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Synthesis of Ti(C,N) ultrafine powders by carbothermal reduction of TiO_2 derived from sol–gel process

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Abstract

Experimental results demonstrate that $TiC_{1-X}N_X$ ultrafine powders can be synthesized by the sol–gel process. The factors influencing the powder synthesizing process, such as temperature, C/Ti ratio in raw materials, holding time and flow rate of nitrogen gas, are discussed. $TiC_{0.5}N_{0.5}$ powders with particle sizes less than 100 nm were produced at 1550°C. The microhardness of hot-pressed $TiC_{0.5}N_{0.5}$ samples at 1750°C was 19.6 GPa and the relative density was 98.9%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbothermal process; Powders-gas phase reaction; Sol–gel processes; Ti(C,N)

1. Introduction

Ti(C,N) is a kind of excellent nonoxide ceramic material with good high temperature strength, thermal and chemical stability, high hardness, high thermal and electrical conductivity.[1] It can be used as wear-resistant parts, cutting tools, electrode and coating materials.

Ti(C,N) exists as a solid solution of TiC and TiN, and it can be expressed as $TiC_{1-X}N_X$ with $0 < x < 1$. The producing methods of Ti(C,N) powders are classified as follows: (1) solid state methods, such as chemical reduction of titanium oxide, titanium chloride, or titanium hydride by carbon, nitrogen, and ammonia;[2,3] direct reaction of TiC with TiN or Ti with C, N;[4–9] self-propagating high-temperature synthesis.[10,11] (2) gaseous state methods, such as chemical vapor deposition process,[12] (3) liquid state methods, such as thermal decomposition process.[13] However, there are many drawbacks for these methods. For example, powders obtained from solid state methods usually have large particle size and low purity. The processes of liquid and gaseous methods cannot be controlled easily and the raw materials are generally very expensive. So there is a necessity to develop a new way to synthesize Ti(C,N) powders conveniently and effectively.

In recent years, the sol–gel process has been widely investigated as a new way to synthesize high purity ultrafine powders. It has many benefits, for instance, good dispersion of the components, narrow distribution of particle sizes, larger specific surface and higher purity when compared with the conventional methods listed above. In addition, this process does not require special equipment and can be finished with low cost. There have been many reports concerning synthesis of ultrafine powders by the sol–gel process. For example, Yan et al.[14] prepared $PbTiO_3$ powders with particle sizes less than 50 nm; Taguchi et al.[15] produced $La_{1-X}Sr_XMnO_3$ powders with particle sizes of about 18 nm. However, research on the synthesis of $TiC_{1-X}N_X$ ultrafine powders by sol–gel methods has so far been lacking. This work presents the synthesis of ultrafine $TiC_{1-X}N_X$ powders by a sol–gel method.

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2. Experimental procedure

The reactants used in this research include $TiO(OH)_2$ sol with pH = 3.5 (Zhuzhou Chemical-engineering Factory), activated charcoal (Nanping Carbon Factory), and nitrogen gas (99% pure).

$TiO(OH)_2$ and activated charcoal were mixed and hydrolyzed in deionized water and gelatinized at 60°C. Subsequently the gel was dried to constant weight at 120°C. The mixture was put into a graphite crucible and the $TiC_{1-X}N_X$ powders were synthesized in a carbon tube furnace at 1400–1600°C in flowing nitrogen gas. The synthesizing reaction can be expressed with the following equation:

$$2\ TiO(OH)_2 + 2(3-x)C + xN_2 = 2\ Ti(C_{1-X}N_X) + 4\ CO + 2\ H_2O \quad (1)$$

Table 1 shows the synthesizing conditions of $TiC_{1-X}N_X$ powders. The initial raw materials and synthesized powders were analyzed by D5000-XRD Analyzer (Simens Corporation). Particle sizes were measured by SKC-2000R Particle Size Distribution Analyzer. To test the sinterability, the synthesized powders were put into a graphite die and hot-pressed at 1550–1850°C for 20 min in flowing nitrogen gas. The heating rate was 20–30°C/min.

Table 1
Synthesizing conditions of $TiC_{1-X}N_X$ powders

	Ratio of C/Ti	Temperature (°C)	Holding time (h)	Flow rate of N_2 (l/min)
$TiC_{0.5}N_{0.5}$	2.5	1550	1	0.2
$TiC_{0.2}N_{0.8}$	2.2	1550	1	0.2

The microstructure of sintered samples was observed by H-800 TEM and JMS-35C SEM. The microhardness of the sintered samples was determined by the MM6 Hardness Detector.

3. Results and discussion

3.1. Synthesis of powders

In this sol–gel process TiO_2 is generated by hydrolyzing a $TiO(OH)_2$ sol and the $TiC_{1-X}N_X$ powder is produced by carbothermal reduction of TiO_2. The particle sizes of the $TiC_{1-X}N_X$ powders obtained from the sol–gel method are small (generally the particle sizes are less than 100 nm) and have a narrow distribution. This method requires lower synthesizing temperature compared with solid state methods. $TiC_{0.5}N_{0.5}$ can easily be synthesized already at 1550°C by the sol–gel method while it is difficult at such a low temperature by solid state methods.[16]

Fig. 1(a) and (b) are TEM micrographs of $TiC_{1-X}N_X$ powders produced by sol–gel and solid state methods[16] respectively. The results show that there are great differences in particle size and shape between these two powders. To explain the differences, XRD analysis was carried out on the powder obtained from the sol–gel process (Fig. 2). The gelatinized mixture of $TiO(OH)_2$ and activated charcoal were heat-treated at 120, 400 and 1500°C, respectively. It can be seen that the mixture is amorphous at 120°C. Anatase appears at about 400°C and the particle size is about 5 nm which can be calculated from half-width of diffraction peak. This size is far smaller than that of commercial TiO_2 used in Ref. [16] (more than 100 nm). Accordingly, the mixture has higher reaction activity than TiO_2 does and $TiC_{1-X}N_X$ powders can be synthesized at a certain low temperature. The

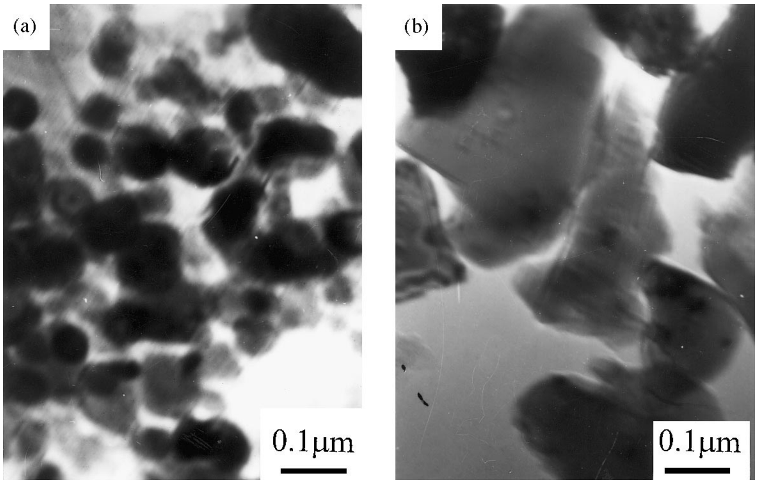

Fig. 1. TEM micrographs of powders synthesized from (a) sol–gel process and (b) solid state method.

diffraction peaks of $TiC_{1-X}N_X$ are viewed at 1500°C. At such a low temperature, grain growth can be suppressed and ultrafine powders can be produced. It was determined by particle size analyzer that the particle size is about 100 nm for the $TiC_{1-X}N_X$ powder synthesized at 1550°C from the sol–gel process.

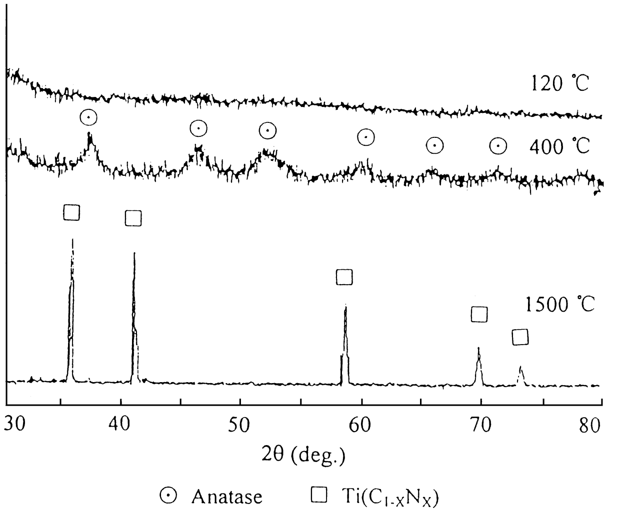

Fig. 2. XRD spectra of raw materials heat-treated at (a) 120°C, (b) 400°C, (c) 1500°C.

3.2. Influence of synthesizing conditions on powder property

3.2.1. C/Ti ratio in raw materials

The carbon content in the raw materials has a significant influence on the purity of synthesized powders. The relationship between the C/Ti ratio and the content of free carbon left in the products is displayed in Table 2. It can be seen that the C/Ti ratio varies from 2.4 to 3 while the x value drops from 0.74 to 0.64, and the free carbon content increases from 0.84 to 11.34 wt%. This

Table 2
Relationship of C/Ti ratio in raw materials to products

No.	C/Ti (molar)	Free C (wt%)	x Value	Color of powders
1	3	11.34	0.64	Black
2	2.8	7.42	0.69	Black–grey
3	2.6	2.52	0.72	Black–grey
4	2.4	0.84	0.74	Grey

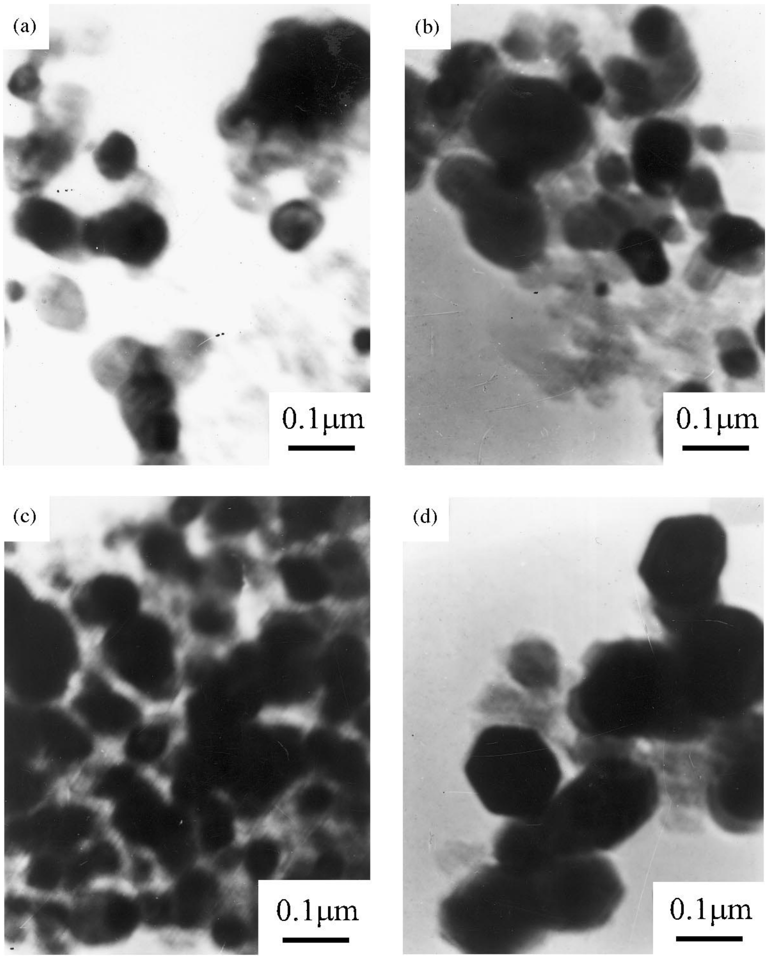

Fig. 3. TEM micrographs of powders synthesized at (a) 1400°C, (b) 1450°C, (c) 1500°C, (d) 1550°C.

result means that the higher C/Ti ratio in the raw materials, the lower the x value in $TiC_{1-X}N_X$ resulting in a higher content of free carbon in the final product. The removal of free carbon is very difficult. In fact, both the crucible and the furnace used in experiment are made from carbon and maybe bring about some carbon contamination. And in general, carbon in the raw materials cannot react with titanium completely from reaction kinetics viewpoint. Accordingly, free carbon always found in synthesized $Ti(C_{1-X}N_X)$ powders.

According to Eq. (1), the molar ratio of C/Ti in the raw materials should be kept less than 3 in order to decrease the content of free carbon left in the products. At the same time, suitable synthesizing conditions should be chosen to ensure that carbon in the raw materials can be consumed as much as possible.

Besides carbon, oxygen is another factor influencing the purity of the products. There are always some oxygen left in the synthesized powders from carbothermal reduction. The influence of oxygen is more complex than that of carbon and will be investigated in further work.

3.2.2. Synthesizing temperature and holding time

In the process of $TiC_{1-X}N_X$ synthesizing, nitrogen does react more easily with titanium compared to carbon. So the key point in the synthesizing process is how to suppress the x value. The TEM micrographs of $TiC_{1-X}N_X$ powders synthesized at different temperatures are shown in Fig. 3. It can be observed that the particle sizes become larger with the increment in temperature, and better crystalline form can be obtained.

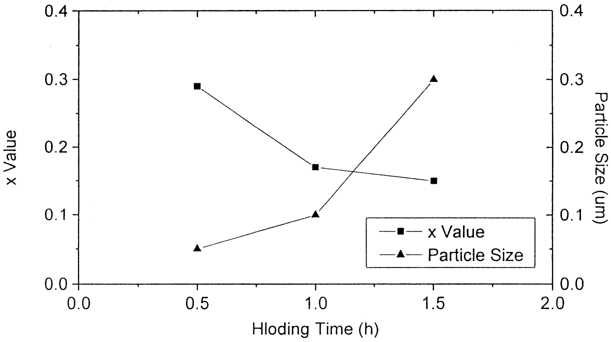

Fig. 4. Relationship of hold time to x value and particle sizes of powders synthesized at 1590°C.

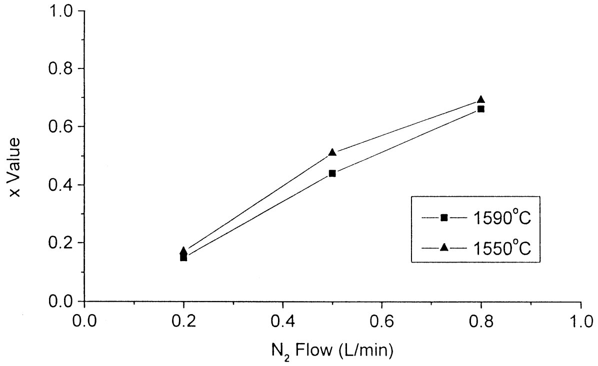

Fig. 5. Relationship of flow rate of N_2 to x value.

The holding time greatly influences the transformation rate of the reactants and the particle size of the products. To study the relationship of holding time with the transformation rate and the particle size, $Ti(C_{1-X}N_X)$ powders were synthesized at 1590°C. Fig. 4 shows that a relative long holding time is beneficial to the reaction of carbon with titanium as well as to a significant decrement of the x value, while the particle sizes increases at the same time. When the holding time is longer than 1 h the drop of x value is limited, and the growth of grains is accelerated. Therefore, it is important to keep the holding time in a suitable range to ensure the property of synthesized powders.

3.2.3. Flow rate of N_2

The flow rate of N_2 is a key factor in the synthetic reaction of $TiC_{1-X}N_X$. Large flow rates will hinder the combination of carbon with titanium because nitrogen reacts more easily with titanium compared to carbon. From thermodynamic calculation, it can be obtained that the temperature of nitrogen begin to react with titanium is about 1160°C, while the temperature of carbon begin to react with titanium is about 1260°C. The larger the flow rate of N_2, the higher the x value of $TiC_{1-X}N_X$ powders. From Fig. 5, it can be seen that the value of x varies from 0.15 to 0.66 (at 1590°C) and from 0.17 to 0.69 (at 1550°C) when the flow rate of N_2 increase from 0.2 to 0.8 l/min. This phenomenon due to that during the temperature increasing process, more titanium react with nitrogen before it can react with carbon ($T < 1260$°C) under a larger flow rate of N_2. Therefore the flow rate of N_2 must be controlled at a certain low level in order to make carbon react with titanium completely.

3.3. Sinterability of synthesized powders

The synthesized powders were hot-pressed at 1550–1850°C and 0.1 MPa nitrogen atmosphere to test their

Table 3
Properties of sintered samples

No.	x Value[a]	Temperature (°C)	Theoretical density (%)	Microhardness (GPa)
5	0.5	1750	98.9	19.6
6	0.5	1650	97.2	17.3
7	0.5	1550	90.1	14.9
8	0.8	1850	98.6	14.1
9	0.8	1800	98.9	14.6
10	0.8	1750	99.3	14.7
11	0.8	1700	97.3	13.1
12	0.8	1650	89.0	11.1

[a] x Value is the composition of starting powder.

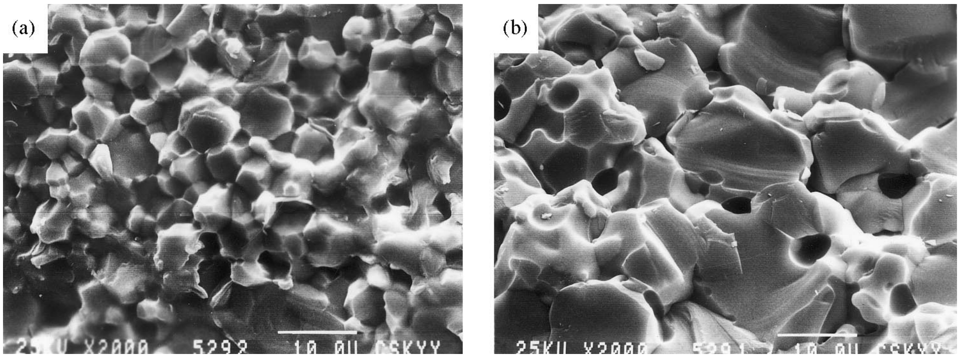

Fig. 6. SEM micrographs of sintered samples at (a) 1750°C and (b) 1850°C.

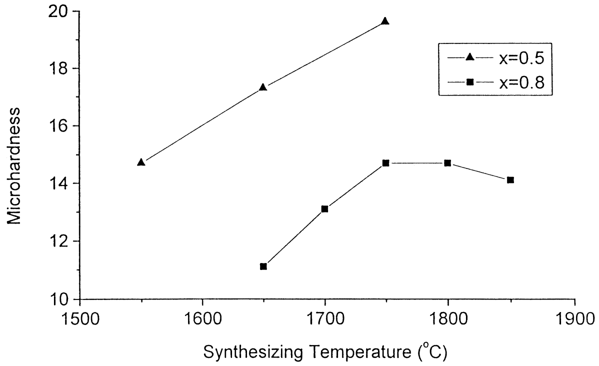

Fig. 7. Relationship of sintering temperature to microhardness.

sinterability. The density and hardness of the sintered bodies are list in Table 3.

The sintering temperature is important to the bulk density of samples. The density increases with the increased sintering temperature and reaches the maximum value of 99.3% theoretical density at 1750°C, but it decreases when the temperature is higher than 1800°C. SEM micrographs of samples sintered at 1750 and 1850°C respectively are displayed in Fig. 6(a) and (b). A more densified and homogeneous microstructure was observed in the sample sintered at 1750°C. However, there are many pores and larger grains in the sample sintered at 1850°C. The results showed that 1850°C is slightly high for sintering of $Ti(C_{1-X}N_X)$ powder compacts in 0.1 MPa nitrogen atmosphere.

Pore formation in sintered samples mainly due to the denitrification phenomenon at high temperature. Denitrification is a common phenomenon during the $Ti(C_{1-X}N_X)$ sintering process. It can be expressed as following equation:

$$Ti(C_{1-X}N_X) \Rightarrow Ti(C_{1-Y}N_Y) + (X-Y)/2\ N_2, \quad \text{where } X > Y \tag{2}$$

This reaction can be controlled by selecting suitable sintering temperature and nitrogen pressure. More details can be obtained by thermodynamic calculation according to Ref. [13].

Another reason for pore formation may be due to the coalescence of vacancies in $Ti(C_{1-X}N_X)_\alpha\square_{1-\alpha}$ ($\square$ is the vacancy) lattice. More experiments to prove this inference will be carried out in further investigations.

The relationship of microhardness to sintering temperature is shown in Fig. 7. The microhardness increases almost linearly with increasing sintering temperature up to 1750°C because the higher density at higher sintering temperature lead to a higher microhardness. When the temperature is above 1800°C, the microhardness decreased significantly due to the lower density.

For samples with different x value sintered at the same temperature (such as samples 5, 6, 10 and 12; Table 3), those with lower x value has the highest microhardness. One of the reasons is that C contributes more to the microhardness than N does in these samples.

4. Conclusion

1. Ultrafine powders of $TiC_{1-X}N_X$ with $x = 0.2$–0.8 and particle sizes less than 100 nm can be successfully synthesized by a sol–gel process at high temperatures in flowing nitrogen gas. $TiC_{0.5}N_{0.5}$ powders can be produced at 1550°C.
2. Increased C content in the raw materials, elevated synthesizing temperature, prolonged holding time and lower flow rate of nitrogen gas are beneficial in order to produce $TiC_{1-X}N_X$ powders with low x value.
3. Synthesized $TiC_{1-X}N_X$ powders show best sinterability at 1750°C and 0.1 MPa N_2 pressure. The sample with composition of $TiC_{0.5}N_{0.5}$, which was hot-pressed at 1750°C for 20 min under 25 MPa, has a 98.9% theoretical density and microhardness of 19.6 GPa.

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References

1. Zhang, S., Titanium carbonitride-based ceramics: processes and properties. *Mater. Sci. Eng.*, 1993, **A163**, 141–148.
2. Alekseev, N. V., Balikhin, I. L., Kurkin, E. N., Samokhin, A. V., Troitskaya, E. V. and Troitskij, V. N., Synthesis of titanium nitride and carbonitride ultra-fine powders from titanium hydride in nitrogen arc discharge plasma jet. *Fizika i Khimiya Obrabotki Materialov*, 1995, **1**, 31–39.
3. Licko, T., Figusch, V. and Puchyova, J., Carbothermal reduction and nitriding of TiO_2. *J. Euro. Ceram. Soc.*, 1989, **5**(4), 257–265.
4. Han, K. and Weatherly, G. C., Transmission electron microscopy investigation in titanium carbonitride. *Philosophical Magazine Letters*, 1997, **76**(4), 247–258.
5. Gibas, T., Walter, J. Jaworska, L. and Krolicka, B., Sinterability of carbide–nitride phases of titanium in high pressure conditions. *Journal of Materials Processing Technology, Proceedings of the 1995 International Scientific Conference on Achievements in Mechanical and Materials Engineering*, Vol. 64(1–3), 30 November–1 December 1995 Gliwice-Wisla, Poland. Elsevier Science Inc, New York, pp. 133–140.
6. Ozturk, Bahri and Fruehan, R. J., Thermodynamics of inclusion formation in Fe–Ti–C–N alloys. *Metallurgical Transactions B (Process Metallurgy)*, 1990, **21**(5), 879–884.
7. Vil'k, Yu.N. and Klimashin, G. M., Effect of carbon on the sinterability of highly dispersed powders corresponding to the TiN–TiC section of the titaniumcarbon–nitrogen system and the properties of the specimens made from them. *Refractories* (English translation of Ogneupory), 1988, **28**(11–12), 647–650.
8. Parkhomenko, V. D., Serdyuk, G. N. and Krasnokutskii, Yu.I., Kinetics of formation of titanium carbonitride at high temperatures. *Physics and Chemistry of Materials Treatment*, 1986, **20**(5), 429–432.
9. Rauschenbach, B., Formation of compounds by high-flux nitrogen implantation in titanium. *J. Mater. Sci.*, 1986, **21**(2), 395–404.
10. Eslamloo-Grami, M. and Munir, Z. A., Mechanism of combustion synthesis of titanium carbonitride. *J. Mater. Res.*, 1994, **9**(2), 431–435.
11. Li, J. T., Liu, W. S., Xia, Y. L. and Ge, C. C., Combustion cosynthesis of Si_3N_4-based in situ composites. *J. Mater. Res.*, 1996, **11**(12), 2968–2979.
12. Slifirski, J. and Teyssandier, F., Titanium carbide and titanium carbonitride obtained by chemical vapor deposition from organometallic precursor in the range 450–800°C. *Journal De Physique Proceedings of the 9th European Conference on Chemical Vapor Deposition* Vol. 3(3), 22–27 August 1993, Tampere, Finland, pp. 391–374.
13. Pastor, H., Titanium carbotitride-based hard alloys for cutting tools. *Mater. Sci. Eng.*, 1988, **A105/106**, 401–409.
14. Yan, H. W., Yuan, Q. H., Quyang, S. X. and Xu, M., Preparation of pure $PbTiO_3$ fine powder by sol–gel technique. *J. Func. Mater.*, 1994, **25**(4), 334–338 (in Chinese).
15. Taguchi, H., Matsuda, D. and Nagao, M., Synthesis of perovskite-type $(La_{1-x}Sr_X)MnO_3$ $(0 \leq x \leq 0.3)$ at low temperature. *J. Am. Ceram. Soc.*, 1992, **75**(1), 201–202.
16. Xiang, J. H. and Xiao, H. N., Effect of technological parameters on the synthesis of Ti(C,N) by carbothermal reduction of TiO. *J. Ceram.*, 1997, **18**(2), 63–66 (in Chinese).