NUCLEATION AND GROWTH OF $M_{23}C_6$ PARTICLES IN HIGH-CHROMIUM CREEP-RESISTANT STEEL

NUKLEACIJA IN RAST IZLOČKOV $M_{23}C_6$ V KROMOVEM JEKLU, ODPORNEM PROTI LEZENJU

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The nucleation of $M_{23}C_6$ particles occurs on the surface of Fe_3C particles with a high content of chromium. The initially high content of iron decreases and the chromium increases to about $Cr_{18}Fe_3Mo_2C_6$, in equilibrium with the ferrite composition. The nucleation and growth of the $M_{23}C_6$ particles depend on the carbide's Gibbs free energy, the content and the diffusion afflux of the carbide-forming elements in solid solution in the ferrite. A simple method is proposed for calculating the average spacing and the average size of the carbide particles in steel with a microstructure of tempered martensite.

Keywords: creep-resistant steel, $M_{23}C_6$ particles, nucleation and growth, assessment of particle spacing and size

Nukleacija izločkov $M_{23}C_6$ poteka na površini izločkov Fe_3C z visoko vsebnostjo kroma. V začetku je vsebnost kroma v izločkih $M_{23}C_6$ visoka, nato pa s trajanjem žarjenja zraste do sestave približno $Cr_{18}Fe_3Mo_2C_6$, ki je v ravnotežju s sestavo ferita. Nukleacija in hitrost rasti sta odvisni od Gibbsove proste energije karbidov ter od vsebnosti in difuzijskega pritoka karbidotvornih elementov v trdni raztopini ferita. Predložena je enostavna metoda za izračun povprečne razdalje in velikosti izločkov v jeklu z mikrostrukturo iz popuščenega martenzita.

Ključne besede: jeklo, odporno proti lezenju, izločki $M_{23}C_6$, nukleacija in rast, povprečna velikost in razdalja med izločki

1 NUCLEATION

High-chromium creep-resistant steels have a microstructure of tempered martensite consisting of a dispersion of different carbide particles in ferrite.[1,2] Steels contain the carbide-forming elements chromium, molybdenum, vanadium, niobium and other elements bound to carbides and in a solid solution of ferrite at the operating temperature of thermal power plants. By tempering of quenched steel, carbide particles precipitate from the solid solution in martensite and grow, with the coarsening rate depending on the temperature, the diffusion rate, the content and the atomic volume of the constituent metals, the particle-ferrite interfacial energy and other physical parameters.[3] All carbide-forming metals are in a substitution solid solution and their diffusion rate is several orders of magnitude lower than for interstitial carbon. Therefore, carbon diffusion is without significant influence on the rate of nucleation and coarsening of the carbide particles. For a given content of elements in steel, the content of a single element bound in a carbide depends on the carbide-solubility product.

The precipitation of two atomic particles, such as VC and NbC, may start with heterogeneous nucleation after the local accumulation of a sufficient number of atoms of both carbide-forming elements.[3,4] Nucleation occurs with lattice elastic straining, which is easier on the lattice imperfections, i.e., the grain boundaries, the sub-boundaries and the intersections of the dislocations.

The probability of the nucleation of a carbide with a molecule made up of several metals, as the carbide $M_{23}C_6$ ($Cr_{23-(x+y)}Fe_xMo_yC_6$) in quenched martensite of creep-resistant high-chromium steels with local accumulation of a sufficient number of atoms of the constituting metals and heterogeneous nucleation, is very low, probably zero.

In the investigated quenched steel,[5–7] the composition and lattice of the carbide particles depended on the tempering time at 800 °C. After short tempering, in particles with the mole fractions 57.8 % Fe and 17.8 % Cr of orthorhombic iron carbide (cementite, $\approx Fe_{2.4}Cr_{0.6}C$) with part of the iron substituted with chromium were found. After longer tempering, the chromium content in the particles increased and by approximately the mass fraction 32 % Cr, particles had the cubic lattice of $Cr_{23}C_6$ and the molar composition of about $Cr_9Fe_{14}C_6$. It is possible that for a small particle size the electron-probe microanalysis (EPMA) was not accurate because the matrix was also included. With longer tempering, the content of chromium increased to about 70 %, the content of iron decreased greatly and a small content of molybdenum was also found. After the longer tempering, the molar composition of the particles was about $Cr_{18}Fe_3Mo_2C_6$, and it remained virtually constant after 1354 h of tempering at 800 °C.

In investigations of the segregations in a 1.0–1.5 % Cr steel,[8] inserts of ledeburite, the eutectic in the Fe-FeC binary system, were also found. The line scanning across

such inserts in **Figure 1** showed a gradual and two-steps like high increase of chromium content. With an accurate examination it was found that the chromium content in the ferrite solid solution increased gradually, than it increased step-like to cementite and increased then step-like again to the central $M_{23}C_6$ particle. The presence of both carbides in the examined steel was confirmed with the X-ray diffraction analysis of the isolate of non-metallic phases. EPMA point analysis showed that the maximum content of chromium in the solid solution was about the mass fractions 6.5 %, in cementite it was in the range of 18.9 % to 21.4 % (about $Fe_{2.3}Cr_{0.7}C$) and in carbide $M_{23}C_6$ it was in the range 32.0 % to 35.2 % (about $Cr_8Fe_{15}C_6$). These findings agree with the results from the examined creep-resistant steel.

The results of the analysis on two steels with different chemical compositions support the conclusion that cementite (Fe_3C) was the predecessor of the nucleation of the $M_{23}C_6$ particles. It is assumed that the nuclei of the $M_{23}C_6$ with a high content of iron form on the surface of the particles of cementite above the limit of the substitution of iron with chromium. In quenched steel, the rate of nucleation and growth of carbide particles depend on the diffusion afflux of the constituent metal atoms and the Gibbs free energy of the carbide phase. Cementite nuclei with a composition similar to the ferrite solid solution are formed because of the rapid afflux of iron and chromium atoms at a small distance from the nucleation site. The diffusion afflux is greater for the iron atoms because of the lower content of chromium. Then, with a rate related to the diffusion afflux of the constituent elements and to the Gibbs free energy of carbide formation [at 800 °C, ΔG (Fe_3C) ≈ −1 kJ/mol and ΔG ($Cr_{23}C_6$) ≈ −63.8 kJ/mol] the content of chromium in the newly formed cementite is gradually increased to the substitution limit, then on the surface of

these particles, nuclei of the carbide $M_{23}C_6$ with a high iron content are formed. With further growth, the effect of the difference of the free energy increases with the substitution of iron by chromium atoms until the equilibrium of the compositions of carbide and the solid solution is achieved.

In the nucleation phase and the growth of the particles up to a determined substitution in cementite of iron with chromium, the effects of the solid solution composition and the diffusion transport prevail, while for the nucleation and growth of $M_{23}C_6$, the effect of the free-energy difference is stronger.

The difference of the Gibbs energy is also the driving force for the change of phases versus the interior of the particles with a non-equilibrium composition. Small inserts of metal with a high content of iron and low contents of carbon and chromium in the interior of $M_{23}C_6$ particles after a longer tempering time in the micrographs in[6,7] are reliable evidence of a change of the composition with the substitution of iron by chromium and a change of the particles $Fe_{3-x}Cr_xC$ to particles of $Cr_{23-(x+y)}Fe_xMo_yC_6$, with chromium and molybdenum diffusion in the interior of earlier grown $Fe_{3-x}Cr_x$ particles. Thus, the data in ref.[6,7] also confirm the proposed explanation of the nucleation of the $M_{23}C_6$ carbide in investigated steel.

Additionally, the similarity of the findings in[5–8] suggests that the process of the formation of the carbide $M_{23}C_6$ is similar for the solidification and for the precipitation from the solid solution in ferrite. The sequence of events of the change of the carbide phase is probably similar for particles at the grain boundaries and in the interior of the ferrite grains, while the change of the carbide type may be faster because of the faster grain-boundary diffusion.

2 ASSESSMENT OF THE AVERAGE M₂₃C₆ PARTICLE SIZE AND SPACING

In martensite-based creep-resistant steels the carbide particles are precipitated in the interior of the grains and at the grain boundaries. According to the Lifshitz-Slyozov-Wagner[3,6,9,10] (LSW) equation (1), the coarsening rate of the precipitates depends on various constants and parameters:

$$\Delta d^3 = d_t^3 - d_0^3 = 8\ S\ \gamma\ \Omega\ D\ t/9\ k_B\ T \qquad (1)$$

with d_t – the particle size at tempering time t, d_0 – the initial particle size, S – the equilibrium molar content of metal bound to the carbide in the matrix solid solution, γ – the carbide particle matrix interfacial energy, Ω – the atomic volume, k_B – the Boltzmann constant, D – the diffusion coefficient and T – the temperature in K.

The particle size exponent 2 was proposed for coarsening, depending on the faster grain-boundary diffusion rate.[6]
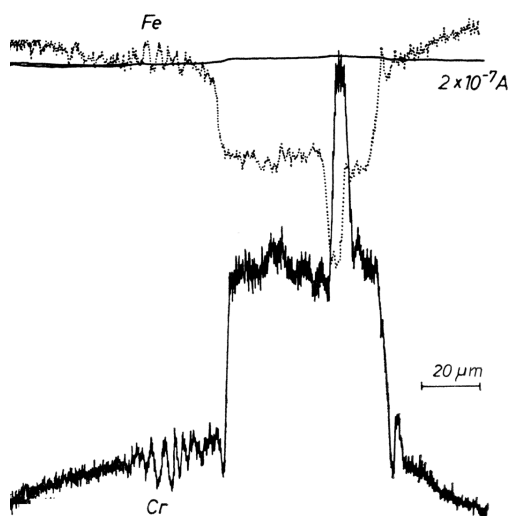

Figure 1: EPMA line scan for chromium and iron over a ledeburite field with a $M_{23}C_6$ particle in 1C-1.5Cr steel[8]
Slika 1: Linijska analiza kroma in železa EPMA preko polja ledeburita z zrnom $M_{23}C_6$ v jeklu 1C-1,5Cr[8]

For the carbide $Cr_{18}Fe_3Mo_2C_6$ and 800 °C, the particle-coarsening rate $k_c = 6.86 \cdot 10^{-27}$ m^3 s^{-1} was calculated for 0.18C11.5Cr1.08Mo0.29V steel using equation (1), while from the experimental data and the tempering up to 1354 h at 800 °C $M_{23}C_6$, the particle-coarsening kinetics was deduced:

$$\Delta d^3 = k_e (t - t_0) \tag{2}$$

with $k_c = 11.70 \cdot 10^{-27}$ m^3 s^{-1}.

Combining equations (1) and (2) we obtain, for the coarsening rate:

$$k_c = 8 S \gamma \Omega D/9 k_B T \tag{3}$$

On the micrometre scale, the linear size (d), the particle spacing and the local particle density are inhomogeneous. In **Figure 2**, the particle size in the range 0.05 μm to 3 μm, the particle spacing 0.1 μm to 5 μm, areas with or without particles and particles with different numbers of direct neighbour particles are found. If data from micrographs similar to that in **Figure 2** are used for the calculations involving the constituents of the microstructure, it should be kept in mind that for a ratio of linear particle size ($d_{max}/d_{min}) \approx 10$, the ratio of the volume size is ($d^3_{max}/d^3_{min}) \approx 10^3$.

The relation of the volume fraction of carbide (f), the average size of the carbide particles (d_a) and the particle spacing (λ) was suggested:[11]

$$\lambda = 4 d_a/\pi f^{1/3} \tag{4}$$

The volume fraction of the carbide phase is calculated from the content of carbide-forming elements in the steel and the carbide composition. In the investigated steel, for tempering at 800 °C only the carbide $M_{23}C_6$ is stable. Assuming that all the carbon is bound to $Cr_{23}C_6$, for the examined carbide the volume fraction of steel is calculated as:

$$f = 0.18 [(18 Cr+ 3Fe + 2Mo + / 6C)] / 7.04 (12.82) =$$
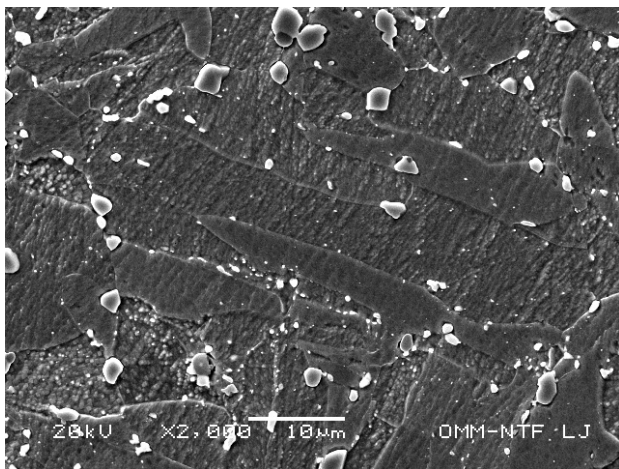$$= 0.0358$$

Figure 2: Microstructure of 0.18C11.5Cr1.08Mo0.29V steel annealed for 672 h at 800 °C
Slika 2: Mikrostruktura jekla 0,18C11,5Cr1,08Mo0,29V, žarjenega 672 h pri 800 °C

with 0.18 g being the content of carbon in 100 g of steel, Cr, Fe, Mo, C are the mole weights of chromium, iron, molybdenum and carbon, 7.04 g/cm^3 is the specific weight of $Cr_{18}Fe_3Mo_2C_6$ and 12.82 cm^3 is the volume of 100 g of steel with a specific weight of 7.80 g cm^{-3}. The specific weight of carbide $M_{23}C_6$ was deduced by assuming that the specific weight of carbide $Cr_{23}C_6$ of 6.50 g cm^3 was increased by the substitution of chromium atoms with heavier atoms of iron and molybdenum.

With modern devices for image analysis it is possible to determine the particle size and spacing as an average of the assessment of the size and the spacing of a large number of particles. However, it should be kept in mind that with an automatic assessment some inaccuracy might originate from an insufficient size and greyness discrimination of the particles and the background of the examined micrographs or specimens. Also, as it is necessary to assess an accurate number of particles with very different sizes, for an examination of high-magnification micrographs for a reliable assessment of particles with a small size, larger particles may be omitted, although their volume share is much greater than the results indicate.[11]

A careful examination of the micrograph in **Figure 2** shows that particles have several neighbours and their position is at the centre of a geometrical form with four (4) or more sides. The size of these forms is variable, and assuming the forms as squares with side s_p, the average side length is equal to the average plane particle spacing λ_p, which is then calculated as:[12,13]

$$\lambda_p = (F/N_p)^{1/2} \tag{5}$$

with N_p being the number of particles on the assessed micrograph area and $F = \Sigma s_p^2$ for the micrograph assessment area.

Combining equations (4) and (5), for the average particle size a relation is obtained:

$$d_a = \pi F^{1/2}f^{1/3}/4 N_p^{1/2} \tag{6}$$

For a constant volume share of the carbide, in the process of coarsening, the size of some particles is increased, while it is decreased for the more numerous other particles. For the examined steel, the share of particles with a size below the average size calculated using equation (5) was above about 90 % also after the longest tempering at 800 °C.[11] Due to the great difference in the volume size of the particles, the accuracy of equations (4), (5) and (6) depends strongly on the accuracy of the size assessment of a number of particles reliably representative for the examined specimen. The checking of equation (6) showed that by counting $N_p > 3000$ on micrographs where particles of $d > 10$ nm size were clearly visible, acceptable differences of particle spacing and size of ±10 % were obtained. In **Table 1** the particle spacing and the size calculated from equations (4), (5) and (6) are shown. An experimental average size of approximately 250 particles

was used in relation (4) and the counting of above 3 000 particles in relations (5) and (6).

Table 1: Average experimental and calculated $M_{23}C_6$ particle size and spacing in the examined steel tempered for 672 h (A) and 1354 h (B) at 800 °C. Volume fraction of $M_{23}C_6$ particles $f = 0.0358$.
Tabela 1: Povprečna eksperimentalna in izračunana velikost in medsebojna razdalja izločkov $M_{23}C_6$ v preiskanem jeklu, žarjenem 672 h (A) oz. 1354 h (B) pri 800 °C. Volumenski delež izločkov $M_{23}C_6$ je: $f = 0,0358$.

Spec.	Magn.	Part. number N_p	Part. size $d/\mu m$	Part. spac. $\lambda/\mu m$
A	$2 \cdot 10^4$	$\approx 250^1$	0.22^1	eq. (4) 0.85
B	$2 \cdot 10^4$	$\approx 250^1$	0.26	eq. (4) 1.00
A	4800	>3000	eq. (6) 0.28	eq. (5) 1.10
B	4800	>3000	eq. (6) 0.42	eq. (5) 1.71

Different values for the particle size and spacing were obtained from micrographs of the same specimen with manual measurement of the particle size and counting of the particles. The data obtained by counting are assumed to be more reliable because for the counting the number of particles considered was more than one order of magnitude higher. On the other hand, individual determination of the particle size requires more time and accuracy; for a reliable assessment of small particles a greater magnification is needed and coarse particles may be omitted, while assessment accuracy is affected less by the omission of smaller particles because of their smaller volume. Also, by counting and by a size assessment of individual particles equal errors may occur because of poor specimen preparation. Thus, it seems justified to conclude that as a method based on the examination of micrographs, counting is more suitable for a fast and sufficiently accurate assessment of particle spacing and average size for the microstructure of tempered martensite with very different carbide particle sizes.

3 CONCLUSIONS

On the basis of theoretical and experimental work we can conclude:
- In the examined steel the nucleation of $M_{23}C_6$ particles cannot be explained by the local accumulation of atoms of the metals chromium, iron and molybdenum. The nucleation of $M_{23}C_6$ occurs on $Fe_{2.4}Cr_{0.6}C$ particles with the formation of $M_{23}C_6$ nuclei with about the mass fraction 33 % Cr when the limit of substitution of iron with chromium atoms in the iron carbide is achieved.
- By tempering, the initial content of chromium in the iron carbide nuclei is gradually increased because by their growth and later by the growth of $M_{23}C_6$ nuclei, the effect of the difference of the Gibbs energy between the $Cr_{23}C_6$ and Fe_3C is stronger than that of the rate of the diffusion afflux of the iron atoms.
- A simple method of assessment of the average particle spacing and size is proposed. It is based on a calculation of the volume share of the carbide phase, counting a sufficient number of particles on SEM micrographs and the assumption that every particle is situated in a square with a side equal to the average particle spacing.
- In the examined steel with the microstructure of tempered martensite with carbide particles of very different size, the average calculated particle spacing and the size obtained applying the proposed assessment method, are more reliable than those obtained with a size measurement of a smaller number of particles.

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