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The self-propagating high-temperature synthesis (SHS) of ultrafine high-purity TiC powder from TiO_2+Mg+C

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The self-propagating high-temperature synthesis (SHS) method has been applied to the preparation of TiC powder from mixtures of TiO_2, Mg, and C. The TiC/MgO product is leached by hydrochloric acid to remove the MgO. The optimum mixing ratio was TiO_2:Mg:C=1:2.2:1.5. The final product TiC had >99.9% purity and relatively uniform particle size of 0.3–0.4 μm.

1. Introduction

High-purity, fine ceramic powders with good sinterability can be prepared by self-propagating high-temperature synthesis (SHS) [1–3] which relies on the large heat of formation of the product from its elements by a rapid reaction. This process is attractive because it requires a simple apparatus and no external supply of heat. Some 200 different materials, including TiC, have been synthesized by this method [1, 4–6]. Titanium carbide has a high melting point (3150–3250 °C), good hardness (Vicker's hardness 3200 kg mm^{-2}), and wear and corrosion resistance [7, 8]. It resists oxidation up to about 700 °C. These properties enable titanium carbide to provide superhard film as well as find much application as an abrasive and a superhard alloy. It is used in an extrusion die, a high-temperature nozzle, and a jet engine turbine.

In this work, high-purity TiC powder was synthesized by the SHS method from a mixture to TiO_2 powder with magnesium and carbon powders. The reaction involved is as follows

$$TiO_2 + 2Mg + C = TiC + 2MgO \quad (1)$$

The magnesium oxide in the product is leached by hydrochloric acid, leaving TiC powder as the final product.

2. Experimental procedure

2.1. Raw materials

The average particle size and the composition of the starting materials TiO_2, magnesium, and carbon powders, are given in Table I.

2.2. Procedure

The predetermined amounts of the three starting powders were thoroughly mixed in a ball mill. The mixture was pressed into pellets of 15 mm diameter and 15–20 mm height. The pellet was placed in an SHS reactor under an argon or air atmosphere and ignited by a tungsten wire connected to a power supply. The produced pellet was quite porous due to the gas generated during the exothermic SHS reaction. The product was leached by hydrochloric acid to remove MgO (see Fig. 1). The remaining TiC product was subjected to X-ray diffraction (XRD) analysis to observe its crystal structure and to scanning electron microscopy (SEM) analysis to examine its microstructure. Its chemical composition was determined by inductively coupled plasma (ICP), energy dispersive X-ray (EDX), and wavelength dispersive spectrometry (WDS). The magnesium content in the leachant was determined by atomic absorption (AA) spectrometry.

3. Results and discussion

The overall reaction show in Equation 1 is believed to take place as a combination of the following two reactions

$$TiO_2 + 2\,Mg = Ti + 2MgO \quad (2)$$

$$Ti + C = TiC \quad (3)$$

The Gibbs' free energies of the relevant reactions are listed in Table II. It is seen that Reaction 1 has a negative ΔG° value, indicating its thermodynamic feasibility. Further, it is seen that magnesium has a greater affinity towards oxygen than carbon or titanium. Thus, it is expected that magnesium first reduces

TABLE I Characteristics of the starting materials

Impurities (wt%)	TiO_2	Mg	C
H_2O (wt %)	0.22	–	–
Fe_2O_3 (wt%)	0.0054	–	–
K_2O (wt %)	0.36	–	–
P_2O_5 (wt %)	0.2	–	–
SO_3 (wt %)	0.10	–	–
Cr_2O_3 (wt%)	0.0003	–	–
MnO (wt %)	0.00028	–	–
CdO (wt %)	0.00018	–	–
ZnO (wt %)	trace	–	–
Particle size (μm)	0.3 ± 0.05		
Purity (wt%)	98.6		
Ca	–	0.05	0.03
Cr	–	0.17	–
Fe	–	0.03	0.02
Mg	–	–	0.01
Si	–	0.25	0.03
Particle size		60–80 mesh	5.0 ± 0.5 μm
Purity (wt %)		99.5	99.9

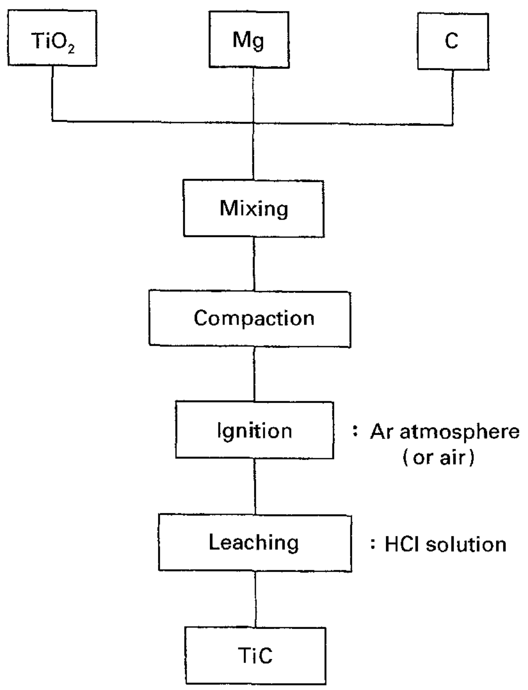

Figure 1 Schematic diagram of the TiC synthesis process.

TABLE II Gibb's free energy changes (298 K)

	$\Delta G°$ (kcal)
1. $TiO_2 + 2Mg + C = TiC + 2MgO$	– 152.8
2. $Ti + C = TiC$	– 45.2
3. $C + O_2 = CO_2$	– 109.3
4. $Ti + O_2 = TiO_2$	– 211.1
5. $2Mg + O_2 = 2MgO$	– 291.3

titanium oxide, and the resultant titanium reacts with carbon to form the final product TiC.

Fig. 2 shows the XRD patterns of the products from mixtures of 1 mol TiO_2 and 1.5 mol carbon with various amounts of magnesium. It is seen that TiO_2 is not completely reduced when the addition of magnesium is less than 2 mol. With an excess of magnesium, TiO_2 is completely reduced, as can be seen in Fig. 2d.

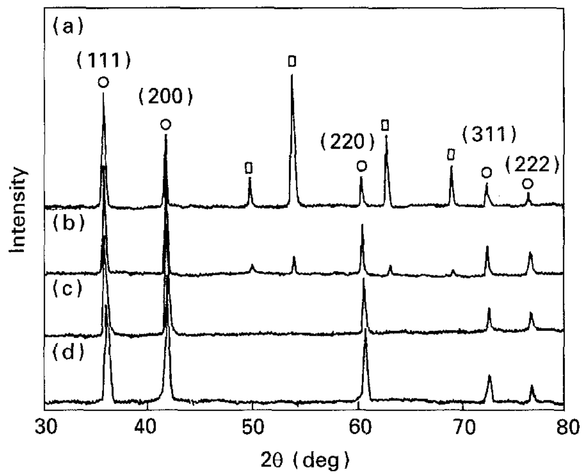

Figure 2 X-ray diffraction patterns of reaction products with various amounts of magnesium (TiO_2:C = 1.0:1.0; Mg size 60–80 mesh; mixing time 5 h, after leaching): (a) 0.5, (b) 1.0, (c) 2.0, (d) 2.5. (○) TiC, (□) TiO_2.

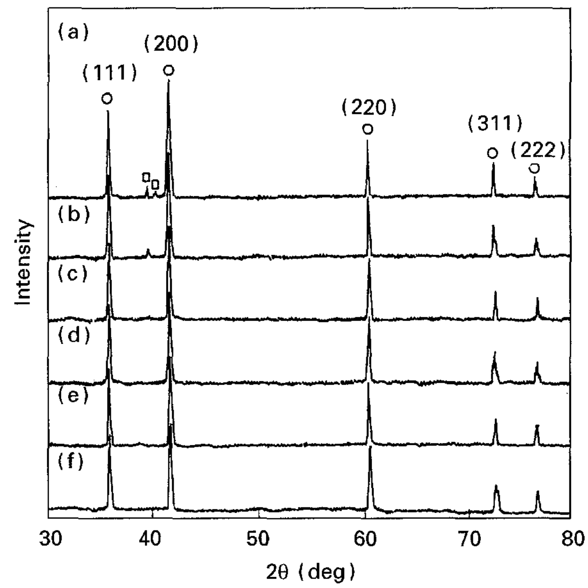

Figure 3 X-ray diffraction patterns of reaction products with various amounts of carbon (TiO_2: Mg = 1.0:2.2; Mg size 60–80 mesh; mixing time: 5 h, after leaching); (a) 0.5; (b) 0.7, (c) 0.9, (d) 1.0, (e) 1.3, (f) 1.5. (○) TiC, (□) Ti.

Fig. 3 shows the XRD patterns of the products from mixtures of 1 mol TiO_2 and 2.2 mol magnesium with various amounts of carbon. The Ti–C phase diagram has a TiC region over the C/Ti ratio of 0.6–0.95. It is seen in Fig. 3 that some unreacted Ti still remains when 0.7 mol carbon is used, but it is completely reacted when more carbon is used. The excess carbon forms CO and CO_2 gases.

Separate tests showed that the compaction pressure in the range 4000–14 000 kg had no effect on the X-ray diffraction pattern of the product.

The product TiC/MgO obtained at the optimum mixing ratio TiO_2:Mg:C = 1:2.2:1.5 was leached with an HCl solution. Fig. 4 shows the magnesium oxide leached by a 6.4 M HCl solution as a function of leaching time at various temperatures. Magnesium oxide is leached rapidly within the first 10–20 min. At

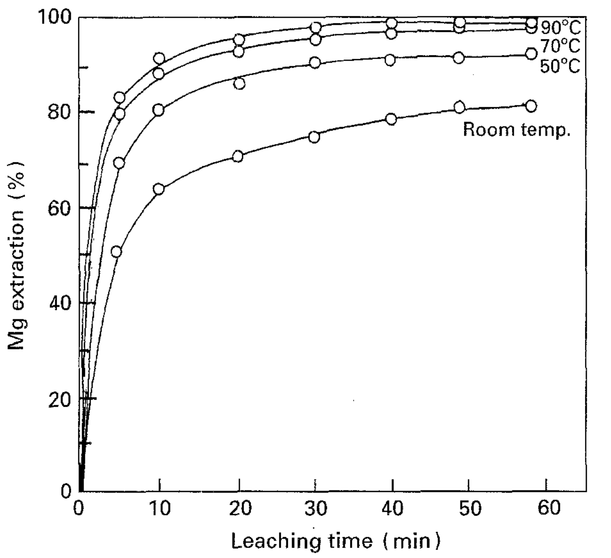

Figure 4 The effect of reaction temperature on magnesium oxide leaching (HCl mole concentration: 6.4 M).

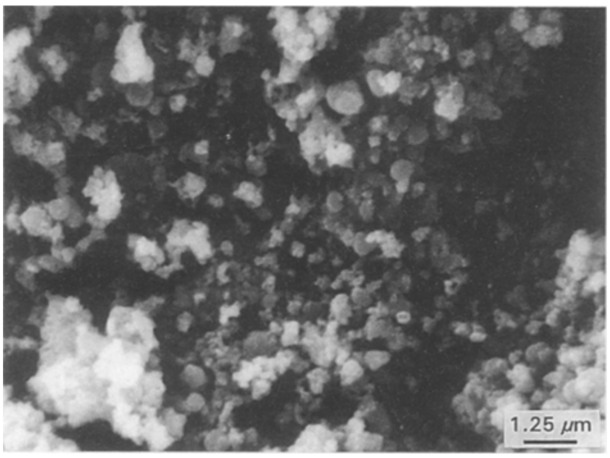

Figure 5 Scanning electron micrograph of the final product TiC after leaching (TiO_2:Mg:C = 1.0:2.2:1.0; Mg size 60–80 mesh, mixing time 5 h)

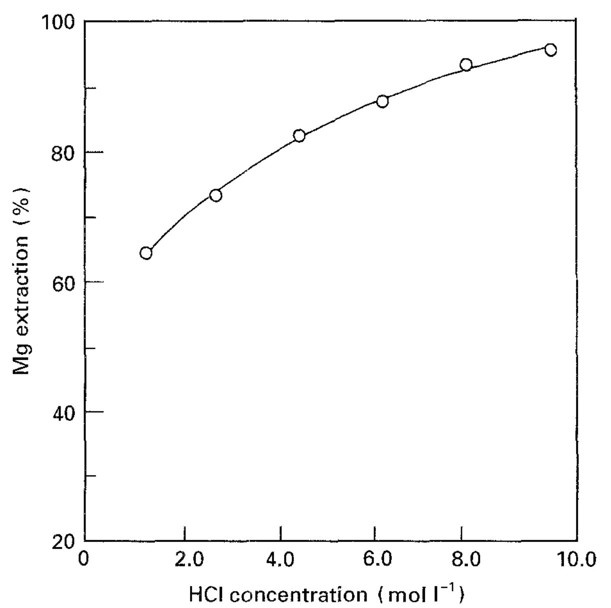

Figure 6 The effect of HCl concentration on magnesium oxide leaching (temperature 50 °C, time 20 min).

TABLE III Chemical composition (wt %) of the final product TiC synthesized by the SHS process

TiC	K	Fe	Na	Ca	Mg	Al
99.925	0.002	0.005	0.005	ND	0.05	0.013

90 °C, almost all the magnesium oxide is leached in about 30 min. The scanning electron micrograph of the final product (Fig. 5) shows agglomerates of relatively uniform 0.3–0.4 μm particles. The effect of the HCl concentration on magnesium oxide leaching is shown in Fig. 6. The leaching rate is seen to increase monotonically with HCl concentration in the range 1–10 M.

The chemical composition of the final product is shown in Table III, in which the TiC purity is seen to be higher than 99.9%. This high purity is due to the fact that the impurities are volatilized due to the high temperature generated during the highly exothermic reaction. Titanium in TiO_2 was essentially all recovered as titanium carbide.

4. Conclusions

The results of this research on the synthesis of TiC powder by the SHS process point to the following conclusions.

1. The amount of magnesium added to the reactant mixture had the greatest effect on the reaction product. Titanium carbide of good crystallinity was obtained when 2.0–2.5 mol magnesium and 1.5–2.0 mol carbon are mixed with 1 mol TiO_2.
2. The rate of leaching of the MgO in the reaction product increased with HCl concentration and temperature. Almost complete leaching was attained in about 30 min at 6.4 M HCl l^{-1} and 90 °C.
3. The final product TiC has > 99.9% purity and a relatively uniform particle size of 0.3–0.4 μm.

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