PLASMACHEMICAL SYNTHESIS OF FINELY DISPERSED TITANIUM CARBONITRIDES

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ABSTRACT

The formation of titanium carbonitrides in the installations of two types was investigated. TiO_2 and $TiCl_4$ were used as raw materials. The influence of synthesis conditions on chemical and phase compositions of products is discussed.

1. INTRODUCTION

The titanium carbonitrides are widely used in different fields of science and engineering[1]. Traditional technology of fine carbonitride powders has low productivity and gives powders, polluted by the admixtures of materials of technological equipment. Therefore the development of a new highly efficient process for unpolluted fine powders producing is one of the urgent and important tasks.

Plasmachemical synthesis allows to obtain the powders of refractory metall compounds with controlled degree of dispersion and chemical composition. Titanium carbonitrides have beem synthesized on installations with r.f. and microwave plasmatrones[2,3].

The oppotunity of titanium carbonitrides synthesis on the installations of two types is discussed in the present paper. A distinctive feature of this installation's operation is rather uniform temperature distribution at the reactor's entrance. Such temperature distribution makes reactor's operation mare stable and provides the compliteness of physicall and chemical convertions in the whole volume of reactor.

2. EXPERIMENTAL

The thermodynamical calculations of equilibrium states of Ti - Cl-C-H-N and Ti-O-C-H-N systems were done in order to evaluate the optium synthesis conditions. Only the existence of TiN, TiC and C in solid phase was taken into account because of thermodynamical data absence for TiC_xN_y, $TiO_xC_yN_z$, TiO_xC_y and TiO_xN_y. It was assumed that formation of solid TiC_xN_y had taken place in the same temperature range as the solid TiN and TiC coexistance. This range, as calculations had shown, was 1000-2700° K.

The vaporisation of raw material particles is, probably, a limiting stage of synthesis TiC_xN_y from TiO_2. The vaporization rate computations were carried out with the help of mathematical model, developed by S.A.Panfilov et al[4]. The results of the computations allowed to estimate energetical and geometrical reactor's performance required for the complete treatment of the raw material. Fig.1 shows the change of particle size during the particle's movement in the reactor with different mass flow rate of the raw material. The increase of mass flow rate of the raw material above some certain value at the one and the same starting tempearture of gas leads to incomplete vaporization of particles.

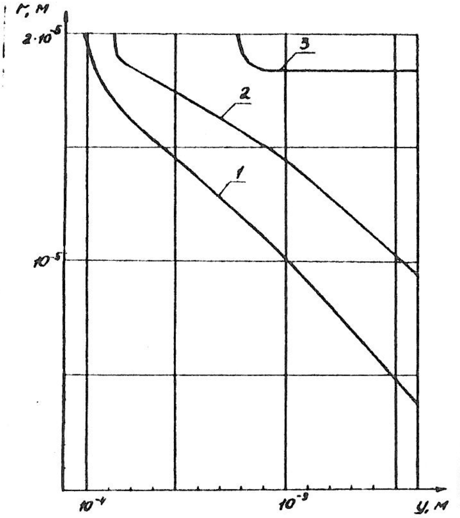

Fig.1. The relation between TiO_2 particle radius, r, and the distance, passed by particle, y. Mean gas temperature 6000°K, gas flow rate 3 g/s, TiO_2 flow rate: 1-0,1 g/s; 2-0,5g/c; 3-1g/s

The investigation of TiC_xN_y synthesis from $TiCl_4$ was carried out on the installation with coaxial plasmatrone (Fig.2). Carbon was used as a material for electrodes. Consume cathode was supplied into the discharge chamber. Sectionalised reactor with carbon fettling was connected to the arc heater. Plasmatron power was 20-50 KW, the strength of the magnetic field of solenoid was 4 A /m Power performances of plasmatrone are given in the paper[5]. Mean temperature of plasma jet at the reactor's entrance was controlled from 2500°K to 5000°K. The vapours of $TiCl_4$ out of feeder were injected into discharge chamber by transporting gas (N_2 + H_2 mixture). In that case the formation of a film consisted of TiC and TiC_xNy was observed on the surface of the electrodes. The rate of film's growth was stabilized, if the weight ratio of the reactants ($TiCl_4/H_2$) had a certain value.

The flow rate of $TiCl_4$ in the given case was determined by the cathode current load, and so in order to provide steady plasmatrone operation some part of $TiCl_4$ was injected into the plasmajet at the entrance of the reactor The propane-butane mixture was feeded into the same place to increase the amount of carbon, since the erosion of consumed cathode ($2,38-2,49\cdot10^{-5}$ g/c, I= 200 - 500 A) had not provide the required amount of carbon. At the reactor's exit high-temperature stream was quenched by cold gas jets. Finely dispersed particles of products were collected at filtration system

The synthesis of TiC_xN_y from TiO_2 was carried out in reactor with three-jets mixing chamber

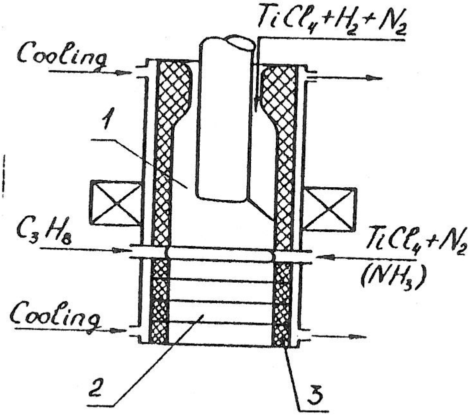

Fig.2.The principal scheme of coaxial plasmatrone reactor. 1- plasmatrone, 2-sectionalized reactor, 3-carbon fettling.

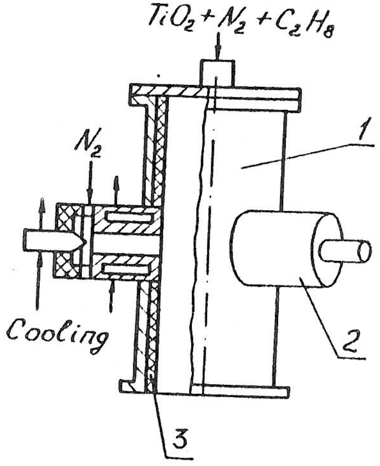

Fig.3 The principal scheme of three-jets mixing chamber 1-chamber, 2-plasmatrone, 3-carbon fettling.

The arc heaters, used in this installation, had the arcs, stabilized by vortex flow. They had copper electrodes; the cathode was supplied with tugsten insert. The heaters were adjusted at the mixing chamber perpendicularly to it's axis and had the angle 120° between the axises of each other. The mixing chamber had a carbon fettling and was adjusted at the reactor, described above.The total installation, had the arcs, stabilized by vortex flow. They had copper electrodes; the cathode was suppliedwith tugsten insert. The heaters were adjusted at the mixing chamber perpendicularly to it's axis and had the angle 120° between the axises of each other. The mixing chamber had a carbon fettling and was adjusted at the reactor, described above. The total installation power was controlled from 30 KW to 90 KW. Mean gas temperature at the entrance of the reactor was varied within the range of 4500-6000 K. Technical nitrogen contained 0,2 - 0,4 % of owygen by volume was used as plasma gas. TiO_2 was injected by transporting gas (N_2) out of powder feeder into the zone of plasma jets collision. Propane-butane mixture (80-90 % by weight C_3H_8) was injected into the same place. Quenching and filtration systems were similar to the systems, which had been used in the installation with coaxial plasmatrone. Mean size of TiO_2 particles, used in experiments, was 18,8; 7,5;2,1 μm.

3. RESULTS

The produced powders were studied by methods of electrone microscopy, roentgenography, and were subjected to element chemical analysis also.

In the case of using $TiCl_4$ as a raw material the products of synthesis are presented by titanium carbonitrides, whose composition varies from $TiC_{0,2}N_{0,8}$ to $TiC_{0,8}N_{0,2}$. With increase of combined carbon content more than 8% by weight free carbon appears, whose content for composition $TiC_{0,8}$NO,2 achieves 12% by weight. Free carbon is present in products in the form of carbine and graphite. The degree of reduction $TiCl_4$ and $TiO2$ in the experiments was 85-99%.

In some experiments carbonitrides, produced from TiO_2 had two compositions (see table 1). The identification of compositions was carried out with the help of carbonitrides lattice period data. The accuracy of the identification was ± 5%. The phase ratio in products was computed on the base of reflex intensivity (220).

Table 1

The composition of carbonitrides phases and their ratio in the products of plasmachemical synthesis

	Period of phase lattice,A	Phase composition	Phase mole ratio
1.	4,290	$TiC_{0,55}N_{0,45}$	0,3
	4,254	$TiC_{0,15}N_{0,85}$	0,7
2.	4,313	$TiC_{0,80}N_{0,20}$	0,4
	4,257	$TiC_{0,20}N_{0,80}$	0,6
3.	4,229	$TiC_{0,65}N_{0,35}$	0,6
	4,254	$TiC_{0,15}N_{0,85}$	0,4
4.	4,297	$TiC_{0,65}N_{0,35}$	0,4
	4,249	$TiC_{0,05}N_{0,35}$	0,6

In these experiments titanium carbonitride phase with high content of nitrogen distinctly dominated over the phase with high content of carbon. The results, given above, are also confirmed by thermographical analysis of products. The ratio of carbonitride phases in the whole range of mass flow rate of raw material is kept practically constant. Only the decrease of a raw material starting velocity up to 8 m/s leads to the contraverse ratio of phases (experiment 3). The amount of free carbon in the products of synthesis also depends on the composition of produced carbonitrides and increases (from 0,4 to 10% by weight) with the growth of combined carbon content as well as in the case of using $TiCl_4$ as raw material. The essential decrease of raw-material starting velocity allows to obtain single phase products, but the productivity of the installation also essentially decreases.

With the help of electrone microscopy it has been found, that titanium carbonitrides are represented by particles of cubic shape, (1-8) $\cdot 10^{-8}$ m in size. Mean particle size, calculated on the base of specific surface measuring data, is (1,5-5)$\cdot 10^{-8}$ m. The regular form of particles points at their formation from gaseous state. We failed to determine the size and morphology of carbine and graphite particles because of their high dispersion and penetration for the electrone beam. At the electrone microscope photos these phases are observes as semitransparency "veil", wraping the titanium carbonitride particles.

The amount of absorbed powders gases (N,O,H_2,CO,HCl,H_2O) varies in the range 2-8 % by weight and depends upon the value of specific surface and conditions of storage. The content of the oxygen at the surface of powders varies from 1 % to 4% by weight.

It is nessesary to point out, that the formation of two compositions of titanium carbonitrides (synthesis in reactor with three-jet mixing chamber) occures in the zones with different synthesis conditions (temperature, concentration of reactants, etc.). The appearance of these zones is, probably, determined by peculiarity of high-temperature gas movement in the given reactor.

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