Formation of Nanocrystalline TiC by a Low-temperature Route

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Nanocrystalline cubic titanium carbide (TiC) powders were successfully synthesized at 450 °C in an autoclave by using Ti, Na, and CCl_4 as the reactants. The X-ray powder diffraction pattern indicates the formation of TiC. Transmission electron microscopy images show that typical TiC crystallites are composed of nanoparticles with the average grain size of about 30 nm.

Titanium carbide (TiC) is a very important non-oxide ceramic for its high melting point (3260 °C), low density (4.93 g/cm^3), outstanding hardness, high chemical stability, good wear resistance and so forth.[1] Because of these attractive properties, TiC has extensive applications in mechanical industry, chemistry, and microelectronics. For example, TiC has been used as wear resistance and aerospace materials.[2]

Traditionally, TiC was prepared by various high temperature reactions, such as direct combination of carbon with metal titanium by self-propagating high-temperature reaction,[3] carbothermal reduction of titanium oxide by carbon over 1900 °C,[4] hydrogen reduction of titanium halides followed by carbonization.[5] Recently, various efforts have been made to synthesize TiC at lower temperatures, control morphology or simplify reaction procedures. For example, Dai et al. reported to synthesize TiC nanorods by carbon nanotube template-mediated growth in which carbon nanotubes were converted into TiC nanorods.[6] Lee et al. prepared TiC nanoparticles by liquid-magnesium reduction of vaporized $TiCl_4$ and CCl_4.[7]

Initially, our group succeeded in preparing TiC nanocrystals by a co-reduction route or a reduction–carbonization route, in which all manipulations need to be carried out in a dry glove box with Ar flowing for the use of easily-hydrolyzed $TiCl_4$.[8,9] In the reduction–carbonization route, a relatively higher reaction temperature (650 °C) is needed. To avoid using easily-hydrolyzed $TiCl_4$ and lower the reaction temperature, we designed a new route to synthesize nanocrystalline TiC at 450 °C by using Ti, Na, and CCl_4 as the reactants based on the following reaction:

$$\mathrm{Ti} + \mathrm{CCl_4} + 4\mathrm{Na} \rightarrow \mathrm{TiC} + 4\mathrm{NaCl}$$

In a typical procedure, 0.03 mol metal Ti, 0.2 mol metal Na (excessive), 0.03 mol CCl_4 were put into an autoclave with a glass tube liner of about 50-mL capacity. The autoclave was maintained at 450 °C for 8 h, and then cooled to room temperature. The product was washed with absolute ethanol, dilute hydrochloric acid and distilled water to remove NaCl and impurities. After drying in vacuum at 60 °C for 4 h, the final black powder product was obtained.

X-ray powder diffraction (XRD) pattern was recorded on a Rigaku Dmax-γ A X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X rays as the excitation source. Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope.

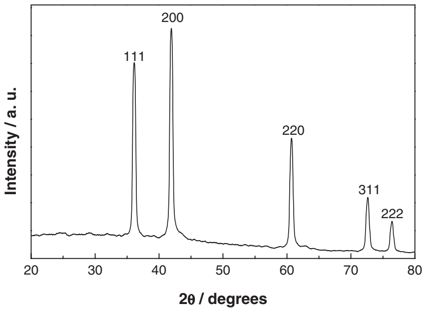

Figure 1. XRD patterns of the TiC sample.

In the XRD pattern (Figure 1), all the peaks can be indexed as cubic TiC. After refinement, the lattice constants, $a = 4.322$ Å, is very close to the reported value for TiC ($a = 4.327$ Å, JCPDS card, No. 730472).

Figure 2 gives the XPS spectra of the as-prepared TiC sample. The Ti2p and C1s core-level regions were examined. The peak at 455.1 eV corresponds to Ti2$p_{3/2}$ binding energy and the peak at 281.6 eV was assigned to the C 1s for TiC.[10] A weaker broad peak at around 285.6 eV was also found, which could be attributed to graphite carbon.[11] A peak that can be assigned to the O 1s core level at 532.10 eV (not shown) indicates O_2 is absorbed on the powder's surface. Based on the calculation of the peak areas, the mole ratio of C/Ti was obtained to be 1.07 and close to the chemical stoichometry of TiC.

Figure 3a shows the TEM images of the sample. It can be seen that typical TiC crystallites are nanoparticles with the average grain size of about 30 nm. Figure 3b shows the selected area electron diffraction pattern of TiC, which is consistent with the high crystallinity of the sample.

In our experiment, the existence of a small amount of graphitic carbon in the product, which was confirmed by the XPS data, suggests that the formation of TiC was based on the reaction of Ti and C. In the reaction process, with the temperature increasing, CCl_4 was firstly reduced by Na to produce carbon. The newly formed carbon particles are so active that they can react directly with metal Ti to form TiC. The possible formation process of TiC could be illustrated as follows.

$$\mathrm{CCl_4} + 4\mathrm{Na} \rightarrow \mathrm{C} + 4\mathrm{NaCl}$$
$$\mathrm{Ti} + \mathrm{C} \rightarrow \mathrm{TiC}$$

According to free energy calculations, the present synthetic

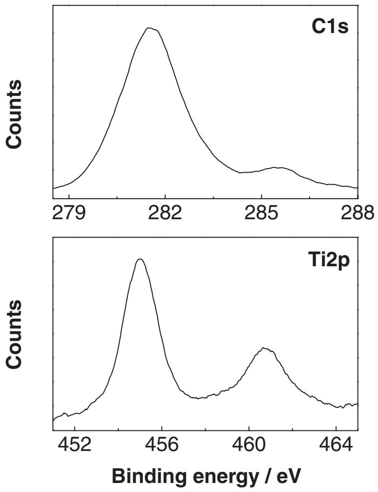

Figure 2. XPS spectra of the TiC sample.

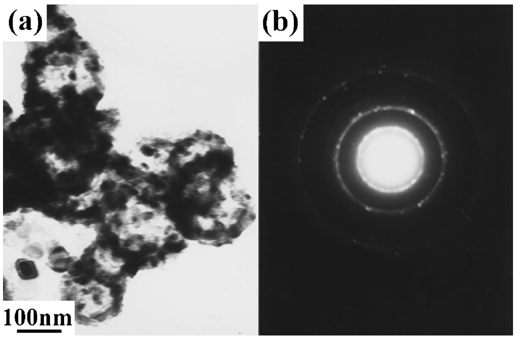

Figure 3. (a) TEM image and (b) Selected area electron diffraction pattern of the TiC sample.

route is thermodynamically spontaneous and highly exothermic ($\Delta G_f{}^\circ = -1659$ kJ/mol, $\Delta H_f{}^\circ = -1701$ kJ/mol). The reaction of Ti, Na, and CCl_4 generates a great deal heat and results in a high local temperature, which favors crystallization of TiC. Meanwhile, the vaporization of CCl_4 (bp = 76.8 °C) during the reaction process can bring about high pressure in the autoclave. Based on the ideal gas law, the highest pressure in the autoclave can be about 3.6 MPa, which is also beneficial to the formation of crystalline TiC. In addition, excessive metal Na (mp = 97.8 °C) existed as liquid during the reaction process. The molten Na not only acts as the medium for the crystallization of the formed TiC, but also absorbs the heat released from the reaction and induced fast cooling, which in turn maintains a relative low overall reaction temperature and avoid the agglomeration of the product.

The influence of reaction temperature and time on the formation of TiC was investigated. An optimum reaction temperature for nanocrystalline TiC is about 450 °C. Although the present synthetic route is thermodynamically spontaneous, TiC could not be obtained at a temperature below 350 °C. At 450 °C, varying the reaction time between 4–24 h did not significantly affect the crystallinity or morphology.

In summary, TiC powders with the average grain size of about 30 nm were successfully synthesized at 450 °C in an autoclave by using Ti, Na, and CCl_4 as the reactants. An atomic ratio of C to Ti of 1.07:1.0 was determined from X-ray photoelectron spectra. In comparison with previous routes, the present route allows for the formation of nanocrystalline TiC through a simpler process.

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References

1 C. K. Narula, in “Ceramic Precursor Technology and its Application,” Marcel Dekker, New York (1995), p 235.
2 N. Durlu, *J. Eur. Ceram. Soc.*, **19**, 2415 (1999).
3 K. S. Vecchio, J. C. LaSalvia, M. A. Meyers, and G. T. Gray, *Metall. Trans. A*, **23**, 87 (1992).
4 I. N. Mihailescu, N. Chitica, V. S. Teodorescu, M. Popescu, M. L. De Giorge, A. Luches, A. Perrone, C. Boulmer-Leborgne, J. Hermann, B. Dubreuil, S. Urdea, A. Barborica, and I. Iova, *J. Appl. Phys.*, **75**, 5286 (1994).
5 K. Thorne, S. J. Ting, C. J. Chu, J. D. Mackenzie, T. D. Getman, and M. F. Hawthorne, *J. Mater. Sci.*, **27**, 4406 (1992).
6 H. Dai, E. W. Wang, Y. Z. Lu, S. S. Fan, and C. M. Lieber, *Nature*, **375**, 769 (1995).
7 D. W. Lee and B. K. Kim, *Scr. Mater.*, **48**, 1513 (2003).
8 Q. Lu, J. Hu, K. Tang, B. Deng, Y. Qian, G. Zhou, and X. Liu, *Chem. Phys. Lett.*, **314**, 37 (1999).
9 J. Hu, Q. Lu, K. Tang, B. Deng, Y. Qian, G. Zhou, X. Liu, and J. Wu, *Chem. Lett.*, **2000**, 474.
10 A. A. Galuska, J. C. Uht, and N. Marquez, *J. Vac. Sci. Technol., A*, **6**, 110 (1988).
11 J. Hrbek, *J. Vac. Sci. Technol., A*, **4**, 86 (1986).

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