

EFFECT OF CHANGE OF CARBIDE PARTICLES SPACING AND DISTRIBUTION ON CREEP RATE OF MARTENSITE CREEP RESISTANT STEELS

VPLIV SPREMEMBE RAZDALJE MED KARBIDNIMI IZLOČKI IN NJIHOVE PORAZDELITVE NA HITROST LEZENJA MARTENZITNIH JEKEL, ODPORNIH PROTI LEZENJU

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The creep rate dependence of particles coarsening and spacing as well as distribution in analysed considering quoted equations. A simple method for assessment of particle spacing is proposed. Accelerated creep rates at 580 °C for CrV and CrVNb steel after different tempering times at 800 °C and 650 °C are calculated and determined experimentally. The rate of microstructural processes increases the creep rate at 800 °C in the CrV steel by 36 times and in the CrVNb by 57 times greater.

Key words: creep resistant steel, creep rate, carbide particles, particles spacing, distribution of particles, tempered martensite

Matematično smo analizirali odvisnost hitrosti lezenja od rasti izločkov in njihove medsebojne razdalje ter porazdelitve. Predlagali smo preprosto metodo za oceno medsebojne razdalje med izločki. Izračunali in eksperimentalno smo določili pospešene hitrosti lezenja pri 580 °C za jekli CrV in CrVNb po različnih časih žarjenja pri 800 °C in 650 °C. Mikrostrukturni procesi, ki vplivajo na zvišano hitrost lezenja, potekajo v jeklu CrV 36-krat hitreje in v jeklu CrVNb 57-krat hitreje pri 800 °C.

Ključne besede: jekla odporna proti lezenju, hitrost lezenja, karbidni izločki, razdalja med karbidnimi izločki, porazdelitev izločkov, popuščeni martenzit

1 INTRODUCTION

Modern creep resistant steels have a microstructure consisting of a distribution of carbide particles in ferrite with a significant content of chromium and molybdenum in solid solution.^{1,2} In these steels particles of intermetallic (Lawes) phases are also found,^{3,4} depending on steel composition and tempering temperature. These particles are generally much coarser than carbide particles,^{3,4} have a minor effect on creep rate and will be omitted in further discussion. The great majority of particles consists of carbides with different stability at increased temperatures, mostly of $M_{23}C_6$ and MC particles. The composition of $M_{23}C_6$ particles depends on annealing temperature, however, the content of chromium is always much higher than the contents of iron and molybdenum.^{5,6} MC particles are mostly vanadium and niobium carbides that may also have a minor content of nitrogen.

The effect of temperature on the solubility of carbide phases is given by the general relation:

$$\lg [M] [C] = A + (B/T) \quad (1)$$

with $[M]$ and $[C]$ mass fractions of elements in solid solution in ferrite, A and B – constants and T/K – temperature.

At low solubility, particles are more stable and coarsen slower because, according to the LSW equation (2), the

coarsening rate depends of volume diffusion transport, which is smaller by low content of carbide forming elements in substitutional solution in ferrite. The solubility products for carbides in ferrite were established for VC and NbC in structural steels with a much lower content of chromium.^{7,8} These products can not be used reliably for creep resisting steels with much higher content of chromium which is a strong carbide forming element and may affect the solubility of MC carbides. Based on a thermodynamic analysis and on solubility product of VC in structural steel, it was calculated that at 873 K (600 °C) the solubility of NbC particles in ferrite was for one order of magnitude lower than for VC carbide.⁹ The solubility can be deduced also by Thermocalc analysis.

The coarsening rate of carbide particles is calculated applying the Lifshitz-Slyozov-Wagner¹⁰ (LSW) equation:

$$\Delta d^3 = d_t^3 - d_0^3 = 8 S \gamma \Omega D t / 9 k_B T \quad (2)$$

With d_t – particles size at tempering time t , d_0 – initial particles size, S – content of carbide constituting metal in solution in the matrix, γ – carbide particle matrix interfacial energy, Ω – volume of diffusing atoms, k_B – Boltzmann constant, D – diffusion coefficient and T – temperature in K. In ref.¹¹ the exponent 2 was proposed for coarsening of grain boundary particles.

For the 0.18C-11.7Cr-1Mo-0.29V steel, the experimental coarsening rate based on the assessment of particles size after tempering of steel specimens up to 1356 h

at 800 °C was $k_{cc} = 1.48 \times 10^{-26} \text{ m}^3 \text{ s}^{-1}$ and in acceptable agreement with the coarsening rate $d^3_{cc} = 7.25 \times 10^{-27} \text{ m}^3 \text{ s}^{-1}$ deduced applying the LSW equation.¹² The increase of size of particles at a determined temperature can be calculated using the simple relation:^{11,12,13,14}

$$\Delta d^3 = k_{ci} t \quad (3)$$

with k_{ci} – isothermal coarsening rate.

Based on the acceptable agreement of calculated and experimental coarsening rate at 800 °C, assuming that by change of temperature in equation (1) only the diffusion constant changed and using as base the coarsening rate calculated for the temperature 800 °C, for the calculation of coarsening rate of $M_{23}C_6$ particles in range 550 °C to 800 °C the relation was obtained:¹²

$$d^3_{cc,T} = k_{cc,Cr,1073} (D_{Cr,T}/D_{Cr,1073}) (T/1073) t \quad (4)$$

with k_{cc} – calculated coarsening rate at 800 °C, T/K – temperature, D – diffusion constant, t/s – time.

The coarsening rate of $2.89 \times 10^{-27} \text{ m}^3 \text{ s}^{-1}$ at 750 °C was calculated for $M_{23}C_6$ particles in the steel 0.18C-11.7Cr-1Mo-0.29V using this equation and $S = 0.277 \text{ J m}^{-2}$ very similar to that reported in ref.¹⁵ of $2.82 \times 10^{-27} \text{ m}^3 \text{ s}^{-1}$ calculated using a model based on equations (1) and (2). At low temperature the differences obtained using equation (4) and experimental data on assessment particle size may be affected by the simultaneous coarsening of particles of different carbides.

For the calculation of the coarsening rate for VC particles at the temperature of 650 °C a modification of equation (4) was proposed with introducing of proper ratio of parameters for chromium and vanadium¹² in equation (1), thus:

$$\begin{aligned} k_{cc,VC} &= k_{cc,Cr} (S_V D_{V,K} \gamma_{M_{23}C_6} \Omega_V / S_{Cr} D_{Cr,K} \gamma_{MC} \Omega_{Cr}) \\ k_{cc,v,923K} &= 4.77 \times 10^{-29} \times 0.01623 = \\ &= 1.28 \times 10^{-31} \text{ m}^3 \text{ s}^{-1} \end{aligned} \quad (5)$$

For the 0.18C-11.7Cr-1Mo-0.29V steel and the temperature of 650 °C the calculated coarsening rate for VC particles was for about two orders of magnitude lower than for $M_{23}C_6$ particles.¹²

Creep increases the number of mobile dislocations in steel and for the calculation of the density of these dislocations the relation was proposed^{12,16}:

$$\rho = \sigma / \alpha M G b \quad (6)$$

with σ/MPa – stress, $\alpha = 0.4$ – constant $M = 3$ (Taylor factor), G – shear modul at creep temperature and b – Burgers vector.

By creep tests at 923 K by 80 MPa stress of a 0.14C-12Cr-1.5Mo-0.2V-0.05Nb-0.05N steel the size of MX particles was assessed in grip and in gauge of tested specimens.¹⁷ Using the simplified relation $\Delta d^3 = k_{ci} t$ it was deduced that the coarsening rate was 3.73 times greater in the gauge than in the grip part of specimens and, according to equation (6), the density of mobile dislocations¹² in the gauge part of specimen was of $2.40 \times 10^{13} \text{ m}^{-2}$. The increased coarsening of particles in

gauge part of specimens is ascribed to higher density of mobile dislocations.

For the dependence of creep rate on different physical parameters related to the tested steel the equation was proposed:^{18, 19}

$$\dot{\epsilon} = \left(\frac{b^2}{k_B T G} \right) \lambda \rho \sigma^2 D \quad (7)$$

with: $\dot{\epsilon}$ – creep rate, b – Burgers vector, k_B – Boltzmann constant, T/K – temperature, G – shear modulus, σ – acting stress, D – diffusion coefficient and ρ – density of mobile dislocations.

A better fit to experimental values of creep rate was found by modification of equation (7) with introduction of a constant (A) accounting also for particles spacing, a stress exponent $n > 2$, the rationalisation of the stress σ with the shear modulus and yield stress at creep temperature and the threshold stress σ_{th} , below which, theoretically, no creep could occur²⁰:

$$\dot{\epsilon} = A \left(\frac{D G b}{k_B T} \right) \left(\frac{\sigma - \sigma_{th}}{G} \right)^n \quad (8)$$

In the detachment concept of interaction of particles and mobile dislocations the particle size is included, as parameter of a real microstructure:^{21, 22, 23, 24}

$$E = G b^2 r \left[(1-k) \left(1 - \frac{\sigma}{\sigma_d} \right) \right]^{3/2} \quad (9)$$

$$\dot{\epsilon} = \left(\frac{6 \lambda \rho}{k_B T} \right) \cdot \exp \left(- \frac{E}{k_B T} \right) \quad (10)$$

with E – creep activation energy, σ_d – detachment stress, r – average particles size and the relaxation parameter $k = T_p/T_m$, with T_m – dislocation line energy in the matrix and T_2 – the dislocation line energy decreased by the attraction force precipitate – dislocation. The value of the parameter k is ($0 < k < 1$).

Theoretically, creep and self diffusion activation energies for pure α iron are about 300 kJ/mol.²⁵ On the base of lifetime of specimens tested at different temperatures,²⁶ creep activation energies of about 600 kJ/mol were calculated.^{27,28} In ref.²⁹ it is suggested that the difference may be related partially to the increase of creep rate due to the change of distribution of particles during creep tests.

The differences in creep rate for 0.18C-11.7Cr-1Mo-0.29V tempered for 672 h and 1356 h at 800 °C calculated according to equation (7) and experimental creep rate were of 1.53 and 2.26 times, while it was of several sizes of magnitudes greater if calculated according to equation (9). This indicates as unreliable the detachment model of interaction of a mobile dislocation and carbide particles in creep resistant steels with the microstructure of tempered martensite.²⁹ In all quoted equations it is assumed that the distribution of particles in ferrite is uniform. However, in steels the particles dis-

tribution is not uniform, since by tempering of martensite carbide particles are precipitated at grain boundaries and subboundaries and in the interior of grains and the coarsening rate is greater for particles situated at grain boundaries, where the diffusion rate is greater.

In investigations on 0.18C-11.7Cr-1Mo-0.29V steel tempered for 2 h to 1356 h at 800 °C³⁰ it was found that the average $M_{23}C_6$ particles size (d) increased with tempering time (t) as $d^3 = 1.48 \times 10^{-26} \times t \text{ m}^3 \text{ s}^{-1}$, which is much slower than the rate of decrease of the number of carbide stringers of $n_s = 3.15 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$. The difference is related to the difference in volume and boundary diffusion rate. Accordingly, the delaying effect of stringers on creep rate, which is very strong by sufficient stringers density, is ended relatively fast and by a critical stringers density of about $0.5 \times 10^2 \text{ mm}^{-2}$ the creep rate is increased for about one order of magnitude (Figure 1).

The particle spacing (λ) can be calculated from the relation¹⁸:

$$\lambda = (4d/\pi \cdot f^{1/3}) \quad (11)$$

with f – volume share of carbides in the investigated steel.

Assuming that carbide particles are uniformly distributed in the micrograph and situated in the centre of a square with the side equal to particles spacing, the spacing could be deduced without prior assessment of particles size and knowledge of the volume fraction of the carbide phases with the relation:

$$\lambda = (F/N)^{1/2} \quad (12)$$

with F – as surface of a micrograph with N carbide particles.

As mentioned earlier, the creep rate for the 0.18C-11.7Cr-1Mo-0.29V steel was calculated using equation (7) for two points in Figure 1 below the critical stringers density using the particles spacing deduced according to

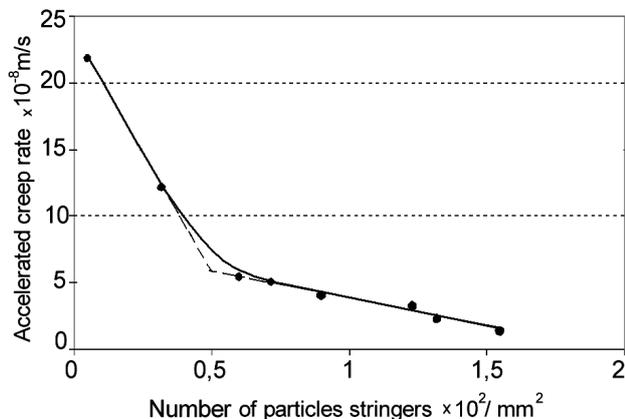


Figure 1: 0.18C-11.7Cr-1Mo-0.29V steel. Dependence of accelerated creep rate on the number of grain boundary stringers of carbide particles in tempered martensite²⁹

Slika 1: Jeklo 0.18C-11.7Cr-1Mo-0.29V. Odvisnost pospešene hitrosti lezenja od števila nizov karbidnih izločkov po mejah zrn v popuščenem martenzitu²⁹

relation (11), the calculated volume of $M_{23}C_6$ carbide content and experimentally assessed average particles size.

Specimens of a 0.18C-11Cr-0.94Mo-0.31V (steel a) and 0.10C-7.9Cr-0.98Mo-0.23V-0.11Nb (steel b) steels with microstructure in Figures 2, 3 and 4 were cut out

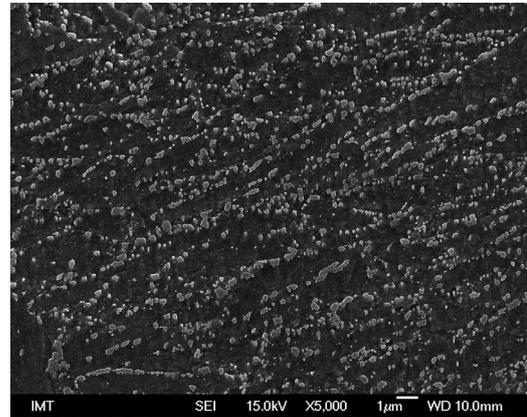


Figure 2: Initial microstructure of steel (a)
Slika 2: Izhodna mikrostruktura jekla (a)

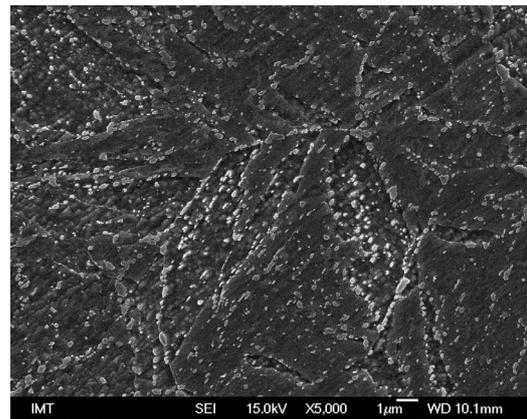


Figure 3: Initial microstructure of steel (b)
Slika 3: Izhodna mikrostruktura jekla (b)

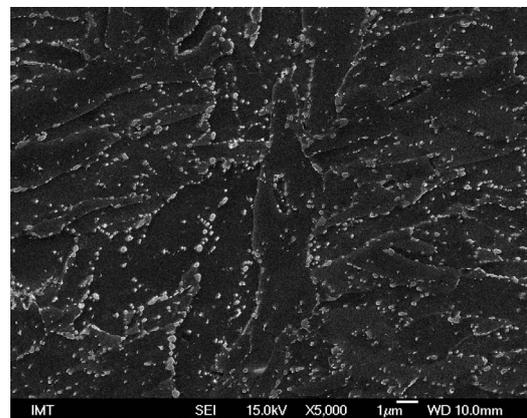


Figure 4: Microstructure of steel (b) after 1 year of tempering at 650 °C

Slika 4: Mikrostruktura jekla (b) po enem letu žarjenja na 650 °C

Table 1: Experimental and calculated creep rate for specimens of steels a) 0.18C-11.7Cr-1Mo-0.29V, b) 0.2C-11Cr-0.94Mo-0.31V and c) 0.10C-7.9Cr-0.98Mo-0.23V-0.11Nb tempered for different times at 800 °C and 650 °C. Test temperature 580 °C, stress 170 MPa and time 100 h.

Tabela 1: Eksperimentalne in izračunane vrednosti hitrosti lezenja za vzorce jekel a) 0.18C-11.7Cr-1Mo-0.29V, b) 0.2C-11Cr-0.94Mo-0.31V in c) 0.10C-7.9Cr-0.98Mo-0.23V-0.11Nb, žarjene različno dolgo pri 800 °C in 650 °C. Temperatura preskušanja 580 °C, napetost 170 MPa in čas 100 h.

Tempering	Particles spacing λ (10^{-6} m)	Creep rate (s^{-1})		Exp./cal.
		experimental	calculated	
800 °C, 672 h, a	1.24	12.2×10^{-8}	7.93×10^{-8}	1.53
800 °C, 1356 h, a	1.50	21.8×10^{-8}	9.62×10^{-8}	2.26
650 °C, 2h, b	0.53	4.76×10^{-8}	3.39×10^{-8}	1.41
650 °C, 8760 h, b	0.61	10.2×10^{-8}	3.90×10^{-8}	2.61
650 °C, 2 h, c	0.507	1.47×10^{-8}	3.24×10^{-8}	0.45
650 °C, 8760 h, c	0.508	2.03×10^{-8}	3.25×10^{-8}	0.62

from industrial tubes and tempered for up to 8760 h (1 year) at 650 °C.³¹ For both steels the accelerated creep rate was determined with 100 h static test at 580 °C and the load of 170 MPa, as for the earlier mentioned steel.³⁰ For the steel (a), the particles spacing was calculated using equation (11) and particles size assessed on SE micrographs at magnification 10^4 and 2×10^4 times, while the particles spacing for steels (b) and (c) was calculated using equation (12) and particles counting on SE micrographs at magnification of 5×10^3 times, where only particles with size of about 0.1 μm (about 20 nm) and more were discernible, sufficiently clearly.

In **Table 1** particles spacings, calculated as well as experimental creep rates are given.

By steel (a) and (b) the ratio of experimental and calculated creep rate is above 1 for both tempering temperature, while it is below 1 for the steel (c) tempered at 650 °C. The different ratio of calculated and experimental rate for the steel (c) may be explained assuming that after both tempering temperatures by steels (a) and (b) on used SE micrographs the great majority of both kinds of carbide particles ($M_{23}C_6$ and VC) was visible, while the resolution of micrographs of steel (c) was too small for NbC particles. This explanation is supported by the different stability of carbides, since after tempering at 800 °C in steel (a) consisted only of $M_{23}C_6$ particles, in steel (b) at 650 °C of $M_{23}C_6$ and VC and in steel (c) of $M_{23}C_6$, VC and NbC particles. Data in **Table 1** indicate that the difference between calculated and experimental creep rate is greater after longer tempering time at both temperatures and independent of particles spacing. As the creep rate is related to the density of particles stringers, it is concluded, that also by longer tempering at 650 °C creep rate was changed by decrease of the effect of stringers of particles.

3 CONCLUSIONS

The following conclusions on the effect of changes in microstructure, i.e. changes in spacings and distribution of carbide particles, are based on data from quoted references and on results of investigations of three creep resistant steels.

- a simple method for assessment of particles spacing was devised based on the assumption that all particles in a micrographs are situated in the centre of a square with the side equal to particles spacing;
- the creep rate delaying effect of stringers of carbide particles at grain and subgrain boundaries is significantly stronger than the effect of particles distributed uniformly in the grains interior;
- when by tempering of the steel the density of particles stringers (number of stringers per unity of the examined surface) is diminished rapidly below a critical level, the creep rate is increased strongly, for about one order of magnitude, in case of tempering the 0.18C-11.7Cr-1Mo-0.29V steel at 800 °C;
- the creep rates determined experimentally and calculated using the Ashby equation with the stress exponent $n = 2$ agree acceptably and differences of both rates depend also on the distribution of particles. The effect of distribution of particles was confirmed for steels with the microstructure with only $M_{23}C_6$ as well as microstructures with $M_{23}C_6$, VC and NbC particles.
- at 650 °C the effect of tempering time on change of distribution of particles is much lower than at 800 °C. In the first case the creep rate was increased 12.1 times after 1356 h of tempering, while at 650 °C, the creep rate was increased for 2.14 times for the CrV steel and 1.38 times for the CrVNb steel after 8760 h of tempering. Thus the processes occurring in microstructure by tempering at 800 °C decrease the CrV creep resistance for about 36 times faster for the CrV steel and 57 times for the CrVNb steel than processes at the for 150 °C lower temperature of 650 °C.

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