The test results are reproduced in Fig. 1, where each experimental point represents an average value obtained for three simultaneously tested specimens. It will be seen that unclad duralumin specimens in superphosphate solutions corrode faster than clad test pieces. However, this difference in the corrosion rate decreases with decreasing concentration of the superphosphate solution (Fig. 2). It is also characteristic that in time the rates of corrosion of clad and unclad duralumin become practically the same (Fig. 3).

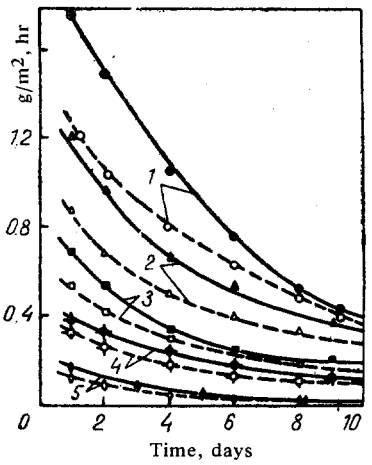

Fig. 3. Time dependence of the rate of corrosion of unclad (continuous curves) and clad (broken curves) duralumin D16AT in aqueous superphosphate solutions. (%): 1) 15; 2) 10; 3) 5.0; 4) 3.0; 5) 1.0.

The examination of the microstructure of corroded specimens showed that the corrosion of clad duralumin leads to a uniform dissolution of the cladding layer and to a reduction in its thickness. This is illustrated by data in Fig. 4 which shows that the thickness

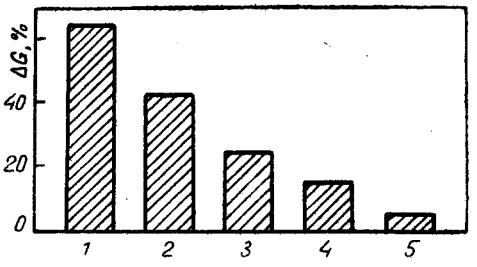

Fig. 4. Quantity of the cladding material ΔG corroded in 10 days in aqueous superphosphate solutions of the following concentrations (%): 1) 15; 2) 10; 3) 5.0; 4) 3.0; 5) 1.0.

of the cladding layer (which is equal to 4–5% of the thickness of the core material) was reduced by 64.5% after 10 days in a 15% superphosphate solution.

As shown in Fig. 2, the rate of corrosion of duralumin in aqueous superphosphate solutions depends on their concentration and ranges from 0.5–0.06 g/m²/hr in a 1.0% solution to 0.7–0.9 g/m²/hr in a 15% solution, (these are the average rates calculated for a 10 days' test). This means that in terms of the standard ten-grade scale of corrosion resistance (GOST 5272-50) both unclad and clad duralumin in the media studied must be regarded as materials with a "reduced" or "low" corrosion resistance (group IV and V on the standard scale).

REFERENCES

1. G. V. Akimov, Theory and Methods of Investigating Metal Corrosion [in Russian], Izd. AN SSSR, 1945.

2. G. V. Akimov, Foundations of the Science of Corrosion and Protection of Metals [in Russian], Metallurgizdat, 1946.

3. S. E. Pavlov, Corrosion of Clad Duralumin [in Russian], Oborongiz, 1940.

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KINETICS OF ANODIC AND CATHODIC REACTIONS OF DEFORMED STEEL IN ACID ELECTROLYTES

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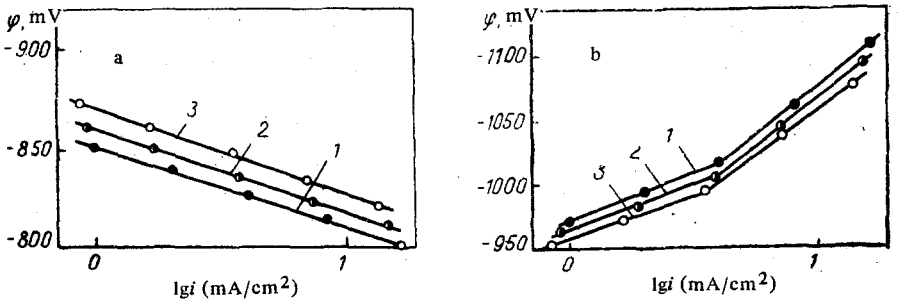
To elucidate the effect of plastic deformation on the kinetics of conjugate electrode reactions accompanying corrosion phenomena, we studied galvanostatic polarization curves obtained in 1.1 N H_2SO_4 solutions for steel St. 20 specimens (cylindrical gauge portion diameter = 4 mm) strained in tension in the electrolytic cell immediately before the measurements.

As shown by the polarization curves (see figure), plastic deformation facilitates both the anodic and cathodic

polarization. The acceleration of the anodic reaction is reflected in a parallel shift of the anodic polarization curve through a distance corresponding to the degree of "debasement" of the equilibrium or standard potential (φ_0 or φ^0, respectively) of the metal [1]. This law is universal and valid not only when the transfer coefficient of the anodic reaction $\alpha = 1$ [1], but also when $\alpha < 1$. In fact, in a general case the anodic current is related to potential φ and standard exchange current i^0 by the following equation:

$$i = i^0 C^{\alpha} \cdot \exp \frac{\alpha(\varphi - \varphi_0)}{b} = k \exp \frac{(\alpha - 1)\varphi^0}{b} \exp \frac{\alpha(\varphi - \varphi^0)}{b} = k \exp \frac{\alpha\varphi - \varphi^0}{b},$$

where k and b are constants and C denotes the ion concentration in the electrolyte. It follows from the above expression that when the standard potential is changed by $-\Delta\varphi^0$ as a result of plastic deformation, the initial point of the anodic curve corresponding to the value of the logarithm of the exchange current $\ln i_0$ (at an arbitrary constant level of C) is shifted to the right by a value $(1 - \alpha)\Delta\varphi^0/b$ (an increase in the exchange current), the entire curve being at the same time shifted upward by a value $\alpha\Delta\varphi^0$. As a final result, the position of the polarization curve will correspond to that produced by its parallel displacement upward by a value $\Delta\varphi^0$ (relative to its initial position) for all the points to the right of the new logarithm of the exchange current.



Kinetics of electrode reactions on steel St. 20 specimens in a 1.1 N H_2SO_4 at 20° C in relation to the elongation of the electrode (%): 1) 0; 2) 10; 3) 30. a) Anodic polarization; b) cathodic polarization. (The potential was measured with reference to a 2N mercury sulfate electrode).

The acceleration of the cathodic reaction is associated with the effect of plastic deformation on the overvoltage of hydrogen evolution which cannot be attributed either to an increase in the real surface area of the metal (due to deformation-induced increase in the surface roughness) or to a redistribution of the carbide phase by a mechanism involving the formation of "atmospheres" around dislocations [2]. The latter effect is impossible since strain aging requires time which is very much longer than the duration of the experiments which last 5-7 min.

The absence of any marked influence of the increase in the real surface area (due to increased roughness) on accelerated corrosion of plastically deformed metals was attributed in [3] to the fact that the increase in the real surface area at the maximum degree of deformation does not exceed 10%.

Experimental data [4] showing that the overvoltage of hydrogen evolution in a neutral electrolyte (i.e., from water molecules) is independent of the degree of deformation and surface roughness of steel electrodes makes it possible to conclude that the change in the surface area is insignificant and that the deformation of the electrode has no effect on the kinetics of the retarded discharge stage which determine the rate of the process during the evolution of hydrogen from water molecules (high overvoltage).

Consequently, in acid electrolytes, in which cathodic reactions are controlled by the retarded discharge stage and by the stage of recombination of adsorbed hydrogen atoms [5], the effect of deformation of the electrode should be manifested during the recombination stage which undoubtedly is influenced by the surface condition in the same way as in catalytic reactions.

The rate of recombination of hydrogen atoms is determined by the number of collisions between reacting atoms and by the activation energy which depends on the strength of bonds between adsorbed atoms and the metal surface. Plastic deformation, which produces surface heterogeneities, leads to nonuniform adsorption of hydrogen atoms which takes place preferentially at "active adsorption centers". Due to smaller distance between atoms in these localized adsorption regions there is an increase in the probability of collision between atoms, while a mutual reduction in the heat of adsorption [6] (strength of bond with the metal) of neighboring adsorbed atoms leads to a reduction in the activation energy for recombination. As a result, increasing the degree of deformation of steel in an acid electrolyte produces an increase in the recombination rate and a reduction in the hydrogen overvoltage.

REFERENCES

1. E. M. Gutman, FKhMM [Soviet Materials Science], nos. 4, 5, 1967.
2. A. Z. Foroulise and H. H. Uhlig, J. Electrochem. Soc., **111**, 522, 1964.
3. J. Talbot, Corros. et anticorros., **15**, no. 2, 43-48, 1967.
4. A. V. Ryabchenkov and M. G. Timerbulatov, Stress Corrosion of Metals and Methods of Protection [in Russian], TsNIITMAsh, vol. 31, Mashgiz, 1950.
5. N. D. Tomashov, N. M. Strukov, and L. P. Bershinina, Zashchita metallov, no. 5, 1967.
6. S. E. Roginskii, ZhFKh, no. 11, 1957.

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EFFECT OF THERMOVIBROMECHANICAL TREATMENT ON THE CORROSION AND STRESS-CORROSION RESISTANCE OF MEDIUM-CARBON STEELS

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The aim of this investigation was to study the effect of thermovibromechanical treatment (TVMT) [1], which is a modification of thermomechanical treatment and which produces a substantial increase in the strength characteristics of many structural steels and in the resistance of steel to corrosion and stress corrosion. A low-allow medium-carbon steel 35Kh (0.40% C, 0.30% Si, 0.50% Mn, 1.20% Cr) was chosen as the experimental material.

The mechanical properties of this steel are noticeably improved by TVMT [2]. And so, a value of UTS which is 20% higher than that of conventionally heat treated steel was recorded for specimens subjected to TVMT in the following way: heating to 840° C; cyclic straining at that temperature with n = 300 and $\Delta E = 0.035$, where n is the number of stress reversals in the elastoplastic range and ΔE is the relative elongation of the outer specimen layers in the direction of principal tensile stresses; cooling in oil to room temperature; tempering for 2 hr at 150° C. The ductility of steel after this treatment is practically the same as after the conventional heat treatment, and the hardness of specimen surface layers reaches HRC = 49-50. As a rule, steel in such a hardened condition is more sensitive to the influence of active media.

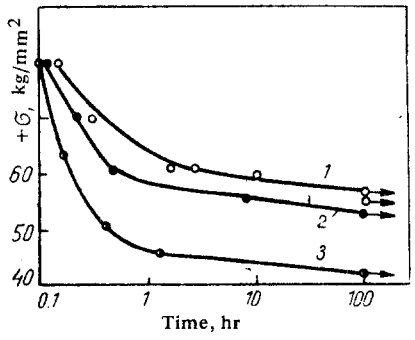

Fig. 1. Variation in the stress-corrosion resistance of steel 35Kh after: 1) conventional heat treatment; 2) TVMT with n = 300 and $\Delta E = 0.035$; 3) TVMT with n = 2500 and $\Delta E = 0.035$.

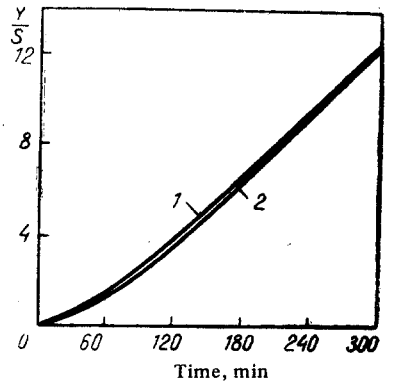

Fig. 2. Variation in the corrosion resistance of steel 35Kh after 1) conventional heat treatment and 2) TVMT.

During this investigation we studied the effect of the TVMT conditions on the stress-corrosion resistance of steel 35Kh and the corrosion resistance of the surface layers of specimens for which the largest increase in strength was obtained after TVMT. For comparison, identical tests were carried out on speciments subjected to a conventional heat treatment (oil quenching from 840° C followed by 2 hr tempering at 150° C).

The stress-corrosion tests were carried out in a 20% H_2SO_4 solution, on machines designed for long-time strength tests under uniaxial tensile loads. Carefully degreased specimens were placed in special devices and mounted in the shackles of the testing machine. After loading a specimen to a given level, an ebonite container of the specimen holding