Reaction Mechanism of ZrB$_2$-ZrC Formation in Ni-Zr-B$_4$C System Analyzed by Differential Scanning Calorimetry

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Abstract: The reaction mechanism of ZrB$_2$-ZrC formation in a 30% Ni-Zr-B$_4$C system under argon was revealed by using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results indicated that the reaction mechanism in the Ni-Zr-B$_4$C system was complex. Initially, Ni$_x$Zr$_y$ and Ni$_x$B$_y$ intermetallics were formed via solid-state diffusion reactions between Ni, B$_4$C and Zr. Then, the eutectic reaction between B$_4$NiB$_3$ and Ni$_x$B$_y$ lead to the formation of Ni-B liquid. The free C atoms dissolved into the Ni-B liquid to form a Ni-B-C ternary liquid, and then part of the Zr powder dissolved into the surrounding Ni-B-C ternary liquid to form Ni-Zr-B-C quaternary liquid. Finally, ZrB$_2$ and ZrC formed and precipitated out of the saturated liquid. The eutectic liquid plays an important role during the formation of ZrB$_2$-ZrC.

Keywords: reaction mechanism; ZrB$_2$-ZrC; combustion synthesis; self-propagation high-temperature synthesis; differential scanning calorimetry

1. Introduction

Boride and carbide of zirconium (ZrB$_2$ and ZrC) exhibit outstanding properties such as high hardness and melting points, low density as well as high resistance to corrosion and wear, which makes them attractive candidates for high-temperature ceramics, cutting tools, corrosion-resistant parts, reinforcing particles in the composites and wear resistant coatings [1–6]. It is believed that double or multiple phase ceramics have better properties than single-phase ceramics [7–9]. Hence, more attention has been paid to develop materials combining ZrB$_2$ and ZrC ceramics [1–5].

Multiphase ceramics can be synthesized by a variety of methods including hot isostatic pressing, spark plasma sintering, pressureless sintering, combustion synthesis, etc. [10–13]. Among them, combustion synthesis (CS) has attracted much attention for preparation of intermetallics, borides, carbides, nitrides and silicides due to the advantages of simple devices, low processing cost, high reaction purity and fast reaction rates [14–18]. CS is generally divided into two types. The first is self-propagating high-temperature synthesis (SHS) by ignition and spread at one end of the sample, and the second is thermal explosion (TE) by heating the whole sample uniformly [19,20]. Up to now, ZrB$_2$-ZrC/Al, ZrB$_2$-ZrC/Cu and ZrB$_2$-ZrC/Co composites have been successfully prepared by the SHS method [1–5].

In a previous paper [21], we successfully synthesized ZrC-ZrB$_2$/Ni cermet powders using a Ni-Zr-B$_4$C system by the SHS method. The SHS-derived feedstock powders were deposited on a magnesium alloy, and atmospheric plasma spraying was used to obtain ZrC-ZrB$_2$/Ni cermet coatings. However, the reaction mechanism of ZrB$_2$-ZrC formation in the Ni-Zr-B$_4$C system needs to be further studied.

In the present work, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to reveal the formation mechanism of ZrB$_2$-ZrC in the Ni-Zr-B$_4$C system during combustion synthesis. It is expected that
these preliminary results will be valuable for promoting the understanding of the reaction mechanism of ZrB$_2$-ZrC formation in the Ni-Zr-B$_4$C system.

2. Materials and Methods

The ZrB$_2$–ZrC/Ni composites were produced according to the following reaction equation:

$$x\text{Ni} + 3\text{Zr} + \text{B}_4\text{C} \rightarrow x\text{Ni} + 2\text{ZrB}_2 + \text{ZrC}$$ (1)

Commercial powders Ni (~99% in purity, ≤48 μm, ST-nano science and technology Ltd. Co., Shanghai, China), Zr (~99% in purity, ≤38 μm, ST-nano science and technology Ltd. Co., Shanghai, China) and B$_4$C (~95% in purity, ≤3.5 μm, Abrasive Ltd. Co., Dunhua, China) were selected as the starting materials. In order to investigate the complex combustion reactions in the Ni-Zr-B$_4$C system, DSC experiments were performed on the mixtures of Zr-B$_4$C, Ni-B$_4$C, Ni-Zr and 30 wt.% Ni-Zr-B$_4$C. In 30 wt.% Ni-Zr-B$_4$C mixture, Zr and B$_4$C powders with a molar ratio of 3:1 were mixed with 30 wt.% Ni. The compositional proportions in the Zr-B$_4$C, Ni-B$_4$C and Ni-Zr mixtures were in accordance with those in the 30 wt.% Ni-Zr-B$_4$C mixture. The weight of powder mixtures subjected to DSC analysis was 15 mg. The reactant mixtures were dry-mixed sufficiently in a container using zirconia balls at a low speed (~50 rpm) for 6 h.

DSC was carried out on a STA 449C Jupiter (Netzsch, Weimar, Germany) apparatus to reveal the reaction mechanism of the Ni-Zr-B$_4$C system. The heating process was set to a rate of 10 °C/min in flowing argon gas (99.9% in purity, flow rate: 40 mL/min). Following DSC analysis, the sintered powders were crushed, and the phase composition was analyzed by XRD (D8 Advance, Bruker, Ettlingen, Germany, Cu-Kα radiation, λ = 0.15406 nm) at a scanning speed of 6°/min and a scanning range of 20–80°. Microstructures of the reacted samples were characterized by SEM (S-4800, Hitachi, Tokyo, Japan) equipped with an energy-dispersive spectrometer (EDS).

3. Results and Discussion

Figure 1 displays the DSC curves of the Zr-B$_4$C, Ni-B$_4$C, Ni-Zr and 30 wt.% Ni-Zr-B$_4$C mixtures heated to 1200 °C with a heating rate of 10 °C/min. Moreover, interrupted experiments were performed in order to elucidate the reaction mechanism during the heating process.

The DSC curve of the Zr-B$_4$C mixture is shown in Figure 1a. A broad exothermic peak appears near 1008 °C. The XRD result of DSC product heated to 1200 °C shows that the product mainly consists of a large amount of ZrB$_2$, ZrC and a small amount of Zr (see Figure 2). The presence of Zr may have been caused by the incomplete reaction of reactants. Hu et al. [1] studied the mechanism of ZrB$_2$ and ZrC generation in the Zr-B$_4$C system and proposed that the solid-phase synthesis reaction was the main formation mechanism. Zhang et al. [2–4] investigated the reaction behavior and formation mechanism in the Cu-Zr-B$_4$C system. Effects of heating rate and B$_4$C particle size on the reaction process in the Zr-B$_4$C system were also explored. Either increasing the particle size of B$_4$C or increasing the heating rate may result in a sluggish solid-state reaction between Zr and B$_4$C, which leads to the residual of Zr and B$_4$C in the DSC products. The diffraction peaks of Zr were also found in the XRD patterns of the above research, but the diffraction peaks of B$_4$C were very weak or absent due to the atomic characteristics and crystalline lattice of B$_4$C [1–4].
Figure 1. The DSC curves of the mixtures heated to 1200 °C with a heating rate of 10 °C/min: (a) Zr-B$_4$C; (b) Ni-B$_4$C; (c) Ni-Zr and (d) 30 wt.% Ni-Zr-B$_4$C.

Figure 2. XRD pattern for the DSC product of the Zr-B$_4$C mixture heated to 1200 °C.
Figure 1b shows the DSC curve of the Ni-B$_4$C mixture heated to 1200 °C. A small exothermic peak was present at 576 °C, and a large endothermic peak was present at 1026 °C. To better interpret the two peaks, the Ni-B$_4$C mixtures were heated to 900 °C and 1030 °C, respectively, before being cooled down. Figure 3 shows the XRD patterns obtained for DSC products when quenched from 900 °C, 1030 °C and 1200 °C, respectively. When the DSC heating was quenched from 900 °C, the product was mainly composed of Ni$_2$B, Ni$_3$B and C, indicating that the solid reaction between Ni and B$_4$C occurred at this time, corresponding to the exothermic peak appearing at 576 °C on the DSC curve. As shown in Figure 3, the DSC product quenched from 1030 °C was mainly composed of Ni$_2$B, o-Ni$_4$B$_3$ and a small amount of NiC$_3$B$_{15}$. When the Ni-B$_4$C mixture was heated to 1200 °C, o-Ni$_4$B$_3$, m-Ni$_4$B$_3$ and a small amount of Ni$_2$B and NiC$_3$B$_{15}$ were formed in the product. Following the Ni-B binary phase diagram [22], a Ni-B melt could be formed due to the eutectic reaction between Ni$_2$B and o-Ni$_4$B$_3$ at 1018 °C, which corresponded to the large endothermic peak at 1026 °C on the DSC curve. At the same time, the Ni-B liquid phase could promote the dissolution of C atoms and form the Ni-B-C melt. The NiC$_3$B$_{15}$ phase was possibly formed and precipitated from it during the cooling process.

Figure 3. XRD patterns for the DSC products of Ni-B$_4$C mixtures quenched at different temperatures.
Figure 1c shows the DSC curve of the Ni-Zr mixture heated to 1200 °C. As indicated, three exothermic peaks appear at 878 °C, 1030 °C and 1074 °C, respectively. Two endothermic peaks appear at 1146 °C and 1181 °C. In order to determine the reactions occurring near these peaks, the Ni-Zr mixtures were heated to 600 °C, 950 °C, 1030 °C, 1080 °C, 1160 °C and 1200 °C, respectively, and then cooled down. XRD patterns for the DSC products of Ni-Zr mixtures quenched at different temperatures are shown in Figure 4. When the Ni-Zr mixture was heated to 600 °C, only the original reactants Ni and Zr were found in the quenched product, and no obvious reaction occurred (see Figure 4). When the Ni-Zr mixture was heated to 950 °C, the diffraction peak intensity of Ni and Zr in the quenched product was obviously weakened. At this time, NiZr, Ni10Zr7 and Ni2Zr were generated, which indicated that there was a solid-state reaction between Ni and Zr, resulting in a wide exothermic peak at 878 °C. When the Ni-Zr mixture was heated to 1030 °C, the content of Ni10Zr7 increased significantly, which corresponded to the exothermic peak at 1030 °C (see Figure 4). As the temperature was raised to 1080 °C, the Ni11Zr9 phase appeared, and the content of unreacted Ni and Zr decreased significantly. The production of Ni11Zr9 led to the presence of an exothermic peak at 1074 °C. As the temperature was raised to 1160 °C, Ni11Zr9 disappeared, and there was a large amount of NiZr and a small amount of Ni11Zr9 in the product. Following the Ni-Zr binary phase diagram [23], Ni10Zr7 and Ni will form a eutectic liquid at 1150 °C, which exactly corresponds to the endothermic peak at 1146 °C in the DSC curve. When the Ni-Zr mixture was heated to 1200 °C, the product mainly consisted of NiZr, Ni11Zr9 and a small amount of Ni3Zr2, in which the content of Ni11Zr9 phase increased obviously. According to the Ni-Zr binary phase diagram [23], NiZr and Ni will form eutectic liquid phase at 1170 °C. Therefore, it can be deduced that the Ni-Zr eutectic liquid will form after the temperature is gradually raised to 1170 °C, which leads to the endothermic peak at 1181 °C. Subsequently, when the mixture was heated to 1200 °C and then cooled down, Ni11Zr9 and Ni3Zr2 eventually crystallized from the Ni-Zr eutectic liquid.

Figure 1d shows the DSC curve of the 30 wt.% Ni-Zr-B4C mixture heated to 1200 °C. As shown, two exothermic peaks were observed at 851 °C and 1088 °C, and two endothermic peaks were observed at 1025 °C and 1159 °C, respectively. In order to make clear the reactions occurring during the heating process, DSC interrupted experiments were carried out for the Ni-Zr-B4C mixtures at 900 °C, 1030 °C, 1060 °C, 1100 °C, 1130 °C, 1170 °C and 1200 °C, respectively, and then cooled down. The XRD patterns for the DSC products quenched at different temperatures are shown in Figure 5. When the Ni-Zr-B4C mixture was heated to 900 °C, a large amount of Ni2B and a small quantity of Ni4B3, NiZr and Ni3Zr were generated in the product, indicating that the wide exothermic peak near 851 °C corresponded to the formation of these Ni3Zr and Ni3B3 phases. This is also consistent with the previous analysis of Ni-Zr and Ni-B mixtures. When the Ni-Zr-B4C mixture was heated to 1030 °C, a very small amount of ZrB2 and ZrC appeared in the product, indicating that a small amount of Zr reacted with B4C at this time. As the temperature was raised to 1060 °C, the diffraction peak intensity of Ni2B and Ni4B3 decreased. According to the analysis of the Ni-B4C mixture, Ni2B and Ni4B3 can form the Ni-B eutectic liquid at 1018 °C, which corresponds to the endothermic peak at 1025 °C in the DSC curve of Ni-Zr-B4C. At the same time, the formation of the Ni-B liquid phase also promotes the contact and reaction between the reactants in the mixture, and the free C atomic can dissolve into the Ni-B liquid phase to form the Ni-B ternary liquid phase, which fully contacts with the surrounding Zr powder and B4C powder. As the temperature was raised to 1100 °C, a large amount of Ni, ZrB2 and ZrC were formed in the product, and a large exothermic peak appeared at 1088 °C in the DSC curve. It is speculated that part of the Zr powder directly reacted with B4C to form ZrB2 and ZrC, and part of the Zr powder dissolved into the surrounding Ni-B-C ternary liquid to form Ni-Zr-B-C quaternary liquid. When the concentration of [Zr], [B] and [C] atoms in the Ni-Zr-B-C liquid achieved the thermodynamic condition for the formation of ZrB2 and ZrC, ZrB2 and ZrC particles precipitated out of the saturated liquid. It is worth mentioning that a large amount of Ni10Zr7 also appeared in the product.
at 1100 °C, which was slightly different from the temperature at which Ni$_{10}$Zr$_7$ appeared in large quantities in the Ni-Zr mixture (1030 °C), which may be due to the influence of the addition of B$_4$C in the Ni-Zr-B$_4$C mixture. When the Ni-Zr-B$_4$C mixture was heated to 1130 °C, the product was mainly composed of a large amount of ZrB$_2$, ZrC and a small amount of Ni$_{10}$Zr$_7$ and Ni$_2$B. When the Ni-Zr-B$_4$C mixture was heated to 1170 °C, the product consisted of ZrB$_2$, ZrC, Ni and a small amount of Ni$_2$B. As the temperature was raised to 1200 °C, the product consisted of ZrB$_2$, ZrC and Ni, indicating that the reaction of the system had tended to be complete. When the temperature rose from 1130 °C to 1170 °C, the content of Ni$_{10}$Zr$_7$ decreased rapidly, which was consistent with the results in the previously studied Ni-Zr mixture. When the temperature reached 1150 °C, Ni$_{10}$Zr$_7$ and Ni could form a Ni-Zr eutectic liquid phase, corresponding to the thermal absorption peak at 1159 °C in the DSC curve of the Ni-Zr-B$_4$C mixture. The formation of Ni-Zr liquid phase promotes the contact and reaction between each component, which makes the reaction of the whole system fast and complete.

Figure 4. XRD patterns for the DSC products of Ni-Zr mixtures quenched at different temperatures.
Figure 5. XRD patterns for the DSC products of 30 wt.% Ni-Zr-B₄C mixtures quenched at different temperatures.

In order to better illustrate the above viewpoints, microstructure analysis of DSC quenching products in the 30 wt.% Ni-Zr-B₄C mixture at different temperatures was carried out. The SEM images are shown in Figure 6. It can be seen from Figure 6a that, at room temperature, the raw material mixed powder presented a loose and uniform microstructure. When the temperature was 900 °C, the Ni powder no longer presented a flower shape, but it became denser and bound more closely with the surrounding Zr powder and B₄C powder, as shown in Figure 6b. Some NiₓBᵧ compounds formed around it by energy spectrum analysis. When the temperature rose to 1060 °C, the formation of a liquid phase was observed (see Figure 6c). Combining the EDS-point scanning spectrum (see Figure 6g) with the SEM image, point 1 was rich in Ni and B and thus mainly contained the Ni-B liquid phase. When the temperature rose to 1100 °C, the EDS-point scanning spectrum (see Figure 6h) of point 2 in Figure 6d contained Zr, Ni, B and C and, thus, possibly mainly contained the Ni-Zr-B-C liquid phases. When the temperature was further increased to 1170 °C, a large amount of liquid phase was formed, and a small number of ceramic particles were precipitated out of the liquid phase (see Figure 6e). When the temperature was increased to 1200 °C, a large number of ceramic particles formed in the product, as shown in Figure 6f. These results indicate that the microstructure evolution of DSC-quenched products is consistent with the previously inferred reaction mechanism analysis.
4. Conclusions

Based on DSC and XRD analysis of Zr-B$_4$C, Ni-B$_4$C, Ni-Zr and 30 wt.% Ni-Zr-B$_4$C mixtures, the reaction mechanism in 30 wt.% Ni-Zr-B$_4$C mixture under DSC conditions is proposed as follows: (i) Firstly, some intermetallic Ni$_x$B$_y$ (mainly Ni$_2$B and Ni$_4$B$_3$) and Ni$_x$Zr$_y$ (mainly NiZr and Ni$_5$Zr) formed via solid-state diffusion reactions of Ni, B$_4$C and Zr at about 851 °C. (ii) Then, Ni$_2$B and Ni$_4$B$_3$ formed a Ni-B eutectic liquid at about 1025 °C, and the free C atoms dissolved into the Ni-B liquid to form a Ni-B-C ternary liquid. When the mixture was heated to about 1088 °C, part of the Zr powder directly reacted with B$_4$C through a solid-state diffusion reaction, and part of the Zr powder dissolved into the surrounding Ni-B-C ternary liquid to form Ni-Zr-B-C quaternary liquid. (iii) Finally, when...
the concentration of [Zr], [B] and [C] in the liquid attained a certain value, ZrB₂ and ZrC formed and precipitated out of the saturated liquid.

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