SYNTHESIS OF FUNCTIONALLY-GRADED CERAMIC MATERIALS VIA LIQUID INFILTRATION TECHNIQUE

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ABSTRACT

SYNTHESIS OF FUNCTIONALLY-GRADED CERAMIC MATERIALS VIA LIQUID INFILTRATION TECHNIQUE. Liquid infiltration technique has been used to synthesise several functionally-graded ceramic materials. In this process, powder as the matrix was uniaxially pressed and then presintered at approximately 1000 °C to obtain green bodies with porosity of 40-45% to increase their strength for liquid infiltration. The green bodies were then fully immersed with suitable liquids. The infiltrated green bodies were sintered at high temperature to allow the formation of new phases and densification of the ceramics. The technique has been applied to produce functionally-graded mullite-aluminium titanate/alumina, aluminium titanate/zirconia-alumina, and zirconium titanate/zirconia composites. The graded profile of each material was characterised using Rietveld x-ray diffraction technique, microanalysis, and electron microscopy. Results showed that the functionally-graded ceramic composites can be produced by infiltration method.

INTRODUCTION

In the past, requirements for industry were mainly focused on materials which exhibit uniform properties. Among them are dispersed, laminated, and fiber-reinforced composites. There is no doubt that these materials are still required. However, a novel type of composite has been developed, termed as functionally-graded materials or functional gradient materials (FGM). This type of material displays character which is spatially inhomogeneous but changes between spatial positions are continuous. From phase distribution point of view, FGM lies between homogeneous or dispersed and laminate composites. It has been shown that the continuous change of characters in FGM provides superior macroscopic properties over other type of materials, especially when residual thermal stresses is taken into account [1]. The idea of synthesising FGM was originated by Japanese scientists led by Niino in 1984 [2]. Beginning with the development for mechanical and thermal properties improvement, FGM has found application in broader fields which include electronics and optics. Methods for producing FGM have also advanced, one of which is liquid infiltration technique. Type of FGM can be combination of two or more basic type of material, ie metals, ceramics, and polymers.

The idea of producing functionally-graded ceramic materials via liquid infiltration technique was inspired by the success of synthesising such materials by sol-gel process. In this process, a powder is mixed with a solution containing a phase precursor. When the mixture is processed, usually by firing, formation of a new phase is allowed or a new phase is introduced into the former matrix resulting in a functionally-graded composite. An alumina/ zirconia functionally-graded
material can be produced [3] by infiltrating a solution of \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) into yttria-tetragonal zirconia polycrystal (Y-TZP). Other systems which have been produced include mullite/alumina with TEOS as infiltrant [4], mullite/ZTA with TEOS as infiltrant [5], and aluminium titanate/alumina with TEOT as infiltrant [6].

In this paper, synthesis of three other types of functionally-graded ceramic materials which have been produced via infiltration technique is reviewed. They are mullite-aluminium titanate (AT)/ZTA with TEOS and TEOT as infiltrants [7], AT/zirconia-alumina [8], and aluminium titanate/ZT)/zirconia [9]. Infiltrant for the later two materials was a solution containing titanium chloride. This paper also reports the characterisation of the material to reveal their graded character.

**EXPERIMENTAL METHOD**

Raw materials used are tabulated as in Table 1. The table also shows the shape, dimensions, sintering temperature and porosity of both green body and as-fired ceramics.

The powder for each system was wet-milled with pure water as the wetting media. Certain amount of \( \text{NH}_4\text{OH} \) was added into each mixture before milling. The purpose of adding \( \text{NH}_4\text{OH} \) was to take up the pH up to 10-12 in order to facilitate the break up of the spray-dried grains. The as-milled mixture was dried in an oven at 100 °C for 24-48 hours. The dried mixture was then sieved until free-flowing with a consecutive grid-size sieves.

Uniaxial press in a metal die was applied into the powder mixture to produce the shape. A partial sintering at 1000 °C was then used to increase its strength but maintain the porosity prior to infiltration. The apparent porosity of the samples was measured following the Australian Standard AS 1774.5 (1989): The Determination of Density, Porosity, and Water Absorption [10].

Infiltration process was conducted by fully immersing the presintered ceramic with the certain solution for 1 - 24 hours. In some cases, control samples, ie. uninfiltrated samples, were also made. The samples were then sintered at high temperature to allow the formation of new phases and densification of the ceramic. The synthesis of the FGM is then finalised. The general procedure of synthesising a FGM can be illustrated using a flow-chart as shown by Figure 1.

Characterisation of the graded profile in the FGMs was made using x-ray diffraction, electron microscopy. The x-ray diffraction technique was not only used to monitor the formation of new phases but also to determine the phase composition within the samples. This quantitative phase analysis was performed using the whole-pattern Rietveld phase analysis LHPM (Hill and Howard 1986). Methods of calculating weight fractions using Rietveld 'ZMV' approach following Pratapa et al. [11] and Hill and Howard [12] were used.

**RESULTS AND DISCUSSION**

There are two indications which can be used to predict that the synthesis is successful, ie. mass gaining and x-ray diffraction pattern from the surface of each sample. Results showed that the green bodies had gained a certain amount of precursor indicated by the presence of positive mass difference between as-fired and uninfiltrated samples. Mass increase of 4.2% was found both in the AT/zirconia-alumina (24 hours immersion) and ZT/zirconia (1 hour immersion) systems. The x-ray diffraction pattern showed that new phases(s) formed in the material. The new phases were believed...

<table>
<thead>
<tr>
<th>No</th>
<th>System</th>
<th>Powder</th>
<th>Infiltrant</th>
<th>Shape</th>
<th>Dimension</th>
<th>Porosity (%)</th>
<th>Sintering Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mullite-AT/ZTA</td>
<td>alumina-zirconia (85:15% by weight)</td>
<td>TEOS and TEOT</td>
<td>disc</td>
<td>13.5 mm diam. 2 mm height</td>
<td>35-40</td>
<td>1550 for 3 hours</td>
</tr>
<tr>
<td>2</td>
<td>AT/zirconia-alumina</td>
<td>alumina-zirconia (90:10% by weight)</td>
<td>solution containing titanium chloride</td>
<td>bar</td>
<td>5 mm x 12 mm x 60 mm</td>
<td>45</td>
<td>1550 for 3 hours</td>
</tr>
<tr>
<td>3</td>
<td>ZT/zirconia (unstabilised)</td>
<td>zirconia</td>
<td>solution containing titanium chloride</td>
<td>disc</td>
<td>13.5 mm diam. 3 mm height</td>
<td>44</td>
<td>1350 for 2 hours</td>
</tr>
</tbody>
</table>

Note: TEOS: tetraethyl orthosilicate as precursor of SiO₂
TEOT: Tetraethyl orthotitanate as precursor of TiO₂
Solution containing titanium chloride as precursor of TiO₂
Porosity: for the green bodies.
to be formed via sintering reaction between the matrix and the introduced precursor. The reaction occurred in each system can be summarised as follows.

1). in the mullite-AT/ZTA system:

\[ \text{mullite} \quad 3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3\text{.}_2\text{SiO}_2 \quad (1) \]

\[ \text{mullite} \quad \text{Al}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Al}_2\text{TiO}_3 \quad (2) \]

2). in the AT/zirconia-alumina system:

\[ \text{Al}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Al}_2\text{TiO}_3 \]

3). in the ZT/zirconia system:

\[ \text{ZrO}_2 + \text{TiO}_2 \rightarrow \text{ZrTiO}_4 \quad (3) \]

While the successful synthesis can only be predicted by those two approaches, the presence of the graded profile in the materials can be observed by diffractometry, microanalysis or electron microscopy. X-ray diffraction patterns were collected from various depths in order to, both qualitatively and quantitatively, see the graded composition within the materials. X-ray diffraction patterns of the AT/zirconia-alumina and ZT/zirconia systems are shown by Figure 2 dan 3. As can be seen from the figures, the AT and ZT peaks reduce in height with depth. By contrast, the alumina and zirconia peak intensities increase with depth. This result indicates the qualitative gradual composition in the samples. Detail information about the refinement and calculation can be found in other reports [8,11].

Applying Rietveld refinement into the collected patterns resulted in the quantitative composition. There were three measures from the refinement which were used to determine the completion of each refinement. Firstly, figures-of-merit from the refinement show that the refinement are acceptable [8,9,11], ie the Bragg R-factor are generally less than 10% and the “goodness of fit” (GoF) are less than 3%. The second measure is the difference plot which also indicates that the refinements are acceptable since the difference profiles are negligible. Representative difference plot from the AT/zirconia-alumina FGM is depicted in Figure 4. The final measure is the standard deviation of each refined parameters which is generally less than 10%. The success in the refinement led to the ability to make use of the cell parameters and scale factor for calculating the weight fraction of each phase.

In the AT/zirconia-alumina system, the absolute weight fraction of AT is 44.5 wt% on the surface and reduces with depth to 9.5 wt% at 0.3 mm, and then to 5.3 wt% at 1.5 mm. On the other hand, the alumina content increases with depth from 44.4 wt% at the surface to 80.2 wt% at 0.3 mm, and then to 85.7 wt% at 1.5 mm.

The quantitative Rietveld phase analysis for the ZT/zirconia system showed that the weight fraction of ZT reduces with depth ie from 12.2% at the surface to 8.4% at 0.2 mm, then to 4.4% at 0.5 mm, and finally to 0% at the center of the FGM. On the contrary, the weight fraction of zirconia increases with depth, ie from 87.8% at the surface to 91.6% at 0.2 mm, then to 95.6% at 0.5 mm and finally to 100% at the center.

The continuous change of the phase content in the FGMs can be expressed as follows (following expression derivation given by Hirai [1] and Markworth et al. [13].

1). AT/zirconia-alumina system [8]:

\[ V_{\alpha T} = -194.0d + 49.3 \quad 0.0 \leq d \leq 0.2 \quad (4) \]

\[ V_{\alpha T} = -5.75d + 11.6 \quad 0.2 \leq d \leq 1 \]

Figure 1. Liquid infiltration steps to produce functionally-graded materials (FGMs).
2) ZT/zirconia system [9]:

a. \( W_{ZT} = 7.1d - 9.2d + 12.1 \) \( (6) \)

b. \( W_{ZrO_2} = -7.1d + 19.2d + 77.9 \) \( (7) \)

where \( W \) is weight fraction.

These expressions show that a graded composition has occurred both in the AT/zirconia-alumina and ZT/zirconia systems. They also show a slight difference in the trend of phase content curves. While the curve for the later system is simply parabolic, that for the former is divided into two linear curves. In the former sample, the gradual change in composition within area around surface is much sharper than that in the later sample. This difference is believed to be caused by the different infiltration time.

From the x-ray diffraction measurements, it can be claimed that the infiltration technique is one powerful ways for producing FGMs, especially ceramic-ceramic system. The diffraction method, on the other side, is a potential technique for revealing the composition distribution within FGMs.

There are other techniques can be used to reveal the qualitative graded profile of a FGM, ie. microanalysis and electron microscopy. They have been utilised to assess such profile in the mullite-AT/ZTA and AT/ zirconia-alumina systems. Making use the microanalysis, Ti and Si dot map and their characteristic x-ray intensities can be acquired from the cross-sectioned surface of the FGMs (Pratapa and Low 1997, Pratapa 1997). Figure 5 shows the x-ray characteristic emissions of TiK\( \alpha \), AlK\( \alpha \), and ZrL\( \alpha \) with depth of the AT/zirconia-alumina sample measured using energy-dispersive x-ray microanalysis. The figure displays the graded character in the TiK\( \alpha \)
of 600 μm and finally to 3.7 μm at depth of 1000 μm. This implies that the presence of AT tends to control the grain growth of alumina.

CONCLUDING REMARK

It can be concluded from the studies that infiltration method has been successfully applied to produce functionally-graded mullite-AT/ZTA, AT/zirconia-alumina, ZT/zirconia ceramic materials. Rietveld x-ray diffraction method has been shown as a novel and potential way in determining the graded composition in FGMs. Other techniques, such as microanalysis and electron microscopy, can also be used to characterise the graded profile of FGMs.

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