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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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A MASS-SPECTRAL METHOD FOR THE ANALYSIS OF OXYGEN IN TITANIUM

(Presented by Academician A. P. Vinogradov, 4 V 1964)

Mechanical properties of most metals depend substantially on the oxygen content in them. The sensitivity achieved in determining oxygen in refractory and rare metals is comparatively low: the chlorination and hydrochlorination methods and the bromine-carbon method have a sensitivity of 10^{-2}%, while the vacuum-fusion and isotope-dilution methods have a sensitivity of 10^{-3}% ([1,2]). If the sensitivity of isotope dilution can still be somewhat increased, then in the vacuum-fusion method it has reached the limit determined by the sorption of the evolved gas on metal deposits and by its incomplete extraction from the sample.

Fig. 1

The good sorption capacity of titanium deposits and the high thermal stability of its oxides have led to the fact that oxygen in metallic titanium, by means of vacuum fusion, is determined only with a sensitivity of 10^{-2}% ([3,4]).

The fundamental possibility of determining gas impurities in metals by the mass-spectral method of a vacuum spark is obvious; to prove this it is sufficient to compare the vapor pressure near the spark-discharge channel ([5]) (10^{-1}—10^{2} torr) and the residual-gas pressure of the vacuum system (10^{-8} torr). However, quantitative interpretation in the determination of oxygen is made difficult by the increased yield of its ions in comparison with the elements of the matrix and impurities, a yield which, moreover, depends on the nature of the analy—

of the substances being analyzed and of the state of the surface of the substance under analysis. The use of standards solves the problem of quantitative analysis, but the absolute magnitude of the O_{16} mass background prevents high sensitivity from being achieved. In the case of titanium, application of this method is also complicated by the superposition on the O_{16}^{+} line of the principal isotope Ti_{48}^{3+}. As was shown in (6-8), the contribution of the association process from the vapor to the formation of clusters in the vacuum spark is small. Therefore the

Fig. 2

Figure 2: Fig. 2

lines of titanium compounds with oxygen, TiO, TiO_2, Ti_2O, Ti_2O_2, Ti_3O, can be used for quantitative determinations of oxygen. Of practical importance for such determinations is line 64 (TiO), as the most intense one (Fig. 1).

Table 1

Characteristics of titanium samples

No.	Oxygen content, wt. %	Brinell hardness	No.	Oxygen content, wt. %	Brinell hardness
1	0.022	60	5	0.4	223
2	0.046	95–110	6	0.6	284
3	0.1	150	7	0.8	286
4	0.2	187	8	1.0	325

To study the dependence of the TiO yield on the oxygen content, titanium samples with known oxygen content were used in the concentration range from 0.02 to 1% (0.06–3.0 at.%). The characteristics of the samples are given in Table 1 (the oxygen content is the arithmetic mean result obtained by the methods of vacuum melting and isotopic equilibration in several laboratories). Each sample was analyzed on an MS-7 instrument (AEI, England) with a spark source at least three times (9). The dependence obtained in these experiments of the TiO concentration on the oxygen content in the sample is shown in Fig. 2. The concentration of the oxygen cluster of titanium corresponds to the oxygen content in the metal and is approximately 100 times smaller than it. The latter is apparently explained by the dissociation of a considerable number of complexes in the spark according to the reaction $TiO \rightarrow Ti + O$, which at the same time is the source of atomic oxygen ions in the mass spectrum. The nonlinear character of the dependence in the region of high concentrations is evidently explained by the appearance of a new oxygen phase.

Fig. 2

The results obtained indicate the possibility of quantitatively determining oxygen in titanium from the concentration of the TiO cluster with an accuracy determined by the reproducibility of the method, which averages 30%. The theoretically attainable sensitivity of this method, if the course of the curve (Fig. 2) toward low concentrations remains unchanged, will be $3 \cdot 10^{-6}$% ($1 \cdot 10^{-5}$ at.%) at the maximum sensitivity of the vacuum-spark method, $1 \cdot 10^{-7}$ at.%. The attainment of such sensitivity will be hindered by zinc impurities in concentrations greater than 10^{-7}%, nickel in concentrations greater than 10^{-5}%,

and also by surface oxides of titanium or a film of chemisorbed oxygen on the sample. In experiments with titanium, oxides were removed from the surface by etching the samples in HF; chemisorbed oxygen was removed by sparking the samples for 30 min in the ion source in a vacuum of 10^{-8} torr.

It appears possible to determine oxygen in niobium, tantalum, zirconium, tungsten, rhenium, molybdenum, and other pure metals by a similar method, provided that the instrument is preliminarily calibrated using standard samples.

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Note: Figure translations are in progress. See original paper for figures.