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Dear Dr. Rocha-Rangel:

It is a pleasure to accept your manuscript entitled "Synthesis Process and Microstructure for Al2O3/TiC/Ti Functionally Materials" in its current form for publication in the 8th Pacific Rim Conference on Ceramics and Glass Technology. The comments (if any) of the reviewer who reviewed your manuscript are included at the foot of this letter.

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Synthesis Process and Microstructure for $\text{Al}_2\text{O}_3/\text{TiC/Ti}$ Functionally Materials

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Abstract

The production of $\text{Al}_2\text{O}_3$-based functionally graded materials (FGMs), with different amounts of fine reinforcement particles of titanium and titanium-dispersed carbide were explored. The FGMs synthesis has been induced by means of both; solid sintering of $\text{Al}_2\text{O}_3$-titanium powders mixed under high energy milling via pressureless sintering and formation of titanium carbide at 500 °C by a cementation pack process. SEM analyses of the microstructures obtained in cemented bodies were performed in order to know the effect of the cementant (graphite) on the titanium in each composite. In this way, it was found that different depths of titanium carbide layer were obtained as a function of the titanium content in the functionally graded materials. On the other hand, the use of reinforcing titanium enhanced significantly density and fracture toughness of the FGMs.

Introduction

Functionally Graded Materials (FGMs) have received considerable attention in recent years, primarily as potential structures for elevated temperature and high heat flux aerospace applications [1]. In contrast to the discrete interface typically formed between two dissimilar materials e.g. ceramics and metals, FGMs are characterized by a well defined graded structure with continuous variation in composition and microstructure along the thickness. It is well know that abrupt transitions in materials composition and properties within a component often result in sharp local stress concentrations. Graded structures in compositions are expected to alleviate this problem. In this sence FGMs offer a significant degree of durability of components exposed to applications where the operating conditions are rigorous, for example, wear-resistant materials, rocket heat shields, heat exchanger tubes, thermoelectric generators, heat-engine components and electrically insulating metal/ceramic joints. FGM can be constituted of carbide ceramics, oxide ceramics and metals, and they can be used in application at high temperatures such as in the construction of gas turbine engines in order to increase their thermal cycle efficiency [2-3]. In this sense, mechanical and physical properties of such sorts of FGMs have been studied as well as their production process [4-5]. However, the high temperature cementation of metal- dispersed carbide composites has not been investigated with detail and there are not reports about the high
temperature cementation of thermal barrier FGM coatings [6]. Since at high temperatures carbon can diffuse through an oxide matrix, metal particle dispersion will cemented in the matrix. The metallic dispersion expands due to cementation thus inducing stresses in the surrounding matrix. As result, fissures can nucleate in the neighboring matrix when the stresses generated by volume of oxide that resulted from metal particles cementation, particularly if the associated compression stresses reach the fracture strength. Eventually, after multiple cracks form, the composite is fractured. Thus, to design FGMs for high temperature applications, high temperature cementation is very important.

Experimental

FGMs were prepared in two stages; in the first one, titanium-dispersed oxide aluminium composites were produced with powders of Al₂O₃ (99.9 %, 1 μm, Sigma, USA) and Ti (99.9 %, 1-2 μm, Aldrich, USA) used as raw materials. The amounts of powder employed were fixed in order to obtain composites with 0.5, 1, 2 and 3 vol % of Ti. The powder mixture was milled in a high energy mill (Simolyer) with ZrO₂ media, the rotation speed of the mill was of 400 rpm during 8 h. The ball-to-powder volume ratio was 20:1. With the milled powder mixture, cylindrical samples of 2 cm in diameter and 0.3 cm in thickness were fabricated by uniaxial pressing using 250 MPa pressure. Then the pressed samples were pressureless sintered in an electric furnace with an inert argon atmosphere. Heating rate was fixed at 5 °Cmin⁻¹, sintering temperature was 1500 °C and holding time 1 h, after sintering the furnace was turned off and the samples were left to cool inside the furnace. In the second stage the fabrication of the FGMs was as follows; the composites produced in the first stage were situate inside a packed with graphite and heated at 500°C during 1 h. and then cooled. Characterization was made as follows: the density of fired specimens was determined using the Archimedes’ method. Cemented samples were analyzed using SEM and energy dispersive spectroscopy (EDS) to observe their microstructure and chemical composition, as well as the thickness of carbide layer as a function of titanium content in each sample. The hardness of samples was evaluated as microhardness using Vickers indentation, toughness was estimated by the fracture indentation method [7].

Results and Discussion

Microstructure

Figure 1 shows SEM pictures of the surface cross section of the different samples after cementation at 500 °C during 1 h. These micrographs depicting general features of the microstructure in studied system. It is possible to view the formation of homogeneous products, because the Ti particles (white points), which retained their very fine sizes were well distributed in the alumina matrix (gray phase). In general the resulting microstructures displayed few pores present in the matrix. Figures (a), (b), (c) and (d) correspond to samples with (0.5), (1), (2) and (3) wt % of titanium respectively. In these pictures, also it can be observed that there are no Ti metal particles in the surface region to a depth of about 50, 83, 107 and 119 μm for samples with (0.5),
(1), (2) and (3) wt % of titanium respectively. For the sake of argumentation, the region in which any Ti metal particles have been completely cemented is defined as the cemented layer. An important observation in all figures is that Al₂O₃-based composite is not fractured by the cementation of titanium. There is a surface layer displaying a different color with respect to the Al₂O₃-based matrix that is similar to the cemented dispersion in the cemented region. Between the cemented layer and the non-cemented region, there is an intermediate region which consists of partially-cemented Ti particles, as the case may be. From the surface, there are three regions with: (1) completely cemented metal particles, (2) partially cemented particles and (3) metal particles without cementation.

In all samples, the Al₂O₃-based matrix, titanium reinforcing metal particles and titanium carbide layer were identified with the help of EDS analysis performed during SEM observations. Figure 2 reports the EDS analysis in the edge and in the core on the sample with 2 % wt Ti, confirming the presence of high carbon contents near the surface. In contrast the carbon concentration in the core of the sample is nonexistent.

Figure 1. SEM secondary electron images of the resulting microstructures of FGMs produced. (a) 0.5 % Ti, (b) 1 % Ti, (c) 2 % Ti and (d) 3 % Ti.
Figure 2. EDS análisis in the edge and in the core of sample with 2 % wt Ti.

Figure 3 shows the depth of the cemented layer, as a function of titanium content in the sample. Growth of the cemented regions appears to follow a parabolic behavior, because in spite that there is an increment on the depth of the cemented layer with the increments of titanium in the samples, this growing is not lineal, and the tendency of the curve indicates that for high titanium concentrations the depth of the cement layer will growth just until certain limit.

Figure 3. Depth of cemented layer as a function of titanium content in the sample.
Table 1 shows the values of the relative density and different mechanical properties measured in the final FGMs. It can be observed that final density is rising with the increments of titanium in the composites. Such situation appears to be verified by a strong contraction of the samples after sintering. Microhardness was evaluated in two different parts of the samples, the first one at the edge of the sample and the other near the core of it. Result of microhardness are reported also in Table 1, it can be observed that in all samples with titanium additions, the hardness in the edge is larger than the hardness in the core of each sample. This behaviour is due to the formation of a hard material near the edge of the sample, in agreements with the next chemical reaction:

$$\text{Ti} + \text{C} \rightarrow \text{TiC}$$  \hspace{1cm} (1)

This chemical reaction is thermodynamically possible because its free formation energy is $-43.2$ Kcal/mol [8]. In this sense if the TiC was formed at the edge of each studied sample it is confirmed that with the cementation processes followed in this experimental sequence it is possible to fabricate $\text{Al}_2\text{O}_3/\text{TiC}/\text{Ti}$-FGMs.

The values of the fracture toughness measured in each one of the materials studied are reported in Table 1. The fracture toughness of all the samples is superior to that of the pure alumina, from which it is possible to conclude that metallic particle incorporation in a ceramic matrix brings in increments to its toughness. Different authors have reported that the reinforcing mechanism here is due to the crack bridging by ductile metallic ligaments [9-10]. On the other hand, the good degree of densification reached by each of the composites is another factor that also influences considerably the toughness improvement observed.

<table>
<thead>
<tr>
<th>System</th>
<th>Relative density (%)</th>
<th>Edge hardness (GPa)</th>
<th>Core hardness (GPa)</th>
<th>$K_{\text{IC}}$ (MPa·m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 % Ti</td>
<td>94.95</td>
<td>11.97 +/- 0.5</td>
<td>11.94 +/- 0.5</td>
<td>3.2 +/- 0.2</td>
</tr>
<tr>
<td>0.5 % Ti</td>
<td>97.64</td>
<td>9.76 +/- 0.3</td>
<td>6.80 +/- 0.3</td>
<td>4.1 +/- 0.2</td>
</tr>
<tr>
<td>1.0 % Ti</td>
<td>97.75</td>
<td>10.01 +/- 0.4</td>
<td>9.13 +/- 0.3</td>
<td>4.8 +/- 0.1</td>
</tr>
<tr>
<td>2.0 % Ti</td>
<td>97.93</td>
<td>10.34 +/- 0.4</td>
<td>9.69 +/- 0.4</td>
<td>5.0 +/- 0.1</td>
</tr>
<tr>
<td>3.0 % Ti</td>
<td>99.76</td>
<td>10.17 +/- 0.5</td>
<td>7.09 +/- 0.3</td>
<td>5.2 +/- 0.1</td>
</tr>
</tbody>
</table>

Table 1. Relative densities and mechanical properties measured in FGMs.
Conclusions

- Al₂O₃-based FGMs with different titanium contents were produced successfully by the combination of techniques such as; mechanical milling, pressureless sintering and cementation.
- The FGMs’ microstructures are constituted by an Al₂O₃ ceramic matrix reinforced with a carbide titanium layer and fine and homogeneous distribution of metallic particles in the core.
- The incorporation of ductile titanium inside hard ceramic matrix incremented its toughness. The probable toughening mechanism is crack bridging due to the presence of a homogeneous ductile metal in the composite’s microstructure.

References