

Temperature Dependences of Age-hardening Austenitic Steels Mechanical Properties in Gaseous Hydrogen

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In recent years much attention has been given to the problems of interaction of hydrogen with structural materials [1–4]. This is explained, on the one hand, by realization of specific projects and programs of alternative energetic and, on the other hand, by a desire to formulate scientific principles of elimination of factors leaning to hydrogen degradation of metals. Despite numerous theoretical generalizations in this direction, the experimental estimation of properties under conditions maximally similar to service ones is the most reliable method for the determination of the susceptibility of structural materials to hydrogen degradation.

The aim of present work was to investigate the influence of high-pressure hydrogen in temperature range 293 – 1073 K on the ultimate strength and plasticity (tensile test properties), low-cycle durability, static and cyclic crack resistance of 05Kh12N23T3MR and 10Kh15N27T3B2MR steels, which hardened mainly by an intermetallic γ' -phase of the type $Ni_3(Al,Ti)$.

Materials and Test Procedure. The chemical composition, heat-treatment modes and original properties are given in Tables 1 and 2.

Table 1. Chemical composition of Steels

| Steel | Content of elements, wt.% | | | | | | | | |
|-----------------|---------------------------|------|-------|-------|------|------|------|------|-------|
| | C | Si | Cr | Ni | Mo | W | Ti | Al | B |
| 05Kh12N23T3MR | 0.05 | 0.37 | 11.35 | 23.17 | 1.48 | - | 2.98 | 0.62 | 0.015 |
| 10Kh15N27T3B2MR | 0.09 | 0.6 | 15.18 | 27.11 | 1.41 | 1.92 | 2.85 | 0.29 | 0.02 |

Table 2. Modes of Thermal Treatment and Mechanical Properties of Steels in Air at Room Temperature

| Steel | Thermal Treatment | | Mechanical Properties | | | | |
|-----------------|--------------------|---------------------------|-----------------------|----------------------|--------------|------------|---|
| | Solution treatment | Mode of aging | σ_u , MPa | $\sigma_{0.2}$, MPa | δ , % | ψ , % | Number cycles to fracture, bending strain 1.6 % |
| 05Kh12N23T3MR | 1373K, 1 h | 1000K, 16 h 923K, 5 h | 1200 | 880 | 29 | 47 | 3000 |
| 10Kh15N27T3B2MR | 1373K, 1 h | 1023K, 16 h 923K, 10 h | 1270 | 870 | 17 | 23 | 2277 |

The most important difference in the chemical composition of steels is the additions of about 2 % W and almost twice larger amount of carbon in 10Kh15N27T3B2MR steel. The presence of tungsten enhances the heat-resistance of steel [5] and the presence of carbon increases its sensitivity to the action of hydrogen [2,4].

Specimens were subjected to static tension in a gaseous hydrogen under the pressure of 0 – 35 MPa with displacement rate $10^{-2} - 10^2$ mm/min. For the used fivefold specimens with a diameter of the working part of 5 mm, this rate lies within the range $7 \times 10^{-6} - 7 \times 10^{-2} \text{ sec}^{-1}$. We determined the low-cycle resistance of polished plane specimens in the pressure range 0 – 35 MPa at amplitudes ε of 0.8 – 1.2 % and frequencies 0.5 Hz.

Fracture toughness was calculated by Srawley–Gross formula [6] with using “F–V” diagrams of static off-center tension with displacement rate 0.1 mm/min of compact specimens with sizes 50×60×20 mm in helium and hydrogen under the pressure of 0 – 30 MPa.

The influence of high-pressure hydrogen on cyclic crack resistance was investigated by three points bending of beam specimens with sizes 160×40×20 mm with frequencies 20 Hz and stress ratio by cycle $R = 0.22$.

To determine the indicated mechanical characteristics in hydrogen, the working chambers were preliminary evacuated, blown-out with hydrogen, again evacuated and filled with hydrogen up to a given pressure. At high temperature, the specimens were held under the test conditions for 30 min up to the attainment of thermal equilibrium.

In order to compare the action of external and internal hydrogen [2–4,7] and study the influence of hydrogen dissolved as a result of long-term operation of structures on the properties of steels, a part of specimens was preliminary held in a hydrogen atmosphere for 10 h under the following conditions: 673 K, 10 MPa (mode 1), 673 K, 35 MPa (mode 2). All these modes ensure the possibility of through saturation of the specimens made up to the concentrations 32 and 60 mole/m³ respectively. The hydrogenated and nonhydrogenated specimens were tested under various pressures in hydrogen, helium or air.

The sensitivity to hydrogen degradation was evaluated by the coefficients β_ψ , β_N and β_K , which were calculated as ratio between the reduction of area, cyclic durability and crack resistance coefficients in hydrogen and in helium or air (e.g., the coefficient of influence of hydrogen on the reduction of area $\beta_\psi = \psi_H / \psi_{He}$).

Influence of the Parameters of Loading on Mechanical Properties in Hydrogen.

For the adequate assessment of the serviceability of materials in hydrogen-containing media, is very important to be able to realize the proper choice of testing the conditions and, first of all, of the modes hydrogenation and loading rates [2,7]. It is shown that the 05Kh12N23T3MR- and 10Kh15N27T3B2MR-type steels have low sensitivity to the action of gaseous hydrogen under the conditions of slow strain rate tension and low-cycle fatigue at room temperature. They are strongly embrittled by hydrogen after preliminary hydrogenation at elevated temperature for the concentrations of hydrogen exceeding 40-45 mole/m³, whereas the properties of hydrogenated specimens at room temperature in air and hydrogen are identical [2,4,7]. However, it is unknown whether these effects are also observed at elevated temperature and, therefore, we determine the mechanical properties of materials in the entire temperature range under the maximum possible pressure for the used installations equal to 35 MPa.

The analysis of influence of strain rate on the coefficient β_ψ , which is one of the most sensitive indicators of hydrogen degradation [1–4,7], shows that the range of strain rates and the degree of decrease in plasticity are determinate by the chemical composition and structure of material (Fig. 1). The 10Kh15N27T3B2MR austenitic steel with elevated contents of carbon and tungsten has much lower plasticity and low-cycle durability in air and is more sensitive to the influence of hydrogen than 05Kh12N23T3MR steel (Table 2, Fig. 1). This was revealed both for nonhydrogenated specimens (Fig. 1, curves 1 and 2) and specimens hydrogenated in mode 2 (Fig. 1, curves 4 and 5). In the case of slow strain rate tension at room temperature, the properties of these steels are deteriorated in gaseous hydrogen only in the presence of hexagonal densely parked intermetallic or carbide phases in there structure [4].

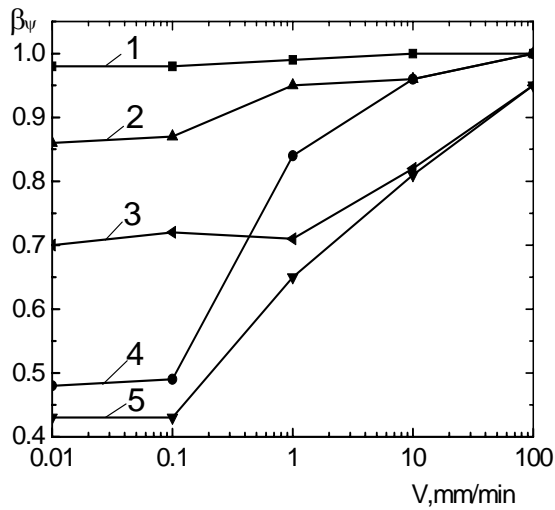


Fig. 1. The coefficient of hydrogen influence on reduction in area β_w for specimens of 05Kh12N23T3MR (1, 2) and 10Kh15N27T3B2MR (3-5) steels versus tensile strain rate V at 293 K (1,2,4,5) and 873 K (3): 1-3 – nonhydrogenated specimens, 4,5 – hydrogenated specimens (623 K, 35 MPa, 10 h).

specimens of 10Kh15N27T3B2MR steel in hydrogen within the analyzed range of strain rates 0.01–0.1 mm/min (Fig. 1, curve 2). Despite the well-known regularities of hydrogen degradation [2,4,8] the degree of embrittlement of this steel in hydrogen media strongly increases as temperature grows from 293 to 873 K. At the same time, the range of strain rates of embrittlement enlarges (Fig. 1, curves 1 and 3).

In view of their chemical composition (Table 1), carbides can be regarded as the cause of an almost 15 % drop of the reduction in area of

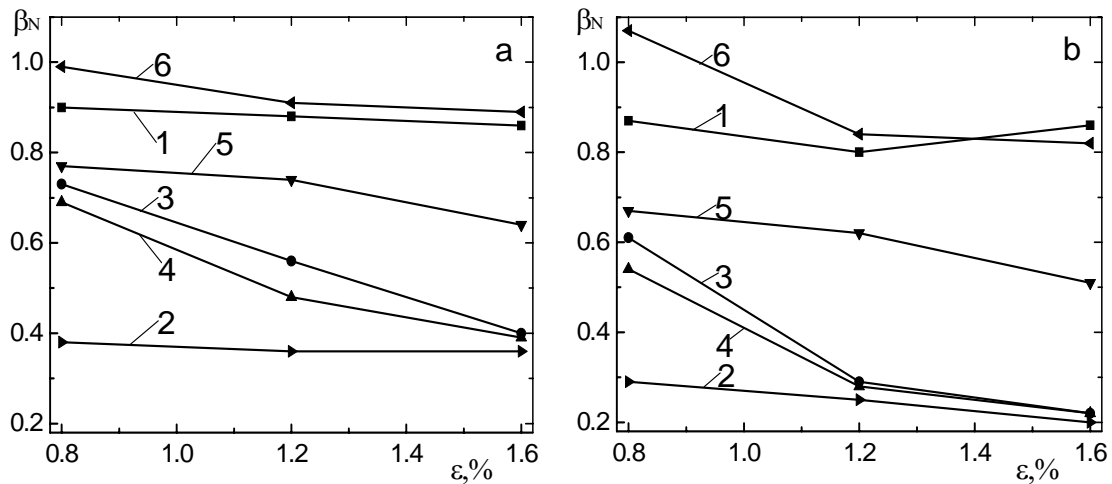


Fig. 2. The coefficient of hydrogen influence on low-cycle durability β_N versus strain amplitude ϵ for 05Kh12N23T3MR (a) and 10Kh15N27T3B2MR (b) steels at the following temperatures: 1,2 – 293 K; 3 – 473 K; 4 – 673 K; 5 – 873 K; 6 – 1073 K. 1,3-6 – nonhydrogenated specimens, 2 – hydrogenated specimens (623 K, 35 MPa, 10 h).

Under the conditions of low-cycle loading, the kinetic process of interaction hydrogen – metals are governed by strain amplitude and frequency. Thus, by decreasing the frequency from 0.5 to 0.05 Hz, it is possible to lower the hydrogen corresponding to the minimum number of cycles to failure for specimens of 03Kh12N10MT steel from 10 to 3 MPa [2]. However, the duration of experiments increases by an order of magnitude. Therefore, in view of the fact that the level pressure used in our test was as high as 35 MPa, they were performed at a frequency 0.5 Hz.

The influence of hydrogen on low-cycle durability of 05Kh12N23T3MR and 10Kh15N27T3B2MR steels increases with the bending strain amplitude (Fig. 2a, b). This is typical of high-strength materials in which plastic zone formed in front the crack tip for high amplitudes is small and hydrogen fairly rapidly penetrates into the region of maximum tensile stresses [2]. The nonhydrogenated specimens of both steels undergoes insignificant

embrittlement (10-20%) at 293 and 1073 K (Fig. 2a, b, curves 1, 6), somewhat greater embrittlement (30-40%) at 873 K (Fig. 2a, b, curve 5), and attains its maximum sensitivity to the action of gaseous hydrogen at 473 and 673 K (Fig. 2a, b, curves 3,4). After preliminary high-temperature hydrogenation, the minima of durability can also be obtained at room temperature (Fig. 2a, b, curve 2) i.e., the stage of penetration of hydrogen into metal is decisive for the hydrogen degradation of the analyzed steels under the conditions of tension and low-cycle fatigue.

Influence of hydrogen on the Static Crack Resistance of Steels.

We estimate the crack growth resistance of materials in the presence of hydrogen according to the values of the parameter K_c determined by using the standard procedures of testing for short-term static crack resistance in neutral media. This method is relatively simple and fast by its application has certain limitations [6]. In our opinion, it should be emphasized that the action of hydrogen is, as a rule, localized and connected with surface and diffusion processes and structural inhomogeneities, whereas the linear fracture mechanics is based on the analysis of homogeneous structures. At the same time, it seems reasonable to perform the comparative analysis of the influence of the stress intensity factor (SIF) K_c and all other characteristics of structural materials under the identical testing conditions.

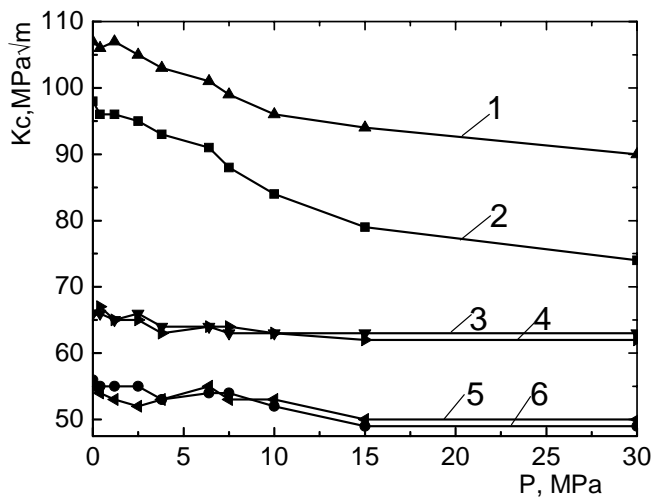


Fig. 3. Dependence of the fracture toughness K_c of the specimens of 05Kh12N23T3MR (1,3,4) and 10Kh15N27T3B2MR (2,5,6) steels at the room temperatures on the pressure of hydrogen P : 1,2 – nonhydrogenated specimens, 3,5 – hydrogenated specimens (623 K, 10 MPa, 10 h) 4,6 – hydrogenated specimens (623 K, 35 MPa, 10 h).

In neutral media, the steels are characterized fairly high plasticity in the entire analyzed temperature range (Table 2). Therefore, the thickness of the specimens is insufficient to get the plain-strain state. The fracture diagrams are curvilinear (of type III) [6] and the fracture surface is ductile-brittle with typical lateral bindings. The regularities of the influence of hydrogen on the quantity K_c (Fig. 3), the low-cycle durability and the characteristics of plasticity [2] are qualitatively similar. For nonhydrogenated specimens of 05Kh12N23T3MR and 10Kh15N27T3B2MR steels (Fig. 3, curves 1, 2), the parameter K_c decreases in the entire range of pressures, i.e., a pressure of 30 MPa is insufficient for the maximum possible deterioration of fracture toughness. As in case of testing for tension and low-cycle durability (Fig. 1 and 3), the minimum values of quantity K_c for this steels at room temperature (independent of the pressure of hydrogen) are attained only after preliminary high-temperature hydrogenation in mode 1 or 2 (Fig. 3, curves 3-6). The concentrations of hydrogen in first case (mode 1) is equal 32 mole/m^3 , i.e., somewhat lower than required for the maximum possible hydrogen degradation of this type of steel under the conditions of short-term static tension (45 mole/m^3) [2,4,7,8].

In the helium the static crack resistance of 10Kh15N27T3B2MR steel first increases but then remains constant in the temperature range 423–693 K (Fig. 4, curve 1). The presence of hydrogen leads to decrease in K_c (Fig. 4, curve 2,3). The internal preliminary dissolved hydrogen plays an important role in the hydrogen embrittlement at medium temperature (Fig. 4, curve 2).

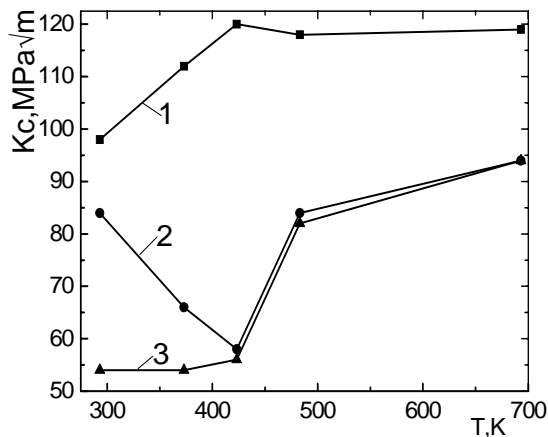


Fig. 4. Temperature dependences of the fracture toughness K_c of the specimens of 05Kh12N23T3MR: 1 – in helium, 2 – in hydrogen under the pressure 10 MPa, 3 – in hydrogen under the pressure 10 MPa after hydrogenation (623 K, 10 MPa, 10 h).

At 423 K, the values of K_c for the nonhydrogenated and hydrogenated specimens of 10Kh15N27T3B2MR steel are identical, which means that the amount of hydrogen penetrating into the material from the gaseous phase at the indicated temperature in the course of the tests is sufficient for its degradation. At temperature increases, the influence of hydrogen becomes weaker, but the 20 % drop of K_c is preserved even at 693 K.

Hydrogen decreases the coefficient of crack resistance and effects the character of fracture. Under the conditions of maximum hydrogen embrittlement, the load displacement diagrams become linear with sharp maxima (as functions of load) and correspondent to type II [6]. The fracture surfaces of specimens are covered with cleavage facets typical of brittle fracture in temperature range 293-693 K (Fig. 5).

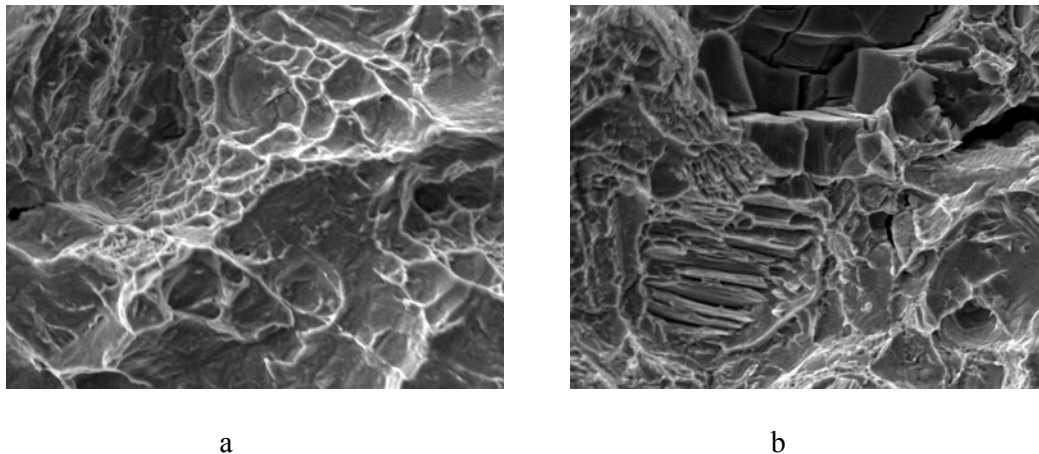


Fig. 5. Microfractograms of 10X15H27T3B2MP steel after crack growth testing at 693 K in helium (a) and in hydrogen under the pressure 10 MPa after hydrogenation (623 K, 10 MPa, 10 h) (b) $\times 3000$.

The values of K_c can be regarded as equal to K_{Ic} , i.e., they satisfy the condition $l, b \geq 2.5(K_c^H/\sigma_{0.2}^H)^2$, where l is the crack length and b is the thickness of specimen [6]. The indicated condition is satisfied at room temperature for 05Kh12N23T3MR and 10Kh15N27T3B2MR steels after preliminary hydrogenation (623 K, 10 MPa, 10 h) for all hydrogen pressure with K_{Ic} is equal 62–66 and 50–55 MPa√m, respectively. The temperature ranges in which the sizes of the specimens under the conditions of maximum possible hydrogen degradation for

05Kh12N23T3MR and 10Kh15N27T3B2MR steels are sufficient to find the quantity K_{Ic} are 293–483 K (Fig. 4). In other cases, in order to get correct estimates of the crack resistance of steels, it is necessary to increase the sizes of the specimens or to apply the other methods [6,9]. For example, for definition of critical moment of state, which prevents the fracture (durability closing) of details of energetic unit the SIF at plane-strain fracture $K_I(a, \sigma)$ can be used. The critical state is consider such, when on the crack contour the maximum SIF value achieves the fracture toughness K_{Ic} . Using Life Assessment Code EPRI IN-103088, IN-1030887 for calculation of retaining ring life with defects we can predict, that with crack depth $a^* = 24 \text{ mm}$ the fracture of retaining ring made from steel 18Mn-18Cr take place after 5 thousand hours of the service [9, 10]. In spite of that, hydrogen factor can decrease drastically at that time, because critical crack size in gaseous hydrogen is less. Thus, it is necessary to take into account the real value of $K_{Ic(H)}$ for working environment. Assessment of modern steels has shown, that high nitrogen 18Mn-18Cr (12Kh18AG18Sh) steel with higher value of fracture toughness enable the safe carrying ability of retaining ring with crack during the higher service time in hydrogen environment, than traditional 8Mn-8Ni-4Cr (60Kh3G8N8V) steel [10, 11]. As a result of the analysis of cracks, detected at the FPP TG retaining rings it is established, that crack propagation rates are commensurable with crack rates, obtained during experimental testing of specimens made of 8Mn-8Ni-4Cr steel in hydrogen containing environments. Crack rates in 18Mn-18Cr steel retaining rings at the some FPP are equal to 0.10...7.0 mm/year and less, than in the retaining rings made of 8Mn-8Ni-4Cr steel.

Conclusions.

The parameters of loading and the modes of hydrogen action for which the mechanical characteristics of the 05Kh12N23T3MR and 10Kh15N27T3B2MR steels are minimum at room temperature can be formulated as follows:

–the strain rate for slow strain rate tensile test $V_{def} \leq 10^{-6} \text{ s}^{-1}$ and the content of preliminary dissolved hydrogen is equal to 60 mole/m³;

–the strain amplitude under the conditions of low-cycle fatigue $\varepsilon = 1.6 \%$ and the content of hydrogen is equal to 32 mole/m³;

–in testing for static crack resistance the content of hydrogen is equal to 32 mole/m³ independently of the hydrogen pressure.

10Kh15N27T3B2MR steel is more sensitive to hydrogen embrittlement than 05Kh12N23MTR, but less sensitive than 60Kh3G8N8V and 12Kh18AG18Sh steels.

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