Microwaves:
Theory and Application
in
Materials Processing III

Edited by
David E. Clark
University of Florida
Diane C. Folz
University of Florida
Steven J. Oda
Consultant
Richard Silbergliedt
FM Technologies, Inc.

Ceramic Transactions
Volume 59
Published by
The American Ceramic Society
735 Ceramic Place
Westerville, Ohio 43081
MICROWAVE SYNTHESIS OF ALUMINUM TITANATE IN AIR AND NITROGEN

M.D. Mathis, D.K. Agrawal and R. Roy
Materials Research Laboratory
The Pennsylvania State University
University Park, PA

R.H. Plovnick
3M Ceramic Technology Center
St. Paul, MN

R.M. Hutcheon
Chalk River Laboratories
Chalk River, Ontario, Canada

ABSTRACT

The effect of microwave heating on solid state reactions is a key issue in materials processing. The microwave-assisted solid state reaction of alumina and anatase to form aluminum titanate was studied. The reaction was carried out in both air and nitrogen atmospheres. It was found that aluminum titanate can be synthesized at 1150°C in air and at 1050°C in nitrogen. Dielectric studies show a three-fold increase in the dielectric constant when processed in nitrogen as opposed to air, indicating the evolution of defects. Comparison of the dielectric measurement data shows the onset of the solid state reaction is enhanced when nitrogen processing is employed. XRD analysis of the resulting materials shows that anatase is converted to rutile before the Al₂TiO₅ reaction occurs. Additionally, Al₂TiO₅ was synthesized from an alumina-defect rutile route in nitrogen. The Al₂TiO₅ was nucleated at 600°C and was about 70% reacted by 900°C.

INTRODUCTION

Microwave processing has produced enhancements during sintering [1-3] when compared with conventional sintering. It has been reported in some cases that the activation energies for sintering are lowered by microwave processing [2] resulting in faster material sintering rates. The reasons for the apparent reduction of activation energies are the subject of debate. Recently microwave synthesis has been attempted on zinc aluminate spinel from zinc oxide and alumina [4] and aluminum titanate made from alumina and rutile [5,6]. In each case the reactions in question showed a reduction in the temperatures and times necessary to synthesize each phase.

Unlike conventional sintering or synthesis, microwave synthesis depends largely upon the ability of one or more phases in the reactant mixture to couple with the applied field. This may...
enhance reaction rates due to the fact that heating occurs throughout the reactant mixture, rather than by heat conduction from the surface to the core of the conventionally processed material. In this work, attempts were made to enhance the microwave absorption of a reactant mixture by introducing defects, in the form of oxygen vacancies, in one of the phases. The incorporation of defects into the crystal structure of a material can increase its dielectric loss [7] by introducing a mechanism for microwave absorption.

In this work Al₂TiO₅ was microwave synthesized from Al₂O₃ and TiO₂ phases in both air and nitrogen environments. In the latter case, the nitrogen gas was not used as a reactant in the system, as in the case of another process described elsewhere [8] in these proceedings, but rather to prevent or slow the oxidation of defect titania during heating and reaction. Al₂TiO₅ is an interesting material because of its low thermal expansion properties [9,10] due its ability to form microcracks.

EXPERIMENTAL

**Alumina-titania (anatase) system:** Equimolar mixtures of alumina (lot A165G, Alcoa Inc.), with a 0.2 µm particle size, and anatase (Cerac, Inc.), with a <5 µm particle size, were wet-milled for 16 hours. The resulting powder was dried by microwave initially and then conventionally. Pellets, weighing approximately 12 grams, were pressed uniaxially to increase particle contact. The pellets had diameters of 1.13 inches and heights of about 0.3 inches for all microwave and conventional experiments.

**Alumina-defect titania (rutile) system:** Anatase was fired to 1100°C under forming gas (5% hydrogen-95% argon, Linde Inc.) for 3 hours to give oxygen-defective rutile. After firing, defect rutile was the main phase detected by X-ray diffraction (XRD). The defect powder was dry-milled with alumina overnight. Pellets, having the same dimension described earlier, were uniaxially pressed from the resulting powder mixture. The pellets were processed in a nitrogen (Linde, Inc.) atmosphere for these experiments.

**Equipment:** The microwave equipment, conventional drying oven and supporting materials used in this work are described elsewhere [11]. Microwave temperature measurements were done by K and C-type thermocouples [11] (Omega, Inc.). The temperatures at the various soak times reported in this work were maintained by the controller [11] cycling the microwave power within soak-tolerance limits (10-15°C of the setpoint temperature). The conventional furnace used for reduction of rutile and high temperature aluminum titanate synthesis was a Rapid Temperature tube furnace (CM Furnaces, Inc.).

**Characterization:** Phase analysis was done by XRD. The instrument used was a Phillips APD model 3600 using copper K-alpha radiation. Scans were done from 5 to 80 degrees 2-theta. Dielectric measurements were made at microwave frequencies over a temperature range of 25°C-1400°C under nitrogen and air. The heat rate was 20°C per minute.

High temperature X-ray diffraction (HTXRD) analysis was done on the anatase-alumina reaction to determine the temperatures for the anatase-rutile transition as well as to determine the temperatures necessary for conventional aluminum titanate production. The sample was heated on a platinum stage at various temperature intervals. At the end of an interval cycle a diffraction pattern was obtained while the sample remains at the final temperature of that
interval. These experiments were done in air, helium and under vacuum as needed by the specifics and limitations of the instrumentation.

RESULTS AND DISCUSSION

Analysis of the Anatase-Alumina Reaction

HTXRD data showed that aluminum titanate is not synthesized conventionally from anatase, but rather from the rutile phase. Anatase is converted to rutile between 900-1000°C in air. The conversion occurs near 800°C when the experiment is done in inert atmospheres or in a vacuum.

Al₂TiO₅ synthesis was not observed by 1200°C when heated in air (the instrument could not be operated above 1200°C in air). In an inert atmosphere or in a vacuum, the reaction began between 1300-1400°C and was not complete by 1500°C, which is the maximum working temperature achievable by the HTXRD.

Aluminum Titanate Synthesis in Air

Tables 1 and 2 summarize the XRD findings of attempts to synthesize Al₂TiO₅ from α-alumina and anatase by microwave and conventional synthesis respectively. Both tables show the relative intensities for representative peaks of the reactant and product phases.

Table 1. XRD Analysis of the Microwave Synthesis of Al₂TiO₅ in Air

<table>
<thead>
<tr>
<th>Temp-Time</th>
<th>α-Al₂O₃</th>
<th>TiO₂ (anatase)</th>
<th>TiO₂ (rutile)</th>
<th>Al₂TiO₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050°C-30 min</td>
<td>71</td>
<td>---</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>1150°C-30 min</td>
<td>42</td>
<td>---</td>
<td>100</td>
<td>(1)</td>
</tr>
<tr>
<td>1250°C-30 min</td>
<td>26</td>
<td>---</td>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>1300°C-15 min</td>
<td>19</td>
<td>---</td>
<td>96</td>
<td>100</td>
</tr>
<tr>
<td>1300°C-30 min</td>
<td>4</td>
<td>---</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>1300°C-45 min</td>
<td>---</td>
<td>---</td>
<td>11</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2. XRD Analysis of the Conventional Synthesis of Al₂TiO₅ in Air

<table>
<thead>
<tr>
<th>Temp-Time</th>
<th>α-Al₂O₃</th>
<th>TiO₂ (anatase)</th>
<th>TiO₂ (rutile)</th>
<th>Al₂TiO₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300°C-30 min</td>
<td>31</td>
<td>---</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>1300°C-45 min</td>
<td>32</td>
<td>---</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>1400°C-45 min</td>
<td>8</td>
<td>---</td>
<td>86</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 1 shows that Al₂TiO₅ begins to nucleate at 1150°C using microwave heating. After 15 minutes at 1300°C the microwave reaction is near completion with minor amounts of alumina and rutile phases remaining. Synthesis by conventional methods does not show any product formation until 1300°C. These findings are consistent with work done by Ph. Boch, et al. [5,6], whereby alumina was reacted with rutile-phase titania. In that work aluminum titanate was nucleated near 1210°C by microwave and near 1300°C conventionally.
Aluminum Titanate Synthesis in Nitrogen

Tables 3 and 4 show the XRD results from Al$_2$TiO$_5$ synthesis from alumina and anatase in nitrogen by microwave (Table 3) and conventional (Table 4) methods. The relative peak intensities were used to compare the composition data at each temperature and time interval.

### Table 3. XRD Analysis of the Microwave Synthesis of Al$_2$TiO$_5$ in Nitrogen

<table>
<thead>
<tr>
<th>Temp-Time</th>
<th>α-Al$_2$O$_3$</th>
<th>TiO$_2$ (anatase)</th>
<th>TiO$_2$ (rutile)</th>
<th>Al$_2$TiO$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>950°C-15 min</td>
<td>52</td>
<td>7</td>
<td>100</td>
<td>--</td>
</tr>
<tr>
<td>950°C-30 min</td>
<td>46</td>
<td>5</td>
<td>100</td>
<td>--</td>
</tr>
<tr>
<td>1050°C-15 min</td>
<td>55</td>
<td>---</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>1050°C-30 min</td>
<td>49</td>
<td>---</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>1100°C-15 min</td>
<td>57</td>
<td>---</td>
<td>100</td>
<td>23</td>
</tr>
<tr>
<td>1100°C-30 min</td>
<td>37</td>
<td>---</td>
<td>100</td>
<td>34</td>
</tr>
</tbody>
</table>

### Table 4. XRD Analysis of the Conventional Synthesis of Al$_2$TiO$_5$ in Nitrogen

<table>
<thead>
<tr>
<th>Temp-Time</th>
<th>α-Al$_2$O$_3$</th>
<th>TiO$_2$ (anatase)</th>
<th>TiO$_2$ (rutile)</th>
<th>Al$_2$TiO$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150°C-30 min</td>
<td>47</td>
<td>3</td>
<td>98</td>
<td>--</td>
</tr>
<tr>
<td>1250°C-30 min</td>
<td>41</td>
<td>---</td>
<td>100</td>
<td>--</td>
</tr>
<tr>
<td>1300°C-30 min</td>
<td>35</td>
<td>---</td>
<td>100</td>
<td>(1)</td>
</tr>
<tr>
<td>1400°C-30 min</td>
<td>18</td>
<td>---</td>
<td>93</td>
<td>100</td>
</tr>
</tbody>
</table>

From the data obtained it appears that in an atmosphere that promotes oxygen defects and reduction of titania, the product phase can be synthesized at lower temperatures. This can further be observed by the dielectric measurements[12,13] done at microwave frequencies in both air and nitrogen atmospheres using the same starting reactants, i.e. alumina and anatase. The dielectric measurements [13] quantify the “real-part” (ε'') and the “imaginary or loss part”(ε'') of the dielectric constant at 2460 MHz as temperature increases. The green and final densities of the sample measured in figure 1 were 1.82 and 2.08g/cm$^3$ respectively.

From the data shown in Figure 1, the reactants heated in air up to 1400°C show an increase in ε' and ε'' starting at about 250°C. This peak varies at 600°C and is possibly due to water evoking from the test sample. The increase in ε' and ε'' starting at 800°C may be consistent with the phase change of anatase to rutile, as shown by HTXRD. The sharp rise in ε' and ε'' starting at about 1160°C is thought to be the nucleation of Al$_2$TiO$_5$, which corresponds to XRD results obtained on the reaction (Table 1). Hence, in this case, dielectric measurements can be used as a technique to follow the reaction in the microwave region.

Figure 2 is the dielectric measurement data (ε' and ε'') for the alumina-anatase reaction in a nitrogen atmosphere. The green and final densities of the test sample were 1.81 and 2.06g/cm$^3$ respectively. The data can be interpreted analogously with Figure 1, with respect to phase transitions; however, what is important to note is that the onset of the Al$_2$TiO$_5$ reaction is at about 1050°C. This information is consistent with XRD results obtained (Table 3). Conventionally (Table 4), the results are almost analogous with Table 2.

Nitrogen processing lowered the onset of reaction about 110°C as opposed to air processing. Additionally, the increase in ε'' starting at 250°C is greater than in the air
measurement case. A value of 1.2 is observed for the nitrogen case, while 0.3 is observed for the air case. In the air measurement case, this peak had dropped by 800°C, after which the peak for the phase transition of anatase to rutile begins. However, in the nitrogen measurement case, the 250°C loss-peak decreased to a minimum by 1000°C and probably includes the phase transition. This may indicate a decrease in the temperature necessary to convert anatase to rutile, which is consistent with HTXRD data. The HTXRD (in inert atmosphere) data showed the phase transition occurred about 100°C lower than in air.

The increase in magnitude likely indicates an increase in electronic conductivity. Conductivity (dielectric loss) continues to increase as temperature rises, indicating an increase in the defect concentration in the nitrogen system.

Figure 1. Measurement of $\varepsilon'$ (-o-) and $\varepsilon''$ (-x-) at 2460 MHz during the Alumina-Anatase Reaction in Air with Conventional Heating

Figure 2. Measurement of $\varepsilon'$ (-o-) and $\varepsilon''$ (-x-) at 2460 MHz during the Alumina-Anatase Reaction in Nitrogen with Conventional Heating
Table 5. XRD Analysis of the Microwave Synthesis of Al₂TiO₅ from Al₂O₃ and Defect TiO₂ in Nitrogen

<table>
<thead>
<tr>
<th>Temp-Time</th>
<th>α-Al₂O₃</th>
<th>TiO₂ (rutile)</th>
<th>Al₂TiO₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C-15 min</td>
<td>44</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>750°C-10 min</td>
<td>40</td>
<td>48</td>
<td>100</td>
</tr>
<tr>
<td>900°C-15 min</td>
<td>49</td>
<td>43</td>
<td>100</td>
</tr>
<tr>
<td>1050°C-15 min</td>
<td>26</td>
<td>21</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 3. Measurement of ε' (-o-) and ε'' (-x-) at 2460 MHz during the Alumina-Defect TiO₂ Reaction in Nitrogen with Conventional Heating

Dielectric measurements (Figure 3) done on the alumina-defect rutile system show overall increases in ε' and ε'' above the case of alumina-anatase in nitrogen synthesis. The green and final densities of the test sample were 2.09 and 2.87 g/cm³ respectively. What is interesting to note is the constant rise in conductivity (ε'') as the mixture heats. From the dielectric studies it
is difficult to pinpoint the nucleation of Al₂TiO₅; however, the area where changes in the slopes of n' and n" occur (starting at about 430°C followed by a brief plateau at 600°C) might be the nucleation. This coincides with the XRD data.

In the actual microwave chamber, the reactants can be heated at about 0.78kw (60% of the total power) without the use of secondary coupling. Heating rates have been found to be near 200°C per minute in some experiments after the temperature reaches about 400°C. In the case of the alumina-anatase nitrogen synthesis, SiC rods were needed as secondary couplers and at no point in the reaction did heating rates reach 200°C/ per minute. These facts are likely attributable to the generation of defects and subsequent defect synthesis.

CONCLUSION

Aluminum titanate has been microwave synthesized from α-Al₂O₃ and TiO₂ (anatase and rutile phases) in air and nitrogen. It was found that before the product phase was formed the anatase conversion to rutile occurred. During this work no anatase phase was found when Al₂TiO₅ was detected by XRD analysis.

It was also found that Al₂TiO₅ could be microwave synthesized from anatase in a nitrogen atmosphere at about 1050°C. In air, the microwave reaction was found to initiate at 1160°C. This would tend to indicate that the microwave field is coupling with the defects that are generated in rutile by nitrogen processing. This can be observed from the dielectric measurements.

Aluminum titanate can be microwave synthesized from α-Al₂O₃ and defect rutile. The reaction is initiated near 600°C after a soak time of 15 minutes. Conventionally the synthesis does not occur until temperatures near 1300°C are achieved. The XRD data shows the microwave reaction nucleates quickly but growth is slowed as temperature increases. This is possibly due to difficulties encountered by the reactants as they attempt to diffuse across the product interface layer. Due to the poor mixing of the reactants in the defect rutile synthesis from dry milling, future work will involve the investigation of wet-mixing. Attempts will be made to synthesize Al₂TiO₅ in a reducing atmosphere. Slowing the oxidation of the defect rutile could result in increased microwave coupling and heightened reaction rates. Attempts are also being made to characterize the microstructure and to quantify defect concentration. Currently there is no information on the relation of defect concentration to the synthesis reaction. Such information might be vital to determining the reaction mechanisms and rates.

ACKNOWLEDGEMENTS

We thank Brian Lynch and Myles Brostrom for the XRD and the HTXRD analyses, respectively.

REFERENCES


