NUMERICAL SIMULATION OF COMBUSTION SYNTHESIS OF ALUMINIDE INTERMETALLIC COMPOUNDS

M. Adeli, M. Shekari, S. H. Seyedein and M. R. Aboutalebi[*]
* *mrezab@iust.ac.ir*

Center of Excellence for Advanced Materials & Processing (CEAMP), School of Metallurgy and Materials Engineering, Iran University of Science and Technology Narmak, Tehran, Iran

Abstract: *Combustion synthesis is a special thermophysico-chemical process applied for production of intermetallic compounds. In the present work, a reaction–diffusion numerical model was developed to analyze the combustion synthesis of aluminide intermetallics by self-propagating high-temperature synthesis process. In order to verify the reliability of the numerical model, an experimental setup was designed and used to perform the combustion synthesis of nickel and titanium aluminides. The developed model was further used to determine the temperature history of a powder mixture compact during self-propagating high-temperature synthesis. The effect of compact relative density on combustion temperature and wave propagation velocity was also studied.*

1. INTRODUCTION

Combustion synthesis, also known as self-propagating high-temperature synthesis (SHS), is known as an effective thermo-physical method of producing a large number of modern inorganic materials such as refractory and intermetallic compounds and their composites in the past three decades [1-6]. This process occurs when a high temperature combustion wave propagates rapidly through a mixture of reactants without additional energy and leaves behind the products of combustion. Initiation of combustion reactions takes place by an external heat source such as an electrically heated element, induction heating, laser radiation, or spark. Some of the most important advantages of combustion process include low energy consumption, simplicity of instruments, quickness and formation of pure products due to evaporation of volatile impurities in the high temperatures involved.

Aluminide intermetallics produced by SHS process have been the subject of numerous research studies during recent years because of their high performance in high temperature applications [7-9]. Mathematical models based on assumed mechanisms have been developed by various authors to better understand the physical behavior of the process as well as the influence of process variables on combustion synthesis of intermetallics [10-13]. In particular, the effects of

ignition method and porosity of the reactants on the rate of combustion synthesis have been studied by Li et al. in several modeling studies [14, 15].

Despite the numerous modeling work performed in the combustion synthesis of intermetallics and their composites, much research work is still demanded to develop comprehensive models capable of predicting the thermal and physical behaviour of the combustion process. The present work has been undertaken to simulate the heat transfer and kinetics of reactions during combustion synthesis of nickel and titanium aluminides in the SHS mode. The model was tested and validated by experiments. The effect of compact relative density on the combustion temperature and reaction wave propagation velocity was evaluated using the developed model.

2. NUMERICAL MODEL

A one-dimensional transient heat flow equation (Equation 1) coupled with the first-order Arrhenius kinetics equation (Equation 2) was utilized to investigate the behavior of the reaction between reactant powders to produce an intermetallic compound:

$$\rho C_p \left(\frac{\partial T}{\partial t} \right) = \frac{\partial}{\partial z} \left(k \left(\frac{\partial T}{\partial z} \right) \right) + \rho Q \phi(T, \eta) - \frac{4h(T - T_0)}{d} \quad (1)$$

$$\phi(T,\eta) = \frac{\partial \eta}{\partial t} = K_o (1-\eta) \exp(-\frac{E}{RT}) \qquad (2)$$

where C_p is mixture specific heat at constant pressure (Jmol^{-1}K^{-1}), T_o ambient temperature (K), h effective heat transfer coefficient (Wm^{-2}K^{-1}), ρ mixture density (kg/m³), k mixture thermal conductivity (Wm^{-1}K^{-1}), **Q** heat of reaction (Jmol^{-1}), d compact diameter (m) and η fraction reacted. $\phi(T,\eta)$, which is the reaction rate, is assumed to obey the Arrhenius law as given in Equation (2).

K_o in Equation (2) is pre-exponential factor (s^{-1}) and E is activation energy (Jmol^{-1}). The second and third terms of right hand side of equation (1) show the heat loss due to convection and radiation from the compact surface and heat generation due to exothermic reaction, respectively.

Different analytical methods such as synchrotron time-resolved X-ray diffraction, Combustion Front Quenching (CFQ), and thermoanalytical methods such as DSC or DTA have been applied by the researchers to understand the mechanism of reactions in SHS process in aluminide systems [8, 16-19]. Despite these efforts, our knowledge of microscopic reaction mechanisms involved in SHS of the aluminide intermetallics is still quite limited.

In this study, the following steps have been assumed for the aluminide intermetallics formation from elemental powders:

a) Melting of aluminum particles

b) Dissolution of higher melting particles in molten aluminum or the diffusion of aluminum melt through product layer

c) Formation and precipitation of intermetallic compound

d) Probable melting of product

Since the adiabatic temperature for the formation of intermetallics in the Ti-Al system is much lower than the Ni-Al system (1518K for the formation of TiAl in comparison with 1912K for NiAl formation [20]), the last step is not usually encountered in the synthesis of titanium aluminides. Among the reaction steps, only the second one is diffusion-controlled and the others have been considered independent of kinetics and have only been included in terms of energy balance. The diffusion-controlled dissolution of higher-melting particles into the molten aluminum pool is presumably governed by the following equation [10]:

$$r_t^2 = r_o^2 - KD\,t \qquad (3)$$

where r_t is the radius of the particle at a given time, r_0 is its initial value, K depends on liquid composition at the particle-liquid interface and bulk liquid composition, and D is the diffusion coefficient given in an Arrhenius form:

$$D = D_o \exp(-\frac{E_a}{RT}) \qquad (4)$$

Increasing the porosity of a material effectively decreases the overall thermal conductivity. Different methods are used in the literature to estimate the effective thermal conductivity (k_{eff}) in a porous media. For example, one of the most popular proposed models to estimate the effective conductivity (k_{eff}) is expressed as Equation (5) [21], in which the concept of a geometric mean is used to determine an effective thermal conductivity for porous media:

$$\frac{k_{eff}}{k_g} = \left[\frac{k_{max}}{k_g}\right]^{S} \left[\frac{k_{min}}{k_g}\right]^{1-S} \qquad (5)$$

In this equation k_{eff} is calculated based on the limiting thermal conductivities of the material, where k_{min} is the minimum thermal conductivity of the material (e.g. thermal conductivity of titanium or nickel in the current work), k_{max} is the maximum thermal conductivity (e.g. , aluminum), and k_g is the thermal conductivity of the gas in the pores. The S in Equation (5) is described as a wetting parameter and an inverse function of the porosity of the products.

In the present work, the compact porosity has been incorporated in the model via modification of thermophysical properties like thermal conductivity and density of compacts. The relationship between porosity and thermophysical properties is evaluated as [13]:

$$k_{(with\ porosity)} = \frac{1-P}{(1+P/2)} k_{(without\ porosity)} \qquad (6)$$

$$\rho_{(with\ porosity)} = (1-P)\rho_{(without\ porosity)} \qquad (7)$$

where P is the volume fraction of compact porosity. The following initial conditions for temperature and fraction reacted (η) have been assumed:

$$T(z,t) = T_0 \quad , \quad \eta(z,t) = 0 \quad \text{at} \quad t = 0 \quad , \quad \forall z \in \{0, L\}$$

The following boundary conditions were considered for energy equation:

$$T(z,t) = f(t) \quad \text{at} \quad t \leq t(\text{time ignition}) \text{ and } z = 0$$

$$q = h(T - T\infty) \quad \text{at} \quad t > 0 \quad \text{and} \quad z = 0, L$$

where f(t) is an exponential ignition function and q represents the convective heat flux at the compact surface.

In this work a cylindrical compact with the diameter of 1 cm and length of 2 cm made of a homogeneous powder mixture of reactants has been considered. The sample has been divided into 1202 nodes in z direction to calculate local temperatures and reacted fractions. According to initial and boundary conditions, numerical solutions for the equations (1) and (2) have been obtained using the finite volume fully-implicit scheme and TDMA iteration procedure. The following convergence criteria were considered for temperature field and reacted fraction calculation:

$$R_T = \sum \left| a_p T_p - \sum a_{nb} b_{nb} T_{nb} - b \right| < 1 \times 10^{-2} \qquad (8)$$

$$R_\eta = \sum \left| \eta^n - \eta^o \right| / \eta^o < 1 \times 10^{-2} \qquad (9)$$

3. EXPERIMENTAL SETUP

In order to validate the numerical model developed in this study, an experimental setup was designed as shown in Fig. 1. Pure Al (99.99%, <45 μm), pure Ti (99.9, <45 μm), and pure Ni (99.9 %,< 45 μm) were used as the starting powders. Appropriate amounts of Al, Ti and Ni powders were weighed out to the compositions of Al-50 at% Ti and Al-50at%Ni, and hand mixed for 10 minutes. Weighed portions of the mixture were compacted under a pressure of 10-12 kN to form cylindrical compacts. In order to investigate the effect of sample green density on the synthesis process, samples were prepared with relative porosities of 45, 40, 35, 30 and 25 vol. %.

The preheating and ignition were conducted utilizing a steel part heated by an induction coil. The electrical power was immediately turned off after the initiation of the combustion reaction. Two R-type thermocouples connected to an electronic data acquisition system capable of recording 10 signals/s were used to record the temperature history at two points. The time-temperature data and wave propagation velocities obtained from experimental measurements were used to evaluate the results predicted by the model.

4. RESULTS AND DISCUSSIONS

4.1. Temperature History

Figs. 2 and 3 represent the temperature profiles obtained from the experimental measurements and the numerical model for nickel and titanium aluminides, respectively. Both temperature profiles for the combustion synthesis of nickel aluminide include approximately four regions, consisting of a very sharp increase in temperature when the combustion front approaches the thermocouple, followed by a small decrease in temperature. After that, temperature curve becomes flattened which usually represents the solidification of liquid NiAl and finally at the fourth region, cooling continues due to heat losses to the surroundings. Similar trend is observed in the temperature histories for the SHS of titanium aluminide as shown in Fig. 3, except that a sharper peak is seen in the curve which shows that no melting and subsequent solidification of the product occurs.

The comparison between experimental and numerical results for temperature histories reveals reasonable agreement between the trends of temperature variation; however, the reaction occurs more rapidly in the numerical results. This shows the complexity of the solid state phenomena involved in the process, giving rise to different kinetic barriers which could not be readily known and included in the model.

5. EFFECT OF RELATIVE DENSITY

The effect of compact relative density was incorporated in the model calculations using equations (6) and (7), in which the density and thermal conductivity were modified. Figs. 4(a) and (b) shows the effect of initial volume fraction of porosity in the green powder compact on combustion temperature for the self-sustained synthesis of nickel aluminides as measured experimentally and calculated by the numerical model.

In the synthesis of NiAl, both experimental and numerical results show an increase in the combustion temperature with decreasing of porosity, which is based on the fact that lower levels of porosity in powder compact lead to the increasing of efficient interfacial contact between the particles, thereby increasing the thermal conductivity and also the heat losses from the reaction zone.

The effect of variation of compact relative density on the combustion temperature for the synthesis of titanium aluminide is shown in Fig. 5. The predictions made by the model show that the combustion temperature increases by increasing the relative density. Although the combustion temperatures measured experimentally also show an increase in the combustion temperature by increasing the relative density up to 65%, there is a decrease in combustion temperatures in higher relative densities. This could be because of higher thermal conductivity of titanium in comparison with nickel. The increasing of effective contact between the particle leads to over-enhancement of the compact conductivity, resulting in high heat transfer rate to the surroundings and to the layers below the surface layers subjected to ignition. The loss of heat to the unreacted regions makes the system further deviate from adiabatic conditions leading to lower combustion temperatures.

Fig. 6 demonstrates the dependence of wave propagation velocity on volume fraction of porosity for the combustion synthesis of nickel aluminide. Ranges of wave front velocities calculated by the present model are approximately similar to the experimental results obtained in the present study as well as the results reported in previous studies. Besides, the simulated and experimental results show almost the same trend in velocity variations with relative densities in the range of 50-65%. The decrease in propagation wave velocity with the decrease in relative density is attributed to the decrease in material's thermal conductivity in the presence of pores, which lowers the rate of heat conducted to the farther unreacted regions.

6. CONCLUSION

In this study, a numerical model for self-propagating high temperature synthesis of nickel and titanium aluminides was developed. The temperature profile for some arbitrary location in compacted samples ignited from one end was calculated. The model was verified by comparison of predicted results with the experimental data obtained in this study. Effect of compact relative density on the combustion temperature and front wave velocity was evaluated. The predictions made by the model showed that the decrease in relative density leads to a decrease in combustion temperature for the synthesis of nickel and titanium aluminides. This was in agreement with experimental results obtained for nickel aluminide. In the case of titanium aluminide the experimental results showed a decrease in the combustion temperature in relative densities higher that 65%. The model also predicted a decrease in wave propagation velocity with a decrease in relative density for the combustion synthesis of nickel aluminide.

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