Reaction Synthesis of Nano-scale ZrC Particulates by Self-propagating High-temperature Synthesis from Al−Zr−C Powder Mixtures

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Nano-scale ZrC particles were synthesized by self-propagating high-temperature synthesis (SHS) reaction from 30–40 mass% Al–Zr–C powder mixtures. The size of ZrC particles evidently reduced from ~160 nm with a nearly spherical shape in 30 mass% Al to ~60 nm with a tetragonal morphology in 40 mass% Al. The reaction mechanism to form ZrC was discussed by DTA and X-ray diffraction analysis. The results revealed that ZrAl3 metastable phase was initially formed by Al–Zr reaction, and then the formation of nano-scale ZrC grain was controlled by the dissolution of C into a Zr–Al melt and the precipitation from the melt. Al in the compact serves not only as a diluent inhibiting the ZrC particle from coarsening, but also as an intermediate reactant participating in the reaction process.

KEY WORDS: ZrC; SHS; microstructure; mechanism

1. Introduction

ZrC ceramic exhibits many exceptional multifunctional properties for its NaCl-type lattice structure, such as extreme hardness, good corrosion resistance and excellent higher temperature tensile and creep strength combined with its metallic electrical and thermal conductivities. Moreover, ZrC particle is a good obstacle for dislocation movement and can increase recrystallization temperature and hinder grain growth which can result in strength increment at elevated temperature. So, as one of the potential advanced engineering structural materials or the good reinforcement candidate in materials, ZrC ceramic has been widely applied as refractory materials for cutting tools and wear resistant parts such as drilling heads, crucibles in the mechanical and nuclear industry and electronic devices, especially as the reinforced-particulates in the metal-matrix composites (MMCs). Conventionally, ZrC particle has been produced by the carbonthermal reduction of ZrO2 at elevated temperature, or synthesized by the mechanical alloying, the solid state metathesis route and so on, while relatively less work has been carried out by Self-propagating high-temperature synthesis (SHS).

SHS possesses many advantages such as the relative simplicity of the process and equipment, higher purity of the products, as well as efficiency in energy and time, and a wide range of its application covers the synthesis of intermetallic compounds, ceramic particles and composites. This method is essentially based on sufficient and self-sustaining chemical exothermic reaction of starting powders ignited by external energy supply. It is well known that the service life of materials can be improved by uniform distribution of fine, clean and thermodynamically stable reinforced-particles, especially those nano-scale particles in the materials. Relative to other methods to produce the nanocrystalline materials such as mechanical alloying, sol-gel process, vapor deposition, etc., the report about SHS to produce nano-scale particles is rather limited. It is difficult to synthesize the nano-size materials by the conventional SHS process because the initial reaction medium is a heterogeneous powder mixtures with particle sizes ranging from 1 to 100 μm and the reaction temperature is high over 2000 K. Nevertheless, in our study regarding Al–Zr–C powder mixtures, nano-scale ZrC particulates with the clean surface and absence from binary and ternary intermediate compounds were successfully synthesized by the SHS method. This paper mainly reports the primary results of studies on the ZrC formation and mechanism.

2. Experimental Procedures

In this experiment, the starting materials consist of carbon black (in nano-size), aluminum (~99%, ~29 μm) and zirconium (~98.5%, ~38 μm). The samples were prepared with Zr/C=1 in at% and 30, 40 mass% Al, respectively. The powders were thoroughly mixed by ball milling for 5 h under the Ar atmosphere and then pressed into a cylindrical preform with 65% theoretical density. The SHS experiment was carried out in a glove-box full of Ar atmosphere. The reaction was ignited by a tungsten arc and its temperature was recorded by a thermocouple inserted into the compact. The TEM sample powder was extracted from the as-prod-
ucts and washed several times with absolute alcohol and distilled water.

The phase constituent of as-products was identified by XRD (Model D/Max 2500PC Rigaku, Japan) and the observation of fractured microstructure was performed by field emission scanning electron microscopy (FE-SEM) (Model JSM-6700F, Japan). TEM image and selected area electron diffraction (SAED) were taken by a transmission electron microscopy (Model JEM-200EX, Japan) using an accelerating voltage of 160 kV. The reaction behavior was determined by DTA (Model DTA/TG-Rigaku, Japan) apparatus and the phase constituent of the quenched bulk sample was identified by X-ray diffraction (Model D8 Discovery, Germany).

3. Results and Discussion

When the flashes and sparks were dazzlingly observed, it suggested the preform being ignited and the self-propagating reaction taking place. The non-steady-state oscillatory motion of the wave during combustion resulted in a typical swelled and stratified structural morphology of the reaction end-products.

The temperature evolution of SHS process with 30 mass% Al–Zr–C mixtures is shown in Fig. 1. After preheating for a long time at 284°C, the Al–Zr solid-state reaction to form ZrAl1 was took place and the temperature rapidly increased to 650°C, indicating preheating the compact can improve the reactivity of mixtures. Anselmi-Tamburini \(^{8}\) found that the ignition of the Al–Zr pellet to form ZrAl1 was impossible unless preheating the sample up to 250°C. Laik \(^{7}\) also reported that ZrAl1 phase can form in the diffusion zone by solid-state diffusion reaction between Zr and Al bulk diffusion couples. During this period, Al–Zr reaction to form ZrAl1 will require some heats to melt Al, and thus unavoidably result in the temperature to fall down. Because the molten aluminum provides an easier route for Al to contact with Zr, more Zr powders can spontaneously dissolve into the Al melt and quickly diffuse. Thus solid–liquid reaction to form ZrAl1 between liquid Al and solid Zr will take place immediately and liberate a mass of heat to promote the temperature abruptly increasing (1675°C). In general, this two steps to form ZrAl1 are a successive process. The first step can be termed incubation reaction which induces a furious subsequent reaction. The non-steady-state oscillatory motion of the wave during combustion resulted in a typical swelled and stratified structural morphology of the reaction end-products.

The temperature evolution of SHS process with 30 and (b) 40 mass% Al–Zr–C mixtures. Fig. 2 shows the XRD results of ZrC/Al as-products. Because of differences in both particle size and lattice structure, graphite and carbon black exhibit extremely different combustion characteristics. Okolovich \(^{11}\) has performed a theoretical analysis of the effect of the particle size of the infusible reactant (C) on the SHS process and concluded that for small particle size of the infusible reactant, the heat-release reaction is rela-
tively homogeneous. Relative to the “bulky” and “crystalline” graphite powder, carbon black has a greatly high reactivity for its non-crystalline surface and its small particle size, thus the conversion reaction of ZrC is very sufficient and homogeneous.

To study the reaction behavior of Al–Zr–C system, 35 mg 30 mass% Al–Zr–C reactant mixtures were heated to 1100°C and quenched at 700°C at 20°C/min rate in DTA apparatus, respectively. As shown in Fig. 3(a), there appears only one endothermic peak at 660°C, corresponding to the melting of Al, and three exothermic peaks at 652°C, 688°C and 988°C, respectively. To identify what is going on at 688°C, the reaction of same mixtures was immediately interrupted in the DTA apparatus just after being heated to 700°C and its DTA curve is also plotted in Fig. 3(b). According to the XRD results of DTA-products (in Fig. 4), it is acceptable that the first exothermic peak at 652°C is the solid-state reaction to form a little ZrAl$_3$ phase, the second sharp exothermic peak at 688°C is the solid–liquid reaction between Al and Zr to form a mass of ZrAl$_3$ phase, and the third exothermic wide peak should mainly result from the formation-reaction of ZrC phase between ZrAl$_3$ and C utilizing the heat released by Al–Zr reaction. Since the enthalpy of formation of ZrAl$_3$ is $-45.3$ kJ/mol, the formation of ZrAl$_3$ is thermodynamically feasible. At the same time, among all zirconium aluminides, ZrAl$_3$ is the most favorable phase than its other counterparts.$^{12}$ Relative to the abrupt reaction at 688°C, the formation-reaction of ZrC at 988°C is much slower.

However, it is noted that, a slight amount of complex ternary carbides such as Zr$_3$Al$_5$C$_9$ and Zr$_5$Al$_5$C$_9$ were identified as well. Compared with the combustion synthesis of the bulk compact, the heat released by a little volume blends in DTA apparatus dissipates into surroundings so rapidly that the dwell time of the reactant in the combustion region is too short to achieve the full conversion equilibrium phase. As to the formation of those ternary phases and their roles, the further study is underway.

To further understand the reaction mechanism of Al–Zr–C elemental powders to synthesize ZrC, the SHS quenching experiment of 30 mass% Al–Zr–C compact was performed in the glove-box under the same condition. Figure 5 indicates the macrograph of reaction evolution and its corresponding X-ray identification of the water-quenched sample. The macrograph of quenched product is unambiguously observed in Fig. 5(a), where the reaction evolution is very clear, i.e. the reacted region, reacting region, unreacted region and their corresponding transition regions appear in turn along the propagation direction of combustion wave. According to the X-ray diffraction patterns in Fig. 5(b), the as-product in the reacted region only consists of ZrC and $\alpha$-Al. However, in the reacting region, besides ZrC and $\alpha$-Al

![Fig. 3.](image-url) (a) DTA curves of 30mass%Al–Zr–C mixtures heated to 1100°C. (b) The insert is DTA plot with same mixtures quenched at 700°C.

![Fig. 4.](image-url) XRD patterns of DTA products with (a) heating to 1100°C and (b) quenching at 700°C.

![Fig. 5.](image-url) Typical macrograph of reaction evolution (a) and its corresponding X-ray diffraction patterns (b) of the water-quenched sample fabricated by SHS reaction with 30mass%Al–Zr–C powders.
phase, some ZrAl3 metastable phases were evidently detected too. In the unreacted region, there were a mass of ZrAl3 phase and raw Zr, Al powders, only a little ZrC phase formed by Zr–C interfacial reaction was identified. In each transition region, there appears a little of ZrAl3 intermediate phase or remnant Zr powder. Based on the results of quenching experiment, it is reasonably believed that the ZrC formation reaction did occur through the reaction between ZrAl3 and C. As to the presence of ZrAl3 phase in ZrC formation reaction did occur through the reaction between ZrAl3 and C. As to the presence of ZrAl3 phase in unreacted region, it should be the Al–Zr solid-state reaction triggered by the heat release from the reacting region.

Figure 6 shows the fractured microstructure of as-products with (a) 30 and (b) 40 mass% Al addition which evidently testifies nano-scale ZrC particles with a clean surface and a uniform distribution were successfully in-situ synthesized by SHS reaction. Al content played an important role both in the shape and the size of ZrC particle. ZrC particle is less than 160 nm with a nearly spherical shape for 30 mass% Al content, but when Al addition is up to 40 mass%, ZrC particle is less than 60 nm with a well-proportioned tetragonal morphology. In SHS reaction, the more Al content, the lower combustion temperature, it leads to a sharp reduction of ZrC particle size because the growth of grains is an exponential function of the combustion temperature.14) Figure 7 reveals the TEM image and SAED of as-prepared ZrC particles with 30 mass% Al. It is seen that the typical nearly spherical morphologies of ZrC particles are 70–160 nm, which further bears evidence of the extremely fine microstructure of ZrC particles synthesized by SHS process. The corresponding SAED dots are in accordance with ZrC [(111), (220) and (311)] and its XRD patterns in Fig. 2.

As analyzed above, in Al–Zr–C system, the reaction of Al and Zr to form ZrAl3 intermediate phase initiates, and then the reaction to form ZrC phase subsequently takes place. One would presume that, not only from their size and distribution but also from their morphologies, the formation of nano-scale ZrC grains in the high-temperature region is considered to be a reaction-precipitation mechanism utilizing the vast heat released by Al–Zr reaction. Because the reaction temperature exceeds the melting point of ZrAl3 (1 580°C), such as 1 953°C for 30 mass% and 1 630°C for 40 mass%, ZrAl3 will be rapidly melted as a binary liquid phase [A] and [Zr]. The molten phase provides an easier path for the movement of particle. C particle diffuses and dissolves into the melt, and hence the ternary phase [A], [Zr] and [C] coexist in the melt. Once the concentration of [A], [Zr] and [C] in the melt favorably meets the thermodynamic formation condition of ZrC, ZrC particle spontaneously precipitates by the reaction of [Zr]+[C]→ZrC. Moreover, the reduced Al melt will spontaneously sever as a diluent to lower the temperature and inhibit the grains from growing. With Al content increasing, its diluent effect will be further strengthened. The liquid Al surrounding ZrC grains will increase the diffusion path and reduce the driving force for ZrC grains growth, which prevents ZrC grains from coarsening within a limited time.

4. Conclusions

The nano-scale ZrC particles (≤160 nm) were in-situ synthesized in Al–Zr–C powder mixtures with Al addition ranging of 30–40 mass%. In Al–Zr–C system, the reaction between Al and Zr to form ZrAl3 metastable phase initiated, and then ZrC particle was synthesized utilizing the heat released by Al–Zr reaction. Al plays an important role in SHS process, not only as a diluent to inhibit the grains from coarsening within a limited time, but also as an intermediate reactant participating in the reaction processing.

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