STUDY OF FEATURES OF PHASE PRECIPITATE FORMATION, STRUCTURAL STATE, AND PROPERTIES OF NB, V-MICROALLOYED LOW CARBON FERRITIC STEELS

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Contemporary methods of optical and transmission electron microscopy, and mechanical property tests are used to study features of phase precipitate formation, structural state, and the properties of low-carbon V, Nb micro-alloyed steels. The effect of nano-sized carbide (carbonitride) V, Nb precipitates formed in austenite during FCC → BCC-phase transformation of steel on the structural state and implementation of different mechanisms is evaluated. Characteristics of similar Ti and Mo precipitates in micro-alloyed ferritic steels are compared.

Keywords: low-carbon micro-alloyed steels, microstructure, nanosize phase precipitates, strength properties, service properties, hardening mechanisms.

An effective direction for development of structural (automobile sheet) and other types of steels providing a set of good indices for strength, ductility, forming capacity, fatigue, and corrosion resistance is creation of new economic low-alloy microalloyed steels of the ferritic class [1]. The unique set of properties for these steels is achieved due to forming a finely dispersed ferritic structure and a volumetric system of nano-size carbide precipitates [1–3]. Initially their structural construction has been based on use of Ti and Mo micro-alloy systems creating conditions for forming carbide (interphase) precipitates during FCC → BCC-phase transformation of steel that has provided preparation of high strength, i.e., up to 700–1000 MPa, with good ductility, stamping capacity, etc. [1–5]. As a result of this in JFESteel (Japan) production has been assimilated for rolled product of this steel type NANOHITEN of various strength classes [1–5]. Subsequently the possibility has been established of using other systems of different and complex micro-alloying and generally V, Nb, Ti, and Mo [6, 7].

Selection of the optimum composition and metal treatment parameters has been delayed by lack of the required fundamental database and adequate methods for predicting the structural state and kinetics of formation for different types of austenitic, ferritic, and interphase carbide precipitates of microalloying elements. In this case the effect of different types of precipitates may differ considerably. For example, formation of interphase nano-size carbide precipitates in titanium-molybdenum microalloyed steels leads to a more significant contribution to strength properties than in ferritic steels [8]. Simultaneously it is possible to change the morphology of the ferritic structure formed, and also to affect strength properties significantly [9]. Interphase precipitates may form with participation of other micro-alloying elements (V, Nb). Therefore, an important task is establishment of features of structural state formation, characteristics of phase precipitates, and the properties of low-carbon steels of the ferritic class in relation to the micro-alloying system used, to which the present study is devoted.

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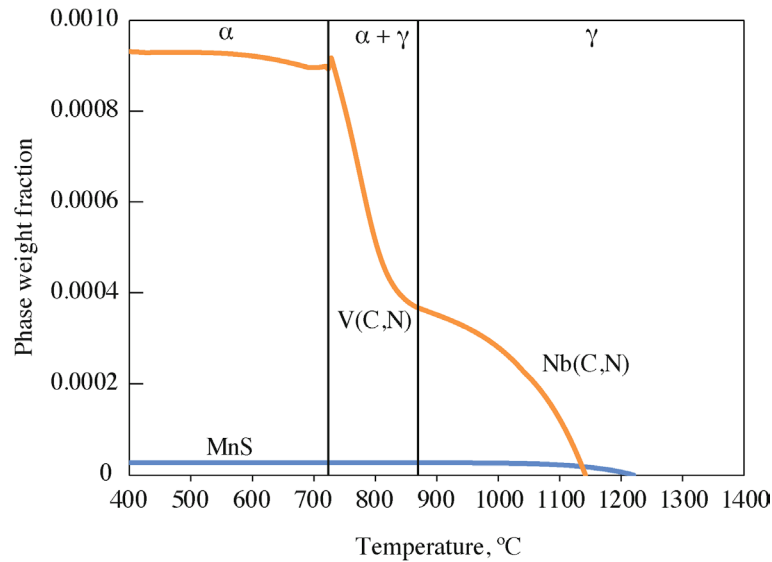
Fig. 1. Temperature ranges for possible formation of type of phase precipitates in test steels.

The object selected was a model of low-carbon microalloyed vanadium-niobium-containing steel from an industrial melt, and results of determination of chemical analysis by spectral analysis according to GOST 18895-97 by means of a OBLF QSN 750 emission spectrometer corresponded, wt.%: 0.06 C, 0.24 Si, 0.59 Mn, 0.008 P, 0.001 S, 0.63 Cr, 0.12 Ni, 0.003 Mo, 0.003 Ti, 0.051 V, 0.031 Nb, 0.029 Al, 0.006 N, and 0.11 Cu. Choice of this composition is due to the well-known capacity of vanadium to form interphase carbide (carbonitride) precipitates [10], which makes it possible to evaluate conditions for their formation and the effect on steel properties. Attention was paid to previously conducted detailed study of Ti-Mo-microalloyed steels of the overall composition, wt.%: 0.08 C, 1.24–1.57 Mn, up to 0.3–0.4 Ti + Mo [8, 9], pointing to the expediency of reducing carbon content to 0.04–0.06 wt.% in order to prevent formation of pearlite, structurally unbonded martensite, and an MA-structural component reducing the level of rolled product properties. In addition, in order to obtain the most promising interphase carbide precipitates within steels of this composition the rate of the FCC → BCC-phase transformation appeared to be too high for their formation, Therefore, retention of the overall level of steel alloying, half of the manganese content in the steel was replaced by chromium, more markedly reducing the intensity of diffusion process and occurrence of FCC → BCC-phase transformation of steel. In order to obtain an idea about the absolute values of parameters for kinetics of V, Nb, Ti phase precipitate formation of different types Mo was excluded was excluded from their composition, considerably accelerating their generation, but retarding growth. In addition, the test steel is characterized by an extremely low content of nitrogen, sulfur, phosphorus capable of causing a competitive effect on carbide precipitate formation of microalloying elements. This is confirmed in results of calculations in accordance with the ideas in [11] by methods forming conditions for possible type of precipitates in the test steel (Fig. 1).

As is seen from Fig. 1, the main types of phase precipitates in the test steel are carbides (carbonitrides) of niobium and vanadium. Their formation commences at ≈ 1150 °C. Due to the low sulfur and nitrogen content the possible amounts of compounds (MnS and AlN) formed are insignificant. In addition, it is well known that formation of AlN is kinetically markedly difficult. With the aim of maximum effective use of microalloying elements before hot rolling it is necessary to provide complete dissolution of the carbide (carbonitride) precipitates. Therefore, the start of hot rolling is recommended at the optimum value of metal temperature of about 1160 °C, and workpiece heating to 1210–1230 °C.

Table 1
Hot Rolling Parameters and Mechanical Property Test Results for Test Steel Rolled Product

Specimen number	T_{er}, °C	T_{wi}, °C	σ_y, MPa	σ_f, MPa	δ_5, %	KCV^{-50}, J/sm^2
1	900	560	455	540	30.0	389
2	905	600	468	550	28.0	369
3	890	580	447	530	32.0	372
4	820	575	475	540	27.0	369
5	825	590	490	550	28.0	405
6	830	580	485	560	28.0	288

It is well known that grain refinement in microalloyed steels facilitates formation during hot rolling of carbide (carbonitride) precipitates of niobium (possibly a complex with vanadium) retarding austenite recrystallization, As is seen from data of Fig. 1 the content of Nb(C, N) precipitates is relatively small. Therefore, a defining role to all appearances may be played by interphase carbide (carbonitride) precipitates of vanadium, whose formation proceeds below 870 °C and leads both to ferrite grain refinement and also to precipitation hardening [10]. It should be noted that according to results obtained [9] for formation of interphase carbide precipitates in Ti- and Ti–Mo-microalloyed steels the end of rolling is optimum at about 900 °C and strip winding on a coil at 600–650 °C. Use of significantly lower temperature for the end of rolling leads to disruption of the interphase mechanism of phase precipitate formation due a high rate of FCC → BCC-phase transformation for steel. However, in the test steel due to alloying with chromium the rate of phase transformations should be slower that may create conditions for formation of interphase precipitates with lower temperatures for the end of rolling. In addition, evidently presence of certain differences in the kinetics of carbide (carbonitride) precipitate kinetics.

In accordance with the situations and discussion presented, specimens selected from intermediate rolled product with a size of $45 \times 110 \times 300$ mm were heated to 1210–1230 °C and held for 1 h. Hot rolling was performed in a DUO 300 reversing laboratory mill for hot rolling for strips 5 mm thick. The temperature for the start of rolling in all cases was maintained in the range 1160–1170 °C and for the end of rolling (T_{er}) at temperatures of about 900 and 820–830 °C. In order to simulate cooling of strip wound on a coil the rolled product obtained was cooled in a stream of air at a rate of 10–15 °C/sec to the required temperature (T_{wi}), placed in a periodically operating furnace and held for 30 min followed by furnace cooling to room temperature during days. Metal samples were selected from the rolled product obtained, and mechanical property tests were performed (according to GOST 1497-84 and GOST 9454-78) (Table 1), and the microstructure was studied by optical and electron microscopy.

In order to evaluate the degree of the effect of metal cooling rate from T_{er} to T_{wi} two specimens of round cross section 10 mm in diameter and 120 mm long were prepared from the original intermediate rolled product. A universal testing Gleeble 3500 complex was used for studying the temperature and deformation treatment regime for specimens No. 1 (see Table 1). Cooling of both specimens from T_{er} to T_{wi} was performed at a rate of 20 and 25 °C respectively. After thermomechanical treatment of specimens they were turned to a diameter of 4 mm in that area where the difference in temperature during performance of a test was not more than 5 °C, and mechanical properties were determined. The values of ultimate strength (σ_f) obtained were 530 and 540 MPa, and yields strength (σ_y) of 450 and 455 MPa for each of the specimens respectively, and compared with data

in Table 1 point to a lack of a significant effect of changes (in the range of values normally used in practice) for cooling rate after rolling on rolled product strength properties.

As is seen from data in Table 1, strength properties, particularly values of ultimate strength for specimens of the rolled product obtained, are quite similar, but the ratio of the values of yield and ultimate strength differ. With lower values of T_{er} the values of σ_y are higher. To all appearances this is caused by differences in the contribution of different steel strengthening mechanisms.

In order to explain the features established the change in mechanical properties a study was made of the structural state and characteristics of phase precipitates present. It has been established that all of the test specimens have a fine-grained ferritic structure uniform over rolled product cross section. With respect to grain size they may be separated into two groups: the first concerns specimens Nos. 1–3 for which there is typically a larger grain size (ferrite grain size number 8–9 according to GST 5369). For the second group, i.e., specimens Nos. 4–6 there is typically a smaller gran size (number 10–111 according to GOST 5369). A typical form of the microstructure on the example of an axial zone of specimens Nos. 1 and 4, where maximum structural inhomogeneity may be observed, is presented in Fig. 2. It is seen from data of Fig. 2b that another feature of the microstructure for specimens of the second group is a difference in grain size, and in fact presence of areas with smaller and larger grain sizes. This may be caused by the end of rolling in a two-phase ferrite-austenite region.

The difference in microstructure characteristics for the two separate groups of rolled product is connected with a considerably different temperature for the end of rolling (see Table 1). More intense grain refinement for the second group of rolled product is caused by the more marked contribution of the grain boundary strengthening mechanism and consequently preparation of similar values of ultimate and yield strength.

Grain-boundary, in contrast to other mechanisms for steel strengthening, hardly worsens ductility indices [12], and therefore it is more promising. The degree of the effect of grain size on yield strength is possibly evaluated by the well-known Hall–Petch equation:

$$\sigma_g = K_g d^{-1/2},$$

where d is grain diameter (length of free travel of dislocations), μm; K_g is a constant having a certain value for each material (for low-carbon steel for K_g the established value in within quite a narrow range of 15.1–18.1 N/mm$^{3/2}$ [12–15].

On the basis of evaluating values of the increase in σ_y with transition from grain No. 8–9 to No. 10–11 (GOST 5639) taking account of the accuracy of determining K_g, a value is determined for the increase in yield strength: 44–53 N/mm^2 with transfer from rolled product of the first to the second groups. This agrees with the change in this property provided in Table 1, and similarly indicates that the change is connected almost entirely with a change in grain size with a change-over from the first to the second group of rolled product.

In order to clarify the role of different types of phase precipitates in forming the structure and properties methods of transmission electron microscopy (TEM) in a JEOL1200CX analytical transmission electron microscope combined with an EM-ASID3D2 scanning attachment and an attachment for energy dispersion X-ray microanalysis LINK SYSTEMS SERIESII were used. With a working magnification from 15 to 30 thousand times, an accelerating voltage of 100–120 kV, and resolution ≈ 1 nm, metal samples were selected from specimens of rolled products Nos. 1 and 4.

A study was made of foils cut from the axial zone of rolled product (Nos. 1o and 4o respectively) at a distance of a quarter of the thickness from the rolled product surface (Nos. 1ch and 4ch respectively). It has been established that steel microstructure is finely dispersed dislocated ferrite with individual pearlite colonies. In addition, extended precipitates of cementite are observed at grain boundaries and at junctions. The thickness
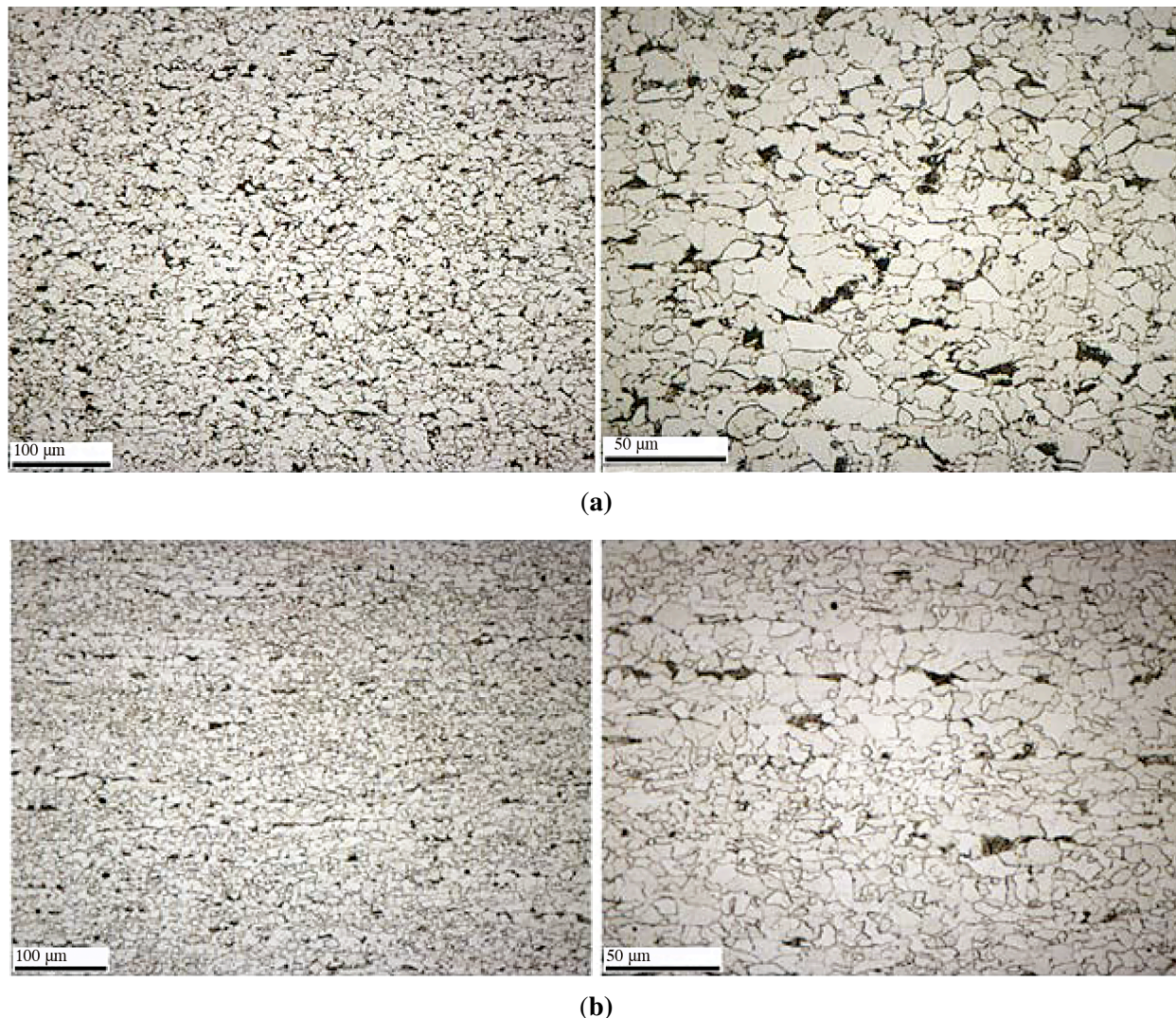
Fig. 2. Macrostructure of specimen No. 1 (a) and No. 4 (b) taken from rolled product axial zone.

of these precipitates ≈ 0.1–0.2 μm, and length ≈ 0.5–1 μm. They do not form a continuous network and encountered relatively rarely. The overall appearance of the steel microstructure, including cementite precipitates, is provided in Fig. 3.

Within the metal of test samples presence has been recorded of nano-size carbide (carbonitride) precipitates of two types: interphase, i.e., smaller size, formed with FCC → BCC-phase transformation of steel, and austenitic, i.e., large sizes formed during hot rolling. Interphase precipitates of V(C,N), possible combined with Nb(C,N), have been recorded in all of the test specimens in a greater amount, and the arrangement of layers (Fig. 4) has the form of equidistantly located chains. This is clearly expressed where a layer is arranged perpendicular to the surface of the foil, and in other cases this arrangement is less clear. In the same specimen the distance between layers may vary somewhat in different parts, which is in good agreement with existing ideas about the random and uneven occurrence of $\gamma \rightarrow \alpha$-transformation in different grains or their areas due existence of a difference in temperature and metal concentration inhomogeneity. Proceeding from this characteristics of interphase precipitates are similar in the test specimens. Their typical size of 2–6 nm and the distance between layers is 20–50 nm.
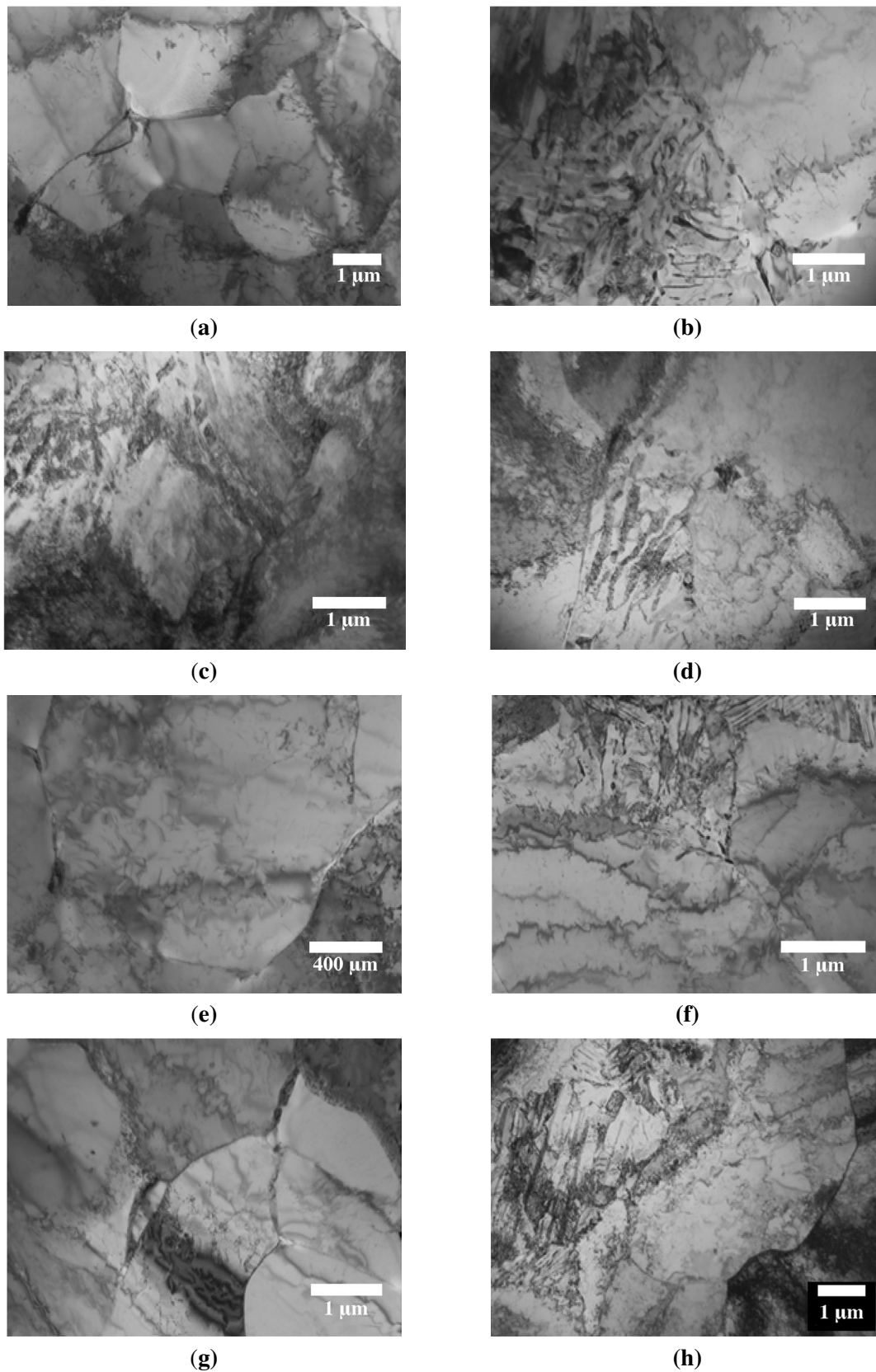
Fig. 3. Appearance of test specimens structure, × 10,000: (a, b) No. 1ch; (c, d) — No. 1o; (e) (× 30,000), (f) No. 4ch; (g, h) No. 4o.
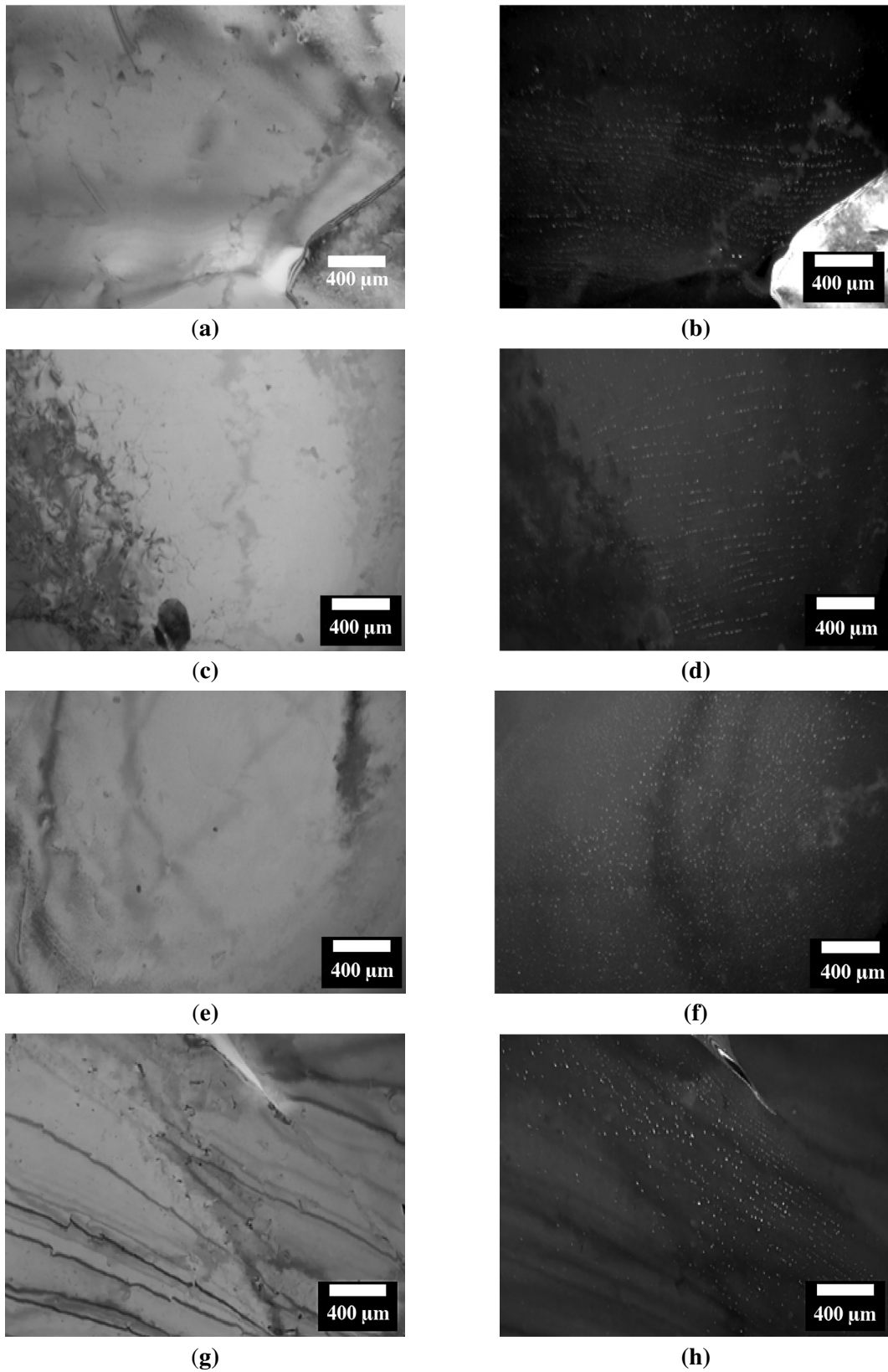
Fig. 4. Nanosize carbide, carbonitride interphase precipitates recorded in test specimens: (a, b) No. 1ch; (c, d) No. 1o; (e, f) No. 4ch; (g, h) No. 4o; (a, c, e, g) light field; (b, d, f, h) dark field image (× 30,000).
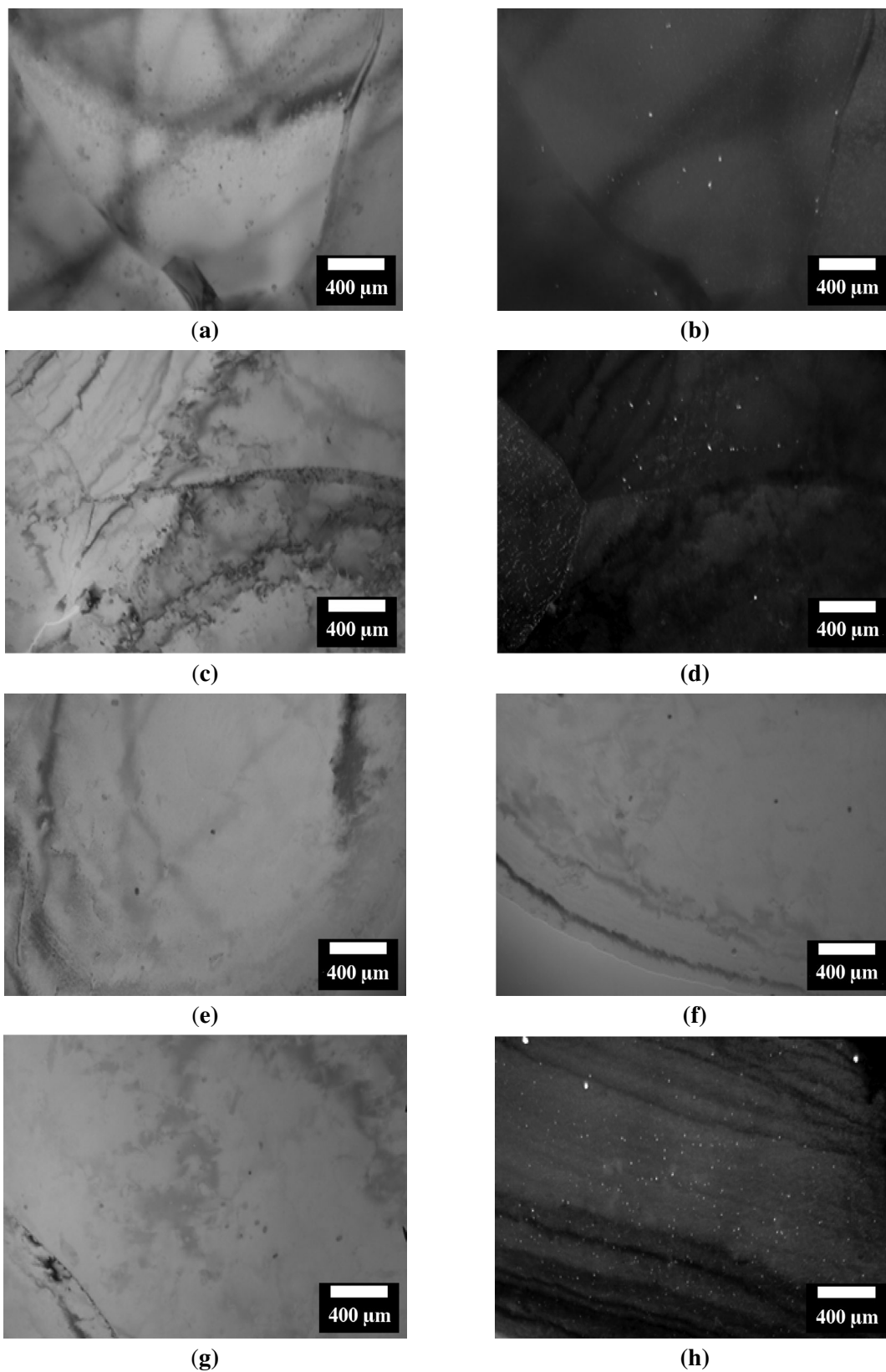
Fig. 5. Nanosize carbide, carbonitride austenite precipitates recorded in test specimens: (a, b) No. 4ch; (c, d) No. 4o; (e, f) No. 1ch; (g, h) No. 1o; (a, c, e, f, g) light field; (b, d, h) dark field image (×30,000).

A marked difference in the structure of test specimens of rolled product may be connected to some extent with the properties of nanosize phase precipitates formed within austenite (Fig. 5). The volume concentration of these precipitates is low in a specimen of metal No. 1 with a size of $\approx$ 20–40 nm. In specimen No. 4 with a greater volume concentration of austenitic precipitates their size is smaller, i.e., $\approx$ 8–15 nm. This is in good agreement with data of Fig. 1, from which it follows that formation of Nb(C,N) precipitates may proceed at relatively high hot rolling temperatures for the steel and their molar fraction is low. A reduction in temperature for the end of rolling facilitates co mpletion of transformation, although due to the faster metal cooling rate there are less clear stimuli for an increase in precipitate size. Nonetheless, from the data obtained it is complicated to follow the yield of the total amount (molar fraction) of austenitic precipitates, and in this case it is quite small.

A marked role in grain refinement may be played by V(C,N) precipitates formed during steel $\gamma \rightarrow \alpha$-phase transformation at a temperature below 870 °C. Due to the lower temperature and limitation of the time for formation, connected with the rate of phase transformation, the size of the precipitates obtained is smaller.

A typical feature of the nanosize precipitates formed within austenite is their somewhat different orientation. In view of this in an individual dark field image in an area of metal only part of the precipitates present is seen, and with some shift in aperture diaphragm it is possible to reveal their additional amount. A light-field image is more indicative in this case. The contrast is absorption and weaker, but almost all precipitates with a size of more than $\approx$ 10 nm are observed.

Therefore, the results obtained indicate that different types of phase precipitates have a different effect on formation of the structural state and steel properties. The Nb(C,N) formed within austenite stimulate grain refinement and implementation of grain boundary strengthening for steel. Interphase carbide (carbonitride) precipitates (mainly V(C,N) lead to both precipitation hardening and also grain refinement [10]. A change in the ratio for the intensity of implementing these mechanisms makes it possible within certain limits to change the ratio of rolled product strength properties.

It should be noted that within the V–Nb-microalloyed steel in question formation of interphase precipitates has been recorded with a change in temperature for the end of rolling over a wide temperature range (820–905 °C), whereas in Ti–Mo-microalloyed steel studied previously for this high values of $T_{er} \approx$ 900–950 °C were required [9]. To all appearances this may be caused by significant stabilization of austenite, and the effect of chromium present within the steel composition. In spite of presence of interphase V(C,N) precipitates, the strength properties obtained are lower than established previously for Ti- and Ti–Mo-microalloyed steel ($\approx$ 1700–900 MPa) [8, 9], which may be connected with morphological features of the low dislocation ferritic structure obtained and characteristics of the interphase precipitates formed. This points to a preference of using microalloying with Ti and Ti–Mo compared with microalloying with V, Nb, or more complex microalloying systems, in order to prepare steels of the ferritic class of a high strength category.

In all cases high values of relative elongation and impact strength have been obtained (see Table 1). Values for the first group of rolled products on average are somewhat better than for the second, in spite of the smaller contribution of grain-boundary strengthening in this case. To all appearances this may be connected with the lower values of consumption of phase-forming components in forming austenitic carbide (carbonitride) precipitates, and correspondingly the larger size of interphase precipitates, and to a lesser extent causing a reduction in the properties in question. Within the microstructure of all of the test specimens presence has been recorded of pearlite colonies and cementite precipitates, also leading to this effect. In order to prevent the unfavorable situation noted, it is expedient in accordance with conclusions in [8, 9] to reduce the carbon content in steel.

CONCLUSION

On the basis of studying rolled product of low-carbon V–Nb-microalloyed steel it has been established that a reduction in temperature for the end of rolling from 890–905 to 820–830 °C leads to an increase in ferrite grain

size according to GOST 5369 from 8–9 to 10–11, yield strength with similar values of ultimate strength, and good indices for relative elongation and impact strength. The features noted are connected to a significant extent with presence in metal of nano-size austenitic and interphase carbide (carbonitride) precipitates. The amount of austenitic Nb(C,N) precipitates retarding austenite recrystallization, stimulating grain refinement and implementation of a grain-boundary strengthening mechanism for rolled product, increases with a reduction in T_{er}. Interphase precipitates, mainly V(C,N), lead to both precipitation hardening and also grain refinement. A change in the ratio of intensity of implementing these mechanisms leads within certain limits to a change in the ratio of strength properties for rolled product. Comparison of the results obtained with those obtained previously for Ti- and Ti–Mo-microalloyed steels points to the preference of the Ti- and Ti–Mo microalloying used compared with V–Nb-additions or more complex systems of microalloying in order to prepare steels of the ferritic class of a high strength category.

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