ROLE OF THE HIGH-TEMPERATURE SYNTHESIS OF THE TITANIUM CARBIDE PHASE IN LOWERING THE LIMITS OF DETECTION OF IMPURITIES IN HIGH-PURITY TITANIUM DIOXIDE

I. A. Grikit, A. S. Kozhevnikova,
S. N. Dotsenko, and Yu. I. Rys'eva

UDC 669.295.721

In the literature a method is described for the direct atomic emission determination of impurities in high-purity titanium dioxide [1] which involves mixing the titanium dioxide with graphite powder in the ratio 1:1 (to ensure the uniform entry of the sample into the discharge zone), placing the mixture in a thin-walled carbon electrode 2 mm in diameter, 4 mm deep, and with a wall thickness of 0.3 mm, excitation of the spectrum in a dc arc (10 A), and spectrographic recording. In addition, a method is known involving the preliminary concentration of impurities, based on separating the matrix component in the form of titanium tetrafluoride [1], as well as a method for the preliminary concentration of the impurities in titanium dioxide by using special evaporators [2]. The evaporation temperature (1773-2473 K) and period (120-390 sec) varies according to the volatility of the element.

On heating titanium dioxide a violent exothermic reaction takes place. To avoid sputtering of the titanium dioxide it is mixed with graphite powder in the ratio 3:1 by mass.

A method has been published for the distillative separation of elements in the analysis of high-purity titanium dioxide, using silver chloride [3]. In the presence of silver chloride the conversion of the impurities into the form of highly volatile chlorides is the result of heterogeneous reactions which take place at the interface of the solid and gaseous phases (i.e., titanium dioxide and chlorine).

Procedures are known, based on the fractional distillation from the base of the elements being determined in the form of readily volatile compounds (chlorides, fluorides, sulfides, etc.) which are formed in the reaction of the sample material with a buffer in a chamber electrode [4]. The methods described are based on the preliminary concentration of the impurities or on the chlorination or fluorination reactions of components in the sample and the fractional distillation of the elements being determined from the base in the form of highly volatile compounds (chlorides, fluorides, etc.) in order to enhance the sensitivity of the analysis of high-purity titanium dioxide.

A special feature of the methods described is the relatively high labor and time requirement for an analysis. It is necessary to prepare chamber or special thin-walled electrodes (requiring control of the analytical gap while they are burning) and to use a compound based on a precious metal (silver) as a support. When large analytical portions of the samples being analyzed are used with highly volatile chlorinating or fluorinating reagents an unstable explosive entry of the reaction products into the discharge zone is observed, as a result of which the convergence of the analytical results is impaired.

However, in the published studies the role of graphite powder in the high-temperature reactions of titanium dioxide has not been studied when the spectrum is excited with an electric discharge, which is used in practice to prevent the sputtering of titanium dioxide.

It has been established by the present investigations that in spite of diluting a titanium dioxide sample with graphite powder (up to 50%), the intensity of the analytical lines from the impurity elements is scarcely lowered at all, while for certain elements it increases (Table 1). Consequently, graphite powder is not just an inert buffer diluting the base of the sample but participates directly in the high-temperature synthesis of titanium carbide by reacting with titanium dioxide.

X-ray analysis was used to study the reaction products formed by the action of a dc arc (10 A) on the mixture of titanium dioxide with graphite powder. The mixture studied consisted of 70% TiO_2 + 30% C.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 51, No. 5, pp. 735-738, November, 1989. Original article submitted October 4, 1988.

0021-9037/89/5105-1129$12.50

TABLE 1. Values for the Relative Intensity (n) of the Analytical Lines of the Impurity Elements on Excitation by a dc Arc of Titanium Dioxide (SO No. 43) on Dilution with Graphite Powder

Element studied	Ratio TiO_2:C		
	pure TiO_2	2:1	1:1
V	0,48	0,53	0,48
Cr	0,35	0,46	0,51
Al	0,54	0,71	0,77
Si	—0,66	—0,51	—0,36
Mn	—0,65	—0,65	—0,52
Fe	—1,43	—1,39	—1,28

TABLE 2. Thermodynamic and Thermophysical Properties of Carbide

Phase	Melting point, K	Heat of formation of carbides from the elements H_{298}, kcal/mole	Phase	Melting point, K	Heat of formation of carbides from the elements H_{298}, kcal/mole
TiC	3530±150	43,85	Cr_3C_2	2168	21,01
ZrC	3803	44,1±0,68	$Mn_{23}C_6$	—	3,3
V_2C	—	35,2	Mn_3C	—	3,6
VC	3103	24,1	Fe_3C	1923	—5,4
Mo_2C	2963	—4,2	Ni_3C	2373	—9,2
MoC	2973	—9,7	Al_2C_2	1695	33±10
$Cr_{23}C_6$	1773	16,38	Al_4C_3	2373	46,7±10
Cr_7C_3	2053	42,51	SiC	3100 (decomp.)	15,8

On studying the reaction products in the crater of a carbon electrode it was established that the reaction takes place according to the scheme

$$TiO_2 + C \rightarrow Ti_3O_5(\text{base}) + TiO + Ti_6O_{11} + CO.$$

The time for the reaction to take place is 15 sec. On increasing this period to 40 sec an oxycarbide (carbonitride) is formed according to the scheme

$$Ti_3O_5 + C \rightarrow TiC(0, N) + CO.$$

Lower oxides of titanium were also detected.

In order to lower the limits of detection of impurity elements in titanium dioxide obtained by the hydrolysis of high-purity titanium tetrachloride it is suggested that use be made of the high-temperature synthesis effect involving the formation of titanium carbide (TiC) on reducing titanium from titanium dioxide by graphite powder. In order to bind titanium (the base of the sample) in low-volatility compounds it is necessary to ensure that the impurities enter preferentially into the plasma of the electric discharge compared with the base of the sample. For this purpose grade OSCh-7-4 graphite powder was chosen as the reductant and the carbide-forming reactant. The ratio of titanium and carbon for the formation of titanium carbide (TiC) in a low-temperature plasma was established from calculations: 80% Ti + 20% C.

Consequently, it is sufficient to add 20% of graphite powder to the material of the sample (TiO_2) in order to combine the reduced titanium in titanium carbide. However, it is necessary here to take into account the losses of carbon which occur during the reduction of titanium in the formation of CO in the discharge plasma, which was confirmed by x-ray phase analysis. It was established experimentally that it is desirable to add 30-50% of graphite powder to the material of the sample (TiO_2), this scarcely lowering the intensity of the analytical lines but improving the convergence of the analytical results.

The heats of formation of the carbides decrease on passing from the carbides of the subgroup IV metals (in this case the metals Ti, Zr) to the metals in subgroups V-VIII (V, Cr,

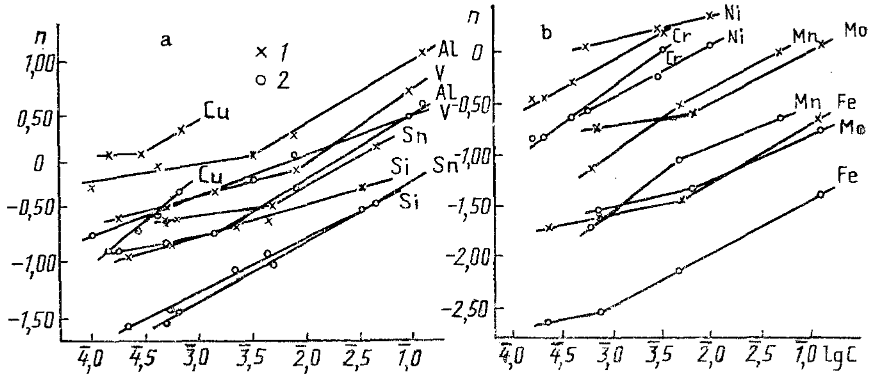

Fig. 1. Calibration graphs for determining impurities in purified titanium tetrachloride: silicon, tin, vanadium, aluminum, copper (a) and iron, molybdenum, manganese, chromium, nickel (b) by the procedure used in production (1) and by the procedure developed (2).

Mo, Mn, Fe, Ni), which indicates a decrease in the Me—C bond energy, determined by electrons and, consequently, by a strengthening of the Me—Me and C—C bonds [5, 6] (Table 2). Therefore in an admixture with carbon the atomization of impurity elements being determined in titanium dioxide takes place more efficiently than for the element of the base (titanium).

Since the carbides of aluminum and silicon are less thermally stable (judging from the melting points) than titanium carbide, atomization of these impurity elements should also be achieved preferentially compared with the element of the base (this is confirmed by the increase in the intensities of the lines from aluminum and silicon), in spite of the heat of formation of aluminum carbide Al_4C_3 being higher than the heat of formation of titanium carbide.

Since zirconium carbide has almost identical thermodynamic and thermophysical properties to titanium carbide no favorable effect was found of an increase in the sensitivity of determining zirconium in titanium dioxide by using carbon powder.

As a result of these investigations a photoelectric atomic emission method was developed for analyzing high-purity titanium dioxide obtained by the hydrolysis of purified titanium tetrachloride. The prepared mixture of titanium dioxide with graphite powder was poured into the craters of the lower and upper OSCh-7-3 grade carbon electrodes 3 mm in diameter and 2 mm deep. The spectra were excited in the 10 A dc arc of a UGÉ-4 generator. The integration period on the DFS-36 photoelectric unit was 30 sec.

Using the proposed method the detection limit for the impurities in purified titanium tetrachloride (Fig. 1) is lowered and for a determination comprises (mass %): iron, silicon, vanadium, chromium, copper 0.0002; aluminum 0.0001; nickel, tin, manganese 0.0005; molybdenum 0.0008.

The relative mean square deviation (Sr) lies within the limits 0.20-0.30.

LITERATURE CITED

1. Z. G. Fratkin, Zavod. Lab., 20, No. 2, 170-172 (1964).
2. V. T. Kalashnikov and A. N. Shteinberg, Zavod. Lab., 20, No. 2, 178-180 (1964).
3. N. F. Zakhariya and O. P. Turulina, Zh. Anal. Khim., 29, No. 6, 1170-1176 (1974).
4. N. T. Shokina and M. E. Shuvalova, Zh. Anal. Khim., 32, No. 6, 1127-1130 (1977).
5. T. Ya. Kosolapova, Carbides [in Russian], Moscow (1968).
6. V. V. Fesenko and A. S. Bolgar, The Volatilization of Refractory Compounds [in Russian], Moscow (1966).