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Synthesis of ultrafine zirconium carbide particles by SHS in an Al–Zr–C system: Microstructural evaluation and formation mode

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ABSTRACT

Due to exhibiting the desirable mechanical and chemical properties, ZrC is widely applied as the multifunctional materials related to reinforced-particulates, engineering structures and electrical devices. Using self-propagating reaction technique, the ultrafine even nanosized ZrC particles were in situ fabricated in an Al–Zr–C powders with 30 and 40 wt.% Al contents, but the ZrC-forming reaction failed to be triggered at 50 wt.% Al content. The Microstructural characteristics of synthesized as-products, coupled with the formation mode of ZrC phase, was considered together. The results reveal that the ZrC particles size is highly influenced by Al content in the compact. For 30 wt.% Al content, the size is about 150 nm, while for 40 wt.% Al content, the clean ZrC nanoparticles with well-developed morphology is about 60 nm. The reaction–precipitation mechanism is responsible for the formation of ultrafine ZrC particles. DTA analysis, combined with the water-quenched treatment during SHS, strictly demonstrated the reaction habit of Al–Zr–C system. It is accepted that the reaction between Al and Zr to form $ZrAl_3$ phase initially take place, and then the reaction between molten $ZrAl_3$ phase and C to synthesize ZrC phase is followed. Al has been playing an important role in controlling the reaction habit of Al–Zr–C system, not only serving as a diluent to inhibit the ZrC particles from coarsening, but also as an intermediate reactant to participate in the total reaction process.

1. Introduction

The refractory transition-metal carbides, such as zirconium carbide (ZrC), have attracted increasing interest in the modern industry both for theoretical and experimental investigations because of exhibiting the various unique physical and chemical properties such as the high wear resistance, ultrahigh hardness, high melting point, as well as excellent thermal conductivities and thermodynamic stability. It is well established that ZrC is of typical NaCl-type lattice structure with mixtures of metallic, covalent and ionic bonding [1]. As one of the potential advanced engineering structural materials or the novel reinforcement candidates in materials, ZrC has been widely applied as the refractory materials for cutting tools and wear resistant parts such as drilling heads, crucibles, electrical devices, and the fuel cladding materials for the 4th generation gas-cooled Fast Reactors or the nuclear reactor core materials [2–4]. In particular, it has been extensively used as the hardening phase of superalloys or the reinforced-particulates in the composites [5].

Conventionally, ZrC was fabricated by the carbonthermal reduction of ZrO_2 at elevated temperature, or synthesized by the solution-based processing at low temperature, the mechanical alloying (MA) method, the chemical vapor deposition (CVD) technique and so on [6–8]. In most cases, however, these methods will give rise to the complication of process and equipment and the larger size particles, especially the MA method will contaminate the end products from its milling equipment during grinding. Furthermore, a high temperature is required for the ZrC-forming process due to the relatively coarse raw powder mixtures (e.g., micrometer-scale), which badly deteriorates the service performance of ZrC-containing materials. It is well known that the mechanical properties and service life of composites can be extremely improved by the uniform distribution of the fine, clean and thermodynamically stable carbide reinforced-particulates, especially those nanoparticles in the matrix. Relative to the conventional ex situ methods such as stirring casting, or those in situ methods to produce the ultrafine even nanocrystalline particles such as MA, sol–gel process, vapor deposition, and laser pyrolysis route [9–11], the report about self-propagating high-temperature synthesis (SHS) to fabricate the nanosized particles still remains limited because its initial reaction medium is a heterogeneous powder mixtures with the larger particle size ranging from 10 to 100 µm and the reaction temperature is higher over 2000 K.

A wide range of SHS applications covers the synthesis of intermetallic compounds, ceramic particulates, metal–matrix

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composites and functional gradient materials [12]. However, owing to the rapidness and usually unstable propagation even the extinguishment of the combustion wave front, the reaction information involved in SHS process still keeps poorly understood. In this paper, Al powder was selected as an additive due to its low liquid phase temperature. The problem of microstructural characteristics of the synthesized ZrC as-products during SHS, as well as the ZrC formation mode analyzed by the DTA testing and the quenching treatment, was considered together. It is expected that the insights into this work could contribute to understand and control the fabrication of ultrafine ZrC and its formation mode during SHS in an Al–Zr–C system.

2. Experimental procedures

The starting elemental powders consist of Al (99% purity, ~29 μm), Zr (98% purity, ~38 μm) and carbon black (in nanosized). The reactant mixtures with Zr:C = 1.0 in at.% and 30, 40, 50 wt.% Al content, were thoroughly mixed by ball milling for 5 h under the argon atmosphere, and then were uniaxially pressed into a cylindrical compact with 22 mm in diameter and 15 mm in height under ~40 MPa pressure to obtain ~65% relative density. Afterwards, the compact was dried in a vacuum oven at 120 °C for 3 h to remove any trace of moisture. SHS experiment was performed in a glove-box full of Ar and was ignited by a tungsten arc heater installed under the compact with supplying a high current pulse (75 A). And the reaction temperature was recorded by a thermocouple inserted into the compact.

After the SHS reaction was completed, the phase constituents of as-products were identified by X-ray powder diffraction (XRD) device (Model D/MAX 2500PC, Rigaku., Japan). And the phase identification of the water-quenched bulk as-products was determined by X-ray micro-diffraction device (Model D8, Discovery., Germany). The reaction habit of the Al–Zr–C powders was analyzed by using a differential thermal analysis (DTA) apparatus (Model DTA/TG, Rigaku., Japan). The microstructural morphology was observed by a field emission scanning electron microscopy (FE-SEM) (Model JSM-6700F, Jeol., Japan) with energy dispersive spectrum (EDS) (Model Inca, Oxford., Britain). TEM image was taken by a transmission electron microscopy (Model JEM-200EX, Jeol., Japan) after extracted from the as-products and washed several times with absolute alcohol and distilled water.

3. Results and discussion

3.1. Phase constituents of as-products

When the compact was ignited by a tungsten arc heater, it emitted dazzling flashes and sparks, which means SHS reaction taking place. The reaction end-products emerged a typical swelled and stratified structural morphology owing to the non-steady-state oscillatory motion of the combustion wave during SHS.

In the SHS reaction, $Zr + C + xAl \rightarrow ZrC + xAl$, the combustion temperature T_c is controlled easily by the amount of Al content. Commonly, the "inert" Al acted as a diluent may lead the combustion temperature to decline even the combustion wave front to extinguish. With Al content increasing, its dilution effect will become more and more intensive, leading T_c to decrease promptly. In terms of the results measured by the thermocouple, three reaction temperatures T_c with 30, 40, 50 wt.% Al contents are 2213, 1893 and 1460 K, respectively.

If taking the final reaction products into account only, it is considerable to presume Al as a dilute only and to ignore the intermediate reaction process. So in the chemical reaction of Al–Zr–C system, the formation of ZrC phase could be, in principle, expressed:

$$\mathrm{Zr} + \mathrm{C} + x\mathrm{Al} \rightarrow \mathrm{ZrC} + x\mathrm{Al} \tag{1}$$

where x denotes Al content (mol.%). The amount of Al is one of the main factors to control the theoretical reaction temperature, *viz.*, adiabatic temperature T_{ad}. If provided the ZrC-forming reaction is homogeneous with a narrow reaction region and the heat loss is negligible during SHS, the standard state enthalpy balance equation could be written [13]:

$$\Delta H^0_{298} + \int_{298}^{T_{ad}} \sum n_j C_p(P_j)dT + \sum_{298}^{T_{ad}} n_j L(P_j) = 0 \tag{2}$$

where H^0_{298} is the standard state enthalpy at 298 K, $C_p(P_j)$ and $L(P_j)$ are the heat capacity and fusion latent heat of the products, P_j and n_j denote the products and the molar number of the components, respectively. Referring to the thermochemical data [14], it can obtain:

$$\begin{aligned} &37.66T + 5.23 \\ &\quad \times 10^{-3}T^2 + 2.6 \times 10^5 T^{-1} + \frac{x}{1-x}(31.75T - 923) + 219,558 = 0 \end{aligned} \tag{3}$$

So, it can calculate the adiabatic temperature T_{ad}, which is 2267, 1932 and 1530 K corresponding to 30, 40, 50 wt.% Al contents in the Al–Zr–C powders system, respectively. Of course, the practical reaction temperature T_c is lower than its theoretical value T_{ad} due to the unavoidable heat loss.

Fig. 1 shows the typical XRD results of ZrC/Al as-prepared products with 30–50 wt.% Al contents. And also as shown in Fig. 1, all the intensity peaks marked by crystal plane indices $\{hkl\}$ were indexed to the standard peaks of *fcc* ZrC phase in the JCPDS-ICDD database (PDF No. 65-0962). It is clearly seen that for both 30 and 40 wt.% Al contents in the compacts, the phase compositions of the synthesized materials closely fit the predictions based on the thermodynamic equilibrium, i.e., the final product contains only the expected ZrC phase and metallic α-Al phase. There is no any evidence of zirconium aluminides ($ZrAl_x$) intermediate phase in XRD level, and maybe these phases contents are below the XRD detection limit. It is completely sure that ZrC particles are synthesized by in situ SHS technique. In the Al–Zr–C system, three reactions, $Zr + C = ZrC$, $4Al + 3C = Al_4C_3$ and $3Al + Zr = ZrAl_3$ can favorably take place. According to the analysis of the reaction Gibbs free energy ΔG^0_T, however, at the temperature range of 873–2873 K, the first reaction, $Zr + C = ZrC$ has the most negative ΔG^0_T, meaning its easiest occurrence. So combined with the final reaction product, ZrC phase is the most thermodynamically stable phase in the Al–Zr–C system.

However, once the "inert" Al content in the compact is up to 50 wt.%, the end-products mostly consists of the predominant $ZrAl_3$ intermediate phase, the residual Al and a spot of ZrC phase, indicating the failure of ZrC-forming reaction during SHS. Considering the results of the latter DTA and water-quenched experiments, when SHS reaction took place in the Al–Zr–C powders,

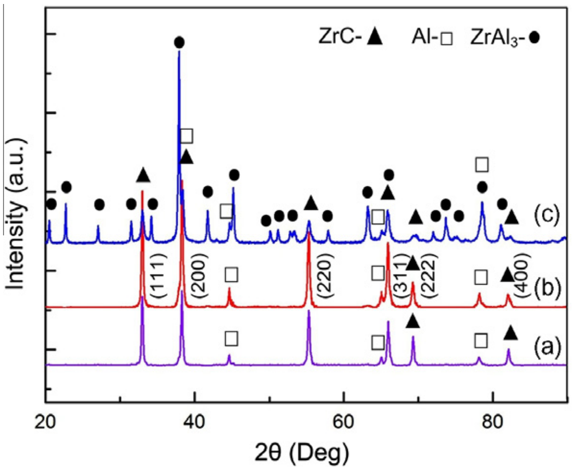

Fig. 1. Typical XRD patterns showing the phases constituents of as-products by SHS in an Al–Zr–C system with (a) 30, (b) 40 and (c) 50 wt.% Al contents, respectively.