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GRAIN BOUNDARIES OF $M_{23}C_6$ PARTICLES IN HIGH CHROMIUM CREEP RESISTANT STEELS, STABILITY AND EFFECT ON CREEP RATE

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Specimens of high chromium creep resistant steel were tempered at 800 °C for different times and examined in SEM. After short tempering stringers of cementite particles are formed at ferrite grain boundaries. By longer tempering, the content of chromium and molybdenum increase up to $Cr_{18}Fe_3Mo_2C_6$ and the number of stringers decreases what gradually increase the creep rate.

Key words: creep resistant steel, tempering, structure, carbides, grain boundaries

INTRODUCTION

High chromium creep resistant steels have a high content of chromium in surplus of the content of carbon that creates a temperature range of stability of chemistry of matrix and carbide particles. In creep resistant steels, carbide particles are $M_{23}C_6$, in fact $Cr_{23}C_6$ with iron and molybdenum in solid solution. On the surface of particles Fe_3C nucleate, than chromium higher Gibbs energy of carbide formation, gradually substitutes iron in cementite up to about ($Fe_{2,7}Cr_{0,3}C$). Then, $M_{23}C_6$ nucleates on their surface [1]. The contents of chromium and molybdenum increase with tempering time up to $Cr_{18}Fe_3Mo_2C_6$ [1-4]. On principle, there is no difference in grain boundary and grain interior nucleation and coarsening of $M_{23}C_6$ with exception of difference of due to greater grain boundary than volume diffusion rate.

According to the LSW (Lifshitz-Slyozov-Wagner) equation, the particle coarsening rate is proportional to diffusion rate:

$$d_t^3 - d_0^3 = \left(\frac{8 \cdot S \cdot y \cdot \Omega \cdot D}{9 \cdot k_b \cdot T}\right) \cdot t \qquad (1)$$

With d_t – particles size at the tempering time t, d_0 – initial particles size, S – atomic content of chromium in solid solution in the ferrite, g – carbide particle matrix interfacial energy, W – volume of diffusing atoms, D – chromium diffusion rate, k_B – Boltzman constant and T – tempering temperature.

For isothermal coarsening of particles, equation (1) can be simplified to $d^3 = kt$, with k – coarsening rate equal to the product in parenthesis in equation (1).

If in equation (1) the content of chromium in at. % is used as parameter S, the difference of experimental and calculated coarsening rate is reasonable [5].

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By surplus of content of chromium and complete binding of carbon to carbide, the matrix and particle compositions are constant by tempering temperature below about 800 °C. In this case, isothermal particle coarsening is a dual process of parallel growth of part and shrinking or even dissolution of part of particles.

EXPERIMENTAL

The creep tests were performed on the 0,18C; 11,5Cr; 1,08Mo; 0,29V steel on specimens oil cooled from temperature of complete dissolution of carbide particles in austenite, tempered at 800 °C and a microstructure of ferrite and $M_{23}C_6$ particles was obtained. At the applied tempering temperature, VC was in solid solution in ferrite. Specimens tempered for different times were examined in SEM and the average particles size was assessed on micrographs at magnification of 10^4 and $2x10^4$ with reliable clarity of linear particles size down to 5 nm. After short tempering, the particles distribution with a great number of grain boundary and subboundary particles stringer was obtained (Figure 1). By longer tempering time, the number of stringers decreased and the complete uniform particles distribution was obtained after 400 h of tempering (Figure 2). The size of particles was in the range of some to about 10^3 nm (Figure 3). By lengthening of tempering, the average particles size d_a increased and the number of particles decreased. The number of particles was calculated as $N_p = 2f/\pi d_a^3$ with f-volume part of carbide $M_{23}C_6$ deduced from the chemistry of steel and carbide [6,7]. The average size of particles was calculated using the modification of equation (1) with the parameter S as at.% content of chromium in solid solution in ferrite [5]. The calculated numbers of particles were N_p =1,16x10^{19} m^{-3} rsp. N_p =1,01x10^{18} m^{-3} after 100 rsp. 10 h of tempering at 800 °C.

The creep rates were deduced from the results of accelerated 100 h creep test at 580 °C by tensile stress 170 MPa.

EFFECT OF TEMPERING TIME ON GB PARTICLES STRINGERS

The coarsening rate of $M_{23}C_6$ particles is depicted in Figure 4 [5]. It is constant and, according to equation (1), it is proportional to diffusion rate of chromium in ferrite. The diffusion of elements in substitutional solution in ferrite is for several orders of magnitude greater at grain boundaries that in grain interior [8, 9]. In Figure 5 the density (number per unity of surface) of particles stringers is shown in dependence of tempering time. The density of gb stringers decreases proportionally to $t^{1/3}$, thus parallely to the coarsening of particles. Thus, it is reasonable to conclude that, while in ferrite grains interior, the growth and dissolution of particles by tempering are in dynamical equilibrium, at grain boundaries the particles dissolution velocity prevails.

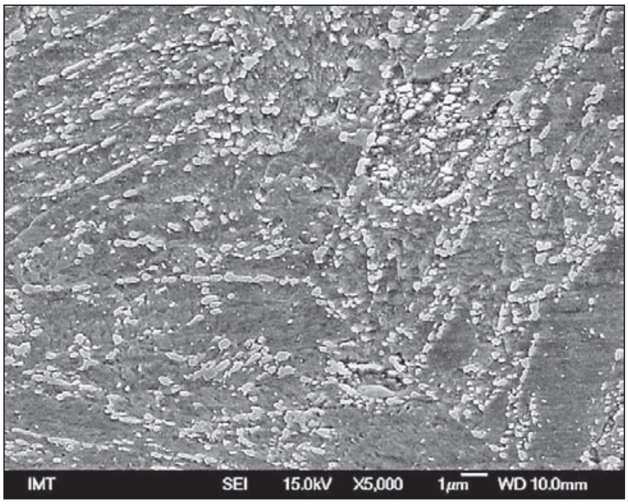

Figure 1 Distribution of $M_{23}C_6$ particles in steel tempered for 2 hours at 800 °C

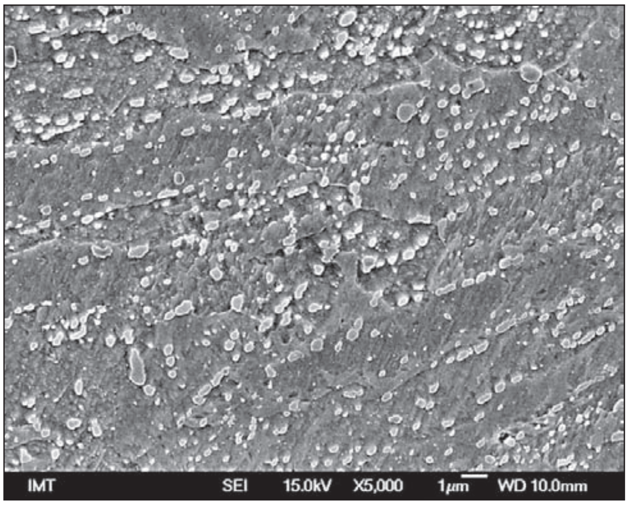

Figure 2 Distribution of $M_{23}C_6$ particles in steel tempered for 400 hours at 800 °C

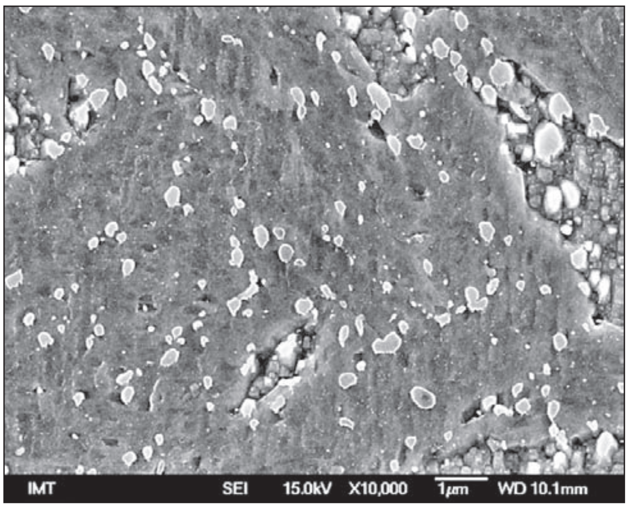

Figure 3 Particles of different size in interior of ferrite grains in steel tempered for 400 hours at 800 °C

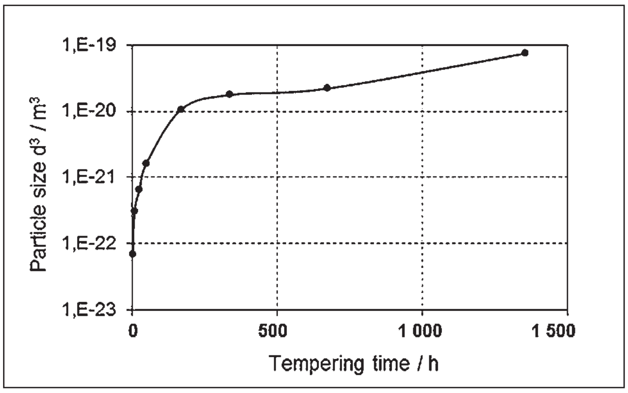

Figure 4 Average size of $M_{23}C_6$ versus tempering time at 800 °C [5]

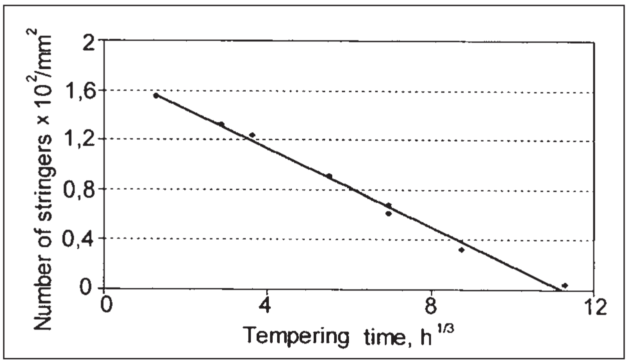

Figure 5 Dependence number of gb particles stringers versus tempering time at 800 °C [1]

However, the logical result of the difference of gb and volume diffusion rate alone would be a greater average size of gb particles. The absence of gb particles stringers supports, as more reasonable conclusion that chromium atoms from the gb dissolved particles are bound to particles in grain interior, or the probability of inclusion of gb stringers in grain interior by grain boundary shifting or increase of chromium content at grain boundaries. The shifting possibility is very low, as grain boundaries are fixed by particles stringers. So far, no experimental observation was found confirming the transport of chromium from gb to the interior of ferrite grains.

EFFECT OF GB STRINGERS ON CREEP RATE

Assuming the particle shape as sphere, the average interparticles distance- average particles spacing- is calculated as $\lambda_a = 4d_a/\pi f$ [6]. In Figure 6 the dependence experimental creep rate – average particles spacing is depicted [1,10]. Above a limit stringers number, about $0,5x10^2$ mm^{-2}, the increase of creep rate is proportional to growth of average spacing and size of particles, as expected from equation (2) [10]:

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

With: *s* = creep stress, *r* = density of mobile dislocations, *D* - diffusion rate, *d* - average particles size, λ_p - average particles spacing, *b* - Burgers vector, *k* - Boltzmann constant, *T* - temperature, *G* - shear modulus, and $k_s = \sigma^{3,65}/\sigma^2$.

Below this limit, the creep rate increases slower and proportionally to the number of stringers. At this moment two hypothetical explanations were suggested for the effect of gb stringers on creep rate of the investigated steel [10]:

– stringers are obstacles to shifting of mobile dislocations because of smaller particles spacing than that by uniform distribution of particles;
– stationary (secondary) creep of the examined steel is a dual process of grain lattice and grain boundary creep. Grain interior creep occurs by glide and climb of mobile dislocations, while grain boundary creep proceeds with shifting of ferrite grains with gb movement of vacancies

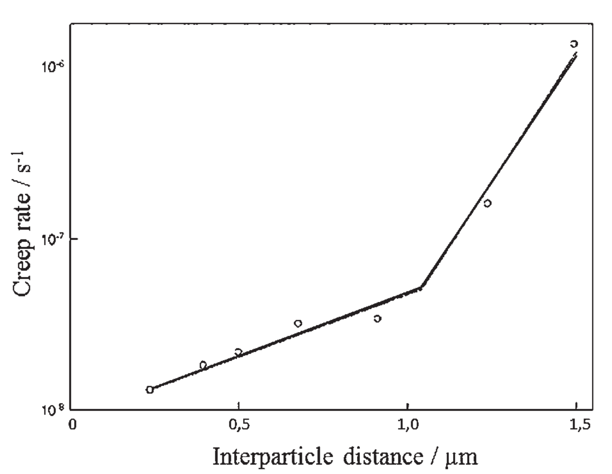

Figure 6 Dependence experimental creep rate versus particles spacing [1]

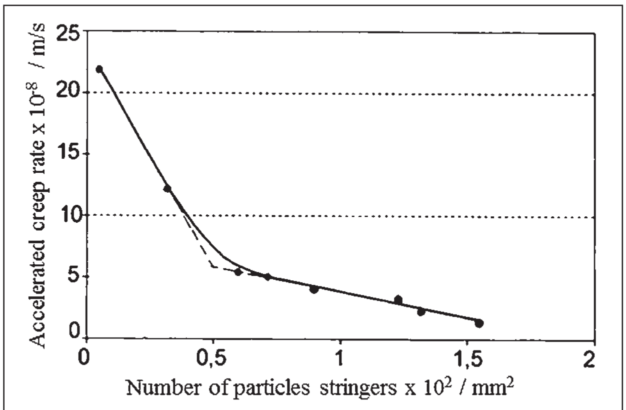

Figure 7 Dependence experimental creep rate versus number of gb particles stringers [1]

The greater creep rate by equal particles size and different ferrite grain size [11] suggest as more probable the second explanation.

CONCLUSIONS

By short tempering of steel quenched from total dissolution of carbide particles in austenite, stringers of cementite particles are formed at great number ferrite grain boundaries and subboundaries. By longer tempering, the content of chromium in particles increases at on the surface of cementite particles of carbide and $M_{23}C_6$ nucleate by about 20 % Cr. By longer tempering, their content of chromium and molybdenum increase to the composition of $Cr_{18}Fe_3Mo_2C_6$.

The number of stringers decreases by longer tempering time parallely to particles coarsening because of gb particles dissolution and lateral diffusion of chromium. By sufficient tempering time, virtually all particles stringers are dissolved and the uniform distribution of particles in ferite matrix is obtained.

Stringers of particles decrease steel creep rate. The steel creep rate increases gradually with decreasing number of stringers. Below a critical number of stringers, it increases much faster by growth of average size and spacing of particles with rate predicted by the creep equation.

The results obtained so far suggest that the lower creep rate of steels with gb particles stringers due to lovering of gb diffusion flow of vacancies.

REFERENCES

[1] F. Vodopivec, J. Vojvodič-Tuma, B. Šuštaršič, R. Celin, M. Jenko, Materials science and technology, 27 (2011) 5, 937-942.

[2] W. Blum, Materials Science and Engineering A, 319–321 (2001), 8–15.

[3] S.R. Holdsworth, Constitutive equations for creep curves and predicting service life, F. Abe, T.U. Kern, R. Wiswanathan (ed.), Woodhead Publ. Lim., Cambridge, England 2008, pp. 403-420.

[4] A. Aghajani, Ch. Somsen and G. Eggeler: Acta Mater., 57 (2009), 5093-5106.

[5] F. Vodopivec, D. Steiner Petrovič, B. Žužek, M. Jenko, Steel research international, 84 (2013) 11, 1110-1114.

[6] E. Hornbogen, Einfluß von teilchen einer zweiten Phase auf das Zeitstandverhalten, W. Dahl, W. Pitsch (ed.), Verlag Stahleisen Düsseldorf, 1980, pp. 31.

[7] J. W. Martin, R. D. Doherty, B. Cantor, Stability of microstructure in metallic systems, 2nd ed., Cambridge University Press, Cambridge 1997, pp. 242- 272.

[8] F. Abe, Materials Science and Engineering A, 510–511 (2009), 64–69

[9] A. Gustafson, M. Hättestrand, Materials Science and Engineering A, 333 (2002), 279–286

[10] F. Vodopivec, B. Žužek, M. Jenko, D.A. Skobir Balantič, M. Godec, Materials science and technology, 29 (2013) 4, 451-455.

[11] F. Kafexhiu, PhD Thesis, Jožef Stefan International Postgraduate School, Ljubljana, 2014.

Note: The responsible for English language is F. Vodopivec, Ljubljana, Slovenia