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KINETICS OF THE FORMATION OF NANOSIZE NIOBIUM CARBONITRIDE PRECIPITATES IN LOW-ALLOY STRUCTURAL STEELS

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A detailed study is made using original methods of kinetic features of nanosize niobium carbonitride precipitate formation in relation to metal temperature and deformation regimes on the example of an industrial melt of low-alloy structural steel. It is established that in the absence of deformation there are considerable kinetic difficulties for niobium carbonitride precipitation, and for its occurrence to some significant extent a time interval of not less than 20–40 min at 900°C is necessary, even in the presence of considerable supersaturation and solid solution supercooling. With equivalent conditions, preliminary deformation considerably accelerates formation of nanosize niobium carbonitride precipitates that commences approximately after 10 sec and ceases after isothermal soaking at 900°C in 200–300 sec. A fundamental dependence is demonstrated for the amount and mechanism of nanosize niobium carbonitride precipitate formation on thermal prehistory. In addition, prior cooling to room temperature and subsequent heating to an exposure temperature of 700°C leads to a marked increase in number of nanosize carbonitride precipitates formed.

Keywords: *low-alloy structural steels, nanosize niobium carbonitride precipitates, heat treatment, deformation, structural state.*

A key factor controlling the structural state and mechanical properties of low-carbon structural steels is connected with formation and evolution of niobium carbonitride and other phase precipitates, including nanosize precipitates [1]. They determine fineness and uniformity of the microstructure obtained, realization of various strengthening mechanisms, and mechanical and other service indices. Nonetheless, as a rule carbonitride and other precipitates required in order to achieve a prescribed set of these property parameters (type, amount, size, morphology, and distribution throughout the metal volume) are predicted by thermodynamic calculation or simple empirical relationships. These methods do not take account of kinetic features of the reactions that occur, do not make it possible to obtain precise information, and often lead to physically inadequate results. For example, complete substantiation from the point of view of fundamental thermodynamic principles of reactions for carbonitride or other precipitate formation is far complete, or entirely lacking. In accordance with this situation, it is important to study features of phase precipitate formation in relation metal treatment parameters.

The research was conducted on low-alloy structural steel of an industrial melt with the following chemical composition, wt.%: C 0.11, Si 0.34, Mn 1.72, P 0.012, S 0.004, Cr 0.027, Ni 0.024, Cu 0.059, Al 0.04, Mo 0.005, Ti 0.004, Nb 0.05, As 0.005, N 0.0062. There was only niobium within the composition of microalloying elements, which points to the possibility of only forming niobium carbonitride precipitates based upon it.

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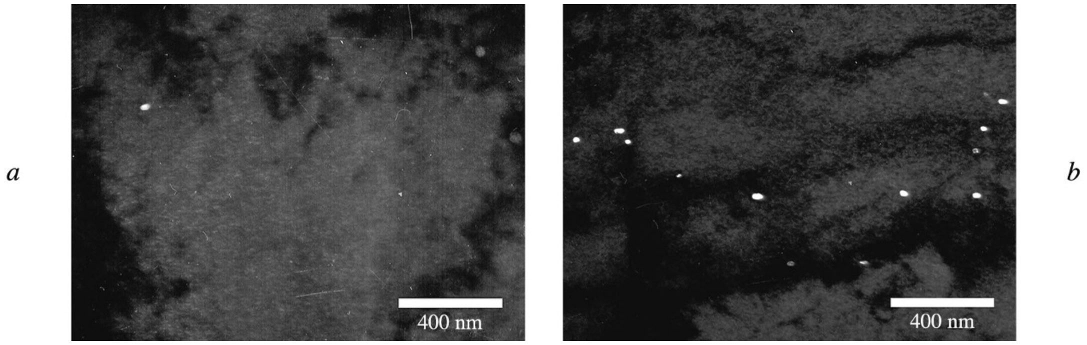

Fig. 1. Dark field image of carbonitride precipitates recorded in steel specimens at 900ºC using different exposure duration: *a*) 20 min; *b*) 40 min.

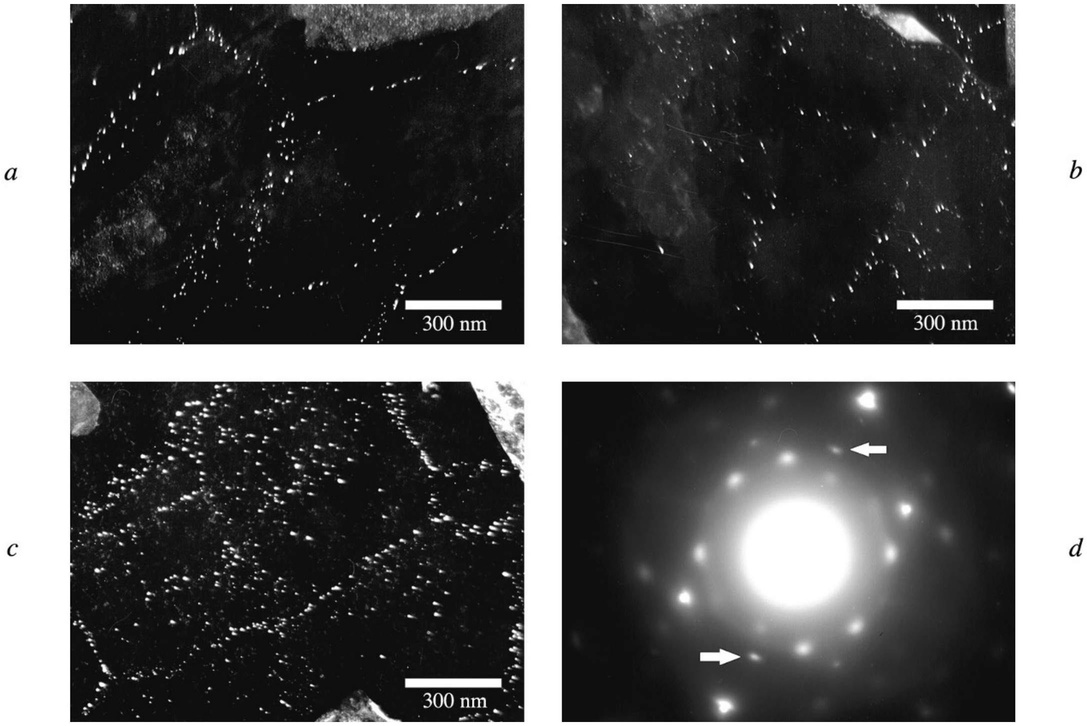

Fig. 2. Dark field image of carbonitride precipitates in steel specimens held after deformation at 900ºC for 60 sec (*a*), 120 sec (*b*), and 300 sec (*c*), and also microdiffraction (*d*) in area of accumulation of a considerable amount precipitates in a specimen held for 300 sec.

The amount and size of precipitates present within specimens was determined by scanning (SEM) and transmission (TEM) electron microscopy in Jeol JSM 6610 LV and JEM200CX instruments, respectively.

Features of precipitation kinetics were studied in the absence and presence of deformation. Studies without deformation were conducted in a modified high-speed Formaster-F dilatometer with an induction heater with power of 3 kW and frequency of 1.7 MHz. In order to accomplish accelerated cooling, the inductor was made in the form of a double tube with a gas nozzle aimed at a test specimen.

Steel specimens cylindrical in shape 10 mm long and 5 mm in diameter were heated to 1300ºC (which, according to calculation in accordance with approaches in [2–4], is higher by almost 100ºC for complete dissolution of niobium carbonitride

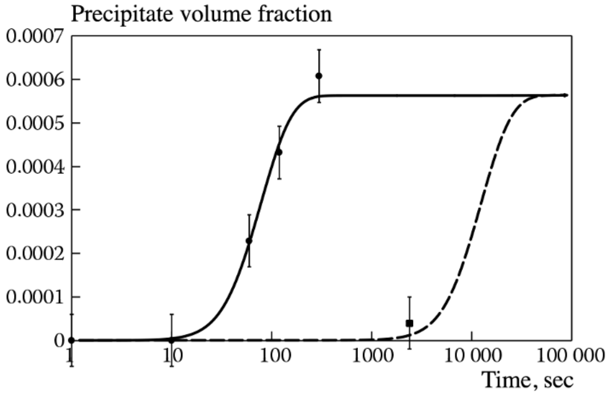

Fig. 3. Isothermal diagram of niobium carbonitride precipitation rate at 900ºC: ——) calculated values with deformation; – – –) calculated values without deformation; ●) experiment with deformation; ■) experiment without deformation.

precipitates) and held for 20 min. After exposure, a specimen was cooled rapidly to the test temperature and held at it for a specific time, then cooled at high speed by a gas stream to room temperature.

A study of niobium carbonitride precipitate formation with the presence of deformation was conducted by means of a BAHR (type 805) dilatometer, simulating controlled rolling with accelerated cooling. Specimens were held for 20 min at a temperature above that for niobium carbide dissolution, then cooled to T_{soak}, held there for 30 sec in order to level out and stabilize the temperature, and 50% reduction was accomplished by means of a hydraulic drive. After this, specimens were exposed for 1, 2, and 5 min followed by accelerated cooling in an inert gas stream at rates of 80–100ºC/sec. The amount and size of precipitates was determined by SEM and TEM in the instruments indicated above.

Undeformed steel specimens were studied at 900ºC (soaking duration 10, 20, 30, and 40 min). Dark field images of niobium carbonitride precipitates obtained by the TEM method are shown in Fig. 1, recorded with different steel specimen soaking duration.

It follows from Fig. 1 that in the case of absence of deformation with significant soaking duration (20–40 min) for a steel specimen at 900ºC in spite of significant solid solution supersaturation there is only formation of individual nanosize niobium carbonitride precipitates, which agrees with data in [5, 6].

In other experiments, after accelerated cooling to 900ºC and soaking for 30 sec, in order to level out the temperature, specimens were given 50% compression with a deformation rate of 1 sec^{-1}, and after different soaking times and cooled rapidly in a stream of argon. Electron microscope studies showed that the phase precipitated is also niobium carbonitride. From the interplanar distance (200) determined from microdiffraction images (Fig. 2), the value of lattice parameter $a = 4.48$ nm, which corresponds to niobium carbonitride. It follows from data in Fig. 2 that after deformation carbonitride precipitate formation proceeds with a significantly shorter soaking time, i.e., 60–300 sec. No precipitates were detected for specimens quenched immediately after deformation and soaked for 10 sec.

The volume fractions of precipitates was evaluated from results of studies. For this, in the images obtained (see Figs. 1 and 2) by mean of Image Expert 3 Pro software the area of all visible precipitates was determined from which their effective diameters were calculated. Then, assuming precipitate shape to be spherical, their proportion within the volume was determined equal to the product of image area by foil thickness (25 nm). Simultaneously, average precipitate radius was evaluated. No fewer than five images were analyzed for each exposure. Data obtained in Figs. 3 and 4 were compared with results of calculation by a model based on classical new phase nucleus generation and growth theory [7]. The conformity of an experiment and calculation is due to the fact that the free parameter of the model (surface energy of niobium carbonitride precipitates) was found by the same experimental data. Nonetheless, results obtained make it possible to draw a number of important conclusions. In fact, with absence of deformation niobium carbonitride precipitation has marked kinetic limitations, which even with a significant degree of solid solution supersaturation and supercooling (more than 300ºC) requires significant time,

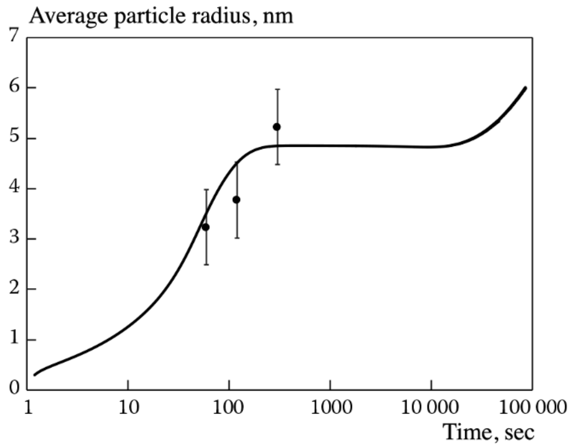

Fig. 4. Dependence of average niobium carbonitride precipitate radius on steel exposure time at 900°C after deformation: ●) experimental data; ——) calculated values.

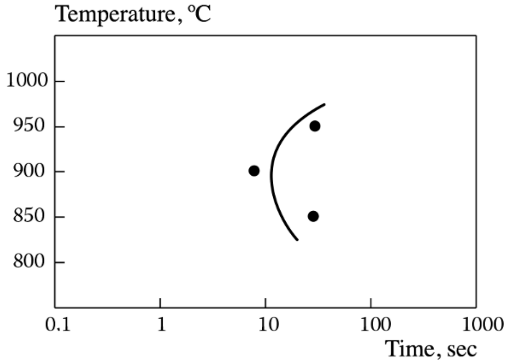

Fig. 5. RTT-diagrams for the start of niobium carbonitride precipitation (5%) in test steel: ——) calculation by model [7]; ●) experimental data [8] for steel of similar chemical composition.

i.e., not less than 20–40 min for formation of some significant amount of precipitates of this phase. It is important that the temperature of 900°C for the test steel corresponds to the most optimum combination of thermodynamic and kinetic stimuli for niobium carbonitride precipitate formation. This is confirmed by comparing (Fig. 5) the PTT diagram for the start of precipitation (5%) of niobium carbonitride calculated by a model [7] with experimental data [8] obtained for steel similar chemical composition (wt.%): C 0.88 and Nb 0.038.

After deformation with isothermal soaking (900°C), the formation of niobium carbonitride precipitates accelerates significantly: it starts with soaking for about 10 sec and ceases in 250–300 sec (see Figs, 3 and 5). It should be noted that the start of niobium carbonitride precipitation in these experiments was not studied in detail by the authors. The minimum recorded average size was more than 3 nm after soaking for 60 sec. Some instrument limitations also exist connected with sensitivity of the methods used and the procedure for revealing precipitates of the smallest sizes. Precise prediction and calculation of the process in question proceeding from first principles is impossible currently, and the physical and phenomenological models (see, for example, [7]) are based on determining three parameters from experimental data. Therefore, the values of time found for the start of niobium carbonitride formation contain a certain error. The time interval established for complete niobium carbonitride precipitation, i.e., of the order of 250–300 sec (see Fig. 3), is quite long for temperature-deformation

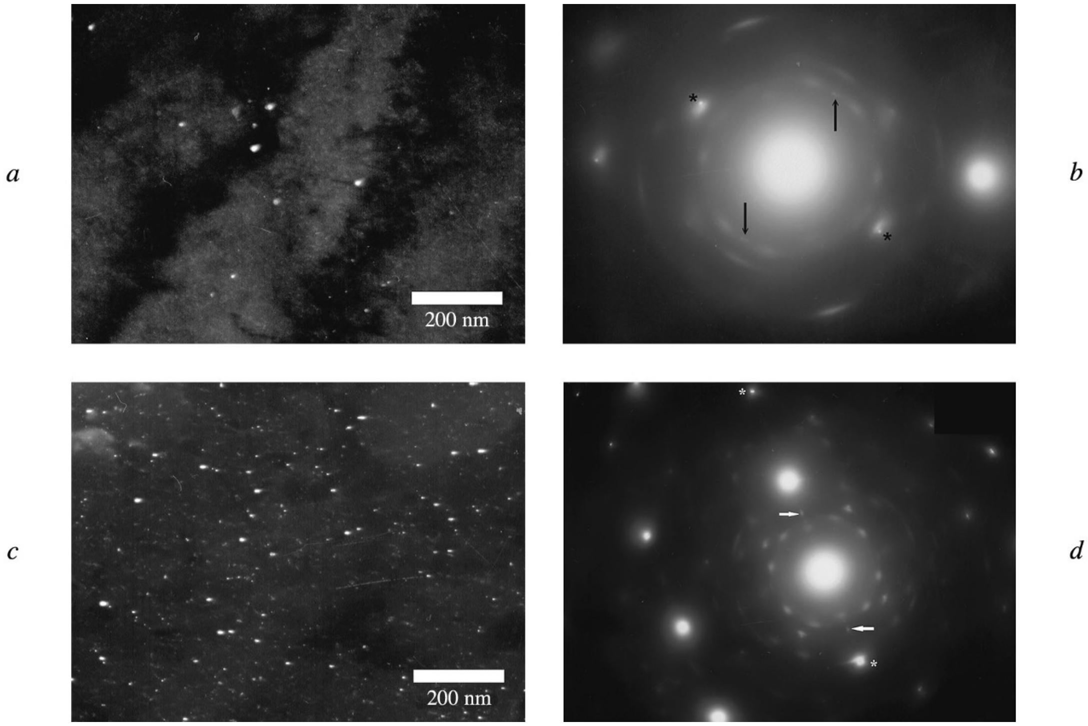

Fig. 6. Steel specimen microstructure (TEM) after isothermal exposure at 700ºC for 30 min immediately after homogenizing annealing (*a*, *b*) and after prior cooling to room temperature (*c*, *d*): *a*, *c*) dark-field image; *b*, *d*) microdiffraction.

treatment regimes normally used for steel in practice, aimed at improving productivity of rolling equipment. This points in favor of the conclusion that during steel hot rolling precipitation of niobium carbonitride and other excess phases as a rule proceeds far from completely and is realized for example during subsequent rolled product heat treatment [2].

It is important that kinetic features of precipitation of niobium carbonitride and other excess phases [9] depend not only on the start of deformation, but also steel heat treatment regime. In order to clarify this situation, test steel after soaking at 1300ºC for 20 for complete dissolution of niobium carbonitride precipitates in the first case was cooled to 700ºC, held for 30 min, and cooled rapidly to room temperature. In the second case, before isothermal exposure it was cooled to room temperature and heated to 700ºC. Heat treated specimens were studied by the TEM method (Fig. 6).

It is seen from Fig. 6 that in the second case the amount of niobium carbonitride formed is significantly greater. In addition, microdiffraction patterns point to niobium carbonitride precipitation in the first case from austenite, and in the second case predominantly from ferrite. Thus, experimental information has been obtained for the fundamental dependence of amount of nanosize niobium carbonitride precipitate and the formation mechanism on preceding steel heat treatment regime. In addition, prior cooling to room temperature and subsequent heating to the soaking temperature of 700ºC leads to a marked increase in the amount of niobium carbonitride precipitate formed. To all appearances, this is connected with occurrence of thermal stresses and active centers for generation during steel cooling, which do not manage to relax on heating and combined with a significantly greater degree of solid solution saturation lead to formation of a greater number of nanosize carbonitride precipitates.

Conclusion. Research results indicate that with presence of deformation niobium carbonitride precipitation has marked kinetic limitations. Even with a significant degree of supersaturation and supercooling (more than 300ºC) for solid solution, a prolonged time is required, i.e., not less than 20–40 min at 900ºC in order to form some significant amount of nanosize precipitates of this phase.

After deformation with isothermal soaking at 900ºC, formation of nanosize niobium carbonitride precipitates accelerates significantly: it starts with soaking for about 10 sec and ceases in 250–300 sec. This interval of niobium carbonitride precipitation is quite long, and comparable with temperature-deformation treatment regimes used normally in practice for steel, which may lead to complete implementation of this process and retention of phase-forming elements in solid solution.

Experimental evidence has been obtained for the fundamental dependence of amount and mechanism of nanosize niobium carbonitride precipitate formation in relation to steel previous heat treatment regime. In particular, a precooling to room temperature and subsequent heating to a soaking temperature of 700°C, leads to a marked increase in amount of carbonitride precipitate formed.

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REFERENCES

1. A. I. Zaitsev, V. S. Kraposhin, I. G. Rodionova, et al., *Complex Nonmetallic Inclusions and Steel Properties*, Metallurgizdat, Moscow (2015).
2. A. I. Zaitsev, I. G. Rodionova, A. A. Pavlov, et al., "Effect of composition, structural state, production technology, on service properties of high-strength low-alloy steel of a main bimetal layer," *Metallurg*, No. 8, 50–58 (2015).
3. N. L. Abramycheva, I. V. V'yimitskii, K. B. Kalmykov, and S. F. Dunaev, "Isothermal cross-section of the phase diagram of the Fe–Ni–Ti system at 1273 K," *Vestn. Mosk. Univ., Ser. 2, Khimiya*, **40**, No. 2, 139–143 (1999).
4. N. G. Shaposhnikov, B. M. Mogutnov, S. M. Polonskaya, et al., "Thermodynamic modeling as a tool for improving heating technology for rolling steel 12Kh18N10T," *Materialovedenie*, No. 11, 2–9 (2004).
5. A. J. De Ardo, "Niobium in modern steels," *Int. Mater. Rev.*, **48**, No. 6, 371–402 (2003).
6. R. Simoneau, G. Begin, and A. H. Marquis, "Progress of NbCN precipitation in HSLA steels as determined by electrical resistivity measurements," *Metal Sci.*, **12**, No. 8, 381–386 (1978).
7. A. V. Koldaev, *Modeling Thermodynamics and Excess Phase Precipitation Kinetics and Prediction of Their Effect on the Structure and Properties of Low-Carbon Microalloyed Steels of the Ferritic Class: Auth. Abstr. Dissert. Cand. Phys.-Mat. Sci.*, Bardin TsNIIchermet, Moscow (2016).
8. J. S. Park, Y. S. Ha, S. J. Lee, and Y. K. Lee, "Dissolution and precipitation kinetics of Nb(C,N) in austenite of a low-carbon Nb microalloyed steel," *Metallurg. Mater. Trans. A*, **40**, No. 3, 560–568 (2009).
9. D. Thivellier, D. Rousseau, and R. Tricot, "Precipitation of aluminum nitride in steels," *Mem. Sci. Revue de Metallurgie*, **74**, 627–637 (1977).