UDC 539.21 (06)

Vestnik SibGAU
Vol. 16, No. 2, P. 491–495

STUDY OF CARBIDE FORMATION IN THE PLASMA OF A LOW-PRESSURE PULSED ARC DISCHARGE

L. Yu. Fedorov[1*], A. V. Ushakov[1], I. V. Karpov[1], A. A. Lepeshev[1,2], A. A. Shaihadinov[1]

[1]Siberian Federal University
79, Svobodny Av., Krasnoyarsk, 660041, Russian Federation
[2]Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences
50, Akademgorodok, Krasnoyarsk, 660036, Russian Federation
[*]E-mail: sfu-unesco@mail.ru

We examine the influence of pressure and gas mixture composition on the preparation of nanomaterials via vacuum arc sputtering of titanium cathodes in carbon-containing media. The formation of carbide phases in various gaseous atmospheres is accompanied by the formation of the low-temperature phase α-Ti (hcp lattice), characteristic of pure titanium. Carbide formation in the plasma synthesis of TiC nanoparticles is determined by the C/H ratio in the molecules of the hydrocarbons used. To raise the yield of carbon-rich carbide phases and reduce the percentage of the residual metal in the resulting nanopowders, it is necessary to use hydrocarbons with a large C/H ratio, for example, benzene and acetylene.

Keywords: titanium carbide, plasma synthesis, nanoparticles, microstructural characteristics, vacuum arc sputtering.

Вестник СибГАУ
Т. 16, № 2. С. 491–495

ИССЛЕДОВАНИЕ ФОРМИРОВАНИЯ КАРБИДОВ В ПЛАЗМЕ ДУГОВОГО РАЗРЯДА НИЗКОГО ДАВЛЕНИЯ

Л. Ю. Федоров[1*], А. В. Ушаков[1], И. В. Карпов[1], А. А. Лепешев[1,2], А. А. Шайхадинов[1]

[1]Сибирский федеральный университет
Российская Федерация, 660041, г. Красноярск, просп. Свободный, 79
[2]Красноярский научный центр Сибирского отделения Российской академии наук
Российская Федерация, 660036, г. Красноярск, Академгородок, 50
[*]E-mail: sfu-unesco@mail.ru

Рассмотрено влияние давления и химического состава газовой смеси при получении нанодисперсных материалов вакуумно-дуговым распылением титановых катодов в углеродсодержащих средах. Формирование карбидных фаз в атмосфере различных рассматриваемых газов происходит с образованием характерной для чистого титана низкотемпературной α-модификации с ГПУ-решеткой.

Ключевые слова: карбид титана, синтез в плазме, наночастицы, микроструктурные характеристики, вакуумное дуговое распыление.

Introduction. Currently, there is still insufficient information about the influence of gas mixture pressure and the chemical composition of individual hydrocarbons on the phase composition of Ti–C nanopowders produced by plasma synthesis. These parameters are known to play a key role in determining the stability of nanoparticle synthesis and the quality of the final product. The distinctive features of the metal dispersion process under the effect of a high-power current pulse and subsequent interaction of vacuum arc discharge (VAD) products with the ambient medium under increased pressure make it possible to extend the technological possibilities of the nanopowder preparation process.

As shown earlier [1–3], a VAD in the synthesis of metal carbides in gaseous media leads to the formation of products containing residual metals, and the resulting carbides are carbon-deficient (Ti_2C, TiC_{1-x}). The applicability of the VAD method in the synthesis of TiC, ZrC, Wc, Ta_2C, and MoC via sputtering in acetylene diluted with argon or hydrogen was demonstrated by Nazarenko [4] and Tikhonov [5], who pointed out that the most efficient hydrocarbon reagent was acetylene, because it has an extremely high stored chemical energy (226.8 kJ/mol), related to the formation of a triple bond. The participation of this bond in carbide formation increases the heat release in the reaction between the

metal and acetylene. The products of vacuum arc sputtering in methane were studied by Nazarenko [4] and Vishnevetskii [6]. The phase composition of the resultant carbide was shown to be independent of the stoichiometry of the reagents and to be determined by the equilibrium conditions in the temperature range 3200–3500 K [4].

Thus, since the concentration of active reagents is considerably higher when metals are sputtered by a vacuum arc discharge, this allows one to increase the yield of chemical compounds and vary their phase composition. To raise the carbide yield and obtain more carbon-rich phases, it is reasonable to raise the pressure in the discharge chamber, which is, however, not always justified technically. Another possibility is to use denser media, which is determined in many respects by the chemical composition of the gas mixture, that is, by the type of hydrocarbon used.

To assess the influence of gas mixture pressure and individual hydrocarbons in gas mixtures on the phase composition of nanopowders produced by a vacuum arc discharge using titanium cathodes, we prepared a number of TiC nanopowders using the Nanostructure Plasma Synthesis/Analysis System at the Siberian Federal University.

Experimental. According to previous results [7–11], the optimal arc discharge parameters for the synthesis of nanoparticles are as follows: discharge current I_d = 500 A; longitudinal magnetic field generated by a focusing coil on the cathode surface, 6366.2 A/m; the cathode for sputtering was of VT1-00 commercial titanium. The particles were deposited on a polished condensation surface of 12Kh18N9T stainless steel (2-mm-thick plate). After the vacuum chamber was pumped down to a pressure of = 1×10^{-3} Pa, a 30 % C_2H_2 + 70 % Ar gas mixture was admitted to it (in experiments aimed at assessing the effect of pressure). Before evaporation, the cathode was heated to a working temperature of 1200 K. The evaporation rate was assessed experimentally, from the reduction in cathode weight [12]. A titanium nitride nanomaterial was produced over a period of 10 min. Specific surface areas were determined by low-temperature BET argon adsorption measurements. The morphology, particle size composition, and structure of the powders were analyzed by transmission electron microscopy (TEM) on a JEOL JEM- 2100 and scanning electron microscopy (SEM) on a JEOL JSM-6490 LV.

To examine the effect of gas mixture composition on the physicochemical properties of carbide nanoparticles, we prepared materials in a series of experiments, using the following hydrocarbons as working media: methane, acetylene, benzene vapor, and toluene vapor. Evaporation was performed at 40 Pa, the optimum gas mixture pressure (see below).

The phase composition and structure of the materials were determined by X-ray diffraction on a Shimadzu XRD 7000 X-ray diffractometer (monochromated CuK_α radiation). Intensity data were collected at room temperature in the angular range 20 30°–120° with a scan step of 0.04°. Microstructural characteristics and unit-cell parameters were determined by the Rietveld profile analysis method [13].

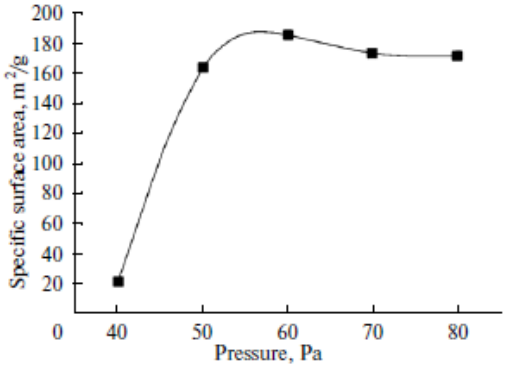

Fig. 1. Specific surface area of TiC nanopowders as a function of the pressure in the plasma reactor

Results and discussion. The formation of carbide phases at elevated reaction gas pressures is due to processes that take place directly in a plasma. The nature and rate of heat and mass exchange processes between particles of the disperse phase and the plasma flow are determined by the energy of the plasma flow, the physicochemical properties of the particles of the finely dispersed phase, the nature of the plasma-forming gas, and the nature of the interaction between the plasma flow and the finely dispersed phase. Fine titanium carbide powders can be obtained using an electric arc [4] resulting from the explosion of a melt bath on the cathode surface, because the sublimation energy of titanium is roughly equal to its ionization energy.

Fig. 1 shows the specific surface area of TiC nanopowders as a function of the pressure in the plasma reactor. As follows from these results, the specific surface area of the TiC powders rapidly reaches the highest level, 190 m^2/g at 40 Pa, and further raising the pressure causes no significant changes in specific surface area. The curve lies in a narrow range of pressures used in the synthesis of carbide nanoparticles. Above a pressure of 80 Pa, we observed arc discharge instability and frequent arc extinctions.

Analysis of TEM images (fig. 2) indicates that the products of the vacuum arc sputtering of a titanium cathode in carbon-containing gases have the form of powders consisting of spherical particles with a large surface area and a diameter from 3 to 15 nm. The micrographs show well-seen spherical particles, with much smaller particles on their surface.

It is also worth noting the presence of large, micron-sized particles, which are agglomerates of finer, submicron-sized particles, which however cannot be disaggregated.

The X-ray diffraction patterns of the powders obtained at various gas mixture compositions (fig. 3) contain peaks corresponding to α-titanium (hcp lattice). Clearly, this is due to the presence of a coarse-particle phase which resulted from cathode splashing. The lattice parameter corresponds to the reference value in the PCPDFWIN database (a = 2.951, c = 4.697 Å). α-Ti is known to be a low-temperature allotrope, existing at temperatures below 882.5 °C. At higher temperatures, it transforms into β-titanium, which has an bcc lattice [14]. Moreover, the observed broadening of the base of diffraction peaks suggests the presence of small TiC particles.

This can be understood in terms of the cathode evaporation mechanism: the cathode material is first splashed as a liquid phase in the cathode spot and then is completely evaporated in the vapor/plasma flow. In addition, the intermixing of metal vapor with an ionized carrier gas flow leads to vapor overheating, which prevents premature condensation. Next, the vapor phase is rapidly saturated with an almost completely dissociated hydrocarbon, and the hot mixture is cooled through gasdynamic expansion. Because of the high cathode temperature, the carbide formation process begins directly on the cathode surface, where the local temperature may considerably exceed the necessary threshold for direct synthesis. The final carbide formation step takes place on a substrate. Moreover, high titanium carbide synthesis temperatures in the vacuum arc sputtering process and the rapid cooling of the forming powders lead to stabilization of metastable carbides [4; 14].

The resulting titanium monocarbide, TiC, has a cubic lattice (B1 (NaCl) structure, sp. gr. Fm3m) with a lattice parameter of 0.430–0.433 nm, which depends on carbon content in the homogeneity range [4; 15]. The lattice parameter of our samples was found to increase in the order $CH_4 \rightarrow C_6H_5CH_3 \rightarrow C_6H_6 \rightarrow C_2H_2$. It is worth pointing out, however, that the lattice parameters obtained differ markedly from reference data.

Titanium carbide has the general formula TiC_{1-x} (x = 0.49–1.00) and is an interstitial phase with a broad homogeneity range. Therefore, the carbon content of the carbide (which increases in going from CH_4 to C_2H_2 and C_6H_6) and the yield of stoichiometric carbide phases depend on the nature of the hydrocarbon, namely, on the C/H ratio.

It is worth pointing out that the well-defined structure of the α-Ti samples suggests that the plasma synthesis of the carbide does not reach completion. To identify the processes responsible for this phenomenon, one should compare spectra of pure titanium and titanium carbides. It is seen that there is a rather large ratio between the peaks of titanium and titanium carbide in acetylene and benzene.

Conclusion. Thus, analysis of the above results indicates that the plasma synthesis of the carbide is more active in C_2H_2 and C_6H_6 owing to the higher density.

Note that the formation of titanium carbides has no significant effect on the nanoparticle coagulation process. This is evidenced by the fact that the particle diameter depends little on whether the powder was prepared using a VAD in carbon-containing gases, nitrogen, or argon.

The carbide formation process during vacuum arc sputtering of titanium cathodes is influenced not only by the gas mixture pressure (which is limited by the arc discharge stability) but also by the C/H ratio in the hydrocarbon molecules: increasing the C/H ratio increases the yield of carbon-reach carbide phases and reduces the percentage of the residual metal in the synthesis products. At the same time, acetylene is more attractive because the synthesis of carbide nanoparticles in a plasma reactor is more technologically attractive.

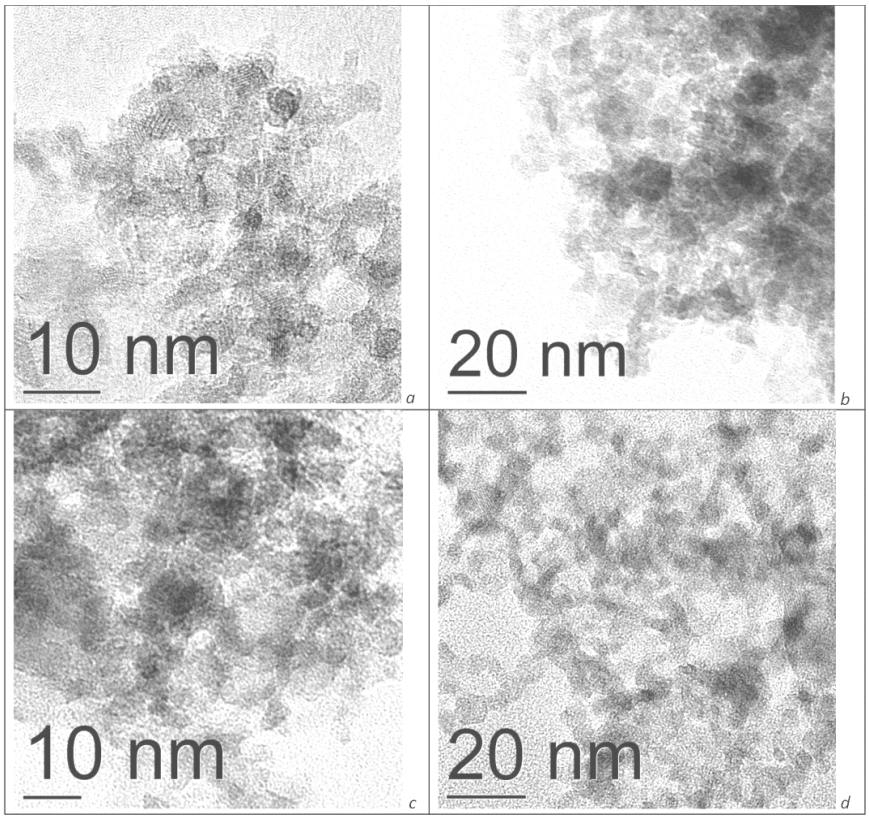

Fig. 2. Micrographs of powders produced by vacuum arc sputtering of a titanium cathode in 30 % C_2H_2 + 70 % Ar (*a*), 30 % $C_5H_5CH_3$ + 70 % Ar (*b*), 30 % C_6H_6 + 70 % Ar (*c*), and 30 % CH_4 + 70 % Ar (*d*)

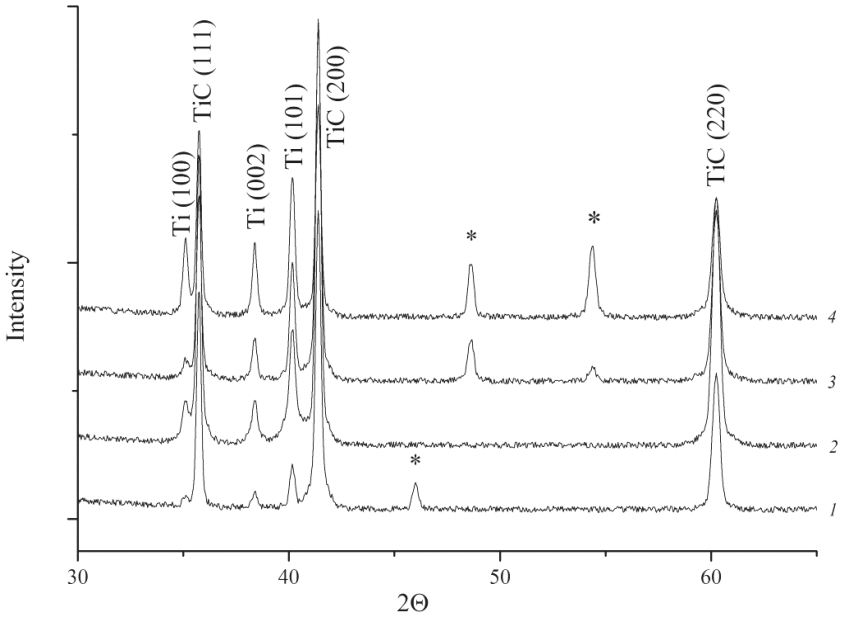

Fig. 3. Portions of X-ray diffraction patterns of freshly deposited TiC samples obtained in various gaseous atmospheres at a pressure of 40 Pa: 30 % C_2H_2 + + 70 % Ar, a = 0.429 nm (1); 30 % $C_5H_5CH_3$ + 70 % Ar, a = 0.426 nm (2); 30 % C_6H_6 + 70 % Ar, a = 0.428 nm (3); 30 % CH_4 + 70 % Ar, a = 0.425 nm (4)

Acknowledgments. This work was partly supported by the Ministry of Education and Sciences of the Russian Federation (projects no. 11.370.2014/K, 11.1287.2014/K).

Благодарности. Данная работа выполнена при частичной финансовой поддержке Министерства образования и науки Российской Федерации (проекты № 11.370.2014/K, 11.1287.2014/K).

References

1. Cook E., Siegel B. Carbide synthesis by metal explosions in acetylene. *J. Inorg. Nucl. Chem.*, 1968, Vol. 30, No. 7, P. 1699–1706, doi: 10.1016/0022-1902 (68)80341-0.

2. Johnson R. L., Siegel B. Chemistry of electrical wire explosions in hydrocarbons. *J. Electrochem. Soc.*, 1968, Vol. 115, No. 1, P. 24–28, doi: 10.1149/1.2410993.

3. Fedorov L. Yu., Karpov I. V., Ushakov A. V., Lepeshev A. A. Influence of Pressure and Hydrocarbons on Carbide Formation in the Plasma Synthesis of TiC Nanoparticles. *Inorganic Materials*, 2015, Vol. 51, No. 1, P. 25–28, doi: 10.1134/S0020168515010057.

4. Nazarenko O. B. *Protsessy polucheniya nanodispersnykh tugoplavkikh nemetallicheskikh soedineniy i metallov metodom elektricheskogo vzryva provodnikov. Dis. dok. tehn. nauk.* [Preparation of nanoparticulate refractory nonmetallic compounds and metals by electrical wire explosions. Dr. techn. sci. diss.] Tomsk, 2006, 289 p.

5. Tikhonov D. V. *Elektrovzryvnoe poluchenie ul'tradispersnykh poroshkov slozhnogo sostava. Dis. kand. tehn. nauk.* [Preparation of ultrafine powders of complex composition by electroexplosion. Cand. techn. sci. diss.] Tomsk, 1999, 212 p.

6. Vishnevetskii I. I. *Issledovanie razlozheniya uglevodorodov v impul'snykh elektricheskikh razryadakh. Dis. kand. tehn. nauk.* [Decomposition of hydrocarbons in pulsed electric discharges. Cand. techn. sci. diss.] Tomsk, 1974, 237 p.

7. Ushakov A. V., Karpov I. V., Lepeshev A. A., Krushenko G. G. [Physicochemical properties of nanomodifiers based on electric arc titanium nitride powder for polymer nanocomposite materials], *Tekhnol. Met*., 2011, No. 3, P. 16–21 (In Russ.).

8. Ushakov A. V., Karpov I. V., Lepeshev A. A. [Synthesis of titanium nitride nanopowders in a low-pressure arc discharge plasma], *Materialovedenie*, 2012, No. 3, P. 48–51 (In Russ.).

9. Karpov I. V., Ushakov A. V., Fedorov L. Yu., Lepeshev A. A. Method for Producing Nanomaterials in the Plasma of a Low Pressure Pulsed Arc Discharge. *Tech. Phys*., 2014, Vol. 84, No. 4, P. 559–563, doi: 10.1134/S1063784214040148.

10. Ushakov A. V., Karpov I. V., Lepeshev A. A., Fedorov L. Yu., Petrov M. I. Study of Magnetic Flux Pinning in Granular $YBa_2Cu_3O_{7-y}$/nanoZrO_2 Composites. *JETP Letters*, 2014, Vol. 99, No. 2, P. 105–109, doi: 10.1134/S002136401402009X.

11. Miheev A. E., Harlamov V. A., Krjuchek S. D., Chernjatina A. A., Homenko I. I. [Study of the Composition and Residual Plasma-forming Gases in the Chamber Vacuum Coaters] *Vestnik SibGAU*, 2013, No. 2 (48), P. 216–219 (In Russ.).

12. Ushakov A. V. *Poluchenie ul'tradispersnykh poroshkov v plazme dugovogo razrjada nizkogo davlenija*. *Dis. kand. tehn. nauk.* [Preparation of ultrafine powders in a low-pressure pulsed arc discharge plasma. Cand. techn. sci. diss.] Krasnoyarsk, 2002, 135 p.

13. Rietveld H. M. Profile Refinement Method for Nuclear and Magnetic Structures. *J. Appl. Crystallogr.*, 1969, No. 2, P. 65–71, doi: 10.1107/S0021889869006558.

14. Gusev A. I., *Strukturnye fazovyeperekhody v nestekhiometricheskikh soedineniyakh* [Structural phase transitions in nonstoichiometric compounds]. Moscow, Nauka Publ, 2005, 308 p.

15. Samsonov G. V. *Karbidy vol'frama* [Tungsten Carbides]. Kyiv, Naukova Dumka Publ, 2008, 175 p.

Библиографические ссылки

1. Cook E., Siegel B. Carbide synthesis by metal explosions in acetylene // *J. Inorg. Nucl. Chem.* 1968. Vol. 30, no. 7. P. 1699–1706. Doi: 10.1016/0022-1902(68) 80341-0.

2. Johnson R. L., Siegel B. Chemistry of electrical wire explosions in hydrocarbons // *J. Electrochem. Soc.* 1968. Vol. 115, no. 1. P. 24–28. Doi: 10.1149/1.2410993.

3. Influence of Pressure and Hydrocarbons on Carbide Formation in the Plasma Synthesis of TiC Nanoparticles / L. Yu. Fedorov [et al.] // *Inorganic Materials*. 2015. Vol. 51, no. 1. P. 25–28. Doi: 10.1134/S0020168515010057.

4. Назаренко О. Б. Процессы получения нанодисперсных тугоплавких неметаллических соединений и металлов методом электрического взрыва проводников : дис. … д-ра техн. наук. Томск, 2006. 289 с.

5. Тихонов Д. В. Электровзрывное получение ультрадисперсных порошков сложного состава : дис. … канд. техн. наук. Томск, 1999. 212 с.

6. Вишневецкий И. И. Исследование разложения углеводородов в импульсных электрических разрядах : дис. … канд. техн. наук. Томск, 1974. 237 с.

7. Физико-химические свойства наномодификаторов на основе электродугового порошка нитрида титана для полимерных нанокомпозиционных материалов / А. В Ушаков [и др.] // Технология металлов. 2011. № 3. С. 16–21.

8. Ушаков А. В., Карпов И. В., Лепешев А. А. Особенности синтеза нанопорошков нитрида титана в плазменной среде дугового разряда низкого давления // Материаловедение. 2012. № 3. С. 48–51.

9. Method for Producing Nanomaterials in the Plasma of a Low Pressure Pulsed Arc Discharge / I. V. Karpov [et al.] // *Tech. Phys*. 2014. Vol. 84, no. 4. P. 559–563. Doi: 10.1134/S1063784214040148.

10. Study of Magnetic Flux Pinning in Granular $YBa_2Cu_3O_{7-y}$/nanoZrO_2 Composites / A. V. Ushakov [et al.] // *JETP Letters*. 2014. Vol. 99, no. 2. P. 105–109. Doi: 10.1134/S002136401402009X.

11. Исследование состава остаточного и плазмообразующего газов в камере установки вакуумного напыления / А. Е. Михеев [и др.] // Вестник СибГАУ. 2013. № 2 (48). С. 216–219.

12. Ушаков А. В. Получение ультрадисперсных порошков в плазме дугового разряда низкого давления : дис. … канд. техн. наук. Красноярск, 2002. 135 с.

13. Rietveld H. M. Profile Refinement Method for Nuclear and Magnetic Structures // *J. Appl. Crystallogr.* 1969. No. 2. P. 65–71. Doi: 10.1107/S0021889869006558.

14. Гусев А. И., Рempель А. А. Структурные фазовые переходы в нестехиометрических соединениях. М. : Наука, 2005. 318 с.

15. Самсонов Г. В., Витрянюк В. К., Чаплыгин Ф. Ч. Карбиды вольфрама. Киев : Наукова думка, 2008. 173 с.