Chemistry

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1960

SovietRxiv

Abstract

Full Text

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Investigation of the Niobium–Tellurium System

There is very little information in the literature on the chalcogenides of niobium. The tellurides and selenides of niobium have not been studied. There is only a report ([1]) that niobium selenide is obtained by the direct interaction of elemental niobium and selenium. Niobium sulfides have been studied in greater detail. Biltz and Kocher ([2]) investigated the niobium–sulfur system by the tensimetric method and by X-ray diffraction and found the compound Nb_2S_3, which dissolves sulfur up to the composition NbS_4, and the compound NbS, which dissolves niobium up to the composition $NbS_{0.5}$.

In the work of Hägg and Schönberg ([3,4]), two phases were found in this system: NbS and NbS_2 with narrow homogeneity ranges, the exact boundaries of which were not established, but their crystal lattices were studied in detail. The NbS phase is noteworthy: depending on the excess content of niobium or sulfur relative to the 1 : 1 composition, its structure changes from the WC type to the NiAs type. The NbS_2 phase crystallizes in a lattice similar to $CdCl_2$.

Our work is devoted to the study of the niobium–tellurium system. Preparations with different contents of niobium and tellurium were prepared by sintering ground powders of niobium and tellurium (niobium of 99.8% purity contained impurities of Fe, Ta, Al, Si; tellurium of 99.99% purity). Weighed amounts of the substances were placed in quartz ampoules, which, after evacuation (10^{-4} mm Hg), were sealed. The ampoules were held for 700 hours at 900°, after which they were slowly cooled to room temperature over the course of 350 hours. Some preparations were obtained in the form of rather large crystals, sometimes reaching several millimeters in size, but most were obtained as gray or black powders. The ampoules were opened in air; in this process, preparations containing 20-30 at. % tellurium heated up noticeably. However, identically prepared preparations opened in benzene or acetone and transferred into capillaries under a layer of organic liquid gave, in X-ray examination, diffraction patterns that did not differ from those obtained for preparations opened in air. Some ampoules in which samples containing more than 60 at. % niobium had been sintered were coated on the inside with a very thin white film. This is apparently the result of interaction between niobium and quartz ([5]). The dense deposit obtained remained on the ampoule walls, and the main mass was easily separated from it. The amount of deposit was negligibly small and practically could not change the composition of the preparation.

Fig. 1. Stick diagrams of specimens of the niobium–tellurium system

Figure 1: Fig. 1. Stick diagrams of specimens of the niobium–tellurium system

The prepared specimens differed from one another in tellurium content by 2–3 at. %.

The preparations were studied by X-ray diffraction, using copper radiation. Their electrical conductivities and thermoelectromotive forces (t.e.m.f.) were also measured.

Samples for X-ray diffraction study were prepared mainly by applying the powder, with the aid of liquid zapon lacquer, to a thin glass fiber of Pyrex glass, containing no heavy-offsetof

atoms. The X-ray study was carried out in an RKD chamber* with a diameter of 57.3 mm. The film was loaded asymmetrically. Powder patterns were measured on a comparator with a measurement accuracy of 0.05 mm. The intensity of the diffraction lines was estimated visually on a ten-point scale.

Fig. 1. Stick diagrams of specimens of the niobium–tellurium system (weak lines with intensity 1–2 points are not shown)

As a result of comparing the constructed stick diagrams, three phases of variable composition with broad regions of homogeneity were found in the niobium—tellurium system.

α-Phase. The lines characterizing the α-phase appear in powder patterns of specimens containing even less than 5 at. % tellurium. The presence of metallic niobium is detected in powder patterns of specimens up to the composition $NbTe_{0.15}$ (13 at. % tellurium). With further addition of tellurium, the lines corresponding to niobium disappear and the lines of the α-phase remain. The diffraction pattern of only the α-phase is obtained in powder patterns of all specimens with tellurium contents from 15 to 48 at. %.

β-Phase. The diffraction pattern of specimens containing 50 and more atomic percent tellurium is completely different from that in the case of the α-phase. It should be noted that some reflections belonging to the β-phase appear already in powder patterns of specimens containing 48 at. % tellurium. The diffraction pattern of the β-phase remains unchanged up to the composition $NbTe_{1.70}$ (63 at. % tellurium).

* The chamber was manufactured at the Scientific Research Institute of Physics of Moscow State University.

γ-phase. The diffraction lines not belonging to the β-phase, found on powder patterns of a specimen containing 65 at. % tellurium, constitute the main pattern on the powder pattern of a specimen containing 66.67 at. % tellurium. But the powder pattern of this specimen contains many lines, although weak ones, belonging to the β-phase. Along with the black powder this specimen contains

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

needle-like crystals. A separately taken powder on the X-ray photograph gave a diffraction pattern characterizing a mixture of β- and γ-phases,

Fig. 2. Dependence of the specific electrical conductivity on composition in the niobium–tellurium system

Fig. 3. Dependence of thermoelectromotive forces on composition in the niobium–tellurium system

whereas the selected and ground needle-like crystals gave a diffraction pattern belonging entirely to the γ-phase. Consequently, the specimen containing 66.67 at. % tellurium is two-phase, consisting of β- and γ-phases. With further addition of tellurium the lines belonging to the β-phase disappeared completely.

In the composition range from 70 to 80 at. % tellurium the diffraction pattern does not change and belongs only to the γ-phase. On the powder patterns of specimens containing more than 80 at. % tellurium, lines appear that belong to elemental tellurium.

For measuring the electrical conductivity and the thermoelectromotive force, the specimens were ground into a fine powder, after which they were pressed under a pressure of 13,000 kg/cm^2. To obtain a uniform density distribution, the specimens were kept under the indicated pressure for 3 min. Pellets with a metallic luster and considerable mechanical strength were obtained, 4 mm in diameter and about 15 mm long. The electrical conductivity and thermoelectromotive force of the specimens were measured on an apparatus assembled according to a somewhat modified scheme described by Middleton and Scanlon ([6]). Potentiometers PPTV-1, PPTN-1, and PP were used for the measurements.

The electrical conductivity was measured by the probe method. The probes were iris diaphragms made of tantalum, tightly enclosing the pressed cylindrical specimen and ensuring good contact.

The thermoelectromotive force was measured both relative to chromel and relative to alumel. The difference between these measurements was always about 41 μV/deg, which agrees well with the difference between the thermoelectromotive forces of chromel and alumel relative to lead (41.3 μV/deg ([7])). The values of the thermoelectromotive force of the specimens that we measured were also recalculated relative to lead. The cold end of the specimens was at 20°. The temperature difference between the cold and hot ends was from 10 to 80°.

The electrical conductivity and thermoelectromotive force of pressed powdered

Fig. 4. Phase boundaries in the niobium–tellurium system (20°)

Figure 4: Fig. 4. Phase boundaries in the niobium–tellurium system (20°)

substances are affected both by impurities and by the conditions of preparing the specimens for measurement. Therefore the values of specific electrical conductivity and thermoelectromotive force found by us are not specific to niobium tellurides. To ensure reproducibility of the measurements and the possibility of comparing them, the specimens were prepared from identical starting substances under identical conditions–

···This made it possible to compare the electrical properties of preparations of the niobium–tellurium system.

The dependence of the specific electrical conductivity on composition is shown in Fig. 2, where the abscissa gives the composition of the samples in atomic percent tellurium and the ordinate gives the logarithm of the specific electrical conductivity. As is seen from Fig. 2, the two-phase regions: $\alpha + \beta$, $\beta + \gamma$, and $\gamma + \mathrm{Te}$ correspond to straight lines (the phase boundaries found by X-ray analysis are indicated by dashed lines). In the region of existence of the γ-phase a shallow minimum is found on the curve near the composition $NbTe_3$.

Fig. 4. Phase boundaries in the niobium–tellurium system (20°)

In the case of the β-phase, the specific electrical conductivity gradually increases from the preparation of composition 50 at.% tellurium to the preparation of composition 63 at.% tellurium. The preparation of gross composition $NbTe_2$ is two-phase. The region with a high niobium content is not shown in Fig. 2, since the values of the specific electrical conductivity in this region vary considerably and irregularly from experiment to experiment. This possibly occurs as a result of surface oxidation of finely dispersed preparations of the α-phase (some of the samples of the indicated compositions were heated when the ampoules were opened). Apparently, the oxide film on the surface of the crystallites, which so strongly alters the course of the electrical conductivity, is present in an insignificant amount and therefore cannot affect the results of the X-ray investigation.

Figure 3 shows the dependence of the thermo-e.m.f. of pressed powders on composition. The ordinate gives the values of the thermo-e.m.f. in μV/deg relative to lead. The dashed lines indicate the phase boundaries determined by X-ray analysis. The region of compositions corresponding to the α-phase is not given because of poor reproducibility.

The numerical values of the specific electrical conductivity and thermo-e.m.f. indicate the semimetallic character of the chemical bond in niobium tellurides.

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named after M. V. Lomonosov

Received

14 VII 1960

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