Facile Synthesis of Nanocrystalline Titanium Carbonitride via a Chemical Metathesis Route

Xin Feng*[†,††] and Li-Yi Shi*[†,†††]
[†]College of Sciences, Shanghai University, Shanghai 200444, P. R. China
[††]School of Material Science and Engineering, Shanghai University, Shanghai 200072, P. R. China
[†††]Nano Science & Technology Research Center, Shanghai University, Shanghai 200444, P. R. China

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Nanocrystalline titanium carbonitride (TiCN) was successfully synthesized at low temperature (450 °C) via a chemical metathesis route using the readily attainable $TiCl_4$, CaC_2 and NaN_3 as source materials. X-ray powder diffraction indicated that the product was cubic TiCN with a lattice constant $a = 4.252$ Å. Transmission electron microscopy revealed that the crystals were composed of spherical particles with the diameter of 66 nm. X-ray photoemission spectra analysed that the atomic ratio was good agreement with the $TiC_{0.4}N_{0.6}$ stoichiometry. The possible formation mechanism was investigated.

Ternary titanium carbonitride (TiCN) concurrently possesses the merits of TiN and TiC, and has some more excellent properties, such as high melting point and thermal conductivity, significant hardness-toughness compromise, good oxidation and wear resistance, and low electrical resistivity, which make it wide applications in strengthening ferrous matrices for wear-resistant surfaces, in fabricating advanced engineering ceramic-based composites, scratch-resistant protective coating on watches and jewellery, and electrical or automatic refractory devices.[1–6] Therefore, much effort has been devoted to preparing the promising material.

TiCN was traditionally synthesized by high-temperature solid-state diffusion from TiN–TiC and TiN–C powder blends,[7] or by a self-propagating reaction between Ti and C in a N_2 atmosphere.[8] Jha et al. prepared TiCN via the reduction of TiO_2 with C in the presence of N_2 over a range of temperatures between 900 °C and 1500 °C.[9] Kerr et al. synthesized TiCN using high-energy ball milling TiO_2 and graphite for 100 h under a N_2 atmosphere and subsequent isothermal annealing at up to 1200 °C.[10] Xiang et al. prepared TiCN at 1550 °C by carbonthermal reduction of TiO_2 derived from sol–gel process.[11] Lichtenberger et al. reported the synthesis of nanocrystalline TiCN by pyrolysis of poly(titanylcarbodiimide) above 1100 °C.[12] Shen et al. utilized a simple route to nanocrystalline $TiC_{0.7}N_{0.3}$ at 600 °C.[13] Other physical and chemical methods, including ion implantation process,[14] chemical vapor deposition,[15–17] were also adopted to prepare TiCN. As a consequence, the methods available for the synthesis of TiCN should be carried out at high temperature or high pressure with complicated manipulation. Thus it is necessary to search facile synthesis routes to achieve this important material.

In this communication, ternary TiCN nanocrystallites, rather than the composites of TiC and TiN, were successfully synthesized at low temperature (450 °C) via a chemical metathesis route. To the best of our knowledge, this is the first time to prepare nanocrystalline TiCN at such low temperature under conveniently controllable conditions.

The starting materials used in this work were analytical pure grade anhydrous $TiCl_4$, CaC_2, and NaN_3. CaC_2 was fully milled to fine powders in a ball-milling machine. In a typical procedure, 3 mL of $TiCl_4$, 0.9 g of CaC_2, and 5.3 g of NaN_3 were put into a stainless steel autoclave of 50 mL capacity. All the manipulations were carried out in a protecting N_2 gas flow. After the autoclave was sealed, it was heated to 450 °C and held 8 h at the temperature and then allowed to cool to ambient temperature in furnace. The product was collected, filtered, and washed with absolute ethanol, hot hydrochloric acid, and distilled water successively to remove unreacted reagent, by-product of NaCl, $CaCl_2$, and other impurities. After being dried fully in vacuum at 60 °C, brown powders were ultimately obtained.

X-ray powder diffraction (XRD) was performed on a Rigaku D max-γA X-ray diffractometer with Ni filtered Cu Kα radiation ($V = 50$ kV, $I = 100$ mA) at a scanning rate of 4°/min. The morphology of TiCN nanocrystals was examined using a Hitachi H-800 transmission electron microscope (TEM) at an accelerating voltage of 150 kV. The composition of TiCN was analyzed by X-ray photoelectron spectra (XPS), which were recorded on a KARTOS XSAM800 X-ray photoelectron spectrometer. Al Kα ($h\nu = 1486.6$ eV) radiation was employed as the excitation source with an anode votage of 12 kV and an emission current of 10 mA.

X-ray powder diffraction (XRD) pattern of the sample is shown in Figure 1. The peaks, excluding the one at $2\theta = 26.4°$, can be indexed to a cubic phase with a lattice constant $a = 4.252$ Å, which is similar to TiC and TiN with *Fm*3*m* space group. No peak separation can be detectable, indicating that the resultant is single phase, other than the composites of TiC and TiN. The average grain size calculated by the Scherrer formula is near 66 nm. The peak at $2\theta = 26.4°$ can be attributed to free carbon produced during the reaction.

The X-ray photoelectron spectrum of the product is shown in Figure 2. The three strong peaks at 282.4, 396.5, and 456.2 eV correspond to C1s, N1s, and Ti2p binding energies, respectively. Calculation of the peak areas gives an atomic ratio

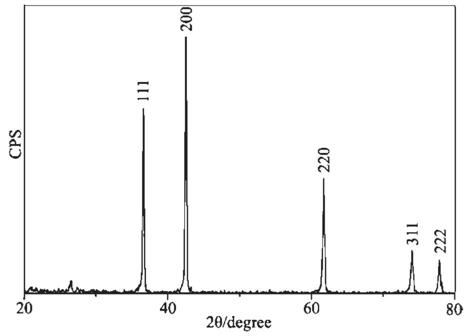

Figure 1. XRD pattern of the as-prepared TiCN.

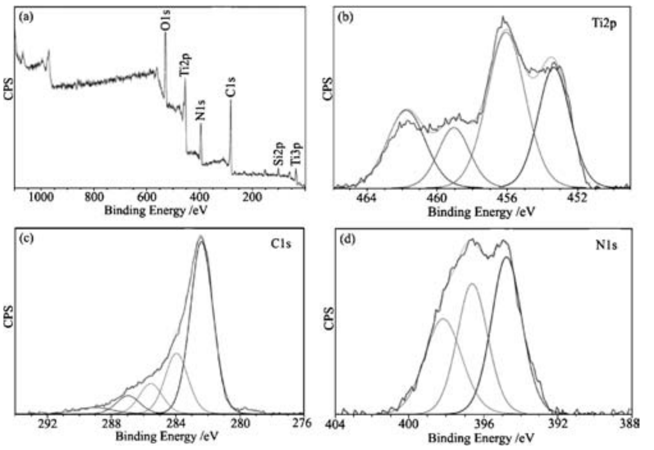

Figure 2. XPS spectra of the as-prepared TiCN nanocrystallites: (a) survey spectrum, (b) Ti2p, (c) C1s, (d) N1s. The three strong peaks at 282.4, 396.5, and 456.2 eV correspond to C1s, N1s, and Ti2p binding energies, respectively.

of Ti:C:N = 1:0.39:0.61, which was very close to the stoichiometry of $TiC_{0.4}N_{0.6}$. From the C regions, the other peaks can be attributed to free carbon (284.3 eV) and CO_2 adsorbed at the sample surface.

Figure 3 shows the typical transmission electron microscopy (TEM) morphology of the TiCN nanocrystals and the corresponding electron diffraction pattern (EDP). It can be seen that the crystals consist mainly of uniform spherical particles of 66 nm or so in size, which is consistent with the result from the XRD pattern. From the EDP, the d values corresponding to the diffraction rings are 2.455, 2.126, 1.503, 1.281, and 1.227 Å, which can be assigned to the planes of (111), (200), (220), (311), and (222) of the cubic TiCN, respectively.

The possible formation mechanism of TiCN nanocrystals was also investigated. With raising the temperature to 450 °C, $TiCl_4$ vaporizes (boiling point: 136.4 °C) and NaN_3 decomposes (decomposition point: 410 °C), as a result, the gas–solid interface is provided. And either of the reactions between $TiCl_4$ and CaC_2 ($TiCl_4 + 2CaC_2 = TiC + 2CaCl_2 + 3C$, $\Delta G_f^0 = -810.6\,\text{kJ/mol}$, $\Delta H_f^0 = -851\,\text{kJ/mol}$) or $TiCl_4$ and NaN_3 ($TiCl_4 + 4NaN_3 = TiN + 4NaCl + 11/2N_2$, $\Delta G_f^0 = -1418.0\,\text{kJ/mol}$, $\Delta H_f^0 = -1193.2\,\text{kJ/mol}$) may start preferentially. However, no matter which of the reactions takes place, it is followed immediately by a rapid and large amount of heat releasing. The heat is transferred instantly to the reactants surrounded, and initiates almost at the same time the other reaction. Thus, in fact, the three reagents participate in the reactions simultaneously, resulting in the formation of ternary TiCN compounds. Although the melting point of CaC_2 is very high (2300 °C), the process can be actually regarded as a chemical metathesis reaction as described in the following equation:

$$\begin{aligned}&2TiCl_4 + CaC_2 + 6NaN_3\\&\quad = 2TiCN + CaCl_2 + 6NaCl + 8N_2.\end{aligned} \tag{1}$$

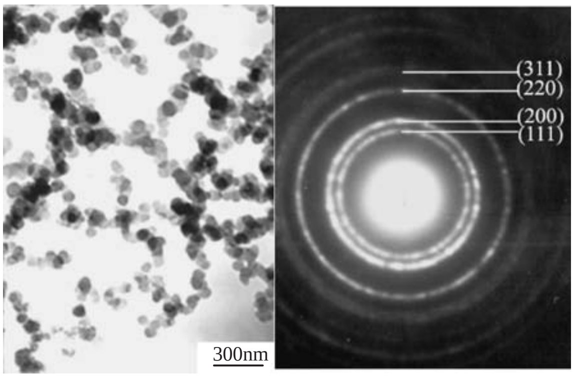

Figure 3. TEM morphology of TiCN nanocrystallites with 66 nm in size and the corresponding EDP.

The heat also results in the transiently molten by-product of NaCl (melting point: 800.8 °C) and $CaCl_2$ (melting point: 775 °C), which is favorable to the formation and crystallization of TiCN. Nevertheless, it is not long enough for ultrafine TiCN to grow into large size because the heat energy produced during the reaction is transferred rapidly to the autoclave and released. Thus obtained nanocrystalline TiCN. Here the by-products NaCl and $CaCl_2$ may also play a significant role in the experiment, which not only limit the maximum reaction temperature but also avoid the agglomeration of the TiCN crystals owing to subsequent solidification.

In summary, TiCN nanocrystals was successfully prepared by the direct reaction of $TiCl_4$, CaC_2, and NaN_3 at low temperature (450 °C) in autoclave. The similar route may be extended to prepare other carbonitrides, which is underway.

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