Nitriding in the reduction of tantalum and niobium oxide compounds with magnesium vapor

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Abstract. The nitriding of the oxide compounds Ta₂O₅, Nb₂O₅, Mg₄Ta₂O₉ and Mg₄Nb₂O₉ was carried out in two stages: 1 — reduction of oxides at the residual pressure of nitrogen or argon in the reactor of 5-10 kPa and a temperature of 820°C for 4 hours; 2 — nitriding of the obtained products in a nitrogen atmosphere at an overpressure of 30-100 kPa and a temperature of 820 or 900°C for 3-12 hours. The phase composition of the powders obtained after magnesium oxide leaching was studied on the DRON-4 diffractometer. The specific surface area was determined by the BET method on the Tristar II 3020 Micromeritics analyzer. Powders were obtained by nitriding Ta₂O₅ and Nb₂O₅ reduction products which are a mixture of nitrides of different composition. The products of the Mg₄Ta₂O₉ and Mg₄Nb₂O₉ reduction are not nitrided.

1. Introduction

Tantalum and niobium nitrides are promising functional materials [1]. The specific surface area of the material is of great importance for a number of applications [2, 3]. One of the nitrides production methods is heat treatment of fine powders of metal or its oxide in ammonia atmosphere [4, 5]. The use of mesoporous powders of tantalum and niobium, obtained by the reduction of their oxide compounds with magnesium vapours, makes it possible to obtain compounds of these metals with nitrogen after 1-2 hours of treatment in an ammonia stream at a temperature of 600-700°C [6, 7]. At the same time, due to the fact that the surface of the powders is determined mainly by pores smaller than 5-10 nm, already at a temperature of 500-600°C it is repeatedly reduced. In addition, the bulk of the powders with a large specific surface area is amorphous oxide [8]. Therefore, tantalum and niobium oxynitrides are formed during the first stage of ammonolysis. The formation of the nitride phase during ammonolysis of niobium powder with a specific surface of 123 m²/g was observed after aging at 700°C [7]. In the ammonolysis of tantalum powder with a specific surface of 56 m²/g even after a three hour exposure at a temperature of 870°C, the reaction product was oxynitride [6].

In this paper, the possibility of obtaining tantalum and niobium nitrides with a large specific surface area during the reduction of oxide compounds by magnesium vapors is investigated. Layers of magnesium oxide, separating the metal particles and determining the structure of the powder [9], should contribute to the preservation of the porosity of the particles and the surface of the resulting nitride. In addition, the reaction products should not contain oxynitrides.
2. Experiment methods and data treatment

Tantalum and niobium pentoxides produced by the Solikamsk Magnesium Works Public corp., as well as tantalate (Mg₄Ta₂O₉) and niobate (Mg₄Nb₂O₉) magnesium were used as precursors. The pentaoxides were additionally heat treated in air at a temperature of 1100°C for 2 hours. Tantalate (TM) and niobate (NM) were synthesized by sintering a mixture of the starting oxides at a temperature of 1300°C for 2 hours.

The process was carried out in a reactor which is a stainless steel retort with a water-cooled flange. Nozzles for connecting to the vacuum system and a thermocouple were in the lid of the retort. The beaker was installed in the retort [10]. A container with magnesium was located at the bottom of the beaker and containers with oxide compounds were placed above it. High-purity nitrogen was fed directly to the reactor without further purification.

The process consisted of two stages in accordance with the results of thermodynamic modelling of interaction in the Та₂О₅-Mg-N₂-Ar system performed using the ASTRA software complex. In the first stage, the oxide compounds were reduced by magnesium vapor for 4 hours at a temperature of 820°C and a residual pressure of nitrogen or argon in the reactor of 5-10 kPa. Next, the reactor was filled with nitrogen and maintaining its overpressure at a level of 30-100 kPa, holding at a temperature of 820 or 900°C for 3-12 hours. The magnesium oxide from the obtained products was leached with a 15% solution of nitric acid. The powder was washed with distilled water and dried at 70°C.

The phase composition of the obtained powders was determined using the JCPDS and ICSD databases. The refinement of the crystal lattice parameters and quantitative phase analysis were performed by Rietveld method.

The X-ray diffraction experiment was performed on an x-ray diffractometer DRON-4 using Cu Kα radiation. Pyrolytic graphite crystal served as a monochromator. The specific surface was measured on a Micromeritics TriStar II 3020 analyzer by the BET method, and the porosity parameters were measured using the BJH method. The content of nitrogen and oxygen was determined by the method of gas-adsorption chromatography in combination with pulsed heating on the K-671 analyzer.

3. Results and discussion

Calculation results of the equilibrium composition of the products in the Та₂О₅-Mg-N₂-Ar system are shown in figure 1. It can be seen that with a sufficient amount of gas for the complete nitriding of tantalum and magnesium, the nitrides of both metals are simultaneously present. With a shortage of nitrogen, the amount of magnesium nitride decreases but free magnesium appears. Experimental results confirmed the simulation results. The reduction of tantalum pentoxide with simultaneous nitriding under nitrogen overpressure did not occur in the reactor, since there is no free magnesium vapor in the system (figure 1a). As a result, only magnesium nitride Mg₃N₂ was obtained. Tantalum pentoxide remained unchanged. This is quite understandable: firstly, the rate of evaporation of magnesium under these conditions is small; secondly, the enthalpy of formation of the nitride Mg₃N₂ is –461 kJ/mol, and TaN is only –252.7 kJ/mol. This means that nitrogen primarily interacted with magnesium. The resulting magnesium nitride is stable at this temperature, there is no free magnesium, therefore, reduction of the oxide and, accordingly, the formation of nitrides does not occur.

After vacuuming to a residual nitrogen pressure of 5-10 kPa, in accordance with the data of figure 1b, magnesium vapors are present in the reactor. The recovery process under these conditions did not differ from the argon carried out at the same pressure. The nitrogen content in the obtained powders depending on the type of precursor and nitriding conditions is shown in figure 2. The figure shows that the temperature and the duration of exposure of the reduction products in the atmosphere of nitrogen in the range of 3-12 hours practically had no effect on its content in the obtained powders.
Figure 1. Phase composition of the Ta-Mg-N₂-Ar system with a sufficient amount of nitrogen for complete nitriding (a) and a shortage of nitrogen 20% (b).

Figure 2. Nitrogen content in powders obtained by reduction and nitriding at temperature 800°C (a) and 900°C (b) depending on the holding time. Precursor: 1 — Nb₂O₅; 2 — Ta₂O₅; 3 — Mg₄Nb₂O₉; 4 — Mg₄Ta₂O₉.

The specific surface area of nitrided powders corresponded to the surface of tantalum and niobium powders obtained by reduction of these precursors under similar conditions without additional exposure in nitrogen atmosphere [10, 11]. When using precursors Nb₂O₅ and Ta₂O₅, it was on average 22 and 25 m²/g respectively. In the case of the precursors Mg₄Nb₂O₉ and Mg₄Ta₂O₉ — 69 and 142 m²/g. The type of sorption and desorption curves after nitriding of the powders corresponds to type IV according to IUPAC.

The shape of the hysteresis loop indicates their mesoporous structure (figure 3). The porosity parameters with changes in temperature and duration of exposure in a nitrogen atmosphere remained almost unchanged when using tantalate or magnesium niobate as a precursor. At the same time, when using tantalum pentoxide as a precursor, an increase in the duration of exposure at a temperature of 820°C from 3 to 12 hours led to an increase in the pore volume from 0.057 to 0.105 cm³/g. Under the same conditions, when using niobium pentoxide as a precursor, the pore volume, on the contrary, decreased from 0.089 to 0.075 cm³/g.

The insignificant nitrogen content in the powders obtained using niobate and magnesium tantalate as a precursor is noteworthy. Based on the size of the surface, the size of the metal particles that make up the skeleton of the formed porous powder particle was calculated. It is 5-6 nm. Therefore, when interacting with nitrogen, any restrictions associated with its diffusion in the metal are absent.

The particle of the reduced oxide compound is a structure consisting of nanoscale metal particles separated by a layer of magnesium oxide of nanoscale thickness [8, 9]. In order for the gas to diffuse and interact with deep metal particles, there must be a free distance between them and magnesium.
oxide. The width of this gap must be greater than the diameter of the gas molecule. The powders obtained by the reduction of tantalates and niobates are characterized by a smaller pore size. This corresponds to thinner layers of magnesium oxide between the metal particles.

![Isoterm Linear Plot](image)

**Figure 3.** Sorption-desorption curves of powders obtained after nitriding at a temperature of 820°C for 6 hours. Precursor: a — Ta₂O₅; b — Nb₂O₅; c — Mg₄Ta₂O₉; d — Mg₄Nb₂O₉.

A comparison of the reaction products nitriding results obtained by the pentaoxides and complex oxides reduction shows that the size of the gap depends on the layers thickness of magnesium oxide. Nitrides were not formed when complex oxides were used as a precursor, because the free distance between the metal and magnesium oxide was insufficient for the penetration of nitrogen molecules into the zone of contact with the metal. In the case of nitriding of the reaction products obtained as a result of the reduction of pentoxides, the initial gap between the metal and magnesium oxide is sufficient for nitrogen to penetrate to the surface of the metal particles in the volume of the reduced particle. Subsequently, due to the absorption of nitrogen, the volume of metal particles increases, the channels of nitrogen supply in the smallest pores overlap. Nitriding at these sites is terminated. As a result, the nitrogen content does not increase and the phase composition of the products practically does not change (Tables 1, 2).

The lower nitrogen content in powders obtained after nitriding for 3 hours (figure 2) is explained by the presence of a metallic phase in their composition.
Table 1. The phase composition of the products of reduction-nitriding Ta$_2$O$_5$

| Nitriding conditions | Phase composition/ICSD |
|---------------------|------------------------|
| $T$, °C | Time, h | $\theta$-TaN/76455 | $\epsilon$-TaN/1396 | Ta$_2$N/76015 | Ta/151407 |
| 820  | 3 | 13 | 4 | 71 | 12 |
| 900  | 3 | 12 | 35 | 34 | 31 |
| 900  | 6 | 3 | 42 | 41 | 17 |
| 900  | 12 | 3 | 59 | 13 | 28 |

Table 2. The phase composition of the products of reduction-nitriding Nb$_2$O$_5$

| Nitriding conditions | Phase composition/ICSD |
|---------------------|------------------------|
| $T$, °C | Time, h | NbN c/604392 | NbN h/76384 | Nb$_2$N/31165 | Nb$_3$N$_3$/76389 | Nb/645059 |
| 820  | 3 | 49 | 20 | 10 | 11 | 10 |
| 900  | 3 | 41 | 38 | 7 | 9 | 5 |

4. Conclusion

It was shown that the production of nitrides in the tantalum and niobium pentoxides reduction with magnesium vapor is possible if the process is carried out in two stages: 1 — reduction with residual pressure of argon or nitrogen in the reactor at 5-10 kPa; 2 — the subsequent exposure of the reaction products in a nitrogen atmosphere. The reduction was carried out at a temperature of 820°C for 4 h, nitriding — at a temperature of 820 or 900°C for 3-12 h. The nitrogen content and phase composition of the products did not change with increasing temperature and duration of nitriding.

The powders are characterized by a mesoporous structure with a specific surface area of 20-28 m$^2$/g. When using Mg$_4$Ta$_2$O$_9$ tantalate or Mg$_4$Nb$_2$O$_9$ niobate as a precursor nitrides were not observed in the obtained products.

The particle of the oxide compound after reduction is a layered structure of alternating particles of magnesium oxide and metal. The size of the gap between the metal and the layers of magnesium oxide should exceed the diameter of the gas molecule to ensure access of nitrogen molecules to the reaction surface. Layers of magnesium oxide are characterized by a much smaller thickness in the reduction products of tantalate and magnesium niobate. The gap between them and the metal is insufficient for the diffusion of nitrogen into the reduced particle.

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