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Preparation of titanium nitride ultrafine powders by sol–gel and microwave carbothermal reduction nitridation methods☆

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Abstract

Titanium nitride ultrafine powders were prepared from tetrabutyl titanate and sucrose by sol–gel and microwave carbothermal reduction methods. The influences of reaction temperature, molar ratio of Ti to C, addition of crystal seeds and amount of NH_4F on the synthesis of titanium nitride were studied. The results show that excess amount of carbon, addition of crystal seeds and NH_4F plays a positive effect on the preparation of TiN at low temperature. The inceptive formation temperature of TiN ultrafine powders is about 800 °C, and pure TiN can be prepared at 1000 °C. Field emission-scanning electron microscopy (FE-SEM) was used to get the micrograph of the TiN powder, it shows that the size of the powders synthesized at 1000 °C is about 0.1–0.5 μm.

Keywords: Sol–gel; Microwave; Carbothermal; Reduction; Titanium nitride; Powders

1. Introduction

Titanium nitride is an important technological material for applications in various fields because of its good combination of physical and chemical properties, such as high melting point (2927 °C), high hardness, and relatively low specific gravity, high wear resistance and high corrosion resistance [1–3].

Traditional synthesis techniques of monolithic titanium nitride include the direct reaction of titanium with nitrogen gas or ammonia at temperatures around 1200 °C for extended periods of time [4]. TiN powders can be also synthesized by a variety of other method, such as nitridation of titanium oxides in the presence of carbon at temperatures higher than 1000 °C [5,6], microwave plasma heating [7,8], self-propagating high temperature synthesis (SHS) [9–12], mechanochemical route [4,13,14], and rapid solid-state metathesis (SSM) reactions of titanium tetrachloride ($TiCl_4$) [15] with various solid nitrogen sources, such as Li_3N [16], sodiumamide ($NaNH_2$) [17–19], Ca_3N_2 [20], NH_4Cl [21].

The sol–gel process is a well-known chemical route to prepare oxide-based materials. Moreover, the use of molecular precursors and the control of the synthesis conditions make it possible to prepare homogeneous and pure multicomponent systems. However, there are only few reports on the preparation of TiN by a homogeneous sol–gel and microwave heating process. The aim of the present work was to investigate the low-temperature preparation of TiN ultrafine powder using sol–gel and microwave carbothermal reduction process. The effects of TiN crystal seeds and addition of NH_4F on the preparation of TiN ultrafine powder were also studied.

2. Experimental procedure

The raw materials utilized in present paper were analytical reagent grade tetrabutyl titanate (≥99.8 wt%, Beijing Chem. Co. Ltd., Beijing, China, $[C_4H_9O]_4Ti$), sucrose (≥99 wt%, Beijing Chem. Co. Ltd., Beijing, China, $C_{12}H_{22}O_{11}$). TiN is obtained by the reaction as following:

$$TiO_2 + 2C + (1/2)N_2 = TiN + 2CO \quad (1)$$

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A stoichiometric amount of sucrose was dissolved in distilled water, the solution was then slowly mixed with tetrabutyl titanate precursor to get the sol, and the sol was placed in air atmosphere for several days to obtain the gel; the gel was then heated in a temperature range of 120–140 °C for 24 h to get a dried gel. Finally, the dried gel precursor was fired in microwave furnace (Model: MW-L0316V, 3 kW, 2.45 GHz, by Changsha Longtech Co. Ltd, Hunan province, China) at 800–1275 °C for 2 h in flowing N_2 atmosphere (N_2 purity about 99.999 wt%) to obtain ultrafine TiN powder. The heating rate was about 20 °C min^{-1}, the plateau temperature could be held within ±5 °C. The gas outlet valve was normally opened on heating and closed at 600 °C on cooling.

X-ray diffraction patterns were recorded from 20° to 100° (2θ) with a step width of 0.02°, using a Philips X'Pert PRO diffractometer (using Cu Kα radiation, Ni as filter and silicon as internal standard, 40 kV, 40 mA, time per step 3.80 s). The Rietveld refinement method, a proven way for the quantitative determination of amorphous and crystalline phases, was used to refine the structure of the phases in the samples. PANalytical X'pert Highscore plus program was used for the refinement analysis. Powder morphology was observed via field emission scanning electron microscopy (FESEM) (Model, JSM-6700F, JEOL, JAPAN).

3. Results and discussion

Table 1 shows the XRD results and the content of phase composition of TiN specimens with different carbon annealed at 800–1275 °C. From the results, it can be seen:

(1) The inceptive formation temperature of TiN by sol–gel and microwave carbothermal reduction way is about 800 °C, pure TiN crystal phase can be prepared at 1000 °C. The five

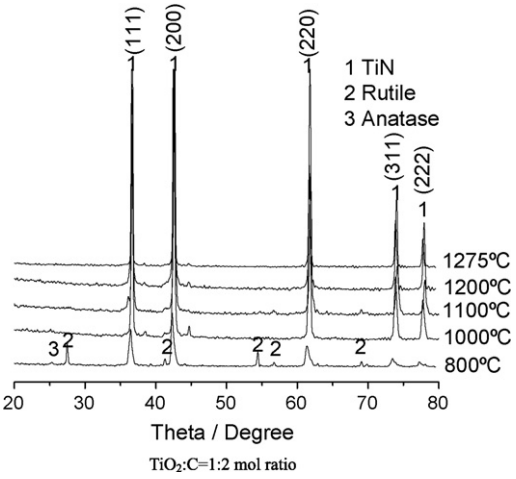


Fig. 1. XRD results of TiN prepared at different temperature (1) TiN, JCPDS 38-1420; (2) TiO_2(R), JCPDS 21-1276; (3) TiO_2(A), JCPDS 21-1272.

diffraction peaks at 2θ of 36.65, 42.54, 61.61, 73.82 and 77.67° can be indexed as the cubic cell of TiN((1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2)), this is clearly illustrated in Fig. 1 showing the XRD patterns of specimen T-1 fired at 800–1275 °C. The temperature (1000 °C) is relatively low compared to other results using TiO_2/carbon as starting materials [22,23], in those reports, bulk TiN is usually synthesized by carbothermal reduction and nitridation at about 1200 °C in nitrogen under high pressure. It is considered that three factors contributed to the lower onset temperature of TiN formation in present paper. Firstly, the sucrose was homogeneously distributed in the TiO_2 precursor, and changed into carbon in the heating process. The produced carbon uniformly covered the surface of TiO_2, and consequently, a large contact area between TiO_2 and carbon was created. Secondly, the particle size of TiO_2

Table 1
Composition content and cell parameters of prepared TiN with different amount of carbon at 800–1275 °C

Sample	TiO_2:C mol ratio	T (°C)	Cell parameter a (Å)	Content of TiN (%)	Content of rutile (%)	Content of anatase (%)
T-1	1:2.0	1275	4.256	100	0	0
		1200	4.244	100	0	0
		1100	4.239	100	0	0
		1000	4.254	100	0	0
		800	4.271	58.6	39.5	1.9
T-2	1:2.2	1275	4.255	100	0	0
		1200	4.245	100	0	0
		1100	4.263	100	0	0
		1000	4.243	100	0	0
		800	4.268	60.0	34.7	5.3
T-3	1:2.5	1275	4.258	100	0	0
		1200	4.255	100	0	0
		1100	4.266	100	0	0
		1000	4.261	100	0	0
		800	4.276	75.5	24.5	0
T-4	1:3.0	1275	4.259	100	0	0
		1200	4.268	100	0	0
		1100	4.265	100	0	0
		1000	4.262	100	0	0
		800	4.281	91.7	8.3	0

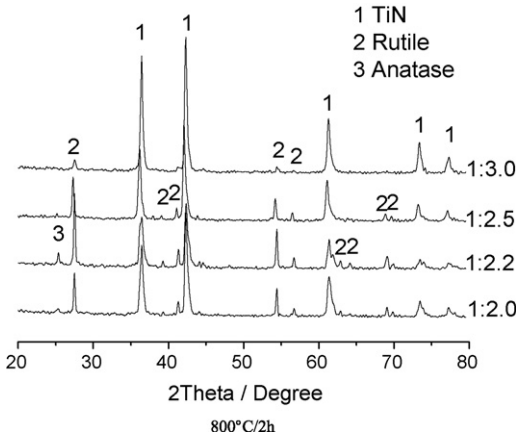


Fig. 2. XRD results of TiN prepared with different amount of carbon (1) TiN, JCPDS 38-1420; (2) TiO_2(R), JCPDS 21-1276; (3) TiO_2(A), JCPDS 21-1272.

prepared from tetrabutyl titanate was also very small. Thirdly, the microwave heating technique enhanced the reaction process. The extent of TiN formation is influenced by amount of C addition at low temperature, excess amount of carbon plays a positive effect on the preparation of TiN at 800 °C, and it can be concluded from the XRD patterns shown in Fig. 2.

(2) When heated at 800 °C, the diffraction peaks of anatase can be still observed in the XRD spectrum (Figs. 1 and 2). The phase transform temperature of TiO_2 nano-particles (from anatase to rutile) is about 650 °C in air. However, anatase remained even at 800 °C under N_2 without the transition to rutile in the present work, which may be due to the presence of carbon, which plays a role of inhibiting the transition of anatase. Over 1000 °C, TiO_2 phase (rutile and anatase) can not be observed in XRD pattern (Fig. 1), this shows that the carbothermal reduction process is complete at this temperature. Carbothermal reduction (see Eq. (1)) is an overall reaction consisting of several steps. It has been reported that TiO_2 is reduced to TiN via various suboxides (Ti_3O_5, and TiO) [24]. However, the peaks of the suboxides were not observed in any XRD spectrum of the specimens heated at 800 °C or above. This may indicate that the change of TiO_2 into TiN is relatively fast during the reduction process using microwave heating.

(3) The lattice parameter of TiN prepared at 800 °C is little higher than that other samples prepared at 1000–1275 °C. The lattice parameter of TiN prepared at 1275 °C is in the range of 4.255–4.259 Å, which is little different with that of the pure cubic TiN phase ($a = b = c = 4.244$ Å, PANalytical ICSD Database code 98-002-1995).

Table 2 shows the phase composition of TiN specimens prepared at 800 °C with crystal seeds added, it indicates that little amount of crystal seeds plays a positive effect on the preparation of TiN, when the crystal seeds addition is 3% (weight ratio), the extent of TiN formation is more than 80%. This indicates that for synthesizing TiN by tetrabutyl titanate and sucrose, the little amount of TiN crystal seeds is effective in promoting TiN preparation at low temperature.

Table 3 shows the phase composition of TiN specimens prepared at 800 °C with NH_4F added, when the NH_4F addition is 15% (weight ratio), the extent of TiN formation is about 90%. This indicates that the addition of NH_4F is effective in promoting TiN preparation at low temperature. The XRD results of the samples (TN series specimens) with different amount of NH_4F are shown in Fig. 3, it clearly indicates the intensity of the diffraction peak of TiO_2 decrease with the NH_4F increase. In the fabrication of nitride powders, ammonium halides are often added to accelerate the reaction process [25]. It shows that NH_4F has been almost fully decomposed at about 250 °C [26], NH_3, N_2 and H_2 will be released as a reaction product during the decomposition process, which will play a positive role on the reduction nitridation process of TiO_2.

SEM images of the synthesized TiN powders at 1000 and 1200 °C for 2 h are shown in Fig. 4. Fig. 4a (FE-SEM) shows that the particle sizes of the TiN powders synthesized at 1000 °C distribute over 0.1–0.5 μm, agglomerations can be observed and most of the particles are comprised of the aggregates with several particles. Fig. 4a also exhibits that a lot of irregular shaped TiN particles are formed in the sample. The particle sizes of the TiN powders synthesized at 1200 °C is about 0.5–1 μm (Fig. 4b). EDS analysis (Table 4) shows the

Table 2
Composition content and cell parameters of prepared TiN with different amount of TiN crystal seeds

Sample	TiO_2:C mol ratio	Seeds amount (wt%)	T (°C)	Cell parameter a (Å)	Content of TiN (%)	Content of rutile (%)	Content of anatase (%)
TS	1:2.0	0	800	4.271	58.6	39.5	1.9
		1		4.263	74.2	25.8	0
		2		4.264	69.6	30.4	0
		3		4.270	82.1	17.9	0

Table 3
Composition content and cell parameters of prepared TiN with different amount of NH_4F

Sample	TiO_2:C mol ratio	NH_4F (wt%)	T (°C)	Cell parameter a (Å)	Content of TiN (%)	Content of rutile (%)	Content of anatase (%)
TN	1:2.0	0	800	4.271	58.6	39.5	1.9
		5		4.272	62.5	34.4	3.1
		10		4.270	67.5	23.8	8.7
		15		4.271	89.5	10.4	0

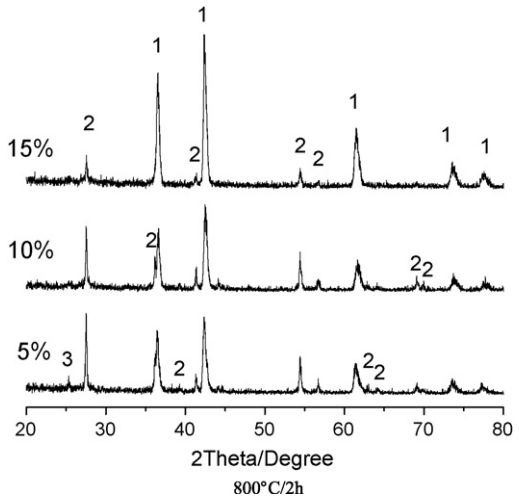
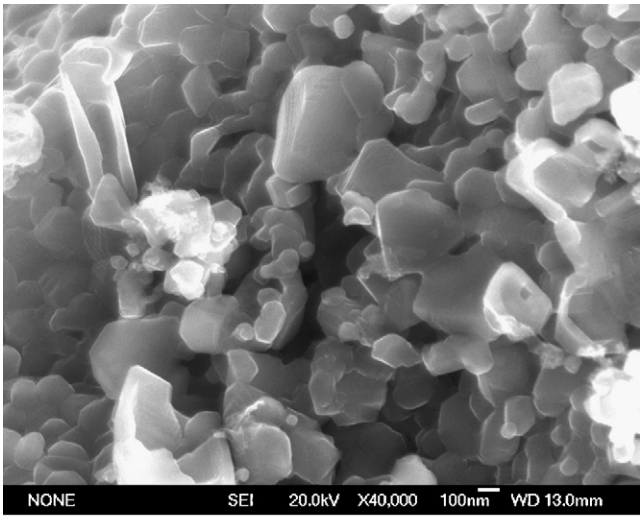
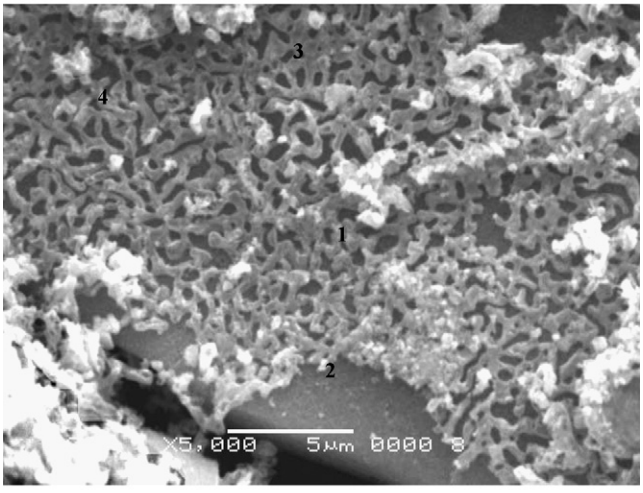


Fig. 3. XRD results of TiN prepared with different amount of NH_4F (1) TiN, JCPDS 38-1420; (2) TiO_2(R), JCPDS 21-1276; (3) TiO_2(A), JCPDS 21-1272.



(a) (1000°C, TiO_2: C=1:2mol ratio)



(b) (1200°C, TiO_2:C=1:2)

Fig. 4. SEM photograph of TiN prepared at (a) 1000 °C and (b) 1200 °C by sol–gel and microwave carbothermal method.

Table 4
EDS results of the selected point in Fig. 4(b) (at.%)

Spectrum	*N*	Ti	Total
Point 1	29.08	70.92	100.00
Point 2	38.62	61.38	100.00
Point 3	37.91	62.09	100.00
Point 4	39.24	60.76	100.00

only presence of Ti and N in the sample, which undoubtedly indicates that the pure TiN powders are prepared.

4. Conclusions

Pure TiN powders were prepared by sol–gel and microwave carbothermal reduction process using tetrabutyl titanate and sucrose as studying materials. This method cannot only lower the reaction temperature and shorten the soaking time, synthesize the ultrafine powders, but also is economical and energy saving.

The initial crystallization temperature of the TiN powder is about 800 °C, whereas that of the fully crystallized TiN appeared at about 1000 °C. The carbothermal temperature, and the content of carbon show obvious effects on the formation of TiN. The addition of crystal seeds and NH_4F play a positive effect on the preparation of TiN at low temperature.

The principal factors influencing ultrafine TiN powder synthesis are: (1) formulation: use of tetrabutyl titanate and sucrose is recommended at TiO_2:C = 1:2 molar ratios and (2) temperature: the suitable firing temperature is 1000 °C. The TiN powders prepared at 1000 °C are granular with size 0.1–0.5 μm.

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