THEORY, PRODUCTION TECHNOLOGY, AND PROPERTIES
OF POWDERS AND FIBERS

PRODUCTION OF FINE NIOBIUM AND TANTALUM CARBIDE POWDERS

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At the present time, parallel with orthodox techniques, new methods are being increasingly used for the production of carbides. One of them is the plasma-chemical process, which yields materials possessing a number of specific characteristics attributable to their large specific surface.

To obtain basic information on the process of formation of carbides from niobium and tantalum chlorides and also hydrocarbons in a high-temperature hydrogen stream, calculations were made of the equilibrium compositions and some processing characteristics of the Me--C--Cl--H system. The following metal-containing components were considered: MeCl, MeCl₂, MeCl₃, MeCl₄, Me₂C, Me, MeC, and C, their thermodynamic properties were calculated from existing data [1-4]. The condensed components Me₂C, MeC, Me, and C were treated as individual phases. The equilibrium in each system was investigated in the temperature range 1000-5000 °K under a total pressure of 10⁵ Pa.

At ratios C : Me ≥ 1 and H : Cl ≈ 10 the monocarbides of Ta and Nb exist in the temperature range 1000-4000 °K with a yield of 100%. A ratio C : Me = 1 ensures the existence of a single-phase condensed product in the form of MeC, while higher carbon concentrations in the system result in its precipitation into condensate.

The temperature range of existence of condensed carbon is determined by the total carbon content of the system; at C : Me = 2 condensed carbon exists in the range 1000-2500 °K (Figs. 1 and 2). Results of calculations show that there are no thermodynamic limitations on the process of synthesis of Ta and Nb carbides in a high-temperature hydrogen stream.

Tantalum and niobium carbide synthesis experiments were carried out in an apparatus with an arc-plasma device. Starting materials were fed into a graphite-lined mixing chamber. The 40-mm-diameter, 300-mm-long graphite reactor was thermally insulated from the water-cooled shell walls. The mean-mass temperatures of the gas stream issuing from the plasma device varied from 2900 °K for pure hydrogen to 3600 °K for an argon-hydrogen mixture with 3 wt. % H₂.

The rates of flow of plasma-forming gas were 40 g/min for the argon-hydrogen mixture and 5 g/min for pure hydrogen. The rate of supply of chloride vapor was varied from 0.5 to 20 g/min and that of the hydrocarbon from 0.1 to 3.0 g/min. In the jet a ratio H : Cl > 20 was always maintained. Increasing the hydrogen concentration in these reactions accelerates the formation of metal vapors and inhibits the cracking of methane.

A ratio C : Me = 1 in the starting reactant mixture is insufficient for the formation of carbides close to stoichiometric. With increase in the amount of hydrocarbon fed into the stream, the carbon content of the product grows. To obtain powders with carbon contents corresponding to the composition MeC₁.₀, a substantial excess of the carbidizing agent is necessary (Fig. 3). Under these conditions the amount of combined carbon attains a certain value close to the stoichiometric Me : C ratio, and with further increase in the rate of flow of the carbidizing agent the amount of free carbon in the product grows. The composition of the carbide depends on the thermal conditions of the process: with increasing mean-mass jet enthalpy the amount of combined carbon grows (Fig. 4). In this work the yield of a fine fraction was more than 90%. The product obtained was collected on a bag filter. The niobium carbide powders contained from 9 to 13% of combined carbon and from 0.4 to 2.0% of free carbon. On the surfaces of the powders there was up to 1.5% of sorbed HCl, which could readily be washed off or removed by heating at 250 °C, leaving a residual content of ~ 0.1%.

Fig. 1. Equilibrium composition of Nb–C–Cl–H system (0.0357TaCl₃ + 0.0714CH₄ + 0.893H₂).

Fig. 2. Equilibrium composition of Ta–C–Cl–H system (0.0357TaCl₃ + 0.0714CH₄ + 0.893H₂).