Fabrication of ceramics/high-entropy alloys gradient composites by combustion synthesis in ultra-high gravity field

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A B S T R A C T

The gradient ceramic/metal composite of TiC-TiB2/Al0.3CoCrFeNi was prepared by combustion synthesis under ultra-high gravity field. Right after the formation of the mixture by combustion, the ceramics and metals are separated in an ultra-gravity field due to the difference in mass density, resulted in a gradient distribution of ceramics (TiC-TiB2) along the gravitational field in the high-entropy alloy (Al0.3CoCrFeNi) matrix. The hardness of the material shows a significant gradient change.

1. Introduction

Recently, high-entropy alloys (HEAs), which contain at least four principal metals, have been explored and attracted more and more attentions[1,2]. Compared with conventional alloy materials, HEAs possess excellent structural stability and comprehensive properties because of the high entropy effect and sluggish diffusion effect[3,4]. Thus, HEAs become a focus in many fields of scientific research, such as heat-resistant HEAs, cryogenic HEAs, HEA wire, HEA film, high entropy ceramics, superconducting HEAs, eutectic HEAs, etc. [5–7]. However, due to the limitations of the preparation technology, ceramic/HEAs gradient composites, which combine the advantages of ceramics and high-entropy alloys, have been rarely reported, although they are desirable for protective structural materials including armor and aerospace shell materials.

In this LETTER, a novel method has been adopted to prepared TiC-TiB2/Al0.3CoCrFeNi gradient composites by ultra-high gravity combustion synthesis, an efficiently approach to produce ceramics, cermet, grade alloys, HEAs, etc. [8–11]. Metal melt and Al2O3 melt are formed through aluminothermic reactions, as well as TiC-TiB2, which are rapidly separated under the influence of ultra-high gravity field, forming the TiC-TiB2/Al0.3CoCrFeNi gradient composites after solidification. The microstructures, mechanical properties and synthesis mechanism of this material are investigated.

2. Experimental procedures

Commercial powders of Co3O4, Fe2O3, Cr2O3, NiO, Ti (99.5% purity), B4C (97% purity), and Al (99.9% purity) are fully mixed according to the formula in Eq. (1).

\[
\begin{align*}
2\text{Al} + 3\text{NiO} &= \text{Al2O3} + 3\text{Ni}; \\
2\text{Al} + \text{Fe2O3} &= \text{Al2O3} + 2\text{Fe}; \\
2\text{Al} + \text{Cr2O3} &= \text{Al2O3} + 2\text{Cr}; \\
8\text{Al} + 3\text{Co3O4} &= 4\text{Al2O3} + 9\text{Co}; \\
3\text{Ti} + \text{B}_{4}\text{C} &= \text{TiC} + 2\text{TiB2}
\end{align*}
\]

(1)

X-ray diffraction (XRD, Rigaku) was used to identify the crystal structure, the scanning rate of 4°/min with a step of 0.02°, and the 2θ scanning range was 10°–90°. JSM-6510A (Japan) scanning electron microscopy equipped with EDS was used for microstructure characterization. The hardness of the material was measured using a micro hardness tester. A load of 0.2 kg applied and the loading time was 10 s.
3. Results and discussion

3.1. X-ray diffraction

The material installation diagram is illustrated in Fig. 1(a), the whole part is the put into the equipment for combustion synthesis under high gravity and adjust the counterweight to achieve equilibrium (Fig. 1b). An ultra-high gravity field \( G = 1500 \text{ g} \) is applied by high-speed rotation. Once the raw material is ignited by the tungsten wire, the chemical reactions take place immediately and the combustion wave is transmitted along the direction of the ultra-high gravity field. The reaction process is shown in Fig. 1(c), the final sample was naturally layered, as shown in Fig. 1(d). The upper layer is porous, presumably \( \text{Al}_2\text{O}_3 \), and the lower layer is a dense alloy ingot, which may be a cermet composite.

Phase compositions are examined by XRD on four spots (Fig. 1e). The main phase of the top layer is \( \text{Al}_2\text{O}_3 \) (region I). The II, III, and IV regions were mainly composed of TiC, TiB\(_2\) and high entropy alloy with FCC structure. The diffraction peak of the fine (\( \text{Cr}, \text{Fe} \))\(_2\)B borides phase was detected, indicating that the region is a composite structure composed of a HEA and ceramics. Along the direction of the ultra-high gravity field, the corresponding diffraction peak relative intensity of the ceramics material (TiC-TiB\(_2\)) is weakening gradually.

3.2. Microstructure

Microstructures and materials along the direction of the ultra-high gravity field are characterized, as showed in Fig. 2(a–f). The number of precipitates on the substrate gradually decreases. The elemental composition of every region (Fig. 2b) was determined several times using EDS, as summarized in Table 1.

The EDS results show that region 1 is the TiB\(_2\) and region 2 is the TiC, the TiB\(_2\) is significantly larger than TiC. Region 3 contains nearly equal elements of Al, Co, Ni and Fe, which is a typical HEA phase with FCC structure. Region 4 has significant Cr enrichment and a certain amount of B and Fe, with the composition close to (\( \text{Cr}, \text{Fe} \))\(_2\)B borides. The slightly high ratio of B left in this region might due to the unintended supplement of C from graphite crucibles during the reaction. The concentrations of the ceramics gradually decrease and shows a significant gradient distribution along the direction of the ultra-high gravity field.

Next, in order to measure the hardness and ceramics volume content distributions, the specimen was divided into 11 layers along the direction of the ultra-high gravity field. The volume content of each layer and the hardness of the composite are measured five times for good statistics at each of these 11 layers. The ceramic volume content and hardness of composites both have a continuous downward trend along the direction of the ultra-high gravity field, as shown in Fig. 2(g). The volume content of the ceramics has dropped from 41 vol% to 4.2 vol%, and the hardness of the composites has dropped from 1200 HV to 552 HV. The two curves are consistent to each other with some correlations. The highest hardness region has the high volumetric ceramics. This is reasonable since the ceramic is much stiffer than metal in this case. Therefore, the volume content of the ceramics is a major factor for the mechanical properties of this composite. At the end of the curve, the volume content and hardness of the materials change smoothly and even slightly increased. We speculate that the graphite crucible supplied the C element during the reactions, resulting in additional amount of TiC.
3.3. Synthesis mechanism

The principle of the combustion synthesis under ultra-high gravity field to preparation gradient material is shown in Fig. 3. The combustion process releases a large amount of heat, the calculated adiabatic temperature for the combustion reaction system is 2938 K, the direction of the propagation of the combustion wave is consistent with the direction of applied gravitation field. Therefore, the gravity field promotes the flow of heat and matter inside the reaction system, thereby accelerating the propagation of the combustion wave. Powdered raw materials react with each other at high temperatures to produce TiC, TiB$_2$, Al$_2$O$_3$ and metal structures, respectively. The subsequent separation of these phases in ultra-high gravity field obeys the Stock’s law [12].

Due to the difference in density between ceramics (4.9 g/cm$^3$ for TiC and 4.5 g/cm$^3$ for TiB$_2$) and melts (>7 g/cm$^3$), directional flow occurs in the ultra-high gravity field, high-density metals flow in the direction of the gravitational field, and low-density ceramics flow in the opposite direction, resulting in volume-mass segregation of metals and ceramics. Due to the large density difference

![Image of microstructures and reaction mechanism](image)

**Table 1**
Elemental composition for regions in Fig. 2(b), (at.%).

<table>
<thead>
<tr>
<th>Region</th>
<th>Phase</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>B</th>
<th>C</th>
<th>Ti</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiB$_2$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>48</td>
<td>13</td>
<td>35</td>
<td>1.5%</td>
</tr>
<tr>
<td>2</td>
<td>TiC</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8</td>
<td>40</td>
<td>48</td>
<td>0.8%</td>
</tr>
<tr>
<td>3</td>
<td>FCC</td>
<td>16</td>
<td>12</td>
<td>2</td>
<td>10</td>
<td>21</td>
<td>22</td>
<td>15</td>
<td>1</td>
<td>0.35%</td>
</tr>
<tr>
<td>4</td>
<td>(Cr,Fe)$_2$B$_2$</td>
<td>–</td>
<td>3</td>
<td>43</td>
<td>8</td>
<td>–</td>
<td>31</td>
<td>5</td>
<td>1</td>
<td>0.15%</td>
</tr>
</tbody>
</table>

![Fig. 2.](image)

(a)–(f) are the microstructures along the direction of the ultra-high gravity field. (b) is microscopic structure enlargement of (a), the numbers of 1, 2, 3, 4 represent different phase regions, respectively. (g) changes in ceramic volume content and hardness of materials along the ultra-high gravity field.

![Fig. 3.](image)

Reaction Mechanism. (a) Before the start of the reaction. (b) Reaction process. (c) After cooling.
between Al<sub>2</sub>O<sub>3</sub> melt and metal, liquid phase separation occurs, resulting in a complete segregation of Al<sub>2</sub>O<sub>3</sub> on one side (Fig. 1d). The difference in density between TiC/TiB<sub>2</sub> particulates and HEA is relatively smaller and compounding can be achieved. Ceramics materials have a much higher melting point (3430 K for TiC, 3500 K for TiB<sub>2</sub>) than HEAs and much less thermal expansion coefficients. Therefore, ceramics have less volumetric change, and the final solidification of the metal structure shrinks.

4. Conclusions

A novel functionally gradient material TiC-TiB<sub>2</sub>/Al<sub>0.3</sub>CoCrFeNi which was successfully prepared in-situ by combustion synthesis under ultra-high gravity field. The ceramic volume content and hardness of composites both monotonically decrease, along the direction of the ultra-high gravity field. The ceramic volume content drops from 41 vol% to 4.2 vol%, and the hardness of the corresponding composites has dropped from 1200 HV to 552 HV. Ceramics-metal gradient composites have both high hardness and toughness of the ceramics, and the gradient change of mechanical properties is tunable. With these unique structural and mechanical properties, this gradient ceramic/HEA composite has promising applications in the field of protective structural materials, including armored protective materials and aerospace shells.

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References