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CORROSION

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CRITERIA FOR ACCELERATED ESTIMATION OF SUSCEPTIBILITY OF PIPE STEELS TO CORROSION CRACKING UNDER OILFIELD CONDITIONS

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Recommendations are developed for selection of criteria for estimation of the susceptibility of steels to corrosion cracking in accelerated tests. The fracture behavior of pipe steels under different loading rates and temperatures is studied experimentally in environments containing hydrogen sulfide and carbon dioxide. Depending on the yield strength of the steel, such criteria are shown to be the breaking stress or the ratio of the failure stresses in the corrosive environment and in air as well as the elongation or the ratio of the elongations in the environment and in air.

Key words: pipe steel, 34KhMA, 485, 09G2S, microstructure, corrosion cracking, accelerated tests.

INTRODUCTION

The operating capacity of the equipment serving at oil and gas deposits with high contents of H_2S and CO_3 is determined to a great extent by the resistance of the materials to corrosion cracking [1 – 4]. The use of corrosion-resistant alloys lowers the risk of failure of the equipment under the impact of corrosion, but application of conventional carbon steels in the oil and gas industry remains advantageous economically [5 – 7].

The pipe steels serving in oil extraction should possess the specified chemical compositions, mechanical and corrosion properties [8]. It should be noted that in contrast to control of the chemical composition and mechanical properties, which is not laborious, the tests for sulfide and hydrogen cracking may last for up to two months or even longer [9, 10]. This makes the development of accelerated methods for estimating the susceptibility of steels and alloys to corrosion cracking a timely task.

Advanced methods for accelerated assessment of the susceptibility of steels to sulfide and hydrogen cracking, for example, electrochemical testing or slow strain rate testing (SSRT) for corrosion cracking, shorten the test time substantially [11 – 15]. Such methods make it possible to determine the threshold stress or another characteristic of the metal in a short time. However, the results of alternative test methods do not converge obviously, and there are no reliable criteria for estimating the susceptibility of steels to corrosion cracking.

An accelerated test requires a correct choice of the strain rate. It should be close to the rate of short-term creep of the steel under the tensile stresses applied and concentrated in the zone of the developing corrosion defect, which acts as a stress concentrator on the surface of the specimen [16, 17]. At a slow strain rate, a protective film forms on the surface of the metal, and corrosion racking is possible only when the strain rate exceeds somewhat the rate of formation of the protection film [18]. An important factor in any test is the temperature. Under the conditions of an oilfield it is usually higher than room temperature, which should also affect the operating capacity of the steel in an environment of hydrogen sulfide or carbon dioxide.

The aim of the present work was to study experimentally the effect of the rate of deformation and of the temperature on corrosion cracking (CC) of steels in hydrogen sulfide and carbon dioxide environments and to choose substantiated cri-

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TABLE 1. Chemical Compositions of Studied Steels

Steel	Content of elements, wt.%									
	C	Si	Mn	Cr	Ni	Cu	Mo	V	S	P
09G2S	0.10	0.75	1.40	0.11	0.17	0.18	—	0.01	0.020	0.027
485	0.04	0.08	1.68	0.05	0.26	0.20	0.15	—	0.002	0.008
34KhMA	0.29	0.17	0.42	0.49	0.06	0.04	0.85	0.08	0.009	0.012

TABLE 2. Mechanical Properties of Steels under Standard Tests for Static Tension at Room Temperature

Steel	$\sigma_{0.2}$, MPa	σ_r, MPa	δ, %	ψ, %
34KhMA	990	1064	18	68
485	540	605	22	69
09G2S	284	431	30	71

teria for estimating the susceptibility of the steels to CC in testing by accelerated methods.

METHODS OF STUDY

We studied steels of three grades differing in the strength class, i.e., commercial steel $09G_2S$; steel DNV SAWL 485FD (to be called 485) used for pipelines, and 34KhMA (P110), the samples of which were cut from a ready casing pipe P110 (according to API 5CT-2011).

The chemical compositions of the steels were determined by atomic emission spectrometry with photoelectric detection of the spectra for assessing the mass fractions of the elements according to GOST R54153–2010 using an "Iskroline-100" spectrometer. The chemical compositions of the steels are presented in Table 1.

The mechanical properties of the steels in the initial condition were assessed by static tests of cylindrical samples (type IV, GOST 1497–84) for uniaxial tension. The tests were conducted at room temperature in an Instron 8850 machine with Instron Bluehill 2.6 software. The mechanical properties of the steels are presented in Table 2.

The tests for corrosion cracking were performed with the help of an UME-10T machine updated for testing for hydrogen sulfide stress corrosion (SSC) and stress corrosion cracking (SCC) at a slow strain rate (about 1×10^{-4} mm/min). The sealed cell with the tested sample had a coil from a corrosion-resistant material inside, which was connected to a thermostat to keep the temperature of the solution at the specified level (20, 40, 60, and 80°C).

A slow strain rate test (SSRT) consists in applying tensile of bending deformation to the sample at a slow stain rate in an environment providing occurrence of electrochemical reactions. The loading is started from a zero load and conducted until failure of the sample. The stress–strain curve is plotted in coordinates $\sigma - \varepsilon$, where $\varepsilon = \Delta L/L$ is the relative strain of the sample and L is the length of the functional part of the sample. The susceptibility of the sample to CC is determined in terms of the ratio of the critical strains and stresses in air and in the corrosive medium. Standard [12] also stipulates the possibility of the use of the ratio of the times of before failure of the sample in air and in the corrosive medium. This involves plotting of two curves at the specified strain rate, i.e., the curve for the air test and the curve for the test in the corrosive medium causing corrosion cracking. If the steel is susceptible to CC, these curves differ. The main criterion in the determination of the susceptibility of the material to CC the in slow strain rate tests is the ratio of the values of plastic strain of the sample that undergoes failure in the corrosive medium and in air. Another criterion is the ratio of the stress at which a crack starts to grow in the corrosive medium to the maximum breaking stress in air. The stress at which the crack starts to grow in the corrosive medium is determined from the point of divergence of the curves for air and for the corrosive medium. If the stress–strain diagrams are not plotted, the criterion may be the ratio of the elongations after testing of the samples in the corrosive medium and in air, as it is recommended in [11].

The metallographic studies were performed for microsections prepared in the longitudinal direction from the functional part of the samples after the slow strain rate test. The surface of the metallographic specimens was polished in a BUEHLER ECOMET 4 mill and etched in a 4% alcoholic solution of nitric acid. The microsections were studied under a Reichert-Jung MeAF-3A microscope using a Thixomet Pro image analyzer.

RESULTS AND DISCUSSION

Figure 1 presents the stress–strain diagrams of steel 34KhMA obtained in air tests at different strain rates. Since there are no significant qualitative or quantitative differences in the curves, we may conclude that the strain rate in the air test does not affect the mechanical characteristics of steel 34KhMA.

Figure 2 presents the stress–strain curves of steel 34KhMA tested with different strain rates in a corrosive medium at room temperature. The corrosive medium is a 5% aqueous solution of NaCl with pH = 2.8 (solution *A* in NACE TM 0177) saturated with H_2S, i.e., we determined the effect of the strain rate on the susceptibility of the steel to SSC. For comparison, we present in Fig. 2 the stress–strain

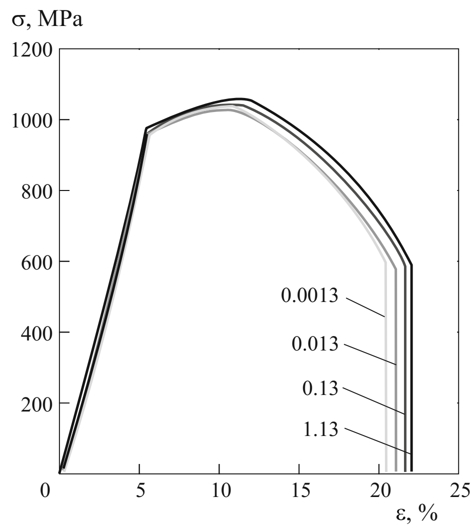


Fig. 1. Stress–strain (σ – ε) curves of steel 34KhMA tested in air at different strain rates (given at the curves in mm/min).

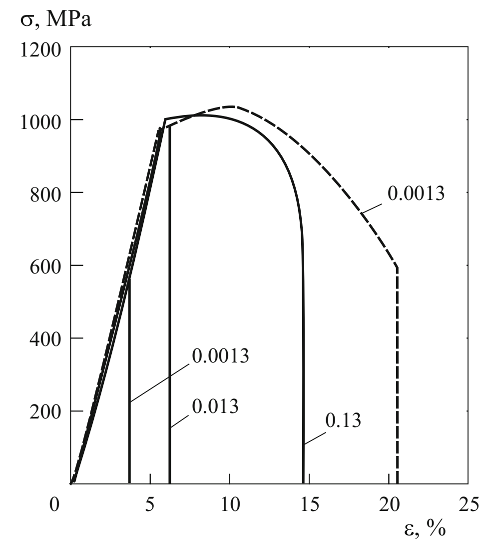


Fig. 2. Stress–strain (σ – ε) curves of steel 34KhMA tested in solution *A* (the solid lines) and in air (the dashed lines) at different strain rates (given at the curves in mm/min).

curve obtained for the same steel tested in air. Table 3 presents the strength and plasticity characteristics of steel 34KhMA.

The tests in solution *A* saturated with hydrogen sulfide have shown that the strain rate affects substantially the mechanical properties of steel 34KhMA. If we treat the maximum stress and strain of the sample tested in air as a unity, the decrease in the strain rate from about 8.53×10^{-5} sec^{-1} to about 8.53×10^{-7} sec^{-1} in the test in solution *A* lowers the ratio of the breaking stress n_σ from 0.97 to 0.54, and the relative strain n_ε responsible for the cracking from 0.71 to 0.19. Further decrease in the strain rate from about 10^{-7} sec^{-1} to about 10^{-8} sec^{-1} virtually does not affect the fracture characteristics of the steel. Similar behavior of ship building steels tested in seawater has been observed in [13].

To estimate the susceptibility of steels of different strengths to corrosion cracking in environments containing H_2S or CO_2 tested at slow strain rates, we should choose criteria for ranking the steels with respect to their resistance to SSC and SCC respectively. For this purpose, we tested the

TABLE 3. Mechanical Properties of Steel 34KhMA at 20°C Tested in Air and in Solution *A* at Different Strain Rates

Medium	v_s, sec^{-1}	σ_{max}, MPa	n_σ	ε, %	n_ε
Air	$8.53 \cdot 10^{-7}$	1040	1	21	1.00
A	8.53×10^{-5}	1010	0.97	15	0.71
A	8.53×10^{-6}	990	0.95	6	0.29
A	8.53×10^{-7}	560	0.54	4	0.19
A	8.53×10^{-8}	550	0.53	4	0.19

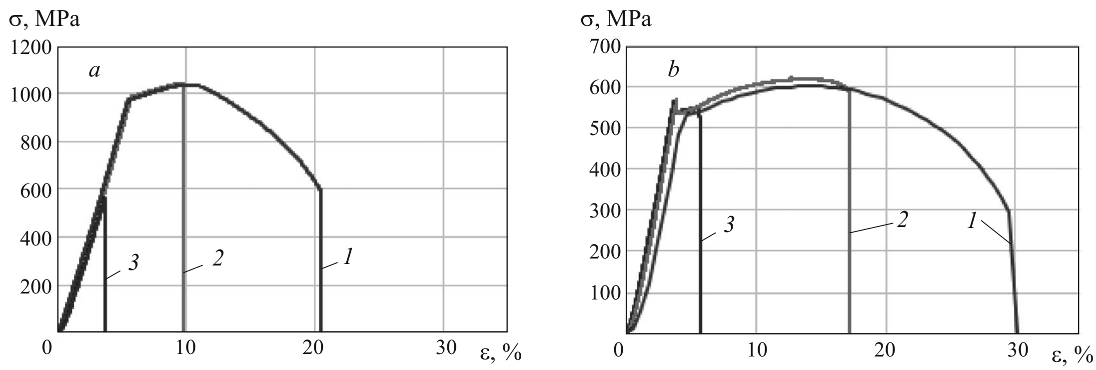
Notations: v_s) strain rate; σ_{max}) maximum stress in the test; ε) relative strain; n_σ and n_ε) ratio of the values of σ_{max} and ε obtained in testing in medium *A* and in air.

pipe steels 34KhMA, 495 and 09G2S with yield stress 990, 540 and 284 MPa, respectively (Table 2). The corrosive medium was a 5% solution of NaCl with pH = 2.8 (solution *A*) saturated with H_2S or CO_2 at room temperature. The study was performed at a strain rate of 8.53×10^{-7} sec^{-1} (0.0013 mm/min). Figure 3 presents the stress–strain diagrams of the steels tested in this medium and in air (for comparison). Table 4 presents the main characteristics of the strength and ductility of the steels.

The steels susceptible to CC in a hydrogen sulfide environment fracture at a stress below the yield strength obtained in the air tests (Tables 2 and 4). For these materials the criterion for estimating the susceptibility to CC may be the ratio of the maximum stresses (0.6) or strains at failure (0.2) obtained in the tests in the corrosive medium and in air.

Figure 4 presents the results of the study of the effect of the temperature of the corrosive medium on the failure stress and the relative strain in the tests of steels 34KhMA, 485, and 09G2S at a strain rate equal to 8.53×10^{-7} sec^{-1} in the environments of hydrogen sulfide and carbon dioxide at 20, 40, 60 and 80°C.

The results of the tests show that elevation of the temperature of the solution causes growth of the failure stress in the medium of hydrogen sulfide for steel 34KhMA (Fig. 4*a*) due to lowering of its concentration in the solution. Lowering of the concentration of hydrogen sulfide reduces the corrosion activity of the solution and this prevents appearance of local surface defects provoking crack nucleation. When the temperature is increased to 80°C, the sample fails at a stress virtually twice higher than at room temperature. When the temperature of the solution used for testing steel 34KhMA in the presence of carbon dioxide is increased (Fig. 4*b*), the negative effect of the corrosion-active substances is reduced,



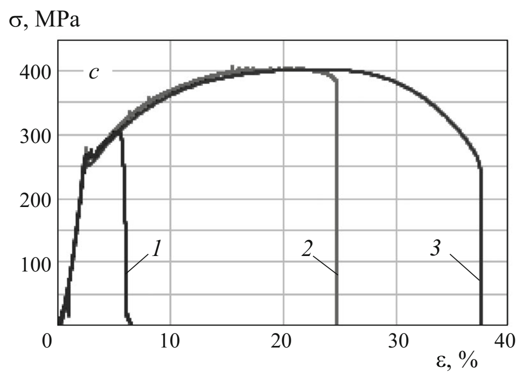


Fig. 3. Stress-strain ($\sigma - \varepsilon$) curves of steels 34KhMA (*a*), 485 (*b*) and 09G2S (*c*) tested at slow strain rates at room temperature: *1*) in air; *2*, *3*) in environments saturated with CO_2 and H_2S, respectively.

especially at 60 and 80°C. At all the test temperatures, steel 34KhMA failed at a stress exceeding the yield one. Under these conditions, the difference on the failure stresses is not considerable, and it is expedient to take the relative plastic strain at failure as a criterion of the susceptibility of the steel to corrosion cracking in carbon dioxide at elevated temperatures of the medium.

Steel 485 failed at room temperature at a stress exceeding the yield one. Failure of steel 485 in the hydrogen sulfide medium at room temperature (Fig. 4*c*) requires a 2% relative strain. The results obtained in the tests of this steel at 40 and 60°C are virtually similar, i.e., the samples failed at a relative strain of 4%. A maximum relative strain of 10% at failure occurred at 80°C. The behavior of the stress–strain curve with growth of the test temperature of steel 485 in the carbon dioxide medium was similar to that in the medium of hydrogen sulfide (Fig. 4*c*). However, the relative strain in this case was 12 – 22% depending on the temperature of the medium. Consequently, with growth of the solution temperature we observed a tendency to growth of the strain preceding failure of the sample both for the hydrogen sulfide medium and for the carbon dioxide medium, i.e., the susceptibility of the steel to cracking in H_2S and CO_2 decreased. The lowering of the susceptibility of the steel to cracking was especially noticeable in the range of 60 – 80°C, which is explainable by substantial decrease in the solubility of hydrogen sulfide and carbon dioxide.

The results of the tests of steel 09G2S show that elevation of the temperature of the medium with hydrogen sulfide has virtually no effect of the fracture characteristics (Fig. 4*d*). The steel fails at a relative strain of 4%. In the medium with carbon dioxide the samples of steel 09G2S fail at 20 and 40°C at a relative strain of 25%; at 60 and 80°C the figure is 33%. Consequently, the susceptibility of steel 09G2S to cracking at elevated temperatures may also be assessed in terms of the relative strain, because it fractures at a stress exceeding the yield point.

TABLE 4. Characteristics of Failure (σ_f and ε_f) of the Steels Obtained in Tensile Tests in Different Media

Steel	Medium	σ_f, MPa	n_σ	ε_f, %	n_ε
34KhMA	H_2S	560/1040	0.54	4/21	0.19
	CO_2	1040/1040	1.00	10/21	0.48
485	H_2S	560/600	0.93	6/30	0.20
	CO_2	630/600	1.05	17/30	0.57
09G2S	H_2S	300/400	0.75	6/38	0.16
	CO_2	400/400	1.00	25/38	0.66

Notations: n_σ and n_ε) ratio of the values of σ_f and ε_f obtained in air tests and in medium *A*.

Notes. 1. The numerators present the values obtained in the air tests; the denominators present those obtained in solution *A* saturated with H_2S or CO_2.
2. The tensile tests were conducted at 20°C at strain rate 8.53×10^{-7} sec^{-1}.

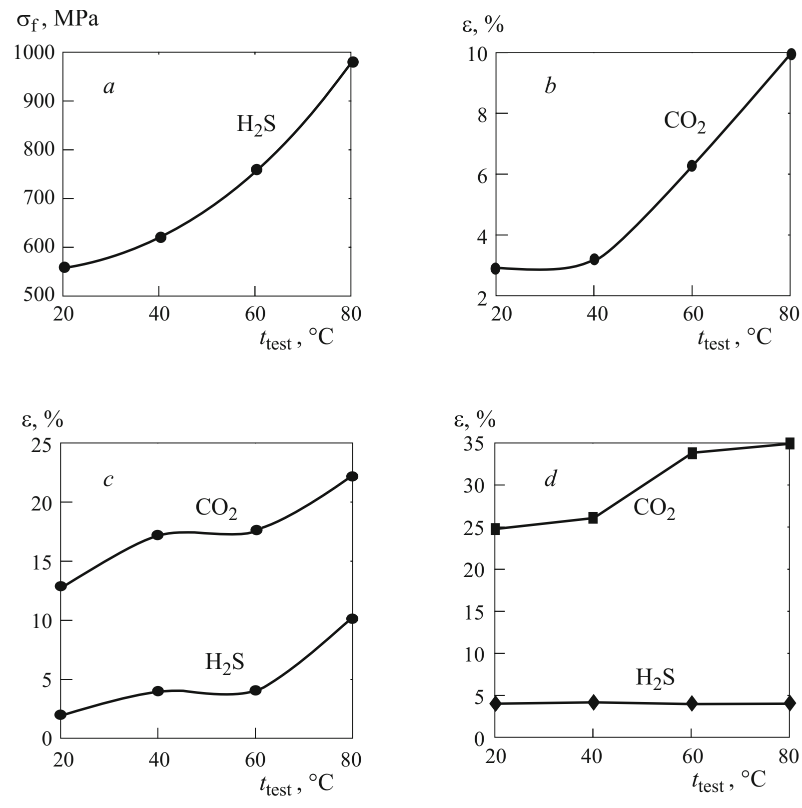


Fig. 4. Dependences of the failure stress σ_f (*a*) and relative strain ε (*b* – *d*) on the temperature ttest of testing of steels 34KhMA (*a*, *b*), 485 (*c*) and 09G2S (*d*) for corrosion cracking at strain rate 8.53×10^{-7} sec^{-1} in solution *A* saturated with H_2S (*a*, *c*, *d*) and CO_2 (*b* – *d*).

The metallographic analysis of the samples tested in the medium with hydrogen sulfide shows a tendency to lowering of the growth of cracks and decrease in their number with increase of the test temperature of all the steels studied (Fig. 5).

The results obtained allow us to conclude that a reliable criterion for assessing the susceptibility of steel 34KhMA to CC in accelerated tests at a slow strain rate in an environment with hydrogen sulfide is the failure stress, which grows with the temperature. In the medium with carbon dioxide, the criterion for assessing the susceptibility of this steel to cracking is the relative strain, which increases abruptly at 60 and 80°C.

For steel 495 the criterion for estimating the susceptibility to CC in the environment of hydrogen sulfide and carbon dioxide is the relative strain, because in both cases the metal fails at a stress exceeding the yield point. Both at 20°C and at 80°C the samples fail in the region of lumped strain.

Steel 09G2S is the least susceptible to corrosion cracking in the medium of hydrogen sulfide under the effect of the temperature as compared to steels 34KhMa and 485. In the medium with carbon dioxide the steel fails in the range of lumped strain independently of the temperature; at 60 and 80°C the failure strain is higher than at 20 and 40°C by 10%.

CONCLUSIONS

The results of the study of the effect of the temperature and of the rate of deformation on the fracture behavior of steels 34KhMA (P110), DNV SAWL 485FD and 09G2S under slow strain rate testing (8.53×10^{-5} – 8.53×10^{-8} sec^{-1}) in corrosion-active environments containing hydrogen sulfide or carbon dioxide allow us to determine the criteria for estimating the susceptibility of the steels to corrosion cracking under accelerated tensile tests. It has been shown that the choice of such criteria depends on a set of parameters including the strength characteristics of the material at room temperature, the composition and the temperature of the environment. For high-strength steels of type 34KhMA the criterion for estimating the susceptibility to corrosion cracking (CC) in the medium with hydrogen sulfide is the failure stress. For steels with a medium (485) and low (09G2S) strength such a criterion is the value of the relative strain at failure. In the medium saturated with hydrogen sulfide the susceptibility of all the steels to CC is determined in terms of the maximum relative strain.

Elevation of the temperature of the medium affects the maximum stress and the relative failure strain of the steels differently. In steel 34KhMA at 80°C in the environments containing hydrogen sulfide or carbon dioxide, failure occurs in the region of lumped plastic strain. Consequently, the steel is not susceptible to corrosion cracking at elevated temperatures in contrast to the tests at room temperature. For steel 485 the temperature of the medium does not virtually affect the susceptibility to corrosion cracking, because this grade remains stable in the environments bearing hydrogen sulfide and carbon dioxide. Elevation of the temperature of the environment changes the fracture behavior of steel 09G2S insubstantially in the presence of hydrogen sulfide, while in the

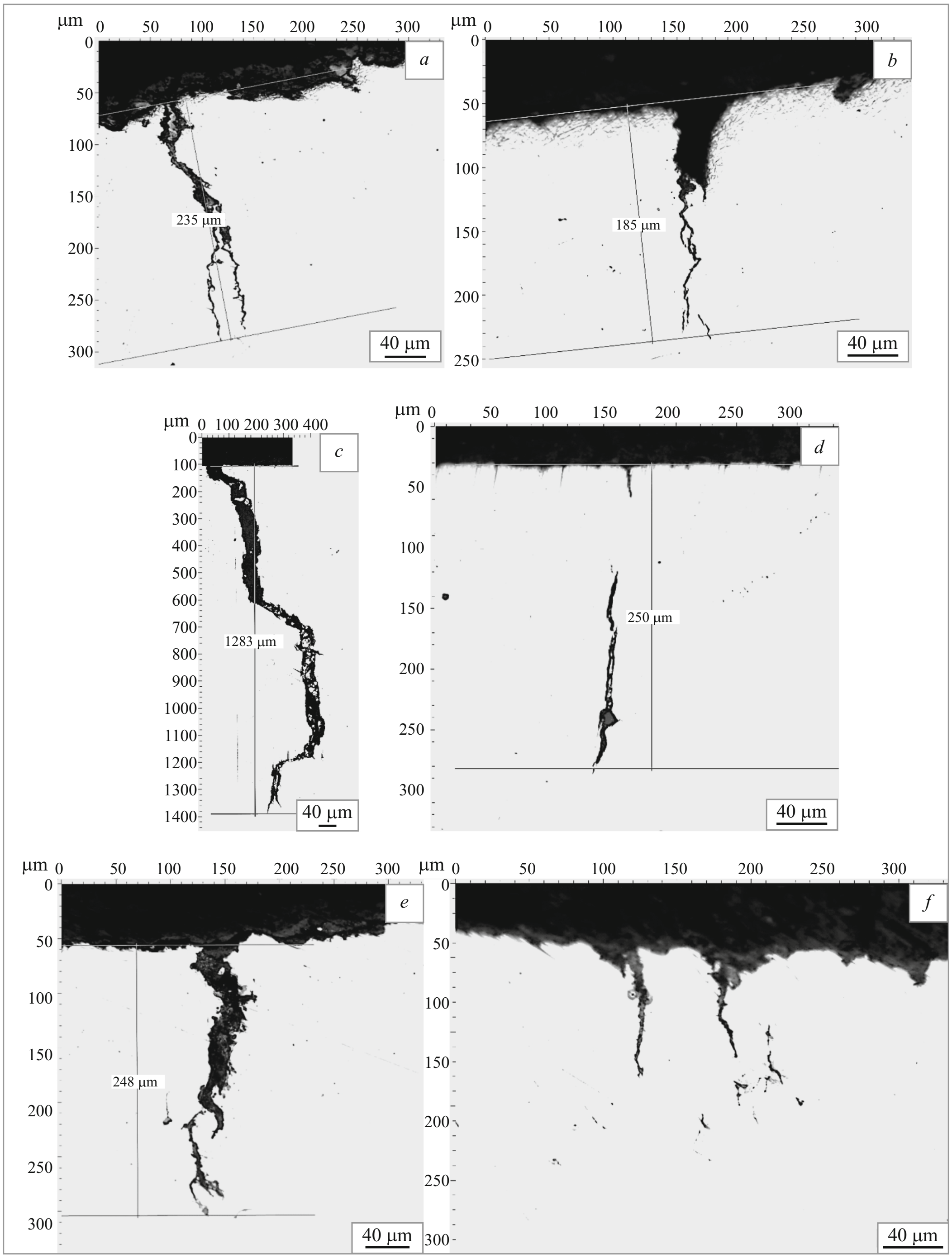


Fig. 5. Cracks in the structure of steels 34KhMA (*a*, *b*), 485 (*c*, *d*) and 09G2S (*d*, *f*) formed in testing for corrosion cracking in a medium saturated with H_2S at strain rate 8.53×10^{-7} sec^{-1} at a temperature of: *a*, *c*, *d*) 20°C; *b*, *d*, *f*) 80°C.

presence of carbon dioxide the temperature influences the fracture behavior of the steel like that of steel 485.

Thus, we can recommend the value of the failure stress as a criterion for assessing the susceptibility of high-strength steel 34KhMa (P110) to corrosion cracking. For steels DNV SAWL 485FD and 09G2S with medium and low strength, respectively, we can recommend for this purpose the value of the relative strain at failure obtained in accelerated tensile tests with a slow strain rate in corrosive environments.

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