplement *Solver* whose adjustment for strongly nonlinear problems with regression parameters differing in many orders is necessary [6]. Only in some cases special regression procedure written in *Pascal* [7] was used which is better than MS Excel if extremely high interrelations between some pairs of regression parameters exist and in addition it gives also standard deviations of regression parameters.

5. Results of regression calculations

The basic problem of using regression function (2) is to determine optimum number of addends n . There are three possibilities how to determine it:

- from theory of decomposition of studied supersaturated solid solution (if sufficiently deeply developed),
- according to the number of stages and phase or structural components, which can be experimentally distinguished during age-hardening in hardened alloy,
- phenomenologically according to the temporal course of studied properties.

In the case when quite complicated alloy (containing three metals and semimetal) is studied and not own but the results of other authors are used for regression without any information about structural development during age-hardening, only item c) remains to be applied.

Regression of growth of this silumin was solved already in previous paper [8] where the values $n = 2$ to 8 were studied. This paper shows which features of the family of kinetic curves are successively described when number n is increasing. For $n = 6$ certain optimum is reached: all basic features of kinetic curves are covered and increasing n gets no substantial improvement, only instability of regression calculations appears. The result of growth regression is presented in Fig. 1.

HB hardness kinetic curves of this silumin are studied newly in this paper (for similar 356.0 silumin were studied in paper [9]). Experience from previous regressions shows that $n = 4$ is the lowest meaningful number of addends in regression function (2) which can cover basic features of the family of those kinetic curves. Also

in this case number n was increased and also for $n = 6$ above mentioned optimum was reached as a compromise between success rate and complexity of the description of kinetic curves. The result of HB hardness regression using regression function (2) with added $a_0 = 71.77$ (initial value of hardness before age-hardening) is presented in Fig. 2.

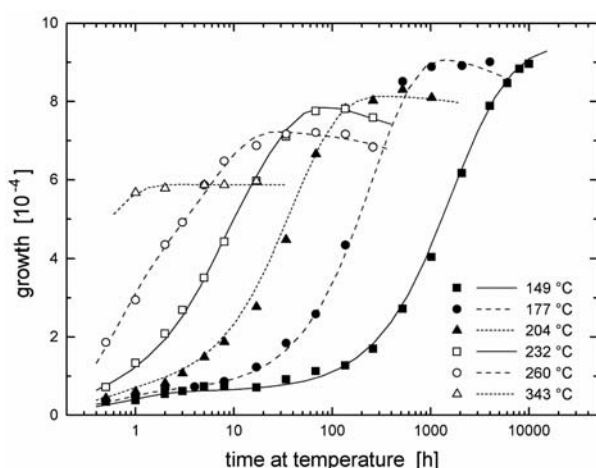


Fig. 1 Regression of growth kinetic curves using regression function (2)

6. Common regression of kinetic curves of more properties

In regression function (2) only parameters a_i (representing proportionality between the proportion of considered structural component in the whole structure mixture and the change of considered property) are connected with considered property, all other parameters (k_i, ε_i) are connected directly with structural changes, therefore they are common for all properties. This fact was used in common regression of growth and HB hardness. While in the case of *separate* regressions of growth and HB hardness with 6 addends in regression function $18 + 18 = 36$ parameters are necessary, in the case of *common* regression only 24 parameters are sufficient. But not only reduction of the number of regression parameters is important – more important is the fact that common parameters can be determined with higher reliability and accuracy. Also assignment of addends in regression function (2) to processes in age-hardened silumin can be easier and more reliable in this case.

Basic problem of common regression is the generalized criterion of regression. Usual regression criterion is a minimum sum of squares of differences between corresponding couple measured value – fitted value of considered property. In the case of common regression when different quantities with values differing in orders are fitted (growth measured in 10^{-4} order and HB hardness measured in 10^1 order), this criterion cannot be directly applied because the quantity with higher values would influence the sum of squares much more strongly than the quantity with lower values. In regression programs it can be solved by rescaling of values or by weighted

sums of squares, which are in fact two sides of the same coin, but constants for rescaling or weight change can be determined by various ways and no unequivocal and universally accepted criterion for choosing the best one exists. In MS Excel supplement *Solver*, which can minimize arbitrary cell by changing other arbitrarily

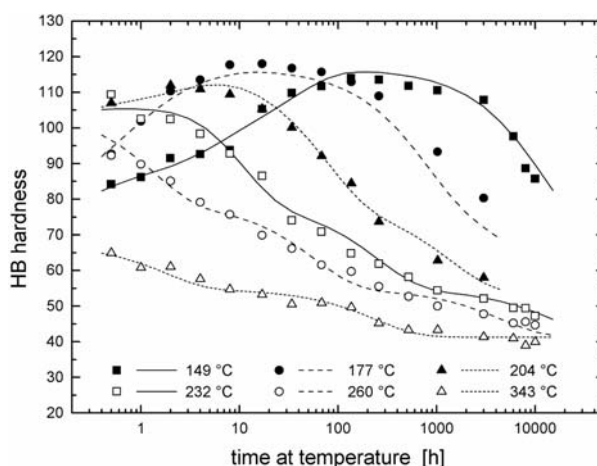


Fig. 2 Regression of HB hardness kinetic curves using regression function (2)

chosen cells, the criterion is very natural: the product of the sum of squares corresponding to HB hardness and sum of squares corresponding to growth is minimized. This approach is independent of scaling of fitted quantities. Common regression of growth and HB hardness with the lowest product of corresponding sums of squares is presented in Fig. 3.

Regression calculations in the case of 24 parameters with regression functions of *double-exponential* type (addends in kinetic equations as well as the Arrhenius equation are of exponential type) represent a very badly conditioned task (especially for experimental curves with high dispersion and low jaggedness). High degree of nonlinearity of regression functions leads to many local minima of regression criterion. Fortunately, most of them can be simply identified by very poor fit of measured dependences or by clearly incorrect final values of regression parameters (e.g. negative or zero values of quantities which must be positive, see rate constants, activation energies etc.). Very specific behaviour of *iteration path* is due to the construction of regression criterion as the product of sums of squares corresponding to hardness and to growth. Depending on initial values of regression parameters, in some cases the fit of growth is improving very quickly i.e. corresponding sum of squares decreases very quickly in initial iterations of regression calculations), while the fit of hardness is improving slowly and does not reach sufficient level (see Fig. 3, corresponding row in Table 1 is *common fit (G)*), while in other cases the situation is opposite (see Fig. 4, corresponding row in Table 1 is *common fit (H)*). As it was already mentioned, the best fit (according to the *product* of corresponding sums of squares) is presented in Fig. 3.

Comparison of sums of squares for separate fit and common fits Table 1

Sum of squares	Growth	Hardness	Product
Separate fits	2.190	483.8	(1060)
Common fit (G)	3.489	870.1	3043
Common fit (H)	7.192	604.5	4783

The regression curve with the worst fit corresponds to the highest temperature (see hardness in Fig. 3 not respecting the jaggedness of experimental dependence as well as growth in Fig. 4 systematically shifted to higher values). All other hardening temperatures are chosen with the step of approx. 28 °C (50 °F), only the distance of the highest temperature is triple. Omitting this temperature, the fit would be much better but it exceeds the limited extent of this paper.

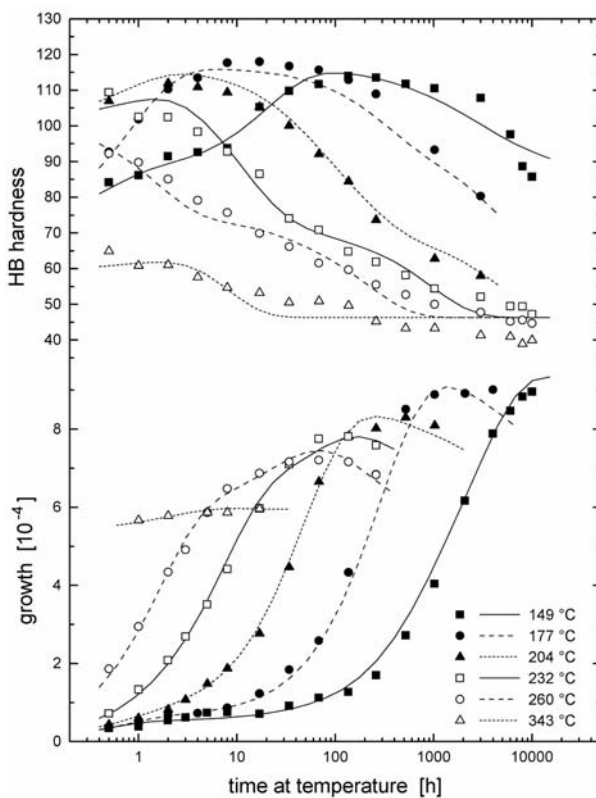


Fig. 3 Common regression of HB hardness kinetic curves and growth kinetic curves using regression function (2) - best fit of growth

The most important characteristics of individual processes, i.e. their activation energies (in kJ/mol), are presented in Table 2. From their values the processes could be identified, which is now only in progress.

Activation energies of individual processes (in ascending order) Table 2

ϵ_i [kJ/mol]	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6
Separate fit G - Fig. 1	14.9	88.6	146.9	243.8	250.0	269.3
Separate fit H - Fig. 2	15.6	22.0	96.6	119.8	149.2	215.2
Common fit (G) - Fig. 3	15.5	50.3	116.1	127.1	169.3	193.6
Common fit (H) - Fig. 4	9.6	81.4	100.0	130.2	147.3	184.8

7. Discussion

Generalized criterion of common regression (minimum product of corresponding sums of squares) can be directly implemented in MS Excel, but not in commercial regression programs. Instead of criterion $S_1 S_2$ also the criterion $\sqrt{S_1 S_2}$ could be considered but it leads to the same results as the previous one. In the case when the fit of one of quantities in common regression is substantially faster than of the other, the criterion $S_1^x S_2^{1-x}$ with suitably chosen $0 < x < 1$ can be considered. Some interesting results have already been obtained with this criterion but systematic study has not yet been done.

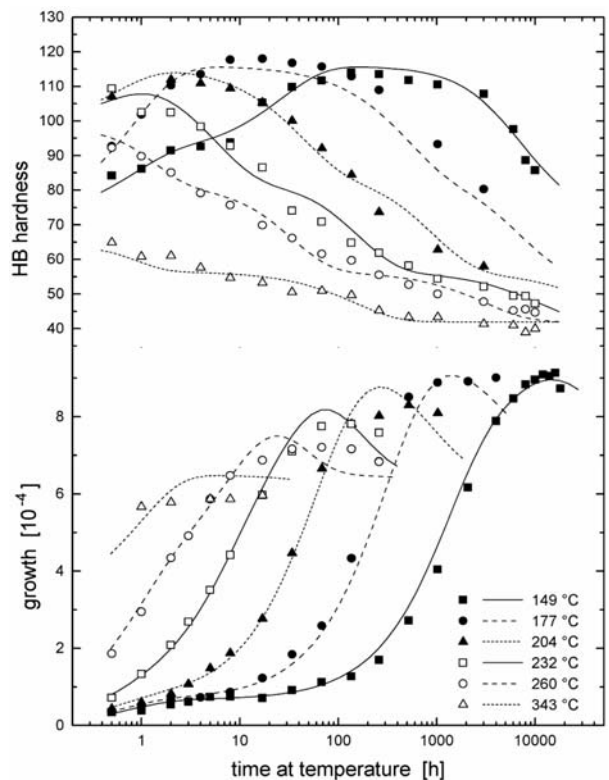


Fig. 4 Common regression of HB hardness kinetic curves and growth kinetic curves using regression function (2) - best fit of hardness

The results of regression show that the condition for replacing consecutive reactions by concurrent (parallel) reactions (i.e. rate constants differing in orders) is mostly fulfilled. Rate constants with extreme values (the lowest one and the highest one) are usually determined with lower accuracy than the others. Therefore, the hardening should be studied in sufficiently wide temporal as well as temperature ranges.

Up to now the author has no reliable tool for common regression giving with the values of regression parameters also their standard deviations. This problem will be solved in near future.

For the development of mentioned approach the simpler alloys should be used, with deep parallel study of microstructure, reliable identification of structural components and unequivocal assignation between addends in Eq. (2) and individual processes taking place in studied material during age-hardening. The proposal of such project will be submitted in next years - after the verification that the approach is really able to give effective and reliable results.

8. Conclusions

The sum of exponential functions with negative arguments containing rate constants, for whose temperature dependence the Arrhenius equation is used, proves to be a very good tool for the description of age-hardening kinetics of supersaturated solid solutions. It can be used not only for separate regression of the family of kinetic curves corresponding to the chosen studied property, but it can be successfully used in common regression of kinetic curves of more properties when rate constants and activation energies are common for all studied properties.

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