INHIBITION EFFECT ON RESISTANCE OF LOW-ALLOYED STEEL TO CORROSION FATIGUE IN NEUTRAL ENVIRONMENTS

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Inhibiting effect of new compounds (aminoderivatives of molybdenum and ferrocyanides) on the 40Kh steel in 3% NaCl solution in conditions of corrosion and corrosion fatigue is investigated. Is shown that the protective effect of the compounds is provided by passivation of the steel surface with a complex anion and adsorption of an organic cation on nonpassivated areas.

INTRODUCTION

There is a general opinion that the resistance of metals to corrosion fatigue is determined by its corrosion resistance in a greater degree than by the mechanical strength. It should be expected that the inhibitors, which are efficient against corrosion, will render protective action also in the conditions of corrosion fatigue. The investigations of inhibition influence on corrosion fatigue of steels concern mainly acidic media. In particular, it was found by Babei and Maksymyshyn (1) that the HOSP-10 inhibitor in a concentration of 6 g/l protects the 40Kh steel from low-cycle corrosion fatigue in sulphuric and hydrochloric acids at all mechanical stress levels. Positive effect on the corrosion fatigue resistance in neutral media is produced by sodium dichromate, hexametaphosphate, and silicate; (Balezin et al (2)), but so essential effects as in acidic environments were not observed. In this connection, several groups of compounds of transitive metals with organic cations, which are coordination compounds or polymolecular salts (Babei et al (3)) were developed: aminoderivatives of tetracyanemolybdate, trimolybdate, octamolybdate; hexacyanoferrates of ortoaminephenol and 2-aminopyridine.

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MATERIAL AND METHODS

The tests were conducted on the 40Kh steel (0,39%C, 0,21%Si, 0,59%Mn, 0,91%Cr, 0,15%Ni, 0,13 Cu) quenched in oil and tempered at 200 °C. Corrosive medium was 3% NaCl water solution. Corrosion fatigue test were performed on: a) high-cycle fatigue at constant load of frequency 50 Hz and pure bending with rotation of cylindrical specimens of a diameter 19 mm (test base was $5x10^7$ cycles); b) low-cycle fatigue at constant deformation of frequency 0,83 Hz and symmetric bending of flat 460x10x1.5 mm specimens.

EXPERIMENTAL RESULTS AND DISCUSSION

Molybdenum Aminoderivatives

The received results testify to achievement of almost full protection at a concentration of the substances of $5x10^{-4}$ mole (Table 1). The corrosion potential became more positive and the differential capacity decreased (Table 2) at the presence of inhibitors. This indicates the chemisorption mechanism of protective action up to formation of phase layers (two maximums on Fig. 1).

TABLE 1 - Dependence of the corrosion rate and the 40Kh steel protection degree on molybdenum aminoderivative concentration

Compound	Concentration, mole/l	K, g/m^2 h	Z, %
3% NaCl	-	0.218	-
$Am_2Mo_3O_{10}$	10^{-4}	0.048	82
	$5\ 10^{-4}$	0.018	93
	10^{-3}	0.010	95
$Am_4[Mo(CN)_8]\ 3H_2O$	10^{-4}	0.030	86
	$5\ 10^{-4}$	0.030	86
	10^{-3}	0.015	93
$K_4[Mo(CN)_4Am]$	10^{-4}	0.065	70
	$5\ 10^{-4}$	0.018	91
	10^{-3}	0.008	96

The lifetime of the specimens in the 3% NaCl solution at the presence of these substances is increased at all stress levels (Fig. 3a). The conventional fatigue limit becomes three times higher. However, the predicted critical concentration has appeared to be insufficient for full protection against corrosion fatigue fracture.

TABLE 2 - Electrochemical properties of the 40Kh steel in 3% NaCl solution with molybdenum aminoderivatives

Compound	-φ, mV	Minimum of C, μF/cm²	Δφ, mV
3% NaCl	560	48	400
$Am_2Mo_3O_{10}$	508	18	650
$Am_4[Mo(CN)_8]\ 3H_2O$	515	14	650
$K_4[Mo(CN)_4Am]$	480	8	800

The inhibitor $K_4[Mo(CN)_4Am]$ of 10^{-3} mole provides 90-93% protection effect against corrosion fatigue (Fig. 2). The reduction of inhibitor concentration to $5x10^{-4}$ mole decreases efficiency of protection by 30 %. The natural ageing of the inhibited solution has practically no effect on protective ability of the substance.

Ferrocyanide aminoderivatives

Efficiency of the investigated ferrocyanide aminoderivatives (Table 3) exceeds the known inhibitor $K_4[Fe(CN)_6]$. Essential shift of the corrosion potential to positive values and decrease of the differential capacity minimum is observed (Table 4).

TABLE 3 - Dependence of the corrosion rate and the 40Kh steel protection degree on ferrocyanide aminoderivative concentration

Compound	Concentration, mole/l	K, gm/m² h	Z, %
3% NaCl	-	0.218	-
$K_4[Fe(CN)_6]$	10^{-3}	0.057	74
$(C_6H_4OHNH_3)_4\ [Fe(CN)_6]$	$5\ 10^{-4}$ 10^{-3}	0.015 0.015	94 94
$(C_5H_4N_2H_3)_4\ [Fe(CN)_6]$	$5\ 10^{-4}$ 10^{-3}	0.030 0.018	86 93

The formation of protective passive films is confirmed by X-ray inspection results. The main product of the inhibitor interaction with the steel surface is $Fe_4[Fe(CN)_6]_3$, for which the lattice spacing (d = 1,041nm) is higher than in pure salts (d= 1,015nm) that is caused by the effect of the organic cation.

TABLE 4 - Electrochemical properties of the 40Kh steel in 3% NaCl solution with ferrocyanide aminoderivatives.

Compound	-φ, mV	Minimum of C, μF/cm^2	Δφ, mV
3% NaCl	560	48	400
$K_4[Fe(CN)_6]$	500	20	580
$(C_6H_4OHNH_3)_4$ $[Fe(CN)_6]$	420	5	800
$(C_5H_4N_2H_3)_4$ $[Fe(CN)_6]$	450	10	670

The conventional corrosion fatigue limit (Fig. 3b) at the presence of 10^{-3} mole of $(C_5H_4OHNH_4)[Fe(CN)_6]$ increases by 2.7 times, and at the presence of $[C_5H_4N_2H_3]_4[Fe(CN)_6]$ - by 3.5 times. The observed effect is related to possibility of 2-aminepyridine effect on the hydrogenation process. In conditions of low-cycle corrosion fatigue (Fig. 4), the efficiency hexacyanoferrate 2-aminopyridine is so high, that the curve in corrosion environment becomes closer to the curve in air.

CONCLUSIONS

Aminoderivatives of molybdenum and ferrocyanides reduce by 14-28 times the corrosion rate of the 40Kh steel in the 3% NaCl solution and increases by 3-4 times the resistance to corrosion fatigue fracture. The mechanism of protective effect of these inhibitors consists in passivation of the steel by the complex anion with the subsequent adsorption of the organic cation on nonpassivated areas.

USED SYMBOLS

φ = Corrosion potential (mV)

Δφ = range of potentials of capacity minimum (mV)

C = differential capacity (μF/cm^2)

K = corrosion rate (g/m^2 h)

REFERENCES

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(3) Babei, Yu.I., Slobodian, Z.V., and Semenyshyn, D.I., Zashchita Metalov, Vol. , No. 4, 1983, pp. 617-620.

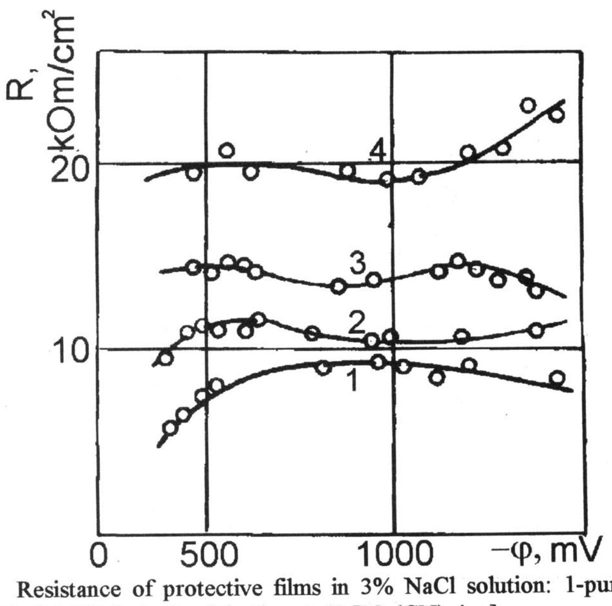

Figure 1 Resistance of protective films in 3% NaCl solution: 1-pure; with: 2- $Am_4[Mo(CN)_8]$ $3H_2O$; 3- $Am_2Mo_3O_{10}$; 4- $K_4[Mo(CN)_4Am]$.

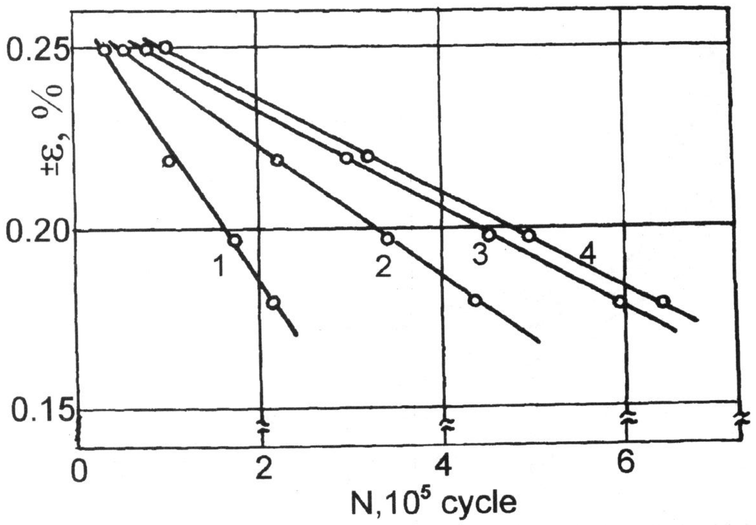

Figure 2 Low-cycle fatigue curves in pure 3% NaCl solution (1), with addition of $K_4[Mo(CN)_4Am]$ of concentration 5 10^{-4} mole (2), 10^{-3} mole (3); and in air (4).

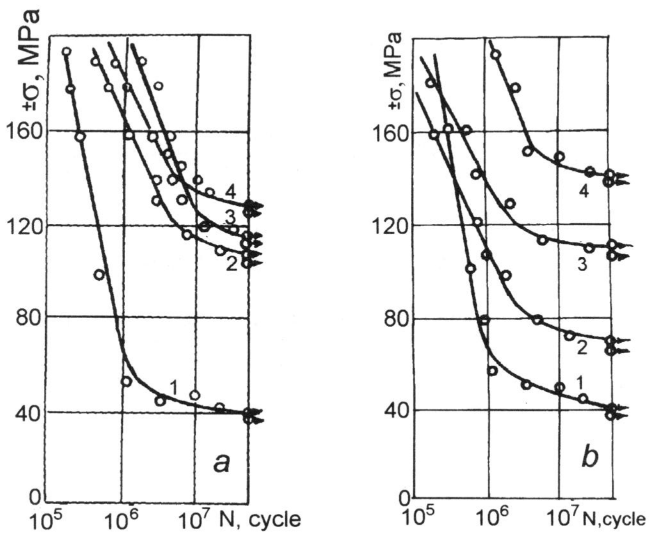

Figure 3 Corrosion fatigue curves in 3% NaCl: 1a,1b - pure and with: 2a - $Am_4[Mo(CN)_8]$ $3H_2O$; 3a- $Am_2Mo_3O_{10}$; 4a- $K_4[Mo(CN)_4Am]$; 2b - $K_4[Fe(CN)_6]$; 3b - $(C_6H_4OHNH_3)_4[Fe(CN)_6]$; 4b - $(C_5H_4N_2H_3)_4[Fe(CN)_6]$.

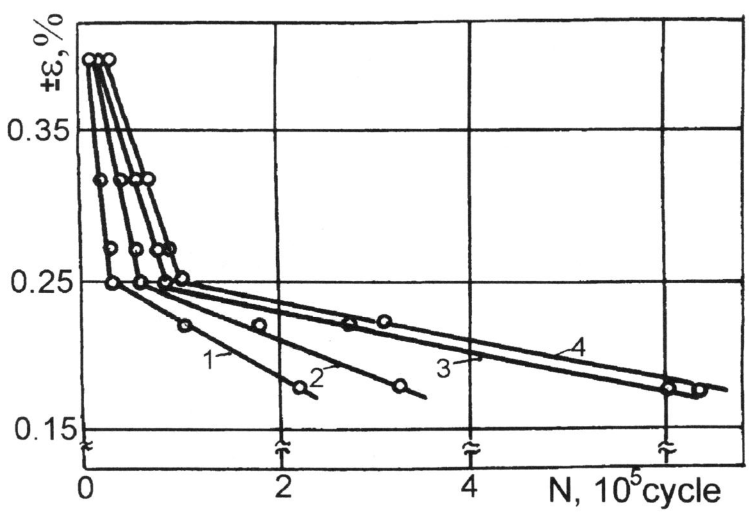

Figure 4 Low-cycle corrosion fatigue curves in 3% NaCl solution: 1- pure, 2 - with $K_4[Fe(CN)_6]$, 3 - with $(C_5H_4N_2H_3)_4[Fe(CN)_6]$; and 4 - in air.