INTRODUCTION

The Fe–Cr–Ni system is of noticeable practical interest, primarily because, similar to Fe–Cr, Fe–Si, and Fe–Ni systems, it is one of the most widely used Fe-based structural alloys, particularly corrosion resistant steels. Therefore, the previous ESTM and ESTS studies of Kh18N10T stainless steel (Fe–17.8% Cr–10.4% Ni alloy) [1, 2] are now supplemented by ESTS and ESTM measurements of specimens of Fe–20% Cr–40% Ni and Fe–20% Cr–70% Ni alloys in air and diluted acid solutions.

Similar to [1–3], the measurements are carried out in air and under electrochemical conditions of the operation of a scanning tunneling microscope in 0.01 N HCl and 0.1 N H\textsubscript{2}SO\textsubscript{4} solutions at the controlled potentials of the specimen and needle using in situ techniques of electrochemical scanning tunneling microscopy (ESTM) and electrochemical scanning tunneling spectroscopy (ESTS). The changes in the potential of Fe–20% Cr–40% Ni alloy specimen fall in ranges of –0.3 to 1.1 V and 0–0.3 V (N.H.E.) in 0.01 N HCl and 0.1 N H\textsubscript{2}SO\textsubscript{4}, respectively, and the changes in the potential of Fe–20% Cr–70% Ni specimen, in ranges of 0.09–0.94 V and –0.1 to 0.5 V in 0.01 N HCl and 0.1 N H\textsubscript{2}SO\textsubscript{4}, respectively. Local spectral dependences of the tunnel current on the tunnel voltage are obtained and processed and the coefficients that characterize the local electrophysical properties of the surfaces are calculated on their basis. It is found that, in the studied acid solutions at the controlled potential, the surfaces are more energetically homogeneous than in air, where a substantially larger dispersion of the properties is observed. It is concluded that the energetic characteristics of separate surface sites of these alloys are determined on the atomic scale by the mutual effects of the neighboring atoms involved in its composition, i.e., by the matrix effect, which was discovered previously in the case of Kh18N10T stainless steel [1].

EXPERIMENTAL

The technique of experiments is similar to that described in [1–3]. The experiments are carried out using an CPM Solver EC electrochemical scanning tunneling microscope (ESTM). 0.01 N HCl and 0.1 N H\textsubscript{2}SO\textsubscript{4} solutions were prepared from bidistilled water. Rolled sheet specimens of Fe–20% Cr–40% Ni and Fe–20% Cr–70% Ni alloys with a thickness of 0.15 mm were preliminarily (before placing in a cell for STM measurements) polished with corundum powder to a mirror luster and thoroughly washed in acetone, alcohol, and bidistilled water. The alloys served as working electrodes in an ESTM cell. The residual electrodes of the ESTM cell, as well as the technique of potentiostating, are described in [1–3].

Platinum–iridium STM needles (containing 30% Ir) electrochemically insulated with a Glassofor polymer coating were used. The quality of the needle tip was controlled with the special test designed for the ESTM unit set, namely, the spectroscopy of the response dependence on the distance between the specimen and the needle, which is gradually taken away from it [4, 5]. ESTM measurements were carried out under \(I_t = \text{const}\) conditions at the controlled potentials of the specimen and needle. The tunnel voltage (\(U_0\)) was set to 0.1 V in all the experiments, while the tunnel current (\(I_0\)) was 0.1 nA. Thus, the controlled tunnel conductivity (\(G_1 = I_0/U_0\)) corre-
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Fig. 1. STM images of (a, c) Fe–20% Cr–40% Ni and (b, d) Fe–20% Cr–70% Ni alloy surfaces in (a, b) air, (c) 0.01 N HCl, and (d) 0.1 N H₂SO₄ at the specimen potentials of 0 and 400 mV respectively. \( U_t = 100 \) mV; \( I_o = 0.100 \) nA; scanning step = 10 nm.

Respecting to the tunnel gap was constant and equal to 1, which provided the same distance between the needle and specimen in all the experiments.

Upon obtaining STM or ESTM images, a series of \( I_{t_ex}, U_t \) curves (STS and ESTS spectra) were recorded, where \( I_{t_ex} \) is the experimentally measured current, which is equal to the sum of the tunnel and Faraday currents (\( I_{t_ex} = I_t + I_{far} \)). In the experiments, a program that ensures the displacement of a needle from one of 400 sites to another over the surface square net was used. The scanned field was 1 \( \mu \)m². The tunnel voltage at each point where a local spectrum was recorded was changed from –0.75 to 0.75 V, then in the reverse direction at a scanning rate \( U_t = \pm 1 \) V/s.

At the beginning and end of each ESTM experiment, the Faraday current (\( I_{far} \)) on a noninsulated part of the needle tip removed from the specimen was recorded depending on the needle potential (\( E_t \)). This background current was then subtracted from the \( I_{t_ex}, U_t \) dependences with the special computer program. The data obtained were processed according to the procedure outlined in [1–3].

RESULTS AND DISCUSSION

Before ESTM series, potentiodynamic polarization curves (±10 mV/s) were recorded on each specimen in an ESTM cell in the acid solutions studied in order to determine the potential ranges where the surfaces are relatively stable. As a result, the following ranges of the potential changes (N.H.E.) were selected for the ESTM studies:

(i) –0.3 to 1.1 V with a step of 0.1 V on Fe–20% Cr–40% Ni in 0.01 N HCl;
(ii) 0–0.3 V with a step of 0.1 V on Fe–20% Cr–40% Ni in 0.1 N H₂SO₄;
(iii) 0.09–0.94 V (0.09, 0.14, 0.24, 0.34, 0.44, 0.54, 0.64, 0.74, 0.84, and 0.94 V) on Fe–20% Cr–70% Ni in 0.01 N HCl;
(iv) –0.1 to 0.5 V with a step of 0.1 V on Fe–20% Cr–70% Ni in 0.1 N H₂SO₄.

Figure 1 shows some STM images of the electronic profiles of the studied alloy surfaces obtained during measurements in air and in the acid solutions at various potentials of the specimen. The scanned field was 1 \( \mu \)m². Comparing the results to the STM measurements in air shows that, at the controlled potential of the specimen, the surface is smoother in the solution than in air. This conclusion is similar to that drawn earlier in the case of the surfaces of Kh18N10T stainless steel, chromium, and nickel [1–3]. The height differences in the solution were several nanometers. This is caused by the normalization of the surface nanostructure in the solution by the selected potential.

Figures 2–6 show characteristic polygons of the distribution histograms of \( \alpha, \beta, \) and \( \gamma \) parameters determined in the measurements on Fe–20% Cr–40% Ni and Fe–20% Cr–70% Ni alloy surfaces in air and 0.01 N