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Abstract

Full Text

CHEMISTRY

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FORMATION OF TANTALUM IODIDES AND IODIDE TANTALUM

The study of iodides and of the properties of metals obtained by thermal dissociation of these iodides is of theoretical and practical importance.

Data on the synthesis of tantalum iodides from the elements are few in the literature and are confined mainly to the works of Rose (^1), Muasson (^2), Korosy (^3) and Alexander and Fairbrother (^4). Rose and Muasson synthesized tantalum iodides at a temperature of 600°; Korosy, Alexander and Fairbrother at 1200–1500°.

Fig. 1. Vessel for thermographic study of the interaction of tantalum with iodine
(labels in the figure: channel for thermocouple; place of charge)

Fig. 2. Heating curve of a mixture of tantalum with iodine (up to a temperature of 390°)

The purpose of the present work was to establish the temperature at which the interaction of tantalum with iodine begins, to obtain tantalum iodides, and also to determine some properties of tantalum obtained by thermal dissociation of its iodides. For the synthesis of tantalum iodides and the production of metal from them, powdered tantalum of 97.8% purity and iodine of chemically pure grade were used. The starting elements were subjected to additional purification. Tantalum was degassed by heating to 400° with continuous pumping off of gases

Fig. 3. Heating curve of a mixture of tantalum with iodine (to a temperature of 670°)

Figure 3: Fig. 3. Heating curve of a mixture of tantalum with iodine (to a temperature of 670°)

Fig. 4. Rod of iodide tantalum. 20×. 1 –on a tungsten core, 2 –on a tantalum core

Figure 4: Fig. 4. Rod of iodide tantalum. 20×. 1 –on a tungsten core, 2 –on a tantalum core

at a residual pressure of 0.05-0.01 mm Hg for 3-4 hours. Iodine was purified by sublimation.

To obtain tantalum from tantalum iodide, the latter was prepared by synthesis from the elements at 550°.

A mixture of tantalum and iodine, with a small excess of iodine relative to stoichiometry, was placed in a dry quartz ampoule, which was evacuated to 0.1-0.05 mm. The sealed ampoule containing the mixture was placed in a furnace and held at 550° for 3 hours. The onset temperature of the interaction of tantalum with iodine was determined by the thermographic method on a Kurnakov pyrometer and was measured with differential platinum-platinum-rhodium thermocouples.

In one quartz vessel (Fig. 1), with a wall thickness of 1-1.5 mm, a mixture of tantalum and iodine was placed; in the other, calcined magnesium oxide, adopted as the standard for the differential recording. The vessels were evacuated to 10^{-2}–10^{-3} mm and sealed. The heating rate was 8-10° per minute.

Fig. 2 shows the heating curve obtained, on which, within the temperature ranges 80-100-200°, an endothermic effect is noted, corresponding to the melting and boiling of iodine. Above 200-250° the curve of the differential thermocouple rises steeply and breaks off at 390°; at this temperature the ampoule exploded.

A quartz ampoule with 3 mm walls was prepared. The heating curve obtained with this vessel is shown in Fig. 3. The first endothermic effect on the curve lies within the same temperature range as in the first case (Fig. 2). At 370° on the curve of the simple thermocouple there is an inflection corresponding to the beginning of the interaction of tantalum and iodine. The rate of the exothermic reaction is so great that no traces of the recording have time to appear on the photographic paper. At a temperature of about 400° there occurs

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desorption of gases from the tantalum powder, which is manifested in a sharp drop of the vacuum in the system during evacuation of the tantalum. This temperature coincides with the beginning of the reaction between tantalum and iodine. From the differential-thermocouple curve it is evident that the interaction between tantalum and iodine proceeds

proceeds with considerable evolution of heat. The end of the exothermic effect is observed at 535°.

X-ray diffraction analysis of the products obtained as a result of the synthesis of tantalum iodides at a temperature of 530–550° revealed the presence of a new substance. According to chemical analysis, the composition of the iodide corresponded to the formula $TaJ_{2.8-3.0}$.

It follows from the thermographic study of the interaction of tantalum with iodine that the reaction begins at 370–400° and kinetically proceeds very rapidly; under the conditions of the experiment performed, the reaction ends at 535°. The tantalum iodide formed undergoes a transformation characterized on the heating curve by an endothermic effect with a minimum at 620°.

In addition to studying the reaction between tantalum and iodine, as a result of thermal dissociation of tantalum iodides we obtained threads of iodide tantalum 0.7 mm in diameter. The character and quality of the deposit obtained on the thread depend on the temperature of the iodide and of the thread, on the position of the iodide relative to the latter, and on the material of the core on which deposition was carried out.

On a tungsten single-crystal thread a deposit with a smooth surface is obtained, consisting of crystals oriented in one direction. The regular arrangement of the crystals is explained by automatic regulation of the rate of crystal growth (Fig. 4, 1). The ends of the thread consist of small, randomly oriented crystals, which is connected with the lower temperature in these places. On a tantalum polycrystalline thread the deposit consists of small, differently oriented crystals (Fig. 4, 2).

The tantalum obtained as a result of dissociation on the incandescent thread, according to spectral analysis, contains almost no gaseous or metallic impurities (iron, tin, lead), possesses plastic properties, and is pressed at room temperature. The microhardness of tantalum perpendicular to the cross section of the wire under a load of 50 g is 130–150 kg/mm^2.

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