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## INFLUENCE OF SODIUM-THERMIC REDUCTION CONDITIONS ON THE PROPERTIES OF THE NIOBIUM POWDERS

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Two variants for process of recreation of niobium from potassium heptafluoroniobate by sodium metal have been studied: «liquid-phase» recreation (supply of liquid sodium on the surface of the melt containing  $K_2NbF_7$ ), and «eterophase» recreation (supply of solid  $K_2NbF_7$  onto the surface of the liquid sodium). The influence of recreation conditions on the specific surface and on the morphology of the niobium powder has been investigated.

Key words: niobium, metallothermic recreation, potassium heptafluoroniobate, sodium, specific surface

Interest in creating capacitors based on niobium appeared with the development of miniature household appliances, in particular mobile communications which do not require the use of particularly reliable products, and the main role is played by the cost and the possibility to reduce the weight and dimensional parameters of products [1,2]. One of the promising methods of obtaining niobium powders with high surface area necessary for these purposes, besides electrolysis of ionic melts [3,4], is sodium-thermic reduction of niobium from melt containing potassium heptafluoroniobate.

The aim of the present work is to study the influence of the conditions of potassium heptafluoroniobate reduction onto the obtained powders characteristics.

In this paper two variants of the recovery process were investigated: supply of liquid sodium on the surface of the melt containing potassium heptafluoroniobate and flux («liquid phase» reduction), and supply of solid potassium heptafluoroniobate onto the surface of the liquid sodium («heterophase» reduction).

To realize the «liquid phase» reduction process, after the assemblage, reactor with load was placed in oven. For a more complete degassing of salts, reactor was heated in vacuo. After reaching a temperature of 450-500 °C and a pressure of 6-8 Pa, retort was filled with argon, salts were melted, and agitator was lowered into the melt and stirred for averaging the melt composition while increasing the temperature gradually. After the desired temperature is reached, desired pressure differential between the container with a reducing agent and the reactor was established, and the feeding of liquid sodium into the reactor with stirring of the melt.

During «heterophase» reduction, liquid sodium in 10-12 % excess of stoichiometry was poured onto the surface of molten eutectic mixture of  $NaCl$  and  $KCl$ . Then, onto the layer of liquid sodium in the reactor, previously heat-treated solid potassium heptafluoroniobate (PHFN) or mixture  $NaCl : K_2NbF_7$  with a molar ratio of (3-4) : 1 was strewn at a certain rate.

Upon completion of the reduction process, the melt is kept under stirring for about 10-15 min., reactor was cooled, nickel crucible was recovered, and reaction mixture was knocked out and ground to a particle size less than 5 mm. The powder was washed free of salts with distilled water, treated with 10 % aqueous hydrochloric acid solution and then washed with distilled water until pH 7, followed by drying in air at a temperature of 348-378 K (depending on the powder particles size).

The bulk density of powders  $\gamma$  was determined in accordance with GOST 19440. The specific surface area  $S$  was measured by thermal desorption of argon according to GOST 23401. Morphological analysis of the powders was carried out using a scanning electron microscope «Hitachi-800».

To determine the specific charge  $Q$ , anodes with diameter  $d = 2.5$  mm sintered in vacuum furnace at residual pressure not more than  $(5-7) \cdot 10^{-3}$  Pa and temperature 1523-1623 K were used. Time of exposure at maximum temperature was 30-45 min. Density of anodes was 1.45-2.57 g/cm<sup>3</sup> depending on the bulk density of the powder. Oxidation of anodes (molding) was carried out at (50-60) °C in 1,5 % solution of phosphoric acid with up to maximum voltage 50-80 V at constant current density of 70-1000 mA/g, and then at constant voltage during (3-4) h.

«Liquid phase» reduction was carried out in melt with initial molar ratio of flux : PHFN = 4-10. As a flux,  $NaCl$ ,  $KCl$ , or their eutectic mixture were used. Initial melting point of the melt, depending on the flux nature and on the quantity thereof was 933-993 K, final – 1023-1123 K. Melting point growth is due to changes in the composition of the melt : PHFN concentration drops, and the content of sodium and potassium fluorides in melt increases. Accordingly, reduction process was carried out in the temperature range 1003-1113 K. From characteristics of powders obtained by «liquid phase» reduction, it is clear that, from melts with various fluxes, but with the same molar concentration of PHFN, powders with similar specific surface and charge were obtained. Decrease of the initial concentration of PHFN in melt allows one to obtain powders with larger specific surface. Smaller surface area of powders obtained with higher PHFN concentration in the initial melt is due to local temperature increase in the reaction zone with rise of quantity of reagents interacting per unit time.

From characteristics of powders obtained by «heterophase» reduction, one can see that, compared with powders obtained by «liquid phase» reduction process, specific surface area of «heterophase» reduction powders is significantly higher. Moreover, a characteristic feature of such powders is much lower (three to four times) bulk density which was 0.28-0.40 g/cm<sup>3</sup>.

Study of the powders morphology has shown that, during «liquid phase» reduction, the bulk powder is represented by almost equated dendrites composed of individual fragments. The fragments constituting particles are interconnected by bridges. Besides particles of such shape, there are two more morphological variations, namely right faceted crystals with are clearly manifested growth stages and platelet-

shaped particles. However, their number is small. Therefore, the contribution of the dendritic shape particles with the most advanced surface into the powders surface area is the determining factor.

When solid PHFN is supplied onto the molten sodium surface, reaction starts at the PHFN particles surface before their melting, which leads to substantial change in the morphology of the powders. The bulk powder is represented by thin plate-like particles with high surface area partially repeating the form of the PHFN crystals.

Comparison of the powders properties has shown that the powders with larger surface area are obtained by supplying the solid  $K_2NbF_7$  onto the liquid sodium surface. The specific surface area of the niobium powder in this case reaches  $2.9 \text{ m}^2/\text{g}$ . The value of the specific charge of the anodes is increased accordingly. Doping powders by phosphorus (0.005-0.010 wt. %) being the sintering inhibitor in this case has reduced the shrinkage of the anodes by 15-20 % and increased their specific charge up to 20-25 %.

*Conclusions.* The influence of conditions of sodium-thermic reduction of PHFN on the characteristics of the obtained niobium powders was studied. Two options of sodium-thermic reduction process were realized. It was shown that more efficient way to obtain powders with high specific surface area is «heterophase» reduction.

#### LIST OF LITERATURE

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