Microstructure Evolution and Model Analysis of $\text{Al}_2\text{O}_3/\text{ZrO}_2$
Hypoeutectic Ceramic During Rapid Solidification

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Rapid solidification of the super high-temperature $\text{Al}_2\text{O}_3/\text{ZrO}_2$ melt was studied by a novel method. The melt was prepared by explosion reaction using $\text{Al}$ and $\text{Zr(NO}_3)_4$ as raw materials and then sprayed to Cu-plate. The heat transfer during the solidification process was analyzed by one-dimensional Finite Element Analysis. The cooling rate of the melt decreased with the increasing distance from the Cu-plate. According to the microstructure evolution, the coating can be divided into four areas: amorphous, nano-crystalline, cellular and dendrite crystal layer. The amorphous and nano-crystalline (50–100 nm) layers can be obtained at the cooling rate of about $1.68 - 7.76 \times 10^4 \text{K/s}$ and $0.48 - 1.68 \times 10^4 \text{K/s}$, respectively, while the cooling rate of the cellular and dendrite crystal layers were about $0.26 - 0.48 \times 10^4 \text{K/s}$ and $0.14 - 0.26 \times 10^4 \text{K/s}$, respectively. The microstructure of the hypoeutectic ceramics shows that the nano-crystalline, cellular and dendritic crystals of the $\text{Al}_2\text{O}_3$ phases were embedded in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic matrix.

Keywords: combustion synthesis, microstructure evolution, model analysis, $\text{Al}_2\text{O}_3/\text{ZrO}_2$, thermal explosion spraying, rapid solidification

1. Introduction

$\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic ceramics have a good combination of physical, thermal and mechanical properties, such as ultra-high hardness, excellent oxidation resistance and strength retention at elevated temperatures. These excellent properties make $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic ceramics potential for a wide range of applications. Generally, eutectic ceramics were mostly prepared by Bridgman method, laser heated floating zone method, micro pulling down method, combustion synthesis method, thermal explosion spraying and so on. In addition, the mechanical properties of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic ceramics are mainly decided by microstructure which is influenced significantly by the cooling rate of the melt.

Rapid solidification technique was usually used to prepare metal, alloy and metallic eutectic because it has the high cooling rate greater than $10^5 - 10^7 \text{K/s}$. However, this method was rarely to prepare eutectic ceramics due to the high melting points of the ceramics. In this paper, thermal explosion spraying was used to realize rapid solidification for eutectic ceramics, which was a new kind of method for high-efficient heating process. By utilizing the highly exothermic reaction between reactants, the thermal explosion spraying can generates a large amount of heat and gas, and the reaction product can melt easily and be sprayed rapidly under high gas pressure. Once encounter the cool substrates, the high-temperature melt can be solidified quickly. Compared to the traditional rapid quenching method, it has the advantages of simplifying process and saving cost and energy. Moreover, this method can reach super high temperatures to realize rapid solidification of the system without any special crucible or extra heating device.

In this paper, $\text{Al}_2\text{O}_3/\text{ZrO}_2$ hypoeutectic coating was prepared by thermal explosion spraying to realize rapid solidification. The heat transfer mechanism of the solidification process was simulated by Finite Element Analysis. The microstructure evolution of the coating under different cooling rates was studied.

2. Experimental Procedure

Aluminum ($5 \mu\text{m}$, ≥ 99% in purity) and zirconium nitrate ($\text{Zr(NO}_3)_4$ A.R. ≥ 99% in purity) powders were used as raw materials in this experiment. The reactant powders were thoroughly dried and mixed by ball milling for 12~24 hours using alumina milling-media, and then the mixed powders were encased into the explosive spraying reaction equipment. The reaction in this study was expected to take place as follows:

$$\text{Al} + \text{Zr(NO}_3)_4 \rightarrow \text{Al}_2\text{O}_3 + \text{ZrO}_2 + 2\text{N}_2 \uparrow \quad (1)$$

In Addition, certain amount of $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ were added to control the reaction temperature of the system. The reactants were ignited by the heat released by the Ni-Cr resistance wire with an 10A electrical current. Once ignited, the reaction instantly generated a large amount of heat, and the system was rapidly heated to a temperature above the melting point of each substance. Meanwhile large quantities of nitrogen produced by the reaction generated a high pressure in the apparatus, so that the melt can spray from the nozzle to the Cu-plate, and the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ hypoeutectic coating was obtained by at rapid cooling rates, as shown in Figure 1.

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The phase composition of the as-sprayed coating was identified by X-ray diffraction (D/MAX-rB, Rigaku, Japan). The cross-sectional microstructure of the coating was investigated by SEM (FE-SEM, S-4700, Hitachi, Japan), EDS (EDAX, USA) and TEM (JEM 2010, Jeol, Japan).

3. Results and Discussion

3.1. Phase composition of the coating

The X-ray diffraction pattern of the as-sprayed coating was shown in Figure 2. It showed that the Reaction 1 proceeded as expected and the reactant was transformed to $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ completely. The reaction between Al and $\text{Zr(NO}_3)_4$ generated a large amount of heat and nitrogen. As a result, the reaction temperature could reach about 3000-4000K. Due to the higher oxidizability of oxygen than nitrogen and sufficient oxygen supply, Al was oxidized to form $\text{Al}_2\text{O}_3$ and no aluminum nitride was observed in the product. Because of the high cooling rate of the coating, most of the $\text{ZrO}_2$ reserved the tetragonal structure, and the residual showed monoclinic structure. The existence of $t\text{-ZrO}_2$ was beneficial to improve the mechanical properties through transformation toughening of $t\text{-ZrO}_2$ to $m\text{-ZrO}_2$.[19,20].

3.2. Microstructure of the coating

The back scattering electron micrograph of the cross-section of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ hypoeutectic coating was shown in Figure 3. The white particles in the figure were Fe, which was formed by the erosion of the nozzle caused by molten $\text{Al}_2\text{O}_3/\text{ZrO}_2$ during the spraying.

According to the microstructure evolution along the growth direction, $\text{Al}_2\text{O}_3/\text{ZrO}_2$ hypoeutectic coating could be divided into four areas: amorphous structure area, nano-crystalline area, cellular crystal area and dendrite crystal area. The boundaries and the center points of the four areas were marked by numbers 1–9, as shown in Figure 3. The changes of the temperature over time as well as the cooling rate of the marked points were shown in Figure 4a, b. With the increase of the distance to the surface of Cu-plate, the cooling rate decreased rapidly. Because of the different cooling rates, the crystallization morphologies of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ coating in different areas were varied significantly.

The amorphous structure, which is shown in Figure 3, occurred in the interface contacted with the Cu-plate. In this area, the maximum cooling rate of $1.68\sim7.76 \times 10^5$K/s was appeared, as shown in curve 2, 3 in Figure 4a. The temperature of the Cu-plate was much lower than that of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ melt so that the heat was transferred to Cu-plate rapidly. As a result, the temperature of the melt dropped suddenly to much lower than the glass transition temperature ($T_g$), and then the amorphous structure formed when the atoms were frozen at the place where they were in the liquid.

The cooling rate decreased with the thickness increasing of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ eutectic coating. When the cooling rate reached about $0.48\sim1.68 \times 10^5$K/s, as shown in curve 4, 5 in Figure 4a, there has a certain period of time to allow the atomic diffusion over a short distance, and therefore crystal...
nucleation process was promoted and Al$_2$O$_3$ nano-crystalline formed finally. Nano-scale Al$_2$O$_3$ particles, as shown in Figure 5a, were observed through TEM in crystalline area b in Figure 3. The particle diameters were about 50-100 nm. The microstructure of the nano-crystalline area showed that Al$_2$O$_3$ phases were embedded in the Al$_2$O$_3$/ZrO$_2$ hypoeutectic structure matrix. Figure 5b showed the strong boundary combination between the crystal and amorphous area in the coating.

As the thickness increasing of the Al$_2$O$_3$/ZrO$_2$ coating, the cooling rate further reduced, and the material diffusion became easier. The nano-sized Al$_2$O$_3$ phase gradually grew up to form cellular crystal. The cooling rate of cellular crystal area (c area in Figure 3) was about 0.26–0.48 × 10$^5$K/s (as shown as curve 6, 7 in Figure 4). X. Mao et al.$^{21}$ pointed out that the higher cooling rate decreased the local solidification time and hindered the nucleus grow fully to dendrites, therefore only cellular crystal could be formed, as shown in Figure 6a.

The phase formation of Al$_2$O$_3$ precipitated ZrO$_2$ to solid-liquid interface during the process of nucleation. When the Al$_2$O$_3$ and ZrO$_2$ proportion in the solid-liquid interface was closed to the eutectic composition, hypoeutectic structure was formed.

Transition region of Nano-crystalline and cellular structure of the Al$_2$O$_3$/ZrO$_2$ coating was shown in Figure 6b. Cellular

**Figure 4.** The temperature over time (a) and the cooling rate at solidification temperature (b) of mark points during Al$_2$O$_3$/ZrO$_2$ melt solidification.

<table>
<thead>
<tr>
<th>mark points</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>cooling rate</td>
<td>7.76</td>
<td>1.68</td>
<td>0.85</td>
<td>0.48</td>
<td>0.35</td>
<td>0.26</td>
<td>0.16</td>
<td>0.14</td>
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<td>x 10$^5$ k/s</td>
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(a)

(b)
Al$_2$O$_3$, with diameter of about 1~2μm were embedded in Al$_2$O$_3$/ZrO$_2$ hypoeutectic matrix.

When the last part of the melt was sprayed, the cooling rate slowed down to the minimum value of 0.14~0.26 × 10$^5$K/s (as shown in curve 8, 9 in Figure 4). The latent heat of the crystallization helped the fully grown Al$_2$O$_3$ cellular crystal to form the secondary dendrite arm and the dendrites. The dendrite region of crystal structure showed that Al$_2$O$_3$ dendrites were embedded in the Al$_2$O$_3$/ZrO$_2$ hypoeutectic structure matrix.

Dendrite Al$_2$O$_3$ crystal structure was shown in Figures 7 and 8, respectively. Figure 7 showed the early stage of the dendrite formation. In this stage pseudo-eutectics formed and dendrite became less due to the high cooling rate. Al$_2$O$_3$ dendrite was embedded in the light gray Al$_2$O$_3$/ZrO$_2$ eutectic matrix, which was demonstrated by EDS shown in Figure 7. When platform of the cooling curve appeared, the low cooling rate and the usual law of solidification conducted the dendrite to form the final morphology. Hypoeutectic products of Al$_2$O$_3$ and ZrO$_2$ were greatly deviated from the eutectic composition, so that a large area of alumina dendrites was formed as shown in Figure 8.

Owing to the characteristics of thermal spraying technique, pores can readily form and deteriorated the properties of the coating. However, the Al$_2$O$_3$/ZrO$_2$ hypoeutectic coating prepared by thermal explosion spraying showed a high relative density and no pores were observed. High relative density of the coating prepared in this experiment was

![Figure 5](image_url1)

**Figure 5.** TEM images of (a) nanostructured Al$_2$O$_3$ crystal and (b) boundary of amorphous and crystal particle.

![Figure 6](image_url2)

**Figure 6.** Back scattering electron images of (a) cellular structure and (b) nano and cellular structure of the Al$_2$O$_3$/ZrO$_2$ coating.
attributed to the strong impact on the coating brought from the explosion spraying, which is favorable for the densification of the coating.

4. Conclusions

Rapid solidification of Al₂O₃/ZrO₂ melt at super high temperature was realized by explosion spraying method. With the increase of distance to the surface of Cu-plate, the cooling rate of the melt solidification decreases gradually and the microstructure evolution of coating could be divided into four crystalline areas: amorphous structure, nano-crystalline, cellular crystal and dendrite crystal. Different cooling rates of these crystalline regions were simulated by Finite Element Analysis.
Reference


