
**STRUCTURE, PHASE TRANSFORMATIONS,
AND DIFFUSION**

The Effect of Creep and Long Annealing Conditions on the Formation of the Z-Phase Particles

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Abstract—The influence of the temperature, applied stress, degree of creep deformation, and aging time on the formation of Z-phase (CrVN) particles in 9% Cr 10Kh9K3V2MFBR martensitic steel at temperatures of 650 and 675°C upon long aging is studied in this work. The particles with a chemical composition determined by energy dispersive spectrometry as 50% (Cr + Fe) and 50% (V + Nb) are detected and identified as particles of the Z-phase. An increase in the creep test time at both temperatures led to the growth of Z-phase particles. An increase in the temperature provokes earlier nucleation of small Z-phase particles with a change in the mechanism of their nucleation. An enlargement of particles is observed upon localization of plastic deformation. Long-term annealing at temperatures of 650 and 675°C does not lead to the formation of Z-phase particles. Plastic deformation has a crucial effect on the formation of Z-phase particles in steels containing 9% Cr. The temperature, time, applied stress, and strain localization are aggravating factors that cause the growth of this phase.

Keywords: heat-resistant steel of the martensitic class, creep, long-term annealing, MX carbonitrides, Z-phase, phase transformation

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INTRODUCTION

The development of materials for power engineering is aimed at increasing the efficiency of coal-fired power plants by increasing their heat resistance [1–3]. Power units operating at ultrasupercritical steam parameters (USCP), in particular, a pressure of 240–330 MPa and a temperature of 620–650°C, are currently put into operation. These steam parameters cannot be attained using traditional ferritic and bainitic steels [1]. Revolutionary changes that occurred in the material science of boiler and turbine steels 30 years ago are associated with the development of a new generation of high-chromium martensitic steels with a V content of 0.24 wt % and a Nb content of 0.05 wt %, while maintaining the C and N contents at a level of 0.1 and 0.05%, respectively. Such alloying allows one to obtain nanosized M(C,N) carbonitrides (where M is V, Nb, and/or Ta) that are not prone to coagulation at high temperatures owing to two-phase separation into VN and NbC [1–13] and ensures the long-term strength of these steels, which is sufficient to increase the steam temperature by 40–70°C. Nanosized M(C,N) carbonitrides uniformly distributed in the volume of the matrix act as obstacles for the movement of dislocations and their rearrangement into subgrain boundaries. The latter fact leads to a sharp increase in the creep rate [14]. However, M(C,N) car-

bonitrides are considered a nonequilibrium phase and in service are replaced by the equilibrium Z-phase (Cr(V,Nb)N), the size of which can reach several micrometers [4–6, 12, 13]. This increases the distance between particles upon creep, which can be an important reason for the premature beginning of the tertiary creep stage thus reducing the long-term strength [4–9].

In previous studies, a mechanism was established for the formation of Z-phase particles under creep conditions at 650°C [6, 12, 13, 15, 16]. This mechanism consisted in the direct rearrangement of the cubic lattice of M(C,N) carbonitrides into the tetragonal lattice of the Z-phase. The process of transformation begins from the peripheral zone of M(C,N) particles and gradually moves towards their core, thereby forming the so-called “hybrid particle”. The rate of growing the Cr-enriched shell composed of the Z-phase along the M(C,N) particle periphery is controlled by the diffusion of Cr atoms from the ferrite matrix and the diffusion of V or Nb atoms from the M(C,N) particle core [5, 12, 13].

The aim of this study was to establish the role of factors such as the temperature, applied stresses, test duration, strain, and scope of its localization on the conversion of M(C,N) carbonitrides into the Z-phase. This information would allow one to clarify the mech-

anism and kinetics of this transformation and to increase the heat resistance characteristics.

RESEARCH METHODOLOGY

In a high-frequency induction furnace at OAO NPO TsNIITMASH, 10Kh9K3V2MFBR steel with the following chemical composition (wt %): Fe (balance content)—0.12C—0.06Si—0.1Ni—0.2Mn—9.5Cr—3.2Co—0.45Mo—2.0W—0.2V—0.06Nb—0.005B—0.05N was cast. The ingots were reformed to rods with square cross sections with a square side of 20 mm by the method of free forging at temperatures in the range from 1150 to 900°C. The heat treatment of steel included normalization at $1050 \pm 10^\circ\text{C}$ followed by tempering for 3 h at $750 \pm 10^\circ\text{C}$. Flat specimens with a working part with a length of 25 mm and a cross-sectional area of $7 \times 3 \text{ mm}^2$ and cylindrical specimens with a working part with a length of 100 mm and a diameter of 10 mm were tested on an ATS2330 lever-type testing machine for the long-term tensile strength at temperatures of 650 and 675°C under applied stresses in the range of 180–80 MPa with a step of 20 MPa.

To study the structure, we used a JEM JEOL-2100 transmission electron microscope (TEM) equipped with an INCA energy dispersive attachment. Foils for TEM were prepared from the gripped and working parts of the sample, as well as from the neck region of the samples for creep tests, and electrolytically polished in an electrolyte composed of a 10% perchloric acid solution in acetic acid at room temperature. Carbon replicas were analyzed to determine the exact chemical composition of the particles without the influence of the matrix when recording the energy dispersive spectrum. The particles of the secondary phases were identified by simultaneously analysing the microdiffraction patterns obtained in a transmission electron microscope (TEM) and the chemical composition of the particles. The techniques are described in more detail in previously published studies [8, 9, 15, 16].

RESEARCH RESULTS

Initial State after Tempering at 750°C

The microstructure of 10Kh9K3V2MFBR steel and the chemical analysis of M(C,N) carbonitrides after normalization and tempering at 750°C were described in detail in previous studies [8, 9, 15, 16]. Briefly, it should be noted that a lath structure of tempered troostite with a high dislocation density inside martensitic laths is formed after the heat treatment. Globular M_{23}C_6 carbide particles with an average size of 90 nm are arranged along the boundaries of the initial austenitic grains and martensitic laths and subgrains, while M(C,N) carbonitride particles are uniformly distributed over the volume of the ferrite matrix. Two types of M(C,N) particles were found in the steel under study [15]. The first type is Nb-enriched

round particles with an average size of 40 nm. These particles precipitated in the course of normalization and tempering to 500°C [2]. The second type is vanadium-enriched particles with an elongated shape and an average size of 20 nm, which precipitated upon tempering at 750°C.

Mechanical Properties under Creep

The dependence of the applied stress on the time to degradation is shown in Fig. 1a. As is seen, after long-term strength tests the steel under study showed a pronounced bend on the long-term strength curve after 2000 h of testing at a temperature of 650°C, while no such a bend was observed at this time point when testing at a temperature of 675°C. Moreover, a bend on the curve may appear, depending on the result of an unfinished test, at 80 MPa (Fig. 1a). The time dependences of the creep rate prior to degradation at temperatures of 650 and 675°C are given in Figs. 1b and 1c, respectively. At a creep temperature of 650°C, the minimum creep rate is $1.2 \times 10^{-10} \text{ s}^{-1}$ at an applied stress of 100 MPa (Fig. 1b). With a decrease in the applied stress from 180 to 100 MPa, the time for which the minimum creep rate is reached shifts from 47 to 3984 h. At a creep temperature of 675°C, the minimum creep rates are 1.4×10^{-8} and $4.6 \times 10^{-9} \text{ s}^{-1}$ with applied stresses of 120 and 100 MPa, respectively (Fig. 1c). With a decrease in the applied stress from 160 to 100 MPa, the time required to reach the minimum creep rate shifts from 10 to 1082 h.

M(C,N) Carbonitrides after Prolonged Annealing at 650 and 675°C

The main change in the tempered troostite lath structure of the studied steel with 9% Cr after prolonged annealing at 650 and 675°C is the precipitation of particles of the Laves phase with an average size of 100 nm (Fig. 2a) [8]. With a further increase in the annealing time, the sizes of M_{23}C_6 carbide particles and Laves phases increase several times [8], while the sizes of V(C,N) and Nb(C,N) carbonitride particles do not change (Fig. 2b), although they increased almost twofold compared to the initial state (Fig. 2b). No evidence of the formation of the Z-phase particles was found after prolonged annealing for 11151 h at 650°C and for 2003 h at 675°C. Slight changes in the chemical composition of the M(C,N) carbonitride particles were detected after prolonged annealing (Fig. 2c). Thus, the vanadium and niobium contents in the V(C,N) carbonitride particles increase, while the chromium content decreases (Fig. 2c). In the Nb(C,N) carbonitride particles, the niobium content increases, while the vanadium content slightly decreases (Fig. 2c). Changes in the chemical composition of small M(C,N) carbonitride particles do not lead to their transformation into particles of the Z-phase.

Formation of Z-Phase Particles after Testing the Long-Term Strength at 650 and 675°C

After the long-term creep under conditions of 650°C/120–100 MPa, the tempered troostite structure strongly evolves and transforms into a subgrain structure with an average subgrain size of above 1.5 μm , while the lath structure with an average size of martensitic laths of about 500 nm is preserved under short-term creep conditions at 675°C/120–100 MPa [8]. The chemical composition of the Nb(C,N) carbonitride particles barely changes; no evidence was found for the enlargement of these particles or their transformation into Z-phase particles upon creep at both temperatures. In the chemical composition of the V(C,N) carbonitride particles, the fractions of vanadium and niobium decrease and the fractions of chromium and iron increase, which leads to their transformation into the Z-phase particles with a composition of 50 wt % (Cr + Fe) and 50 wt % (V + Nb) in accordance with the results of energy dispersive spectrometry under creep conditions at both temperatures (Fig. 3). At a temperature of 650°C, several small particles of the Z-phase with an average size of 70 nm were detected after 4869 h of testing under an applied stress of 120 MPa [8, 15]. The substantial enlargement of Z-phase particles up to 200 nm was detected after 11151 h of creep testing under an applied stress of 100 MPa. Large particles of the Z-phase coexist with the V(C,N) carbonitride particles (Fig. 3). The effect of strain localization on the formation of the Z-phase particles was investigated in detail in [16]. It can be briefly noted that the creep localization changes the mechanism of nucleation of the Z-phase particles from the direct rearrangement of the cubic lattice of the V(C,N) carbonitride particles into the tetragonal lattice of the Z-phase in the region of uniform deformation to the heterogeneous nucleation of the Z-phase particles at the V(C,N)/ferrite interface. The simultaneous presence of very small and large particles leads to an accelerated enlargement of Z-phase particles near the degradation site.

The average size of Z-phase particles reached 300 nm in the region closest to the degradation region. The ratio of fractions of the Z-phase particles to V(C,N) particles ranged from 1 : 1 in the region of uniform deformation to 9 : 1 in the region of maximum localization of the plastic flow [16].

Under creep conditions at a temperature of 675°C and an applied stress of 120 MPa, the time prior to degradation is 773 h and very small Z-phase particles with a cubic lattice were found on the surface of the V(C,N) carbonitride particles in the region of strain localization (Fig. 4). An increase in the creep time (applied stress 100 MPa) to 2003 h led to the enlargement of the Z-phase particles with a cubic lattice to 41 nm and the appearance of individual Z-phase particles with a tetragonal lattice with an average size of 60 nm, while the ratio of all Z-phase particles to V(C,N) particles was 1 : 4 in the region of uniform deformation

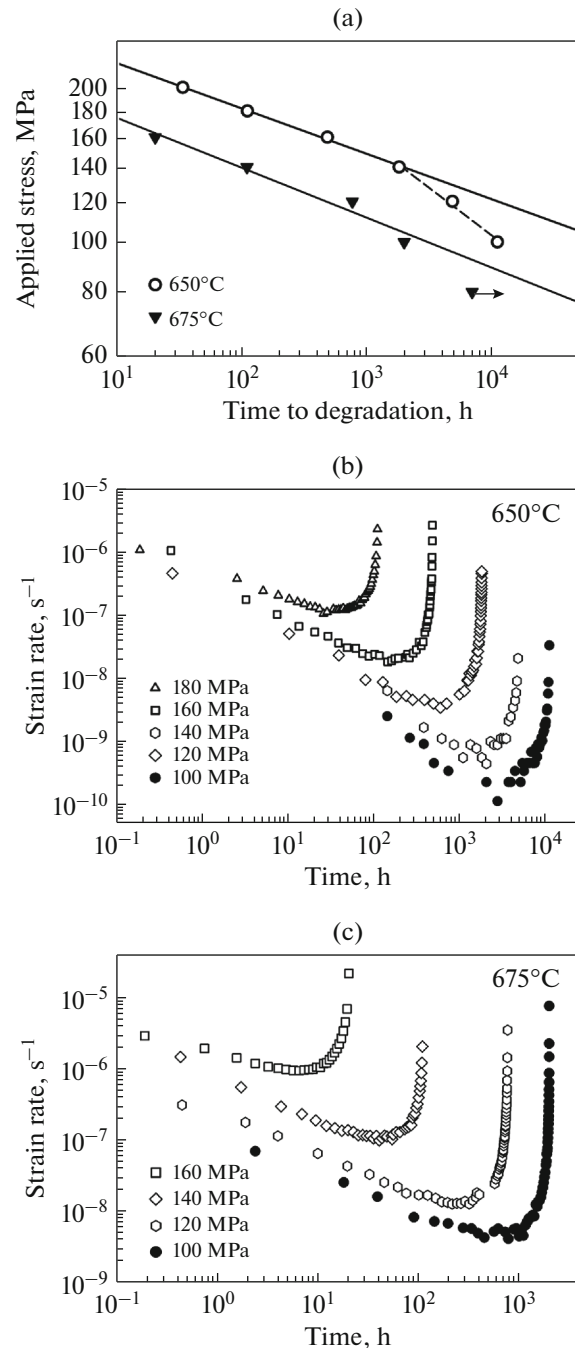


Fig. 1. (a) Dependence of the stress on the time to failure at test temperatures of 650 and 675°C for 9% Cr steel under study additionally alloyed with 3% Co and (b, c) the deformation–time curves obtained (b) with applied stresses of 180, 160, 140, 120, and 100 MPa at a temperature 650°C and (c) with applied stresses of 160, 140, 120, and 100 MPa at a temperature of 675°C.

(Fig. 5). It should be noted that the chemical compositions of the Z-phase particles with a tetragonal lattice that are formed upon creep at 650°C (Fig. 3d) and the Z-phase particles with a cubic and tetragonal lattices that are formed upon creep at 675°C (Figs. 4b and 5d)

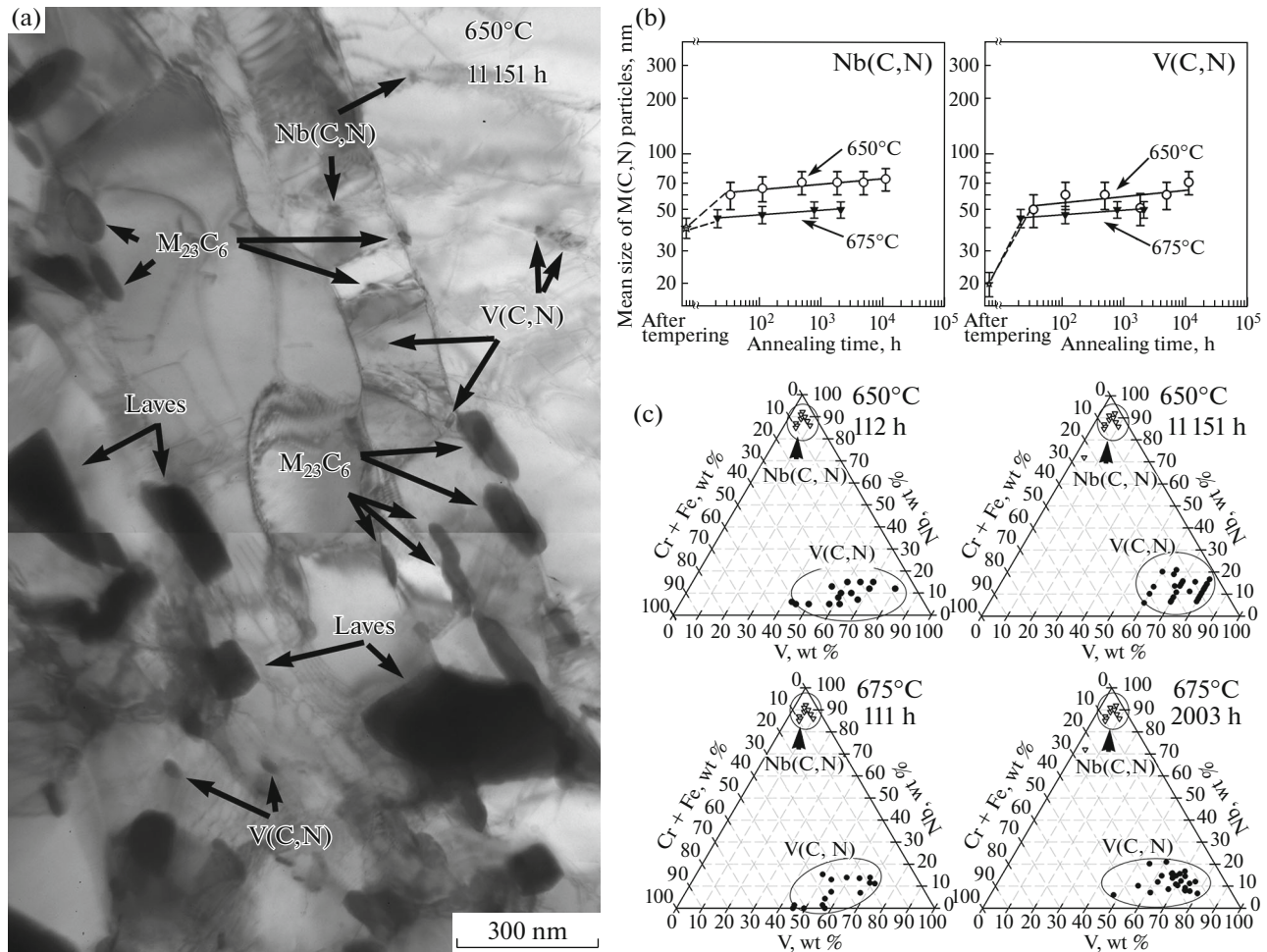


Fig. 2. (a) Microstructure of the studied steel containing 9% Cr and additionally alloyed with 3% Co in the gripped part of the sample tested for long-term strength under the following conditions: 650°C, 100 MPa, and time to degradation 11151 h; (b) the time dependence of the changes in the size of Nb(C,N) and V(C,N) carbonitride particles at annealing temperatures of 650 and 675°C; and (c) a change in the chemical composition of M(C,N) carbonitride particles upon annealing with various times and temperatures.

are the same and do not depend on the temperature or on the type of crystal structure.

DISCUSSION

Particles of Nb(C,N) carbonitrides are stable under creep. The size of these particles and their chemical composition do not change with increasing the test temperature, the test time, or the degree of deformation, which indicates the high stability of these carbonitride particles against coarsening at high temperature upon creep. No transformation of the Nb(C,N) carbonitride particles into Z-phase particles was detected. Moreover, the V(C,N) carbonitride is not a stable phase at $T = 650$ and 675°C . According to the thermodynamics of alloys, the existence of unstable phases in an alloy does not correspond to the minimum Gibbs energy [16] and, consequently, they must dissolve. The calculation results obtained using the

ThermoCalc software package show that the Z-phase with a chemical composition of 50% (Cr + Fe) and 50% (V + Nb) is an equilibrium phase at 650 and 675°C. This is consistent with the published data [5, 12, 13] stating that the Z-phase is the most stable nitride in steels with 9–11% Cr. In this case, the amount of the Z-phase depends on the temperature and the exposure time, as well as on the concentration of Cr in the steel [4]. At both creep temperatures of 650 and 675°C, a process of transformation of small V(C,N) particles into the Z-phase is observed.

It should be noted that the formation of the Z-phase particles has an insignificant effect on the mechanical behavior of the steel under study and does not lead to the appearance of a bend on the long-term strength curve at a temperature of 675°C (Fig. 1a). Moreover, it was found in earlier studies that the appearance of a bend on the long-term strength curve at a temperature of 650°C is caused by other structural

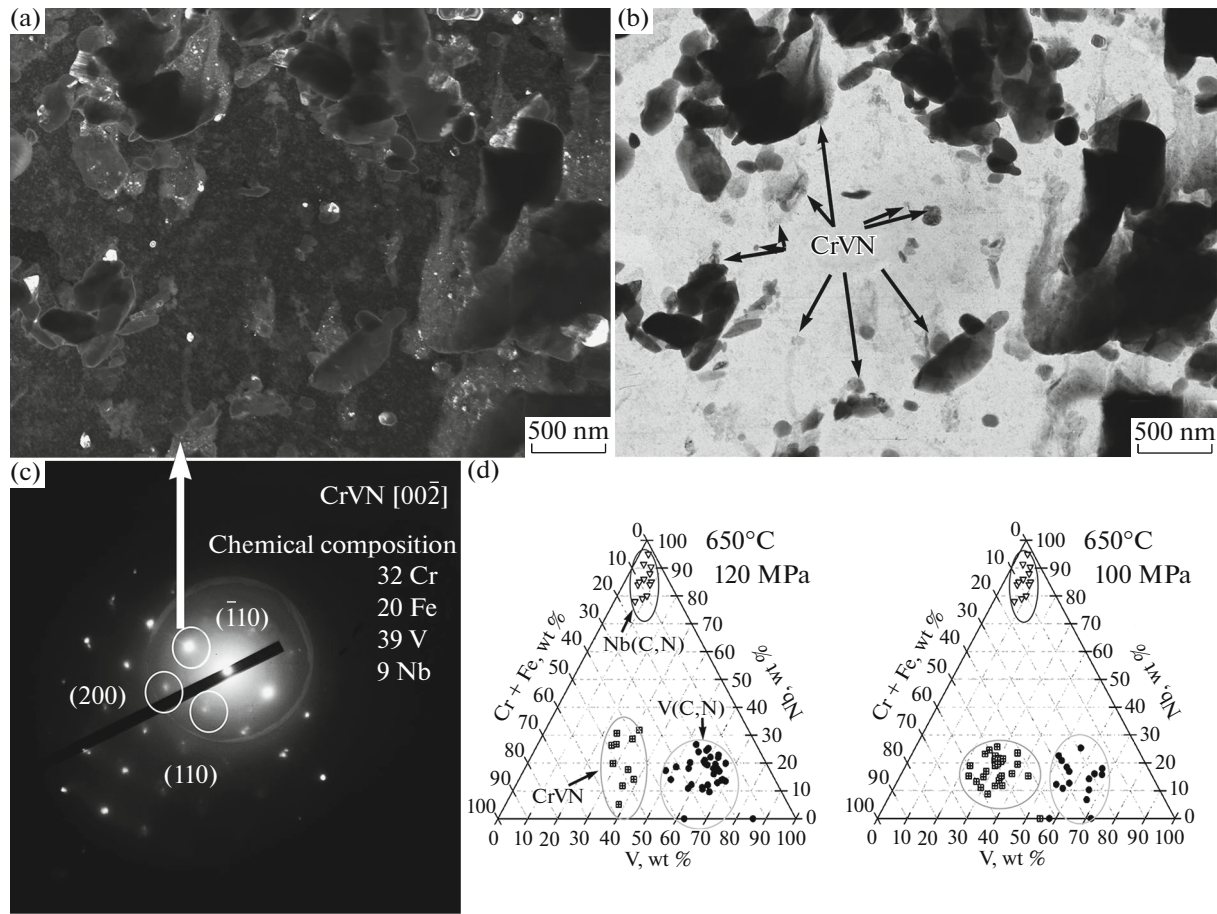


Fig. 3. (a) Dark-field and (b) bright-field TEM images of Z-phase particles obtained from the (-110) reflection (c) after creep at $650^{\circ}\text{C}/100\text{ MPa}$ in the region of strain localization; and (d) a change in the chemical composition of M(C,N) carbonitride and Z-phase particles upon creep at 650°C under stresses of 120 and 100 MPa.

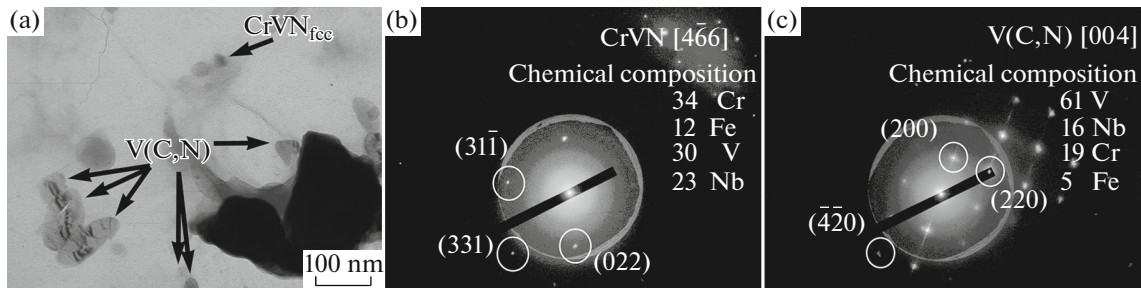


Fig. 4. (a) Bright-field TEM image of Z-phase and V(C,N) carbonitride particles with corresponding electron diffraction patterns of (b) a Z-phase particle with a cubic lattice and (c) a V(C,N) carbonitride particle after creep under conditions of $675^{\circ}\text{C}/120\text{ MPa}$.

changes in the microstructure of the steel under study [8]. The substitution of V(C,N) carbonitride particles by the Z-phase does not have an effect on the slope of the curve in the region of the tertiary creep stage at both temperatures of 650 and 675°C with a decrease in the applied stress (Figs. 1b and 1c). The absence of changes in the slope of the curve in the region of the tertiary creep stage with a decrease in the applied stress

indicates that the formation of Z-phase particles does not make a significant contribution to the structure degradation if at least 50% of the V(C,N) carbonitride particles from the initial amount are retained [15].

As was shown in [6, 7, 18], small particles of the Z-phase do not have a negative effect on the long-term strength in steels with 12% Cr, while the appearance of a bend on the long-term strength curves is associated,

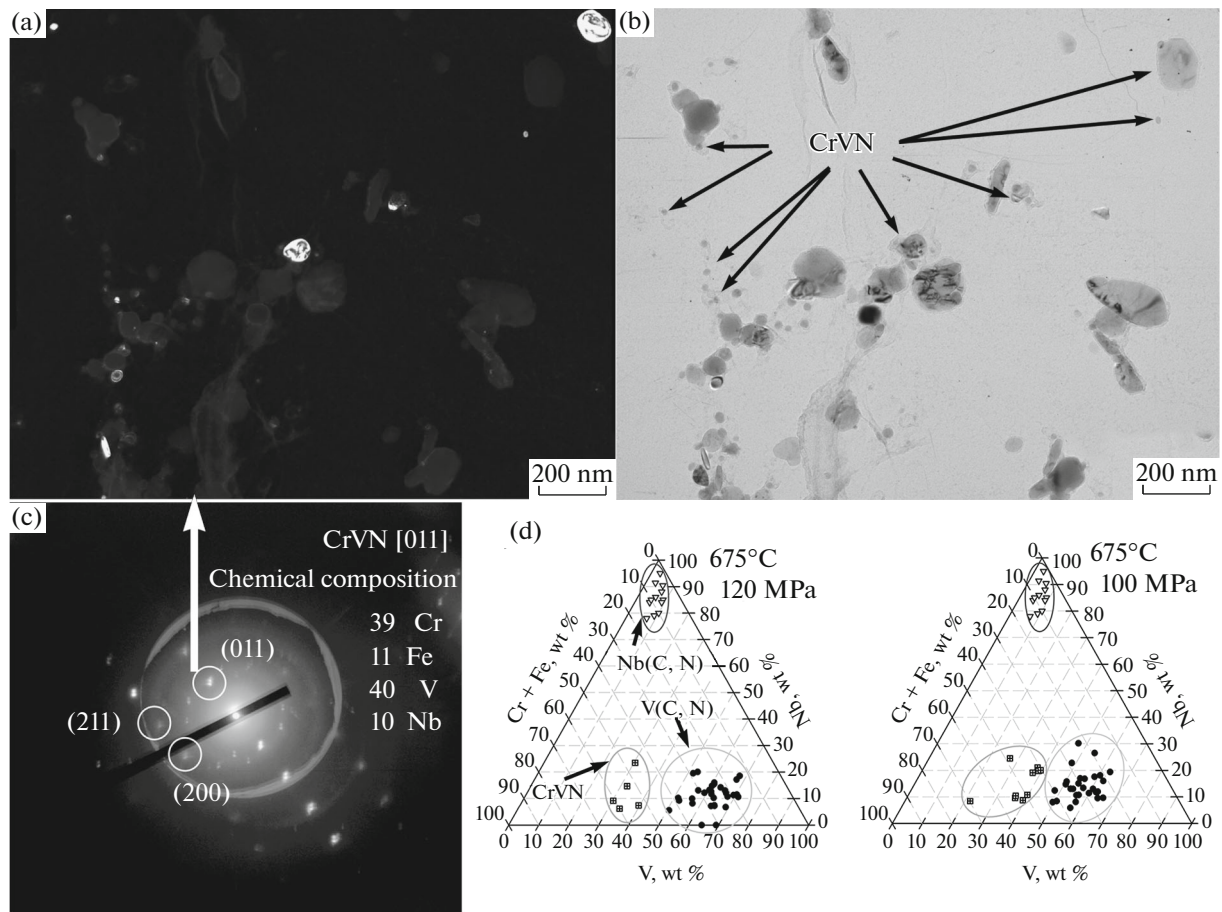


Fig. 5. (a) Dark-field and (b) bright-field TEM images of Z-phase particles obtained from the (011) reflection (c) after creep under conditions of 675°C/100 MPa in the region of uniform deformation; and (d) a change in the chemical composition of M(C,N) carbonitride and Z-phase particles during creep at 675°C under stresses of 120 and 100 MPa.

regardless of the test temperature, with the enlargement of the Z-phase particles. The higher the fraction of these large particles, the steeper the slope of the long-term strength curve and the lower the long-term strength threshold.

A decrease in the applied stress and, accordingly, an increase in the creep time stimulate the formation of Z-phase particles and cause the growth of this phase. In this case, an increase in the test temperature causes the formation of nuclei of the Z-phase particles in the studied martensitic steel for shorter creep times (Fig. 4). Thus, an increase in the temperature by 25°C reduced the time prior to the start of nucleation of the Z-phase particles by a factor of almost five. The addition of deformation to a high temperature upon creep gives rise to nucleation of the Z-phase particles regardless of the test temperature. Thus, the conversion of the V(C,N) carbonitride particles into the Z-phase particles at a creep temperature of 650°C was recorded with an applied stress of 120 MPa only in the deformed working part of the sample, while Z-phase particles were not detected in the region of grips, in which long aging without plastic deformation takes place. At a

creep temperature of 675°C, the beginning of transformation of the V(C,N) carbonitride particles into the Z-phase particles was detected at an applied stress of 120 MPa in the sample deformation localization region (Fig. 4), and this transformation develops with a decrease in the applied stress to 100 MPa and propagates into the region of uniform deformation of the sample (Fig. 5). At the same time, no Z-phase particles were detected in the gripped region of the samples. The prolonged annealing stabilizes the V(C,N) particles without transformation into the Z-phase (Fig. 2). It is plastic deformation that contributes to the replacement of the less stable V(C,N) phase with a more stable Z-phase, since vanadium particles in its absence are stable both in size and in chemical composition. They remain unchanged for a sufficiently long time regardless of the test temperature. It is possible to slow down or eliminate the formation of particles either by decreasing the operating temperature (which is unacceptable) or by changing the alloying scheme toward reducing the amount of nitrogen, which requires changing the steelmaking scheme to the vacuum induction or vacuum arc melting.

CONCLUSIONS

Plastic deformation plays a key role in the formation of Z-phase particles, which only appear upon creep. An increase in the degree of deformation leads to a strong increase in the specific volume of the Z-phase and to its enlargement. The lower the applied stress and, consequently, the longer the time to degradation, the more intensive the process of formation of Z-phase particles. The higher the test temperature, the shorter the time of formation of Z-phase particles; furthermore, the particle formation mechanism depends on the temperature.

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