UDK 669.14.018.44:546.261
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 46(6)661(2012)

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

IZRAČUN AKTIVACIJSKE ENERGIJE ZA STACIONARNO HITROST LEZENJA ZA JEKLO Z MIKROSTRUKTURO Z ENAKOMERNO PORAZDELITVIJO KARBIDNIH IZLOČKOV

Borut Žužek, Franc Vodopivec, Bojan Podgornik, Monika Jenko, Matjaž Godec

Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
borut.zuzek@imt.si

Prejem rokopisa – received: 2012-10-05; sprejem za objavo – accepted for publication: 2012-10-15

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 $M_{23}C_6$ 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

Dosedanje raziskave kažejo povezavo med porazdelitvijo karbidnih delcev v martenzitu in hitrostjo pospešenega lezenja, pri čemer je hitrost lezenja odvisna od števila karbidnih delcev na enoto površine in njihove medsebojne razdalje. Cilj našega dela je bil izračun aktivacijske energije za različne velikosti karbidnih delcev in njihovih medsebojnih razdalj. Izračun je temeljil na modificirani enačbi za izračun hitrosti lezenja. Aktivacijska energija procesa lezenja je bila izračunana za jeklo, odporno proti lezenju, z mikrostrukturo iz ferita in enakomerno porazdelitvijo karbidnih izločkov $M_{23}C_6$. Izračun je bil izdelan za temperaturno območje od 540 °C do 630 °C in velikost karbidnih zrn med 0,1 µm in 0,4 µm. Rezultati izračuna so pokazali enako povečanje hitrosti lezenja za vse 4 velikosti karbidnih izločkov. Na podlagi hitrosti lezenja je bila izračunana tudi aktivacijska energija lezenja v vrednosti 248,7 kJ/mol, ki se je izkazala za neodvisno od velikosti izločkov. Izračunana aktivacijska energija procesa lezenja se le malo razlikuje od aktivacijske energije za samodifuzijo v α-železu.

Ključne besede: jeklo, odporno proti lezenju, mikrostruktura, velikost karbidnih izločkov, izračun hitrosti lezenja, aktivacijska energija za lezenje

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.[1,2] 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:[3]

$$\dot{\varepsilon} = \dot{\varepsilon}_i \cdot \exp^{-\left(\frac{Q}{RT}\right)} \tag{1}$$

where $\dot{\varepsilon}_i$ is the creep rate at temperature T_i, 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 $M_{23}C_6$. The creep deformation occurs with dislocation movement, consisting of slip and climb.[3,4] The creep deformation of ferrite is, therefore, the result of dislocation movement, with the creep rate is calculated as:[5,6]

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

where b is the α-iron Burgers vector, σ is the acting stress, ρ 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:[7]

$$\rho = \left(\frac{\sigma}{\alpha \cdot M \cdot G \cdot b} \right)^2 \tag{3}$$

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 polyhedric 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:

$$\dot{\varepsilon} = \frac{c_d \cdot b^2 \cdot \sigma^n \cdot \rho \cdot D \cdot (\lambda - d)}{k \cdot T \cdot G} \tag{4}$$

where λ is the particle spacing, d is the particle size for a uniform distribution of particles and c_d 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, σ, λ, d and k are independent of the temperature, while the parameters ρ, 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 ρ, 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:

$$\ln \dot{\varepsilon}_1 = \ln \dot{\varepsilon}_0 - \frac{Q}{RT_1} \quad \text{and} \quad \ln \dot{\varepsilon}_2 = \ln \dot{\varepsilon}_0 - \frac{Q}{RT_2} \tag{5}$$

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:

$$Q = \frac{R(\ln \dot{\varepsilon}_1 - \ln \dot{\varepsilon}_2)}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \qquad 6)$$

In eq. 4 the particle spacing can be expressed as:[5]

$$\lambda = \frac{4d}{\pi \cdot f^{1/3}} \tag{7}$$

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 $M_{23}C_6$ particles can be obtained by tempering at 800 °C.[16] The volume share of $M_{23}C_6$ carbide particles f can then be calculated according to[17]:

$$f = \frac{0.18 \left(\frac{23Cr + 6C}{6C} \right)}{6.5 \cdot (12.82 + 0.487)} \tag{8}$$

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 $Cr_{23}C_6$ 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):

$$D_T = D_0 \cdot \exp^{-\left(\frac{Q}{RT} \right)} \tag{9}$$

where the frequency factor for iron $D_0 = 2.8\ 10^{-4}\ m^2\ s^{-1}$, and the activation energy Q = 251 kJ/mol.[18]

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: $b = 2.5 \cdot 10^{-10}$ m, $k_b = 1.381 \cdot 10^{-23}$ J/K, σ = 170 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 ρ 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
Tabela 1: Parametri, odvisni od temperature, upoštevani pri izračunih

Temperature, T		D	G	ρ
°C	K	m^2/s	MPa	m^{-2}
540	813	2.09E–20	58600	9.35E+13
570	843	7.83E–20	57400	9.75E+13
600	873	2.68E–19	56000	1.02E+14
630	903	8.46E–19	54600	1.08E+14

Table 2: Creep temperature, particle size, calculated particle spacings and calculated creep rates
Tabela 2: Temperature lezenja, velikosti izločkov, izračunane razdalje med izločki in izračunane hitrosti lezenja

Temperature, T		Particle size, d	Particles spacing, λ	Creep rate, $\dot{\varepsilon}$
°C	K	µm	µm	s^{-1}
540	813	0.10	0.38	7.25E–09
		0.20	0.76	1.51E–08
		0.30	1.15	2.38E–08
		0.40	1.53	3.34E–08
570	843	0.10	0.38	2.68E–08
		0.20	0.76	5.58E–08
		0.30	1.15	8.79E–08
		0.40	1.53	1.23E–07
600	873	0.10	0.38	9.07E–08
		0.20	0.76	1.89E–07
		0.30	1.15	2.98E–07
		0.40	1.53	4.18E–07
630	903	0.10	0.38	2.84E–07
		0.20	0.76	5.91E–07
		0.30	1.15	9.32E–07
		0.40	1.53	1.31E–06

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
Tabela 3: Aktivacijska energija za lezenje pri različnih temperaturnih območjih za velikost delcev 0,1 µm

T_1/K	813	843	873	813
T_2/K	843	873	903	903
ε_1/s^{-1}	7.25E–09	2.68E–08	9.07E–08	7.25E–09
ε_2/s^{-1}	2.68E–08	9.07E–08	2.84E–07	2.84E–07
Q/(kJ/mol)	248.0	248.9	249.1	248.7
$Q_{average}$/(kJ/mol)	248.7			

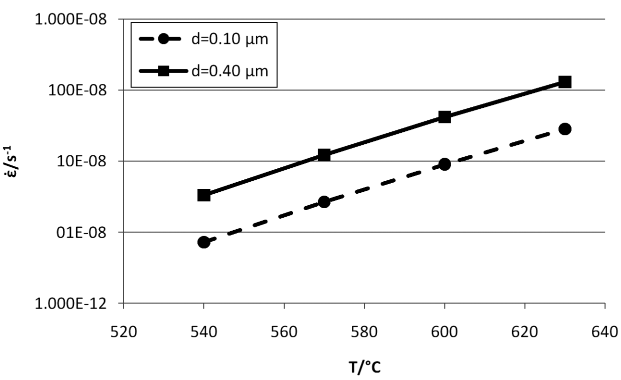

Figure 1: Dependence of accelerated creep rate versus temperature for particle sizes 0.10 µm and 0.40 µm
Slika 1: Odvisnost med izračunano hitrostjo lezenja in temperaturo za velikosti izločkov 0,10 µm in 0,40 µm

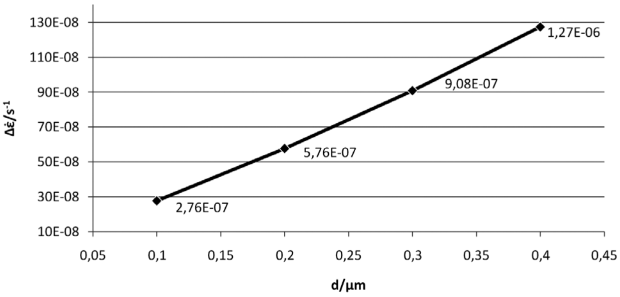

Figure 2: Dependence of creep rate increase versus particles size during an increase of temperature from 540 °C to 630 °C
Slika 2: Odvisnost spremembe hitrosti lezenja od velikosti izločkov pri povišanju temperature iz 540 °C na 630 °C

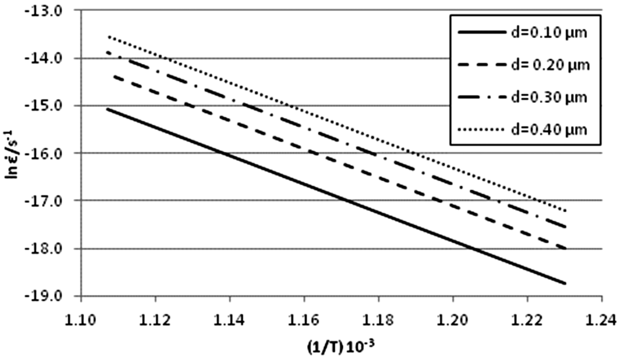

Figure 3: Arrhenius dependence in temperature range 540 °C to 630 °C for different particle sizes

Slika 3: Arrheniusova odvisnost v razponu temperature od 540 °C do 630 °C za različne velikosti izločkov

given in **Figure 3**. From **Figure 2** it is clear that for a temperature increase of 90 °C the creep rate increase for the smallest particle size of 0.10 μm is 2.76E–07 s^{-1} and this increases to 1.27E–06 s^{-1} for the largest particles size (0.40 μm). Furthermore, as the particles become larger also the rate of increase in the creep rate increase gets larger. Finally, as shown in **Figure 3**, for all the particle sizes included in this investigation, the lg of creep rate was found to decrease inversely in proportion to the temperature.

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 α-iron 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 $M_{23}C_6$ 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

[1] F. Vodopivec, J. Vojvodič - Tuma, B. Šuštaršič, R. Celin, M. Jenko, Mater. Sci. Technol., 27 (**2011**) 5, 937–942

[2] F. Vodopivec, J. Vojvodič - Tuma, M. Jenko, R. Celin, B. Šuštaršič, Steel Research Int., 81 (**2010**) 7, 576–580

[3] R. W. K. Honeycombe, The Plastic Deformation of Metals, Edward Arnold, London 1984, 91

[4] R. E. Reed - Hill, R. Abbaschian, Physical Metallurgy Principles, 3th ed., Pws Publ. Comp., 1994, 118–119

[5] M. F. Ashby, The mechanical effects of a dispersion of a second phase, Proc. Sec. Int. Conf. On Strength of Metals and Alloys, 1970, 507–541

[6] E. Hornbogen, Einfluss von Teilchen einer zweiten Phase auf das Zeitverhalten, Festigkeits und Bruchverhalten bei höheren Temperaturen, Verl. Stahleisen, Düsseldorf 1980, 31–52

[7] K. Maruyama, K. Sawada, J. Koike, ISIJ Intern., 41 (**2001**), 641–653

[8] E. Artz, D. S. Wilkinson, Acta Metall., 34 (**1986**), 1893–1898

[9] E. Artz, J. Rösler, Acta Metall., 36 (**1988**), 1053–1060

[10] J. Rösler, E. Artz, Acta Metall., 36 (**1988**), 1043–1051

[11] J. Čadek, V. Šustek, M. Pahutova, Mater. Sci. Eng., A 225 (1**997**), 22–28

[12] V. Sklenička, K. Kuharova, A. Dlouhy, J. Krejči, Materials for Advanced Power Engineering, part I, Kluver Academic Publishers, 1994, 435–444

[13] B. Ule, A. Nagode, Mater. Sci. Technol., 23 (**2007**), 1367–1374

[14] B. Ule, A. Nagode, Scripta Mater., 57 (**2007**), 405–408

[15] S. Spigarelli, E. Cerri, P. Bianchi, E. Evangelista, Mater. Sci. Technol., 15 (**1999**), 1433–1440

[16] D. A. Skobir, F. Vodopivec, M. Jenko, S. Spaić, B. Markoli, Z. Metallkd., 95 (**2004**) 11, 1020–1024

[17] F. Vodopivec, D. A. Skobir-Balantič, M. Jenko, B. Žužek, M. Godec, Mater. Tehnol., 46 (**2012**) 6, 633–636

[18] H. Oikawa, Y. Iijima, Diffusion behaviour of creep resistant steels, Ed. F. Abe, T. U. Kern, R. Viswanathan, Creep resistant steels, Woodhead Publ. LTD., Cambridge, England 2008, 241–266

[19] Y. F. Yin, R. G. Faulkner, Physical and elastic behaviour of creep resistant steels, Ed. F. Abe, T. U. Kern, R. Viswanathan, Creep resistant steels, Woodhead Publ. LTD., Cambridge, England 2008, 217–240