Near-Infrared Emission Property of ZrC-TiC Solid Solution Prepared by Combustion Synthesis

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Abstract. ZrC-TiC solid solutions are considered as a promising candidate for ultra-high-temperature structural applications. ZrₓTi₁₋ₓC (ₓ=0, 0.2, 0.4, 0.6, 0.8, 1.0) solid solutions have been prepared by combustion synthesis method using Zr, Ti and C elemental powder. The effect of Zr/Ti mole ratio on the phase composition, microstructure, oxidation resistance and near-infrared emission property of the synthesized samples were investigated. It was found that the prepared samples with different Zr/Ti mole ratio all have formed a single cubic structure. The grain size of Ti rich solid solution developed to a larger size than that of Zr rich samples. ZrₓTi₁₋ₓC solid solution with x=0.4 has a higher starting oxidation temperature of ~650°C than that of the other solid solution samples. The prepared solid solution with x=0.4 also shows the largest emissivity of 0.79 in 0.75-2.5 μm and 0.76 in 3-5 μm wavelength range. The prepared ZrₓTi₁₋ₓC solid solution samples by combustion synthesis method, which exhibit good near-infrared emission property could be regard as a promising ablation resistant material.

1. Introduction
ZrC-TiC solid solutions possess high melting point, high hardness, good oxidation and ablation resistance, and excellent thermal shock resistance, are promising candidates for applications in extreme environments, such as aerospace engineering and hypersonic flight vehicles[1-4]. Up to now, ZrC-TiC solid solutions with various compositions have been synthesized by different methods, such as Spark Plasma Sintering (SPS)[5], Hot-Pressed (HP)[6,7], liquid metal infiltration reaction[8-11], and so on. The mechanical, anti-oxidation and ablation resistance properties of the ZrC-TiC solid solutions have been well studied. From the prospective of heat transfer, the infrared radiation properties of ZrC-TiC solid solutions played an important role in controlling the temperature of the materials. Because, more than 80 % of heat is transmitted by radiation at over 1000 °C, and more than 76 % of the radiation energy is mainly concentrated in 0.75-5 μm near-infrared wavelength[12]. However, the infrared radiation properties of ZrC-TiC solid solutions with different compositions have never been fully investigated.

Combustion synthesis (CS) has emerged as a facile and energy-saving technique for the preparation of advanced ceramics, catalysts and nano-materials[13,14]. Owing to its high reaction temperature, high purity, high reaction rate, high uniformity, and flexible adjustment to the ratio of Zr/Ti, it is suitable to fabricate ZrC-TiC solution with different ratios of ZrC-TiC.
In this study, we synthesized Zr$_{1-x}$Ti$_x$C($x=0, 0.2, 0.4, 0.6, 0.8, 1$) solution with Zr, Ti, C powders by CS. The effect of Zr/Ti mole ratio on the microstructure, phase composition, thermal properties, infrared radiation and oxidation resistance were investigated.

2. Experimental

2.1. Materials and methods
Ti powder (99% pure, 300 mesh, General Research Institute for Nonferrous Metals, Beijing, China), Zr powder (99% pure, 400 mesh, Shanghai Yunfu Nanotechnology CO.LTD, China) and carbon black (Beijing chemical Co., China) were used as starting reactants. The combustion reaction was carried out under an inert gas atmosphere of high-purity argon (99.9%, Huayuan Gaseous Co., Beijing, China) to prevent oxidation. Zr$_{1-x}$Ti$_x$C (ZT-$x$) samples were prepared by combustion synthesis method. Zr, Ti, C elemental powders were dried and mixed at a ratio of Zr : Ti : C = 1-$x$ : $x$ : 1 ($x=0, 0.2, 0.4, 0.6, 0.8, 1$). Subsequently, the powder mixture was cold-pressed into cylindrical bars and placed into a special reaction chamber for combustion synthesis. The reaction chamber was evacuated and then the sample was ignited by passing an electric current through a tungsten coil in argon atmosphere.

2.2. Characterization
The phase composition of the samples was identified by X-ray diffraction (XRD, D8 Focus, Bruker, Germany) with a step of 0.02° and a scanning rate of 0.1°/sec. The microstructure of the samples was observed using a scanning electron microscope (S-4300, Hitachi, Japan). The accelerating voltage and accelerating current were set to 10 kV and 10 μA, respectively. Gold spraying was performed before the test. The oxidative behaviour of samples were performed using a differential scanning calorimeter (Setsys Evolution 18, Setaram, Caluire, France) at a heating rate of 10°C/min from room temperature to 1200°C. To measure the oxidation resistance of the samples, the Zr$_{1-x}$Ti$_x$C samples were fully ground into powders. After been placed in an equal size alumina crucible with equal mass powders, the samples were put into a furnace at a temperature of 600 °C in air atmosphere. The weight of the sample was measured at intervals of 1 hour. The trend of weight was used to evaluate the oxidation resistance of the samples. The absorption spectrum in the wavelength range of 250-2500 nm were recorded by an ultraviolet-visible-near infrared spectrophotometer (UV-VIS-NIR, Cary 5000, Varian, Sunnyvale, CA) equipped with an internal integrating sphere at room temperature. And the dual-band infrared emissivity measurement instrument (IR-2, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, China) was taken to measure the infrared emissivity of the sample. The experimental temperature was room temperature, and the measurement band was 3-5 μm.

3. Results and discussion

3.1. XRD analysis
Figure 1 shows the XRD spectra of the combustion synthesized Zr$_{1-x}$Ti$_x$C solid solutions. There is only TiC (ZrC) phases peak position at $x=1$($x=0$) which means the raw powders have been reacted competently. No other peaks appear on all the spectra, indicating that the products are all single-phase. As the value of $x$ increases, the Zr atoms in the solid solution are instead by the Ti atoms gradually, which lead to the shifts of peak position. The diffraction peak of (111) plane of the Zr$_{1-x}$Ti$_x$C solid solutions is presented in figure 2(a). The lattice constant of the cubic structure Zr$_{1-x}$Ti$_x$C solid solutions were calculated based on the diffraction peak of (111) plane. The theoretical lattice constant of each sample can be calculated using the Vegard Law, as shown in figure 2(b).

Since Ti atomic radius is smaller than Zr atomic radius, the lattice constant of the solid solution would decrease. As shown in Figure. 2, the experimental values of remaining samples are basically consistent with the theoretical prediction values except ZT-0.6. With Zr and Ti contents close to each other, the energy barrier for forming the substitutional solid solution increases, which leads to a broader peak shape, smaller crystallite site and lower crystallinity, as indicated in the XRD pattern.
At $x=0.6$, the value of lattice constant is much larger than that predicted by the Vinegar law. As combustion synthesis is a transient ultra-high temperature synthesis method, a relatively wide composition of solid solutions could have been synthesized before the forming of a uniform solid solution.

**Figure 1.** XRD spectra of the combustion synthesized Zr$_{1-x}$Ti$_x$C solid solutions.

**Figure 2.** The lattice constant and (111) diffraction peaks of the Zr$_{1-x}$Ti$_x$C solid solutions.

3.2. **SEM microstructures**

Figure 3 shows the SEM microstructures of the combustion synthesized Zr$_{1-x}$Ti$_x$C solid solutions. The holes and grain boundaries between grains can be seen clearly. Due to the release of gas during the reaction there appeared pinhole. Here the source of gas is the hydrogen released from the reaction between the surface of the metal surface oxide and $C[14]$. From the clean and smooth surface of the
crystal grain, it can be presumed that the crystal grows from the liquid nucleation and the crystal grains grow completely. The change in grain size is consistent with the XRD test results, grain size gradually decreases from figure (a) to figure (c), and then increases from figure (e) to figure (f).

Figure 3. SEM microstructures of the Zr1-xTixC solid solutions for (a) x=0, (b) x=0.2, (c) x=0.4, (d) x=0.6, (e) x=0.8, (f) x=1.

3.3. Oxidation behavior test
The oxidation resistance of the Zr1-xTixC solid solutions were tested at 600 °C in air atmosphere. The weight gain of the powder samples were measured at intervals of 1 hour. The oxidized mass is converted using equation (1) to obtain the weight gain of a sample per mole metal atom.

\[ x_n = \frac{M(M_n - M_1)}{M_1 - M_0} \]  

Where \( M \) is the molar mass, \( M_n \) is the mass obtained from the nth measurement, \( M_1 \) is the mass of the initial powder, and \( M_0 \) is the mass of the crucible. The weight gain per unit mass of different samples is plotted in Figure 4(a).

For Zr1-xTixC solid solution, the mass increment per mole is a constant number which is independent with the molar mass of the substance, so that eliminates the error caused by the large difference in the molecular weight of Zr and Ti atoms and can characterize the degree of oxidation of the substance. When solid solution is completely oxidized, the theoretical mass gain per unit mass should be 20. As seen in Figure 4(a), TiC shows the strongest anti-oxidation performance and ZrC shows the weakest. However, oxidation resistance of Zr1-xTixC does not change monotonously in relation to \( x \), and which is weaker than TiC. Among them, Zr0.8Ti0.2C and Zr0.2Ti0.8C have higher oxidation resistance than ZrC, but weaker than Zr0.6Ti0.4C and Zr0.4Ti0.6C. The prepared Zr1-xTixC solid solution with approximate identical Zr and Ti mole content features better oxidation resistant.

The results of the DSC are shown in Figure 4(b). A characteristic exothermic peak can be seen at around 600°C, mainly due to the exothermic oxidation reaction of the solid solution. The exothermic peak temperature represents the most intense temperature of the reaction. A higher peak temperature means better oxidation resistance of solutions. It can be seen that the peak temperature of Zr0.6Ti0.4C and Zr0.4Ti0.6C are both at a higher position, consistent with the results of the previous oxidation experiments. When Zr (Ti) atoms are introduced into TiC (ZrC) to form a solid solution, Zr atoms displace Ti atoms in TiC, which lead to lattice distortion, increase the number of defects, decrease the stability of solid solution and degrade the oxidation resistance. When the number of atoms of Zr and Ti in the solid solution becomes similar, lattice distortion increases which blocks the diffusion of oxygen in the crystal, leading to the increase of oxidation resistance.
It was observed in the sample that little graphite remains in the product in sample ZT-0.4 and ZT-0.6. These graphite remains in the samples can also be a reason for the increases of the oxidation resistance. A difference between the actual and theoretical weight was also observed in Figure 4. So the chemical formula of the solid solution should be corrected to Zr\(_{1-x}\)Ti\(_x\)C\(_y\) (y \leq 1). When it was fully oxidized, the amount of mass per unit mass increases (32-12\(y\)). We calculate the \(y\) value according to the data in Figure 4 and show it in Table 1. The value of \(y\) is close to 1, so the loss of graphite can be ignored.

| sample  | \(x\) | Increase per mol. at \(T_n\) | \(y\) |
|---------|------|-----------------|------|
| ZT-0    | 0    | 19.99027        | 1.00 |
| ZT-0.2  | 0.2  | 19.95808        | 1.00 |
| ZT-0.4  | 0.4  | 20.35943        | 0.97 |
| ZT-0.6  | 0.6  | 20.05768        | 0.995|
| ZT-0.8  | 0.8  | 20.37733        | 0.968|

3.4. Infrared radiation test

Figure 5(a) shows the absorption spectra of Zr\(_{1-x}\)Ti\(_x\)C samples with different Zr and Ti contents in the wavelength range of 0.25-2.5 \(\mu\)m. Figure 5(b) shows the cumulative absorption of Zr\(_{1-x}\)Ti\(_x\)C samples calculated using the curves of Figure 5(a) at 0.25-2.5 \(\mu\)m. The emissivity of the samples in the wavelength range of 3-5 \(\mu\)m were tested by IR-2 and were shown in Figure 5(b). It can be seen that, the emissivity of the Zr\(_{1-x}\)Ti\(_x\)C was improved compared to the single-phase TiC. All the samples exceeded the requirements of the aerospace thermal barrier coating with an emissivity greater than 0.7 and can be used for the thermal barrier coating. Among them, the absorption rates of Zr\(_{0.6}\)Ti\(_{0.4}\)C and Zr\(_{0.4}\)Ti\(_{0.6}\)C samples is the highest. 3-5\(\mu\)m is the most important band for enhanced radiative heat transfer, and the emissivity measurement results are similar to the above. The Zr\(_{0.6}\)Ti\(_{0.4}\)C and Zr\(_{0.4}\)Ti\(_{0.6}\)C samples are better overall, and the Zr\(_{0.6}\)Ti\(_{0.4}\)C emissivity is greater.
Figure 5. Infrared radiation of samples (a) absorption spectra of Zr$_{1-x}$Ti$_x$C at 0.25-2.5μm, (b) average emissivity of Zr$_{1-x}$Ti$_x$C at 0.25-2.5μm and 3-5μm.

It can be seen that, the Zr$_{1-x}$Ti$_x$C solid solutions possess much higher oxidation resistance and near-infrared emissivity when the Zr/Ti ratio close to 1, i.e. $x=0.4$ and 0.6. Radiation heat dissipation is the main heat dissipation method for high temperature objects, and high emissivity means good radiation dissipation capability. At 600°C, about 53% of the radiant energy is distributed in the range of 0.75-5 μm, and the proportion of radiant energy in this range will increase with increasing temperature. The high emissivity of this range is beneficial to the heat dissipation of the sample and thus exhibits excellent oxidation resistance. Testing the emissivity in this wavelength range can effectively predict the oxidation resistance of similar components.

4. Conclusions
Zr$_{1-x}$Ti$_x$C solid solutions with different Zr/Ti mole ratio prepared by combustion synthesis all have formed a single cubic structure. The grains of Ti rich solid solution grow more larger than that of Zr rich samples for its higher generating energy. Zr$_{1-x}$Ti$_x$C solid solution with $x=0.4$ has a higher oxidation onset temperature. The prepared solid solution with $x=0.4$ also shows the largest emissivity
of 0.79 in 0.75-2.5 μm and 0.76 in 3-5 μm wavelength range. The Zr_{1-x}Ti_xC solid solutions are potential candidate for ablation resistant materials due to its good near-infrared emission property.

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