

A METHOD OF INVESTIGATING CORROSIVE AND ELECTROCHEMICAL PROPERTIES OF METALS IN A STRAINED CONDITION

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The phase oxide film on the surface of metals in many cases possesses a considerable electrical resistance which depends not only on the nature but also on the physical condition of the film. When the sample is strained, the film cracks, thus affecting both the electrical resistance and capacitance. By the amount and speed of variation of the capacitance and resistance it is possible to judge of the degree of destruction of the oxide film.

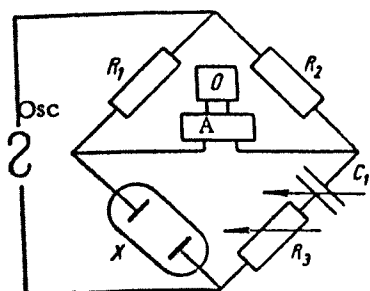


Fig. 1. Schematic of the measuring equipment: R_1, R_2 are fixed resistances; R_3 is a variable resistance (KMS-6); C_1 is a capacitance box (from 0.001 to 100 μf); A is an amplifier; O, an oscillograph; Osc is an oscillator type ZG-10; X is the sample under test.

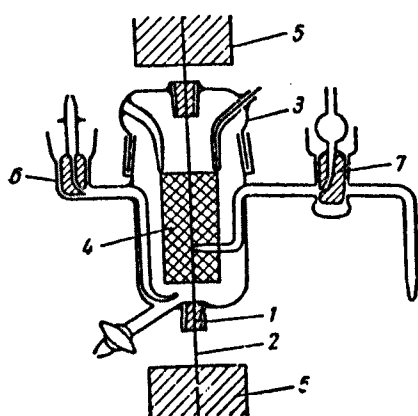


Fig. 2. Container for studying the electrochemical properties of metals under strain.

We developed an equipment for investigating the condition of surface oxide films of materials under tensile strain by means of an optical capacitive method based on this principle.

The schematic of the measuring equipment is shown in Fig. 1. The value of the ac potential supplied by the oscillator is 10-15 mv. It is inadvisable to use higher potentials since this can lead to considerable one-sided (anode or cathode) polarization of the sample under test. The circuit is balanced by capacitance C_1 and resistance R_3 .

The checking is carried out in a special container (Fig. 2) along whose axis the sample 2 under test, consisting of 1-2 mm diameter wire, is fixed by means of two packing pieces 1. Since during testing the sample is extended, lid 3 of the container is made to slide. Platinum cylinder 4, 40 mm high and 20 mm in diameter, is used as the second electrode for measuring the capacitance and resistance of the film. The length of the test part of the sample is 40 mm. The rest of the sample is lacquered. The ends of the sample are fixed in the jaws of the tensile machine 5. The solution is poured in through funnel 6. The ground-in stopper 7 serves to measure the electrochemical potential of the sample.

Figure 3 shows the effect of mechanical tension on the relative variation of the capacitance (C) and resistance (R) of aluminum anodized in a 20% solution of H_2SO_4 at an anode current density of 5 amp/ dm^2 during 15 min at room temperature. Measurements are made immediately after the required load is applied to the metal, hence the corrosive effect of the solution (0.1 NaCl) can be neglected.

The results given in Fig. 3 clearly show that at tensions not exceeding 9-10 kg/ mm^2 the values of capacitance and resistance remain constant. This indicates that despite the considerable lengthening of the sample the film remains intact. At greater loads the film becomes destroyed thus leading to a rise in capacitance and a decrease in resistance.

The results given in Fig. 4 refer to electrolytically polished aluminum. The electrolytic polishing was carried out for 25 min in a bath which contained 150 g/liter of Na_2SO_3 , and 50 g/liter of Na_3PO_4 at a terminal voltage of 13 v and a temperature of 85°C. In this case changes in the oxide film can be observed at higher tensions (11-12 kg/ mm^2) and the changes themselves

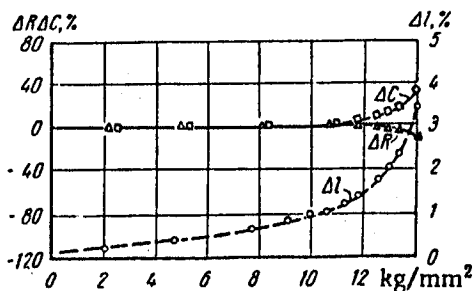


Fig. 3. The effect of tension on relative variations in capacitance, resistance and length of anodized aluminum.

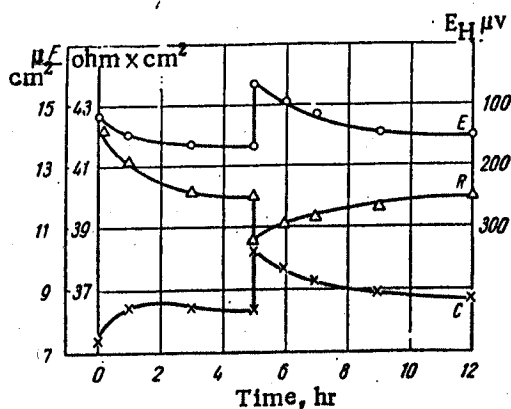


Fig. 5. Variations with time of the capacitance C, resistance R and electrochemical potential E of stainless steel 3X13 in a 0.1N solution of NaNO₃.

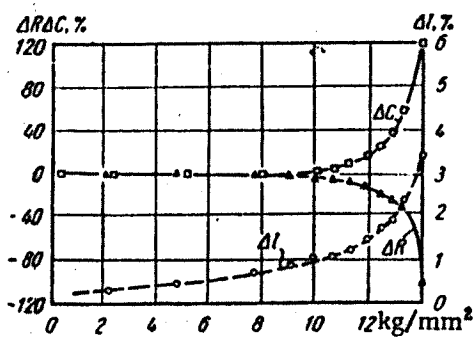


Fig. 4. The effect of tension on the relative variations in capacitance, resistance and length of electrolytically polished aluminum.

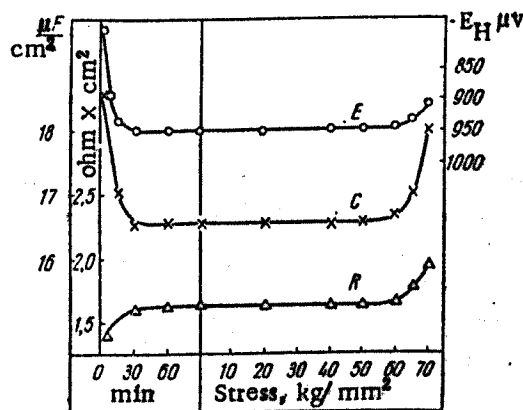


Fig. 6. Relation of capacity C, resistance R and electrochemical potential E to the mechanical loading of stainless steel 3X13.

are smaller at equal tensions. This indicates that the oxide film obtained in electrolytic polishing is more elastic and less subject to cracking than the anodized film.

The oxide films on carbon steel (0.73% C) are considerably less robust ($\sigma_B = 260$ kg/mm² and $\sigma_S = 190$ kg/mm²); they were obtained by treating the samples in a 0.1N solution of KMnO₄. Such oxide films lose their continuity at tensions well below the elastic limit. At tensions which do not produce cracks the oxide films offer good protection in a 1N solution of NaNO₃. If, however, the steel is extended to a value at which the continuity of the film is broken, then in only 1-1.5 hours parts of the sample begin to show signs of corrosion noticeable with the naked eye.

The method also provides the possibility of studying the surface of metals under strain (Fig. 5). At the instant the load which establishes a stress of 65 kg/mm² is applied, the capacitance rises and the resistance falls and the electrochemical potential becomes more negative. This change is followed by a slow return of the characteristics to their initial values. Above phenomenon is due to the portions of metal, which had become active under stress, becoming passive again by interaction with the surrounding solution.

Results shown in Fig. 5 indicate that with a given deformation the metal returns to its initial condition only after some 7-9 hours from the time the load has been applied.

In all the cases examined above, when the strain produced ruptures in the continuity of the oxide film, the capacitance of the film increased, the resistance decreased and the electrode potential became more negative.

This occurs when the newly formed protective layers in the cracks of the film have a lower electrical resistance than the resistance of the original film.

However, cases may occur when the newly formed films will be less conducting than the original film. This is the case, for instance, with stainless steel type 3X13 in a 12 N solution of HNO_3 (Fig. 6). The straining of the sample in this case leads to an increased capacitance and resistance of the surface film. This relation between the measured values is sustained when the sample remains under a given load for a long time (1-2 days). Such behavior of stainless steel 3X13 may be due to the formation in the strong nitric acid over the cracks in the original oxidation film of a new thinner, but less porous film which has a higher resistivity than the original film.

Above experimental results show that the combined measurement of the capacitance and resistance of the double electrical layer, and of the electrode potential can be of great use for investigating the behavior of protective oxide films on metals under strain.

DETERMINATION OF THE TENDENCY OF Al-Mg ALLOYS TO STRESS CORROSION FROM THE MICROSTRUCTURE

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The tendency of Al-Mg alloys with a high Mg content to stress corrosion depends on the type of structure viz. the presence almost continuous rings of the β -phase (or an intermediate chemical compound) along the grain boundaries.

In the present work we have studied the tendency of AMg6T alloy to corrosion cracking depending on the type of microstructure after the thermal treatment. During the investigations, the degree of the decomposition of the solid solution and the distribution of the decomposition products in the grains of the solid solution were studied.

Corrosion Tests on the Specimens of AMg6T Alloy Subjected to Various Thermal Treatments

Thermal treatment	Number of specimens	Time interval from the moment of immersion to the appearance of the first crack, days
Heated at 350° for 1 hr, cooled in air	2	> 160
Tempered at 50°C for 24 hrs	2	> 100
Tempered at 100°C for 24 hrs	2	> 125
Tempered at 200°C for 5 hrs	2	< 16
Tempered at 300°C at 5 hrs	2	> 125
Quenched from 450°C in water	2	> 125

The specimens were in the form of plates 210 x 15 x 2 mm. To obtain various structures, we subjected the specimens to different thermal treatments. After being heated at 350°C in an air furnace for one hour some specimens were cooled in air and then were tempered at 50°C (24 hrs), at 100°C (24 hrs), at 200°C (5 hrs) and at 300°C (5 hrs). Some specimens were quenched from 450°C in water. Simultaneously with the corrosion tests, a microscopic study was carried out.

For corrosion tests the plates were bent into a loop and immersed in a corrosive medium (3% NaCl and 0.1% H_2O_2 in water). The specimens were continuously immersed. The solution was changed every 15 days. The time which elapsed before the appearance of a crack visible to a naked eye was taken as the measure of the corrosion resistance. The results of the corrosion tests are given in the table.

The results show that an increased tendency to stress corrosion in the specimens becomes manifest only after tempering in the region of 200°C.