JOURNAL OF SOLID STATE CHEMISTRY, **18**, 377–380 (1976)

Preparation of a Continuous Series of Solid Solutions in the Ta_2O_5–Nb_2O_5 System

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Received April 7, 1975; in revised form March 10, 1976

A continuous series of Ta_2O_5–Nb_2O_5 solid solutions was obtained by anodically dissolving calculated amounts of tantalum and niobium in a saturated solution of NH_4Cl in methanol (at room temperature), evaporation of the solvent, and thermal decomposition of the product at temperatures not exceeding 750–800°C. X-ray diffraction analysis showed that at all Ta:Nb ratios the product was isomorphic with β-Ta_2O_5 (γ-Nb_2O_5); all reflections could be indexed in an orthorhombic cell, with a increasing linearly from 6.170 to 6.192 Å and c decreasing linearly from 3.935 to 3.885 Å as Ta was substituted for Nb. The changes in parameter b as a function of composition were less pronounced and its values were between 3.657 and 3.662 Å. The method may be used for the preparation of various mixed oxides that are difficult to prepare by other techniques.

Introduction

The preparation of true (i.e., solid-solution) mixed oxides in the Ta_2O_5–Nb_2O_5 system has hitherto encountered difficulties, and data from the literature are controversial. Most authors (*1–4*) have reported that solid solutions exist only over a limited range of compositions. For instance, Holtzberg and Reisman (*1*, *2*) and Mohanty *et al.* (*3*, *4*) prepared and characterized a mixed compound $2Nb_2O_5 \cdot Ta_2O_5$ and solutions of Ta_2O_5 in that compound but were unable to obtain single-phase isomorphous mixed oxides over the entire range of compositions. Earlier reports on the preparation of such a continuous series of isomorphous solid solutions (*5*) were subsequently proven incorrect by Holtzberg and Reisman (*2*).

Indeed, the preparation of a continuous series of isomorphic mixed oxides in the Ta_2O_5–Nb_2O_5 system by solid-state reactions between the pure oxides at high temperatures seems to be impossible because of the fact that Nb_2O_5 is monomorphic (i.e., only α-Nb_2O_5 is stable and all other forms transform to it at ~1100°C) regardless of the method of preparation, while Ta_2O_5 is dimorphic (the low-temperature modification is orthorhombic β-Ta_2O_5 while the high-temperature modification is tetragonal α-Ta_2O_5) with a phase transformation at 1360°C. The stable α-Nb_2O_5 is monoclinic and is thus not isomorphic with either of the stable Ta_2O_5 forms so that any attempt to prepare true mixed oxides by high-temperature reactions would not be successful

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[*] In partial fulfillment of Ph.D. thesis, Hebrew University, Jerusalem.

in spite of the close similarity between the Nb^{5+} and Ta^{5+} ions.

However, one of the metastable forms of Nb_2O_5, namely, γ-Nb_2O_5, which exists at temperatures below 750–800°C, is isomorphic with β-Ta_2O_5. A continuous series of isomorphic mixed oxides could thus be prepared if the temperature during preparation is kept below that range. Earlier attempts to prepare such solutions have failed because this condition was not observed. Indeed, since the synthesis and crystallization were carried out at much higher temperatures, the products consisted (*1*, *2*) of α-Nb_2O_5 and β-Ta_2O_5 based solutions in the concentration ranges 0–25 and 51–100 mole% Ta_2O_5, respectively, and of mixtures of phases at intermediate compositions.

In this paper we report the preparation of a continuous, isomorphic series of solid solutions in the title system by an approach that made it possible to overcome the above problem. Calculated quantities of Ta and Nb metals were anodically dissolved in an alcoholic electrolyte and the resulting complexes were decomposed under controlled conditions at moderate temperatures yielding noncrystalline mixed oxides, which were subsequently crystallized at temperatures not exceeding 800°C.

Experimental

(*a*) *Materials and Equipment*

The starting materials were high purity tantalum and niobium foils from A. D. Mackay & Co. and analytical grade methanol and ammonium chloride. The electrolyte used in the anodic dissolution consisted of a saturated (at room temperature) solution of NH_4Cl in methanol, which was prepared and used in the laboratory atmosphere without taking special measures to reduce the water content or prevent absorption of moisture. Under these conditions it was established (by Carl–Fischer analysis) that the water content of the electrolyte was in the range 0.3–0.5 wt.%. At these concentrations, water had no adverse effect on the subsequent dissolution or decomposition, or on the stability of the solutions. Previous studies (*6*) had established that such electrolytes would tolerate up to ~1% water without adverse effect and that the presence of a small amount of water is probably essential for the anodic process. The anodic dissolution was carried out in a conventional three-neck 50-ml electrolysis cell made of Pyrex glass and fitted with a water-cooled condenser; there was no separation of anolyte from catholyte. Controlled direct current was supplied by a Kepco BHK-1000 power supply, with continuous recording of current and potential. Alumina crucibles and an alumina-tube furnace, made in our laboratory and equipped with an Eurotherm temperature control, were used in all heating steps. A Philips diffractometer was used for the X-ray analysis.

(*b*) *Procedures*

In the dissolution step, tantalum and niobium were consecutively made the anode in the electrolysis cell containing 50 ml of fresh methanol–NH_4Cl solution. The amount of each metal to be dissolved was calculated in advance and the necessary anodic current (determined by Faradaic calculations) was passed at a c.d. of 50 mA/cm^2 at room temperature. A platinum wire was used as the cathode; the initial anode-to-cathode surface ratio was 5:1 but this decreased with time, as the dissolution of the anode proceeded. At the end of dissolution, the methanol was evaporated by slow heating (~60°C) in an evacuated system, H_2O was expelled at 110°C, and residual NH_4Cl was decomposed at 350°C. The product, which had an amorphous structure, was crystallized by heating for 24 h at 600–800°C (as a rule, higher crystallization temperatures were required with increasing Ta_2O_5 content, up to 800°C for pure Ta_2O_5). Heating to still higher temperature might conceivably result in these solid solutions reverting to the stable two-phase system as equilibrium is approached.

The products were analyzed by X-ray diffraction (Cr$K\alpha$ radiation). Relatively long wavelength radiation was selected in order to allow better resolution of nearly overlapping peaks. Indexing of the pattern and calculations of cell dimensions were made with the aid of the PIRUM program (*7*).

Results and Discussion

Weighing of the tantalum and niobium anodes before and after the electrolytic dissolution showed that the Faradaic current efficiency was 100%, i.e. tantalum and niobium dissolved as the Ta^{5+} and Nb^{5+} ions, without noticeable contribution from side reactions. The overall chemical recovery of Ta and Nb as the mixed crystallized oxide was also 100%, i.e., there were no losses upon heating. The X-ray diffraction analysis showed that all products were well crystallized and consisted of a single phase. All reflections could be indexed in an orthorhombic cell; the lattice parameters are listed in Table I for pure Ta_2O_5 and Nb_2O_5 and in Table II for the mixed oxides. The effect of oxide composition on structure is summarized in the figures. The entire series of mixed oxides is isomorphic with β-Ta_2O_5 (i.e., also with γ-Nb_2O_5).

The experimental data (Figs. 1 and 2) showed that all oxides form a continuous series of substitutional solid solutions. The lattice parameters a and c of the mixed oxides $(Nb_xTa_{1-x})_2O_5$ changed linearly with x. The values of the parameter b for the mixed

TABLE I

LATTICE PARAMETERS (IN Å) OF ORTHORHOMBIC γ-Nb_2O_5 AND β-Ta_2O_5 AT ROOM TEMPERATURE; COMPARISON WITH LITERATURE VALUES

	a	*b*	*c*
	γ-Nb_2O_5		
This work	6.170	3.661	3.935
Holser (*8*)	6.19	3.67	3.94
Terao (*9*)	6.174	3.658	3.932
Waring (*10*)	6.168	3.664	3.938
Brauer (*11*)	6.21	3.67	3.95
	β-Ta_2O_5		
This work	6.192	3.662	3.885
Holser (*8*)	6.20	3.67	3.90
Lehovec (*12*)	6.20	3.66	3.89
Terao (*13*)	6.197	3.660	3.884
Aladjem *et al.* (*14*)	6.18	3.66	3.88
Stephenson (*15*)	6.198	3.663	3.888
Vermilyea (*17*)	6.18	3.65	3.88

TABLE II

LATTICE PARAMETERS (IN Å) OF ORTHORHOMBIC Nb_2O_5–Ta_2O_5 SOLID SOLUTIONS

Sample	Mole fraction Nb_2O_5	*a* (±0.002)	*b* (±0.002)	*c* (±0.001)
1	0 (β-Ta_2O_5)	6.192	3.662	3.885
2	0.085	6.191	3.662	3.888
3	0.197	6.189	3.662	3.898
4	0.268	6.187	3.657	3.898
5	0.390	6.183	3.660	3.903
6	0.465	6.182	3.659	3.906
7	0.565	6.180	3.658	3.913
8	0.632	6.178	3.659	3.918
9	0.719	6.175	3.657	3.917
10	0.812	6.173	3.659	3.925
11	0.925	6.172	3.659	3.929
12	1.0 (γ-Nb_2O_5)	6.170	3.661	3.935

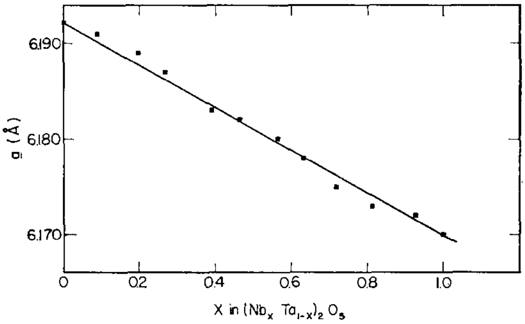

FIG. 1. Parameter a as a function of x in $(Nb_xTa_{1-x})_2O_5$.

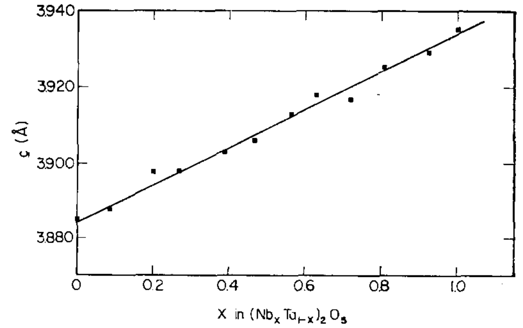

FIG. 2. Parameter c as a function of x in $(Nb_xTa_{1-x})_2O_5$.

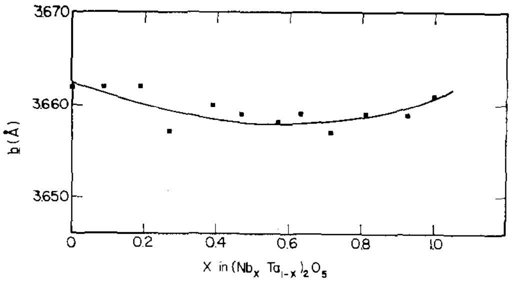

FIG. 3. Parameter b as a function of x in $(Nb_xTa_{1-x})_2O_5$.

oxides were somewhat lower than the respective values for pure β-Ta_2O_5 or γ-Nb_2O_5 but the deviations were too small to show a definite trend. A superstructure has been indicated in the literature for niobium and tantalum oxides in the b direction (*10*, *15*, *17*), but the subject is still controversial and high-resolution lattice image electron microscopy would be needed to establish superstructure in the mixed oxides.

Conclusions

A continuous series of crystalline substitutional solid solutions isomorphous with β-Ta_2O_5 was prepared in the Ta_2O_5–Nb_2O_5 system by electrolytic dissolution and thermal decomposition, limiting the maximum temperature during any stage of synthesis or crystallization to ~800°C. The lattice parameters a and c changed linearly with increasing x in the mixed oxide $(Nb_xTa_{1-x})_2O_5$ while parameter b was relatively constant.

Acknowledgment

The authors are most grateful to P. E. Werner (Institute of Inorganic Physical Chemistry, University of Stockholm, Sweden) who kindly allowed us to use the detailed PIRUM program in our calculations.

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