

THE ELECTROCHEMICAL SEPARATION AND INVESTIGATION OF THE CONNECTING AND CARBIDE PHASES OF HARD TUNGSTEN-COBALT ALLOYS

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A technique has been developed for the electrochemical separation of the carbide and connecting phases in WC-Co alloys. The Co phase was isolated with 6 M HCl, at a current density of 0.03 A/cm² and a potential difference between the electrodes of 0.8-0.9 V; the WC phase was isolated with 6 M NaOH, at a current density of 0.6 A/cm² and a potential difference of 3 V.

The method of electrochemical phase separation, with subsequent chemical analysis of the alloying components, was used to determine the composition of the connecting phase in WC-Co alloys. The electrolytes were caustic soda and hydrochloric acid in which, respectively, the carbides of tungsten and cobalt had been dissolved. Polarization curves were first obtained for electrodes of pure cobalt and of tungsten carbide. The cathode was spectral pure graphite. In HCl solution, with an anode potential about 0.1 V and a current density about 0.03 A/cm², there was intense dissolution of cobalt (Fig. 1, curve 1). The potential of a tungsten carbide anode (Fig. 1, curve 2), without application of an external emf, was about 0.5 V. When this was increased to 1.1-1.2 V, gaseous chlorine was evolved and this oxidized the carbide.

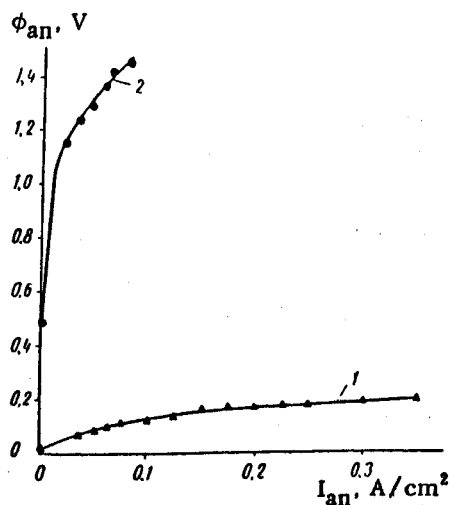


Fig. 1. Anodic polarization curves of 1) cobalt and 2) tungsten carbide at 25°C, in 3 M HCl.

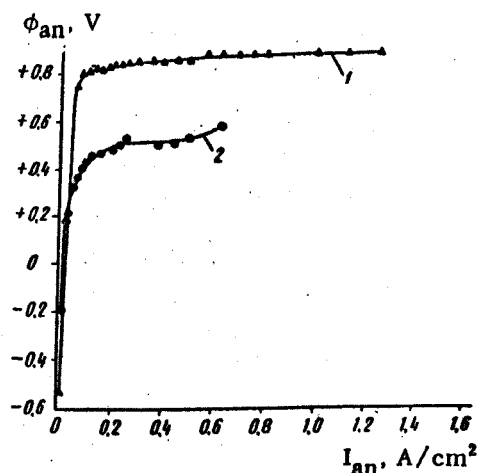


Fig. 2. Anodic polarization curves of 1) cobalt, and 2) tungsten carbide, at 25°C, in 6 M NaOH.

The anodic potentials of cobalt and of tungsten carbide in 6 M NaOH, without an externally applied emf, were -0.5 and -0.20 V respectively (Fig 2). For a tungsten carbide anode (curve 2), a bend in the curve was observed at 0.5 V. A current density of about 0.6 A/cm² corresponded to the point of intense oxygen discharge at the anode. The tungsten carbide was oxidized to WO₃, and this then dissolved in the alkali to give sodium tungstate. At a cobalt anode (curve 1), oxygen evolution* and passivation of the anode occurred at about 0.8 V. Thus the large difference between the anodic polarization potentials of tungsten carbide and cobalt made it possible to carry out an electrochemical separation of the connecting and carbide phases of WC-Co alloys.

*N. M. Popova, M. F. Rybina, Zavodskaya laboratoriya, XIV, 5 (1948).

A study was made of the behavior of tungsten carbide and cobalt in electrolytes of various concentrations. The results, given in Table 1, showed that, even at high current densities, there was selective dissolution of the phases. However, in the electrochemical phase separation of cermet hard alloys, the behavior of the carbide and cobalt phases might differ from that of the individual components.

TABLE 1. The Electrochemical Dissolution of Tungsten Carbide and Cobalt in Various Electrolytes (Constant Current, Graphite Cathode)

Anode	Electrolyte	Electrolysis Conditions			Change in weight, g	Results of qualitative analysis
		Voltage between electrodes, V	Current density, A/cm ₂	Duration, h		
WC	3-m. HCl	1	0.05	3	—	No W
WC	6-m. NaOH	4	1.1	2	3.580	Much W
Co	3-m. HCl	1	0.05	3	1.5624	Much Co
Co	6-m NaOH	4	1.1	2	—	No Co

This might happen, firstly, because the connecting phase in WC-Co alloys a solid solution of tungsten and carbon in cobalt (the content of dissolved tungsten carbide in cement alloys is 1-5%), which might lead to a partial displacement of the cobalt potential and hence to a partial dissolution of the cobalt on electrolysis in NaOH.

With this in mind, we carried out experiments on the electrochemical dissolution in NaOH of WC-Co alloys, which contained various amounts of cobalt, and qualitatively determined the cobalt content of the solutions. In all cases, no dissolution of cobalt was observed.

Secondly, dissolution was accompanied by accumulation of one of the components on the sample surface. This was particularly significant in the electrochemical dissolution of cobalt in acid, when the sample surface became isolated from the electrolyte by tungsten carbide. The current density on the individual particles of Co phase would then increase markedly, the anode potential would alter, and chloride ion discharge would begin, leading to oxidation of the tungsten carbide (see Fig. 1). This could be avoided by renewing the sample surface by special means, and by maintaining the current density constant.*

TABLE 2. The Results of Electrochemical Dissolution of the Connecting and Carbide Phases of Hard WC-Co Alloys

Grade	Change in sample weight after dissolution	Contents of elements in solution, g	Error of determination, % rel.
V20*	0.0738	0.0708	4
V20	0.9972	0.9175	8
	0.6066	0.5940	2
V15	0.4040	0.3697	8
	0.3160	0.2923	8
V8V	1.5530	1.4918	4
V6V	1.0366	1.0619	3
V6*	0.0908	0.0978	7
V6	0.7512	0.6554	13
V6	0.7700	0.7056	8
V4*	0.0594	0.0617	4

* With the alloys marked, the cobalt was separated in 6 M HCl, at 0.8 to 0.9 V, and at an initial current density of 0.03 A/cm². With the other alloys, the tungsten carbide was separated with 6 M NaOH, at 3 V and 0.6 A/cm².

We used an alternative method. The potential difference between the electrodes was held constant during electrolysis at 0.8-0.9 V, so that the anode potential hardly altered and the current density decreased. Electrolysis was continued for 3-4 h so as to ensure that the necessary quantities of cobalt and alloying elements for analysis were dissolved. There was less danger from the formation of a cobalt film on the sample surface during the electrochemical dissolution of tungsten carbide in caustic soda, since an increase in anode potential to 0.8 V led only to passivation of the cobalt (see Fig. 2).

Table 2 shows the results for qualitative determination of tungsten carbide and cobalt. The investigations were carried out on alloy moldings of dimensions 5 × 5 × 35 mm. In the case of dissolution of connecting phase in acid, cobalt and tungsten were determined, and then the tungsten carbide was calculated from the tungsten. It is clear from Table 2 that there was satisfactory agreement between the weight of dissolved material, as found by weighing the sample before and after electrolysis, and the weight calculated from chemical analysis of the solution.

Electrochemical separation of the carbide and connecting phases was carried out on WC-Co alloys, alloyed with molybdenum, chromium, and aluminum, under the same conditions for electrolysis and quantitative determination of the alloying components. These alloying elements dissolved without formation of a deposit. Table 3 shows the compositions of the original alloys and the results of electrochemical and chemical determinations of the alloying elements. For the purpose of chemical analysis, the samples were first powdered and sieved. Powder samples were then treated with a mixture of concentrated sulfuric acid and ammonium sulfate. The alloying elements in solution, after electrochemical separation, were determined as follows: aluminum gravimetrically, chromium by the persulfate-silver method (titration with ferrous ammonium sulfate), and molybdenum colorimetrically.

TABLE 3. Results for the Separate Phase Analysis of Alloyed VK15 Alloys

Alloying element	Chemical composition, %		Content of alloying element in alloy, %, according to:			
	Co	WC	Electrochemical separation			Chemical analysis
			In carbide phase	In cementing phase *	Total content	
6% Mo	9	85	6.18	0.5	6.68	2.80
3% Cr	11.4	85	2.06	0.76	2.82	1.86
1, 2% Al	11.5	85	1.46	0.70	2.16	1.60

* Content of alloying constituent.

TABLE 4. Results for the X-ray Structural Investigation of the Cementing Phase in Hard WC-Co Alloys

Grade	Phase composition		Lattice parameter of Co phase A		WC content of Co phase, %	
	Surface untreated	Surface treated*	Surface untreated	Surface treated	X-ray structural analysis	Chemical analysis
V4	Impossible	Traces of WC	Impossible	3.552	2.3	2.44
V6	Not determined	The same	3.554	3.554	3.0	3.03
V6V	Main phase WC with traces of Co.	Lines of CoWO_4	3.547	3.552	2.3	2.18
V12	Not determined	The same	3.554	3.558	2.7	Not determined
V15	The same	—	3.569; 3.572	3.572; 3.574	5.7; 6.0	The same
V20	The same	—	Not determined	3.554	3.0	2.82

* Cobalt was present in the main phase of all the alloys after surface treatment.

The method of separation was applied to the x-ray structural investigation of the connecting phase in hard tungsten-cobalt alloys of various cobalt contents (Table 4). The surface layers of the alloys were first removed by electrochemical dissolution in 3 M HCl, at 3 V, for 10-15 min, followed by washing with alkali.

Electrochemical enrichment in cobalt of the alloy surface made it possible to determine the phase composition and lattice parameter of the cobalt phase in alloys containing 4%, or less, of cobalt. In the case of the untreated alloy surface, the value of the Co phase lattice parameter was distorted by changes in the composition and structure of the phase, and by microstrains, produced by differences between the linear expansion coefficients of the phases in WC-Co alloys. This distortion was not present in the surface layer enriched with cobalt (see Table 4). The tungsten contents of the connecting phase were determined chemically in the acid solution, after electro-

chemical separation from the Co phase, and agreed well with the values calculated from the lattice parameters of the Co phase in the enriched surface.*

THE SEPARATION, WITHOUT USING ACID, OF OXIDE INCLUSIONS FROM CARBIDES AND SULFIDES IN CARBON STEEL

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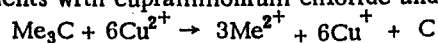
The Ukrainian Scientific Research Institute for Metals

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A method is proposed for the rapid determination of oxide inclusions in carbon steels, based on separation of the oxides from carbides and sulfides by successive treatments with cuprammonium chloride and with iodine. It has been confirmed that methods involving salts and halogens, without acids, show advantages over methods involving acids and oxidizing agents.

In carbon steels and lightly alloyed steels the characteristic carbides are of the cementite type, corresponding to the composition Me_3C . For separation from oxides, the cementite can be decomposed with dilute acids, halogens**, or salts whose cations have sufficient potential to oxidize iron carbide (salts of mercury and copper); treatment of the anodic residues with a solution of iodine in ferric iodide may also be used.*** However, acid decomposition is unreliable, and treatment with iodine solution is slow (5-6 h). Shapiro and Larina**** decomposed carbides in ball bearing steels by using a solution of cuprammonium chloride, containing ferrous ions.

The special features of the iodine and cuprammonium methods enabled us to isolate the oxide phase from carbon steels by successive treatments with cuprammonium chloride and with iodine:



The iodine consumption was considerably reduced because the main bulk of the carbides was removed by the cuprammonium chloride.

The method was tried out on carbon steels containing 0.32 and 0.68% of C. The carbides were decomposed by treatment at 30, 60, and 90°C for an hour. In most of the experiments the amount of copper salt precipitated increased with the rise in temperature. These copper salts dissolved when the deposit was washed with a hot solution of ammonium citrate and ammonia.

Analysis of the residues, after treatment by the method of Shapiro and Larina, showed that, even after treatment at 90°C, there were increases in the iron and manganese contents (assuming that only oxide phase was retained in the residue). Microscopic investigation of the nonmetallic inclusions showed considerable amounts of iron and manganese sulfides (figure, a), which were only decomposed completely after further treatment with a solution of iodine in potassium iodide, at 70-80°C, for 45-60 min (figure, b).

Comparison of the results for oxygen determination in oxides, obtained by various methods, with results for direct oxygen determination in the metal by vacuum fusion (see table), showed that the acid-oxidizing agent method led to partial decomposition of the oxides, even in killed steels. On the other hand, the iodine and cuprammonium-

*A. E. Koval'skii and L. Kh. Pivovarova, *Izvestiya AN SSR, Otdelenie tekhnicheskikh nauk*, 6 (1959).

**Yu. A. Klyachko, A. G. Atlasov, and M. M. Shapiro, *The Determination of Gases, Nonmetallic Inclusions, and Carbides in Steels* [in Russian] (Metallurgizdat, 1953), p. 374-381.

***N. F. Leve, A. B. Gurevich, and L. M. Turubiner, *Zavodskaya laboratoriya*, XX, 1, 26 (1954).

****M. M. Shapiro and O. D. Larina, *Zavodskaya laboratoriya*, XVII, 6, 650 (1951).