Kinetics and Product Composition of Exothermic Reacting Systems Consisting of Binary Nanopowders

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Abstract

Kinetics of the formation of intermetallic compounds, such as NiAl, Ni_3Al, and $MoSi_2$ in a self-propagating high temperature regime is investigated as a function of reactant particle size. Elemental powders ranging from 50 to 150 nm are utilized and the activation energy is evaluated using differential scanning calorimetry. In-situ combustion synthesis and densification experiments are conducted in vacuum or argon atmosphere in a uniaxial hot press with densification pressures up to 200 MPa and preheating temperatures up to 1,500 K. The effect of preheating temperature, ignition sequence, and densification pressure on phase composition, product morphology, and the density of combustion synthesized products will be discussed as well.

Introduction

Self-propagating High-Temperature Synthesis (SHS) also called combustion synthesis (CS) is a well known technique for the synthesis of advanced ceramic and intermetallic materials [1-2]. SHS utilizes the highly exothermic character of the main reaction to generate a sufficient amount of energy to maintain self-propagating conditions and lead to the formation of desired condensed phase products. During the combustion temperatures exceeding 3000 K can be generated in a few seconds. In general SHS reactions are characterized by short reaction times, large thermal gradients $\sim 10^5$-10^6 K m^{-1}, and high reaction temperatures.

Traditional synthesis utilizes powder reactants pressed into a pellet and ignited locally or uniformly heated to ignition. Without consolidation the products of SHS reactions are normally quite porous. To date several techniques for consolidation have been utilized, such as hot isostatic pressing, hot pressing, and centrifugal forces [3]. These techniques have resulted in dense products with a relatively large grain size (microns) due to initial reactant size and long exposure to high temperatures. Until recently the majority of research in academia and industry was focused on utilization of micron size reactant powders, however with the research explosion in the area of nanoscience there has been a significant interest in understanding the formation of consolidated nanocrystalline materials. These materials show improved mechanical, electrical, or optical properties. However, the challenge associated with the densification of nanopowders has remained difficult to overcome [4]. Densification of such materials requires elevated temperatures, however, in order to preserve the nanostructure it is essential to complete the densification process in a very short time [5, 6].

The advantage of using nanopowder reactants is the availability of a high number of contact points between heterogeneous solid reactants and a short diffusion path. This critically impacts the reaction kinetics and leads to better homogeneity of the resulting products. With a solid understanding of the reaction kinetics, product quality and properties of these materials may be tuned by proper processing. The complex nature of gasless combustion reactions involving two or more species has limited the understanding of the SHS mechanism. Various analytical methods have recently been applied including; temperature profile studies [7], combustion wave velocity [8], time-resolved X-ray diffraction [9], and high temperature thermal methods (DSC [10] and DTA [11]). Thermal analysis methods are often preferred due to continuous measurement and easy adjustment of experimental conditions (heating rate, atmosphere). However, these methods are not applicable to all reactions.

Experimental

The objective of this experimental study was two-fold: i) in-situ densification of combustion synthesized nanocomposites and ii) measurement of reaction kinetics in the gasless reaction system consisting of nickel and aluminum nanopowders. The following powders were used: 1) nickel powder from Argonide, d_{avg}=72 nm; 2) aluminum powder from Technanogy Inc., d_{avg} = 50 nm, 3) aluminum powder from Nanotechnologies Inc., d_{avg} = 50 nm, 80 nm, and 100 nm, 4) molybdenum powder from Atlantic, d_{avg}= 5 µm, and 5) silicon powder from Ellkem, d_{avg}= 10 µm. Wet mixing technique was used to mix the reactant powders and is described elsewhere [5]. In-situ combustion synthesis and densification experiments were performed, in argon and vacuum, with varying uniaxial pressure conditions in a grafoil lined die. Schematic of the densification equipment is shown in Figure 1.

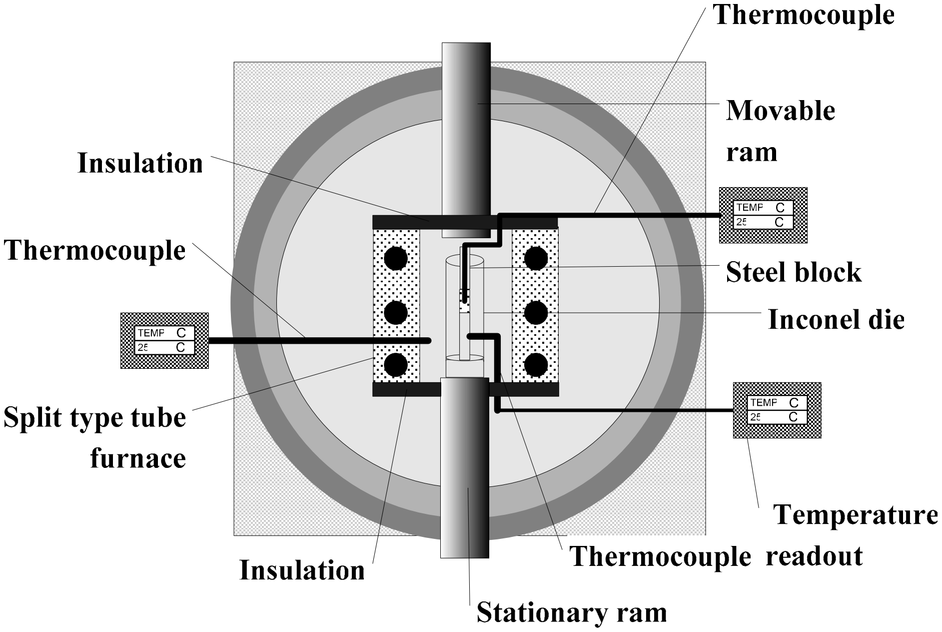

Figure 1. *Experimental set-up for densification of in-situ synthesized nanocomposites.*

Simultaneous TGA/DSC SDT Q600 instrument was used to study the reaction kinetics as a function of average particle size. Pellets were prepared from reactant mixtures, cold pressed at a pressure of 140 MPa in a uniaxial die, and a sample piece of 3-10 mg was loaded in the instrument and a DSC scan was run with varying heating rates from 1 to 20 K in accordance with the ASTM Method E698-79 [15].

Results

Nanocomposites

The reactions, as shown below, were considered for synthesizing composites from a binary mixture of nanoreactants:

$$Ni + (Al + x\,Al_2O_3) \longrightarrow NiAl + x\,Al_2O_3 \quad (1)$$
$$3Ni + (Al + x\,Al_2O_3) \longrightarrow Ni_3Al + x\,Al_2O_3 \quad (2)$$
$$Mo + 2Si \longrightarrow MoSi_2 \quad (3)$$

The best results for formation of NiAl- Al_2O_3 from nanoreactants were obtained when a uniaxial pressure was applied at the moment of ignition. Figure 2 shows the SEM images of the NiAl-Al_2O_3 composites synthesized. The use of nanopowders as intial reactants leads to densified samples exhibiting sub-micron structure with grain sizes in the range of 100-200 nm and density in the range of 3.49-4.49 g/cc [17].

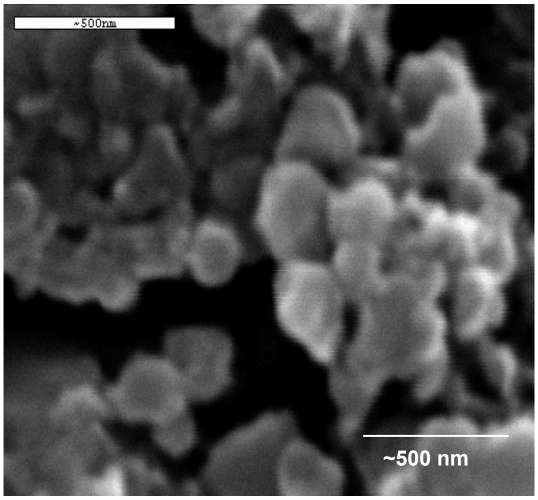

Figure 2. *SEM image of NiAl- Al_2O_3 composite synthesized by preheating nano-size reactant powders to ignition temperature of 588 °C and pressing at ignition with a uniaxial pressure of 140 MPa [17].*

Investigation of the second reaction to form Ni_3Al-Al_2O_3 from nanoreactants has resulted in composites with density in the range of 5.22-5.78 g/cc. However, Ni_3Al is not the only phase present; NiAl and Ni are present in the sample. This is due to quenching of the reaction from excessive heat losses. The combustion temperature of reaction two is significantly less than reaction one, (1524 K vs. 1911 K). However, the use of micron-size reactants has lead to the desired product with the same synthesis conditions which indicates the impact reactant particle size has on the reaction kinetics. Currently, further work to form the desired nanostructured dense Ni_3Al-Al_2O_3 composites is underway.

The formation of $MoSi_2$ was first investigated with micron size powders to determine what product was formed with the available synthesis conditions. In order to utilize in-situ densification a reactant mixture of Ni and Al (reaction one) was used as the ignition source for formation of $MoSi_2$. Results indicate that the reaction did not go to completion resulting in

$MoSi_2$, Mo_5Si_3, and unreacted Mo. This is an indication that there is not a sufficient amount of energy in the system to overcome heat losses in the die. Therefore, the combustion temperature most likely did not reach the melting point of Si and proceed to full combustion. It has been shown that the reaction between Mo and Si proceeds when liquid silicon reacts with solid molybdenum in the combustion front [18]. In-situ densification is then ineffective due to the lack of plasticity of the material and the resulting pellet does not retain its shape when removed from the die. In order to overcome this a more energetic system must be introduced, such as Ti-C, and a composite material formed. The use of a system such as Ti-C will vastly increase the combustion temperature. This is currently being investigated using nanopowders, of the four reactants, to form nanostructured $MoSi_2$–TiC composites.

Measurement of Kinetic Parameters

Several methods exist for evaluating kinetic parameters of condensed phase exothermic reactions [7-12]. In the case of very fast reactions involving nanoreactants (e.g. Al-Bi_2O_3, Al-CuO, Al-Fe_2O_3, Ni-Al, etc.) the differential scanning calorimetric technique seems to be by far more suitable [15,16]. This method is applicable to reactions whose behavior can be described by the Arrhenius equation and power law kinetics. The basic procedure is described elsewhere [17]. A typical DSC plot for 50 nm aluminum powder reacting with nanosize nickel at different heating rates is shown in Figure 3.

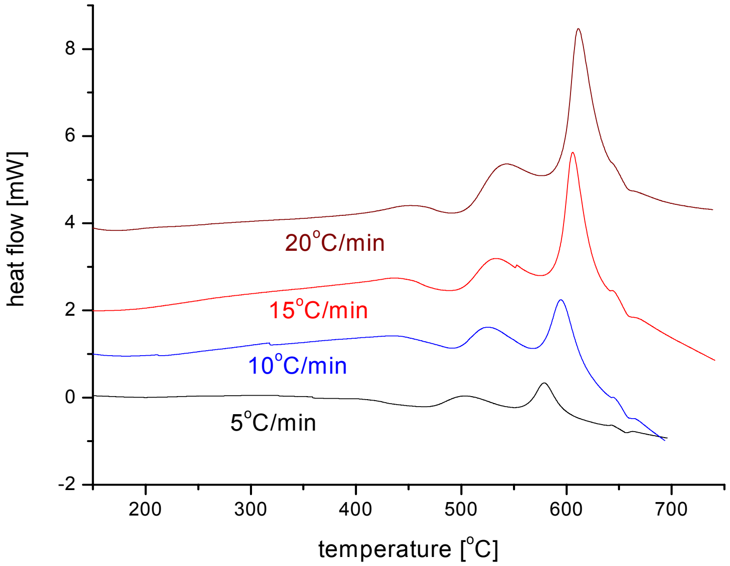

Figure 3. *DSC curves for Ni (72 nm) -Al (50 nm - Technanogy) system with a heating rate of 5, 10, 15, and 20 °C/min. The curves are shifted along the ordinate for clarity [17].*

Determination of activation energies for nickel nanopowder with the average particle size of 72 nm and three aluminum nanopowders with different average particle sizes (50, 80, and 100 nm) was made using both major observed DSC peaks. A plot of heating rates as the function of the inverse absolute temperature of the first and the second peaks for Ni (72 nm) and Al (50 nm) are shown in Figure 4. The evaluated activation energies for both DSC exothermic peaks are presented in Table 1.

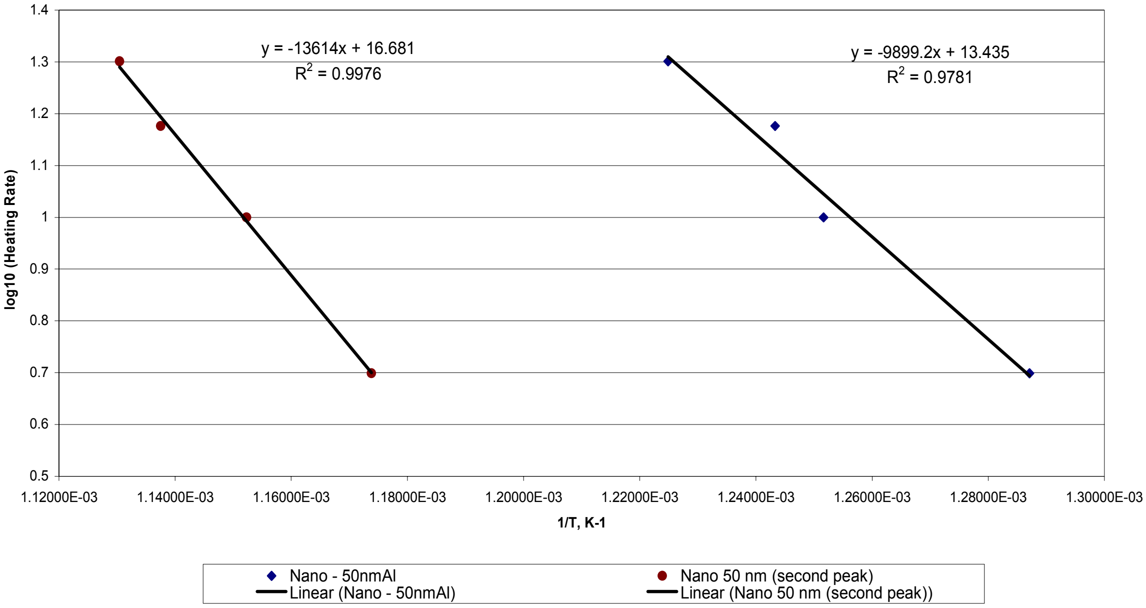

Figure 4. *Evaluation of activation energy using DSC method for Ni (72 nm) -Al (50 nm from Nanotechnology) reacting system [17].*

Table 1. Values of activation energies at the initial stage of the formation of $NiAl_3$ and Ni_2Al_3 [17] .

Avg. Particle Size of Al nanoreactant, [nm]	Activation Energy (first DSC peak) [kJ/mole]	Activation Energy (second DSC peak) [kJ/mole]
50	176.4	246.4

The activation energies measured by the DSC technique, as reported in Table 1, for the reacting system consisting of Ni and Al nanopowders are different for both DSC peaks. They are consistently higher for the second DSC peak. However, less weight should be assigned to these results as the analysis method may not describe a consecutive reactions case very well. Still, the results reported in Table I for the initial reaction (first DSC peak) are higher than the effective activation energies reported in the literature for micron size reactant powders 140 kJ/mole [13] and 170 kJ/mole [14]. There might be several reasons inducing that difference. First of all, non-isothermal techniques lead to the evaluation of the apparent activation energy, which may be reflecting several consecutive reaction steps leading to the formation of the final, desired nickel aluminide phase. The presented DSC technique allows evaluating the kinetic parameters during the initial stage of the reaction (formation of $NiAl_3$), which seems to be the essential reaction step leading to the ignition of Ni-Al mixture. The second reason might be associated with the presence of significant amounts of oxides on the surface of aluminum and nickel nanoreactants.

Conclusions

Simultaneous combustion synthesis and densification of Ni and Al reacting system led to the formation of nanostructured products with average grain size in the range of 100-200nm. The reactions to form Ni_3Al and $MoSi_2$ are not energetic enough to overcome heat losses to the equipment. Currently the addition of a more energetic system, Ti-C, is being investigated. The DSC technique has been found to be a suitable method for evaluating kinetic parameters of the initial stage of exothermic condensed phase reacting systems involving nanoreactants.

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