Spherical Powders of Titanium Carbide and Oxide by Thermal Plasma Spheroidization and Oxidation of Titanium Carbide

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Abstract

Titanium carbide (TiC) and titanium oxide (TiO2) are important intermetallic carbide and functional oxide ceramics, respectively, which have important applications as structural and functional materials. Titanium carbide is used as cutting tools and coatings in components for thermal and ceramic-based components, while titanium oxide is widely utilized as pigments, photoconductors, sensor materials and dental ceramics and has been investigated successfully recently as a new generation of photocatalysts. In this study, spheroidization of the TiC particles in an AC plasma and the formation characteristics of the TiO2 particles in the thermal plasma oxidation were discussed.

1. Introduction

Titanium carbide (TiC) and titanium oxide (TiO2) are important intermetallic carbide and functional oxide ceramics, respectively, which have important applications as structural and functional materials. Titanium carbide is used as cutting tools and coatings in components for thermal and ceramic-based components, while titanium oxide is widely utilized as pigments, photoconductors, sensor materials and dental ceramics and has been investigated successfully recently as a new generation of photocatalysts. In this study, spheroidization of the TiC particles in an AC plasma and the formation characteristics of the TiO2 particles in the thermal plasma oxidation were discussed.

Plasma synthesis offers advantages in production of spherical powders and generation of new structure and phase by virtue of its high processing temperatures (8000 °C), high heating and cooling rates (10^6-10^8 K/s). Synthesis of fine spheroidized TiC and TiO2 powders has been performed by a number of researchers by plasma-induced vapor phase reactions using vapor or liquid reactants. Evaporation of titanium TC particles by plasma heating has been mentioned in an early literature, with emphasis on the evaporation process to generate fine TiC particles by vapor-condensation mechanism. Treatment of amorphous TiC in a thermal plasma-assisted aerosol reactor was carried out by Kang et al. and a significant change in powder composition after the plasma treatment was observed.
In the present work, we report on preparation of well-defined spherical particles of titanium carbide and titanium nitride, respectively, by plasma spheroidization and evaluation of irregularly shaped commercial titanium carbide infant powders. The TiC powder produced is highly crystallized, a property which is not exhibited by the powder derived from spherical particles along the wet chemical route, which is attributed to the high synthesis temperature in the thermal plasma process. We describe the behavior of sphericalization of TiC and oxidation of TiC to spherical TiO2 powders in thermal plasma synthesis, characteristics of the synthesized powders, and the their processing behavior.

2. Theory and Experimental

For spheroidization of TiC, a total melt of the powders under plasma heating is required. Vacuum furnace was performed to estimate the time of melting of TiC powder in Ar-He plasma. A simple technique of thermal conduction for small particles in high temperature plasma was used to estimate the time of heating and melting time for TiC particles at non-nucleation temperatures in high-temperature plasma in this work. The results indicate that a total melting of the TiC particles occurs within 2 ms. However, the time of melting is dependent on the temperature of the high-temperature plasma zone. The experimental results obtained from the thermal plasma zone are about 2 ms, which is in agreement with the simulation results for the reaction of TiC powders and only hydrogen.

A high temperature in Ar-He plasma is thermodynamic equilibrium calculation with the standard of enthalpy program for electroplated powders after nucleation. The free energy of formation of all possible total products was compared. The possible total product in the TiC-He system has been shown in Figure 1. It demonstrates that the thermodynamically stable phase is a carbide of titanium (TiC). The TiC can be formed by oxidation at 1500 °C under the plasma oxidation conditions. When the temperature exceeding 2000 K, all products are vapor phases. In the TiC-He system, the total products are formed in the TiC-He system.

Figure 1 Thermodynamic calculations of equilibrium formation of TiC in carbon in Ar-He thermal plasma. Figure 2 Thermodynamic calculations of equilibrium formation of TiO2 in Ar-He thermal plasma.

Spheroidization and oxidation of TiC powders were carried out in a thermal-plasma assisted gas-atomizer in Ar-He plasma and Ar-O2 plasma respectively. The high temperature thermal plasma was generated by an induction plasma torch (Model PT-6000, TEKNA Plasma Systems, Sherbrooke, Quebec, Canada) connected with a radio frequency (RF) power supply system of 13.56 MHz. Nihon Kosha Co. Ltd., Yokohama, Kanagawa, Japan. The starting TiC powders were a commercial product of Lit-Al, Nippon New Metal, Osaka, Japan with a mean diameter of 35 μm and a composition of TiC. The particles were axially injected from the top of the plasma torch into the center of the plasma region by a powder feeder by meansVK and were processed in Ar-He or Ar-O2 plasma. Synthesis conditions for the
plasma-melted and oxidized treatment are listed in **Table 1**. The plasma-treated and oxidized powders were collected from the wall and bottom of the reactor chamber and were characterized in terms of morphology, microstructure and particle size distributions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Sheath gas and flow rate</td>
<td>Total oxygen: 90% H2</td>
</tr>
<tr>
<td>for spheroidization of Ti</td>
<td>Argon: 10% Furan: 1%</td>
</tr>
<tr>
<td>Ratio of Ti oxidation</td>
<td>Nitrogen: 1%</td>
</tr>
<tr>
<td>Powder feeding rate (Rf)</td>
<td>Argon: 300 ml</td>
</tr>
<tr>
<td>Reactor Pressure</td>
<td>Ar: 300 W</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Spheroidization of Titanium Carbide

Processing of the irregularly shaped Ti particles at Ar plasma conditions, spheroidized Ti spherical particles with a mean diameter of 1 μm out of the starting powder as shown in figure 4. The ratio of the spherical particles to the irregular or amorphous state increases with hydrogen input in the plasma spheroidization process. Figure 6 shows that at a spheroidization ratio of 85%, a 90% Ti powder was achieved with hydrogen input in the plasma zone.

![Morphology of the starting Ti powder and the plasma-treated powder](image)

The enhanced melting of Ti particles was attributed to the elevated thermal conductivity of the plasma zone as the hydrogen content increases, which allows the total melting of the particles even in the high-temperature region in the plasma zone. As shown in figure 7, the enhanced melting at low-temperature regions as the hydrogen input increases, causes more Ti powder in the high-temperature zone. This increases the weight fraction of Ti powder in the treated products by 85-90%, as shown in the starting Ti powder, because of the greatly increased kinetic of evaporation as the particle size decrease.
3.2 Oxidation of Titanium Carbide to Titanium Dioxide

3.2.1 Synthesis

Oxidation of TiC particles in Ar+O plasma yields TiO powder or a mixture of Ti and TiO in the oxidized products. The extent of oxidation increases with the oxygen input to the plasma sheath gases, and nearly complete oxidation was attained at the oxygen flow conditions (10 L/min) (Fig. 5).

The as-oxidized TiO powders exhibit typically a bimodal size distribution (Fig. 6). The larger size particles have a particle diameter of ~1.4 μm which is slightly smaller than the starting TiC particles size, while the smaller size particles are ~1.1 μm in micro-diameter (Fig. 7). However, there were appreciable amount of nanosize TiO particles condensed directly from vapor phase existing in the oxidized products.

Detailed microstructure examination of the as-oxidized particles suggests that the larger size particles are formed through a direct oxidation of TiC droplets, while the smaller size particles are formed from the vapor-condensed droplets. As the TiC particles went into the downstream of high-temperature plasma chamber, they were partly evaporated and were oxidized in a gas phase, followed by vapor liquid condensation and solidification resulting in the micrometer-sized powder. As summarizing this process, the TiC particles were oxidized inside the chamber, which led to the bimodal size particles.

![Figure 6](image6.png)

![Figure 7](image7.png)

3.2.2 Sedimentation Treatment

The different constituents in the as-synthesized products can be separated easily from their mixture by performing a simple sedimentation treatment using common alcoholic solvents. The sedimentation velocity, \( V \), for spherical particles of diameter \( R \) is given by

\[
V = \frac{\rho_p - \rho_f}{\rho_p} \frac{g R^3}{6 \mu}
\]

where \( \rho_p \) and \( \rho_f \) are densities of the spheres and fluid respectively, \( g \) is the gravitational constant, and \( \mu \) is the viscosity of the fluid.

We dispersed the as-oxidized powder in ethanol at 10% by volume in pure ethanol and the suspension was then dispersed by the assistance of ultrasonic vibration. By control of the

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
</tr>
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<tbody>
<tr>
<td>TiC</td>
<td>4.5</td>
</tr>
<tr>
<td>TiO</td>
<td>4.2</td>
</tr>
<tr>
<td>C</td>
<td>2.25</td>
</tr>
</tbody>
</table>
4. Conclusion

The LiF micron powders have been effectively spheroidized in Ar/H2 thermal plasma. The spheroidization rate increases with hydrogen input in the plasma sheath gases (Ar-H2), and by increase of the hydrogen input up to 10% max, spheroidization rates >90% have been achieved.

The LiF micron powders have been produced by evaluation of the micron powders in Ar/H2 thermal plasma. The powders are in spherical shape, highly crystallized and nano-sized, and exhibit typically a binodal size distribution. A simple sedimentation using organic solvents was performed to efficiently separate the two different size particles (LiF A and LiF B).

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References
