Fabrication of Al₂O₃/TiC/Ni Functionally Graded Materials by Pulsed-Electric Current Sintering and Their Mechanical Properties

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SYNOPSIS

Dense Functionally Graded Materials (FGMs) in the systems of Al₂O₃/TiC/Ni and (Al₂O₃-WC/Co)/TiC/Ni were fabricated at 1300°C and 10 minutes by pulsed-electric current sintering method. The grain growth was effectively prevented and fine microstructure could be obtained by this rapid sintering. The residual stress produced in the outer Al₂O₃ and Al₂O₃-WC/Co layers of FGMs, which was induced by the thermal expansion mismatch between the inner TiC/Ni layer and the outer layers, was in the range of -180 MPa to -300 MPa. The compressive stress and the dispersion of WC/Co particles enhanced the toughness of the outer ceramic layers and developed steep R-Curve behavior.

KEYWORDS

FGM, R-curve behavior, Al₂O₃/TiC/Ni, (Al₂O₃-WC/Co)/TiC/Ni, toughness, residual stress

1 Introduction

Ceramics have high resistances against heat, abrasion, oxidation, and corrosion. However, the brittle nature limits applications in structural and engineering uses. Many researches have been devoted to improving the toughness of ceramics. The fracture toughness is reportedly reached about ~10 MPa·m^1/2 by microcracking toughening, 15 ~ 25 MPa·m^1/2 by particles dispersion toughening, and ~20 MPa·m^1/2 by transformation toughening. It has been manifested that the compressive stress existing in the surface of ceramics can improve the toughness and strength as well. The compressive stress can be introduced in layered ceramics by employing the transformation of unstabilized tetragonal ZrO₂ to monoclinic phase in the outer layers upon cooling or the thermal expansion mismatch between the inner and outer layers of a sandwiched structure. New symmetric FGMs such as the TiC/Ni/TiC and the Cr₃C₂/Ni/Cr₃C₂ were fabricated by Pityulin and Merzhannov in Russia, and the Al₂O₃/TiC/ Ni by Miyamoto and J.S. Lin in Japan. These symmetric FGMs were fabricated by SHS compaction and SHS/HIP, respectively. Strong residual compressive stress is preferable for restraining the initiation or growth of microcracks. This concept of the stress-enhanced toughening has been applied to fabrication of cutting tools, resulting in the extension of tool life.

In the present study, the symmetric FGMs of the Al₂O₃/TiC/Ni system were fabricated by pulsed-electric current sintering and their mechanical properties were evaluated and discussed. Pulsed-electric current sintering is a new process providing a means by which ceramic powders can be easily sintered at lower temperature and shorter time than conventional sintering methods.

2 Experimental

The starting materials used are Al₂O₃, TiC, Ni, WC, and Co powders with an average particle size of 0.4 μm, 1.4 μm, 1.0 μm, 1.0 μm and 1.0 μm, respectively. These powders were wet-mixed in pre-determined compositions for over 48 hours by ball milling, and then dried in a vacuum oven. The sample was designed to have a symmetric five-layer structure. The compositions of every layer are shown in Fig. 1. In order to increase the compressive residual stress of the outer layer, the Al₂O₃-WC/Co composite with a lower thermal expansion coefficient than Al₂O₃ was also used. The mixed powders were carefully placed into a graphite die with 30 mm diameter and subjected to pulsed-electric current sintering. The sintering condition was 1300°C with a heating rate of 100°C/min for 10 minutes under pressure of 30 MPa.

The sintered sample was disk with 30 mm in diameter and 6 mm in thickness, which was polished to a diamond
surface finish of $3\mu m$. The compressive stress at the surface of FGMs was determined by the $\sin^2\phi - 2\theta$ method using an X-ray diffraction peak (416) of $\text{Al}_2\text{O}_3$. Hardness and indentation toughness were measured by using a Vickers hardness-testing machine with an indentation load of 98 N for 10 seconds. The indentation-induced crack length, $2c$, was measured using an optical microscope and the indentation toughness, $K_c$, was calculated using the following equation \(^9\):\[ K_c = \frac{H_v E}{(2H_v - E)\phi} \approx 0.129\left(\frac{C}{a}\right)^{3/2} \] where $\phi$ is a material-independent constant. $H_v$, $E$, and $a$ are Vickers hardness, Young's modulus, and half-diagonal length of the indentation, respectively.

The sintered sample was cut into rectangular bar specimens with the size of $2 \times 6 \times 25 \text{mm}^3$. The surface of a specimen was ground and the edges were slightly chamfered and the tensile faces were polished to a $1\mu m$ finish. Flexural strength was measured by means of three-point bending test with a span length of 18 mm and crosshead speed of $0.5\text{mm} \cdot \text{min}^{-1}$ using Instron 1185 machine. The indentation-strength method was used to evaluate the R-curve behavior of the FGMs \(^{10,11}\). The indentations with loads of 9.8 - 196 N were applied at the center of a sample beam, and subsequently fractured by three-point bending. The indentation strength, crack length and load in bending experiments were used to calculate the R-curve: $K_R = k(Ac)^m$, where $K_R$ is the fracture resistance, $Ac$ is crack extension, and $k$, $m$ are material constants. The fracture surface was observed by scanning electron microscopy (SEM).

3 Results and Discussion

Fig. 2 shows the fracture surfaces of two different FGMs of the $\text{Al}_2\text{O}_3$/TiC/Ni and the $\text{Al}_2\text{O}_3$-WC/Co/TiC/Ni systems. The photos (a) and (b) show the surface layers of the $\text{Al}_2\text{O}_3$ and the $\text{Al}_2\text{O}_3$-WC/Co, respectively. Photos (c), (d), (e) and (f) show the interfacial regions of the first/second layer, second layer, interfacial region of the second/central layers and central layer of $\text{Al}_2\text{O}_3$/TiC/Ni system, respectively. The grain growth could be effectively prevented and fine microstructures obtained, that was resulted from the lower temperature and shorter time condition by pulsed-electric current sintering. No microcrack was observed at the layer boundaries.

The mechanical properties of FGMs are listed with reference to the monolithic $\text{Al}_2\text{O}_3$ in Table 1. Because of the existing of compressive stress, the local fracture toughness of every outer layer was effectively enhanced. The value of toughness increased with increasing the compressive stress in the outer layers. Especially for the $\text{Al}_2\text{O}_3$-WC/Co FGM, the bridging and deflection effects due to WC/Co particles to the crack propagation are considered to act besides the stress effect as seen in Fig. 3. The WC particles coagulated with Co metal and dispersed in the $\text{Al}_2\text{O}_3$ matrix. As a crack reached the WC/Co particles or the $\text{Al}_2\text{O}_3$/WC interface, the ductile cobalt metal around WC particles lead to crack blunting or deviation along the interfaces.

The residual stress can be determined according to the indentation fracture mechanics for a half-penny flaw \(^{12}\). The indentation toughness, $K_c$, and crack length can be related by the following equation:\[ K_c = K_c^0 - 2\sigma_R (C/\pi)^{1/2} \] where $K_c^0$ is the toughness of a ceramic without stress, $\sigma_R$ is the residual stress in a ceramic and $C$ is the indentation crack length. $K_c^0$ and $\sigma_R$ can be obtained by a linear fitting associated with $K_c$ and $C^{1/2}$. Fig. 4 shows the plots of $K_c$ versus $C^{1/2}$ of the two FGMs. The indentation loads are 49 N, 98 N, and 196 N. For the $\text{Al}_2\text{O}_3$/TiC/Ni and the $\text{Al}_2\text{O}_3$-WC/Co/TiC/Co FGMs, the toughness rose with the increase of crack length. The calculated and measured $K_c^0$ and $\sigma_R$ are listed in Table 2. Both values showed good coincidences.

R-curve behavior arises because the additional energy is consumed in the process zone of a crack besides the fracture energy dissipated at the crack tip. The shape of an R-curve reflects the ability of ceramic to tolerate the crack extension and thus the strength reliability. It is very important, therefore, to characterize and understand the R-curve behavior of ceramics as well as the development of
materials having an appropriate R-curve behavior. It has been manifested that the surface compressive stress can introduce a steep R-curve in a ceramic by a three-dimensional finite element analysis. In this study, the compressive stress was induced by the thermal expansion mismatch between the outer and inner layers. Due to the addition of about 20 vol.% nickel whose thermal expansion coefficient is as high as $16 \times 10^{-6}/^\circ\text{C}$, an apparent difference in thermal expansion coefficient of $1 - 2 \times 10^{-6}/^\circ\text{C}$ exists in the central and outer layers of the Al$_2$O$_3$/TiC/Ni FGMs, that causes a strong compressive stress of $-180 - -300\text{MPa}$ in the outer layers. The central layer of TiC/Ni has a tensile stress of $300 - 400\text{MPa}$, which can withstand because of the high strength of about 1000 MPa. The fracture resistance $K_R$ and the crack extension length, $\Delta c$, satisfies the following relationship:

![Fig.2 SEM images of fracture surface (a) Outer Al$_2$O$_3$/WC/Co layer, (b) Outer Al$_2$O$_3$ layer, (c) Interfacial region of Al$_2$O$_3$/Al$_2$O$_3$-TiC layer, (d) Al$_2$O$_3$-Ti layer, (e) Interfacial region of Al$_2$O$_3$-TiC/TiC-Ni layer, (f) Center TiC-Ni layer.](image-url)
Table 1 Mechanical properties of symmetric FGMs and an Al₂O₃ ceramic.

<table>
<thead>
<tr>
<th>Property</th>
<th>Al₂O₃-WC/Co FGM</th>
<th>Al₂O₃ FGM</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kᵣ(MPa·m¹/₂) by IF(98N)</td>
<td>8.4</td>
<td>6.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Hardness(GPa) (98N load)</td>
<td>19.8</td>
<td>19.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Flexural Strength(MPa)</td>
<td>670</td>
<td>670</td>
<td>500</td>
</tr>
<tr>
<td>Residual Stress(MPa) (measured by X-ray)</td>
<td>-300</td>
<td>-180</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ k_R = k(Δc)^m \]  \quad (3)

where \( k \) is a constant and \( m \) is a characteristic exponent that describes the sensitivity of R-curve behavior. When \( m \) is zero, \( k_R \) is invariant with the crack extension. The exponent \( m \) can be obtained from a slope \( β \) of a log-log plot of post-indentation strength, \( S \), versus indentation load, \( P \).

\[ m = \frac{(1 - 3β)}{(2 + 2β)} \]  \quad (4)

\[ k = \frac{γ}{P} \alpha (βγ)^{-\frac{1}{2}} \]  \quad (5)

\( (α \) is obtained from the intercept of the log-log plot; \( γ = P/ \)

\( a_i^{2(1+β)} \) where \( a_i \) is the initial crack length.

The ratio of the crack length \( a_c \) and the initial crack length, \( a_i \), can be obtained by the initial crack length \( a_i \) from the following equation:

\[ a_c/a_i = \left[ \frac{4}{(1-2m)} \right]^{2(3+2m)} \]  \quad (6)

Table 3 gives the values of \( k \), and, \( m \), of the two FGMs and the monolithic Al₂O₃. Fig. 5 shows their R-curves. The FGMs exhibited steep R-curves with the residual compressive stress in the outer layers, that can lead to higher crack growth resistance and damage tolerance.

Table 2 Comparison of calculated and measured \( K_c^0 \) and \( σ_b \).

<table>
<thead>
<tr>
<th>Materials</th>
<th>( K_c^0 )(MPam¹/₂) calculated</th>
<th>( K_c^0 )(MPam¹/₂) measured</th>
<th>( σ_b )(MPa) calculated</th>
<th>( σ_b )(MPa) measured (by x-ray)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ FGM</td>
<td>4.0</td>
<td>4.5</td>
<td>-150</td>
<td>-180</td>
</tr>
<tr>
<td>Al₂O₃-WC/Co FGM</td>
<td>5.0</td>
<td>_</td>
<td>-260</td>
<td>-300</td>
</tr>
</tbody>
</table>

Fig.3 A SEM image showing the crack deflection and bridging in the outer layer of Al₂O₃-WC/Co/TiC/Ni FGMs.

Fig.4 Indentation toughness vs crack length.
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Table 3 Parameters defining the R-curve for two different FGMs and a monolithic $\text{Al}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolithic $\text{Al}_2\text{O}_3$</td>
<td>11.9</td>
<td>0.112</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$/FGM</td>
<td>31.9</td>
<td>0.188</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-WC/CoFGM</td>
<td>80</td>
<td>0.278</td>
</tr>
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</table>

Fig.5 R-curve as a function of the crack extension for two different FGMs and a monolithic $\text{Al}_2\text{O}_3$.

4 Conclusions

Dense symmetric FGMs in the systems of $\text{Al}_2\text{O}_3$/TiC/Ni and $\text{Al}_2\text{O}_3$-WC/Co/TiC/Ni were successfully fabricated at 1300°C, 10 minutes and 30 MPa by pulsed-electric current sintering. This rapid sintering resulted in the grain growth effectively prevented. Because of the residual compressive stress tailored in the outer ceramic layers which is induced by the thermal expansion mismatch of the inner and outer layers of the FGMs, the outer ceramic layers were strongly toughened. The compressive residual stress in the surface can develop a steep R-curve behavior of FGMs and significantly enhance the crack growth resistance and damage tolerance.

References: