Recent progress in dilatometry for quantitative analysis of precipitation kinetics

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Abstract. A high-stability non-contact dilatometer based on two-beam Michelson interferometry was developed recently, enabling isothermal measurements of relative length changes in the sub-$10^{-5}$ regime with minimized drift over times as long as $10^6$ s. This advanced technique opens up novel potentials for quantitative studies of precipitation phenomena, which are associated with tiny relative length changes that have not been accessible before. Using a dilute Al-Mg-Si alloy as a case study, the amount of the metastable coherent $\beta''$- and of the semi-coherent $\beta'$-phase, as well as the amount of the stable $\beta$-phase could be determined quantitatively from isothermal length change measurements. This is accomplished by the distinct length change features that arise from the volume excess due to the precipitates, on the one hand, and the contraction of the matrix upon precipitation of solute atoms, on the other hand. Moreover, reaction-rate analyses of isothermal length change variations yield the kinetic parameters for the formation and transformation of the precipitates.

1. Introduction: Dilatometry as tool in materials science
The principle of dilatometry, i.e., of measuring volume changes caused by physical or chemical processes, dates back to the nineteenth century [1]. Meanwhile, dilatometry has developed to a powerful toolbox with a number of measurement routines applicable to various phenomena in materials science.

Concerning lattice defects, dilatometric measurements of the macroscopic length change $\Delta L/L$ in combination with X-ray diffraction for determining the change of lattice constant $\Delta a/a$, yields access to the concentration of thermal lattice vacancies in pure metals [2, 3]. For high vacancy concentrations and low vacancy diffusivities as in various intermetallic compounds, both the vacancy formation and migration enthalpies can be determined by isothermally monitoring the length change which is associated with vacancy equilibration after a temperature jump [4, 5].

Furthermore, deformation-induced lattice defects are detectable by means of their excess volume since this gives rise to a length contraction upon annealing with respect to a defect-free reference sample [6]. In favourable cases when it is possible to assign the length change in a temperature window to the annealing out of a certain defect type, rather specific information for this defect can be obtained. For instance, for ultrafine-grained Ni and Cu prepared by extreme plastic deformation, a structural key quantity of grain boundaries, namely the grain boundary excess volume, could be determined in this way [7, 8]. In the same manner the concentration of deformation excess vacancies became measurable by dilatometry for ultrafine-grained Ni [9, 10]. Moreover, as dilatometry by its nature can be applied as function of orientation, the anisotropic behaviour of vacancy annealing, which arises from
structural anisotropy in this material, allowed conclusions to be made regarding the vacancy formation and relaxation volume \[9\].

For studying transformation processes in alloys dilatometry has also turned out to be a powerful tool \[11, 12, 13, 14, 15, 16\]. For example, dilatometry is capable of studying the precipitation kinetics in shape memory alloys \[12\] or determining the induced dislocation density in bainitic steel \[13\]. Furthermore, precipitation in Al-alloys with a high concentration of alloying elements can also be monitored by dilatometry \[14, 15\].

However, the amount of precipitation has been quantitatively studied by dilatometry so far only for cases where the associated relative length change exceeded $10^{-4}$ and, moreover, when this took place on short time scales of the order of minutes. Therefore, most relevant alloy systems, such as Al alloys of the 6xxx series with low amounts of Mg and Si, until recently have not been amenable to study by dilatometry so far due to the low amount of precipitation and due to the long time scale necessary to reproduce practical relevant processing conditions. In order to get access to this regime, a highly stable non-contact dilatometer was developed that enables isothermal measurements of relative length change measurements in the sub-$10^{-5}$ regime with minimized drift over times as long as $10^6$ s \[17\]. Using commercial grade Al-Mg-Si alloy (EN AW-6060) as model system, the potential of this technique has been demonstrated recently \[18, 19\]. A summary will be given in the following, after a brief description of the chosen alloy system.

2. Short literature survey on precipitation processes in Al-Mg-Si
The Al-Mg-Si alloy EN AW-6060 was chosen as model system because of the complex precipitation sequence, involving metastable phases, and because of the comprehensive research done before on the precipitation processes in this alloy (for reviews see, e.g., Refs. \[20, 21\]). Summarizing briefly, precipitation proceeds via three metastable phases (clustering, $\beta''$, $\beta'$) before the final equilibrium $\beta$-precipitates are formed. Initial clustering is a highly complex multistage process \[22\], presumably starting with single element clusters which transform into co-clusters \[23\]. The formation of the $\beta''$-phase takes place via one or more transition stages, designated, e.g., GP-II, pre-$\beta''$, initial-$\beta''$ \[24, 25\]. Coherency between $\beta''$-precipitates and the Al-matrix causes hardening. The associated strain field strongly influences the crystal structure of $\beta''$ which most likely is monoclinic Mg$_4$Al$_3$Si$_4$ \[26, 27\]. Subsequently, the semicoherent metastable $\beta'$-phase (hexagonal Mg$_9$Si$_5$ \[28\]) is formed associated with a loss in hardness. Additional metastable phases are reported (named U1, U2, B or A, B, C), the number densities of which usually are much lower \[29\]. The finally formed equilibrium $\beta$- phase is Mg$_2$Si with the CaF$_2$-structure \[30\].

3. Experimental procedure
The length change measurements reported here were performed by means of a non-contact dilatometer based on two-beam Michelson interferometry. The dilatometer, with a self-developed housing and furnace, optimized for high stability, is described in detail elsewhere \[17\]. The cylindrically shaped samples (length: 20 mm, diameter: 5.7 mm) were solution annealed in the dilatometer at 540 °C (30 min), subsequently quenched in a He gas stream, then held at 32 °C for 4 min, and finally rapidly heated at a rate of 100 °C/min to the temperature of isothermal precipitation treatment between 170 °C and 260 °C.

4. Results and discussion
4.1. Resolving $\beta''$- and $\beta'$-precipitation by dilatometry
Figure \[1\] shows the dependence of the relative length changes $\Delta L/L$ on time $t$ for various isothermal aging temperatures between 180 °C and 240 °C. As outlined in detail elsewhere (see \[18\]), the clear time correlation of length change and hardness during aging indicates that the length increase arises from the formation of the metastable coherent $\beta''$-phase and the length decrease from the formation of the metastable semicoherent $\beta'$-phase. It is a highly remarkable fact that the two phases can be
Figure 1. Dependence of relative length change $\Delta L/L$ on time $t$ measured at the quoted annealing temperatures. The horizontal lines mark the quantitatively estimated length changes arising from $\beta''$- and $\beta'$-formation (see Table 1).

Table 1. Relative length change associated with precipitation of $\beta''$ and $\beta'$. $\Delta L/L_{\text{matrix}}$: matrix contraction; $\Delta L/L_{\text{prec}}$: expansion upon precipitation; $\Delta L/L_{\text{calc}}$: sum; $\Delta L/L_{\text{exp}}$: measured value deduced from the extrema of the $\Delta L/L$ curves. For details see ref. [18].

| Precipitate Composition | $\beta''$ | $\beta'$ |
|------------------------|----------|---------|
| $\Delta L/L_{\text{prec}}$ | $10^{-4}$ | 3.47 | 5.23 |
| $\Delta L/L_{\text{matrix}}$ | $10^{-4}$ | -3.08 | -5.93 |
| $\Delta L/L_{\text{calc}}$ | $10^{-4}$ | 0.39 | -0.71 |
| $\Delta L/L_{\text{exp}}$ | $10^{-4}$ | 0.53 | -0.61 |

4.2. Precipitation kinetics from analysis of isothermal length change

Knowing the absolute amount of precipitates as function of time and temperature (see above), also the underlying kinetics of the precipitation processes can be determined. The formation of $\beta''$ is described by JMAK-type kinetics (Avrami exponent of $n = 1$) combined with a second term describing the $\beta'' \rightarrow \beta'$ transformation. For higher temperatures in addition to the $\beta'' \rightarrow \beta'$ transformation, also a direct formation of $\beta'$-precipitates has to be taken into account. This yields the following set of three differential equations:

\[
\frac{dP_{\beta''}}{dt} = k_{\beta''} \left(1 - \frac{P_{\beta''}}{P_{\text{total}}}\right) - k_{\beta''}^{\beta'} \frac{P_{\beta''}}{P_{\text{total}}} \frac{P_{\beta'}}{P_{\text{total}}} \\
\frac{dP_{\beta'}}{dt} = k_{\beta''}^{\beta'} \frac{P_{\beta''}}{P_{\text{total}}} \frac{P_{\beta'}}{P_{\text{total}}} - k_{\beta'} \left(1 - \frac{P_{\beta'}}{P_{\text{total}}}\right)
\]
Figure 2. Arrhenius plot representation of reaction rates $k_1$, $k_2$, $k_3$ determined from fitting the $\Delta L/L$-curves according to the solution of rate model (equations (4–6)).

Figure 3. Time-temperature-precipitation (TTP) characteristic for the formation and dissolution of $\beta''$ and $\beta'$. The iso-concentration lines are calculated from the solution of the rate model (equations (4–6)).

coupled rate equations:

\[
\dot{c}_{\beta''}(t) = k_1 \left\{ c_0 - \left[ c_{\beta''}(t) + c_{\beta'}(t) + c_{\beta'\text{dir}}(t) \right] \right\} - k_2 c_{\beta''}(t), \tag{1}
\]

\[
\dot{c}_{\beta'}(t) = k_2 c_{\beta''}(t), \tag{2}
\]

\[
\dot{c}_{\beta'\text{dir}}(t) = k_3 \left\{ c_0 - \left[ c_{\beta''}(t) + c_{\beta'}(t) + c_{\beta'\text{dir}}(t) \right] \right\}, \tag{3}
\]

for the atomic fractions of the precipitate phases with $c_0$ as the maximum amount finally attained. Here, $k_1$ denotes the rate for formation of the precipitate phase $\beta''$, $k_2$ that for formation of $\beta'$ from $\beta''$, and $k_3$ that for direct formation of $\beta'$.

With the initial conditions of a vanishing amount of precipitates for $t = 0$, the solution of the set of rate equations yields the following temporal evolutions:

\[
c_{\beta''}(t) = c_0 \frac{k_1}{k_2 - (k_1 + k_3)} \left\{ \exp(-(k_1 + k_3)t) - \exp(-k_2 t) \right\}, \tag{4}
\]

\[
c_{\beta'}(t) = c_0 \frac{1}{k_2 - (k_1 + k_3)} \left\{ \frac{k_2 k_1}{k_1 + k_3} \exp(-(k_1 + k_3)t) + k_1 \exp(-k_2 t) \right\} + c_0 \frac{k_1}{k_1 + k_3}, \tag{5}
\]

\[
c_{\beta'\text{dir}}(t) = c_0 \frac{k_3}{k_1 + k_3} \left\{ 1 - \exp(-(k_1 + k_3)t) \right\}. \tag{6}
\]

By means of this set of solutions, the experimental isothermal $\Delta L/L(t)$-curves can be fitted (see [19]). For each temperature the three rate constants $k_i$ ($i = 1, 2, 3$) as obtained from the fit are shown in the Arrhenius plot (figure 2). Linear fits of the temperature variations $k_1(T)$ and $k_2(T)$ according to Arrhenius-type behaviour yields the corresponding activation energies $Q_1 = (0.90 \pm 0.30)$ eV and $Q_2 = (1.42 \pm 0.28)$ eV. A comparison of the temperature variations of $k_2$ and $k_3$ shows that for temperatures above 200 $^\circ$C the rate of direct $\beta'\rightarrow\beta''$ transformation exceeds that of $\beta''\rightarrow\beta'$ transformation. The deduced activation energies are similar to those found earlier for Al-Si-Mg alloys [15]; they also can be considered as characteristic for metastable precipitates in Al-alloys [31, 32].
Analyzing isothermal measurements as in the present case compared to non-isothermal ones has the distinct advantage that the resulting kinetic parameters, such as the activation energies, only vary insignificantly with the reaction model [33]. JMAK-theory with an Avrami exponent of $n = 1$, applied here, was found to be suitable giving analytical solutions even in the present case where formation of the precipitate phases is interdependent and occurring in parallel. Comparative kinetic analyses with various reaction models yielded similar results.

4.3. Time-temperature-precipitation (TTP) diagrams

Dilatometry data have been used previously to construct transformation diagrams both for ferrous metals [34] and for non-ferrous metals [35], including Al alloys. However, measurements of this kind have so far been restricted to relatively highly alloyed systems where the volume changes upon precipitation are much larger compared to those studied here. By means of the kinetic parameters obtained from the analysis of the $\Delta L/L(t)$ curves, the concentrations of $\beta''$ and $\beta'$ for each time and temperature can be calculated from the solution of the rate model (equations (4−6)). This allows to construct an important part of the technologically most relevant TTP-diagram of this alloy as shown in figure 3.

The hatched area marks the parts where the concentration of one or both of the phases exceeds 10% of the respective maximum concentration. As expected, with increasing temperature the transformations are shifted to shorter times. Within the temperature−time regime where $\beta'$ has not yet started to form at a noticeable amount, the iso-concentration lines of $\beta''$ show an almost linear behaviour related to the logarithmic time scale.

The crosshatched area marks the overlapping regime where the concentrations of both phases exceed 10%. As can be discerned from the crossing of the iso-concentration lines 100% $\beta''$ and 10% $\beta'$, for low temperatures, and correspondingly long times, a noticeable amount of $\beta'$ is formed only after the maximum amount of $\beta''$ has been reached. For high temperatures and correspondingly fast kinetics, the formation of $\beta'$ in appreciable amounts sets in prior to reaching the maximum amount of $\beta''$.

5. Outlook

As demonstrated by the present case study, the recent progress in dilatometry regarding sensitivity and stability opens up a novel pathway for quantitative analysis of complex precipitation kinetics in alloys. The method not only appears to be particularly relevant for elucidating precipitation processes in the technologically important class of light-weight alloys, but also for other materials classes, such as, e.g., maraging steels. The dilatometer system described was recently mounted in an improved temperature-stabilized enclosure ($\Delta T \leq 0.2^\circ\text{C}$). With this additional stability improvement long-time processes associated with even smaller length changes, occurring as for instance upon natural aging of Al alloys, are within reach.

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