Preparation of Titanium Nitride: Microwave-Induced Carbothermal Reaction of Titanium Dioxide

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Carbothermal reduction and nitridation of TiO₂ was performed in a 2 kW, 2.45 GHz microwave furnace. Carbon, generally added for the removal of oxygen from TiO₂ lattice also served as the low-temperature susceptor in these experiments. At temperatures >1200°C, the mixtures started reacting vigorously (self-burn), which was never observed with the respective pure compounds. In the self-burning state, the minimum duration required for complete titanium nitride transformation was ~20 min with stoichiometric amounts of carbon. With excess C, the transformation duration dropped to just 1 min. CO removal and subsequent N₂ fixation occur more directly in microwave-induced reactions than in conventional nitridation procedures. Intermediate formation of successive Magneli phases (Ti₂ₙO₃₋ₙ₋₁) was not found in the microwave-induced reactions. The combination of microwave processing and combustion makes this route of economical interest.

I. Introduction

Properties such as high-melting point, thermal conductivity, low-electrical resistivity, high hardness, toughness, and moderate oxidation resistance make titanium nitride (TiN) useful for a wide range of applications. TiN is used in modern ceramic cutting tools as an important ingredient in the layered structure due to its high-fracture toughness and thermal conductivity. The hardness—stiffness combined with high conductivity—makes TiN a potential encapsulation material in power transmission cables. TiN coatings are also widely used in electronic and ornamental applications; in tools, they are reported to improve wear-resistance by minimizing cutting-edge buildup and cratering.

Preparation of TiN using carbothermal reduction and nitridation of TiO₂ is a well-known process. The underlying reduction and nitridation mechanisms are well understood. TiO₂ reacts with C in the following manner:

\[ \text{TiO}_2 + 2\text{C} + \frac{1}{2}\text{N}_2(g) \rightarrow \text{TiN} + 2\text{CO}(g) \]  \hspace{1cm} (1)

The Gibbs free energy of formation for the previous reaction is \( \Delta G^\circ = 376 \text{kJ/mol} \) at 1469 K. Researchers have observed a minor amount of CO₂ in the effluent gas, which does not exclude the following possibility:

\[ \text{C} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]  \hspace{1cm} (2)

\[ \text{C} + \text{CO}_2(g) \rightarrow 2\text{CO}(g) \]  \hspace{1cm} (3)

TiN may also be formed by reacting TiO₂ with CO. The corresponding reaction can be written as

\[ \text{TiO}_2 + 2\text{CO}(g) + \frac{1}{2}\text{N}_2(g) \rightarrow \text{TiN} + 2\text{CO}_2(g) \]  \hspace{1cm} (4)

Moreover, TiN does not appear to form in one step. The phase diagram suggests that the loss of oxygen from the TiO₂ structure leads to the formation of oxygen-deficient Magneli phases, namely Ti₅₋₄O₄₋₄, with 4 > n > 10. Experimentally, a reaction sequence involving the formation of various titanium-rich phases, such as Ti₃O₄, and Ti₄O₆, was observed by many researchers. The combination of excess C and higher temperatures always led to the formation of TiC.

The combustion synthesis of a variety of simple and complex non-oxide phases is well known. Interestingly, pure metals are almost always involved as reactants by themselves or in association with oxides in these processes; however, reports on microwave field-assisted combustion synthesis are scarce. The understanding of such a process is very complex because of the involvement of a vast number of unconstrained parameters. In conventional processes, the high degree of adiabaticity observed in combustion reactions is attributed to various material-dependent parameters, such as particle size, particle-particle contact, and particle packing (green density). In this paper, we present only the experimental observations concerned with TiN synthesis, not the effect of the previously mentioned parameters, because of the inseparable nature of microwave and the SHS process. More details about combustion synthesis can be found in the excellent review articles of Munir.

Recent research work from this lab has demonstrated a major advance in the use of microwave energy in materials processing. Advantages such as rapid heating, selective material coupling, and enhanced reaction kinetics make the microwave process an attractive route for materials synthesis. Several reports are available on preparation of various oxides, nitrides, carbides, and silicides. Many materials couple directly with microwaves; other reactions use the heat generated by indirect microwave coupling as well as direct microwave-material interactions. The shorter processing time in microwave synthesis compared with conventional synthesis is one factor clearly evidenced from most of these reports. Despite this fact, microwave-material coupling and the electromagnetic field effect are not yet well understood and still remain a subject of research. The principles of microwave processing and related details can be found elsewhere.

In this paper, we report microwave-induced preparation of TiN ceramic powder starting from TiO₂. The involvement of microwave energy and subsequent combustion makes this process relatively simple, fast, and economically promising.
The process involves the introduction of thermal energy induced by the microwave field that spreads throughout the sample volume, which is believed to accelerate the carbonitridation reactions.

II. Experimental Procedure

High-purity TiO₂ (impurities: Fe 0.008\%, Pb 0.008\%, and Zn 0.008\%; average particle size, 0.41 \( \mu \)m; specific surface area, 4.32 m²/g) (Fisher Scientific Co., Pittsburgh, PA) and activated C (impurities: <100 ppm Fe, <30% H₂O; average particle size, 8.56 \( \mu \)m; specific surface area, 1.17 m²/g) (Aldrich Chemical Co., Milwaukee, WI) were used as the starting reagents. Various ratios of TiO₂ and C were thoroughly mixed in an acetone medium using an agate mortar for ~30 min. The mixed powder was then transferred to a mullite tube with one end closed, which was then placed at the center of a 2 kW tubular microwave furnace (Model RC/20SE, Amana Refrigeration, Inc., Amana, IA). Less than 70% of the total microwave power was used in the experiments. More details about the description of the microwave furnace and its operation are reported elsewhere. All reduction experiments were conducted in a forming-gas (95% N₂, 5% H₂) environment. A constant flow rate of 200 mL/min was maintained throughout the experiments. Temperatures were measured using a single wavelength infrared (IR) pyrometer (Model MA2SC, Raytek Co., Santa Cruz, CA) that was focused through a transparent quartz window on the center of the charge. An average emissivity value of 0.5 was used for the TiO₂ + C mixture. This value was chosen because it lies between the emissivity values of pure TiO₂ and pure C. Generally, in compositionally changing ceramic systems, the emissivity value is subjected to variations with time and temperature and, hence, on many occasions, the value may not be the same for the entire reaction range. The measured temperatures (>750°C) were occasionally cross-verified using dual-wave and optical pyrometers, and the temperature matching suggested that the chosen emissivity value was nearly accurate. The IR intensity lost through the quartz window seems to be negligible. This was confirmed by making sample measurements with and without using the quartz window. The IR pyrometer was positioned exactly 27 inches from the sample with a 2-mm-diameter spot size. The position, focus, and measurement point of the pyrometer were unaltered during the sequence of experiments to obtain the best possible temperature readings. Heating rate curves were plotted against time. These graphs were capable of showing even fine changes in temperature during the reaction process. The reacted powder was characterized using X-ray diffraction (XRD) (Scintag Inc., Cupertino, CA) and scanning electron microscopy (SEM) (Model S-3500N Hitachi Ltd., Tokyo, Japan).

III. Results

(1) Microwave Absorption of TiO₂ and C

Microwave absorption behavior of activated charcoal and TiO₂ powders was determined by their time-temperature behavior. Previous studies by various researchers proved that C, a good absorber of microwaves, can be used either directly or indirectly for materials processing. Although the absorption behavior of charcoal powder is noted by some authors, the mechanisms for such high-temperature losses are yet to be understood. The time-temperature behavior of charcoal powder used in the present experiments is shown in Fig. 1. Even at room temperature, C shows a strong microwave-absorbing behavior. Within the first 15 s of microwave exposure, adiabatic heating rates of ~1400°C/min are observed (see Fig. 1). After 1 min, however, the heating rate decreased to ~1000°C/min. On the other hand, pure, unmixed TiO₂ powder did not show any increase in temperature, even after 10 min of microwave exposure (not shown in Fig. 1). A homogeneous mixture of TiO₂ + C is believed to result in an "anisothermal reaction" caused by selective microwave heating of individual powders. Compared with pure TiO₂, the TiO₂ + C mixtures showed a heating rate similar to pure C at the initial stage, but stretched slightly longer, finally resulting in much higher temperatures. After the first 5 min of microwave exposure, the charge (TiO₂ + C) started to react vigorously. This is specified by the wavy region in Fig. 1 that corresponds to wide temperature fluctuations during the exothermic reaction. Microwave energy may be responsible for this effect, as the self-burning effect completely stopped when the microwave power to the system was halted. Additionally, earlier published works on conventional routes for TiN preparation do not mention the occurrence of any such effects. Interestingly, in the present experiments, the exothermic reaction and associated self-burning phenomenon were more pronounced when the sample tube was reused.

![Graph of heating rate versus time for various TiO₂ + C mixtures used in the experiments.](attachment:image.png)
(2) Effect of TiO₂:C Ratio on Microwave Heating

Microwave heating rate curves of TiO₂ + C mixture with varying C content is given in Fig. 2. All these experiments were conducted for a maximum time period of 10 min each. This graph demonstrates that pure C shows very high heating rates initially and then saturates to a lower value after ~40 s. With the addition of TiO₂, the heating patterns were remarkably different from that of pure C.

(3) Phase Formation in Microwave-Induced Carbothermal Synthesis

Figure 3 shows the XRD pattern of the reaction products formed during microwave induced carbothermal reaction between TiO₂ and C with a stoichiometric ratio (C/TiO₂ = 2:1). The time indicated above each pattern represents the duration of soaking after the mixture started to self-burn. These XRD patterns clearly indicate a conversion
of >50% after just 1 min. Similar reactions in conventional carbothermal reaction involved a sequence of phase formations before complete TiN formation. The reaction time involved for complete TiN formation in the conventional process is ~4 h at 1300°C, and in the microwave process, it does not exceed 20 min. To reach the self-burning point from room temperature, the charge takes <8 min. Allowing ~30 min for the microwave furnace to cool, the entire cycle time will be just <60 min.

A second set of experiments was conducted with excess C. Figure 4 shows XRD patterns of the products formed. Comparing Fig. 3 and Fig. 4, two interesting points can be observed: (i) with higher carbon content, no Ti2O3 or any other Magneli phases are formed at any stage of reaction; and (ii) complete conversion to TiN occurs after just 1 min of reaction. However, excess carbon removal by oxidizing at 700°C was a problem because of the high oxidizing nature of TiN. Despite quicker TiN formation in the presence of an excess C compared with a stoichiometric mixture, the removal of C must be optimized to be superior to the stoichiometric process.

Figure 5 shows an SEM micrograph of the TiN powder particles produced by this method. It can be noticed that the particles are submicrometer sized and uniformly shaped.

Lattice parameters calculated using the (111) peak for TiN are tabulated in Table I. The lattice parameter values are comparable to the commercial TiN powder (Bukowski International Corp., Charlotte, NC); however, inherent O always seems to exist in both commercial and powders prepared using this method. This was also confirmed qualitatively by energy-dispersive X-ray analysis (EDAX). TiN prepared with excess C shows the presence of lesser amounts of O in the lattice.

IV. Discussion

First we attempt to understand the following observations (see Fig. 1): (i) initial heating rates of 1400°C/min and the subsequent microwave induced self-burning phenomenon and (ii) sustained microwave coupling of TiN.

The absence of combustion in pure C, the presence of combustion in C+TiO2 mixture, and the previously discussed observations lead to the idea of a possible anomalous microwave heating effect. It is known that when TiO2 is reduced in a N2/H2 atm from 700° to 1100°C, the following reaction occurs:

\[ \text{TiO}_2 \rightarrow \text{TiO}_{2-x} + x\text{H}_2\text{O} \]  

(5)

The inclusion of C may remove O faster from the TiO2 structure. At lower temperatures, the formation of oxygen-deficient structures can be written as

\[ \text{TiO}_2 + x\text{C} \rightarrow \text{TiO}_{2-x} + x\text{CO}(g) \]  

(6)

Previous reports from this laboratory clearly established that reduced oxide, TiO2-x, is a very strong microwave susceptor.22,23 This fact seems to contribute to the early stages of the present combustion reaction, where the heating rate of the mixture surpasses the heating rate of carbon. However, its contribution to the SHS process is still unclear.

To analyze the microwave susceptor nature of TiN at elevated temperatures, a microwave heating experiment using a mixture of carbon and commercial TiN powder was performed. Surprisingly,
Table I. Lattice Parameter Values of the TIN Power Prepared by the Microwave Combustion Process

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO\textsubscript{2}-C ratio</th>
<th>Reaction time (min)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1:2</td>
<td>1</td>
<td>4.204</td>
</tr>
<tr>
<td>C2</td>
<td>1:2</td>
<td>5</td>
<td>4.210</td>
</tr>
<tr>
<td>C3</td>
<td>1:2</td>
<td>10</td>
<td>4.204</td>
</tr>
<tr>
<td>C4</td>
<td>1:2</td>
<td>15</td>
<td>4.204</td>
</tr>
<tr>
<td>C5</td>
<td>1:2</td>
<td>20</td>
<td>4.193</td>
</tr>
<tr>
<td>TC1</td>
<td>1:3</td>
<td>1</td>
<td>4.204</td>
</tr>
<tr>
<td>TC2</td>
<td>1:3</td>
<td>5</td>
<td>4.226</td>
</tr>
<tr>
<td>TC3</td>
<td>1:3</td>
<td>10</td>
<td>4.225</td>
</tr>
<tr>
<td>TC4</td>
<td>1:3</td>
<td>30</td>
<td>4.234</td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
<td>4.201</td>
</tr>
</tbody>
</table>

*(111) plane was used for calculations.*

The powders mixture also produced a wavy pattern in heating rate-time curve (see Fig. 6). Figure 6 also shows that pure C did not produce a wavy pattern in a temperature-time (T-t) graph. At room temperature, pure TIN did not couple with multimode microwaves at all. With the mixture (TIN + C), however, the microwave heating of carbon increased the mixture temperature to the point where the burning process initiated (see Fig. 6). At present, we believe that TIN becomes microwave absorbing at increased temperatures and is thus responsible for the observed temperature fluctuations at >1200°C.

Recently, it was established that very fine metal powders not only heat, but also sinter to full density when exposed to a normal 2.45 GHz microwave field. The increased metallic nature of submicrometer TIN particles at high temperatures could have caused a surface heating (eddy current heating), which later spread throughout the charge volume to create anomalous heating effect in these experiments. According to White et al., TIN formation starts at ~1100°C. Here, because the ignition of the self-burning phenomenon starts at ~1200°C, at least a small fraction of TIN that was formed at this temperature appears to be sufficient for ignition. Experimentally, it was repeatedly observed that ignition originated at the top surface of the charge, which was relatively closer to the magnetron. Despite having various supportive evidences for anomalous heating effect in TIN, the involvement of a number of unconstrained parameters makes this discussion section purely speculative. Additional experiments are in progress to understand this effect in a more detailed fashion.

We now try to explain the remarkable difference in heating rates between C and TiO\textsubscript{2} + C mixtures. Figure 2 shows that, in these mixtures, the initial heating is driven by C evidenced by the overlapping of rising heating rate curves and the occurrence of heating rate maxima in the same region. The higher magnitude observed in the heating rate curves could be due to additional absorption by the reduced TiO\textsubscript{2} phases (i.e., TiO\textsubscript{2-α}).

Two other significant features are evident from Fig. 1: (i) the time of ignition (t\textsubscript{ig}) is independent of TiO\textsubscript{2}-C ratio and (ii) there is discontinuity in the heating rate pattern.

The time of ignition (t\textsubscript{ig}) variations in these experiments are not well understood. They might depend on several factors, such as TiO\textsubscript{2}-C particle contacts, homogeneous particle distributions, the intermediate phases formed, and their absorption behavior. Additional experiments were not performed in this study to understand the dependence of all these parameters on t\textsubscript{ig}. One limitation in measuring t\textsubscript{ig} was frequent shattering of the sample-containing mullite tubes due to extremely high heating rates produced in the reactant mixture.

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Fig. 6. Graph of heating rate versus time for a 1C:1TIN mixture.

Fig. 7. Typical reaction sequence in the microwave-induced carbonitridation of TiO\textsubscript{2} with a C/TiO\textsubscript{2} ratio of 2:1.
Figures 3 and 4 show that the reaction sequences for microwave reactions are from conventional processes. Reactions in a conventional carbothermal reduction reaction involved a sequence of phase formations before complete TiN formation. In the work by White et al., the phase field indicates an overlapping of Magneli phases Ti₄O₉ and Ti₅O₈. The reduction reactions involving formation of these phases can be represented generically by

$$4\text{TiO}_2 + C \rightarrow \text{Ti}_4\text{O}_9 + \text{CO}_2$$  \hspace{1cm} (7)

Further reduction of Ti₅O₈ may lead to

$$3\text{Ti}_5\text{O}_8 + C \rightarrow 4\text{Ti}_4\text{O}_9 + \text{CO}_2$$  \hspace{1cm} (8)

These stepwise reductions to Ti-rich Magneli phases were not observed in the microwave-induced reactions. Figure 4 shows that the coexistence exclusively of the Ti₄O₉ phase with Ti₅O₈ phase (see Ref. 8) was observed after 1 min soaking. However, after 20 min of reduction reaction, XRD detects only TiN and no Ti₄O₉. It must be noted that XRD is insensitive to detect phases <5%, but during conventional synthesis of TiN, these phases are reported to form in major quantities. Full width at half maximum (FWHM) of the (111) XRD peak also confirms formation of highly crystalline TiN. The reaction sequence is schematically depicted in Fig. 7. Unlike in conventional heating, in microwave heating, the very rapid rise of temperature does not allow enough time for other intermediate phases to form, finally leading to a different reaction path. In an ambient nitrogen atmosphere, the reaction sequence that occurs in the conventional process can be written as

$$\text{TiO}_2(\text{anatase}) \rightarrow \text{TiO}_2(\text{rutile}) \rightarrow \text{Ti}_4\text{O}_9 \rightarrow \text{Ti}_5\text{O}_8 \rightarrow \text{TiN}$$

whereas, in the microwave process, the reaction is

$$\text{TiO}_2(\text{anatase}) \rightarrow \text{Ti}_5\text{O}_{8-x}(\text{transient}) \rightarrow \text{Ti}_4\text{O}_9 \rightarrow \text{TiN}$$

V. Conclusions

TiN powder was prepared by a microwave carbothermal reduction and nitridation technique. Heating rates of TiO₂ + C mixtures were as high as 1400°C/min and resembled that of C at the initial stages, but rose to higher values after that. After about 5 min of microwave exposure, TiO₂ + C mixtures showed a self-sustaining combustion, which was never observed with pure TiO₂ and C powders. Experiments proved that higher heating rates in TiO₂ + C mixtures were due to the increased microwave susceptibility of TiO₂, that was formed in the earlier stages of reaction. The subsequent self-burning effect was possibly induced by the microwave coupling of the freshly formed TiN, which is believed to behave similar to a metal powder at higher temperatures. Inclusion of excess carbon in the mixture enhanced the reaction rate, leading to much faster TiN formation. Formation of successive Magneli phases did not occur in microwave synthesis, as is often observed in conventional TiN synthesis. Presently, the microwave experiments are under way to study the relationship between time, temperature, and atomic substitutions in TiN.

References