

Nano-sizing titanium into titanium carbide by 1-chlorobutane

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(Received 10 May 2002; accepted 3 September 2002)

TiC nanoparticles (average diameter 10–150 nm) were prepared by reacting bulk Ti powders (average diameter 20 μm) with gaseous 1-chlorobutane at a relatively low temperature (1073–1273 K). 1-Chlorobutane provided the carbon atom in the TiC and the chlorine atom that assisted the shrinking of the size of the original Ti powders. The apparently simple procedure is a complex heterogeneous process combining etching, deposition, and carburization reactions.

Due to their special properties, such as high melting point, low density, extreme hardness, and high resistance to corrosion and oxidation, early transition metal carbides have many potential industrial applications.^{1–3} For example, they can be used in rocket nozzles and drill bits. Recently, there were reports about the potential application using early transition metal carbides as diffusion barriers for Cu metallization in microchip fabrication.⁴ Traditionally, transition metal carbides are prepared via high-temperature routes. For example, TiC can be synthesized by reducing TiO_2 with carbon black at 2000–2400 K.² Recent reports have shown that it is possible to prepare TiC through reduction–carburization,^{5–7} gas–solid reaction,⁸ polymeric precursors obtained from titanium alkoxides with other organic compounds,^{9–11} and solid-state metathesis (SSM) methods.^{12,13} The last two examples are the so-called “bottom-up” strategy for the preparation of small-size materials. The strategy employs molecular precursors as the building blocks to form solid materials through chemical bond formation. To implement the strategy effectively, much chemistry knowledge is required. Another strategy is to employ the “top-down” approach. For example, bulk solid materials can be shrunk through the physical evaporation–deposition process. But this high-energy route suffers from the requirement of maintaining a vacuum environment, low production efficiency, and frequently forming highly reactive powder products. Alternatively, bulk solid materials can be shrunk through a high-energy mechanical milling process. For example, synthesis of TiC powders by this route has been reported.^{14,15} But the process frequently employs a long period of reaction time. Carburization of metals directly by hydrocarbons at high

temperatures is a simple method to prepare metal carbides.^{2,8} But the process usually does not shrink and carburize the bulk metal particles effectively. For example, reacting Ti metal with methane at 1173 K for 8 h can only transform about half of the metal into the carbide.⁸ Here, we wish to report a simple chemical method to prepare nano-sized TiC powders by reacting bulk Ti metal powders with 1-chlorobutane at a relatively low 1073–1273 K. The reaction is a combination of etching, deposition, and carburization processes.

Ti powders (2.0 g, 42 mmol) (Strem, 2N-325 mesh) or a piece of Ti foil ($1 \times 1 \text{ cm}^2$, Strem, 99.6+%, thickness 0.025 mm) in an alumina boat were placed in a 30-mm quartz tube and heated by a horizontal tube furnace (873–1273 K). At 1 atm, 1-chlorobutane at 298 K was bubbled into the reactor under the assistance of a constant flow of Ar (20–100 sccm). Under a flow of 20 sccm Ar, the consumption rate of liquid 1-chlorobutane was 0.04 ml/min. While under a flow of 100 sccm Ar, 1-chlorobutane was evaporated at a rate of 0.1 ml/min. After 2–4 h, black powders of TiC were collected. The results are summarized in Table I. In this work, x-ray diffraction (XRD) studies were carried out using a MAC MXP-3 (MAC, Japan) diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) and electron diffraction (ED) data collection were accomplished on a JEOL JEM-2000FX (JEOL, Tokyo, Japan) instrument. High-resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM-2010 microscope. Scanning electron microscopy (SEM) data collection was performed using a JEOL JSM840A instrument. Atomic force microscopy (AFM) images were obtained using a Digital Nanoscope E (Digital Instrument, Santa Barbara, CA). The x-ray photoelectron spectroscopy (XPS) measurements were carried out using a Perkin-Elmer PHI-1600 (Norwalk, CT) spectrometer with $\text{Mg K}\alpha$ (1253.6 eV) radiation. The volatile products were analyzed by a Perkin-Elmer System 2000 Fourier transform infrared (FTIR) spectrometer.

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Dark black powders were obtained when 1-chlorobutane was passed over Ti powders with an average particle size of 20 μm (by SEM) and a crystal size exceeding 1 μm (estimated from the XRD pattern using Scherrer equation) at 873–1273 K under atmospheric pressure. The general reaction conditions and observations are summarized in Table I. In addition, deposition of brown and purple solids on the quartz tube was observed. They were identified to be TiCl_2 and TiCl_3 , respectively. The powders prepared at 873 K were very reactive in the air and not characterized. Other volatile products, such as HCl, TiCl_4 , and hydrocarbons, were detected also and will be discussed below.

The XRD patterns of the powders synthesized at 873–1273 K are shown in Fig. 1. Figure 1(a) shows the XRD from the purchased Ti metal powder. There was no reaction taking place until the temperature reached 873 K. The signals of Ti metal diminished and broadened under this condition [Fig. 1(b)]. For the samples prepared at 1073 and 1273 K [Figs. 1(c) and 1(d), respectively], the signals at 2θ of 36.33, 42.30, 61.30, 73.40, and 77.32 deg are assigned to the (111), (200), (220), (311), and (222) reflections of a face-centered cubic (fcc) structure. The diffraction peaks are broadened due to the small domain size of the products. The average crystal sizes estimated from the Scherrer equation¹⁶ are 13 and 15 nm for the products prepared at 1073 and 1273 K, respectively. The cell constant a is calculated to be 0.431 nm, which is close to the reported value of cubic TiC,

$a = 0.43274 \text{ nm}$.¹⁷ In Fig. 2(a), the TEM image of the powders prepared at 1073 K is shown while the particle size is about 10–150 nm. The crystal size is estimated to be near 15 nm. The ED pattern, shown in Fig. 2(b), indicates that the nanocrystals have an fcc structure with an estimated lattice parameter a of 0.43 nm. This is close to the XRD data and the reported value of TiC. The result of HRTEM studies of the sample prepared at 1273 K is shown in Fig. 3. The micrograph in Fig. 3(b) reveals a nanocrystalline nature. The patterns of the lines identifies them to be (111) and (200) of TiC. The ED in Fig. 3(c) shows dot patterns that correspond to single-crystal TiC. In addition, there are some graphite-like lattice images around the metal carbide, as observed in the HRTEM experiments, indicating the presence of excess carbon materials.

TABLE I. Summary of reaction conditions and results.

Metal source	Reaction temp. (K)	Ar flow rate (sccm)	Reaction time (h)	Yield (%)	Cryst. size (nm)	Surf. area (m^2/g)
Ti powder	873 ^a	100	4
Ti powder	1073	20	4	60	13	17.93
Ti powder	1273	20	2	69	15	7.05

^aThe yield was too low to be estimated at this temperature.

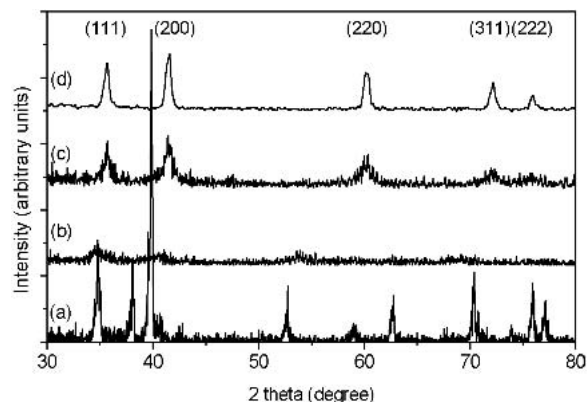
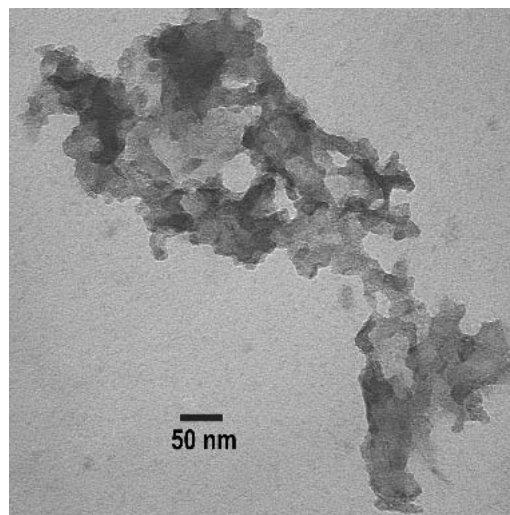
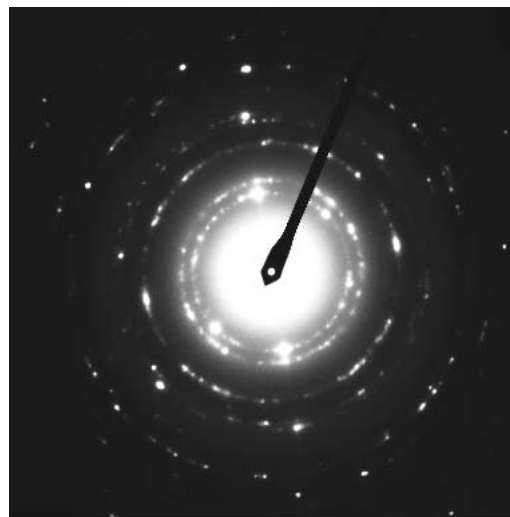


FIG. 1. XRD patterns of (a) as purchased Ti powder and (b) 873, (c) 1073, and (d) 1273 K prepared TiC powders.



(a)



(b)

FIG. 2. (a) TEM image and (b) ED pattern of TiC powders obtained at 1073 K.

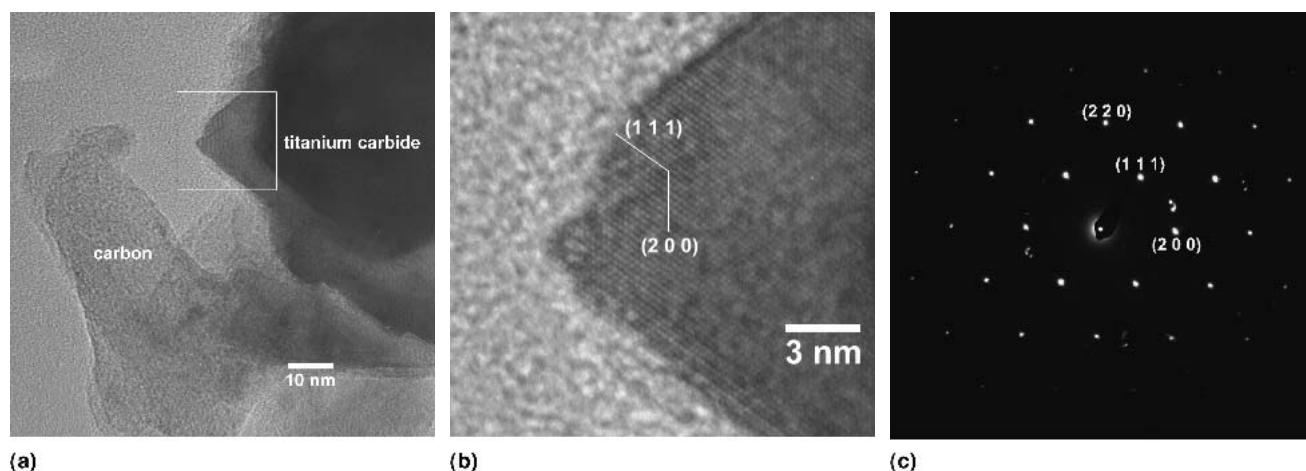


FIG. 3. TEM studies of a TiC crystal obtained at 1273 K: (a) TEM image; (b) HRTEM image of the selected area shown in (a); (c) ED pattern.

XPS survey spectra showed the presence of Ti and C as the major components after Ar⁺ sputtering. Shown in Fig. 4(a), high-resolution Ti signals are observed at 454.9 and 460.8 eV, corresponding to Ti 2p_{3/2} and Ti 2p_{1/2} electrons,^{18,19} respectively. The major C 1s signal at 281.8 eV [Fig. 4(b)] is assigned to the carbon atoms in a

metal carbide environment while the minor signal at 284.5 eV is designated to the presence of graphitic carbon. The quantity of carbidic carbon is twice that of graphitic carbon, estimated from the integration of the spectra. The surface area was estimated by the BET method²⁰ (Table I). Assuming that the products are

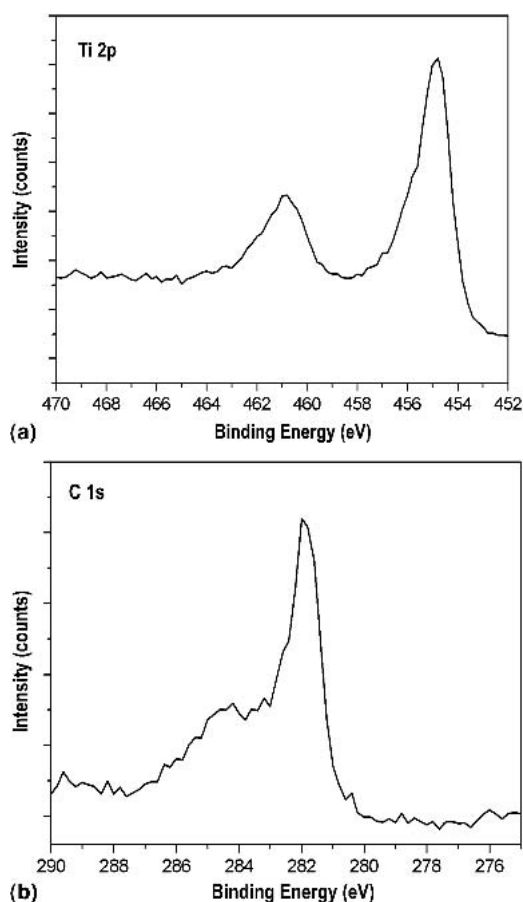


FIG. 4. High-resolution XPS spectra of TiC powders prepared at 1273 K: (a) Ti 2p region; (b) C 1s region.

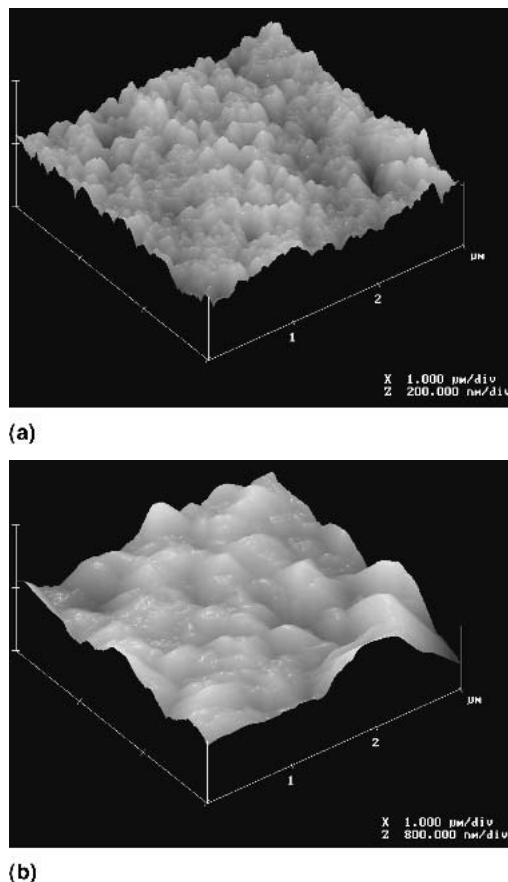


FIG. 5. AFM images of a Ti foil surface: (a) as-received, roughness = 20 nm; (b) after reacting with 1-chlorobutane at 873 K, roughness = 95 nm.

spherical, the mean diameters are estimated to be 68 and 173 nm, for the samples prepared at 1073 and 1273 K, respectively. This observation is in good agreement with the TEM image in Fig. 2(a), which shows aggregation of TiC nanoparticles to form larger powders. This study and the TEM data clearly show that the size of the Ti powder was shrunk by two to three orders of magnitude.

Clearly, 1-chlorobutane provided the source of carbon in metal carbide. On the other hand, it also acted as a source of chlorine atoms, capable of removing Ti atoms as titanium chlorides. To understand the reaction further, the following experiment was carried out. A Ti foil of 0.025 mm thick was exposed to 1-chlorobutane at a reaction temperature of 873 K for 1 h. As shown by the AFM images in Fig. 5, the Ti surface was clearly etched. The surface roughness increased significantly from an original value of 20 to 95 nm after the reaction. The observation suggests that the etching process probably plays an important role to shrink the size of the Ti powder. An XPS study also showed that the surface consisted of Ti metal and graphitic carbon atoms. But the concentration of carbidic carbon atoms was below the XPS detection limit. Therefore, under this temperature, the Ti surface was etched but not converted to TiC.

Using an on-line FTIR instrument, the gas-phase products were studied. No volatile products were observed below 773 K. From 873 to 1073 K, significant amounts of hydrocarbons, including CH_4 , C_3H_6 , C_4H_{10} , and C_4H_8 , were detected. Above 1173 K, additional products, HCl , CH_4 , and TiCl_4 , were identified. The result suggests that the reaction threshold was near 773 K. Above this temperature, the chlorine atoms from 1-chlorobutane etched the Ti surface to form lower valent TiCl_2 and TiCl_3 deposits mentioned earlier. Also, above the threshold, a major portion of the butyl groups underwent a β -hydrogen activation pathway to form C_4H_8 and C_4H_{10} . Some butyl groups underwent a C–C bond activation process to form CH_4 and C_3H_6 . This process also provided the route to incorporate the carbon atoms into the Ti lattice to generate TiC. The low-valent TiCl_x molecules are known to disproportionate into TiCl_4 and elemental Ti solids,⁵ providing another source of nanometer-sized particles. The process is summarized in Fig. 6.

In conclusion, we have demonstrated that the reaction between 1-chlorobutane and bulk Ti metal powders can

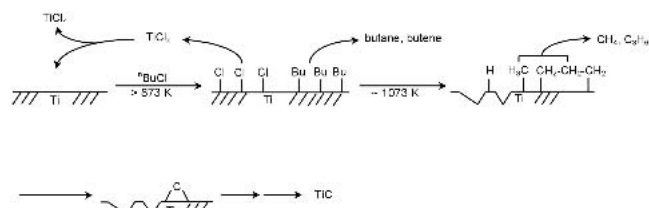


FIG. 6. Proposed reaction pathway.

generate nano-sized TiC particles at a relatively low temperature, 1073–1273 K. 1-Chlorobutane not only acts the carbon source to carburize the Ti metal but also provides the chlorine atoms to etch the Ti metal into smaller size and generating volatile TiCl_x molecules. The disproportionation of TiCl_2 and TiCl_3 provides another growth route of the nano-sized metal powders, with the evolution of TiCl_4 vapor. The apparently simple procedure is a complex heterogeneous process combining etching, deposition, and carburization reactions.

ACKNOWLEDGMENTS

The authors thank the National Science Council of Taiwan, Republic of China, for financial support (Grant NSC-892113-M-009-013). Professor Chi-Young Lee is appreciated for FTIR consulting.

REFERENCES

1. S.T. Oyama, in *The Chemistry of Transition Metal Carbides and Nitrides* (Blackie Academic & Professional, Glasgow, U.K., 1996).
2. P. Schwarzkopf, R. Kieffer, W. Leszynski, and F. Benesovsky, in *Refractory Hard Metals: Borides, Carbides, Nitrides and Silicides* (MacMillan, New York, 1953).
3. H.O. Pierson, in *Handbook of Refractory Carbides and Nitrides* (Noyes Publications, Park Ridge, NJ, 1996).
4. H-Y. Tsai, S-C. Sun, and S-J. Wang, *J. Electrochem. Soc.* **147**, 2766 (2000).
5. C-Y. Lee, *J. Mater. Synth. Proc.* **6**, 49 (1998).
6. J-Q. Hu, Q-Y. Lu, K-B. Tang, B. Deng, R. Jiang, Y-T. Qian, G-E. Zhou, and L. Yang, *Chem. Lett.* **5**, 474 (2000).
7. Y. Gotoh, K. Fujimura, M. Koike, Y. Ohkoshi, M. Nagura, K. Akamatsu, and S. Deki, *Mater. Res. Bull.* **36**, 2263 (2001).
8. Y-J. Kim, H. Chung, and S-J.L. Kang, *Composites A* **32**, 731 (2001).
9. Z. Jiang and W.E. Rhine, *Chem. Mater.* **3**, 1132 (1991).
10. S. Dutremez, P. Gerbier, C. Guerin, B. Henner, and P. Merle, *Adv. Mater.* **10**, 465 (1998).
11. Y. Kurokawa, S. Kobayashi, M. Suzuki, M. Shimazaki, and M. Takahashi, *J. Mater. Res.* **13**, 760 (1998).
12. A.M. Nartowski, I.P. Parkin, A.J. Craven, and M. MacKenzie, *Adv. Mater.* **10**, 805 (1998).
13. A.M. Nartowski, I.P. Parkin, M. MacKenzie, A.J. Craven, and I. MacLeodb, *J. Mater. Chem.* **9**, 1275 (1999).
14. N.J. Welham, and D.J. Llewellyn, *J. Eur. Ceram. Soc.* **19**, 2833 (1999).
15. M.S. El-Eskandarany, *Metall. Mater. Trans. A* **27**, 2374 (1996).
16. H.P. Klug and L.E. Alexander, in *X-Ray Diffraction Procedure for Polycrystalline and Amorphous Materials*, 2nd ed. (John Wiley & Sons, New York, 1974).
17. Powder Diffraction File, Card No. 32-1383, JCPDS, International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081.
18. H. Ihara, Y. Kumashiro, A. Itoh, and K. Maeda, *Jpn. J. Appl. Phys.* **12**, 1462 (1973).
19. L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, and C. Nordling, *J. Phys. Chem. Solids* **30**, 1835 (1969).
20. T. Allen, in *Particle Size Measurement* (Chapman and Hall, London, U.K., 1990).