

**STABILITY OF MC CARBIDE PARTICLES SIZE IN CREEP RESISTING STEELS**

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Theoretical analysis of the dependence microstructure creep rate. Discussion on the effects of carbide particles size and their distribution on the base of accelerated creep tests on a steel X20CrMoV121 tempered at 800 °C. Analysis of the stability of carbide particles size in terms of free energy of formation of the compound. Explanation of the different effect of VC and NbC particles on the resistance to accelerated creep rate.

**Key words:** *steel, accelerated creep rate, VC and NbC carbide particles, size and stability, ferrite matrix, residual solubility of vanadium and niobium*

**Stabilnost MC karbidnih čestica u čelicima otpornim na puzanje.** Dana je teoretska analiza ovisnosti brzine puzanja o mikrostrukturi. Rasprava o utjecaju veličine karbidnih čestica i njihove raspodjele na temelju ispitivanja ubranog puzanja kod čelika X20CrMoV121 žarenog pri 800 °C. Analiza stabilnosti veličine čestica na temelju slobodne energije stvaranja karbida. Obrazloženje razlike u utjecaju VC i NbC čestica na ubrano puzanje.

**Ključne riječi:** *čelik, ubrano puzanje, karbidne čestice VC i NbC, veličina i stabilnost, feritni matriks, rezidualna topljivost vanadija i niobija*

**INTRODUCTION**

The two most important properties of creep resisting steels are the initial resistance to creep deformation and its stability by long operation time of thermal power works. The operation temperature of some parts of these works is at the level enabling a slow diffusion of atoms of elements in substitutional solid solution in ferrite, which is the matrix of the steel microstructure. The rate of diffusion of carbon in ferrite is several orders of magnitude greater than that of substitutionals, it is, for this reason, without significant affect on the processes related to the resistance to creep deformation [1].

The microstructure of steels with the greatest creep resistance consists of a distribution of carbide particles in ferrite obtained with tempering of the steel quenched to martensite. In steels with lower creep resistance both constituents of the microstructure, carbide and ferrite, coexist as distinct phases, mostly as polygonal grains of ferrite and pearlite or bainite. In all steels a small share of resistance to creep is obtained also with the dragging of vacancies due to atoms some alloying elements in solid solution. Tungstene and molybdenum could also produce

a limited increase of creep resistance with the formation of particles of intermetallic phases [2].

**CREEP DEFORMATION**

Theoretically, the creep rate of an alloy with a microstructure consisting of a homogeneous distribution of particles in a softer metallic phase is [3]:

$$\dot{\epsilon}' = \frac{b^2}{kTG} L\sigma^2 D_{Fe} N \quad (1)$$

with:

- $b$  - Burgers vector,
- $K$  - Boltzmann constant,
- $T$  - temperature / K,
- $G$  - shear modulus,
- $L$  - average particle to particle distance,
- $\sigma$  - stress,
- $D_{Fe}$  - coefficient of diffusion resp. autodiffusion in the matrix solid solution and
- $N$  - number of dislocations per unity of volume.

For other parameters constant, the creep rate is proportional to the average particle to particle distance. For the same steel chemical composition, the creep resistance

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is the smaller, the greater is the average size of particles, as the average particle to particle distance is:

$$L = \frac{4}{\pi} \frac{d}{f^{1/3}} \quad (2)$$

with:

$d$  - particle size (diameter) and  
 $f$  - volume share of particles.

The particle to particle distance is proportional to the size of particles and inversely proportional to the cubic root of the volume fraction of the carbide phase. This shows that, in terms of creep resistance, more can be gained by control of the stability of the particles size than from the increase of the volume fraction of the carbide phase.

The activity of constitutive atoms in the carbide phase (a) depends on the size of particles and it is [4]:

$$RT \ln a = 2\gamma \frac{V}{r} \quad (3)$$

with:

$R$  - universal gas constant,  
 $\gamma$  - surface energy and  
 $V$  - molar volume of the compound.

The surface energy of the carbide depends on the physico-chemical nature of the surface and it is, like the specific volume, constant by constant chemical composition. Since, the activity increases proportionally to the decrease of the size of particles, coarse particles grow on expense of smaller and for a homogeneous distribution of particles of different size, the coarsening kinetics is [5, 6]:

$$d_t^3 - d_0^3 = \frac{k}{RT} VD\gamma t \quad (4)$$

with:

$d_t$  - average diameter of the particle at the time  $t$ ,  
 $d_0$  - the initial diameter of particles and  
 $D$  - diffusion coefficient of carbide constitutive elements in solution in ferrite.

For a 0,2C Cr-Mo steel a time related  $t^{1/3}$  kinetics of growth of cementite particles and the  $t^{1/5}$  kinetics of growth of MC particles coherent with the ferrite matrix are reported [7]. The  $t^{1/5}$  kinetics is explained in terms of pipe diffusion of niobium, vanadium and molybdenum atoms.

In steels containing atoms of elements with a free energy of formation of the carbide phase greater than that of

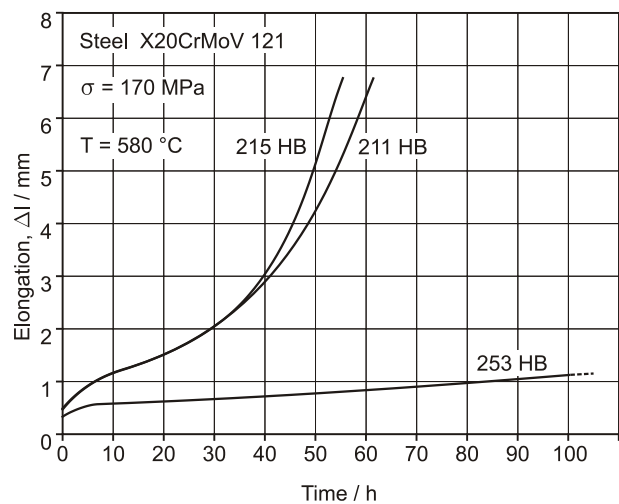


Figure 1. Accelerated creep rate and hardness of specimens of steel X20CrMoV 121 cut out from the same overheater tube after approximately 57000 h. of operation at the nominal temperature of 560 °C [9]

Slika 1. Brzina ubrzanog puzanja i tvrdoća čelika X20CrMoV 121 odrežanog iz cijevi predgrijača pare poslije približno 57000 sati rada kod nominalne temperature 560 °C [9]

iron carbide, the kinetics depends also on the exchange rate of atoms between the matrix solid solution and the carbide phase. This explanation was proposed for the  $t^{0,27}$  coarsening kinetics of  $M_m C_n$  carbide particles in the quenched steel X20CrMoV 121 (X20) tempered at 800 °C [8]. It was established that the equilibrium chemical and phase composition of carbide particles were not achieved even

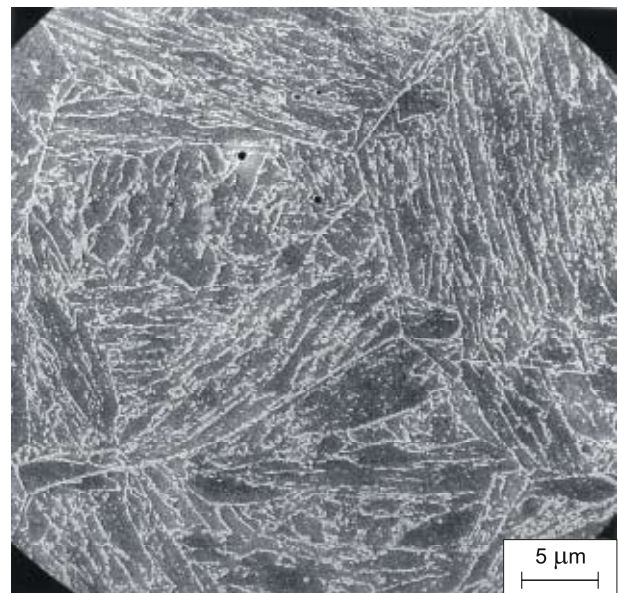


Figure 2. Microstructure of tempered martensite in the steel in Figure 1. cut out from one side of the tube

Slika 2. Mikrostruktura otpuštenog martenzita na jednoj strani cijevi na slici 1.

after 1344 h of annealing at 800 °C. During the isothermal tempering the carbide phases evolved in the sequence  $M_3C \rightarrow M_{23}C_6 \rightarrow M_7C_3$  with the substitution in carbide of iron with chromium atoms, and to a smaller extent, also with molybdenum atoms from the solid solution in ferrite [8]. The phase change  $M_3C \rightarrow M_{23}C_6$  occurred approximately by the content of chromium of 21 % and the phase change  $M_{23}C_6 \rightarrow M_7C_3$  at approximately by 58 % of chromium in the carbide [8].

Tests on specimens cut out from the same overheater tube after an operation time of approximately 57000 h at the nominal steam temperature of 560 °C have shown that the accelerated creep rate was much greater on one than on the diametral side (Figure 1.). On this side, a local overheating caused the internal recrystallisation of martensite grains and the change of the distribution of precipitates from that typical for tempered martensite (Figure 2.) to an aleatory distribution of particles in the ferrite matrix (Figure 3.). The hardness was greater for the steel with the martensite habitus, while, the accelerated creep rate was much greater for the aleatory distribution of particles [8].

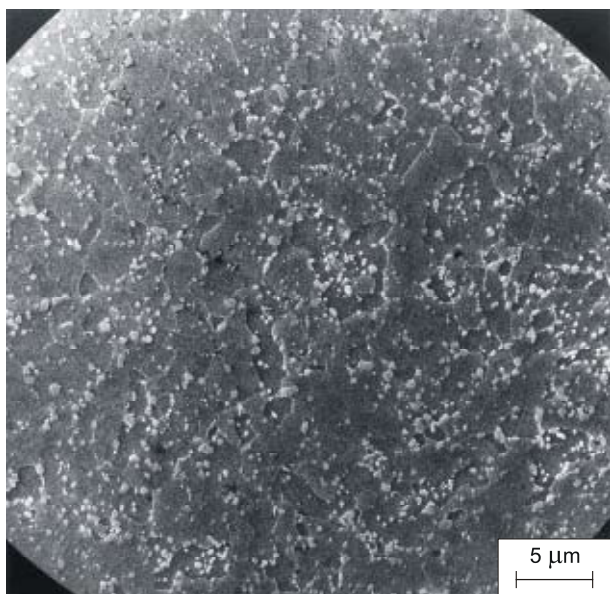


Figure 3. Microstructure of the steel in Figure 1. cut out on the opposite side than the specimen in Figure 2.  
Slika 3. Mikrostruktura čelika na slici 1. na uzorku sa suprotne strane cijevi od uzorka na slici 2.

The difference in average size of carbide particles was too small to explain for the difference in accelerated creep rate, and it was assumed, that the difference in creep rate was related also to the distribution of carbide particles.

In an investigation aimed to determine the effect of particles size on accelerated creep rate for the heat resisting steel X20, it was established [10] that the creep rate increased proportionally to the particle to particle distance, as predicted in equation (1), and that of side a crytical dis-

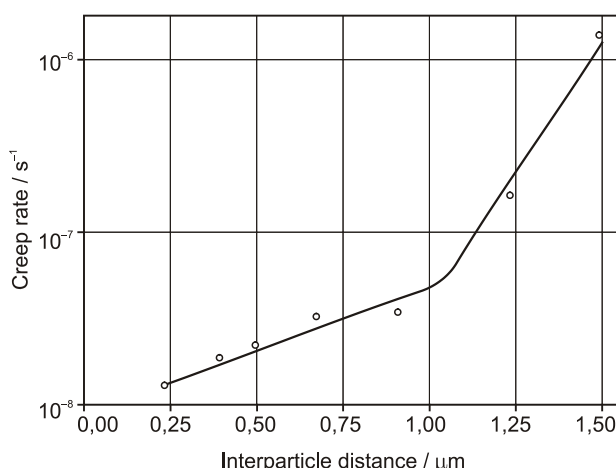


Figure 4. Accelerated creep rate versus the dependence average particle to particle distance for the steel X20CrMoV 121 tempered for different times at 800 °C. Testing conditions as in Figure 1.

Slika 4. Brzina ubrzanog puzanja u ovisnosti o udaljenosti između čestica za čelik X20CrMoV 121 žarenog različito vrijeme pri 800 °C. Uvjet ispitivanja kao na slici 1.

tance the creep rate increased by approximately 4,5 times (Figure 4.). Approximately at the critical point, internal recrystallisation occurred in martensite grains and the distribution of precipitates changed from that typical for the interior of tempered martensite grains to a prevailing

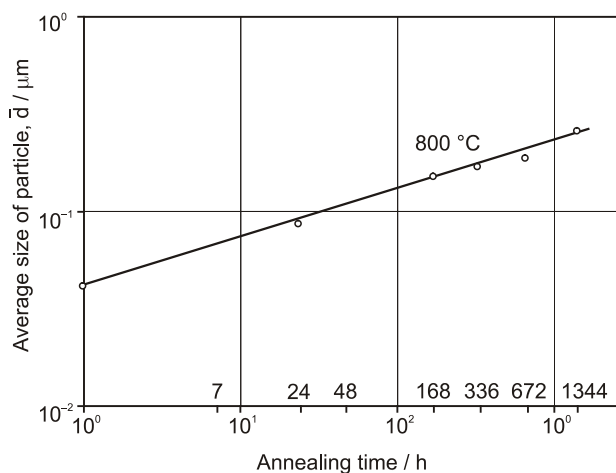


Figure 5. Kinetics of coarsening of average size of  $M_{23}C_6$  carbide particles in the quenched steel X20CrMoV 121 tempered at 800 °C

Slika 5. Kinetika okrupnjavanja čestica karbida  $M_{23}C_6$  u kaljenom čeliku X20CrMoV 121 žarenom pri 800 °C

aleatory distribution of particles in ferrite grains and a strong decrease of the number of martensite subboundaries decorated with carbide particles. By further prolonging of the tempering, the average particle to particle distance increased (Figure 5.) with the same rate as before the internal recrystallisation occurred [11].

The increase of yield stress ( $\Delta\tau$ ), which is proportional to the stress required for the dislocation to overcome a string of precipitates, is [12]:

$$\Delta\tau = 0,85 \frac{3Gb}{2\pi L} \ln \frac{d}{x} \quad (5)$$

with:

$x$  - diameter of the dislocation core.

The average particle to particle distance in stringers in Figure 1. is significantly smaller than the stringer to stringer distance in the same martensite grain, and it is also smaller than the particle to particle distance in the microstructure in Figure 2. It is concluded, that the presence of carbide particles in stringers is of essential importance for the steel creep resistance. The dislocations can glide through a tempered martensite subgrain faster than overcome the subboundary stringer of particles. For this reason, the microstructure of tempered martensite is heterogeneous in terms of resistance to creep rate.

After a tempering time short in comparison to the operation time of a thermal power work, in the microstructure of the steel P.91 two groups of carbide particles are found (Figure 6.): particles of size of  $10^3 - 10^2$  nm of carbide of

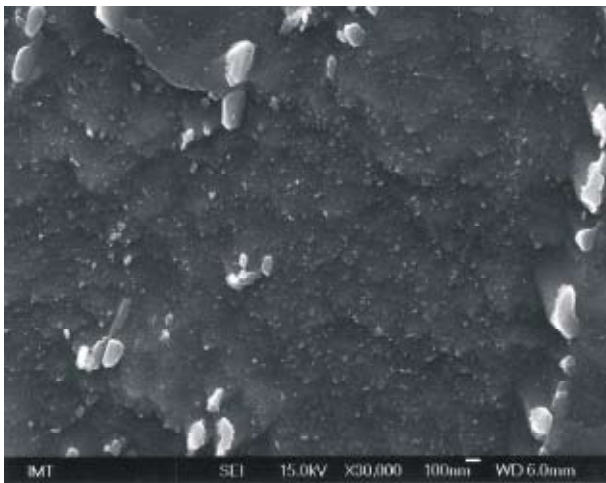


Figure 6. Coarse  $M_{23}C_6$  particles and small MC precipitates in a P.91 steel quenched and tempered for 8 h. at  $650^\circ\text{C}$

Slika 6. Velike čestice karbida  $M_{23}C_6$  i male čestice karbida MC u čeliku P.91 kaljenom i žarenom 8 sati pri  $650^\circ\text{C}$

composition  $M_mC_n$  with chromium, molybdenum and iron on the M place and much smaller particles of MC carbide. The coarse particles are located in stringers at martensite subgrain boundaries and represent carbide formed with the change of chemical composition and of phase of the initial cementite. The smaller particles consist of VC car-

bide in steel X20 and NbC and VC carbides in niobium - vanadium steel P.91. These carbide particles nucleate independently, their nucleation rate is much smaller than that of the carbide  $M_mC$  and their distribution is not related to the martensite habitus [7].

### STABILITY OF PARTICLES SIZE

The stability of carbide particles size depends on their solubility in ferrite and the diffusion rate of constitutional elements in the ferrite matrix. The rate of diffusion of carbon is several orders of magnitude greater than that of other elements bound in the carbide phase. Iron atoms are separated from the carbide compound only by the phase boundary. For this reason, the exchange rate of iron atoms between the carbide particle - solid solution does not depend on the diffusion in the matrix. However, iron and chromium diffusion in the carbide phase could affect significantly the kinetics of the change of the chemical composition of this phase. The content of chromium in the steel is in excess over that necessary for the formation of a pure chromium carbide. Using stoichiometry rules it can be deduced that if all carbon in the X20 steel (0,18 % C and 12 % Cr) was bound to the carbide  $Cr_{23}C_6$ , the content of chromium in solid solution in ferrite would be decreased from 12 to approximately 11,2 %, only. This justifies the conclusion that the diffusion of chromium in solid solution could not affect significantly the coarsening kinetics of carbide particles. A similar analysis allows to conclude that the diffusion of molybdenum could have only a minor effect on the kinetics of coarsening of carbide particles. It should be noted, that the role of different elements in the reaction of exchange of atoms between the solid solution and the carbide phase and on the rate of this reaction was not explained, so far.

The coarsening of  $M_3C$  particles is fast and their initial composition corresponds to that of the matrix solid solution. By further annealing, coarsening occurs parallelly to the change of chemical composition and the change of phase.

The content of vanadium and niobium in steel is much lower than that of other carbide forming elements. The transport of atoms of these elements in the ferrite matrix depends on their diffusion rate and on their content in solid solution. The net flux of atoms from the plane  $X$  to the plane  $Y$  of the solid solution lattice is proportional to the content of the element in solid solution [1]:

$$J_{X \rightarrow Y} = \frac{1}{6\tau} n_A a \quad (6)$$

with:

$\tau$  - average time of stay of the diffusing atom at the lattice site,

$n_A$  - number of atoms of the diffusing element per unit of volume of the solid solution and  
 $a$  - lattice constant.

With Auger analysis of a great number of particles in the steel X20 the carbide phase  $M_mC_n$  was found free of vanadium [8].

It is reported in [7] that vanadium and niobium are bound only to very small MC particles.

The stability of different carbide phases above the temperature level allowing chemical and phase transformation depends on the free energy of formation of the compound. The greater in this energy, the more stable is the compound and the lower is its solubility in the solid matrix [13]. In Figure 7. it is shown that the free energy of formation of carbide decreases from niobium, over vanadium, chromium and molybdenum to iron.

The atomic concentrations of carbon and of the metal M in solid solution in equilibrium with the carbide  $M_mC_n$  are related through the equations [13]:

$$[M]^m [N]^n = K \tag{7}$$

$$K = K_0 e^{-\frac{\Delta H}{RT}} \tag{8}$$

with:

$[M]$ ,  $[N]$  - content of elements constituting the compound in the alloy,

$m$ ,  $n$  - number of atoms of both elements in the compound. For vanadium and niobium carbide  $m = n = 1$ ,

$\Delta H$  - free energy of formation of the compound and

$K$ ,  $K_0$  - empirical constants.

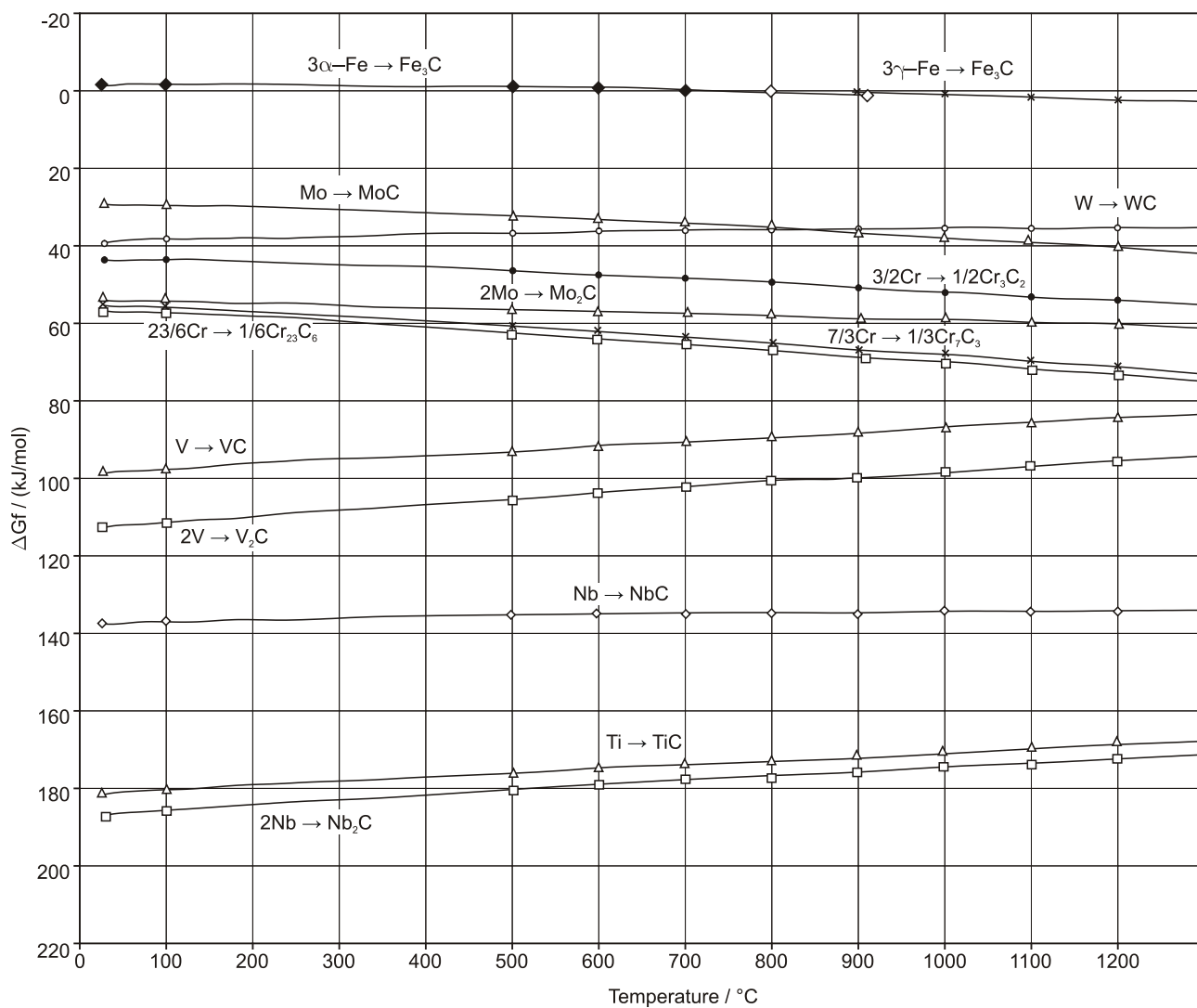


Figure 7. Free energy of formation of carbides of alloying elements in creep resistant steels  
 Slika 7. Slobodna energija stvaranja karbida legiranih elemenata u čeliku otpornom na puzanje

The solubility of niobium and vanadium carbide respectively carbonitride in austenite is calculated from the solubility product developed combining equations (7) and (8) with empirical data. For a structural steel with up to 0,2 % C, 1,5 % Mn and 0,05 % V the solubility product for vanadium carbide is [14]:

$$\log [V] \times [C_v] = -\frac{9500}{T} + 1,48 \quad (9)$$

with:

[V], [C<sub>v</sub>] - content of vanadium and carbon in solution.

In a steel with 0,1 % C, 0,2 % V the content of vanadium in solution in ferrite at 650 °C is of  $2,68 \cdot 10^{-4}$  %.

Equations (7) and (8) show that the equilibrium atomic content of both elements in solid solution is exponentially related to the value of free energy of formation of their compound, in this case of the carbide. Let us deduce, based on the product [V] × [C<sub>v</sub>], the content of carbon in solid solution [C<sub>Nb</sub>] at 650 °C for a steel with 0,10 % C, 0,2 % V and 0,10 % Nb using the equations (7) and (8). In atomic % the contents of these elements in the steel are: 0,46 % C, 0,22 % V and 0,058 % Nb. The carbides Ca carbon atom, both have a cubic lattice, both have a small solubility in ferrite and by the both form precipitates by the same mechanism. Let us then, assume for the calculation that  $K_{0V} \approx K_{0Nb}$ . Applying this assumption the following relation can be deduced from equations (7) and (8):

$$\frac{[Nb] \times [CNb]}{[V] \times [C_v]} \approx \frac{e^{-\frac{\Delta H_{Nb}}{RT}}}{e^{-\frac{\Delta H_v}{RT}}} \quad (10)$$

The free energy of formation of the carbide NbC is of  $-134,7 \text{ kJ/mol} \cdot \text{K}$  and for VC is of  $-90,7 \text{ kJ/mol} \cdot \text{K}$ . Introducing the corresponding values in equation (10) the content of carbon in equilibrium with 0,1 % Nb in solution in ferrite of  $[C_{Nb}] = 5,44 \cdot 10^{-6}$  % is obtained for the temperature of 650 °C. Thus, the presence of 0,1 % Nb lowers theoretically the residual content of carbon in the solid solution with 0,2 % V at 650 °C for  $[C_v]/[C_{Nb}] = 2,68 \cdot 10^{-4}/5,44 \cdot 10^{-6} = 49$  times.

Based on the same data, and assuming as base the content of carbon in steel, it is calculated that by the total content of 0,1 % C the quantity of vanadium in solution in ferrite at the temperature of 650 °C would be of  $[V] = 2,7 \cdot 10^{-3}$  %, thus, by 74 times lower than the total content in the steel of 0,2 % V. The content of niobium in solid solution is calculated to  $[Nb] = 1,9 \cdot 10^{-5}$  % by 526 times lower than the total content of niobium in the steel.

In spite of the simplification used in the calculation, it seems justified to conclude that the content of vanadium

and niobium in solid solution in ferrite are significantly lower than the total content of both elements in steel.

Considering that the diffusion flux of atoms of solute elements depends, according to equation (6), on the number of atoms per unit of volume, respectively the content of the element in solid solution, that the diffusion of carbon is much faster than that of vanadium and niobium and considering the results of the presented calculations, it is justified to conclude, in spite of the assumption used, that the greater stability of NbC particles, which is proportional to their decreasing effect on creep rate, is due to the very small residual content of niobium atoms in solid solution in ferrite in equilibrium with the content of carbon. The residual content of vanadium atoms in ferrite is greater and the increased diffusion flow enables a faster coarsening of VC particles in comparison to NbC particles. For this reason, the effect of vanadium addition on creep rate decreases faster than that of niobium by the temperature, which enables the coarsening of carbide particles because of the faster diffusion transport in ferrite.

Steels X20 and P.91 were quenched and annealed for different times at 750 °C and then submitted to accelerated creep tests in the same conditions as the steel in Figure 1. [15]. After 8 h of tempering the accelerated creep rate was for 8,6 times greater for the steel X20 than for the steel P.91, after 2880 h of annealing the accelerated creep rate was even for 260 times greater for the steel X20. Since, the content of carbon was higher in the steel X20, the increased difference can not be ascribed to a change in the number of  $M_{23}C_6$  particles per unit of volume. It is, thus, evident that the increased difference in creep rate after longer annealing is related to the greater stability of precipitates of niobium carbide, as expected from the difference in the residual content of niobium and vanadium in solid solution in ferrite.

## CONCLUSIONS

Based on theoretical calculations and empirical data, the following conclusions are proposed:

- the chemical stability of carbide phases in creep resisting steels increases from  $M_3C$  over  $M_{23}C_6$  and VC to NbC;
- by the content of 0,1 % of carbon in steel the residual content of vanadium and especially of niobium in solid solution in ferrite at the temperature of operation of these steel in thermal power works is very low. It is for vanadium more than one order of magnitude lower and more than two orders of magnitude lower for niobium in comparison to the nominal contents of both elements in steel;
- the content of both elements in solid solution in ferrite, affects the diffusion flux of their atoms in solid solution, the coarsening rate of carbide particles and of the number of particles per unit of volume;

- the coarsening rate is for niobium carbide particles smaller than that for vanadium carbide particles because at the same temperature the residual content of niobium solid solution in ferrite is lower than that of vanadium;
- the lower accelerated creep rate for the steel P.91 than that for the steel X20CrMoV121 after long time tempering of steels at a temperature of significant diffusion of substitutionals in solid solution in ferrite is explained in terms of the greater number of NbC particles per unity of volume due to the smaller coarsening rate of these particles than that of vanadium carbide particles.

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