PHYSICO - CHEMICAL PROBLEMS OF THE NITRIDE SYNTHESIS IN A SHF-DISCHARGE PLASMA

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ABSTRACT

Problems associated with the synthesis of ultrafine transitional-metal-nitride powders have been considered. The TiN powder dispersion is shown to be controlled within the range 10 to 100 nm, and the VN_x composition within its homogeneity range by varying the basic characteristics of the plasmochemical process. Physico-chemical properties of these powders are investigated.

1. INTRODUCTION

The process design to produce ultrafine nitride powders by hydrogen reduction of chlorides in a SHF nitrogen plasma flow /1 to 5/ gives rise to the following problems: quest for optimal kinetic conditions in a plasmochemical reactor to ensure a thermodynamically possible yield of nitrides; control of the powders dispersion in a wide particle-size range using the basic parameters of the plasmochemical process; formation of the needed phases throughout their homogeneity range; revealing of physico-chemical characteristic features of the nitrides obtained.

Preliminary thermodynamical calculations of M-Cl-H-N systems, where M - Ti, Zr, Hf, suggest that a correlation between the starting components of the gross-reaction $2MCl_4+4H_2+N_2=2MN+8HCl$ being stoichiometric, due to the presence of chlorides in the equilibrium (MCl_4 and MCl_3 in a moderate temperature range, MCl_2 and MCl at high temperatures) the conversion efficiency of MCl_4 into MN is insignificant and has a maximal value in a relatively narrow temperature range (fig.1). In order to fix the nitrides under these conditions, the reaction products must be "quenched" and the nitrides be further separated from lower chlorides. The calculations show that in the case, that the excess of hydrogen and nitrogen is greater than 100-fold, as compared with stoichiometry, there exists a wide temperature range wherein chlorides undergo a 100% conversion into corresponding nitrides. Therefore, in ensuring of the thermodynamically necessary conditions, the real parameters of the process have to be determined by its kinetic characteristics.

A kinetic consideration of said process is difficult due to the fact that studies of heat and mass transfer in a plasmochemical reactor are in an early stage. For simplicity, the diffusion processes occurring in the reactor can be presented as an interaction of various-size turbulent globules of initial hydrogen and chloride jets with the surrounding nitrogen plasma flow. Molecular intermixing and heating of the reactants, as they

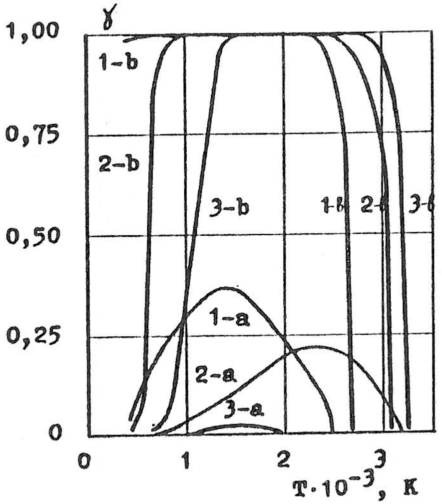

Fig.1. Temperature dependences of nitrides yield with $MCl_4:H_2:N_2$ ratios (here M - Ti (1); Zr (2); Hf (3)) being 2:4:1 (a) and 2:4000:1000 (b).

stay in the high temperature zone (τ_{dif}), occur in the turbulent globules. The rates of chemical reactions being great at elevated temperatures and under the operation of active plasma particles gives evidence to presume that the limiting stage of the process is the stage of molecular mixing and heating of the starting materials in the flow to be completed at a definite path length ($L \sim w_o \tau$). The molecular intermixing time ($\tau \sim \delta / C_{dif}$) depends on the diffusion rate ($C_{dif} \sim f(T)$) and the turbulent globule size. The latter may be determined by Reynold's criterion ($\delta \sim f(w_o d_o / \nu)$). The diffusion length and, accordingly, the conversion efficiency of the starting materials (A) will mainly be determined by the consumption of the reactants introduced into the reactor (w_o), by the channel diameter to introduce the reactants (d_o), by the temperature of the process and by several other factors which allow for the flow gas dynamics, physico-chemical properties of the intermixing masses, apparatus linear dimensions etc. ($L(A) \sim f(w_o,\ d_o,\ T,\ \ldots,\ k_i)$). Despite of the fact that these reasonings are not yet a correct formulation of said problem, they indicate the direction of the quest for optimal parameters of the process.

2. EXPERIMENTAL

An experimental investigation of the above mentioned dependence has carried out for different conditions to introduce a chloride-hydrogen mixture into the nitrogen plasma flow. The investigation results are presented in fig.2.
A comparison between curves I and II shows that a channel diameter diminution intensifies noticeably the intermixing process and, accordingly, increases the total efficiency of the star-

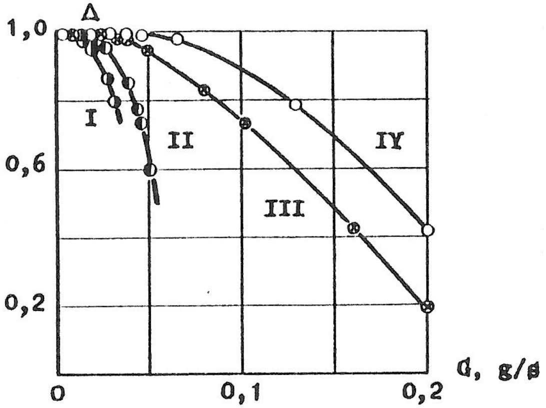

Fig.2. $TiCl_4$ total conversion efficiency as a function of its consumption in various versions of the reactor: I- transversal introduction of $TiCl_4$ via one 2 mm dia channel into a plasma flow at T=4500K, the reactor walls temperature being 400K; II- the same via four 0,75 mm dia channels; III- the same via six 0,8 mm dia channels, the temperature of the reactor walls being 1100K; IY- axial introduction of $TiCl_4$ via one 2,5 mm dia channel into a plasma flow at T=3000K, the temperature of the reactor walls being 1100K.

ting chloride conversion. The reaction completeness is still greater affected by the reactor temperature conditions (curves II and III). An increase of the reactor-wall temperature from 400 to 1100 K results in a smoothed temperature profile of the reacting flow and increased energy contribution to the process due to a decrease of heat losses in the reactor.

A comparison between curves III and IY shows that despite a somewhat lower power supply and worse mixing conditions due to a larger channel diameter, the total $TiCl_4$ conversion efficiency and the consumption range at which chloride reduction is 100% are greater for the case of an axial introduction of the reactants. This proves evidence for a fuller use of the central region enthalpy of the plasma flow.

In the case of a 100% $TiCl_4$ conversion the total amount of volatile admixtures in TiN does not exceed 1to 2% (0,8 to 1,5% NH_4Cl and 0,2 to 0,5% amidochlorides and low Ti chlorides). Allowing for the fact that in TiN the titanium-containing admixtures are less than 1%, one can assume that under said conditions of 100% $TiCl_4$ conversion efficiency the TiN yield is close to 100% as well. In case IY at chloride consumption 0,05 g/s the power consumption to produce 1 kg TiN makes up 130 MJ. That agrees with the thermodynamical calculation results.

As no developed crystallization theory allowing for the kinetics of chemical reactions in the flow is available and because of a variety of operative factors in the experiment, one has to investigate the general effect of different characteristics of the production process, as well as of the equipment, on the dispersion of the nitrides obtained. An averaged characteristic of this dispersion can be the specific surface value (F_{sp}) measured by the low temperature krypton adsorption. The experiments have shown that an F_{sp} change of the nitride powders has a different character depending on the chloride consumption (Fig 3a), the dispersion minimum being apparent within a $TiCl_4$ consumption range $(1{,}7$ to $2{,}8)\cdot10^{-2}$g/s. Here, a smaller $TiCl_4$ particle size and a more pronounced dispersion change with respect to the $TiCl_4$ consumption are observed at an axial introduction of the reactants into the reaction zone. A most likely causative factor for this fact is a lower (as compared with a transversal scheme) temperature level of the process and a smaller effect of coagulation on the particle growth.

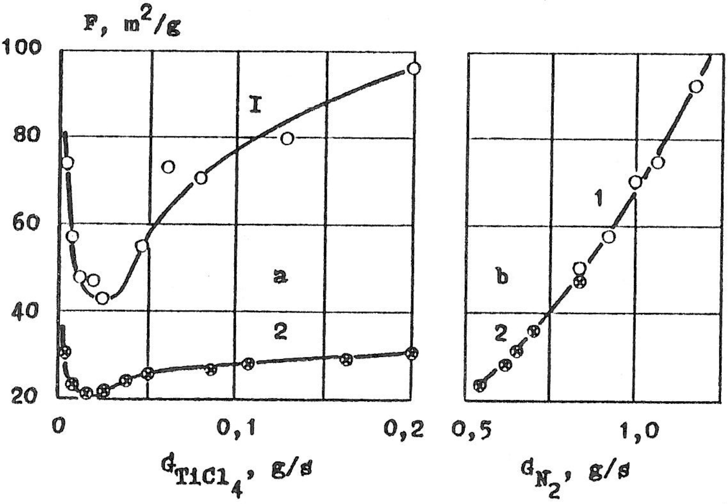

Fig.3. TiN specific surface as a function of the $TiCl_4$ consumption (a) and of the nitrogen consumption (b) at an axial (1) and transversal (2) introduction of the reactants.

The investigations of TiN F_{sp} as a function of the plasmoforming nitrogen consumption at a constant $TiCl_4$ consumption $(1{,}7\cdot10^{-2}$g/s) under its 100% conversion have shown that the two schemes to introduce the reactants are mutually complementary over the dispersion range, and enable one to prepare TiN powders with a mean particle size being 10 to 100 nm.

Due to the error of a chemical analysis of superfine nitrides the compositions cannot be always distinguished from the homogeneity range, therefore the crystal lattice parameter was used as a characteristic to trace the nitride composition. As seen from fig.4, under said conditions, the VN_x composition got changed, actually, throughout the homogeneity range, whereas the TiN composition is close to a stoichiometric one at a sufficiently wide change of the production process characteristics. X-ray investigations of ultrafine powders have shown that TiN crystal lattice gets contracted (fig.5). After a vacuum anneal

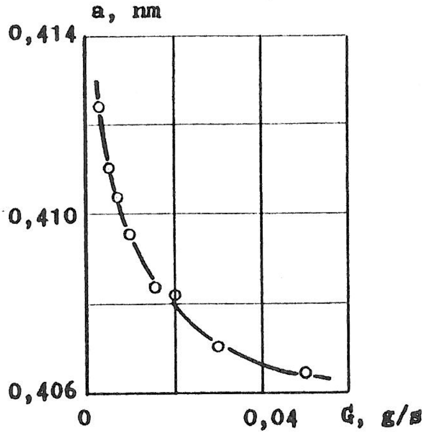

Fig.4. Change of VN_x unit cell parameter at different consumptions of VCl_4 introduced into the plasma flow by reactor scheme III.

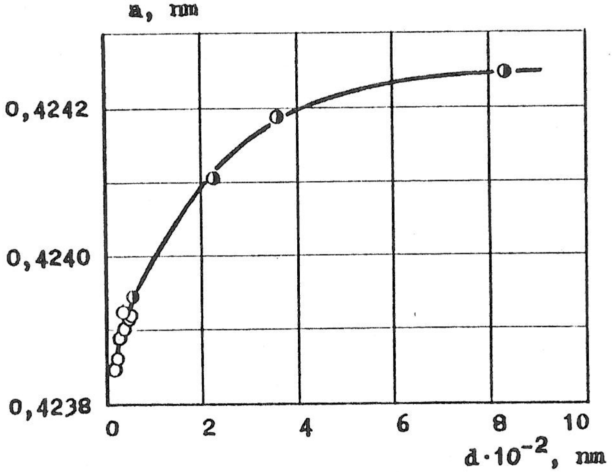

Fig.5. TiN unit cell parameter as a function of a mean particle size.

of the samples at T=1300 K the lattice period increases by $4 \cdot 10^{-4}$ nm, that exceeds the measurement error by an order of magnitude. The same samples demonstrate a noticeable static displacement of atoms from their equilibrium positions to give rise to energy excitation of near-to-surface atoms by 0,02 to 0,03 eV, which is equivalent to the sample heating up to 500 to 650 K. Size effects of physical-chemical properties are also demonstrated by ultrafine nitride powders. Thus, in niobium nitride a size effect of the phase transition was observed to be manifested in the fact that for a 0,04 m mean-particle size powder the activation energy of the phase transition of a metastable cubic phase into a stable hexagonal one is 2,5 times lower than that for nitride with a particle size of the order 100 m. The thermal-oxidative stability of nitrides produced under different conditions obeys the general law of the form $T_{ox}=T_m(F/F_m)^{-n}$, where T_{ox} is the sample temperature at which the oxidation degree reaches 1%, T_m and F_m characterize a massive sample with a mean particle size 1 mm. The parameters of this equation for the nitrides investigated are tabulated in Table:

Nitride	TiN	HfN	ZrN	VN
T_m	1110	1020	980	890
n	0,064	0,065	0,073	0,075

For TiN superfine powders the starting sintering temperature, (i.e. the heat treatment temperature for free-poured powder in vacuum, at which a bend of a graphic F_{sp} dependence on T_{an} is observed and F_{sp} starts dropping) obeys the law of the form: $T_{in}=T_m \exp -c(l_m-l)/l$, where l is a mean particle size of the powder; T=1630 K; l_m=1 mm; $c=9,2\cdot10^{-6}$.

The investigations of the superconducting properties of TiN using 10 nm mean-particle powders /6/ showed that their magnetic field was stronger by an order of magnitude than that of a massive sample, and that the screening ability of TiN small particles, dispersed in a matrix was greater.

3. RESULTS

The thermodynamical and macrokinetic conditions are established for a 100% chloride conversion into nitrides in the plasma flow providing for the preparation of powders with a mean particle size ranging from 10 to 100 nm with an increased nonequilibrium of the crystal lattice.

Considerable size effects are shown to be manifested in the activation process, in particular, in phase transitions, sintering, oxidation of transitional-metal nitrides.

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