DEVELOPMENT OF THE METHOD OF STUDY OF METALS MICROELECTROCHEMICAL HETEROGENEITY

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Abstract – The method of microelectrochemical investigations has been developed in a mobile drop of electrolyte for the estimation of structural heterogeneity of materials, which is based on using a microelectrode as a capillary probe. Thus a sample horizontally moved with a speed of 10 micron per second in a microscope sight field. Character of microelectrochemical heterogeneity of the sample surface was scanned by a capillary (d=1-2 micron) in a film and a drop of different solutions and in a mobile drop of the solution $45 \cdot 10^{-3}$% H_2SO_4 + 0,14% H_2O_2 + $5 \cdot 10^{-6}$% $K_2Cr_2O_7$ (MEX), that flows out of it (capillary diameter = 15-20 micron).

The systems steel 20 – nickel and zinc coating in 3% NaCl, distilled water and MEX have been investigated with the use of a capillary probe, filled with these solutions. It is shown that low conductivity of electrolyte and high currents of metals dissolution are necessary conditions for the reliable estimation of local electrode potentials values. According to these conditions for the microelectrochemical scanning of steel 20 surface the solution of MEX has been chosen. When measurings potentials of electrochemical heterogeneous metals the best resolution is noticed in a drop of electrolyte, comparatively with the solution film, what is proved by diminishing the distance of their interaction. The advantage of microelectrochemical scanning of the sample surface in a mobile drop of electrolyte is shown. Subsequent microelectrochemical investigations of the surface heterogeneity were conducted in a mobile drop of MEX.

Microelectrochemical investigations of steel 20, that corroded in chloride-sulfide solutions have been conducted. It is shown that under passivation the microelectrochemical heterogeneity of surface is higher, than after its active dissolution. That is the passive film does not even the difference of potentials between the separate areas of the surface. During mechanical fracture of surface films by a diamond chisel in air the microelectrochemical heterogeneity increased to 280…320 mV, that will promote the development of local corrosion processes.

Keywords: microelectrochemical heterogeneity, mobile drop, corrosion, capillary probe, scanning

INTRODUCTION

Structural heterogeneity of alloys is an important factor, which determines the speed of their corrosion. The efficiency of the functioning of galvanic microelements on alloys' surface depends on structural heterogeneity, which is a pre-condition of the development of local corrosion [1]. For the estimation of electrochemical properties of materials on a microlevel special methods are used. The most widespread among them are the methods based on using a microelectrode as a capillary probe and the determination of electrochemical properties in a film and a drop of electrolyte [2-4].

The aim of the work was to estimate informativity of microelectrochemical research with a capillary probe in a film, a drop and a mobile drop of the studied solutions.

EXPERIMENTAL METHOD

Apparatus and materials

The specimens from steel 20 on the part of which inflicted the electrolitic zinc coating was applied were tested. This zinc coating was from a sulfate(pH 4.6, t=25°C, i= 300 A/m^2) obtained electrolyte. The microelectrochemical heterogeneity of the sample surface was studied in water solutions: $45 \cdot 10^{-3}$% H_2SO_4 + 0.14% H_2O_2 + $5 \cdot 10^{-6}$% $K_2Cr_2O_7$ (MEX) [5], conductivity $\kappa = 0,38$ Cm·m^{-1}, 3% NaCl ($\kappa = 4,7$ Cm·m^{-1}) and distilled water ($\kappa = 9 \cdot 10^{-5}$ Cm·m^{-1}).

Procedure

The microelectrochemical properties of materials were evaluated, using the method of microelectrode with a capillary probe. The scanning of surface was conducted in a film of solutions (minimum thickness which is determined by the surface tension), in a drop of solutions a size 2-3 mm, that applied from the outside, here capillaries with the internal diameter of 1-2μm were used and by a continuous scanning by a capillary (d= 20 micron) with a speed of 10 micron per second in a mobile drop (d=50 micron) of water solutions. A drop flowed out from to the capillary as it moves. Capillaries were filled with solutions in which research were carried out. Potentials are presented with respect to the values of silver-silver chloride reference electrode.

Microelectrochemical heterogeneity of steel 20 studied after 15 h holding in solutions which contain chloride- and sulfide-ions different pH: 0.7%Na$_2$S (pH 12.25) and 0.4%NaOH (pH12.45), 3.7% HCl (pH1.4), 3.5% NaCl (pH5.95) and 0.7% Na$_2$S+3.5% NaCl (pH 12.15).

EXPERIMENTAL RESULTS AND DISCUSSION

Microelectrochemical heterogeneity of the surface

The investigation of zinc coating – steel 20 galvanic couple by a capillary probe showed, that in a 3% solution NaCl potential at a different distance from the laterface (to ~ 10 mm) both in the film and in a drop remains constant (E=-965 mV). This is related to high conductivity of solution which provides complete polarization of the specimen surface. When using of the distilled water a difference of potentials between separate components of galvanic couple and in the film and in a drop is already recorded, but there is more a smooth transition from potential of Zn to potential of steel (Fig. 1).
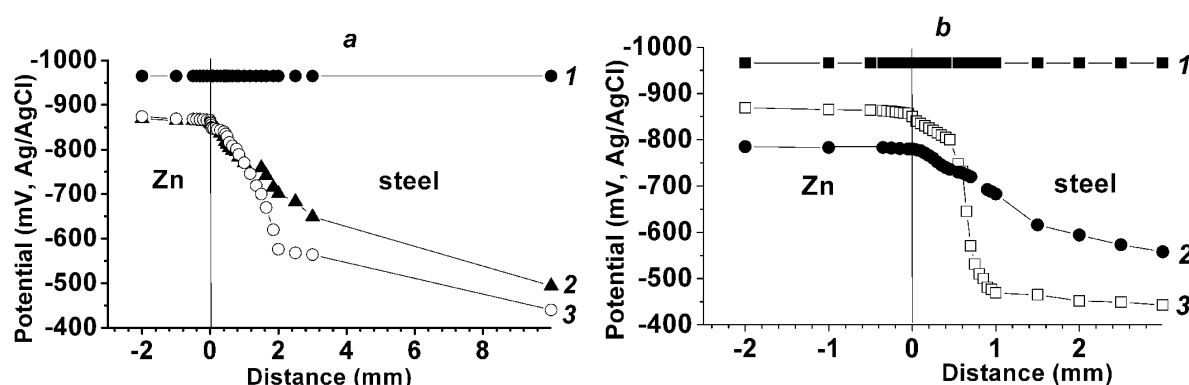

Figure 1. Change of the potential of specimen surface in the system zinc coating – steel 20 :
a – in a solution film; b – in a solution drop; 1 – 3% NaCl; 2 – the distilled water;
3 – $45 \cdot 10^{-3}$% H_2SO_4 + 0,14% H_2O_2 + $5 \cdot 10^{-6}$% $K_2Cr_2O_7$.

At the presence of unknown constituents in the galvanic couple it will in cause difficulty their identification.

In solution of MEX for the surface scanning by a capillary from zinc coating a potential practically does not change when approaching the boundary of metals contact. Farther he gradually displaces to the side of positive values and at a distance ~ 0,5 mm (fig. 1) it changes sharply. At a distance of 10 mm in a film and 2 mm in a drop of the studied solution the electrode potential practically stabilizes and arrives at values which characterizes steel.

When using a mobile drop method in the MEX solution the resolving capacity of measurings grows: the different constituents of galvanic couple are fixed in the distance ~ 30-35 micron (Fig. 2). The use of solutions with greater conductivity (3% NaCl) does not diminish sensibility of the method, potential of steel is stabilized also on that distance ~ of 30-35 micron (Fig. 3).
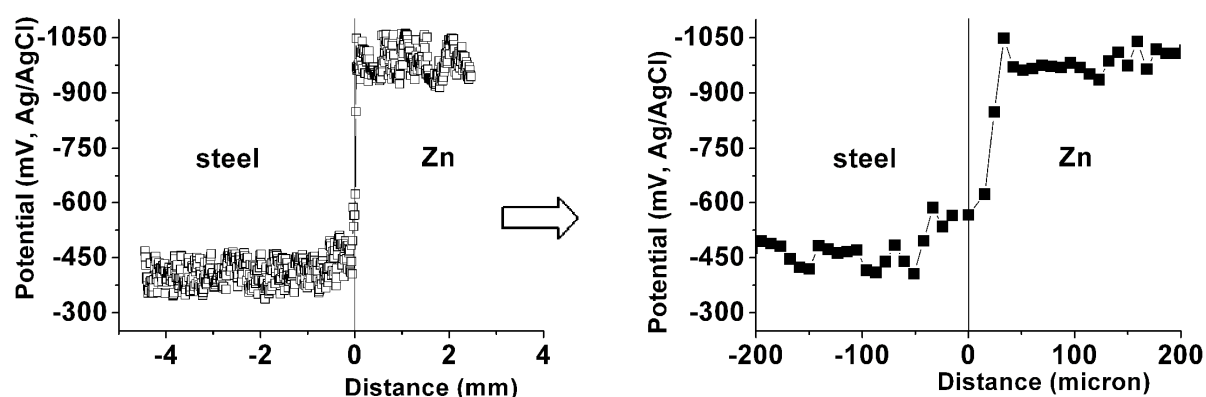

Figure 2. Change of potential of specimen surface in the system steel 20 – zinc coating in a mobile $45 \cdot 10^{-3}\% \ H_2SO_4 + 0{,}14\% \ H_2O_2 + 5 \cdot 10^{-6}\% \ K_2Cr_2O_7$ drop.
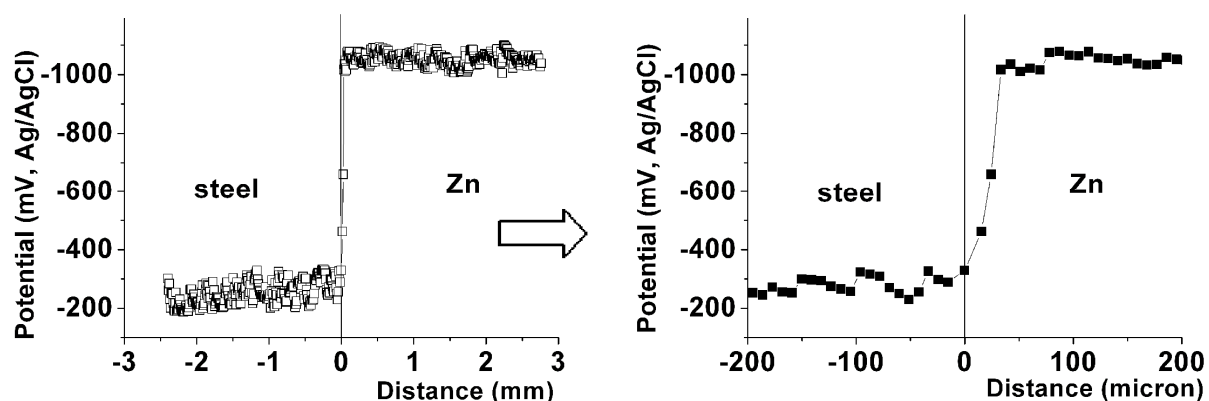

Figure 3. Change of potential of specimen surface in the system steel 20 – zinc coating in a mobile 3% NaCl drop.

When measurings potentials of electrochemical heterogeneous metals in a moving electrolite drop the best resolving ability of electrolyte, than in a film and a drop of solution which shows up in

diminishing of their interaction distance. In is noticed scanning surface in the a mobile drop of solution conductivity is not a determining factor for the reliable estimation of local electrode potential values. That is for microelectrochemical research it is possible to use those solutions in which the process of corrosion occurs, not using special solutions.

Microelectrochemical heterogeneity after corrosion

For the estimation of microelectrochemical heterogeneity of steel 20 after its corrosion in different solutions the method of a mobile drop MEX was used. It is shown that the difference of potentials (ΔE) on the separate areas of steel 20 initial surface of a ength 8…10 mm makes ~10…80 mV (Fig. 4a).
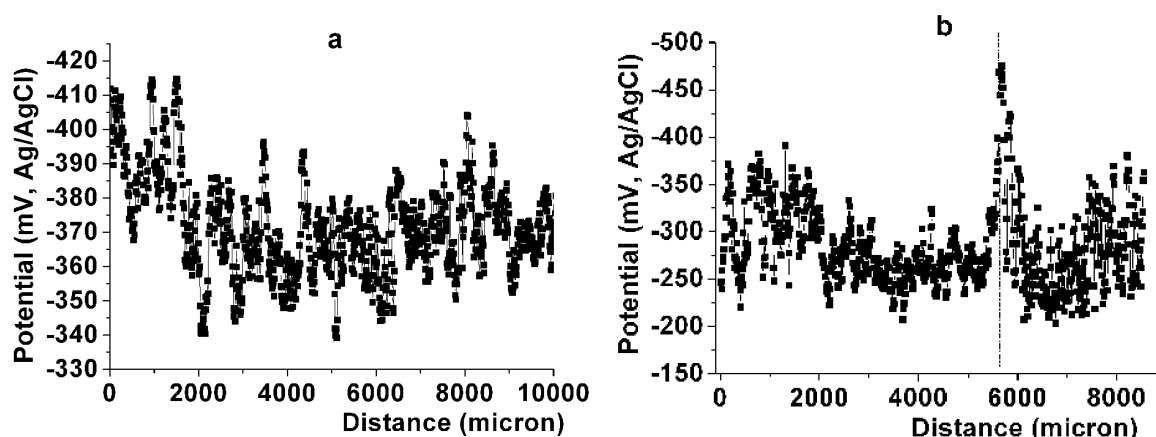

Figure 4. Change of local potentials of steel 20 initial surface in a mobile drop of solution $45 \cdot 10^{-3}\%$ H_2SO_4 + 0,14% H_2O_2 + $5 \cdot 10^{-6}\%$ $K_2Cr_2O_7$ (a) and after corrosion in the 0.7% Na_2S + 3.5% NaCl solution (b).

The specimen surface was covered with a homogeneous grey dull film after holding in the 3.7% HCl solution and mechanical removing of loose products of corrosion. Change of local potential of steel 20 surface is $\Delta E = 30…110$ mV, and after their complete removal of corrosion products by the diamond chisel the potential of damage site I more negative by $\Delta E' = 60…170$ mV in comparison to the other surface (Table 1). The steel surface is evenly covered with loose corrosion products which are easily taken off after corrosion in 3.5% NaCl. Microelectrochemical heterogeneity of the surface in comparison to the initial grows and is $\Delta E = 20…100$ mV, $\Delta E' = 40…140$ mV. The difference of surface local potentials makes $\Delta E = 40…160$ mV and $\Delta E' = 50…220$ mV after corrosion of steel 20 in 0.4% NaOH solution. Comparing results, after holding in obtained acid and alkali, it is possible to establish, that passivation of steel surface in 0.4% NaOH solution does not reduce the microelectrochemical heterogeneity of the surface, and on the contrary, increases it. After specimens holding in 0.7% Na_2S solution and mechanical removal of corrosion products on the surface an even point corrosion is observed: $\Delta E = 40…180$ mV and $\Delta E' = 160…320$ mV. The character of steel corrosion is analogical in the solution 0.7% Na_2S + 3.5% NaCl, $\Delta E = 20…180$ mV and $\Delta E' = 80…280$ mV (Fig. 4b).

The obtained results show (Table 1) that in corrosion of steel 20 in solutions, where passivation (0.4% NaOH; 0.7% Na_2S; 0.7% Na_2S+3.5% NaCl) was observed, they microelectrochemical heterogeneity of the surface is higher, than after its active dissolution. Consequently, the passive film does not level the difference of potentials between the separate areas of the surface. But due to their

passivation and low currents of dissolution the microelectrochemical heterogeneity does not bring the corrosive processes localization.

Table 1. Results of microelectrochemical investigations of steel 20 surface after corrosion

Potentials difference	Solutions				
	3.7% HCl, pH = 1,4	3.5% NaCl, pH = 5,95	0.4% NaOH, pH = 12,45	0.7% Na_2S, pH = 12,25	0.7% Na_2S+ +3.5%NaCl, pH= 12,15
ΔE, mV	30-110	20-100	40-160	40-180	20-180
$\Delta E'$, mV	60-170	40-140	50-220	150-320	80-280

The research of the influence on microelectrochemical properties of the surface films mechanical fracture a diamond chisel in air show, that the greatest difference of potentials was observed for the steel 20 after its corrosion in Na_2S solutions – to 280…320 mV. It is considered [6] that the intensity of corrosive processes grows sharply, if the difference of contacting metals potentials or their neighbour areas exceeds 200 mV. Therefore mechanical fracture of surface films and increase of microelectrochemical heterogeneity of steel 20 surface in chloride-sulfide environments can assist in the development of local corrosive processes.

CONCLUSIONS

The method of microelectrochemical investigations has been developed in a mobile drop of electrolyte for the estimation of structural heterogeneity of materials, which is based on using a microelectrode as a capillary probe. The advantage of using MEX solution when scanning of steel 20 surface in its film and a drop has shown : the resolving ability of method grows almost by 2 orders. The low conductivity of the solution is not the necessary condition of reliable estimation of local electrode potentials values when scanning the surface in a mobile drop of solution. The advantage of microelectrochemical scanning of specimens surface is shown in a mobile drop of electrolyte. It has been established that under passivation conditions the microelectrochemical heterogeneity of the surface is higher than after its active dissolution. It is has been found that in chloride-sulfide solutions at the films fracture on the steel 20 surfaces local corrosive processes can develop which will result in a subsequent local accelerated damage .

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