Preparation of Nanodisperse Transition Metals Carbonitrides by the Plasmachemical Method

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Abstract

A series of nanodisperse powders of carbonitrides of IV-VI group transition metals (for example, TiC_xN_{1-x}, ZrC_xN_{1-x}, NbC_xN_{1-x}, $Cr_3C_{1,6}N_{0,4}$), their hard alloys (for example, $Ti_xNb_{1-x}C_yN_{1-y}$) and mixtures (for example TiC_xN_{1-x}-$Cr_3C_{1,6}N_{0,4}$), as well as their compositions with metals (Ti(C,N)-Ni,Mo, (Ti,Nb)(C,N)-Fe,Ni,Cr,Mo, $Cr_3C_{1,6}N_{0,4}$-Ni, Ti(C,N)-$Cr_3C_{1,6}N_{0,4}$-Ni) with a medium particle size of 50 - 200 nm have been prepared by the method of plasmachemical synthesis. Due to the dynamic conditions of synthesis (starting products evaporation or decomposition, mixing and condensation of the end product is lasting for some tenths of second) the product is formed in a form of nanodisperse powder, mainly as a monocrystals with a numerous concentration of the crystallic lattice defects. This determines high chemical activity of these powders, including increased sintering rate and decreased sintering temperature (for example, in the case of TiC_xN_{1-x} and NbC_xN_{1-x} this temperature is 400-600 °C lower in comparison with the traditional powders).
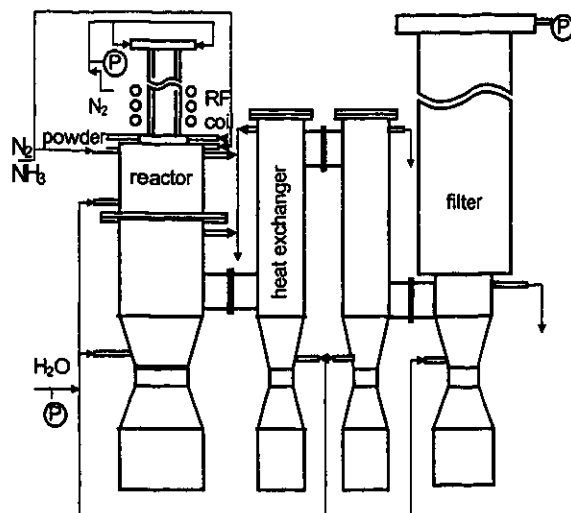
1. Introduction

Due to the development of new hard alloys, including non-tungsten materials, the interest is lasting on preparation methods of transition metal carbides, nitrides and their hard solutions – carbonitrides. It is necessary to develop new methods of their preparation to satisfy the increase of their use. One of such methods is the plasmachemical method allowing to obtain a nanodisperse product. This paper deals with the interaction of IV-VI group transition metals with high temperature nitrogen flow in a presence of carbon in order to obtain nanodisperse carbonitride powders.

2. Experimental

2.1. Investigations of nanodisperse powders

Nanodisperse carbonitride powders and their composites are prepared by evaporation of coarse commercially available powders of chemical elements and subsequent condensation of products in a radio frequency inductively coupled nitrogen plasma. The elaborated experimental apparatus (Fig. 1) consists of radio-frequency (5.28 MHz) oscillator with maximum power of 100 kW, quartz discharge tube with induction coil, raw powder and gas supply systems, water cooled stainless steel reactor and heat exchanger, and cloth filter for collecting of powder. The flow rate of the plasma-forming gas (nitrogen) is 6,9-8,0 m^3/h and the feed rate of raw powders is 1,0-2,2 kg/h.

Figure 1. Schematic view of plasma apparatus.

The calculated fractions of raw powders of chemical elements are premixed and introduced into plasma tail through 4 or 8 tubes by carrier gas. Conditions of injection and particle size are determined by theoretical calculations and preliminary experiments. The complete evaporation of raw powders can be reached by varying the particle size and their injection rate, feeding rate, plasma velocity and temperature. The formation of products, their particle size, chemical and phase composition are controlled by introduction the cold nitrogen and hydrocarbon into reaction chamber.

Titanium (purity 99,1 wt.%), niobium (98,6%) and chromium (99,2%) powders, gaseous hydrocarbons (methane, mixture from propane and butane and others) were used as raw materials. High purity nitrogen (99,99%) was used as a plasma-forming gas simultaneously used also as one of reaction components.

The chemical composition (Me, N, C and C_{free}) and phase composition of synthesized powders were determined by conventional chemical and X-ray powders diffraction analysis. The size and shape of particles were stated by the transmission electron microscopy (TEM), particle size distribution by photon correlation spectroscopy (PCS) by apparatus Zetamaster S 5002 ZEM, specific surface area by the BET argon adsorption – desorption method.

It was experimentally stated that making synthesis in a great excess of nitrogen, it is possible to change chemical composition of the carbonitride phase in a wide range changing the ratio carbon/metal in a raw material (Fig. 2).

It is known that titanium easily forms cubic phases – nitride, carbide and continuous raw of its hard solutions (carbonitrides) [1]. In a pure nitrogen plasma the nanodisperse nitride powder forms with the composition close to the stoichiometric – TiN_x, where $x = 0,95 - 0,97$. Carbonitride TiN_xC_y ($x+y \approx 1$) forms in plasma in a presence of hydrocarbons. It is possible to regulate the carbonitride composition in a range from $TiC_{0,1}N_{0,9}$ to $TiC_{0,6}N_{0,4}$ changing the amount of hydrocarbons or the ratio C : Me. The crystalline lattice parameter changes linearly with the change of chemical composition (Tab. 1). If the amount of fixed carbon increases above 4 – 5 wt.%, free carbon appears in the reaction product and its content increases with the increase of hydrocarbons. This could be explained by a great affinity of titanium to nitrogen and by a great excess of nitrogen in a system.

Metals of the V-th group differ from metals of the IV-th group and can form carbonitrides of cubic (NaCl-type) structure as well as hexagonal structures – $Me_2(C,N)$. If there are no hydrocarbons in system, niobium forms cubic nitride NbN with the admixtures of hexagonal Nb_2N. In the presence of hydrocarbons the hexagonal phase disappears and product consists of only the cubic phase – NbC_xN_{1-x}. In comparison with the IV-th group metals, metals of the V-th group possess higher

affinity to react with carbon, resulting in carbonitride with increased content of fixed carbon, even if the excess of nitrogen is high.
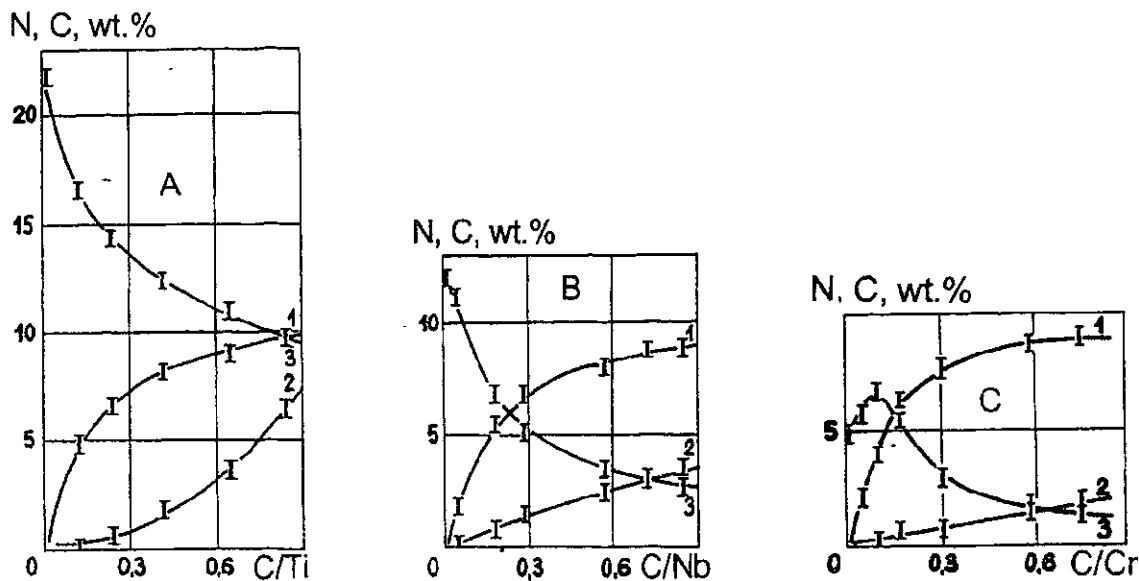

Figure 2. The dependence of chemical composition of reaction products on ratio C:Me for titanium (A), niobium (B) and chromium (C): 1 − C_{fixed}, 2 − C_{free}, 3 − N.

Metal	Phase content	Chemical composition, wt.%				Formula of the cubic phase	Lattice para-Meter, a, Å
		Me	N	C	C_{free}		
Ti	TiN	77,2	21,8	----	----	$TiN_{0.97}$	4,248
	Ti(C,N)	77,8	16,5	4,7	0,2	$TiC_{0,29}N_{0,74}$	4,265
	Ti(C,N)	77,7	12,5	8,1	0,7	$TiC_{0,41}N_{0,56}$	4,276
	Ti(C,N)	74,6	9,8	9,7	5,2	$TiC_{0,52}N_{0,46}$	4,288
Nb	NbN, Nb_2N	86,2	12,6	----	-----	$NbN_{0,96}$	
	Nb(C,N)	87,0	10,8	1,0	0,1	$NbC_{0,09}N_{0,83}$	
	Nb(C,N)	86,3	6,4	5,4	1,0	$NbC_{0,48}N_{0,49}$	
	Nb(C,N)	84,3	2,9	8,6	3,2	$NbC_{0,76}N_{0,22}$	
Ti-Nb (75:25)	(Ti,Nb)(C,N)	62,9/16,5	10,2	8,6	1,0	$Ti_{0,83}Nb_{0,12}C_{0,48}N_{0,50}$	
Ti-Nb (25:75)	(Ti,Nb)(C,N)	26,6/56,8	19,2	4,5	0,5	$Ti_{0,48}Nb_{0,52}C_{0,32}N_{0,66}$	

Table 1. Phase and chemical composition of titanium and niobium carbonitrides.

It is known from literature that metals of the VI-th group, especially chromium can form several compounds in system Me-C-N. The carbon-containing phase is $Cr_2C_xN_{1-x}$, whose exact chemical composition has not been stated, because of the presence of other phases in product. If the ratio C:Cr increases, the content of another carbonitride phase grows, this phase has been identified [2] as $Cr_3C_{1,6}N_{0,4}$ (Tab. 2).

The mechanism of IV-VI-th group carbonitride formation is the same and therefore a similar synthesis conditions could be used for simultaneous preparation of several carbonitrides. Introducing the mixture of two or more metal powders into the reaction zone under certain

conditions it is possible to obtain complex IV-V-th group metal carbonitrides, or their mixtures with chromium carbonitrides, or VI-th and Fe-group metals (Tab. 1,2). Practical experience shows that the presence of IV-th group metals (for example, Ti) facilitates the formation of the cubic phase both in the case of V-th group metals (δ-Nb(C,N), δ-Ta(C,N)) and VI-th group metals (α-MoC) [3]. In the system of IV-V-th group metal carbonitrides we obtain their hard solutions $(Me_I, Me_{II})(C,N)$ instead of mixture of separate carbonitrides (Tab. 1).

Nominal chemical formula of carbonitrides	Content of elements, mass.%						SSA[*] of Particles, m^2/g	ES[**], μm
	Ti	Cr	Ni	N	$C_{tot.}$	O		
$Cr_2(C_{0,54}N_{0,35})$	-	89,9	-	4,2	5,5	0,2	1,2	0.7
$Cr_3C_{1,6}N_{0,4}$		87,0	-	1,2	11,3	0,2	2,6	0.4
$TiC_{0,49}N_{0,51}$ - $Cr_3C_{1,6}N_{0,4}$ (7:3)	56,1	25,1	-	9,1	8,7	0.9	6,0	0.18
$Cr_3C_{1,6}N_{0,4}$ – Ni	-	67,5	21,1	0,5	10,2	0,6	8,5	0.10
$TiC_{0,49}N_{0,51}$ - $Cr_3C_{1,6}N_{0,4}$ – Ni	19,3	51,8	14,9	4,0	9,2	0,5	12,8	0.09

[*] Specific surface area, [**] Effective size

**Table 2.** Examples of some compounds on the basis of chromium carbonitride.

All mentioned compounds have been prepared as nanodisperse powders (NDP) with the specific surface area in the range of 10 – 60 m^2/g. The particle size of the reaction product is of 10 – 500 nm, moreover, the main amount is of size in the range of 20 – 200 nm (Fig. 3, 4), being in good agreement with the medium particle size which is calculated from the measurements of specific surface area. Particles of synthesized carbonitrides are mostly monocrystallic.

1   **0,2 μm**   **0,1 μm**   2
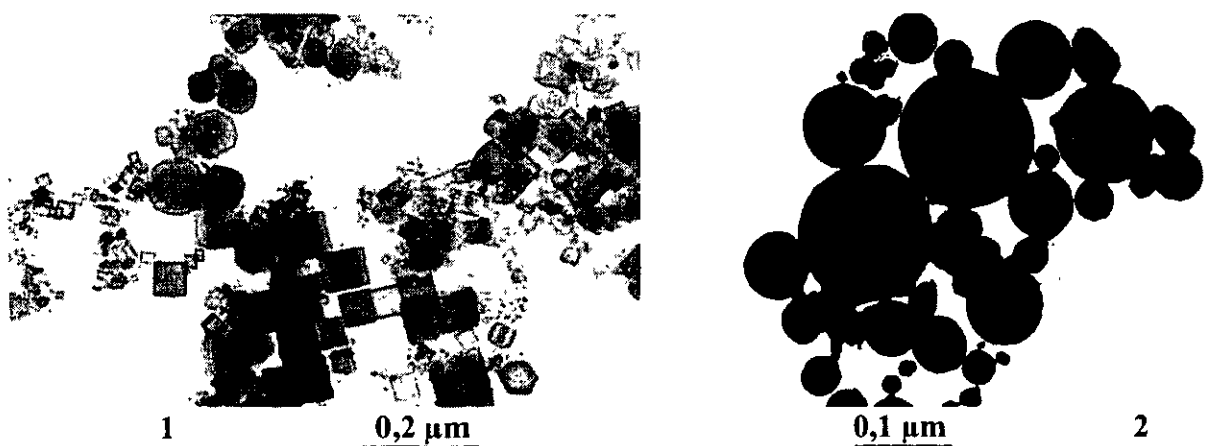
Figure 3. Characteristic shape and particle size of Ti(C,N) (1) and $Cr_3C_{1,6}N_{0,4}$ (2) powders.

High dispersity and concentration of structural defects is the reason of increased activity of plasma synthesis products: high surface of powders results in adsorption of oxygen and water vapor explaining increased content of oxygen (1,2–2,5 wt.%) during long lasting storing. The starting

temperature of NDP oxidation is significantly lower than for powders of the standard dispersity – 240–350 °C. Increased activity reflects also during sintering of these powders – sintering temperatures are significantly lower (for Ti(C,N) the difference is 400-600°) and sintering rate is higher.
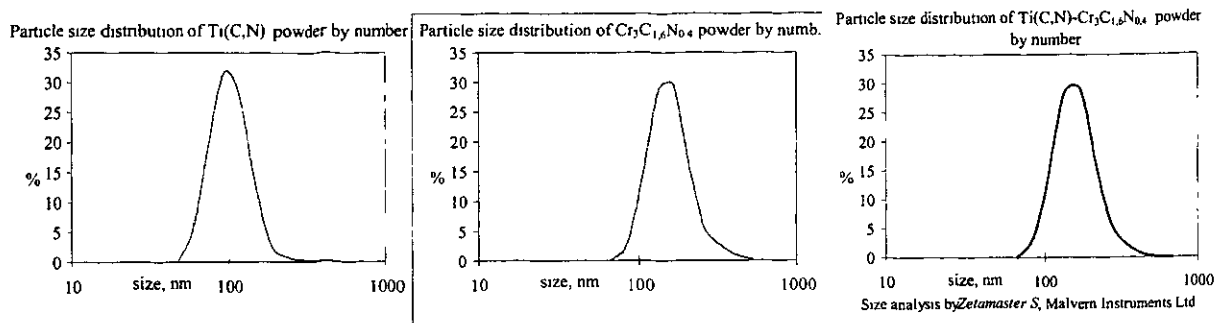
Figure 4. Particle size distribution of Ti(C,N), $Cr_3C_{1,6}N_{0,4}$ and Ti(C,N)-$Cr_3C_{1,6}N_{0,4}$ powders.

2.2. Some examples of nanodispertse powders application

If we use carbonitride powders with different dispersity, it is possible to obtain single-phase material with smaller grain size and inresed properties (Fig. 5, Tab. 3) [4]. The best strength properties have the carbonitrides of intermediate composition - mixtures of traditional industrial powders with NDP, but in the case of 100 % NDP these properties are somewhat higher than those for powder of low dispersity (Tab. 3). The application of plasmachemical NDP at the mentioned conditions ensures the increase of toughness of carbonitrides approximately for 20- 30 %.

A   B   C   D   10μm
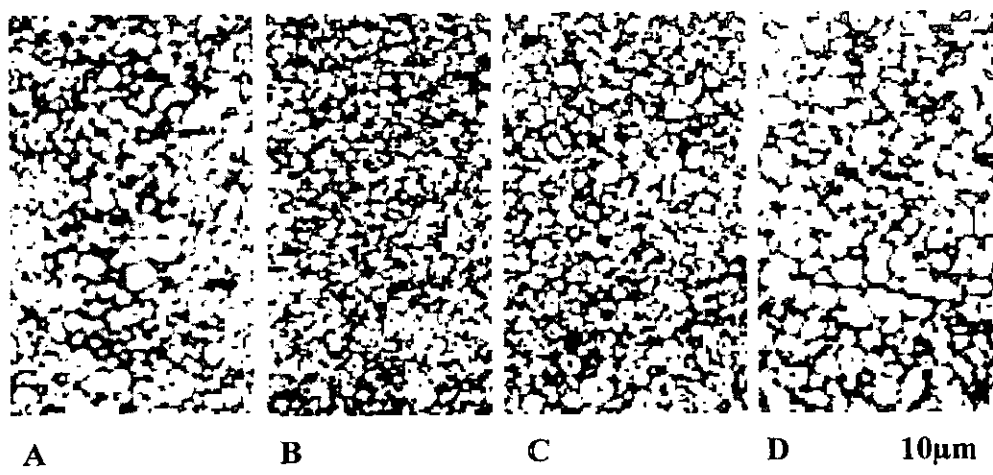
Figure 5. Microstructure of titanium-niobium carbonitride ($T_{sint.}$=1800°C, τ=1h).
A- 0% of NDP, B- 33% of NDP, C- 66% of NDP, D- 100% of NDP.

Due to the different $Cr_3C_{1,6}N_{0,4}$ / Ti(C,N) ratio in composition it is possible to change material properties in a quite wide range (Tab. 4), reflecting in cermets properties.

Chromium carbonitride is characteristic with increased plasticity properties in comparison with Cr_3C_2. The break of pure chromium carbonitride, although have mixed trans- and inter-crystallite character, in it's structure a viscous fracture occupies considerable part, evidenced by great amount of holes and imprints of strong local deformations. It is visible from Table 5. that hard alloy on the basis of chromium carbonitride (with somewhat lower density) exceeds in hardness and especially in flexural strength alloy on the basis of chromium carbide.

	Content Of NDP, %	P_{op}, %	d, kg/m^3 x 10^{-3}	σ_{bend}, Mpa	H_μ, GPa	ρ, $\Omega \cdot m$ x 10^8	λ, W/(m·°C)	E, GPa
A	0	1,6	5,0	450	21,7	48	17	447
	33	1,0	5,1	550	23,1	46	17	456
	66	1,2	5,1	600	22,0	45	15	459
	100	1,5	5,1	460	21,8	45	14	447
B	0	1,2	5,6	700	22,5	64	16	470
	33	0,8	5,6	900	22,9	54	15	503
	66	0,8	5,6	870	23,2	50	15	470
	100	0,8	5,6	750	23,8	49	14	450

P_{op}.- opened porosity; d- density; σ_{bend}- bend strength; H_μ- micro hardness; ρ- specific electric resistivity; λ- thermal conductivity; E- Young's modulus.

Table 3. Some physical and mechanical properties of $TiC_{0,5}N_{0,5}$ (A) and $Ti_{0,75}Nb_{0,25}C_{0,5}N_{0,5}$ (B), sintered at 1700 °C and 1650 °C, respectively, isothermal holding time 1h.

Composition of Sample	$T_{sint.}$, °C	Density, g/cm^3	$P_{op.}$, %	HV, GPa	$\sigma_{bend.}$, MPa
$Cr_3C_{1,6}N_{0,4}$	1550	6,07	0,4	16,5	310
$Cr_3C_{1,6}N_{0,4}$ – $TiC_{0,5}N_{0,5}$ (7:3)	1600	6,15	0,2	17,5	550
$Cr_3C_{1,6}N_{0,4}$ - $TiC_{0,5}N_{0,5}$ (3:7)	1600	5,66	0	22,0	530
$TiC_{0,5}N_{0,5}$	1700	5,10	1,5	22,0	460

Table 4. Physico-mechanical characteristics of sintered titanium - chromium carbonitride.

Alloy	Density, g/cm^3	HRA	$\sigma_{bend.}$, MPa
$Cr_3C_{1,6}N_{0,4}$ - 20% Ni	6,5	85,0	890
Cr_3C_2 - 20% Ni	6,88	83,0	700

Table 5. Some properties of alloys on the basis of chromium carbonitride and chromium carbide with 20 wt.% of Ni [5].

References:

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