A New Reduction-Carburization Route to Nanocrystalline TiC

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Nanocrystalline TiC was synthesized through a new reduction-carburization route by using metallic Na as the reductant, and tetrachlorotitanium ($TiCl_4$) and carbon as Ti and C sources at 650 °C. The present route allowed for the formation of nanocrystalline TiC with fine particle sizes, narrow size distribution (8-12 nm). A possible formation mechanism for nanocrystalline TiC was proposed.

Titanium carbon, TiC, is an important material due to a very high melting point (3260 °C), extreme hardness, a low density (4.93 g cm^{-3}), and a high resistance to both corrosion and oxidation.[1,2] It has great potential applications in key technologies from mechanical industries to chemistry and microelectronics.[3]

There are several methods for synthesizing TiC powders. The carbo-thermal reduction of TiO_2 in a temperature range of 1900-2700 °C has been applied primarily in industry:[4]

$$TiO_2 \text{ (s)} + 3C \text{ (s)} \rightarrow TiC \text{ (s)} + 2CO \text{ (g)} \qquad (1)$$

The self-propagating high-temperature synthesis (SHS) from titanium and carbon particles has been reported intensively:[5-7]

$$Ti \text{ (s)} + C \text{ (s)} \rightarrow TiC \text{ (s)} \qquad (2)$$
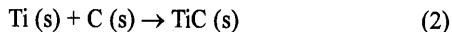
The reaction of $TiCl_4$, H_2, and C by using an incandescent tungsten or carbon filament as the igniting agent was proposed. Due to the corrosion of the by-product HCl, special precaution has to be taken:[4]

$$TiCl_4 + 2H_2 + C \rightarrow TiC + 4HCl \qquad (3)$$
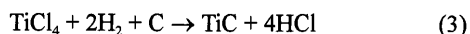
Polymeric precursors made from titanium alkoxides are better suited for the preparation of TiC powders as they can provide an intimate, molecular scale mixture of titania and carbon.[8] Recently, other methods such as a nontransferred-arc thermal-plasma,[9] the mechanical alloying (MA),[10] and the spark erosion technologies[11] have been developed to prepare TiC ultrafine powders.

In this letter, we describe a novel chemical synthetic route to nanocrystalline TiC at 650 °C by using $TiCl_4$ and C as source materials, metallic Na as the reductant. The reaction was carried out in an autoclave and was represented by Eqn (4):

$$TiCl_4 + C + 4Na \rightarrow TiC + 4NaCl \qquad (4)$$

The reaction was based on the reduction of $TiCl_4$ by Na and subsequent carburization of the reduced titanium particles.

All of the manipulations were carried out in a dry glovebox filled with argon. In a typical procedure, 0.02 mol $TiCl_4$ (excess), 0.01 mol C, and 0.04 mol Na were put into a titanium alloy autoclave of 50 ml-capacity. The autoclave was sealed and maintained at 650 °C for 4-10 h and then allowed to cool to room temperature in furnace. The product was collected and washed several times with 0.1 M hydrochloric acid and distilled water to remove α-Ti, NaCl and the other impurities. After being dried in vacuum at 70 °C for 2 h, a dark gray product was
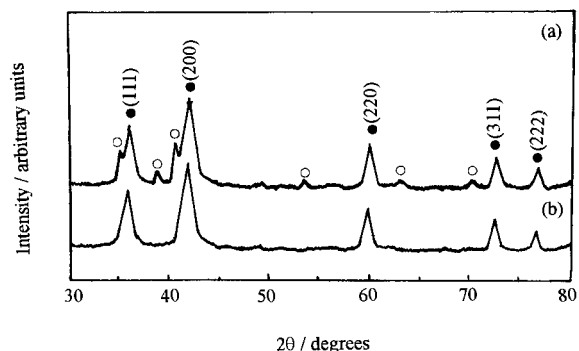

Figure 1. XRD pattern of the TiC samples prepared through a reduction-carburization route by using $TiCl_4$ and C as source materials and Na as reductant at 650 ℃ for 8 h. (a) washed with distilled water and (b) washed with 0.1 M hydrochloric acid and distilled water.

obtained with a density of 4.84 g cm^{-3}. The value is lower than the literature value (4.93 g cm^{-3}). This may be due to a small amount of the residual carbon in the product (the density of carbon is lower than that titanium carbide, so the density of the product was lower than the idea density of titanium carbide).

The samples were characterized by X-ray powder diffraction (XRD) method, operating on a Japan Rigaku Dmax-γA X-ray diffractometer with graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Figure 1(a) shows the product washed with distilled water. The peaks marked with dots could be indexed as main phase TiC (NaCl-type structure) with cell constant a = 4.312 Å, in agreement with the reported data in literature (a = 4.3274 Å).[12] The other peaks marks with circles could be with impurity phase α-Ti.[13] Figure 1(b) shows the final product washed with 0.1 M hydrochloric acid and distilled water. All reflections were indexed as the pure phase TiC. No impurities such as TiO_2 or α-Ti were detected in the XRD pattern. The broadened nature of the peaks indicated that the grain sizes of the samples were on the nanometer scale. The average sizes of the particles were 10 nm, as estimated by the Scherrer formula.

Transmission electron microscope (TEM) images and electron diffraction (ED) patterns were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200kV. Figure 2(a) shows the TEM images of as-prepared nanocrystalline TiC. It can be seen that TiC powders consist of uniform spherical particles with an average size of 15nm, in agreement with the XRD result. Figure 2(b) shows the ED pattern of the nanocrystalline TiC sample. The three polycrystalline rings [(111), (200), and (220)] confirm the XRD result.

To give further evidence for the formation of TiC, the binding energy of the electrons on Ti2p level was investigated, which was performed on a ESCALAB MKII X-ray photoelectron spectrometer with Mg Kα (hν = 1253.6 eV) as the exciting
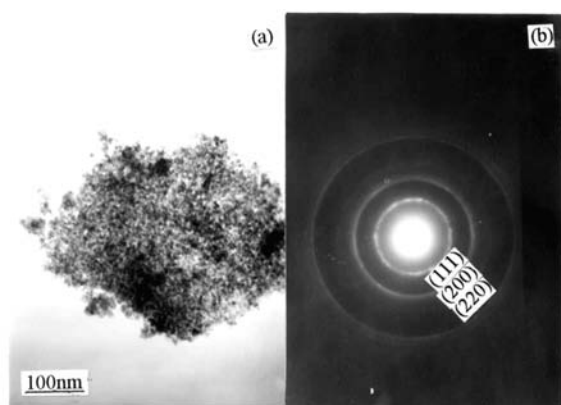
Figure 2. (a) TEM micrograph and (b) ED pattern of the same sample as in Figure 1(b).

source. The peaks at 455.20, 459.15 eV in XPS spectra (as shown in Figure 3) were corresponded to the Ti-C bond in TiC, in accord with the data (Ti2p$_{3/2}$: 454.80 eV) in literature.[4,14] No obvious peaks ascribed to the Ti-O bond were observed. Quantification of the peak intensities gave an atomic ratio of Ti to C of 1: 1.10.
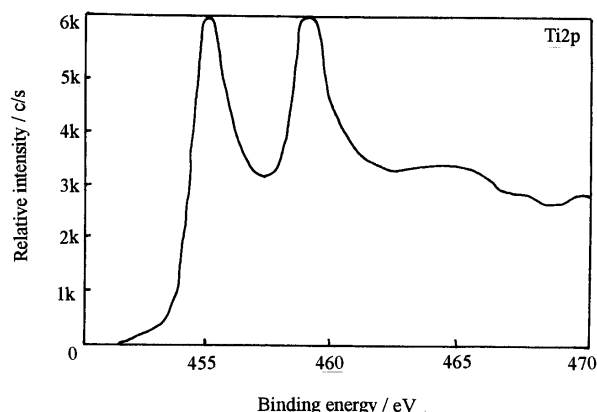

Figure 3. XPS spectra of the same sample as in Figure 1(b).

The influences of temperature and reaction time on the formation for the nanocrystalline TiC were investigated. It was found that an optimum reaction condition for the nanocrystalline TiC was at the temperature of 650 °C for longer than 4 h. If the temperature was lower than 550 °C, TiC can not be obtained and the product mainly consisted of unreacted carbon. As the temperature was higher than 600 °C, the crystallinity of TiC increased evidently. If the temperature is higher than 700 °C, the grain sizes grew easily up. A suitable temperature for nanocrystalline TiC was about 650 °C. The reaction time of longer than 4h at 650 °C did not obviously affect the crystallinity and the yield (about 60%, according to the amount of TiCl$_4$) of TiC. However, the time was shorter than 3 h, the reaction was incomplete and the yield and crystallinity were lower. The results demonstrated that the present route differed from the known SHS reaction mode.[15,16]

The fact that α-Ti formed in the product suggested that the formation for TiC could be attributed to the reaction of the formed α-Ti with carbon. So, it is believed that the synthetic reaction is based on the reduction of TiCl$_4$ by Na and subsequent carburization of α-Ti particles. We call it the reduction-carburization route in reaction (4). The schematic formation process of TiC would then be formulated as follows:

$$TiCl_4 + 4Na \; \rightarrow \; \alpha\text{-Ti} + 4NaCl \qquad (5)$$

$$C + \alpha\text{-Ti} \rightarrow TiC \qquad (6)$$

According to free energy calculations, reaction (5) is thermodynamically spontaneous and exothermic (ΔG_f^0 = -191 kcal mol^{-1}, ΔH_f^0 = -201 kcal mol^{-1}).[17] Once the reaction is initiated, the large heat generated of formation for α-Ti not only provides a driving force to the reactions but also melts by-product NaCl (NaCl : mp of 801 °C).[17] So, the carburization of α-Ti (reaction (6)) was carried out in a NaCl molten flux, which could favor the reaction by increasing the difusivity of C atoms. The formed TiC may be amorphous and was crystallized by the heat remaining in the NaCl flux. Meanwhile, excess TiCl$_4$ existed as vapor-phase at the reaction temperature and could adjust the reaction temperature, which would be beneficial to the formation for the nanocrystalline TiC. To summarize, the formation of nanocrystalline TiC was via two steps, i.e. α-Ti particles from the reduction formed first and then carburized in the NaCl molten flux.

In conclusion, a new reduction-carburization route to nanocrystalline TiC has been developed by using TiCl$_4$ and C as the source materials at low temperature (650 °C). The present route allows for the formation for nanocrystalline TiC with fine particle sizes, narrow size distribution (8-12 nm). A possible formation mechanism for nanocrystalline TiC was proposed. This route described could be extended to synthesize other refractory carbides, which might offer opportunity for technological applications.

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