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ScienceDirect
Journal of Nuclear Materials 374 (2008) 241–247
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Laboratory production of zirconium carbide compacts for use in inert matrix fuels

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Received 2 April 2007; accepted 6 August 2007

Abstract

Zirconium carbide is being actively considered for use as an inert matrix material in composite nuclear fuel for gas-cooled fast reactors. ZrC can be produced either by the endothermic carbothermal reduction of zirconium dioxide or by the direct exothermic reaction of pure zirconium and graphite powder mixtures. The exothermic reaction is classified as combustion synthesis or self heating synthesis. Experiments were conducted to demonstrate the combustion synthesis reaction of zirconium and graphite powders and measure the ignition and adiabatic temperatures. The heat released during this short reaction time was sufficient only to partially sinter the compacts to less than 40% theoretical density. Subsequently, compacts of ZrC were similarly produced by combustion synthesis followed by a short, high temperature hold at 2440 °C to relieve residual stresses in the compacts following the rapid reaction sintering. External pressures of up to 5.2 MPa were used as an additional driving force for sintering. The effects of reactant particle size and degree of uniaxial pressing on the product density and porosity were also studied. Higher densities in the fabricated compacts were noted for higher uniaxial pressures irrespective of powder size. Also, smaller powder sizes produced compacts up to 92% TD, while larger particle sizes produced compacts up to 84% TD for the same pressure. The compacts were characterized based on composition, microstructure, and density/porosity. Results of the different experiments are presented.

1. Introduction

Inert matrix fuels [1,2] are under consideration for gas-cooled fast reactor (GFR) applications. One such proposed fuel form consists of mixed carbide or nitride fuel microspheres dispersed in an inert matrix [2–6]. GFR fuels are expected to operate at nominal temperatures of 1400 °C similar to fuels for high temperature reactors (HTR) [1,2,6]. However owing to the differences in design, the maximum transient temperatures may exceed 1600 °C [6]. Hence the fuel bearing matrix is expected to have certain desirable high temperature characteristics such as high thermal conductivity, high melting point, and resistance to corrosion by fission products in addition to good strength and good neutronic properties [1–10]. Zirconium carbide (ZrC) is being considered as one of the candidate materials for the production of the inert matrix due to its favorable high temperature characteristics mentioned above [1–10].

To establish the fact that ZrC was being produced by combustion synthesis followed by reaction sintering, it was found necessary to divide the experiment into two phases. In the first phase, it was sought to demonstrate combustion synthesis and resulting pressureless, reaction sintering of zirconium and graphite powders. The adiabatic temperature (T_{ad}) [9–12] and the ignition temperatures (T_{ig}) [11–14] were recorded during combustion synthesis. These samples were characterized for porosity/density, chemical composition, and microstructure.

In the second phase, induction heating was employed to initiate combustion synthesis and subsequent sintering of the powders. The mixture was placed in a graphite die-punch assembly and heated to 2440 °C. To accommodate

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doi:10.1016/j.jnucmat.2007.08.016

advanced fuels involving minor actinide recycle [2–6], it was sought to develop fabrication methods that limit the time that the compacts are exposed to high temperatures. Hence in these experiments, the samples were held at the maximum temperature for only 15 min to allow the reaction to complete and relieve any residual stresses in the compacts following the very high temperature combustion reaction and subsequent rapid cooling. The size of the reactant particles and applied pressure were varied to observe the changes in product characteristics such as density and porosity. The samples were characterized for porosity/density, chemical composition, and microstructure.

The two experiments were conceived as a bridge between combustion synthesis, reaction sintering, and hot pressing to understand and establish an overall ZrC compact production methodology. The results of both experimental phases are presented. The ultimate goal would be to then extend this methodology to the formation of composite fuels containing dispersed fuel microspheres.

2. Thermodynamical background

ZrC powder can be produced in the laboratory by several methods such as carbothermal reduction of zirconium dioxide (ZrO_2) by graphite powder, the reaction of zirconium hydride with carbon, solution based processing, and by the direct reaction of zirconium (Zr) and graphite [12,16–19,23–25].

The carbothermal reduction and solution based processing methods are endothermic processes which require an external high temperature heat source. The reported temperature ranges for the carbothermic conversion is 1900–2100 °C [17,18] and that of solution based processing is 900–1500 °C [18]. The presence of inherent oxygen and other dissolved impurities in the product alters its purity and stoichiometry. It often takes long periods of heating and processing to complete the reaction and produce products of desired purity. In cases where sintering of the end product and formation of compacts is required, additional heating (at least two-thirds the melting point of ZrC) has to be provided for long periods of time. The purity of the end products, processing time and the processing temperatures involved in these methods make them less attractive specifically for production of materials for use in nuclear reactors where a compromise on the purity of the material can change the entire set of desired properties such as thermal conductivity under operating and transient conditions.

The production of ZrC by reacting zirconium hydride with graphite [17,19] is also not uncommon. This reaction is exothermic and falls under the category of combustion synthesis reaction. Since zirconium hydride is highly pyrophoric at room temperature, extreme care has to be taken while handling the reactants.

The other method involves the production of ZrC by the direct reaction of zirconium and graphite powders. The reaction is represented as follows [12]:

$$\mathrm{Zr} + \mathrm{C} = \mathrm{ZrC} \tag{1}$$

The reaction is highly exothermic and is also classified as self heating high temperature synthesis (SHS) or combustion synthesis [11–14]. The product purity is almost guaranteed with this method and handling under an inert atmosphere in a glovebox and vacuum chamber is required due to the pyrophoric nature of zirconium powders. Fine powders of zirconium and graphite thoroughly mixed and pressed to form green bodies of desired shapes are heated to a particular temperature known as the ignition temperature (T_{ig}) within a short period of time. Beyond this point, a combustion wave starts and propagates through the compact converting the reactant mixture into ZrC. External heating is required to ignite the compact unless the auto-ignition temperatures of the mixture is close to standard room temperature under an inert atmosphere. The heating can be achieved by several methods from simple direct resistance heating [11] to induction heating.

Once the ignition starts, minimal external heating may be required depending on the amount of heat released. The entire process occurs in a short period of time (few milliseconds). During the conversion reaction, the sample reaches a temperature known as the adiabatic temperature (T_{ad}). The adiabatic temperature is the maximum temperature attained by the compact during the reaction [11]. T_{ad} can be calculated using the formula given by

$$\Delta H = \int_{298}^{T_{\mathrm{ad}}} C_{\mathrm{p}} \mathrm{d}t, \tag{2}$$

where ΔH is the change in enthalpy of the reaction and C_{p} is the sum of the heat capacities of the reactants [11,12].

Many refractory materials have been successfully fabricated by this method [11–15]. Pure reactants used in this method ensure the purity of the end product. The heat released during the reaction can also be used to simultaneously sinter the compact by applying a small pressure during the course of the reaction. This process is referred to as reaction sintering.

Under normal circumstances, the reaction, T_{ig} , T_{ad}, and sustenance of the wave depend on various thermodynamic and thermophysical parameters such as: the external heat rate (before reaching T_{ig}), initial size of the reactant particles, the degree of compaction (pressure applied before or during the reaction), and mixing time of the reactants. At slow heat rates the process competes with solid state diffusion. If the heat rate is very high, the entire reaction becomes an explosion reaction where a physical explosion occurs destroying the green body.

It has been observed that the chances of a stable combustion synthesis reaction are dependent upon the size of the reactant particles. The smaller the size of the particles, the greater is the probability of the reaction and greater is the probability of wave sustenance, which can be explained in part by higher surface to volume ratios and higher packing density leading to increased contact between reactant particles [11]. A thoroughly compacted green body