PHYSICAL FOUNDATIONS
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Formation of Z-Phase Particles in a Martensitic 9% Cr Steel during Creep at 650°C and Their Influence on the Creep

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Abstract—The mechanism of the nucleation of Z-phase (CrVN) particles in a martensitic 10Kh9K3V2MFBR steel (9 wt % Cr) during creep at a temperature of 650°C is studied. The nucleation mechanism of Z-phase particles at a creep temperature of 650°C is found to be restructuring of the crystal lattice of V(C,N) carbonitrides due to the diffusion of chromium atoms. The transformation of nanosized V(C,N) carbonitrides into Z-phase particles is shown to weakly contribute to the structural degradation in the steel and not to cause its premature fracture during creep at 650°C if at least 50% V(C,N) carbonitrides of the initial volume fraction of these particles are retained (even at a large average size ($\approx$200 nm) of Z-phase particles).

1. INTRODUCTION

Martensitic steels containing 9% Cr belong to promising materials for boiler elements and the steam conduits of new power-generating units operating at supercritical steam parameters (direct steam temperature of 600–620°C, pressure of 35 MPa, power-generating unit efficiency of 44%) [1, 2]. A significant increase in the long-term strength of these steels is related to the dispersion of nanosized M(C,N) (M = V, Nb) carbonitrides, which is characterized by high coarsening resistance at high temperatures [2–6]. Nanosized M(C,N) carbonitrides, which precipitate uniformly in the matrix volume, are assumed to be obstacles to the restructuring of free dislocations into low-energy configurations or to the incorporation of free dislocations into the existing lath dislocation boundaries [2–6]. The precipitation hardening induced by these particles is considered to substantially contribute to the hardening of martensitic 9% Cr steels, stabilizing a tempered lath troostite structure during operation [1, 2, 5].

However, M(C,N) carbonitrides are nonequilibrium and replaced by the equilibrium Z phase (CrVN), the size of which can reach several microns, in time. The replacement of M(C,N) carbonitrides with Z-phase particles becomes possible, since the base metallic composition of the Z phase is similar to the composition of M(C,N) carbonitrides [3]. In 11% Cr steels, the Z phase is mainly located along the boundaries of the former austenite grains and/or along packet boundaries, increases the interparticle distances during creep, and can cause premature strength

loss in a relatively short time (tests for 15 000 h) [4, 5]. As was shown experimentally [6–9] and during simulation on an atomic level [10–12], the main problem of 11% Cr steels is the multiple acceleration of Z-phase formation during creep. Moreover, the Z-phase formation mechanism changes when the chromium content increases: it changes from nucleation at the M(C,N)/ferrite interface to a transformation of the crystal lattice of vanadium-rich M(C,N) carbonitrides. As a result, Z-phase particles almost 1 μm in size form and M(C,N) carbonitrides dissolve completely, and steel fully loses its ability to withstand creep in 10 000 h [13].

The Z-phase formation has not been considered as a problem for 9% Cr steels earlier, since the operating temperature of these steels was lower than the temperature at which the transition of M(C,N) carbonitrides into the Z phase is maximal, namely, 600 and 650–700°C [3, 14]. However, additional cobalt alloying of these steels increased their operating temperature to 650–675°C, which provoked Z-phase formation after relatively short creep tests. The purpose of this work is to study the formation of Z-phase particles in a martensitic cobalt-alloyed 9% Cr steel during creep at 650°C and various applied loads.

2. EXPERIMENTAL

We investigated the 10Kh9K3V2MFBR steel made in an open induction furnace in NPO TsNIITMASh. This steel contained (wt %) 0.12 C, 0.06 Si, 0.1 Ni, 0.2 Mn, 9.5 Cr, 3.2 Co, 0.45 Mo, 2.0 W, 0.2 V,
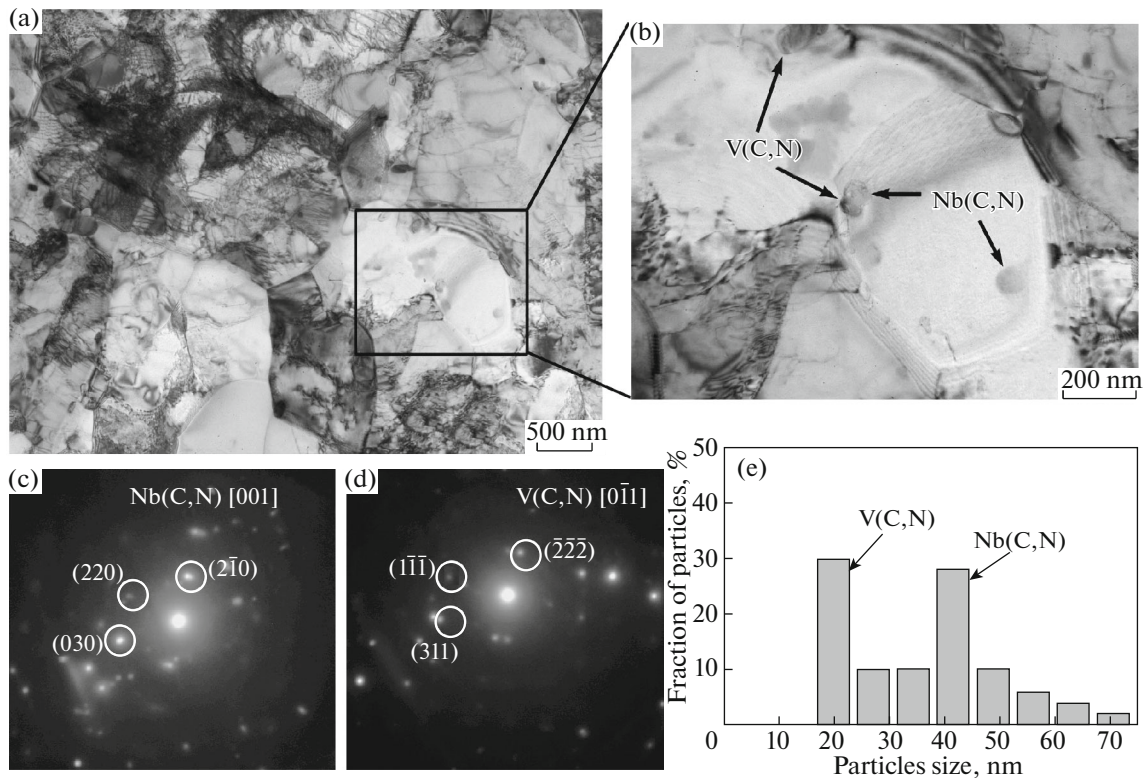
Fig. 1. (a−d) Microstructure of the 10Kh9K3V2MFBR steel after tempering at 750°C with electron diffraction patterns of particles and (e) second-phase particle size distribution.

0.06 Nb, 0.005 B, and 0.05 N. The ingots were forged to form rods with a square cross section and a side of 20 mm using free forging in the temperature range 1150−900°C. The rods were then subjected to normalization from 1050 ± 10°C and subsequent annealing at 750 ± 10°C for 3 h. For long-term strength tests, we cut cylindrical specimens 10 mm in diameter with a gage length of 100 mm from the rods. The specimens were tested to failure at 650°C and an applied stress of 120 or 100 MPa on a lever-type ATS2330 tensile-testing machine.

The structures of foils and carbon replicas were studied on a JEOL JEM-2100 transmission electron microscope (TEM) equipped with an INCA energy dispersive attachment for determining the chemical composition of particles. TEM foils were cut from the gage portion of the creep specimens and were electropolished in a 10% solution of perchloric acid in acetic acid at room temperature in a Struers Tenupol-5 automatic electrolytic thinning device. The lath/subgrain sizes were determined by the random intercept method for all subgrains visible in TEM images. The free dislocation density inside laths or subgrains was found using the number of dislocation exit points on a surface and at least six TEM images for each state. Carbon replicas were used to refine the chemical composition of particles (without the influence of the matrix in an energy dispersive spectrum). Secondary-

phase particles were identified using electron diffraction patterns and the chemical composition of particles. The average secondary-phase particle size was estimated using 15 TEM images for each state.

3. RESULTS

3.1. Carbonitrides in the Steel Tempered at 750°C

The microstructure of the 10Kh9K3V2MFBR steel subjected to normalizing and tempering at 750°C consists of a lath troostite structure and a subgrain structure (Fig. 1a), and it was described in detail in [15, 16]. The average subgrain size and the transverse size of martensite laths are 0.60 and 0.38 μm, respectively. A high dislocation density (2×10^{14} m^{-2}) was detected inside martensite laths and subgrains. Globular M$_{23}$C$_6$ carbides with average size of 90 nm are located along the high-angle boundaries of the former austenite grains and along low-angle martensite lath and subgrain boundaries, and M(C,N) carbonitrides are uniformly distributed over the ferrite matrix volume (Figs. 1a−1d).

The M(C,N) carbonitrides are represented by niobium-rich (Nb(C,N)) or vanadium-rich (V(C,N)) particles. The Nb(C,N) particles are spherical and have a cubic lattice with a parameter $a = 0.447$ nm and an average size of 40 nm (Figs. 1e, 2). The V(C,N)
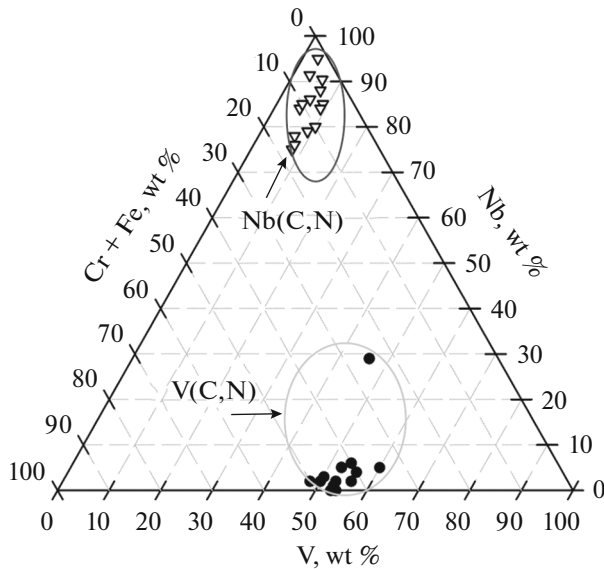
Fig. 2. Concentration triangle with the fields of Nb(C,N) and V(C,N) carbonitrides after tempering of the steel at 750°C.

have a cubic lattice with a parameter $a = 0.414$ nm and a lamellar shape with an average transverse size of 20 nm (Figs. 1e, 2). A small number of large niobium-rich carbonitrides was observed along the boundaries of the former austenite grains [15]. These large particles did not dissolve in normalizing.

3.2. Creep Characteristics of the 9% Steel at 650°C

As follows from the data obtained for creep at 650°C, a decrease in the applied stresses from 120 to 100 MPa doubles the time to failure of the steel, decreases the minimum creep rate fourfold, and weakly increases the strain to failure (Fig. 3, Table 1).
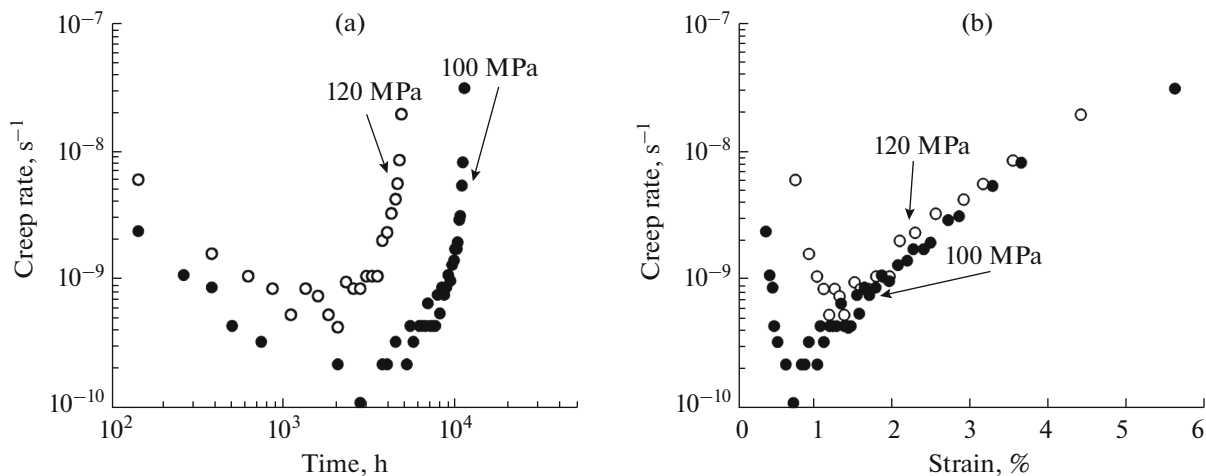
Abe [17] found a relation between microstructural degradation m, defect parameter d, exponent n in the power law of creep $\dot{\varepsilon}_{min} \sim A\sigma^n$, deformation localization i, and the mechanical behavior of steel determined from the slope of the creep curve $(d\ln(\dot{\varepsilon})/d\varepsilon)$ during tertiary creep. $d\ln(\dot{\varepsilon})/d\varepsilon$ during tertiary creep is determined as the strain dependence of the creep rate,

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(n\varepsilon)\exp(m\varepsilon)\exp(d\varepsilon)\exp(i\varepsilon),$$
$$d\ln(\dot{\varepsilon})/d\varepsilon = n + m + d + i.$$

Here, n is the exponent in the power law of creep ($n = 12$ at a creep temperature of 650°C [16]), m is the microstructural parameter, d is the parameter of the defects caused by pore formation during creep, and parameter i describes the influence of localized deformation and is estimated from the relative reduction of area of the specimen (see Table 1). Since pores were not detected by microstructural analysis in the material volume during creep, we did not take into account parameter d and determined the slope of the curve using the following three components: $n + m + i$.

For applied stresses of 120 and 100 MPa, we detected no differences in the slopes of the curves during tertiary creep at 650°C: the slopes of the $d\ln(\dot{\varepsilon})/d\varepsilon$ curves were 116 and 114 for stresses of 120 and 100 MPa, respectively (see Table 1). These data point to long-term creep at 650°C. According to [18], the transition from short-term to long-term creep is accompanied by a sharp increase in the slope of the curve in the tertiary creep range from 50 to 110−150.

3.3. Z-Phase Formation

The chemical composition of the Nb(C,N) carbonitrides does not undergo significant changes during creep at 650°C (Fig. 4), and these particles did not grow or transform into Z-phase particles. However,

Fig. 3. Creep rate of the 10Kh9K3V2MFBR steel vs. (a) time and (b) strain after long-term strength to failure tests at 650°C and an applied stress of 120 and 100 MPa.

the V(C,N) carbonitrides grew substantially and transformed into Z-phase particles.

The beginning of transformation of nanosized V(C,N) carbonitrides into Z-phase particles was detected after tests at a stress of 120 MPa for 4869 h (Figs. 5a−5c). Irregular particles with the average chemical composition 50 wt % (Cr + Fe) + 50 wt % (V + Nb) were identified as the Z phase (CrVN). These particles were detected near or in contact with V(C,N) carbonitrides and were represented by "hybrid" particles consisting of a core of the cubic V(C,N) carbonitride of the corresponding chemical composition (see Fig. 4a) and a shell of the tetragonal Z phase (CrVN) with lattice parameters $a = 0.286$ nm and $c = 0.739$ nm. The average size of the V(C,N) particles is 62 nm and that of the Z-phase particles is 59 nm. Z-phase particles that were substantially smaller than the V(C,N) particles were not detected (Fig. 6). The ratio of the numbers of Z-phase particles to V(C,N) carbonitrides after creep tests at a stress of 120 MPa for 4869 h was 1 : 5.5.

An increase in the creep time to 11151 h at a stress of 100 MPa caused the growth of V(C,N) carbonitrides and the continuation of their transformation into the Z phase according to the mechanism of hybrid particle formation (Figs. 5d, 5e) due to the diffusion of chromium atoms to the surface of the V(C,N) carbonitrides (Fig. 5f). The average V(C,N) particle size increased to 70 nm, almost all small particles (up to 30 nm in size) dissolved, and the fraction of particles 120−180 nm in size increased. Large (about 100 nm in size) V(C,N) particles turned out to be more resistant to the transformation into the Z phase (see Fig. 6b).

Table 1. Creep characteristics of 10Kh9K3V2MFBR steel at 650°C and various applied stresses

Characteristics	120 MPa	100 MPa
Time to failure, h	4869	11151
Strain to failure, %	4.4	5.6
Minimum strain rate, s^{-1}	4.4×10^{-10}	1.2×10^{-10}
Strain for reaching the minimum strain rate, %	1.4	0.7
Time for reaching the minimum strain rate, h	2064	2724
Slope of curve during tertiary creep $d\ln(\dot{\varepsilon})/d\varepsilon$	116	114
Relative reduction of area at failure	43	45

The ratio of the numbers of Z-phase particles to V(C,N) carbonitrides after creep tests at a stress of 100 MPa for 11151 h was 1 : 1.

The average Z-phase particle size increased significantly (to 200 nm), and the fraction of large particles more than 275 nm in size was 22% of the total number of particles (see Fig. 6d). Thus, as in the case of creep at 120 MPa, the Z-phase particles the size of which is smaller than the size of V(C,N) particles are absent after creep at a stress of 100 MPa, which indicates gradual restructuring of the cubic lattice of the V(C,N) carbonitrides into the tetragonal lattice of the Z phase. The average chemical composition of the Z phase remained unchanged (50 wt % (Cr + Fe) + 50 wt % (V + Nb)), and the fraction of vanadium and
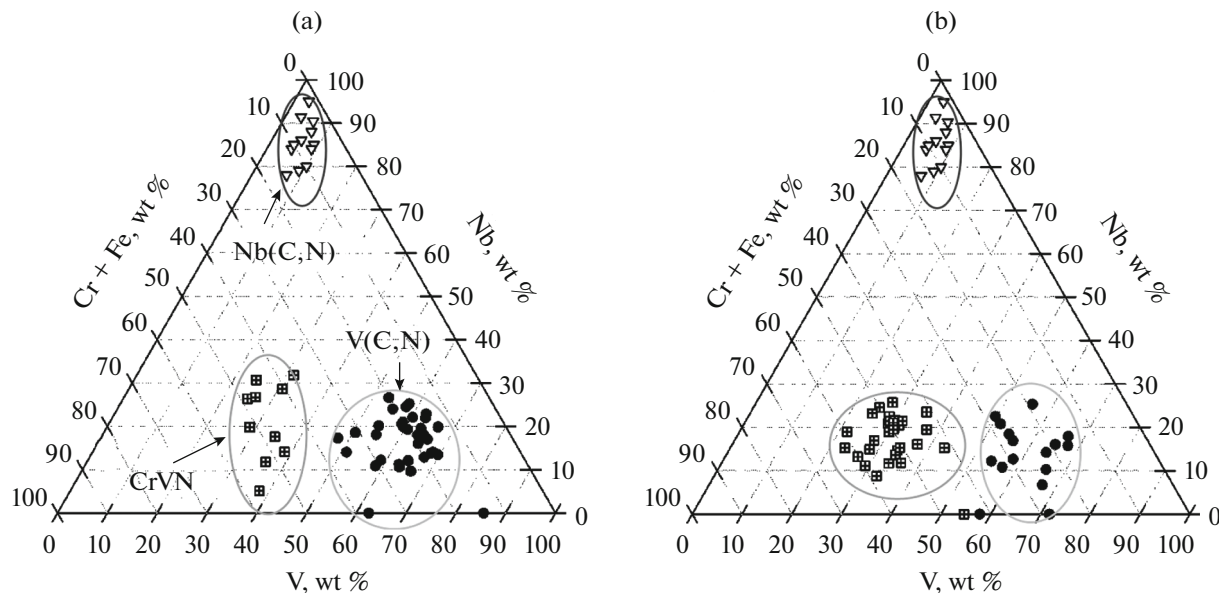

Fig. 4. Concentration triangle with the fields of Nb(C,N) and V(C,N) carbonitrides and the Z phase (CrVN) after long-term strength tests at 650°C and a stress of (a) 120 and (b) 100 MPa. The elemental compositions of the fields indicated in (b) are the same as in (a).
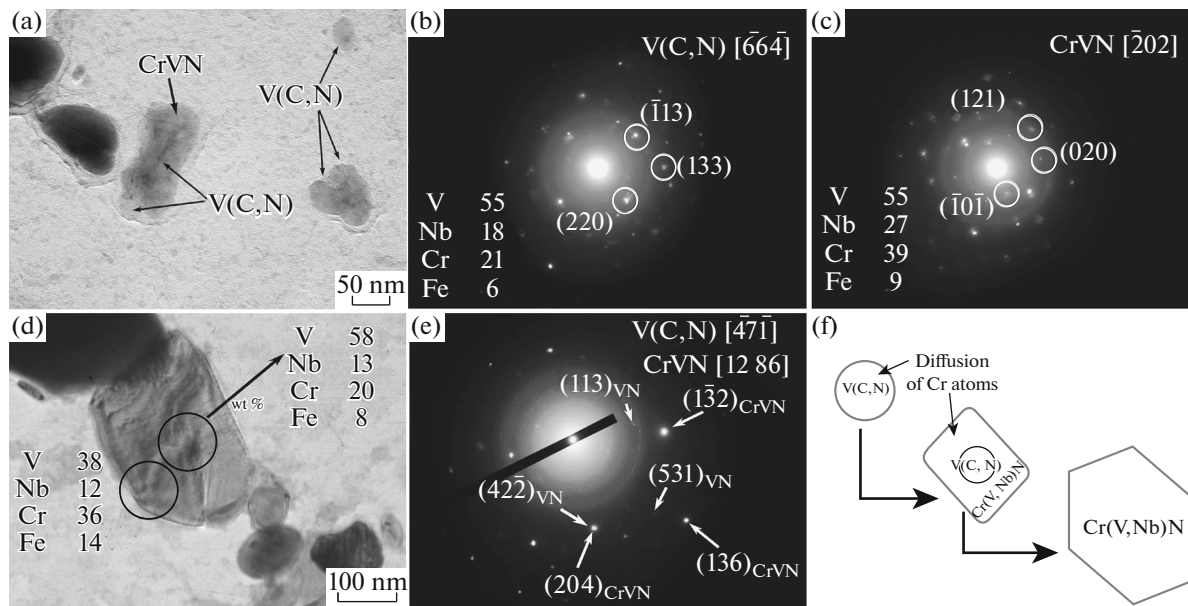
Fig. 5. M(C,N) carbonitride and Z-phase particles with their electron diffraction patterns and chemical compositions after long-term strength to failure tests at 650°C and an applied stress of (a–c) 120 and (d, e) 100 MPa. (f) Scheme of the V(C,N)−Z phase transformation [14].

niobium in the V(C,N) carbonitrides decreased (see Fig. 4b).

4. DISCUSSION

The experimental results demonstrate that an increase in the creep time stimulates the transformation of nanosized M(C,N) carbonitrides into Z-phase particles. In [16], we did not detect substantial differences between the structures of specimens of the steel under study after creep tests at 120 and 100 MPa. We also found that the coarsening of grain-boundary $M_{23}C_6$ particles and Laves phases led to transformation of a lath tempering troostite structure into a subgrain structure, and the grain-boundary particle sizes, the subgrain sizes, the dislocation density, and the tungsten, molybdenum, and cobalt contents in a solid solution after long-term strength tests at 120 and 100 MPa were almost the same. The only substantial difference between the structures of the specimens failed after tests at 120 and 100 MPa was the replacement of M(C,N) carbonitrides with the Z phase. It should be noted that this process did not affect the mechanical behavior of the steel: it did not increase the slope of the curve during tertiary creep when the applied stress decreased (see Table 1).

The slope of the curve is mainly determined by microstructural parameter m (provided n and i are the same at the same creep temperature) and characterizes structural degradation [17]. The absence of a change in the slope of the curve during tertiary creep at a decrease in the applied stress points to the fact that the transformation of nanosized M(C,N) carbonitrides

into Z-phase particles weakly contributes to the structural degradation and does not cause premature fracture of a specimen for at least 50% V(C,N) carbonitrides of the initial volume fraction of these particles even at a large average Z-phase particle size.

Several mechanisms of Z-phase particle formation in 11−12% Cr steels are known to exist [9−13]. In the first mechanism, the cubic lattice of V(C,N) carbonitrides directly transforms into the tetragonal lattice of the Z phase beginning from the periphery of V(C,N) particles and then moving to their core. According to the second mechanism, Z-phase nuclei form at the V(C,N)/ferrite interface. Nucleated Z-phase particles have the $B1$ (NaCl) cubic lattice with a parameter $a \approx$ 0.404 nm. Since the Z phase is metastable, it transforms into the thermodynamically stable tetragonal phase with parameters $a = 0.286$ nm and $c = 0.739$ nm [13].

The formation of Z-phase particles in the martensitic 9% Cr steel at a creep temperature of 650°C occurs according to the first mechanism (see Fig. 5f), which is corroborated by the presence of coarse particles with the tetragonal lattice and different chemical compositions over their cross section. The chemical composition of the cores of the particles corresponds to the V(C,N) carbonitride composition, and the shell composition corresponds to the Z-phase composition (see Fig. 5d). No Z-phase particles with the $B1$ (NaCl) cubic lattice were detected in this case. An indirect indication of the Z-phase particle formation according to this mechanism is the absence of Z-phase particles that are smaller than V(C,N) carbonitrides. If Z-phase particles formed via the formation of nuclei at the V(C,N)/ferrite interface, Z-phase particles that
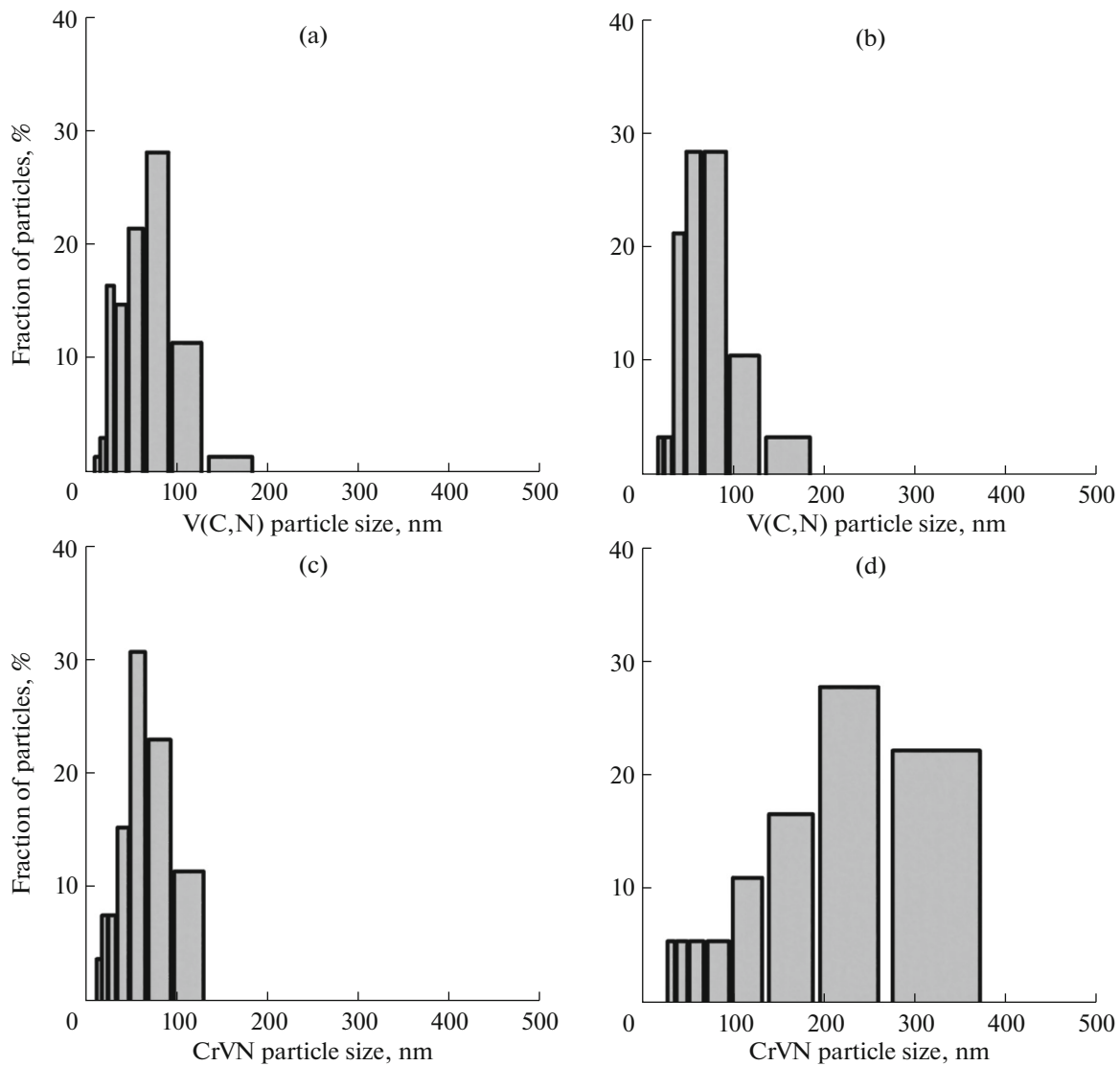
Fig. 6. Size distribution of (a, b) V(C,N) carbonitrides and (c, d) Z-phase particles after long-term strength to failure tests at 650°C and an applied stress of (a, c) 120 and (b, d) 100 MPa.

are smaller than V(C,N) carbonitrides would be present in the steel after creep.

The interaction between dislocations and V(C,N) carbonitrides creates additional short ways for the diffusion of chromium and vanadium. The incorporation of chromium atoms into the surface layers of cubic V(C,N) carbonitrides stimulates the formation of a chromium-rich Z-phase shell around V(C,N) particles; this shell is the tetragonal distortion of the body-centered cubic lattice with double layers of alternating identical atoms (chromium or vanadium) along the c axis, CrCrVVCrCrVV... [8].

The crack growth in the chromium-rich Z-phase shell around V(C,N) particles is controlled by the diffusion of chromium atoms from the ferrite matrix and vanadium atoms from the vanadium-rich core of V(C,N) particles [13, 19]. The formation of a continu-

ous chromium-rich Z-phase shell hinders the motion of carbon from the core [13, 19]. As a result, the "hybrid" particles retain their two-phase structure, which consists of a vanadium-rich V(C,N) core and a chromium-rich Z-phase shell. This mechanism takes place during creep at 650°C for more than 4500 h. This result corresponds to the creep data obtained for 11–12% steels, where the rate of Z-phase formation was found to be maximal at 650°C [3, 19].

5. CONCLUSIONS

The mechanism of formation of Z-phase particles during creep at 650°C consists in the transformation of the cubic lattice of V(C,N) carbonitrides into the tetragonal lattice of the Z phase beginning from the periphery of V(C,N) particles and propagating to the

their core. The average sizes of the Z-phase and V(C,N) particles are the same, and the ratio of the numbers of Z-phase to V(C,N) particles at the beginning of the transformation is 1 : 5.5. An increase in the creep time to 11151 h stimulates the formation and growth of Z-phase particles from ≈60 to 200 nm, and the ratio of the numbers of Z-phase to V(C,N) particles is 1 : 1. The transformation of nanosized M(C,N) carbonitrides into Z-phase particles during creep weakly contributes to structural degradation and does not cause premature fracture when at least 50% V(C,N) carbonitrides of the initial volume fraction of these particles are retained at a large average size of Z-phase particles.

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