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Preparation of Ti(N, C) Based Nanosized Powders and Their Densification

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The nanosized powders of titanium carbonitride find application in manufacture hard corrosion resistant materials, cutting tools and metal matrix composites. The aim of present work was preparation of nanosized titanium carbonitride powders and manufacture dense bodies. The nanosized powders were prepared by evaporation of titanium or titanium hydride in an inductively coupled nitrogen plasma. The formation and growth of product particles were controlled by introducing cold nitrogen, hydrocarbon or their mixture with ammonia into the vapour region. Presence of ammonia in the plasma flow promotes formation of titanium carbonitride with high content of carbon and eliminates decomposition of hydrocarbons. Particle size of the produced powders is in the range of 20 – 100 nm depending on the process parameters. Ti(N, C) particles have a characteristic cubic shape. The nanosized particles of Ti(N, C) with the specific surface area in the range of 33 – 43 m^2/g are stable in air at room temperature but depending on the specific surface they absorb 1.8 – 3.2 wt.% of oxygen. The Ti(N, C) based bodies were prepared by hot pressing and sintering at 1600 – 1800 °C. The density of ceramics depends on sintering temperature, particle size, and composition of powders and strongly on content of carbon.

Keywords: titanium carbonitride, nanosized powders, plasma chemical synthesis, hot pressing.

1. INTRODUCTION

Titanium carbonitride due to its interesting mechanical characteristics finds application in manufacture hard corrosion resistant materials, cutting tools and metal matrix composites as well as for modification of metal structure [1 – 4]. Since it has lower sinterability with respect to titanium nitride the development of synthesis methods for TiNC nanosized powders with higher activity is important.

Fine active TiNC particles have been prepared in an arc plasma [5] or by chemical interaction of titanium tetrachloride vapours with hydrocarbons and nitrogen in microwave discharge nitrogen plasma [6]. However, high partial pressure of nitrogen with respect to hydrocarbon promotes formation of TiNC with low content of carbon. The attempts to prepare $TiC_{0.5}N_{0.5}$ or $TiC_{0.7}N_{0.3}$ by increasing ratio of hydrocarbons and titanium led to increase of free carbon in products up to 5 and 15 wt.%, respectively.

Regarding above-mentioned background the aim of the present work is preparation of nanosized titanium carbonitride powders with reduced content of free carbon and studies of their densification.

2. EXPERIMENTAL

The nanosized powders of titanium carbonitride were prepared by evaporation of coarse-grained commercially available titanium or titanium hydride powders and subsequent interaction of their vapours with hydrocarbons into radio frequency discharge nitrogen plasma. The experimental apparatus consists of radio frequency (5.28 MHz) oscillator with maximum plate power of 100 kW, water-cooled cylindrical reactor, heat exchanger, gas and powder supply systems and bag filter for collecting of products [7]. The flow rate of plasma forming gas – nitrogen was 8.5 m^3/h and feed rate of powder was 0.9 – 1.2 kg/h. The raw powder was introduced into the plasma flame through 8 tubes with diameters of 2 mm by carrier gas nitrogen. The best conditions of evaporation of the raw powders were determined by studying specific surface area and product particle size in dependence on injection parameters – velocity, feeding rate, injection angle.

On the basis of these studies the optimal titanium and titanium hydride particle size of 20 – 40 μm, injection velocity of 12 – 14 m/s and injection angle of 75° were estimated. The additional reactants - hydrocarbons or their mixture with ammonia were injected into reactor together with powder or at a distance of 15 – 60 mm below the introduction plane of Ti. The optimal flow rate of hydrocarbons was determined by studying the dependence of phase and chemical composition of the products on the ratio of titanium/carbon.

The chemical and phase composition was determined by conventional chemical analysis and X-ray powder diffraction analysis.

The specific surface area (SSA) of powders was determined by the BET argon adsorption-desorption method. Particle shape and size were controlled by transmission electron microscopy. The produced nanosized powders were consolidated by hot pressing at 1600 – 1800 °C with the holding time one hour.

3. RESULTS

According to the results of the studies the formation of titanium carbonitride, its chemical and phase composition, content of the free carbon depends strongly on the ration of the distance of the hydrocarbon injection point from powder introduction plane (*L*) and the diameter of the reaction chamber (*D*) as well as on the ammonia additive (Table 1).

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Table 1. Dependence of the characteristics of produced powders on the distance (L/D) of injection hydrocarbon or mixture of hydrocarbon and ammonia, where D is diameter of reaction channel and L is distance from the injection point of titanium

No	L/D	Reactants	Chemical composition, wt.%			XRD
			N	C	C_{free}	
1	0.0	Ti, N_2, C_nH_m	16.2	5.1	1.2	Two phases
2	0.0	Ti, N_2, C_nH_m, NH_3	16.4	4.6	0.8	Two phases
3	0.25	Ti, N_2, C_nH_m	16.0	5.3	1.3	Two phases
4	0.25	Ti, N_2, C_nH_m, NH_3	16.3	4.8	0.5	Single TiNC phase
5	0.5	Ti, N_2, C_nH_m	16.1	5.6	1.5	Single TiNC phase
6	0.5	Ti, N_2, C_nH_m, NH_3	16.7	4.8	0.3	Single TiNC phase
7	0.8	Ti, N_2, C_nH_m	17.4	5.3	1.8	Single TiNC phase
8	0.8	Ti, N_2, C_nH_m, NH_3	17.0	4.3	0.5	Single TiNC phase
9	1.0	Ti, N_2, C_nH_m	18.2	5.1	1.1	Two phases
10	1.0	Ti, N_2, C_nH_m, NH_3	17.2	4.4	0.6	Two phases

If the hydrocarbons are injected into the nitrogen plasma flow together with powder ($L/D = 0$) or at distance $L/D = 0.25$, the X-ray patterns of produced products show splitting of maxima (Fig. 1) that evidences on inhomogenity of carbonitride, on formation of two carbonitride phases with different content of carbon and nitrogen.

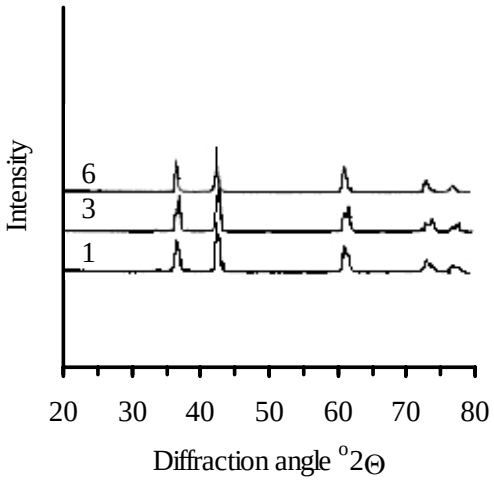

Fig. 1. Diffraction patterns of TiNC samples 1, 3 and 6 referenced in Table 1

Besides this the products contain relatively high amount of free carbon. Ammonia additives to the hydrocarbons remarkably decrease admixture of free carbon and increase nitrogen content in carbonitride. These results can be explained by decomposition of hydrocarbons at temperatures higher as formation temperature of titanium carbonitride resulting in condensation of solid carbon which reactivity is low. According to thermodynamic calculations presence of ammonia in the nitrogen-carbon plasma flow leads to formation of active gaseous products of carbon such as HCN, CN [8] and therefore reduces the amount of free carbon particles. From estimated data follows that injection of hydrocarbon and ammonia mixture at the distance $L/D = 0.25…0.50$ provides preparation of single-phase titanium carbonitride with low admixture of free carbon. The further increase of the injection distance of hydrocarbon results in obtaining two phase carbonitride powders again with increasing content of free carbon. In this case, due to the rapid decrease of the plasma and titanium vapour temperature growth of titanium nitride particles starts before injection point of hydrocarbons and therefore the formation of carbonitride is limited partially by diffusion of carbon into nitride.

Interaction of the titanium or titanium hydride vapours with nitrogen and carbon compounds at the best injection conditions of hydrocarbons and ammonia results in obtaining nanosized titanium carbonitride powders with specific surface area in the range of 33 – 43 m^2/g (Table 2). The chemical composition of the products is close to stoichiometric. The content of N and C is determined by the ratio of raw titanium and hydrocarbons.

Table 2. Characteristics of prepared nanosized powders of titanium carbonitride.

No	SSA, m^2/s	$\bar{d}$, nm	Chemical analysis, wt.%			
			N	C	O	C_{free}
1	33	35	16.9	4.9	3.4	0.3
2	42.2	27	145	7.2	2.7	1.2
3	41	28	10.7	9.9	1.8	1.5
4	43	27	7.1	14.6	1.6	1.8

The increase of chemically bounded carbon in TiNC is followed by a small increase of free carbon but its content is much lower than in powders produced from $TiCl_4$ and hydrocarbons in nitrogen microwave discharge plasma.

According to XRD analysis the prepared samples consists of single-phase titanium carbonitride (Fig. 2). Only at low content of carbon a slight asymmetry of diffraction maxima highlights some inhomogeneity of carbon and nitride distribution. Therefore, presence of ammonia ensures preparation of nanosized titanium carbonitride in nitrogen plasma with content of chemically bounded carbon up to 12.8 wt.% without remarkable admixture of free carbon.

All prepared samples contain admixture of oxygen after exposure in air but amount of oxygen decreases with

increase of bounded and free carbon. Possibly the carbon and its compounds admixture on the carbonitride surface leads to surface passivation.

The nanosized particles of titanium carbonitride with specific surface area in the range of 33 – 43 m^2/g are stable in air at room temperature. According to the DTA analysis oxidizing of TiNC starts at 280 – 300 °C and reaches maxima at 360 – 450 °C depending on the content of the carbon and specific surface area. The oxidizing temperature of the titanium carbonitride decreases with increase of chemically bounded carbon content. The titanium carbonitride with specific surface are higher as 50 m^2/g are pyrophorous.

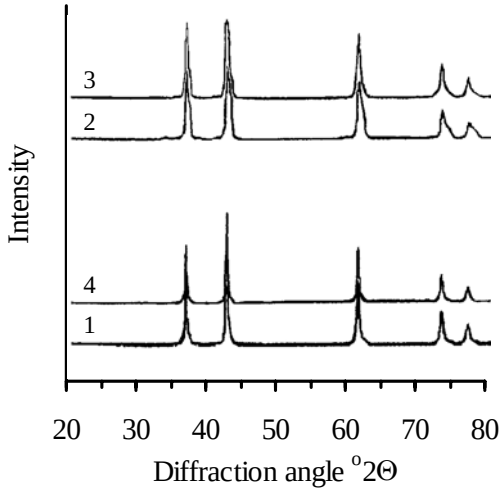

Fig. 2. Diffraction patterns of TiNC samples 1,2,3 and 4 referenced in Table 2

The particles of prepared titanium carbonitride have a characteristic cubic form indicating their growth by mechanism vapour-solid state (Fig. 3).

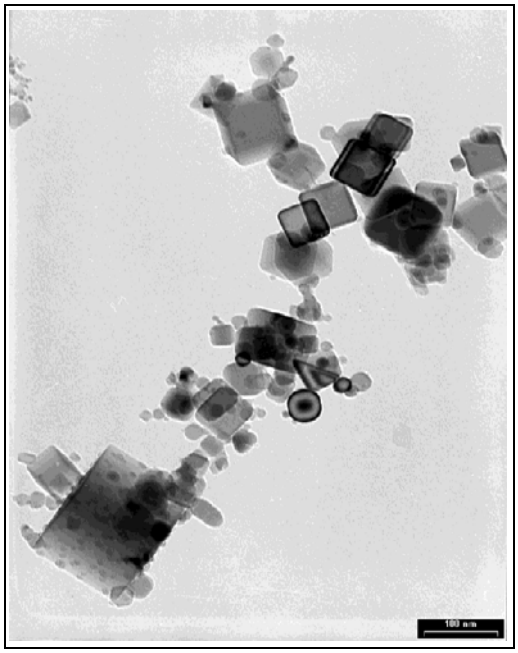

Fig. 3. Micrograph of TiNC particles

The particle size is in the range of 20 – 100 nm and can be varied by changing concentration of titanium vapours in the plasma flow and the cooling rate of product particles. The maximal cooling rate is achieved by introducing cold nitrogen into the reaction chamber. In this case, the specific surface area of prepared titanium carbonitride is 86 m^2/g and calculated average particle size is 14 nm.

Densification of nanosized powders starts at 750 °C and involves three maxima of shrinkage rate at 950, 1300 and 1450 °C (Fig. 4). Th highest shrinkage rate is in the temperature range of 1200 – 1500 °C. The densification

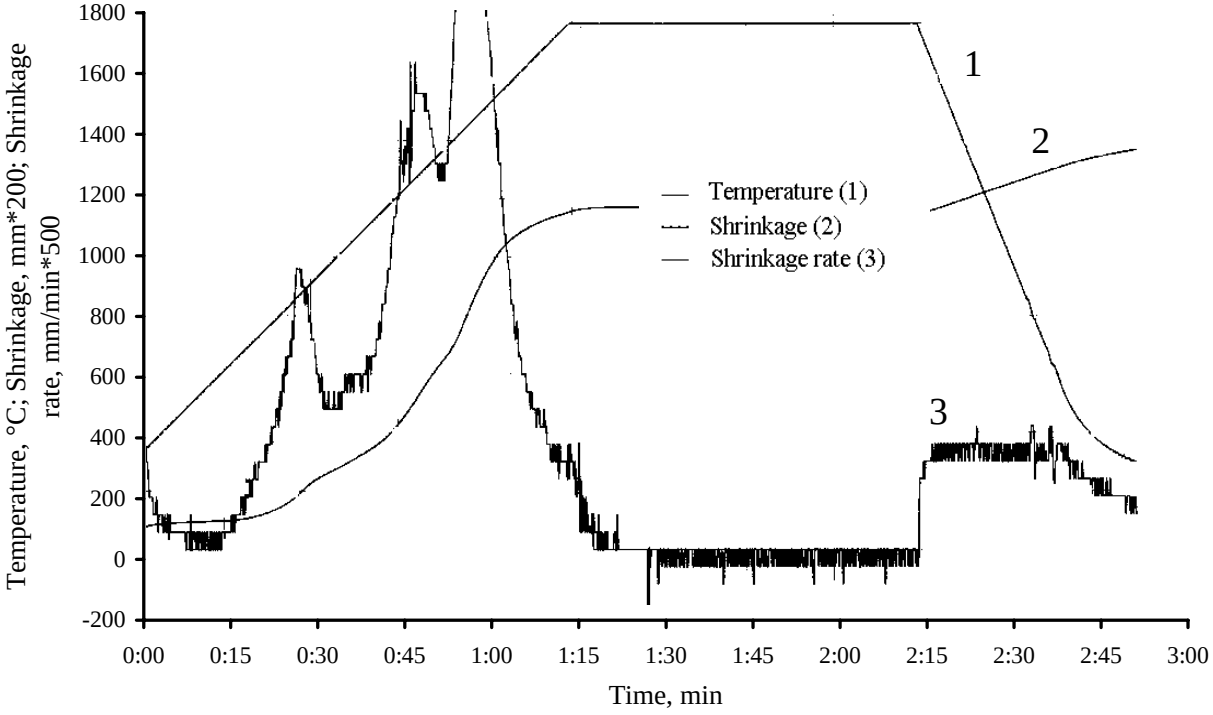

Fig. 4. Parameters of TiNC hot pressing process

process finishes after reaching 1800 °C high temperature. Keeping of samples for an hour has a little influence on their density. The density of hot pressed samples is in the range of 93 – 97 % depending on the content of carbon.

Therefore, despite the small particle size of prepared carbonitrides, their conventional hot pressing demands high temperature. That can be partially explained by presence of free carbon and oxygen.

The microstructure of hot pressed samples is fine and grain size is in the range of 0.5 – 1 μm (Fig. 5).

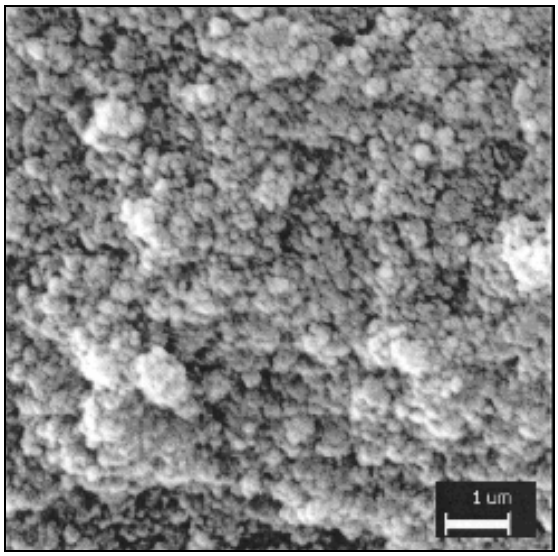

Fig. 5. Microstructure of $TiN_{0.5}C_{0.5}$ (pressed at 1800 °C)

Obviously, further decrease of the TiNC grains and improvement of density could possibly be reached by optimizing chemical composition and purity of samples and such parameters of hot pressing as temperature and time.

CONCLUSIONS

1. Evaporation of titanium or titanium hydride in nitrogen plasma and subsequent interaction of vapour with mixture of hydrocarbons and ammonia allows to prepare nanosized carbonitride powders with carbon content up to 12.8 wt.%.

2. The chemical and phase composition of titanium carbonitride depends on the injection point of hydrocarbons and ammonia, the ratio of hydrocarbons and titanium.

3. The nanosized titanium carbonitride particles have characteristic cubic form and size in the range of 20 – 100 nm.

4. Hot pressing of nanosized TiNC powders at 1800 °C leads to formation of bulk material with density 93 – 97 % and fine-grained microstructure.

Acknowledgments

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