CALCULATION OF ACCELERATED STATIONARY CREEP RATE ACTIVATION ENERGY FOR A STEEL MICROSTRUCTURE WITH A UNIFORM DISTRIBUTION OF CARBIDE PARTICLES

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Recent research has shown a dependence of the accelerated creep rate on the carbide particle distribution in martensite, with the creep rate depending on the number of carbide particles per unit of surface and their mutual distance. The aim of our work was to calculate the activation energy for different carbide particle sizes and particle spacings, using a modified equation for the creep rate calculation. For creep-resistant steel with a microstructure of ferrite matrix and a uniform distribution of M23C6 carbide particles the creep rate was calculated in the temperature range 540 °C to 630 °C and a carbide particle size between 0.1 μm and 0.4 μm. An equal effect on the creep rate increase was found for all four carbide particle sizes. From the calculated creep rates a creep activation energy of 248.7 kJ/mol was calculated, independent of the particles size. The calculated creep activation energy was found to be close to the self-diffusion activation energy in α-iron.

Keywords: creep-resistant steel, microstructure, carbide particle size, calculation of creep rate, creep activation energy

1 INTRODUCTION

Recent research has shown that the accelerated creep rate depends on the carbide particle distribution in martensite, with the creep rate depending on the number of carbide particles per unit surface and their mutual distance. However, the equations used for the creep rate calculation do not usually take into account the size and the distribution of the carbides, thus limiting the possibility of analyzing these effects.

The solid-state reaction rate increases with temperature. The increase of the energy necessary for a reaction is defined by the Arrhenius equation, which for the creep rate increase can be written as:

$$ \dot{\varepsilon} = \dot{\varepsilon}_0 \cdot \exp \left( \frac{Q}{RT} \right) $$

(1)

where $\dot{\varepsilon}_0$ is the creep rate at temperature $T_0$, $Q$ is the creep activation energy, $R$ is the universal gas constant and $T$ is the creep temperature (K).

The microstructure of high-chromium creep-resistant steel consists of a dispersion of carbide particles in a matrix of ferrite, which is a solid solution of chromium, vanadium, niobium, molybdenum and other elements in α-iron. The quoted elements also form different carbide phases, e.g., MC and M23C6. The creep deformation occurs with dislocation movement, consisting of slip and climb. The creep deformation of ferrite is, therefore, the result of dislocation movement, with the creep rate is calculated as:

$$ \dot{\varepsilon} = \frac{b^2 \cdot \sigma \cdot \rho \cdot D}{k_B \cdot T \cdot G} $$

(2)

where $b$ is the α-iron Burgers vector, $\sigma$ is the acting stress, $\rho$ is the density of the mobile dislocations, $D$ is the iron self-diffusion coefficient, $k_B$ is the Boltzmann constant and $G$ is the matrix shear modulus.

The density of the mobile dislocations is calculated as:
The creep activation energy was proposed:

\[
\rho = \left( \frac{\sigma}{\alpha \cdot M \cdot G \cdot b} \right)^{2}
\]

where (constant) = 0.4, \( M = 3 \), and \( b \) is the Burgers vector.

The carbide particles in tempered martensite are obstacles to the dislocation movement. According to theoretical models the carbide particles can be surmounted either by a dislocation line looping or by the detachment of the dislocation line from the polyhedral free surface enveloping the carbide particles. \( ^{5-10} \) Recently, a model based on the effect of particles transferring acting stress on the dislocation movements was suggested and for the creep rate the following equation was proposed:

\[
\dot{\varepsilon} = \frac{c_a \cdot b^2 \cdot \sigma^2 \cdot \rho \cdot D \cdot (\lambda - d)}{k \cdot T \cdot G}
\]

where \( \lambda \) is the particle spacing, \( d \) is the particle size for a uniform distribution of particles and \( c_a \) is the parameter related to the effect of the particle distribution on creep rate = 1.

Using the stress exponent \( n = 3.65 \) a good fit between the calculated and the experimental creep rate was obtained for a uniform distribution of particles of two sizes. In equation (4) the parameters \( b, \sigma, \lambda, d \) and \( k \) are independent of the temperature, while the parameters \( \rho, D \) and \( G \) depend on the creep rate testing temperature. This means that by increasing the temperature at a constant stress, the creep rate will increase due to the lower shear modulus and the greater iron self-diffusion rate, enhanced by the greater mobility of vacancies.

The creep activation energy is the energy needed for a diffusion of one additional mole of atom to start. Accurate calculations of the creep activation energy are possible with two assumptions:

1. The presence of a uniform particle distribution, since creep is strongly affected by stringers of particles distributed along grain boundaries. \( ^{11} \)

2. In the range of the testing temperature, only the parameters \( \rho, D, T \) and \( G \) are changing in equation (4).

For this reason, reliable results on creep rates are obtained only in the temperature range where no change of average particles size and spacing occurs during the testing. However, significant changes in the quoted parameters of equation (4) and the microstructure may occur during long-term testing at sufficiently high temperatures. Accordingly, the calculated creep rate is affected by the change of these parameters. Due to changes in the microstructure, the creep rate and the activation energy are independent of the creep mechanism in these cases. Therefore, conclusions about the values of the activation energy \( ^{12-15} \) are based on insufficiently verified experimental data. Accordingly, the creep activation energy obtained without taking the changes of some influencing parameters into account was twice that calculated for the creep of the ferrite matrix.

Therefore, the aim of our work was to analyse the effect of carbide particle size and spacing on the creep rate and the creep activation energy. For this purpose the equation for the creep rate calculation was modified (eq. 4) in such a way that the size of the carbide particles and their mutual distance are taken into account.

### 2 ACTIVATION-ENERGY CALCULATION

A more correct creep activation energy can be calculated using the data of the creep rate calculated according to equation (4). First, equation (1) is written for the creep rate obtained at two different temperatures:

\[
\ln \dot{\varepsilon}_1 = \ln \dot{\varepsilon}_0 - \frac{Q}{RT_1} \quad \text{and} \quad \ln \dot{\varepsilon}_2 = \ln \dot{\varepsilon}_0 - \frac{Q}{RT_2}
\]

By subtracting both equations:

\[
\ln \dot{\varepsilon}_1 - \ln \dot{\varepsilon}_2 = \frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

the final equation for the creep activation energy calculation can be written as:

\[
Q = R \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \left( \ln \dot{\varepsilon}_1 - \ln \dot{\varepsilon}_2 \right)
\]

In eq. 4 the particle spacing can be expressed as:

\[
\lambda = \frac{4d}{\pi \cdot f^{1/3}}
\]

In this work the creep rate and the creep activation energy were calculated for the 0.18C11.5Cr0.29V steel in which a uniform distribution of \( M_23C_6 \) particles can be obtained by tempering at 800 °C. \( ^{16} \) The volume share of \( M_23C_6 \) carbide particles \( f \) can then be calculated according to:

\[
f = \frac{0.18 \cdot \frac{23\text{Cr}+6\text{C}}{6\text{C}}}{6.5 \cdot (12.82+0.487)}
\]

where 0.18 is the content of carbon in 100 g of steel, Cr and C are the atomic weights of chromium and carbon, 6.5 is the specific weight of \( \text{Cr}_2\text{C}_6 \) in g/cm\(^3\), 12.82 is the volume of 100 g of steel with a specific weight of 7.80 g/cm\(^3\) and 0.487 is the volume of carbide particles in 100 g of steel.

The creep rate was calculated for particle sizes of 0.10 μm, 0.20 μm, 0.30 μm and 0.40 μm and according to equation (7) particle spacings of 0.38 μm, 0.76 μm, 1.15 μm and 1.53 μm at temperatures of 540 °C, 570 °C, 600 °C and 630 °C. The iron self-diffusion coefficient for every temperature \( T \) was calculated using equation (9):

\[
D_1 = D_0 \cdot \exp \left( \frac{Q}{RT} \right)
\]
where the frequency factor for iron 
\[ D_0 = 2.8 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}, \]
and the activation energy \( Q = 251 \text{ kJ/mol} \).

At 630 °C the iron self-diffusion in ferrite is about 200 times slower than at the tempering temperature of 800 °C. From this it is evident that during creep tests, independently of the test time, no significant change in the particle size could be expected.

The values of the parameters used in equation (4) were as follows: \( b = 2.5 \times 10^{-10} \text{ m}, \ k_B = 1.381 \times 10^{-23} \text{ J/K}, \ \sigma = 170 \text{ MPa}, \ n = 3.65 \) as used in ref\(^4\), while the shear modulus was deduced from the data in ref\(^19\) for the P91 steel.

### 3 RESULTS

The temperature-dependent parameters \( D, G \) and \( \rho \) calculated for the investigated temperature range according to equations 3 and 9 and taken from ref\(^19\) are given in Table 1. On the other hand, the creep rates calculated for the given temperatures, particle sizes and spacings (eq. 7) according to equation 4 are summarized in Table 2, and the activation energy calculated for a particle size of 0.1 μm using equation 6 in Table 3.

#### Table 1: Calculated temperature-dependent parameters

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>( D )</th>
<th>( G )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>K</td>
<td>m²/s</td>
<td>MPa</td>
</tr>
<tr>
<td>540</td>
<td>813</td>
<td>2.09E-20</td>
<td>58600</td>
</tr>
<tr>
<td>570</td>
<td>843</td>
<td>7.83E-20</td>
<td>57400</td>
</tr>
<tr>
<td>600</td>
<td>873</td>
<td>2.68E-19</td>
<td>56000</td>
</tr>
<tr>
<td>630</td>
<td>903</td>
<td>8.46E-19</td>
<td>54600</td>
</tr>
</tbody>
</table>

#### Table 2: Creep temperature, particle size, calculated particle spacings and calculated creep rates

<table>
<thead>
<tr>
<th>Temperature, ( T )</th>
<th>Particle size, ( d )</th>
<th>Particles spacing, ( \lambda )</th>
<th>Creep rate, ( \dot{\epsilon} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>( \mu m )</td>
<td>( \mu m )</td>
<td>\text{s}^{-1}</td>
</tr>
<tr>
<td>540</td>
<td>0.10</td>
<td>0.38</td>
<td>7.25E-09</td>
</tr>
<tr>
<td>570</td>
<td>0.20</td>
<td>0.76</td>
<td>1.51E-08</td>
</tr>
<tr>
<td>600</td>
<td>0.30</td>
<td>1.15</td>
<td>2.38E-08</td>
</tr>
<tr>
<td>630</td>
<td>0.40</td>
<td>1.53</td>
<td>3.34E-08</td>
</tr>
<tr>
<td>813</td>
<td>0.10</td>
<td>0.38</td>
<td>2.68E-08</td>
</tr>
<tr>
<td>843</td>
<td>0.20</td>
<td>0.76</td>
<td>5.58E-08</td>
</tr>
<tr>
<td>873</td>
<td>0.30</td>
<td>1.15</td>
<td>8.79E-08</td>
</tr>
<tr>
<td>903</td>
<td>0.40</td>
<td>1.53</td>
<td>1.23E-07</td>
</tr>
</tbody>
</table>

In Figure 1 the dependences of creep rate versus creep temperature calculated for particle sizes of 0.1 μm and 0.4 μm are shown. For both particle sizes the increase of the temperature causes an increase in the creep rate. In the case of a particle size of 0.1 μm the creep rate increased from 7.25E-09 s⁻¹ to 2.84E-07 s⁻¹ as the temperature increased from 540 °C to 630 °C, thus showing an almost linear dependence on the temperature. The same is true for large particles. However, the creep rate in the case of a particle size of 0.4 μm is 4.6 times larger than calculated for the particle size of 0.1 μm, as shown in Table 2 and Figure 1.

The dependence of the creep rate increase in the temperature range from 540 °C to 630 °C versus particle size is shown in Figure 2, and the Arrhenius dependence

#### Table 3: Creep activation energy for different temperature ranges for a particle size of 0.1 μm

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>( T_1/K )</th>
<th>( T_2/K )</th>
<th>( \dot{\epsilon}_{s1}/\text{s}^{-1} )</th>
<th>( \dot{\epsilon}_{s2}/\text{s}^{-1} )</th>
<th>( Q/(\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>813 – 843</td>
<td>813</td>
<td>843</td>
<td>2.68E-08 – 9.07E-08</td>
<td>2.84E-07 – 2.84E-07</td>
<td>248.0 – 249.1</td>
</tr>
<tr>
<td>843 – 873</td>
<td>843</td>
<td>873</td>
<td>7.25E-09 – 9.07E-08</td>
<td>7.25E-09 – 2.84E-07</td>
<td>249.1 – 248.7</td>
</tr>
<tr>
<td>873 – 903</td>
<td>873</td>
<td>903</td>
<td>7.25E-09 – 9.07E-08</td>
<td>7.25E-09 – 2.84E-07</td>
<td>248.0 – 249.1</td>
</tr>
</tbody>
</table>

#### Figure 1: Dependence of accelerated creep rate versus temperature for particle sizes 0.10 μm and 0.40 μm

#### Figure 2: Dependence of creep rate increase versus particle size during an increase of temperature from 540 °C to 630 °C

Slika 1: Odvisnost med izračunano hitrostjo lezenja v temperaturo za velikosti izločkov 0.10 μm in 0.40 μm

Slika 2: Odvisnost spremembe hitrosti lezenja od velikosti izločkov pri povišanju temperature iz 540 °C na 630 °C
4 DISCUSSION

From Figure 3 it is evident that in the examined temperature range of 90 °C (difference from 540 °C to 630 °C), the log of the creep rate decreases inversely in proportion to the temperature, independently of the particle size. However, as shown in Figure 1, the creep rate is greater for coarse particles and greater particle spacings. Furthermore, the effect of temperature on the creep rate increase was found to be more pronounced for the microstructure with coarser particles, as shown in Figure 2. With an increase of the particle size from 0.10 μm to 0.40 μm, thus by a factor of 4, the creep rate increased from 2.76E–07 to 1.27E–06, this is for a factor of 4.61, being almost linear. The effect of temperature on the creep rate was found to be virtually equal for all the particle sizes that were investigated (Figure 1), as indicated by the equal slope of dependence, which corresponds to an activation energy of 248.7 kJ/mol. The calculated activation energy differs little from the self-diffusion activation energy of 241 kJ/mol to 268 kJ/mol, quoted in [3,18].

The results show an equal creep activation energy for martensite with different particle sizes. Although the particle size ratio changes by a factor of 4, the volume ratio by a factor of 64 and the particle spacing ratio by a factor of 4.03 this does not affect the creep activation energy. The small difference between the creep activation energy and the self-diffusion activation energy observed in this work suggests that also atoms in solid solution in ferrite have only a limited effect on the creep activation energy.

5 CONCLUSIONS

The creep rate was calculated for the steel microstructure of tempered martensite with $\text{M}_6\text{C}_6$ particles ranging from 0.10 μm to 0.40 μm, and for the temperature range 540 °C to 630 °C. Based on the results the following conclusions can be made for the range of examined temperatures and particle sizes:

- the creep rate increases inversely in proportion to the creep temperature;
- the creep activation energy of 248.7 kJ/mol is independent of the particle size and spacing;
- the elements in solid solution in ferrite may have only a very limited effect on the creep activation energy;
- with an increase in the temperature, the creep rate increase is more pronounced for coarser particle sizes.

6 REFERENCES