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STUDY OF ANODIC PROCESSES IN THE CORROSION CRACKING OF METALS

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Corrosion cracking, being one type of corrosion destruction of metals, is characterized by the fact that in the process of destruction of metals, along with the corrosive action of the medium, the presence of mechanical tensile stresses plays a major role.

Of the numerous explanations previously proposed for the mechanism of corrosion cracking, the electrochemical theory has proved to be the most universal; it explains the process of corrosion cracking by a considerable increase in the anodic dissolution of the metal in a crack in a mechanically stressed metal. A clear interpretation of this theory was given in the works of foreign investigators —Mears, Brown, Dix [1] and Herouda [2]—and in our country by A. V. Ryabchenkov and co-workers [3,4]. Of great importance in the process of corrosion cracking of metals is also the effect, discovered by P. A. Rebinder and co-workers [5,6], of an adsorption-induced decrease in the strength of metals.

Thus, mechanical stresses, the electrochemical process of anodic dissolution of the metal, and the adsorption effect of reduced strength are the principal mutually complementary factors in the entire process of corrosion cracking of metals.

In the present work the electrochemical factors of corrosion cracking of a metal are considered. According to the electrochemical theory, the growth of a corrosion crack is due to a considerable facilitation of the anodic process in the crack. The basis for this hypothesis is the ennoblement of the electrode potential of the metal observed during loading and during the period of crack growth. However, there are no quantitative data in the literature indicating the degree to which the anodic process is facilitated during the growth of a corrosion crack. Since the time of crack growth is usually short, it is not possible to study the polarizability at various stages of corrosion-crack growth by the widely used method of recording polarization curves, in which a steady value of the potential at specified current densities is fixed.

In the present work, by means of automatic recording of the potential and pulsed polarization with a Π-shaped current waveform, together with precision measurement of the electrode potential at the tip of a growing crack, experimental material has been obtained that makes it possible to give a quantitative estimate of the degree of facilitation of the anodic process at any period of crack growth, from the moment of its initiation to complete destruction of the metal.

Fig. 1

Figure 1: Fig. 1

For the investigation an alloy of the MA2-1 type was selected, having the following chemical composition: Al 4.5%; Zn 1.1%; Mn 0.6%; Mg—the balance. The ultimate strength was 28.1 kg/mm^2, and the proportional limit 17.2 kg/mm^2. With sufficiently high corrosion resistance, this alloy exhibits a very high tendency toward corrosion cracking in many media. The experiments were carried out on flat specimens cut from sheet along the rolling direction. The cross section of the specimen in the working part was equal to 5×1 mm^2. In the process

of the experiment, the tensile mechanical stress was constant and amounted to 15 kg/mm^2 of the initial cross section of the specimen. Before being put to the test, the specimens were subjected to the following treatment. After mechanical polishing with No. 14 emery paper, the specimens were etched for 30 sec in a 20% NaOH solution at 90°, after which they were thoroughly washed in distilled water and placed in a desiccator for 48 h. Another batch of specimens, after mechanical polishing, was subjected to anodizing in a solution of 240 g/l NaOH at 80° for 30 min at $J_a = 1$ A/dm^2. After anodizing, the specimens were washed with distilled water and kept in a desiccator for 48 h. The potential was recorded automatically on the photographic film of a loop oscillograph equipped with an electronic amplifier with an input resistance of 10^{10} ohm ([7]). The potential in the crack was measured using a glass capillary with an internal diameter of 3–5 μ. The tip of the capillary, with the aid of a micromanipulator, was positioned directly (not more than 1–2 μ) above the crack tip and was continuously moved as it developed.

Fig. 1. Anodic polarization of alloy MA2-1 with a continuous increase in current at a rate of 0.1 mA/cm$^2 \cdot$ sec; **1**—without stress; **2**—during the development of a corrosion crack

Some information on the degree of polarizability of the alloy during crack development is provided by polarization curves obtained with a continuous and sufficiently rapid increase in the polarizing current (0.1 mA/cm$^2 \cdot$ sec) and automatic recording of the potential on the photographic film of an oscillograph. The results obtained for the air-oxidized alloy MA2-1 in a solution of 20 g/l K_2CrO_4 + 35 g/l NaCl are presented in Fig. 1. They show that in the absence of mechanical stresses (curve 1) the anodic polarizability of the alloy is rather high and, within the range of current densities up to 0.1 mA/cm^2, averages 5800 V $\cdot$ cm^2/A. Recording the anodic curve during crack development (curve 2) showed that the polarizability in the crack decreases sharply and, in the same range of current densities, does not exceed 450–500 V $\cdot$ cm^2/A. Thus, even this method makes it possible to note that the development of a corrosion crack is accompanied by a decrease in anodic polarizability in the crack by approximately a factor of 10 compared with the initial value. More complete quantitative in-

Fig. 2

Figure 2: Fig. 2

formation on the degree of decrease in the anodic polarization resistance at any moment from

Fig. 2. Potential drop (discharge) for alloy MA2-1 with time after switching off the external anodic current: **a**—surface oxidized in air; **b**—surface anodized. **1**—before application of stress to the specimen; **2, 3, 4, 5, 6, 7** correspond to times 10, 20, 40, 60, 80, and 100 sec from the beginning of crack development. The broken line below shows the form of the polarizing current.

from the beginning of the development of the corrosion crack to complete failure of the specimen are given by the results of pulse polarization.

Since any electrochemical cell is a system consisting of a capacitance C with a common resistance R connected in parallel, the rate of discharge (or charge) of such a system will be determined by the magnitudes of C and R. The drop in potential during discharge is associated with the occurrence of an electrochemical reaction, and, for a known value of C, it will be determined by the magnitude of the resistance R, which is the sum of the polarization (P) and ohmic (R_{ohm}) resistances, i.e. $R = P + R_{\text{ohm}}$. In solutions with good conductivity $R_{\text{ohm}} \ll R$, and, consequently, one may take $R \simeq P$. Thus, under anodic polarization the magnitude of the total resistance R is mainly the polarization resistance of the anodic process, denoted in the present case by P_a.

The potential drop ΔE_τ (V) over the time τ (sec) after switching off the external polarizing current i_0 (mA/cm^2) can be determined [8] from the equation:

$$\Delta E_\tau = b \cdot \ln\left(\frac{i_0 \tau}{bC} + 1\right),$$

where C is the electrode capacitance (F); b is the Tafel equation constant for the anodic process. From this equation, knowing i_0 and ΔE_τ (from the experimental discharge curves), one can determine the capacitance of the electrode under study at any stage in the development of the corrosion crack.

In Fig. 2, for alloy MA2-1 in a solution of 20 g/l K_2CrO_4 + 35 g/l NaCl, a series of discharge curves is presented for pulsed anodic polarization with a Π-shaped current; the limits of current variation are 0–0.5 mA/cm^2. The curves refer to different periods in the development of the crack. Curves 1a and 1b refer to the specimen before loading; curves 7a and 7b were recorded 1–2 sec before failure of the specimen. Analysis of the discharge curves in Fig. 2 shows that they obey sufficiently well the equation for the discharge of a capacitor C shunted by a resistance R:

$$E_\tau = E_0 \cdot e^{-\frac{\tau}{RC}},$$

where E_τ is the potential (V) after the time τ (sec) from the moment the current is opened; E_0 is the potential before the current is opened. In the case under consideration, the resistance R is the anodic polarization resistance P_a.

It is easy to show that when $\tau = P_a C$, $E_\tau = 0.63E_0$, i.e. it amounts to 63% of E_0. Further, by determining from the curve in Fig. 2 the magnitude of the change in potential during complete discharge, one can determine the product $P_a C$ (the time constant of the system, sec) as the time during which the system discharges by 63% relative to the initial state. Hence, knowing at each stage the value of $P_a C$ and C, one can determine P_a.

Fig. 3. Dependence of the anodic polarizability of alloy MA2-1 on the time of development of a corrosion crack: *a*—for material oxidized in air; *b*—for anodized material; 1, 2, 3 correspond to specimen working surface areas of 0.5; 0.05; 0.005 cm^2.

Figure labels: vertical axis, $\lg P_a$; horizontal axis, crack-development time, sec.

Figure labels (inset): vertical axis, $\lg P_a$; horizontal axis, crack-development time, sec.

In Fig. 3 the curves of the change in anodic polarizability at different stages in the development of a corrosion crack are presented for the alloy under study—

in MA2-1 in a solution of 20 g/l K_2CrO_4 + 35 g/l NaCl. They show that crack growth is associated with a significant decrease in the value of the anodic polarizability at the crack tip. In the case of very small initial working surfaces of the specimen (0.005 cm^2), when the internal surface of the crack walls is comparable with the total working surface, the anodic polarizability changes: for an air-oxidized surface from $6 \cdot 10^3$ V $\cdot$ cm^2/A to 15-20 V $\cdot$ cm^2/A; for an anodized one from 10^6 V $\cdot$ cm^2/A to 20-25 V $\cdot$ cm^2/A.

These results give grounds for asserting that the rapid development of a crack during stress-corrosion cracking is due to a very sharp drop in anodic polarizability (by up to 6 orders of magnitude) in the crack-growth zone. Other conditions being equal, as the initial working surface decreases, the drop in anodic polarizability during crack growth becomes more significant. As the initial working surface decreases, the anodic zone, while on average remaining unchanged in area, occupies a larger fraction relative to the entire working surface area and, consequently, the effect of the decrease in anodic polarizability (referred to the entire working surface) becomes more pronounced.

Visually (with the aid of a microscope) one can observe vigorous hydrogen evolution at 10-20 μ ahead of the visible crack tip. In these areas hydrogen is evolved in the form of alternating "fountains" emerging from beneath the oxide film of the metal. Hydrogen evolution along the sides of the visible crack tip is

insignificant. Along the sides of the crack, at a distance of 40–50 μ from the tip, hydrogen evolution almost does not occur.

The experimental material makes it possible to draw certain conclusions about the kinetics of stress-corrosion crack growth. The moment at which the crack appears is accompanied by a strong (stepwise) decrease in anodic polarizability. In subsequent periods the anodic polarizability decreases more slowly. This indicates that, in stress-corrosion cracking, the effective anode is not the whole crack but a comparatively small region concentrated at its tip. The slow decrease in anodic polarizability observed during crack growth indicates that, as the crack tip advances, the anodic effectiveness of its lateral surface gradually decreases with distance from the tip.

Visual observations show that the most effectively operating cathodes are the regions of metal outside the crack, closely adjoining the tip of the continuously growing stress-corrosion crack.

Thus, the experimentally demonstrated significant decrease in anodic polarizability (by 5–6 orders of magnitude) and the concentration of the effectively operating anodic zone at the tip of the stress-corrosion crack are the principal electrochemical factors determining the process of stress-corrosion cracking of metals.

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Note: Figure translations are in progress. See original paper for figures.