Activation Energy of Recovery Process in a Heat-Resistant Alloy Type RR58 with Zirconium

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Abstract. Influence of zirconium on activation energy of the recovery process of Al alloy type RR58 is presented in this paper. By following changes in micro-hardness as a function of time for different temperatures and at different zirconium contents, activation energy of the recovery process, which served as an indicator of the creep resistance of the alloys, was determined. A mathematical model, which enables to evaluate and predict required quality of alloys was also defined.

Introduction
On the basis of the literature data [1-6] and previously obtained results [7,8], it was concluded that the transition metals with relatively low solubility in solid solution (manganese, chrome, zirconium, as well as lanthanides), added to the aluminum alloys can be used for strengthening of grain and sub-grain boundaries, due to precipitation in the form of fine dispersed particles. In this way, the recovery resistance can be increased and creep velocity decreased, which leads to high values of hardness parameters at raised working temperatures.

Since one of the heat-resistance criteria is yield creep, taking into account that difficulties in the recovery process mean at the same time difficulties in the creep process, the accent was put on the investigation of the recovery process.

Calculated activation energy and relative recovery factor values served as the indicators of the difficulties in development of the recovery process, i.e. effect of zirconium on the creep resistance. In this paper, only the results relating to the activation energy of the alloys containing zirconium were presented.

Experimental
The initial material for the experiments was an Al-based heat-resistant alloy, type RR58 (AA2618), of a complex composition, produced by the standard melting process, while zirconium was added in the form of Al-Zr5 master alloy. Chemical composition of manufactured alloys is given in Table 1.
Table 1. Chemical composition of the produced alloys [mas%].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Mg</th>
<th>Si</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>2,10</td>
<td>0,96</td>
<td>1,21</td>
<td>1,28</td>
<td>0,30</td>
<td>-</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>2,15</td>
<td>0,91</td>
<td>1,20</td>
<td>1,26</td>
<td>0,29</td>
<td>0,0834</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>2,10</td>
<td>0,93</td>
<td>1,20</td>
<td>1,25</td>
<td>0,28</td>
<td>0,1763</td>
</tr>
<tr>
<td>Alloy 4</td>
<td>2,10</td>
<td>0,91</td>
<td>1,18</td>
<td>1,24</td>
<td>0,28</td>
<td>0,244</td>
</tr>
</tbody>
</table>

Casting process was followed by homogenization at the temperature of 510-515 °C for 22 hours, and then by hot forging and cold rolling process. Recovery process was performed on all alloys at five selected temperatures, at a range of 150-350 °C, and for nine different time period.

Results and discussion

**Activation energy of the recovery process.** Activation energy of a recovery process in this paper was defined on the basis of analysis of the changes in micro-hardness with time, at different temperatures and with different zirconium contents [8]. Figure 1 shows time dependence of micro-hardness for the Alloy 1 (base alloy).

![Fig. 1. Changes in micro-hardness for Alloy 1.](image)

Quantitative definition of the dependence of the recovery rate on time and temperature is usually followed by a complex procedure. In some cases, however, a simplified analysis can be applied [9]. Certain physical or mechanical properties (micro-hardness in this case) during recovery process of the deformed metal was analysed. According to Eq. 1:

\[
d\Delta X / dt = K / t
\]

(1)

decrease or increase of velocity of any characteristics \((\Delta X)\) is inversely proportional to the recovery time \((t)\) [10]. Parameter \(K\) in Eq.1 is constant for the given temperature and it depends on activation energy of the process \((Q)\), according to the Arrhenius equation. If \(X_d\) indicates value of micro-hardness after deformation, i.e. prior to the recovery process, micro-hardness after recovery is denoted by \(X\), then the total change occurring during recovery can be expressed as \(X_u = X_d - X\). Parameter \(X_u\) is proportional to the volume error concentration \(C\), occurring during deformation [9]. According to those statements, changes of the investigated parameters values with time can be given by:
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\[
\frac{dX_u}{dt} = \frac{dC}{dt} = \frac{d(X_d - X)}{dt} \tag{2}
\]

Error annulment velocity, \( \frac{dC}{dt} \), during recovery, depends on the error concentration \( C \) and its mobility. If error annulment is considered as chemical reaction, the velocity can be written as follows:

\[
\frac{dC}{dt} = AC^n \exp\left(-\frac{Q}{RT}\right) \tag{3}
\]

where \( A \) is a constant, \( n \) is an integer which is 1 for the reaction of the first order, 2 for the reaction of the second order, \( Q \) is activation energy for the process, \( R \) and \( T \) have their usual meaning.

Results of Equations 2 and 3 after combining and integrating may be expressed as:

\[
\int \frac{d(X_d - X)}{(X_d - X)^n} = A\exp\left[-\frac{Q}{RT}\right] dt \tag{4}
\]

Thus, the final solution for the first-order reaction is:

\[
\ln(X_d - X) - B = A\exp\left[-\frac{Q}{RT}\right] dt \tag{5}
\]

Measuring the time, \( t \), which is necessary for inducing always the same change \( (X_u = X_d - X) \) at different temperatures, \( T \), left side of the Eq. 5 becomes a constant:

\[
D = t \exp\left[-\frac{Q}{RT}\right] \tag{6}
\]

Then the solution is:

\[
\ln t = \ln D + \frac{Q}{RT} \tag{7}
\]

Numerical processing of the experimental results. Isothermal curves of the recovery process were good basis for the definition of the activation energy as function of alloying elements contents. EViews3 program package, for data processing, statistical analysis, graphic presentation, estimation, prediction and simulation, was used for the interpolation of the data through the average squared error minimization. This procedure was applied in two phases of the numerical data analysis [8].

Applying the identical procedure for all manufactured alloys the mean values of activation energy were calculated and shown in Table 2.

| Table 2. Activation energy of the recovery process for the produced alloys. |
|---|---|---|---|
| Alloys | 1 | 2 | 3 | 4 |
| \( Q_{\text{mid}} \) [kJ/mol] | 31.34 | 47.43 | 51.00 | 75.72 |
It is obvious that zirconium influences the increase of the activation energy from 31.34 kJ/mol to 75.72 kJ/mol, depending on its content. Therefore, zirconium strongly affects the recovery process. The intensity of this influence is directly proportional to zirconium content. Activation energy as a function of the alloy chemical composition and micro-hardness (shown in Figure 2 in the form of 3D diagram). The non-linear dependence which confirms the previous statements is found.

**Fig. 2. Activation energy as a function of the chemical composition and micro-hardness for alloys containing zirconium.**

**Mathematical model.** Experimental results in Figure 2 have been treated by interpolation models, on the basis of which corresponding graphic presentation were obtained. Analysis shows that cubic interpolation is in a good accordance with the obtained results. Further analysis of the cubic interpolation, introducing additional coefficients, leads to an adequate mathematical model of activation energy dependence on the chemical composition of the investigated alloys. Complete cubic interpolation can be expressed as follows:

\[ Q_{H(34.30)} = C_1 + C_2 Zr(0-0.24\%) + C_3 Zr^2(0-0.24\%) + C_4 Zr^3(0-0.24\%) \]  

Using an original program in MATLAB, the cubic polymon was developed and the following analytical expression is obtained:

\[ Z = a_1 + a_2 xy + a_3 xy^2 + a_4 xy^3 \]

Where, \(a_1-a_4\) are the coefficients of interpolation area, \(x\) is micro-hardness, \(y\) is zirconium content, \(Z\) is required activation energy.

Graphic interpolation of this dependence is shown in Figure 3. It can be seen that the mathematical model is in good accordance with the experimental results shown in Figure 2. This means that the choice of the cubic interpolation is highly reliable for the simulation of the recovery process.
On the basis of the presented results and theoretical considerations, it can be concluded with a high probability that the applied model is valid within a wider concentration interval and different chemical compositions. Therefore, it should be taken into account that the manufactured alloys are very complex system, which are, due to numerous influential factors and complexities in the quantitative determination of the recovery rate, dependent on time and temperature. In spite of that, the applied model gave satisfactory data for its further use.

Conclusions
- Activation energy of the recovery process at a given temperature is a function of micro-hardness.
- Activation energy of the recovery process is directly proportional to the zirconium content.
- Zirconium influences the decrease of recovery rate, i.e. delays creep process and in this way, it may have the effect on the change of the required mechanical properties at the elevated working temperature.
- Presented mathematical model can be used for estimation and prediction of some mechanical properties of wrought heat-resistant Al alloys.

References