Thickness, μm	0.45	1.35	2.2	3	6.56	9	13.1
S_{pore}, cm^2 ($\times 10^5$)	63	23	18	7	0.7	0.1	0.12

Previously [11] we have shown that the protective capacities of silver coatings 3, 6, 9, and 12 μm thick deposited in similar conditions are characterized by the following corrosion currents ($\mu A/cm^2$): 0.53, 0.37, 0.20, 0.12. Comparing these data with results on the porosity, we see that fairly large corrosion currents can exist, especially, it would seem, when the thickness does not exceed 1.5-2 μm. This enables us to interpret the conclusion of Slepushkin et al. [3] that 1.5 μm of silver gives 100% protection as too categorical.

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METHOD OF DETERMINING THE COMPOSITION OF ELECTRODEPOSITED IRON–CHROMIUM ALLOYS

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In our investigation of the mechanism of formation of protective galvanic coatings of iron–chromium alloys, we have developed a method of analysis of these coatings which might be used to attack other problems. For research purposes the alloy was deposited on an inert substrate, and therefore the method of analysis included complete solution of the coating and analysis of the solution products by atomic absorption spectroscopy.

The dissolution of the coating had to be sufficiently complete, and the atomic absorption analysis regime of the solution had to rule out interference from compounds used to remove the deposit and from the mutual interference between iron and chromium simultaneously present in the solution (it is known [1] that iron salts can strongly distort the absorption of chromium).

To eliminate the interfering action of iron in the determination of chromium, a number of methods have been proposed, based either on quantitative allowance for the influence of iron ions in the sample [1, 2] or on selection of optimal conditions for the atomization of chromium [3, 4]. There are also combined methods belonging to both groups.

Quantitative allowance for the influence of iron ions can be made either by using calibration solutions containing iron and chromium in the same ratio as in the test sample [2], or by adding excess iron ions to the calibration and test solutions [1]. Such methods cannot be applied to the analysis of iron–chromium coatings: The first is inapplicable because by the nature of the problem it is necessary to analyze alloys of unknown composition; the second

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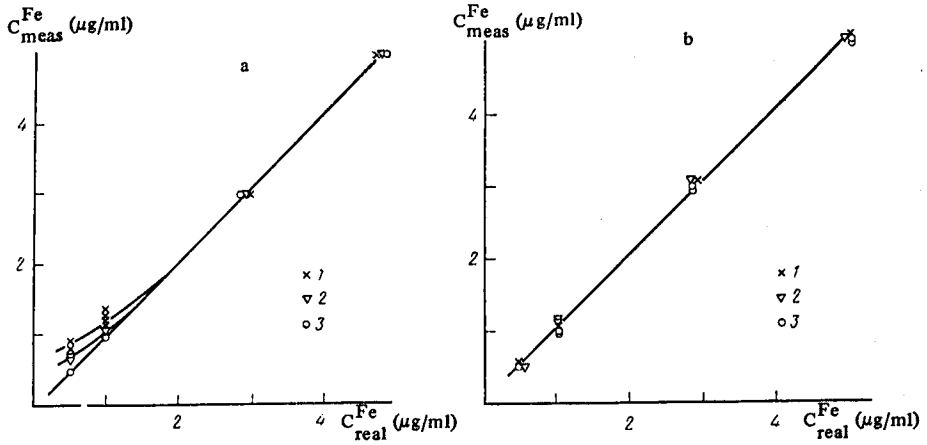

Fig. 1. a) Comparison between real concentrations (C_{real}) of iron in solutions containing added chromium and those calculated from the calibration curve based on solutions with no chromium (C_{meas}) for various HCl concentrations (N): 1) 1.0; 2) 0.5; 3) $5 \cdot 10^{-5}$. b) The same after correction for iron content of acid.

TABLE 1

Fe concn. in sample, μg/ml	Fe:Cr ratio in sample	Determined Fe concn., μg/ml	Error, %
3,00	1 : 0	2,97±0,03	1,7
	1 : 9	3,00±0,05	
	1 : 49	3,10±0,05	
	1 : 99	3,00±0,05	
1,00	1 : 0	0,90±0,04	4,0
	1 : 1	1,00±0,04	
	1 : 49	1,00±0,04	
	1 : 99	1,00±0,04	
0,50	1 : 0	0,48±0,03	5,6
	1 : 1	0,50±0,03	
	1 : 9	0,55±0,03	
	1 : 49	0,45±0,03	
	1 : 99	0,55±0,03	

is inapplicable because in these conditions iron and chromium cannot be determined from a single sample, and because of the great reduction in the sensitivity of determination of chromium.

The interfering influence of iron ions can also be avoided by adding to the test solution spectral buffers such as ammonium chloride or sodium dodecyl sulfate [3, 4], which facilitate the atomization of chromium by reducing the surface tension of the solution or preventing the formation of involatile chromium compounds [5]. However, this method is only applicable if the relative iron content of the sample is low, and this limits its use.

Another way of solving the problem is based on choice of composition of the fuel gas mixture [6, 7]. Thus, we can use a high-temperature flame from a mixture of nitrous oxide and acetylene which practically completely eliminates errors due to the influence of iron ions in the sample [6]. This method, however, is applicable only to a high chromium content, i.e., it cannot determine the compositions of thin galvanic coatings. In this connection, a more promising mixture is one of acetylene with air, which was chosen as the fuel mixture. The problem then reduced to finding an acetylene–air ratio to give complete atomization of chromium and to ensure both correctness of the analysis and adequate sensitivity to solutions containing iron and chromium ions over a wide range of concentration ratios against a background of the solution chosen to dissolve the deposit from the substrate.

The first step was to choose a solution for removing the coating from the platinum substrate on which it had been deposited by electrolysis of solutions based on sulfates of divalent iron and trivalent chromium with added urea and ammonium sulfate [7]. Electrolysis was

effected in galvanostatic conditions with a current density of 0.2 A/cm^2 at 65°C for 5-10 min. The deposits so obtained were thrice washed with double-distilled water in order that traces of electrolyte might be completely removed from the surface, and then dried in air at room temperature.

By performing a series of experiments on the dissolution of iron–chromium coatings in solutions of sulfuric and hydrochloric acids of various concentrations, we established that the most efficient etching is obtained in concentrated hydrochloric acid (about 10 N). In this solution, coatings of the thickness under investigation are completely removed at 80-90°C in 1-3 min. A sufficient ratio of the acid solution volume to the electrode surface is 1 ml:1 cm^2. Completion of dissolution was judged visually from the cessation of evolution of gas bubbles, and also on the basis of experiments with repeated etching of the substrate in several portions of hydrochloric acid and analysis of the repeated-etching products by the atomic absorption spectroscopy method to be described below. For analysis, the solution was diluted at least ten times to avoid corrosion of the atomizer and burner of the atomic absorption spectrometer. It was found that neither iron nor chromium is detected from the repeat etching. Considering the sensitivity found for the method, this result leads us to conclude that in the above conditions over 99% of a 3-μm deposit is removed.

The regime was developed with solutions obtained by dissolving accurately weighed samples of metal in concentrated hydrochloric acid and diluting them. The Fe:Cr mass ratio ranged from 99:1 to 1:99 against the background of hydrochloric acid in various concentrations.

To construct calibration graphs for iron, we used solutions containing only iron ions, diluted to concentrations between $5 \cdot 10^{-7}$ and 10^{-6} g/ml. The atomic absorption measurements were made on a Perkin–Elmer-5000 spectrometer at a wavelength of 248.3 nm with a 0.2-nm slit. The acetylene–air ratio in the gas mixture corresponded to that recommended for the instrument when used with iron.

The calibration curves were used to determine the known amounts of iron in solutions with various amounts of added chromium at various concentrations of hydrochloric acid (Fig. 1, Table 1). We see that the results of the iron determination are independent of the presence of chromium ions up to very large relative amounts, but at low concentrations of iron they depend on the hydrochloric acid content of the solution. This may be attributed to the presence of iron as impurity in the acid used to prepare the solutions.* The error due to this cause was eliminated by subtracting from the readings for the sample the corresponding readings for a solution containing only hydrochloric acid in the given concentration. The results thus corrected are plotted in Fig. 1b.

In order to find the optimal conditions for analysis of chromium, we chose an atomization regime in which solutions with the same chromium content but different iron concentrations gave the same, and moreover the maximum, absorption. We found that this regime is obtained when the acetylene–air ratio in the mixture is 3.3:24 (i.e., close to that calculated for the reaction $C_2H_2 + 2.5\ O_2 = 2CO_2 + H_2O$). Chromium was determined at a wavelength of 357.9 nm with a 0.7-nm slit.

The results, listed in Table 2, show that in the chosen conditions the error due to the presence of iron ions in the solution is practically eliminated. The precision of determination of chromium is also independent of the hydrochloric acid content of the sample (in concentrations not exceeding 1 N). There is some reduction in the characteristic concentration of chromium found when the proposed diluted acetylene–air mixture is used (in comparison with the usually recommended enriched mixture), but it imposes practically no limitation on the applicability of the method to the analysis of electrodeposited iron–chromium alloys.

The minimum thickness of electrodeposited Fe–Cr coatings required for determination of both components by the above method depends on the relative iron and chromium contents of the alloy. Thus, if the two components are present in the alloy in comparable amounts, the minimum coating thickness permitting analysis is 0.03 μm. If the content of one component is about 10%, the thickness is 0.15 μm; if 1%, it is 1.5 μm. With low iron contents, thinner layers of electrodeposited alloys can be analyzed if purer hydrochloric acid is used to dissolve the deposit.

As an illustration of the proposed method of analysis, Fig. 2 shows data on the influence of potential on the partial rates of deposition of iron and chromium in an alloy from a solu-

*We used acid of very high purity grade (OSCh).

TABLE 2

Cr concn. in sample, μg/ml	Cr:Fe ratio in sample	Quantity of chromium determined for HCl concns. (N) of:			Error
		1	0,5	$5 \cdot 10^{-5}$	
2,00	1:0	1,95	2,06	1,97	±0,08; 2,5%
	1:1	1,95	1,90	1,95	
	1:9	1,86	1,74	1,80	
	1:49	1,95	2,00	1,98	
	1:99	2,10	1,95	2,00	
1,00	1:0	1,10	1,00	1,00	±0,02; 0,2%
	1:1	0,99	1,00	1,00	
	1:9	1,00	0,88	1,00	
	1:49	1,00	0,88	0,94	
	1:99	1,00	1,06	1,08	
0,50	1:0	0,50	0,48	0,48	±0,01; 2,0%
	1:1	0,50	0,46	0,46	
	1:9	0,46	–	0,46	
	1:99	0,46	0,46	0,50	

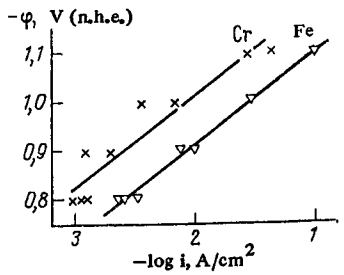

Fig. 2. Partial rates of deposition of iron (▽) and chromium (×) in alloy vs potential.

tion containing 0.48 M $Cr_2(SO_4)_3$, 0.40 M $FeSO_4$, 2 M urea, and 2 M $(NH_4)_2SO_4$ (pH = 2.0) at 65°C.

The method can also be used to determine the rates of dissolution of Fe–Cr alloys in hydrochloric acid.

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