

Sorption phenomena on the surface of steel in solutions of nitrilotrimethylphosphonic acid

Makhina Vera Sergeevna, Serov Alexander Nikolaevich, Vagramyan Tigran Ashotovich
Russian Chemical-Technological University named after D.I. Mendeleev (Russia, Moscow)
frau.mahina@yandex.ru

Abstract: Corrosion behavior of plain steel in alkaline copper-containing solutions was studied. Cementation of steel is inhibited by formation of the passive film on the steel surface. Formation of the film is due to the reacting steel and complex of divalent copper complex with ATMP.

KEY WORDS: IMPEDANCE SPECTROSCOPY, ATMP, ADSORPTION, STEEL CEMENTATION INHIBITION

1. Introduction

When copper or copper-containing galvanic coatings are deposited onto a steel base, there is a risk of contact copper deposition after immersing an item in the electrolyte but before cathodic polarization is applied. Copper deposited in contact manner adversely affects the adhesion of the coating deposited later by impairing its adhesion to the steel base. Moreover, contact exchange results in contamination of the electrolyte with iron ions that can adversely affect the performance of the electrolyte, especially in case of the electrodeposition of alloys.

The most popular method to solve the issue of contact exchange in electrolytes for deposition of copper and its alloys involves binding copper ions into complex compounds [1-3]. At the same time, practical recommendations for the operation of alkaline cyanide-free copper plating electrolytes that are most common in the industry, such as loading parts into the electrolyte under current, indicate that these complexes are not strong enough to prevent the contact deposition of copper on a steel surface [4]. According to literature data, the stability constants of organophosphate copper complexes are comparable to the stability constant of the pyrophosphate copper complex [5].

In the development of an alkaline cyanide-free electrolyte for bronzing based on nitrilotrimethylphosphonic acid, it was noted that in the absence of external polarization, the formation of contact copper is not observed on the surface of a steel electrode even after prolonged exposure of steel to the electrolyte, though, in accordance with literature data on instability constants, its formation is possible. Thus, it can be assumed that the inhibition of the contact exchange reaction is due not only and not so much to the binding of copper into a complex ion but also to the adsorption processes on the steel surface involving the organophosphorus ligand.

This work deals with a study on the mechanism of inhibition of the contact reduction of copper on the surface of steel in solutions containing components of cyanide-free electrolyte bronzing.

2. Experimental

Experiments were carried out at solutions listed below

Solution 1. ATMP 0,25M, pH 10

Solution 2. ATMP 0,25M + CuSO₄·5H₂O 0,11M, pH 10

Experiments were carried out at solution temperatures of 20 and 55°C. The measurements were carried out in solutions without stirring or with stirring with a magnetic stirrer at 700 rpm.

Polarization and impedance measurements were performed using an IPC-Pro MF potentiostatic complex with an FRA-2 unit (Russia). The measurements were carried out using a temperature-controlled three-electrode cell with a volume of 250 ml. A silver chloride electrode was used as the reference electrode, and a platinum anode with an area of 3 cm² served as the auxiliary electrode.

To measure the currentless potential of the electrode, we used an IPC-Recorder (Russia) that allows one to record the potential variation over time. The measurements were carried out for at least 5 minutes until a constant potential was attained.

The frequency dependences of the impedance were obtained in potentiostatic mode at the open circuit potentials, with superposition of a harmonic signal with an amplitude of 10 mV in the frequency range of 20 kHz - 0.13 Hz. The impedance spectra obtained were processed and equivalent circuits that adequately reflect the experimental plots were simulated using the ZMonitor and DCS

programs.¹ Each measurement was carried out at least in duplicate.

3. Results and Discussion

The electrochemical impedance spectroscopy method is widely used to study the interface processes in electrochemical systems. The advantage of this method is not only that it allows one to estimate the corrosion resistance of a metal under the effect of various factors but also that information about the mechanism of reactions occurring on the metal being studied can be obtained.

Figure 1 shows the Nyquist diagrams obtained in the solutions studied. The lowest rate of corrosion processes and the greatest hindrance of charge transfer across the interface are observed in the cold solution in the absence of stirring (Figure 1A, curve 1).

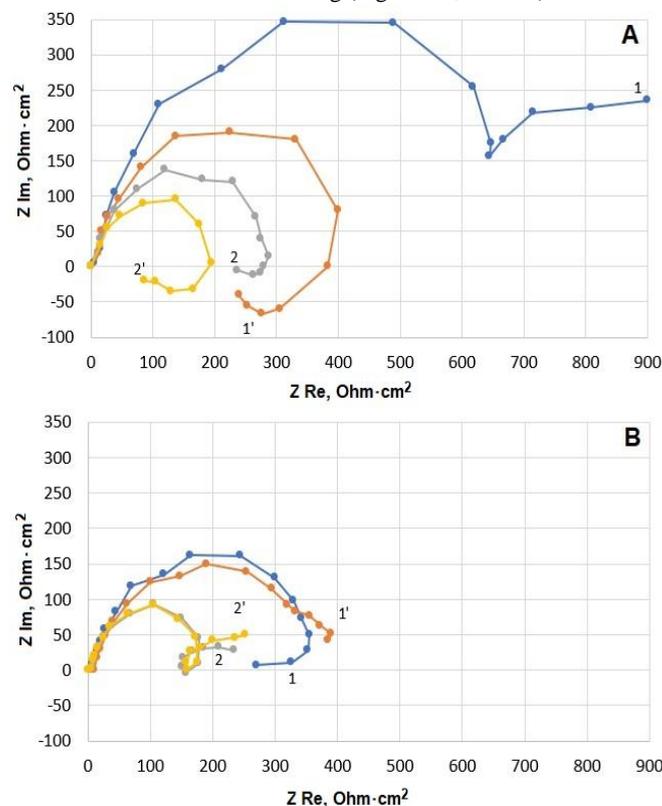


Figure 1. Nyquist plots. A - solution 1; B - solution 2; 1, 1' - 20°C; 2, 2' - 55°C; 1, 2 - without stirring; 1', 2' - with stirring.

According to the Pourbaix diagrams (Fig. 2), at about pH 10 iron dissolves either to give the Fe²⁺ ion (Fig. 2A) or the FeOH⁺ ion (Fig. 2B).

Under conditions of corrosion with oxygen depolarization in an alkaline medium, the near-electrode layer can be alkalinized by the reaction O₂ + 2H₂O + 4e → 4OH⁻ (1). Alkalinization can give rise to the formation of iron hydroxide films on a steel surface. The formation of a new non-conductive phase on the electrode surface causes an increase in the polarization resistance in the low-frequency part of the plot, which is consistent with the appearance

¹The **ZMonitor** and **Dummy Circuits Solver** programs were designed by V.E. Kasatkin specifically for use in combination with the IPC-FRA electrochemical complex.

