Thus, the determination of iron in ores reduces to measurements of η_1 and η_2, and the iron content is then found with the aid of a calibration graph from the intersection of the straight line for η_2 with the curve for constant η_1.

The root-mean-square error is $\sim 0.3\%$ Fe with a maximum value of 0.6% Fe.

INVESTIGATIONS RELATING TO THE THEORY OF ELECTROCHEMICAL PHASE ANALYSIS OF ALLOYS

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In the preceding paper on electrochemical phase analysis [1] it was shown that the relative polarizability of the phases is of principal significance for phase separation by this method. The polarization of the anode phase depends on the composition of the electrolyte and the electrolysis conditions, i.e., the current density, temperature, duration of electrolysis, etc. Later, Koch and his associates [2] obtained interesting polarization curves for steel in halide and citrate solutions. These investigations provide a basis for research in the field of electrochemical phase analysis of metals, but they are inadequate for more concrete generalizations, as they are concerned with only one metal – steel.

The materials studied in the present investigation were nickel-based alloys of the nimonic type; here it is necessary to separate at least three phases – the basic solid solution, the intermetallic compound, and the carbide. The main difficulty lies in the separation of the first two phases, as they are similar in composition and properties.

TABLE 1

Chemical Composition of Samples*, %

Sample No.	C	Cr	Ti	Al
1	0.02	20	2.76	0.62
2	0.29	20	2.60	0.68
3	0.74	19.9	2.63	0.52

*Remainder is nickel.

The aim of the present work was an electrochemical study of methods of phase analysis of nickel-based alloys, including those proposed by us in this paper and earlier [3], and those developed by N.I. Blok and his associates [4].

Three groups of samples were prepared for the investigation; their composition is given in Table 1. The choice of the alloy compositions was determined by the necessity to have three phases in the appropriate heat-treatment. Samples of each composition were subjected to three different heat-treatments, which resulted, respectively, in simultaneous separation of carbide and intermetallic compound, separation of the carbide only, and nonseparation of disperse phases* (the first treatment was: t = 1080°, exposure 8 hours, cooling in air and aging at 800° for 24 hours, cooling in air; second treatment: t = 1080° for 8 hours, cooling in air; third treatment: t = 1250° for 4 hours, cooling in water).

Phase separation was effected by the following methods:

1) isolation of the intermetallic compound and carbide by the TsNIIChM** [3] method – anodic dissolution of the sample in an electrolyte containing 3% $FeSO_4 \cdot 7H_2O$ + 3.5% NaCl + 5% H_2SO_4, at current density 0.025 to 0.05 amp/cm^2 for 1-1.5 hours;

2) isolation of the intermetallic compound and carbide by the method of N.I. Blok et al. [4], with an electrolyte of the composition 0.9% $(NH_4)_2SO_4$ + 0.9% citric acid, current density 0.05 amp/cm^2;

*The selection of alloys and heat treatments was based on advice from G.V. Estulin.

**TsNIIChM = Central Scientific Research Institute of Ferrous Metallurgy – Publisher's note.

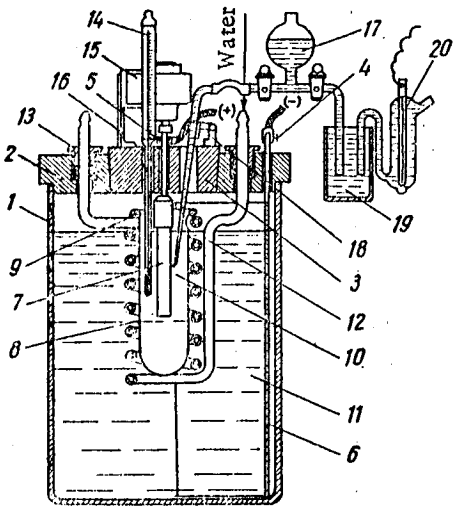

Fig. 1. Measurement apparatus and the TsNIIChM-2 cell: 1) electrolysis vessel; 2) lid; 3) insert; 4) cathode bar; 5) anode bar; 6) cathode; 7) anode; 8) collodion bag; 9) ring; 10) anolyte; 11) catholyte; 12) coil; 13) socket; 14) thermometer; 15) motor; 16) support; 17) electrolytic bridge; 18) clamping device; 19) intermediate vessel; 20) calomel half-cell.

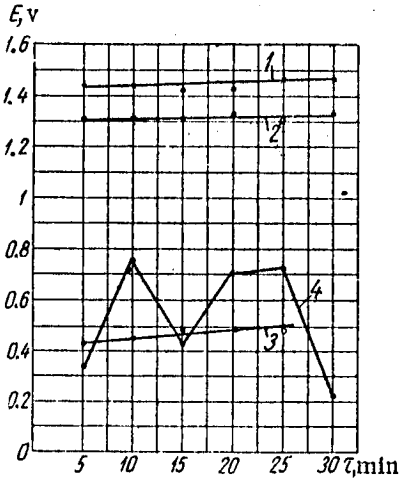

Fig. 2. Anode potentials during dissolution of samples: 1) TsNIIChM method [3]; 2) N.I. Blok's method [4] (electrolyte – 0.9% $(NH_4)_2SO_4$ + + 0.9% citric acid); 3) N.I. Blok's method (electrolyte 1150 ml of methanol + 50 ml HCl); 4) new TsNIIChM method for carbides.

3) isolation of the carbide by the method of N.I. Blok et al., with an electrolyte consisting of 1150 ml of methanol + 50 ml HCl (sp.gr. 1.19), at current density 0.05 amp/cm^2, with cooling;

4) isolation of the carbide by our new method, with an electrolyte containing 15% NaCl + 2.5% tartaric acid, current density 1.0 amp/cm^2. Carbide was also isolated by the method proposed by us earlier, in which the electrochemical residue after dissolution by the TsNIIChM method was treated with 5% sulfuric acid solution on warming (but not boiling) for one hour.

All the electrochemical dissolution processes were accompanied by determinations of anode potentials used for the plotting of "potential-time" curves; the determinations were performed by the compensation method with the aid of the LP-5 electronic potentiometer; the reference electrode was a saturated calomel half-cell. The most suitable apparatus for the determinations was devised and tested; this consisted of an electrolytic bridge filled with the electrolyte, and an intermediate vessel containing potassium chloride solution, in which the tip of the calomel electrode was inserted. This apparatus is shown in Fig. 1 together with the TsNIIChM-2 electrolytic cell, in which the anolyte can be heated or cooled, the sample rotated, and the potential measured. The sample dissolves during electrolysis and a gap is formed between the electrolytic bridge and the sample. The lid of the electrolytic cell is fitted with a clamping device for elimination of this gap, which changes the value of the measured potential.

Table 2 contains analytical results for the electrolytic precipitates obtained by the first and second methods from samples of all three compositions after heat-treatment which resulted in separation of the intermetallic compound and carbide. The measured pH values are given; these changed little during the electrolysis because of its brief duration.

Table 3 contains analytical results for carbide residues obtained by different methods from samples containing either two disperse phases or the carbide phase only. The purity of the carbide residues was confirmed by x-ray structural analysis. Figure 2 shows the results of determinations of anode potentials during dissolution of the samples in all four electrolytes.

TABLE 2

Composition of the Isolated Phases in Relation to the Electrolyte Composition (Current density 0.05 amp/cm^2)

Sample No.	pH	Electrolyte composition, %	Amount of phase isolated, %	Composition of electrolytic precipitate (% on the metal)				
				Cr	Ni	Al	Ti	Fe
1	2.0	3% $FeSO_4 \cdot 7H_2O$ 3.5% NaCl 5% H_2SO_4	3.96	0.23	2.28	0.22	1.16	0.076
	3.5	0.9% $(NH_4)_2SO_4$ 0.9% citric acid	4.19	0.27	2.41	0.23	1.21	0.07
2	1.9	3% $FeSO_4 \cdot 7H_2O$ 3.5% NaCl 5% H_2SO_4	7.38	2.31	4.22	None	0.82	0.03
	3.4	0.9% $(NH_4)_2SO_4$ 0.9% citric acid	7.72	2.42	4.38	None	0.9	0.025
3	2.0	3% $FeSO_4 \cdot 7H_2O$ 3.5% NaCl 5% H_2SO_4	4.57	4.01	0.17	None	0.32	0.076
	3.2	0.9% $(NH_4)_2SO_4$ 0.9% citric acid	4.82	4.21	0.24	None	0.31	0.06

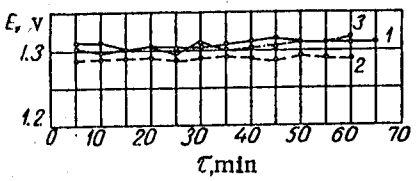

Fig. 3. Variation of potential with time for different heat-treatments: 1) sample 2; 2) sample 2a; 3) sample 5 (disperse phases not isolated).

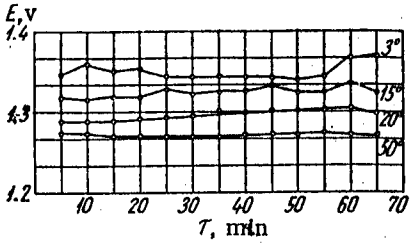

Fig. 4. Variations of potential with time at different temperatures (sample 1).

Next, the role of phase composition of the alloy in establishment of the anode dissolution potential was determined. The expected results of heat-treatment were confirmed by analysis. Figure 3 shows potential-time curves for a number of samples differing in phase composition, determined in the TsNIIChM electrolyte used for isolation of the intermetallic compound. In all cases the anode dissolves at almost the same potential, which must evidently be the decomposition (dissolution) potential of the passive anodically-polarized basic metallic phase (solid solution). This potential varies only slightly with changes in the concentrations of the alloying elements in the solid solution.

The effect of temperature on polarization was also studied; Fig. 4 gives data on anode potentials which show that the potential decreases with increase of temperature, evidently as the result of depassivation. At temperatures above 5°, about 10% of the intermetallic compound phase is lost, probably as the result of solution of the depassivated fine particles of the compound.

The possibility of using high-current densities with the TsNIIChM electrolyte for isolation of intermetallic compounds was investigated. Increase of current density leads to sharp fluctuations of potential with a tendency

TABLE 3

Composition of Carbides

Sample No.	Characteristics of samples	Isolation method	Composition of carbides, %*	
			Cr	Ti
1	Intermetallic compounds and carbides present	Electrolyte: 3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4. Intermetallic compounds dissolved in 5% H_2SO_4	None	0.08
		15% NaCl + 2.5% citric acid; D = 1.0 amp per cm^2	None	0.07
1a	Carbides only present	3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4; without treatment in H_2SO_4	None	0.1
2	Both phases present	Electrolyte: 3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4. Intermetallic compounds dissolved in 5% H_2SO_4	2.31	0.12
		15% NaCl + 2.5% citric acid; D = 1.0 amp per cm^2	2.2	0.09
2a	Carbides only present	3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4; without treatment in H_2SO_4	2.5	0.01
2b	Both phases present	3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4; intermetallic compounds dissolved in 5% H_2SO_4	3.89	0.26
3	Both phases present	15% NaCl + 2.5% citric acid; D = 1.0 amp per cm^2	3.36	0.2
4	Carbides only present	3% $FeSO_4$ + 3.5% NaCl + 5% H_2SO_4; without treatment in H_2SO_4	3.6	0.3

*No nickel or iron.

to transient shifts very high positive values. It seems that at high current densities the higher decomposition potential of the passive intermetallic compound is reached, but after it has been partially dissolved the main phase of the solid solution is again attacked, etc. Analysis showed that the intermetallic compound is not dissolved completely in the process.

The metal is not dissolved uniformly in the TsNIIChM electrolyte for isolation of carbides; uniform dissolution occurs only in the range of D_A = 0.9-1.2 amp/cm^2. Further increase of current density merely leads to even sharper fluctuations of potential, and is of no advantage for the analysis. The results of determinations of the anode potentials are given in Fig. 5.

The carbide electrolyte (of the All-Union Scientific Research Institute of Aviation Materials), which has high resistance, can be used for isolation of carbides at low current density (0.05 amp/cm^2).

Comparison of the analytical data with the values of the potentials leads to the conclusion that the level of the anode potential, or the degree of anodic polarization, is of determining significance in the isolation of any particular phase. Indeed, both the electrolytes used for isolation of the intermetallic compound under the conditions described – the TsNIIChM and the Blok electrolytes – are characterized by approximately the same value for the potential which becomes established during dissolution (1.3-1.4 v). The electrolytes which can be used for isolation of the carbides only under these conditions are characterized by much lower, but also similar, values of the established potentials (0.4-0.7 v). It is clear that in the isolation of phases, neither the electrolyte pH (the TsNIIChM electrolyte is considerably more acid than the Blok electrolyte), nor such characteristics as the conductivity (this is also higher for the TsNIIChM electrolyte) and current density, nor any characteristics of electrolyte composition (the current density for carbide isolation is high in the TsNIIChM method and low in the Blok method; Blok's "carbide" electrolyte is nonaqueous, while the TsNIIChM electrolyte is aqueous) play a decisive role. All these factors are significant insofar as they ensure the necessary level of anodic polarization.

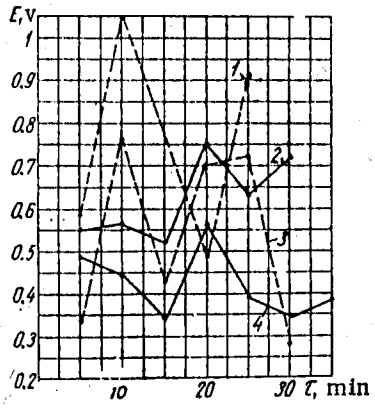

Fig. 5. Variations of potential with time in electrolyte containing 15% NaCl + 2.5% citric acid at the following current densities: 1) 1.25 amp/cm^2; 2) 0.9 amp/cm^2; 3) 1.1 amp/cm^2; 4) 1.20 amp/cm^2.

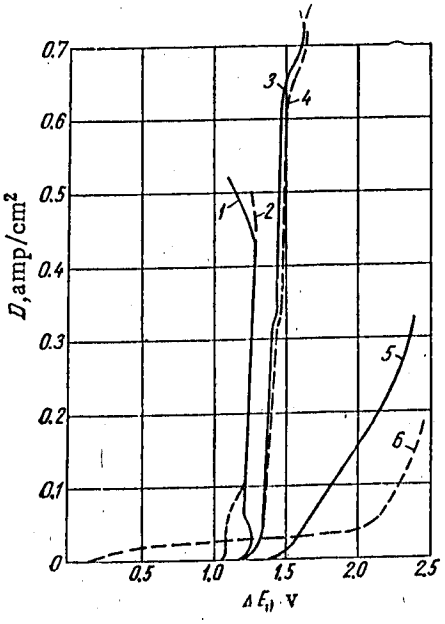

Fig. 6. Anodic polarization curves for electrolytes of 2-2.3 N anionic concentrations of: 1) NaCl + tartaric acid; 2) HCl; 3) $FeSO_4 + H_2SO_4$; 4) H_2SO_4; 5) Na_2HPO_4; 6) H_3PO_4.

To explain these results, polarization curves were plotted for a sample with two disperse phases, in TsNIIChM electrolytes and certain other solutions (Fig. 6). The metal dissolved with considerable polarization in all the electrolytes; this indicated that the metal surface became passive. The slope and the small limiting-current region of the curve for sulfuric acid electrolyte indicate that the lower branch of the curve corresponds to dissolution of the passivated anodically-polarized solid-solution phase (the α-phase), and the upper branch – to that of the intermetallic phase (α'-phase), which differs only slightly from the latter. It follows that fine regulation of potential is necessary in analysis of the metallic phases in these alloys; analysis with control of the anode potential is advisable for this purpose.* It is possible that the systematic small difference between the amounts of electrolytic residue obtained in the TsNIIChM and Blok methods (see Table 2) is due to the fact that in the latter method a somewhat lower anode potential becomes established, and the α'-phase is therefore isolated more completely. It is significant that in aqueous chloride electrolytes the polarization potential decreases at higher current densities. This result is of great theoretical significance, which is discussed below. The same value for the potential is obtained in methanol electrolyte at moderate current densities (see Fig. 2). The decreased passivity leads to dissolution of all the metallic phases, and permits isolation of the carbide phase.

Certain basic principles of a general theory of anodic dissolution in relation to the phase analysis of alloys may be formulated from the results of the present investigation and the data of other workers [1, 2].

1. The important role of passivity has been demonstrated – the values of the dissolution potentials indicate that metal is dissolved when in a more or less passive state.

For separation of phases which differ sharply in thermodynamic properties (metal-carbide, or metal-nonmetallic inclusions), considerable passivation of the metal is not necessary; on the contrary, retention of the metal in a relatively active state assists separation.

2. Polarizability of metallic phases depends on the nature of the metal, and more especially, on the nature of the electrolyte used, namely, on the anion present in the latter. Therefore, two laboratories, working independently, empirically chose sulfate electrolytes for separation of intermetallic compounds, and chloride electrolytes for separation of carbide phases, in phase analysis of alloys of the nimonic type.

The experimental results, as a whole, indicate that the electrolyte anions form compounds with the metal cations on the surface of an anodically polarized sample. A given metallic phase is dissolved when the dissolution potential of these surface chemical compounds is reached.

3. The stability of the surface chemical compounds on the anode (the degree of passivity) depends, for a

*A special potentiostat has been designed for this purpose in our laboratory; this will be described in another communication.

given metal, on the charge and deformability of the dominating anion. It is higher for bivalent than for univalent anions; and higher for trivalent than for bivalent anions; etc. It is higher for the easily deformed iodide ion than for chloride or bromide ions; and higher for large organic anions than for elementary inorganic anions.

4. In addition to the principal passivation agents, anions, electrolytes for phase analysis also contain various activators; these are anions of lower valence than the principal anions, or hydrogen ions, or metal cations of lower valence (such as Fe^{2+}).

5. For the anode process to occur in the dissolution region of the surface compound, a correct relationship must be maintained between the rate of the electrochemical process and the rate of the chemical process in which the surface compound is formed. If the rate of the electrochemical process is too high because of an excessive current density or, conversely, the chemical process is retarded because of difficulties in migration of the anions to the anode, for example, in a nonaqueous electrolyte of high resistance, the metal passes into solution from a nonpassive or only partially passive state. This accounts for the paradoxical decrease of polarization potential at high current densities in chloride electrolytes, and for the possibility of isolating carbide in a methanol electrolyte with simultaneous dissolution of all the metallic phases.

6. The closer the phases, such as the α- and α'-phases in nimonic alloys, are in properties, the higher is the degree of passivity necessary, as in such cases the stability of the surface chemical compounds formed by the phases with the same anion differs appreciably (compare the limiting-current plateau on the polarization curves for alloys of the nimonic type in sulfate electrolytes).

7. The temperature may also be significant in activator action.

The foregoing considerations can now be used for the planned development of methods of anodic dissolution for phase analysis of metallic alloys. These considerations probably have wider significance, and may also be applicable to electrical etching and polishing processes.

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PHASE ANALYSIS OF NITRIDED STEELS

N.I. Blok, M.N. Kozlova, N.F. Lashko and A.G. Andreeva

The hardness, wear resistance, and corrosion resistance of steels are increased by surface saturation with nitrogen. Nitriding, even under the optimum conditions, produces layers in which the corrosion resistance varies in depth. As a result of this, milled nitrided parts are liable to severe corrosion in use. Layer tests revealed the existence of several zones of different corrosion properties and different electrode potentials.

For elucidation of the causes of differences in the corrosion resistance of the nitrided layers of stainless austenitic steels, we developed methods for phase analysis of nitrided steels, and studied the nature of the phases and distribution of the alloying elements between the phases and solid solution at different depths of the nitrided layer. The investigation was performed* with 25Kh18N8V2 steel.

*Senior technician N.M. Rudneva took part in the experimental work.