EVALUATION OF THE EFFECT OF GEOTHERMAL ENVIRONMENT ON CORROSION FRACTURE OF TITANIUM ALLOY AND STEEL

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The corrosion fatigue and electrochemical behavior of 15Kh11MF martensitic-ferritic steel (Wt%: 0.15 C; 11.25 Cr; 0.41 Ni; 0.72 Mo; 0.36 Si; 0.32 Mn) and TS-5 titanum pseudo-α-alloy of the system Ti-5Al-3Sn-2V-3Zn in a model for geothermal environment with and without a mixture of hydrogen sulfide and carbon dioxide has been evaluated.

It was shown that sinegrism of impact of mineralized environment and dissolved gases causes the decrease of fatigue limit of TS-5 alloy specimens by more than 20%. For 15Kh11MF steel the resistance to the corrosion fatigue fracture drastically decreases.

Specific features of corrosion processes of titanium alloy and steel in geothermal environment model at 20°C and 90°C have been established by electrochemical potentiodynamic investigations.

INTRODUCTION

Service operation of plants is defined, first of all, by corrosivity of the service geothermal heat-transfer medium, which is caused by the presence of hydrogen sulphide and carbon dioxide in water and steam (1,2). Since, the majority of accidents at geothermal power plants is conditioned by failure of turbine parts, and in particular, of the working blades and pipe systems of heat-exchange equipment (2), the reliability of geothermal power units can be improved by an employment of new structural materials (3,4) and development of the effective anticorosive-errosive methods (5).

Stainless steels and titanium alloys are widely used in chemical industry, power engineering and machine building. These materials, titanium alloys especially, used for highly loaded blades of turbines are very prospective in production of geothermal plant equipment. The effect of a very aggressive and highly mineralized environment, saturated with hydrogen sulphide and carbon dioxide, on fatigue fracture resistance of these material has been studied inadequately.

This paper presents the researches of the effect of a model of geothermal water (MGW) at room and elevated (90°C) temperatures on corrosion fatigue and electrochemical characteristics of the specimens made from the stainless martensitic-ferritic steel and one of the widely used titanium alloys.

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MATERIALS AND EXPERIMENTAL PROCEDURE

TS-5 Titanium pseudo-α-alloy and 15Kh11MF martensitic-ferritic steel (Table1) have been investigated. They were heat-treated according to the conditions in Table 2.

TABLE 1 - Chemical composition of the materials (weight %)

Material	C	Cr	Mo	Ni	Mn	Si	V	P	S
15Kh11MF steel	0.15	11.25	0.72	0.41	0.32	0.36	0.32	0.025	0.012
Material	AL	Sn	V	Zn	C	N_2	Si	Fe	O_2
TS-5 alloy	5.33	3.15	1.95	2.06	0.03	0.05	0.04	0.04	0.13

TABLE 2 - Mechanical properties of the materials.

Material	Heat treatment conditions	$\sigma_{ys,}$ MPa	$\sigma_{uts,}$ MPa	δ,%	Ψ,%
15Kh11MF steel	Hardening ,1000°C, 1 hour in oil; tempering , 680°C ,4 hours	750	890	18	64
TS-5 alloy	Annealing, 880°C , 2 hours;	745	872	6.7	25

Metallographic studies showed that the structure of TS-5 titanium alloy is lamellar as concerns the form of the particles of the primary α-phase, which is typical of deformed alloys; at the same time, the metal of the forging had a coarse-grain structure with equiaxed β-grains, The internal volume of the β-grains is dissected by the α-particles that are grouped into packets [α-colonies].The α-particles are lamellar in shape; the mean diameter of a β-grain is 400 -800 μm, and the average linear dimension of the α-colonies is greater than 100 μm.

The structure of heat-treated 15Kh11MF steel is a high-tempered martensite with a uniformly distributed numerous inclusions of σ-ferrite.

Fatigue pure bending tests have been carried out at the frequency of machine rotation of 50 Hz. Test base was 5 x 10^7 cycles. Smooth cylindrical specimens 5 mm in diameter with a fivefold length of its working part were used for tests. The influence of stress concentration was studied on the specimens with V-shaped annular grove and concentration factor α_σ=1.99. The section of working part of the specimen was measured with an accuracy no poorer than 0.01 mm. The total error in loading during fatigue tests of the specimen did not exceed ± 3% of the measurement.

Tests of the corrosion fatigue of the materials under study were carried out in a model of the medium at the Mutnovsk (Kamchatka peninsula, Russia) geothermal deposit (containing 805 mg/l of Na_2SO_4 x 10 H_2O; 30 mg/l of KCl; 25 mg/l of $CaCl_2$; 85 mg/l of $NaHCO_3$; 5 mg/l of $MgCl_2$ x $6H_2O$, and 9000 mg/l NaCl) with and without a mixture of hydrogen sulphide and carbon dioxide in a ratio of 1:3 by volume. This enabled separate appraisals to be made of the influence of the cation-anion composition of the medium on the fatigue of the materials under the study and of the synergism of its impact on the dissolved hydrogen sulphide, carbon dioxide.

Potentiodynamic (the scanning speed of the potential was 2mV/s) and kinetic investigation of corrosion process were carried out in the above mentioned environments at 20°C and (90 ± 2)°C. The electrode potentials there were reduced to the normal hydrogen scale.

RESULTS AND DISCUSSION

The results of the fatigue tests of smooth specimens and specimens with stress a concentrator, which were made from TS-5 titanium alloy and 15KhMF steel are presented in Table 3, which shows the influence of the geothermal environment on fatigue limit of the materials under study, and also in Fig.1 and 2.

TABLE 3 - Fatigue limit of 15Kh11MF steel and TS-5 alloy vs. specimen type and composition of geothermal environment.

Material	Air		Geothermal water model		Geothermal water model + ($H_2S + CO_2$)	
Smooth specimens	σ_{-1}	$\sigma_{-1} / \sigma_{uts}$	σ_{-1}^{cor}	$\sigma_{-1}^{cor} / \sigma_{uts}$	σ_{-1}^{cor}	$\sigma_{-1}^{cor} / \sigma_{uts}$
15Kh11MF steel	390	0,44	90	0,10	unnoticed	-
TS-5 alloy	280	0,32	250	0,29	220	0,25
Notched specimens	σ_{-1k}	$\sigma_{-1k} / \sigma_{uts}$	σ_{-1k}^{cor}	$\sigma_{-1k}^{cor} / \sigma_{uts}$	σ_{-1k}^{cor}	$\sigma_{-1k}^{cor} / \sigma_{uts}$
15KH11MF steel	170	0,19	40	0,04	unnoticed	-
TS-5 alloy	230	0,26	200	0,23	180	0,21

The obtained data show that joint action of the hydrogen sulphide and carbon dioxide in MGW resulted in a further decrease of the fatigue limit (σ_{-1}^{cor}) of smooth specimens (Fig.1) as well as the fatigue limit (σ_{-1k}^{cor}) for notched TS-5 alloy specimens (Table.3) by 12 and 10%,respectively ,as compared with the results of tests conducted in geothermal medium without hydrogen sulphide and by 22% as compared with tests conducted in air.

Tests of 15Kh11MF steel in MGW without hydrogen sulphide revealed that tentative fatigue limit exists for smooth specimens (Fig.2) , as well, as for specimens with a stress concentrator .The tentative fatigue limit for smooth specimens amounts to 90 MPa This is evidence of a great drop (by 77%), as compared to air tests, in the fatigue limit caused by corrosive environment. The same reduction of corrosion fatigue limit is typical of the specimens with a stress concentrator (see Table.3)

An investigation of smooth specimens (Fig.2), as well, as of 15Kh11MF steel specimens with a concentrator, in MGW with hydrogen sulphide showed that the limit of corrosion fatigue of the steel changes considerably due to the action of this hydrogen-containing medium. A drastic reduction in the endurance is observed after of more than 80% reduction of the applied stresses level. Such a reduction of serviceability of steel in

MGW can be also observed due to additional presence of oxygen in it. The negative effect of oxygen on the chromium steel fatigue was revealed by Suhr [6].

To evaluate the process on the surface of the materials under study, and to find the probability of surface microdefects initiation and propagation, the electrochemical potentiodynamic tests of specimens in environments were conducted.

At 20°C, without hydrogen sulphide, the steel corrodes with mixed oxygen - hydrogen polarization; oxygen polarization here is predominant (Fig.3, curve 1′). The cathodic branch is similar to that for the limiting diffusion current. The corrosion potential (φ_{cor}= - 0.225 V) for the steel is established in the region of pseudopassivity, the small corrosion current and ,therefore, a small rate of continuous corrosion is probably due to the formation of chemisorbed oxygen-bearing surface layers.

When the solution at room temperature is saturated with hydrogen sulphide, the conjugate process of anodic dissolution of the steel and cathodic liberation of hydrogen are sharply intensified (curves 3 and 3′). The corrosion current increases by almost an order of magnitude. Corrosion of the steel proceeds predominantly with hydrogen polarization , because the pH of the model medium, saturated with H_2S, drops from 6.1 to 4.0, and the concentration of the dissolved oxygen sharply falls. The steel corrosion potential (φ_{cor} = -0.365V) in this solution is established in the cathodic region.

An increase of the solution temperature to 90°C changes the run of the polarization curve : the anodic branch moves in the direction of negative potentials, while the section corresponding to the limiting diffusion current for oxygen disappears in the cathodic branch (Fig.3, curves 2 and 2′). The positive shift of the corrosion potential (φ_{cor} = -0.165V) is evidence that the anodic process of oxidation of the metal takes place more easily at higher temperatures of the solution and that the influence of oxidation on the corrosion current is predominant.

Introducing hydrogen sulphide into the solution at given temperature conditions (curves 4 and 4′) changes the form of the anodic polarization curve; a peak of active dissolution, as well, as narrow section of passivation of tens of millivolts, appears. The steel corrosion potential in this solution is established in the region of potentials for incipience of repassivation.

The polarization curves plotted for TS-5 alloy in MGW at temperature of 20 and 90°C virtually do not differ in nature (Fig.4, curves 1, 1′ and 2, 2′). However, the limiting anodic diffusion current that features the inclination of the alloy to passivation in a hot solution is somewhat smaller than in solution at 20°C. This is evidence that the given alloy is more susceptible to passivation at higher temperatures.

Saturation of the solution with hydrogen sulphide changes the form of the anodic, as well, as the cathodic , branch of the polarization curve (Fig.4, curves 3, 3′ and 4, 4′). Small peaks of anodic dissolution appear in the anodic curves, and the capability for passivation is greatly reduced. However, when the temperature of the solution, containing hydrogen sulphide, rises to 90°C, the passive film does not break down for potentials up to 2.0 V (Fig.4,curve 4). The kinetic dependence of the electrode potential of the titanium alloy in all the cases that were studied attest to the fact that anode control is predominant in corrosion phenomena.

The evaluation of the serviceability of materials contributed to production of the geothermal power systems and stations with titanium heatexchanges, having a heat rating of 20 MW, and separators at the Kaluga turbine works (Russia).

CONCLUSION

The following can be concluded from the obtained results :
- the geothermal medium without hydrogen sulphide reduces the fatigue limit of 15Kh11MF steel (depending on specimen type) by 76 - 77% and that of TS-5 titanium alloy by 11 - 13%;
- synergism of impact of the model for geothermal medium with dissolved hydrogen sulphide and carbon dioxide results in irretrievable drop in fatigue durability of 15Kh11MF steel; the fatigue limit of TS-5 titanium alloy under the same conditions decreases by 22%;
- volatile components significantly increase the cathodic and anodic processes of 15Kh11MF steel; stimulate the growth of the 15Kh11MF steel corrosion rate by an order of magnitude; intensify hydrogenation;
- hydrogen sulphide does not influence the run of the anodic polarization curves for TS-5 alloys in the geothermal medium; moreover , the susceptibility to passivation of the alloy increases as the temperature rises, the passivation area grows to 2.0 V.

SYMBOLS USED

σ_{ys} = yield stress (MPa)

σ_{uts} = ultimated tensile strength (MPa)

δ = elongation (%)

Ψ = reduction of cross-section area (%)

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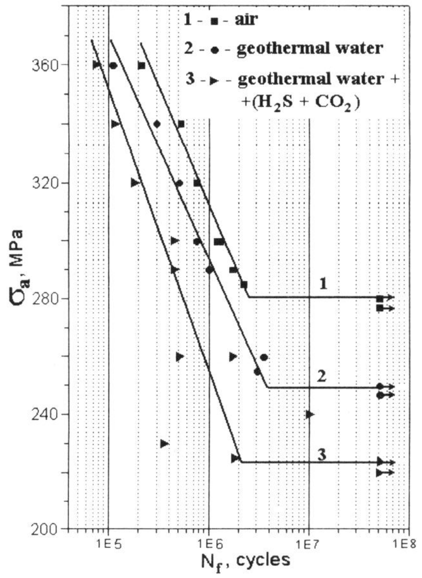

Figure 1 Fatigue endurance (S-N curves) for smooth TS-5 alloy specimens

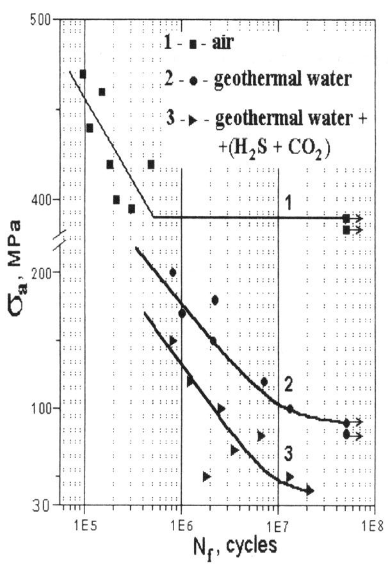

Figure 2 Fatigue endurance (S-N curves) for smooth 15Kh11MF steel specimens

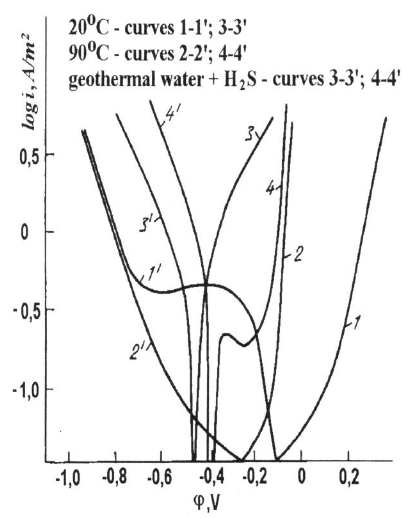

Figure 3 Potentiodynamic polarization curves for 15Kh11MF steel

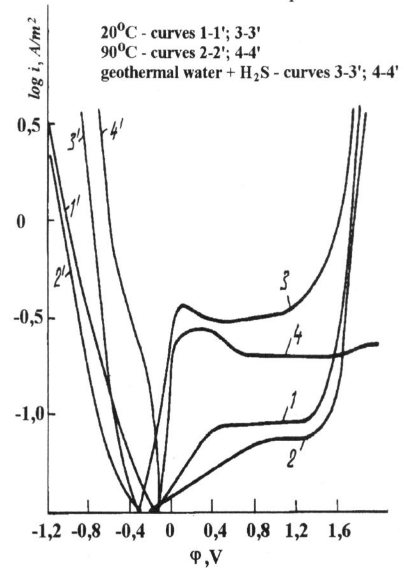

Figure 4 Potentiodynamic polarization curves for TS-5 alloy