

FORMATION OF THE Z-PHASE AND PROSPECTS OF MARTENSITIC STEELS WITH 11% Cr FOR OPERATION ABOVE 590°C

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Prospects of commercial use of new-generation martensitic thermomechanical steels created on the basis of Fe – 11% Cr steels are considered. The physical causes of degradation of mechanical properties in the process of creep of these steels at $\geq 590^\circ\text{C}$ are studied in detail. It is shown that the degradation is connected with formation of the Z-phase. The mechanisms of formation of the phase are described.

Keywords: steels of martensitic class, Z-phase, creep, mechanical properties.

INTRODUCTION

Several types of high-chromium ($\geq 9\%$ Cr) steels of martensitic class have been developed in the last 15 years for making boilers, conduits, and turbines of coal-fired power generating units with supercritical steam parameters ($t = 600 - 620^\circ\text{C}$, $p = (250 - 340) \times 10^5 \text{ Pa}$) [1, 2]. Two steels created by the Nippon Steel and Sumitomo Metal Industries Companies and certified by ASME as P92 (0.1% C, 0.4% N, 9% Cr, 1.8% W, 0.6% Mo, 0.2% V, 0.06% Nb) and P122 (0.1% C, 0.07% N, 11% Cr, 2% W, 0.5% Mo, 0.24% V, 0.07% Nb, 1% Cu) have found the widest use [3, 4]. The former is a classical martensitic steel with 9% Cr, and the latter has been created on the basis of the Fe – 11% Cr composition. At first the steels were treated as equivalent ones. However, the results of their industrial use in the last 15 years show that the undoubted leader is steel P92 despite the obvious advantages of P122 in weldability and resistance to oxidation in steam atmospheres [5]. The latter property, caused by the high refractoriness of steels with 11% Cr, is especially important for further improvement of the chemical and phase compositions of this class of steel with the aim of raising the operating temperature from 600 to 650°C. Formation of wüstite at a temperature of about 637°C on the surface of pipes produced from steel with 9% Cr makes it necessary to use a special operation of preliminary surface oxidizing with a low amount of oxygen in an argon atmosphere for forming a dense protective film of Cr_2O_3 on the surface in order to

prevent further penetration of oxygen into the metal in service. This complicates the process of production of the power equipment. Steel with 11% Cr does not require such treatment, because its heat resistance ensures operation of pipes produced from it at 650°C without using special methods of surface treatment. The dense layer of chromium oxides formed on the surface of the steel ensures high heat resistance in an atmosphere of live steel [5, 6].

However, all these merits of steels with 11% Cr have not compensated for the catastrophic degradation of their creep resistance after service for about $3 \times 10^4 \text{ h}$ in coal-fired power generating units at a temperature of 600°C and higher [4, 7 – 10]. The causes of this phenomenon have remained unknown until present. In the last 2 – 3 years the loss in the creep resistance of steels with 11% Cr of type P122 after operation for $> 10^4 \text{ h}$ has been attributed to the formation of the Z-phase in their structure [7 – 13].

In Russia the results of works [7 – 13] are virtually unknown though a number of research projects have been started with the aim of development of domestic martensitic steels for thermal power plants [1]. An active discussion is carried out on the choice of a base composition (9 or 11% Cr) for the new-generation domestic thermotechnical steel. Steels with 11% Cr are expected to be a very promising variant. The mentioned advantages of steels with 11% Cr are also confirmed by the positive experience of such steels as 14Kh12V2MF (É1756), 1Kh12VNMF (É1802), 2Kh12VMBFR (É1993), and 15Kh12VM1BFR (ÉP752) created in the time of the Soviet Union and used at $\leq 545^\circ\text{C}$ [14]. The service temperature of parts from these steels did not exceed 545°C, which has eliminated the possibility of formation of the Z-phase in long-term operation. For this rea-

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TABLE 1. Permissible Stresses according to ASME and Corrected Values according to the Rules of the Ministry of Economy, Trade and Industry (METI) of Japan [4, 15]

Steel		Permissible stresses, MPa, at a temperature of, °C			
		566	600	625	650
P92	ASME Code Case 2179 (1994)	119	85	65	45
	METI (2005)	114	78	56	30
P122	ASME Code Case 2180 (1994)	124	85	65	47
	METI (2005)	118	68	46	27

son catastrophic failure of parts from steels with 11% Cr has not been detected in the earlier-built power plants.

The aim of the present paper was to review the latest researches of foreign authors on creep of steels with 11% Cr, to analyze in detail the causes of the impossibility of their service at a temperature exceeding 590°C without marked changes in the chemical composition and modes of heat treatment, and to determine the conditions under which these steels would become promising materials for service at thermal power plants of the new generation. We will consider only the characteristics of heat resistance. Such important mechanical properties as the impact toughness and the notch sensitivity in static testing, also not quite favorable in steels with 11% Cr, will not be analyzed at present.

RESULTS AND DISCUSSION

High-Temperature Strength of Steels with 11% Cr

Permissible stresses for steel P122 and for steel P92 for comparison are presented in Table 1. It should be noted that the properties of heat resistance of P92 are considered in detail in [2]. Fifteen years ago, when the production of these steels was started, the permissible stresses determined for them by testing of specimens according to ASME were 4×10^4 h. In eleven years these permissible stresses were corrected to lower values [4] after testing according to the Rules of the Ministry of Economy, Trade and Industry of Japan, which require testing of individual specimens for 1.2×10^5 h and longer times. This correction was confirmed after additional testing at the ECCC (European Committee for Creep) and producer companies. Analysis of Table 1 shows that at $t < 600^\circ\text{C}$ the correction of the permissible stresses due to extension of the test base is inconsiderable. This means that at $t = 575^\circ\text{C}$ steels of type P122 can be used just as well as P92. At these temperatures the good weldability of steel P122 is its main advantage over P92. Consequently, steels with 11% Cr can be used without limit at $t \leq 575^\circ\text{C}$.

At 600°C the correction of permissible stresses for steel P92 attains 10%, which is treated as a norm and does not re-

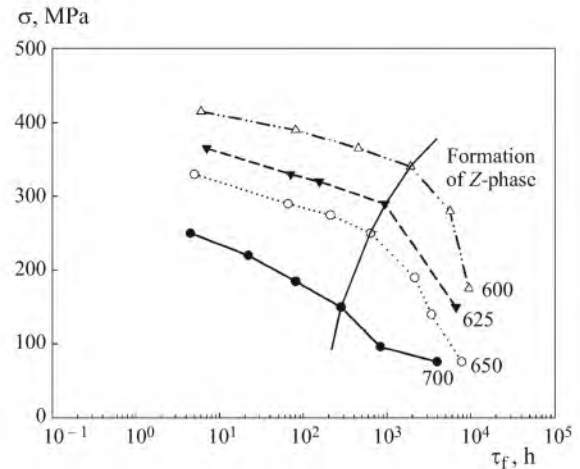


Fig. 1. Applied stresses (σ) as a function of the time before failure (τ_f) for steel with 11% Cr, 3% W, 3% Co, 0.2% V, 0.06% Nb, and 0.07% N [7, 12] at various temperatures (given at the curves in °C).

quire anticipatory replacement of parts. For steel P122 such correction is 25%. At 625°C the correction is 16% for steel P92 and 41% for steel P122. The latter value is unacceptable. At 650°C the corrections of permissible stresses for both steels are unrealistically high. On the basis of the corrected values of permissible stresses the maximum recommended temperature for steel P92 has been preserved at a level of 620°C ; for steel P122 it has been reduced to 590°C . It should be noted that at this temperature the elevated heat resistance of steel P122 has no principal value, because steel P92 exhibits satisfactory erosion resistance in an atmosphere of live steam at up to 620°C [5, 6].

The reason behind the catastrophic correction of permissible stresses for steels with 11% Cr at $t \geq 600^\circ\text{C}$ is the transition from linear dependence of the applied stresses on the time before failure to a descending parabolic dependence (Fig. 1) [7], i.e., starting with a specific time of operation under load steels of type P122 exhibit catastrophic degradation of creep resistance. This makes prediction of permissible stresses at long service times impossible by short-term testing. Materials characterized by such dependences of the long-term strength on the test time in a specific temperature range cannot be used in power engineering at these temperatures [27].

The main reason behind this behavior of thermotechnical steels is instability of the microstructure under creep [2]. In steels of type P92 it consists in formation of Laves phases and coarsening of Me_{23}C_6 carbides [2, 10, 15, 16], which gives rise to dynamic cell formation and softening of the material. In steel P122 the change in the sizes of carbides upon growth in the hold time under creep at 600 and 650°C is the same as in steel P92; the size of the particles of the Laves phases is even three times smaller [17]. Consequently, the processes of coarsening of carbides and segregation of Laves phases during creep, which lead to lowering of the ultimate

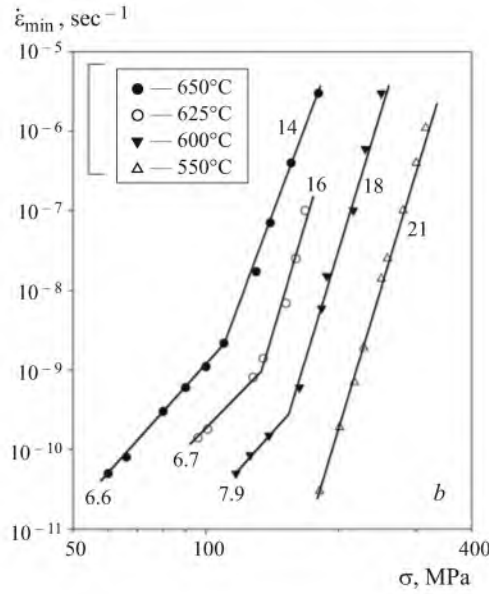
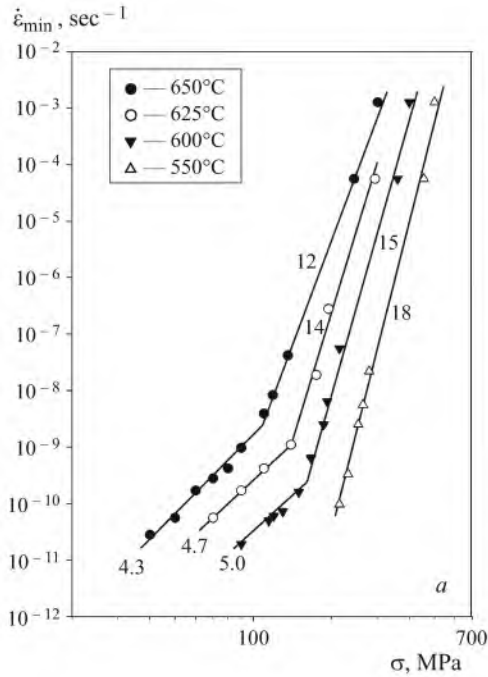


Fig. 2. Minimum rate of creep as a function of applied stress [the figures in the plot present the values of exponent n in equation (2)] for steels P122 [19] (a) and P92 [18] (b) at different temperatures.

long-term strength of steel P92 at $t \geq 600^\circ\text{C}$ [2], cannot be the cause of catastrophic degradation of creep resistance in steels of type P122. In order to understand the nature of this degradation we should analyze the mechanisms of creep in steels P92 and P122 using the data of [18, 19].

It has been shown earlier in [2] that the deformation-induced behavior of thermotechnical steels is describable by the equation

$$\dot{\epsilon} = A [(\sigma - \sigma_{th})/G]^{n^*} \exp\left(-\frac{Q}{RT}\right), \quad (1)$$

where $\dot{\epsilon}$ is either the creep rate in the steady stage or the minimum creep rate, σ_{th} are the threshold stresses below which straining does not occur, G is the temperature-dependent shear modulus, σ is the stress, Q is the activation energy of the deformation, R is the universal gas constant, and T is the absolute temperature. The quantity n^* in Eq. (1) has “true” values obtained experimentally [20]. In order to evaluate the threshold stresses we plot dependences of $\dot{\epsilon}^{1/n}$ on σ for each of the studied deformation temperatures. The true value of n^* is chosen as the value n at which the experimental dependence of $\dot{\epsilon}^{1/n}$ on σ is approximated by a straight line with maximum regression coefficient.

True values of n^* range from 4 to 8. The experimental values of exponent n in equation

$$\dot{\epsilon} = A \sigma^n \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

for steels belonging to the class of precipitation-hardening materials range from 10 to 40. The higher the value of n , the higher the permissible stresses obtained by extrapolation of

data of short-term tests for long-term life. In our previous work [2] we considered the possibility of operation of refractory materials as a function of factor n ; the value of $n \sim 8$ in Eq. (2) should be treated as the lowest one at which the material can be used as a refractory one.

Figure 2 presents dependences of $\dot{\epsilon}_{min}$ on σ plotted in logarithmic coordinates for steels P122 [18] and P92 [19]. It should be noted that each line characterized by its own slope and hence its own value of factor n has been plotted for at least four experimental points [18, 19]; the mean number of points for one line is 7 [18, 19]. It can be seen that at a temperature of 550°C $n \geq 18$ for both steels (Fig. 2), which makes them suitable for operation at this temperature within the permissible stresses without constraint. At 600°C we observe, for steel P92 at $\dot{\epsilon}_{min} = 2.8 \times 10^{-10} \text{ sec}^{-1}$, transition from dependence (2) with $n \approx 18$ to a similar dependence but with $n \approx 8$. This allows steel P92 to serve at this temperature but at the limit of its possibilities. In steel P122 the transition at almost the same $\dot{\epsilon}_{min}$ occurs from $n = 15$ to $n \approx 5$ (Fig. 2), i.e., at a temperature of 600°C and $\sigma \leq 160 \text{ MPa}$ this steel undergoes hot deformation, which is impermissible for a refractory material. Such a transition is explainable only by disappearance of threshold stresses that characterize the metal in the presence of nanosize particles. Steel P122, which should possess MeC-type carbides less than 40 nm in size and Me_{23}C_6 carbides with a size of about 100 nm, behaves as a solid solution at these stresses [20–23]. It can be assumed that at $n \approx 5$ fine particles less than 100 nm in size are dissolved in the steel during creep.

When the temperature is increased to 650°C , factor n in steel P122 decreases further in the range of low deformation

rates (to $n \approx 4$). This value of parameter n is typical only for solid solutions containing no fine particles [20–23]. It follows from the results of creep tests of steel P122 at 625°C and $\sigma \leq 140$ MPa that the fine particles disappear from it and the alloying of the solid solution does not ensure suppression of the high-temperature creep of lattice dislocations controlled by volume diffusion [2]. At the same time, the value of n in steel P92 remains higher than 6.6 even at 650°C (Fig. 2b). Consequently, creep of steel P92 at 650°C occurs in the range of hot deformation, which makes it suitable for short-term operation at this temperature, which is undoubtedly critical for the metal [24]. Steel P92 can exhibit such deformation behavior only if it bears fine particles less than 100 nm in size [2, 17].

Typical creep curves for steel P122 at $t = 650^\circ\text{C}$ are presented in Fig. 3. It should be noted that the steady stage of creep is absent as in steels of the martensitic class [2, 15, 16]. The transition stage of the creep is replaced immediately by the stage of accelerated deformation; the minimum creep rate $\dot{\epsilon}_{\min}$ is attained at $\epsilon \approx 4\%$ as in steel P92 [15, 16]. Accordingly, the analysis of the mechanisms presented above refers fully to this degree of deformation.

The time before failure τ_f obeys the Monkman–Grant relationship, i.e.,

$$\tau = C/\dot{\epsilon}_{ss}, \quad (3)$$

where C is a constant and $\dot{\epsilon}_{ss} = \dot{\epsilon}_{\min}$. This implies a single mechanism of failure due to creep in steel P122 at $\sigma \leq 160$ MPa and $t \geq 600^\circ\text{C}$.

Changes in the Microstructure of Steels with 11% Cr in the Process of Creep

The necessity to explain the catastrophic decrease in the creep resistance at long holds requires careful study of the evolution of the morphology and of the distribution and nature of the particles of secondary phases in steels of type P122 during creep [4, 7–13]. At the same time, data on the evolution of the dislocation structure of troostomartensite in the process of creep in steels with 11% Cr are virtually absent, which complicates interpretation of the results of phase analysis.

High creep resistance is ensured in steels P92 and P122 by carbonitrides of type Me(C, N) [2]. It is the formation of nanoparticles of these nitrides due to complex alloying that has made it possible to raise the operating temperature of these steels by almost 70°C relative to that of the steels used in the heat power industry earlier [2]. The Me(C, N) particles are arranged in the α -matrix according to the orientation relation of Baker–Nutting [15], i.e., $(100)_{\text{Me(C, N)}} \parallel (100)_\alpha$, $[010]_{\text{Me(C, N)}} \parallel [011]_\alpha$. The fcc lattice of the carbonitrides matches the NaCl type. The lattice parameters [the distances between planes (111)] are 0.248 nm for vanadium carbides and 0.258 nm for niobium carbides. These values are close to

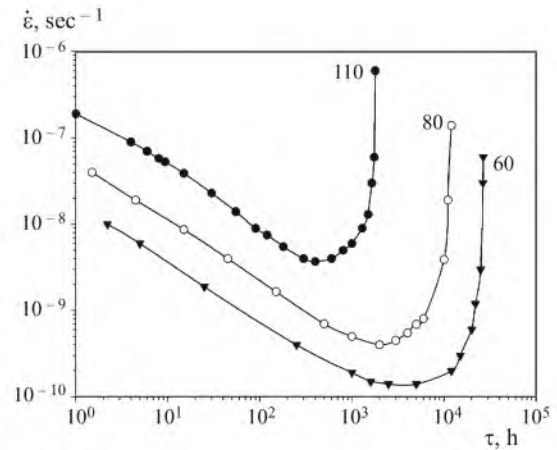


Fig. 3. Deformation rate of steel P92 as a function of time at 650°C [19]. The figures at the curves denote the applied stresses in MPa.

the lattice parameter of ferrite (0.287 nm), which is responsible for the coherent and semicoherent nature of the phase boundaries between them and the ferrite matrix. The carbides enriched with niobium and vanadium have the shape of spheres and plates [15, 25, 26], respectively. In some cases the observed niobium-enriched carbonitride has a round shape with wings [15]. Many researchers analyzing phase transformations in high-chromium steels treat vanadium and niobium carbonitrides as one carbonitride with different contents of V and Nb and, accordingly, different parameters of the cubic lattice [4, 10–12, 26].

It is the dissolution of Me(C, N) nanoparticles in operation that leads to catastrophic softening of steels of type P122 due to creep; this agrees with the analysis of the mechanisms of high-temperature deformation of these steels mentioned above. All investigators of microstructural changes agree in this respect. The authors of [7, 8, 10–12], and [9] disagree about the proportion of the stages of phase transformations and the disability of steel P122 to resist creep. However, in our opinion, this disagreement has no principal value and is a result of the absence of detailed studies of the evolution of the dislocation structure of troostomartensite in creep. Carbonitrides of type Me(C, N) dissolve in creep due to formation and growth of a Z-phase (Fig. 4), which is a carbonitride with the lowest internal energy [29]. Accordingly, creep in steels of type P122 at $t \geq 590^\circ\text{C}$ is accompanied by dissolution of a metastable hardening Me(C, N) phase with particle size of several tens nanometers, which is less stable thermodynamically than the Z-phase [29], and by formation of a stable phase (Z-phase) with particle size of about 1 μm (Fig. 4). This process is similar to a change in stages of aging of aluminum alloys, which leads to a transition from phase (hardening) aging to overaging (softening aging). In fact, in this phase reaction the carbonitrides of type Me(C, N) play the role of a metastable phase and the Z-phase plays the role of a stable phase [12, 29]. The transformation of a less stable phase into a more stable phase in the process

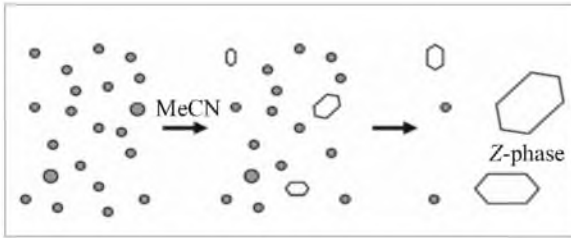


Fig. 4. Scheme of changes in the distribution of phases in creep of steel P92 [7].

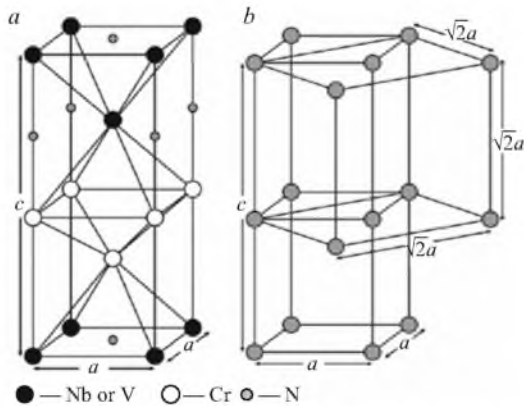


Fig. 5. Crystal lattice of the Z-phase in steel P122: *a*) tetragonal lattice of a modified Z-phase in martensitic steels [11]; *b*) coexistence of cubic and tetragonal lattices reflecting the stages of formation of a Z-phase through a "hybrid" (*Z'*-phase) in the upper part of the lattice [8].

of creep of steel P122 removes the effect of precipitation hardening due to the nanoparticles of Me(C, N). This is responsible for halving of the permissible stresses upon growth in the time of operation at 650°C, which is an optimum temperature for formation of the Z-phase. This leads us to an important conclusion, i.e., the contribution of Me(C, N) nanoparticles to the permissible stresses of steels of the martensitic class is about 50%. It should be noted that the temperature of the dissolution of the Z-phase in a steel with 11% Cr is 800°C [8, 12].

In the steels with 11% Cr subjected to large holds, creep is accompanied by segregation of what is known as a modified Z-phase, i.e., Cr(V, Nb)N (Fig. 5) with tetragonal lattice ($c = 0.739$ nm, $a = 0.286$ nm) represented by periodically alternating layers of VN and Cr [11–13]. As a rule, the Z-phase has the form of plates with a low length-to-thickness ratio and the axis of zone [001] lying perpendicularly to the plane of the plate [11–13]. This phase is said to be modified because a Z-phase was first discovered in austenitic steels and the parameters of its lattice differ somewhat from the parameters of its lattice in high-chromium steels [4, 11, 12]. The Z-phase and the Me(C, N) carbonitrides contain the same elements except for the content of chromium, which varies in the Z-phase from 38 to 54% [8, 25]. It should be

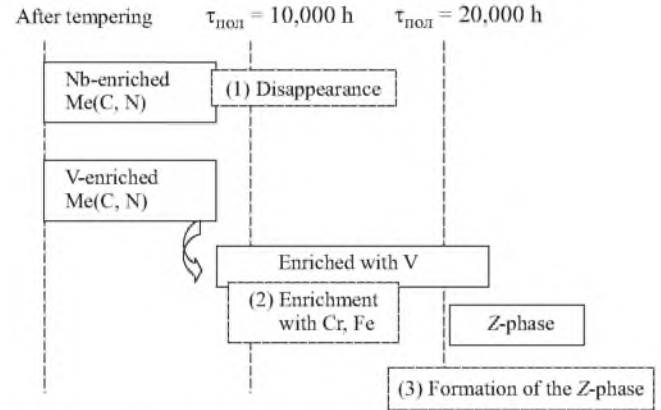
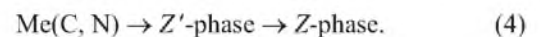


Fig. 6. Scheme of transformations of Me(C, N)-type carbonitride into the Z-phase during creep [4] in steel P122. The figures in parentheses denote the stages of formation of the Z-phase.

noted that while the mean size of the Me(C, N)-type carbonitrides depends but weakly on the chemical composition of high-chromium steels and varies from 10 to 49 nm, the mean size of the Z-phase depends strongly on the chemical composition of martensitic steels and on the hold time during creep and varies from 80 nm in a steel with 9% Cr [25] to 0.5–2 μm in steels with 11% Cr [7–11]. Accordingly, in steel P92 the formation of a Z-phase causes an inconsiderable decrease in the specific volume of carbonitrides of type Me(C, N) [25], whereas in steels of type P122 the Me(C, N)-type carbonitrides dissolve virtually completely (Figs. 4 and 6). Let us consider the causes of this phenomenon in detail [7–11].

The difference in the influence of formation of Z-phase on the creep resistance of steels P92 and P122 is connected with the fact that when the chromium content increases from 9 to 11%, the mechanism of formation of Z-phase in the creep process changes. It should be noted that it is just the mechanism of initiation of the phase that plays the key role in the influence of the Z-phase on the ultimate long-term strength [28]. In steels of type P92 the first Z-phase particles sometimes form after a hold of 10^5 h and their size is less than 100 nm; in steels of type P122 the particles of a Z-phase of micron size can be detected after a hold of 10^3 h [28]. In steels of type P122 a Z-phase is formed from a carbonitride of type Me(C, N) through formation of an intermediate *Z'*-phase with cubic lattice called a "hybrid" [4, 7, 8, 11, 28] by the mechanism of internal rearrangement of the lattice. The succession of phase transformations for steels of type P122 can be written as follows:



The *Z'*-phase is metastable with respect to the Z-phase and more stable with respect to the Me(C, N) carbonitride at chromium content exceeding 20% [28, 29]. The *Z'*-phase forms after creep with a hold of several hundred hours,

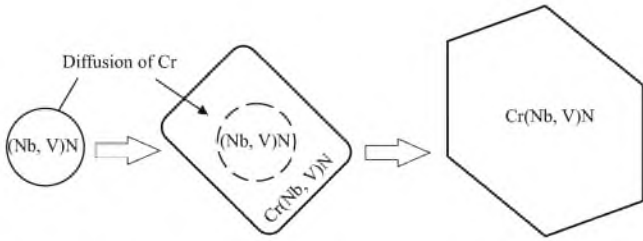


Fig. 7. Scheme of formation of the Z-phase in ferrite matrix of steel P122 due to diffusion of chromium into a Me(C, N) carbonitride [7, 8].

whereas the Z-phase usually appears after a hold of several tens of thousand of hours [28, 29].

In the process of creep, chromium penetrates through the phase boundary into nanoparticles of Me(C, N) (Fig. 7) due to diffusion. The content of chromium in the carbonitride of type Me(C, N) increases from 5 to 20%. It can be concluded from the data of [10 – 12, 25, 26] that 20 wt.% Cr is the limiting content for a Me(C, N) carbonitride to preserve its lattice; a higher content of chromium causes transformation of Me(C, N) into the Z'-phase with cubic lattice (see Fig. 5b). This transformation consists of growth in the lattice constant to 0.416 nm [8], which is connected with a change in the chemical composition of the nanosize dispersion from Me(C, N) to Cr(V, Nb)N. This leads to a loss in coherence over the $(100)_{\text{Cr(V, Nb)N}} \parallel (100)_{\alpha}$; the phase boundaries of the nanoparticles become incoherent. It should be noted that the experimentally observed [28] crystallographic relations between the Z'-phase and the Me(C, N)-type carbonitride corresponds exactly to Fig. 5b.

The rate of coagulation of particles by the Ostwald mechanism is described by the equation [25]

$$r^m - r_0^m = k\tau, \quad (5)$$

where r^m and r_0^m are the mean radii of particles of second phases at the current and initial moments of time, m is an exponent determined by the mechanism that controls the coagulation (if the coagulation is controlled by volume diffusion, $m = 3$), k is the coagulation rate constant, and τ is the time. For Me_AC_B carbides the value of k is determined by the equation [25]

$$k = \frac{8(A+B)\sigma VD u_{\text{Me}}}{9ART(u_{\text{Me}}^p - u_{\text{Me}})^2}, \quad (6)$$

where σ is the energy of the interphase energy of the carbide, V is the molar volume of the carbides, D is the coefficient of volume diffusion of the Me atoms, u_{Me} and u_{Me}^p are the contents of the Me atoms in the matrix and in the carbide respectively.

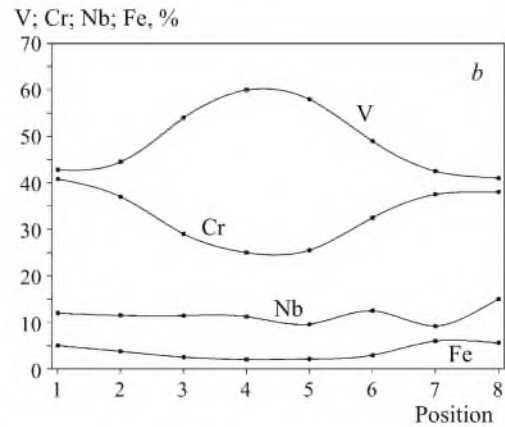
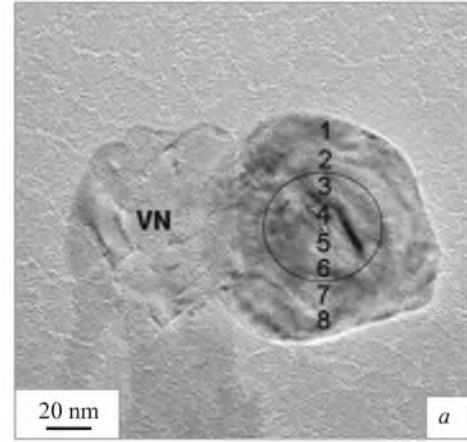


Fig. 8. Hybrid particle (Z'-phase) after creep for 1.2×10^4 h at 660°C in a steel with 12% Cr (a) and distribution of metals in it as a function of the position [7] (b).

The energy of a coherent boundary is over 10 times lower than the energy of an incoherent boundary. Accordingly, coagulation of nanoparticles of the Z-phase with coherent boundaries develops at a rate almost 1000 times lower in accordance with Eqs. (5) and (6) as compared to coagulation of particles of the same phase with incoherent boundaries. In our opinion, it is the formation of particles of the Z-phase with incoherent boundaries that is responsible for its intense coagulation resulting in complete dissolution of the particles of Me(C, N)-type carbonitrides. Formation of the Z-phase by reaction (4) by the mechanism of rearrangement of the lattice of a Me(C, N)-type carbonitride causes formation of coarse Z-phase particles with chemically inhomogeneous composition; a Z'-phase with reduced chromium content and elevated vanadium content is in the center (Fig. 8). In a great number of coarse Z-phase particles observed experimentally [7, 10 – 12] the chemical composition and the lattice in the center corresponded to Me(C, N) (Fig. 8). A chromium-enriched and vanadium-depleted Z-phase with tetragonal lattice has been observed over the edge of a particle (Figs. 7 and 8). Consequently, all the three phases partici-

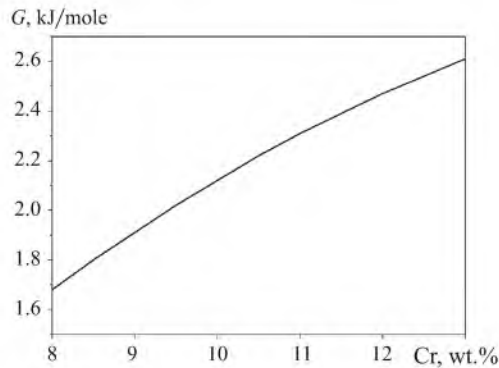


Fig. 9. Effect of chromium content in steel on the driving force G of segregation of the Z-phase [29].

pating in reaction (4) can be observed experimentally for one Z-phase particle.

First, the niobium-enriched carbonitride transforms by the reaction $\text{Nb}(\text{C}, \text{N}) \rightarrow \text{Z-phase}$ (see Figs. 6 and 7) [4]. Formation and growth of the Z-phase causes a leading dissolution of $\text{Nb}(\text{C}, \text{N})$ carbonitrides (Fig. 6) [4]. In the second turn, the vanadium-enriched carbonitride transforms by reaction $\text{V}(\text{C}, \text{N}) \rightarrow \text{Cr}(\text{V}, \text{Nb})\text{N}$ [4]. After a hold of about 3×10^4 h the transformation $\text{Me}(\text{C}, \text{N}) \rightarrow \text{Cr}(\text{V}, \text{Nb})\text{N}$ ends virtually completely (Fig. 6) [4]. After this, only the Z-phase is retained in the steel with 11% Cr; the $\text{V}(\text{C}, \text{N})$ carbonitrides dissolve completely. It should be noted that though a Z-phase bearing no vanadium does exist, a Z-phase without niobium has not been detected yet in the absolute majority of studies [10, 11, 25, 26] despite the fact that its existence had been predicted by thermodynamic computations [29]. Such a phase has been detected in steel X20 (0.2 – 0.025% N – 11.5% Cr – 0.9% Mo – 0.5% Mn – 0.7% Ni – 0.3% V) that contains no niobium after a hold for 1.5×10^5 h [12]. Note that only several particles of micron size have been detected. Formation of the Z-phase in this steel has not led to an experimentally determinable decrease in the specific volume of the $\text{V}(\text{C}, \text{N})$ carbonitrides. Thus, we have every reason to assume that a Z-phase containing no niobium cannot form in modern high-chromium niobium-alloyed steels.

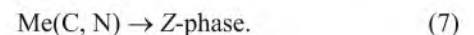
One more feature of Z-phase is its heterogeneous segregation over boundaries of former austenitic grains and boundaries of martensite packets, which causes formation of near-boundary zones free of $\text{Me}(\text{C}, \text{N})$ particles in addition to coarse particles over these boundaries [8, 30, 31]. This is responsible for the early failure of steels with 11% Cr. Note that the change in the dependence of the stresses applied on the time before failure (see Fig. 1) occurs at longer test times than the time in which the Z-phase starts to form [30, 31]. This inflection (Fig. 1) is observed at a hold in which the major part of the $\text{Me}(\text{C}, \text{N})$ carbonitride dissolves near the boundaries of the former austenite grains and packets; chains

of coarse Z-phase particles form over these boundaries [30, 31].

Effect of Alloying on Formation of the Z-Phase

It is known today that the development of transformation (4) affects the following elements: Cr, Ni, Nb, and N. When the content of chromium is decreased from 11 to 9%, the driving force for formation of Z-phase is decreased by almost a factor of 1.5 (Fig. 9) [29]. This is the main reason behind the almost full suppression of formation of the Z-phase in the process of operation of steels of type P92; the rate of formation of the Z-phase in these steels decreases by several orders of magnitude. For example, at 650°C a Z-phase forms in steel P92 after a hold for 10^4 h; in steel P122 with 11% Cr, which does not contain δ -ferrite, this occurs after 10^3 h; in steel P122 with 12% Cr, which bears 5% δ -ferrite, a Z-phase forms after a hold of 2×10^2 h. It should be noted that steels P91/P92 contain individual particles of the Z-phase after several tens of thousand hours of creep [25, 30, 31]. However, their size is comparable with the size of Me_{23}C_6 carbides, and their specific volume is much lower than the specific volume of the $\text{Me}(\text{C}, \text{N})$ particles. Accordingly, the formation of the Z-phase in steels with 9% Cr does not create problems with the long-term strength. At the least, the growth of Me_{23}C_6 carbides and Fe_2W Laves phases in steels of type P92 leads to more significant softening. As a result, the effort of researches aimed at increasing the high-temperature strength of steels of type P92 is concentrated on limiting the processes of coagulation of Me_{23}C_6 carbides and Fe_2W Laves phases. Formation and growth of the Z-phase in steels with 9% Cr has been studied until the present only for special steels with high nitrogen content and low content of carbon [25, 26, 32].

The results of [25, 26, 32] allow us to make the following conclusion: in steels with 9% Cr segregations of the Z-phase are fine and its formation does not cause dissolution of most carbonitrides of type $\text{Me}(\text{C}, \text{N})$ and thus does not lead to substantial softening of these steels in the process of creep. The causes of this phenomenon have remained unclear for the authors of [25, 26, 30 – 32]. However, analyzing the electron micrographs presented in these works we may assume that in steel with 8% Cr a Z-phase forms as a result of heterogeneous nucleation on the ferrite/ $\text{Me}(\text{C}, \text{N})$ phase boundary (Fig. 10) rather than by the mechanism of lattice restructuring. Accordingly, the transformation of carbonitrides of type $\text{Me}(\text{C}, \text{N})$ into a Z-phase in steels of type P92 occurs by the reaction [25]:



Several factors are responsible for the very low rate of transformation (7). Firstly, the heterogeneous nucleation even on the phase boundary requires simultaneous concentration and energy fluctuations in contrast to the mechanism of lattice rearrangement of $\text{Me}(\text{C}, \text{N})$ -type carbonitrides. The

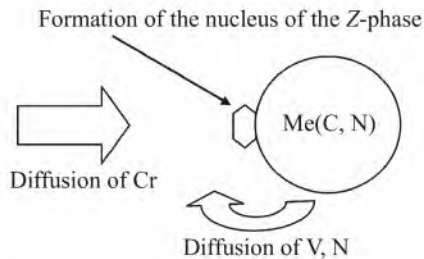


Fig. 10. Scheme of formation of Z-phase in steel P122 by the mechanism of heterogeneous nucleation on a Me(C, N)/ferrite phase boundary [28].

probability of this is extremely low with allowance for the complexity of the crystal lattice of the Z-phase [28]. This very fact makes independent nucleation of a Z-phase impossible; its formation requires the presence of Me(C, N)-type carbides [28]. Secondly, the rate of growth of Z-phase particles formed by the scheme presented in Fig. 10 is also considerably lower than by the mechanism presented in Fig. 7. This is explainable by the lower energy of the phase boundary σ in equation (6), by the necessity for additional diffusion of vanadium and nitrogen through the ferrite matrix, and by the lower rate of diffusion of chromium. The “ a ” parameter of the tetragonal lattice of the Z-phase coincides with high accuracy with the lattice parameter of the ferrite. It is possible that this leads to the formation of Z-phase particles less than 80 nm in size during creep, half of the boundaries of which are coherent or semicoherent. This explains their lower energy σ with respect to the energy of some incoherent particle boundaries formed by reaction (4). Accordingly, the susceptibility of these particles to growth should be much lower than the same susceptibility of the Z-phase particles with incoherent boundaries by the reasons considered above.

It has been shown in [25] that the content of Cr in the Z-phase of steels of type P92 does not exceed 40%, i.e., is at the bottom limit. The mean content of chromium in the Z-phase of steels of type P122 amounts to 50% [11, 12, 28]. Decrease in the gradient of chromium concentration between the Z-phase and the ferrite matrix also lowers the rate of coagulation of the Z-phase in accordance with equation (6). We should say in conclusion that formation and growth of the Z-phase in steels of type P92 stimulates only inconsiderable dissolution of particles of Nb(C, N). It is natural that this softens the steels with 9% Cr but not as strongly as in the case of formation of Z-phase particles of micron size in steels with 11% Cr. The carbonitride phase of type Me(C, N) with a mean size of 40 nm present in the structure of the steels with 9% Cr ensures precipitation hardening and hinders cell formation. For this reason [12], the formation of the Z-phase does not result in an early decrease in the creep resistance in steels with 9% Cr.

The negative action of nickel on the high-temperature strength of thermotechnical steels has been known for a long time. For this reason new steels of martensitic class contain

no nickel at all despite its favorable effect on the impact toughness. Accordingly, experimental works devoted to segregation of Z-phase in new martensitic steels with nickel are virtually absent and the data available are contradictory. In the opinion of the authors of [13] growth in the nickel content accelerates segregation of Z-phase. However, the thermodynamic computations of [29] show that the driving force of formation of Z-phase is independent of the content of nickel.

Another important element is copper. Data on the influence of copper on segregation of Z-phase are absent. Copper is introduced into martensitic steels with 11% Cr for two reasons. Firstly, in steels with 11% Cr and a high content of $\Sigma(W + Mo)$ it provides the possibility of normalization from the austenitic range, because it is a γ -stabilizer and virtually compensates the “excess” 2% Cr (α -stabilizer) in steel P122 ($Ac_1 = 805^\circ\text{C}$) [3] as compared to steel P92. Secondly, copper is introduced to ensure nucleation of Laves phases during creep [2] on the copper/ferrite interface [33] and thus to ensure a marked decrease in the size of the Fe_2W -type particles (from 300 to 30–60 nm). It should be noted that catastrophic softening is observed both in boiler steel P122 with copper and in Japanese steel TAF650 for turbine rotors, which bears no Cu but is additionally alloyed with 3% Co [10–13]. Consequently, a Z-phase forms in steels with 11% Cr both with copper and without it. We may only presume that copper, like cobalt, produces no effect on the formation of Z-phase.

Growth in the content of Nb accelerates the formation of the Z-phase. Thermodynamic computations have shown [29] that growth in the content of Nb increases somewhat the driving force of formation of Z-phase. In steel of type P122 bearing no Nb the content of the Z-phase after creep is inconsiderable [12]. This is connected with the fact that as a rule, as we have shown above, a Z-phase does not form in martensitic steels without niobium (see Fig. 6). Thus, in steels of martensitic class bearing niobium, creep is accompanied by formation of a Z-phase, whereas a Z-phase does not form in them in the absence of niobium. From this standpoint it seems reasonable to replace niobium with titanium, which prevents formation of a Z-phase. However, in [34] such a replacement has resulted in formation of coarse MeX-type carbides in steel of type P92, which is virtually similar to transformation (4) with respect to the influence on creep resistance. This is connected with the fact that the size and distribution of titanium carbonitrides are virtually uncontrollable by heat treatment due to the negligibly low solubility of titanium both in austenite and in ferrite.

It is just the absence of nitrogen in the metal that leads to the formation of a Z-phase in high-chromium steels. It should be noted that nitrogen in an amount of up to 0.05 wt.% gets into the composition of these steels naturally in the process of melting in open furnaces. In a Z-phase nitrogen cannot be substituted by carbon. Therefore, any growth in the nitrogen content with simultaneous decrease in the content of carbon

accelerates the formation of Z-phase, because the chemical composition of the Me(C, N)-type phase shifts from carbonitride to nitride. Increase in the nitrogen content to 0.06% and any decrease in the carbon content stimulate growth in the driving force for formation of Z-phase [29]. The dependence of the rate and of the mechanism of formation of the Z-phase on the content of nitrogen and carbon is almost critical for the long-term strength of new-generation steels created on the basis of P92 due to the replacement of Me_{23}C_6 -type carbides by carbonitrides of type Me(C, N) [17, 25, 26, 32]. It has been shown that growth in the nitrogen content above 0.05 wt.% accelerates considerably the formation of the Z-phase in steels with 9% Cr [25 – 27, 32]. For this reason the content of nitrogen in martensitic steels with 9% Cr is limited by this value. At higher nitrogen concentrations the rapid formation of Z-phase is also accompanied by formation of coarse Cr_2N particles, which causes intense softening.

Prospects of Application of Steels with 11% Cr

All the facts presented allow us to infer that the known steels with 11% Cr cannot be used as a heat-resistant material at $t \geq 600^\circ\text{C}$. For service at high temperatures their chemical and phase composition should be modified and the heat treatment modes changed. Today foreign developers of improved versions of these steels are unanimous in their opinion that it will be impossible to prevent formation of a Z-phase in them in the creep process. However, the composition of steels with 11% Cr can be changed so that the phase will be segregated in the process of tempering and uniformly distributed in the volume of the material; its mean size should not exceed 60 nm. Intense works on creation of such steels are carried out today within the framework of the COST European project. In principle [8], such an approach is implementable. At the same time, a long duration of tempering (3×10^3 h at 650°C) [8] is unacceptable for commercial production. Should developers find a way for alloying of steels with 11% Cr such that nanoparticles of Z-phase form rapidly in the process of tempering at 650°C and are stable in creep, the steels would again be considered as promising candidates for heat power engineering.

CONCLUSIONS

1. In steels of martensitic class with 11% Cr a Cr(V, Nb)N a Z-phase forms in long-term creep tests and is the cause of catastrophic deterioration of their resistance to high-temperature strain.

2. The formation of the Z-phase and its coagulation lead to dissolution of the (V, Nb)(C, N)-type carbonitrides, which is responsible for intense softening of martensitic steels.

3. The highest rate of formation of the Z-phase in steels with 11% Cr is observed at 650°C .

4. Steels with 11% Cr would serve well at a temperature exceeding 650°C only in the case of development of compo-

sitions and heat treatment methods preventing the formation of the Z-phase during creep or ensuring formation of Z-phase particles less than 60 nm in size during tempering.

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