Predicting the Adiabatic Temperature of Transparent $Y_3Al_5O_{12}$ Prepared via Combustion Synthesis under Ultra-High Gravity

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In this paper, the adiabatic temperature of a transparent yttrium aluminum garnet (YAG) preparation using a NiO/Al/Y$_3$O$_5$ aluminothermic system was calculated based on a thermodynamic theory. The results show that the adiabatic temperature without preheating reaches the 2891 K, which is higher than the melting points of YAG and Ni. The liquid phase mixture products can be separated and densified under ultra-high gravity (UHG). In the preheating temperature range of 620 K~2790 K to the reactants of this system, the adiabatic temperature is the same as 3156 K, the boiling point of Ni products. The theoretical analyses and experimental results prove the effectiveness of the YAG fabricated via combustion synthesis under an ultra-high gravity field. [doi:10.2320/matertrans.M2010266]

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1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is an important ceramic material with promising chemical stability, and optical and mechanical properties that make it widely used in laser materials, luminescence systems, window materials for a variety of lamps, and fiber materials for the preparation of ceramic composites.$^{1,8}$ Traditional solid-state reaction techniques for the preparation of YAG require repeated mechanical mixing and extensive heat treatment ($> 1923$ K) to achieve the desired phase purity.$^{1,2}$ These processing conditions do not allow facile control over the microstructure, grain size, and grain size distributions in the resulting powders or shapes.$^{1,4}$ Moreover, most of the approaches described so far suffer from time consuming procedures and/or complicated equipment requirements or costly starting materials.$^{4,6}$ Thus, there has been a general consensus among researchers that exploring a simpler method for YAG preparation should be a priority.

Combustion synthesis, called self-propagating high-temperature synthesis (SHS),$^{9-11}$ can generate high temperatures without requiring alternative energy sources. For example, the adiabatic temperatures of NiO/Al and Fe$_2$O$_3$/Al aluminothermic systems reach 3524 K and 3622 K, respectively, which are above the melting points of products investigated thus far in the literature.$^{12}$ Further chemical reactions then occur between the high temperature production alumina (Al$_2$O$_3$) and yttria (Y$_2$O$_3$) in the raw materials. The YAG is obtained in this manner through the reaction 5Al$_2$O$_3$ + 3Y$_2$O$_3$ = 2Y$_3$Al$_5$O$_{12}$. The liquid phase mixture products (ceramics and metallic) of the aluminothermic systems are separated under ultra-high gravity (UHG) owing to their different densities. Moreover, the ultra-high centrifuge field enables the production of dense, low porosity, or pore-free YAG bulk materials, which can make the YAG materials transparent. In fact, recent interest towards the behavior of various systems under gravity conditions has become the impetus for a variety of investigations. The method of combustion synthesis under the UHG field is being researched widely by material researchers.$^{13,14}$

The adiabatic temperature $T_{ad}$ analysis plays an important role in thermodynamic studies on combustion synthesis.$^{15-18}$ Firstly, the adiabatic temperature is a crucial variable governing the possibility of a self-sustainable reaction. It is generally accepted that the combustion reaction for every system will not become self-sustaining unless $T_{ad} > 1800$ K$^{15,19-21}$ in the SHS community. Secondly, the final state, which affects the microstructure and properties of the reaction products, can be determined through the adiabatic temperature calculation. That is, high temperatures may indicate the complete melting of the product, which is necessary for joining or coating applications. However, the high temperature results in some defects such as shape changes, heterogeneous coarse microstructures, large shrinkage voids, and so on. Yet, the adiabatic temperature can be controlled by preheating and/or by using different mass fractions of the diluent additives in raw materials. The reaction temperature can be controlled to produce desirable results, by predicting the theoretical adiabatic temperature accurately. Therefore, it appears to be important for the YAG to be prepared by combustion synthesis under a UHG field to calculate the adiabatic temperature of the aluminothermic system. To date, there have been no previous reports or studies on the theoretical temperature prediction, to the authors’ knowledge.

In this paper, the thermodynamic parameters of YAG ($Y_3Al_5O_{12}$) are collected first. Based on the thermodynamic theory of adiabatic temperature calculations combined with the computer simulation, the adiabatic temperatures of the YAG prepared by the aluminothermic system are calculated. The reliability of the calculation results was verified experimentally; after analyzing the mechanism of this method, the experimental and theoretical transparent YAG samples were compared.

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2. Thermodynamic Theory for Adiabatic Temperature Simulations

The first assumption in predicting the adiabatic temperature, \(T_{ad}\), is that the enthalpy of the reaction heats the products and that no heat energy is lost to the surrounding environment.\(^{15-18}\) \(T_{ad}\) is the temperature at which the enthalpies of the products are equal to those of the reactants. The oxidation-reduction reaction used to fabricate the YAG bulk can be written in a general form as:

\[
a\text{Al} + b\text{MeO} + c\text{Y}_2\text{O}_3 \rightarrow d\text{Y}_3\text{Al}_5\text{O}_{12} + e\text{Me} + \Delta H. \tag{1}
\]

Here, Me is a metal or an alloy, MeO is its corresponding oxides, and \(\Delta H\) is the heat generated by the reaction. The coefficients \(a, b, c, d,\) and \(e\) indicate the molar quantities of the reactants and products.

Suppose that the reaction is conducted under adiabatic conditions and completed by chemical stoichiometry. According to the first law of thermodynamics, the isobaric enthalpy of an isolated system is a constant, which means that the enthalpy of the reactants at temperature \(T_0\) is equal to one of the reaction products under the adiabatic temperature, \(T_{ad}\).

The reaction can be expressed as follows:

\[
\sum m_i H(T_0) = \sum n_j H(T_{ad}), \tag{2}
\]

where \(H\) represents the enthalpy, and \(m\) and \(n\) are the molar quantities of the reactants and products, respectively. The subscript \(i\) and \(j\) denote the components of the reactants and products, respectively.

It should be noted that different forms of formulae for the enthalpy calculation of one substance are found in literature. For example, the formula found on the NIST Chemistry WebBook (http://webbook.nist.gov) is

\[
H_T = AT + BT^2/2 + CT^3/3 + DT^4/4 - E/t + F - H, \tag{3}
\]

while Dalman\(^{22}\) presents a different formula as follows:

\[
H_T = B_1 T + B_2 T^{-3/2} + B_3 T^{-5/2} + B_4 T^{-7/2} + B_5, \tag{4}
\]

where \(A, B, C, \ldots\) and \(B_1, B_2, B_3, \ldots\) are coefficients, and \(H_T\) is the enthalpy of substance at \(T (K)\). In eq. (3), the variable parameter is \(t = T/1000\).

Despite the different formulae available, the results of the enthalpy calculations of one substance using different formulae, agree well with each other. In order to solve eq. (2), the loop trial value and the linear interpolation method are used. The computational principle of determining \(T_{ad}\) and the flowchart of the computer calculation program are shown in Fig. 1. The calculation program of the adiabatic temperature is compiled using TurboC2 computer software and then its reliability was verified by comparing the results from literature with the calculated ones.\(^{23}\)

3. Results and Discussion

3.1 Definition of the thermodynamic parameters

The adiabatic temperature of the NiO/Y\(_2\)O\(_3\)/Al aluminothermic system used to fabricate the YAG bulks is calculated as an example. The chemical reaction of the aluminothermic system is:

\[
10\text{Al} + 15\text{NiO} + 3\text{Y}_2\text{O}_3 = 2\text{Y}_3\text{Al}_5\text{O}_{12} + 15\text{Ni}. \tag{5}
\]

It is essential to define the enthalpy of reactants and products together with the temperature variations. From the literature,\(^{24}\) the relationship between the solid specific heat, \(C^s_p(T)/\text{J/(mol·K)}\), and the temperature of the YAG material is given by:

\[
C^s_p(T) = \frac{573.3126 + 7.5312 \times 10^{-3} T - 12653462.0}{T^2} - \frac{2070.9615 + 1.02270684 \times 10^9}{T^3}, \tag{6}
\]

for 298 K \(\leq T \leq 2213\) K (the melting point of YAG), \(C^s_p(T)\) given in J/(mol·K) and \(\Delta H(298) = -7250905.48\text{ J/mol, and S(298) = 285.4618311}\text{ J/(mol·K)}\). The heat of fusion
Table 1 Equations for enthalpies at various temperatures of YAG.

<table>
<thead>
<tr>
<th>Enthalpy (J/mol)</th>
<th>Equations</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\text{YAG}}(T)$</td>
<td>$573.3126T + 3.7656 \times 10^{-2}T^2$</td>
<td>298–2213</td>
</tr>
<tr>
<td>$-5.1135 \times 10^{-2}T^2 - 136383.9753$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Thermodynamic parameters of reactants and products of the NiO/Y$_2$O$_3$/Al system.$^{22,24,25}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al</th>
<th>NiO</th>
<th>Y$_2$O$_3$</th>
<th>Y$<em>3$AlO$</em>{12}$</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ (kJ/mol)</td>
<td>0</td>
<td>$-240.35$</td>
<td>$-1903.57$</td>
<td>$-7250.91$</td>
<td>0</td>
</tr>
<tr>
<td>Melt point (K)</td>
<td>933</td>
<td>2257</td>
<td>2693</td>
<td>2213</td>
<td>1728</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>2790</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>3156.58</td>
</tr>
<tr>
<td>Heat of fusion $\Delta H_f$ (kJ/mol)</td>
<td>10.56</td>
<td>/</td>
<td>/</td>
<td>420.00</td>
<td>17.48</td>
</tr>
<tr>
<td>Enthalpy of vaporization $\Delta H_v$ (kJ/mol)</td>
<td>330.0</td>
<td>/</td>
<td>/</td>
<td>430.12</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta H_f$ and liquid specific heat $C_p(T)$ of YAG are $4.2 \times 10^5$ J/mol and 546 J/(mol·K), respectively.$^{25}$

According to Kirchhoff’s law $\int_{T_0}^{T} dH(T) = \int_{T_0}^{T} C_p(T) dT$, the enthalpy calculation formula of YAG is:

$$H_{\text{YAG}}(T) = \int_{T_0}^{T} C_p(T) dT + \Delta H_f + \int_{2213}^{T} C_p(T) dT.$$  \hspace{1cm} (7)

The equations for the enthalpies at any temperature of YAG are listed in Table 1 below.

3.2 Adiabatic temperature of the NiO/Y$_2$O$_3$/Al system

The adiabatic temperature of the NiO/Y$_2$O$_3$/Al aluminothermic system was calculated using a reliable calculation program established and verified previously.$^{25,26}$ The chemical reaction is eq. (5). The thermodynamic parameters of the reactants and products are listed in Table 2.

As is known, the adiabatic temperature generally increases if reactants are preheated. Hence, it is necessary to explore the law of adiabatic temperature variations in conjunction with the reactants’ preheating temperature, shown in Fig. 2. In Fig. 2, the adiabatic temperature of the reaction (eq. 5) is 2891.9 K without preheating, which is above the empirical criterion temperature ($T_{\text{adl}} > 1800$ K) and demonstrates that this reaction is self-sustainable. Furthermore, this adiabatic temperature 2891.9 K is also above the melting points of the products, 1728 K of Ni and 2213 K of YAG. The products of eq. (5) are liquid phase mixtures, which can be separated and densified under UHG due to their difference in densities. With increasing the reactants’ preheating temperature from 298 K to 620 K, the adiabatic temperature of the reaction increases from 2891.9 K to 3156 K. Above 620 K until 2790 K of the preheating temperature, the adiabatic temperature remains the same as 3156 K, the boiling point of a Ni product. Therefore, in the temperature range of 620–2790 K, a partial Ni product exists in a gas phase, increasing the preheating temperature increases quantities of Ni gas and does not affect the adiabatic temperature of the system.

The existing of Ni gas phase has an adverse effect on the products being adequately separated under the UHG field and a subsequent effect on the transparent capabilities of the YAG ceramic. Even though the higher the adiabatic temperature, the more easily and completely the mixture composite propagates the reaction eq. (8). The adiabatic temperature variation in the reaction eq. (9) as a function of the preheating temperature is shown in Fig. 4. In the preheating temperature range of 298 K–2790 K, the adiabatic temperature of the reaction eq. (9) is 3156 K, the boiling point of Ni. Further calculations indicate that there is approximately

![Fig. 2 Relationship between the adiabatic temperature and the preheating temperature of the NiO/Y$_2$O$_3$/Al system.](image-url)
6.37\% of gas phase of Ni under a preheating temperature of 298 K.\(^\text{23,26}\) Comparing Fig. 2 and Fig. 4, however, within 620 K, the adiabatic temperature of the system decreases because of preheating the Y\(_2\)O\(_3\) reaction which can lead the Al\(_2\)O\(_3\)/Y\(_2\)O\(_3\) reaction self-propagating. In fact, the reaction eq. (9) provides supplemental energy source and Al\(_2\)O\(_3\) reaction for the reaction eq. (8).

According to the above calculations and analyses for the NiO/Y\(_2\)O\(_3\)/Al aluminothermic system, when the system is ignited, the reactions must occur step-by-step: (i) when the thermit begins, the reaction eq. (8) starts, a large amount of heat is generated, and a liquid Al\(_2\)O\(_3\) is produced. (ii) The Y\(_2\)O\(_3\) reactant is heated, and the reaction eq. (8) is occurred and self-propagated. (iii) The liquid phase mixture products (YAG and Ni) are obtained. The mixtures are separated under UHG. Then, the YAG melt is densified by the UHG field, which can probably fabricate the bulk transparent Y\(_3\)Al\(_5\)O\(_12\) via combustion synthesis.

### 3.3 Adiabatic temperature calculation of other aluminothermic systems

In order for the other oxidation-reduction reactions in the aluminothermic system to fabricate the YAG bulk materials, the adiabatic temperatures were calculated at the preheating temperatures of 300 K, 400 K and 500 K for the reactants. The results are displayed in Table 3.

### 3.4 Verification of the experiment and calculation results

Al (purity 99.9\%, particulate size 100 \(\mu\)m) powders, NiO (purity 99.99\%, particulate size 44 \(\mu\)m) powders, and Y\(_2\)O\(_3\) (purity 99.98\%, particulate size 10 \(\mu\)m) powders were used in the combustion synthesis system. The reactant powders were mixed by ball milling in ethanol with a mol ratio of Al/NiO/Y\(_2\)O\(_3\) = 10 : 15 : 3. 200 g of dried reactant powders was cold pressed into a graphite crucible with an inner diameter of 30 mm. The density of the powder compact was approximately 55\% of the theoretical value. The thermite mixture was ignited using a W coil by passing an electrical current through the mixture. A colorimetric infrared temperature detector (CIT-1MD) was used to test the temperature when the thermit began, whose parameters are within the temperature range of 1173 K~3273 K, with an error of indication of ±1.2 K, and response time of 67 ms. The experimental temperature was approximately 2881 K, which is close to the calculation temperature of 2891.9 K.

The apparatus used to undertake the combustion synthesis experiment is based on that presented in the literature.\(^\text{27,28}\) The procedure parameters included an acceleration of 800 g, a pressure chamber with 10\(^{-3}\) MPa, and cooling in the chamber after the thermit finished. Based on the results of the adiabatic temperature of the Al/NiO/Y\(_2\)O\(_3\) system, the preheating temperature for the powder mixture is 573 K.
The Ni ingot and YAG ingot were obtained and were separated from each other. The diamond grinding wheel caused a YAG chip slice, approximately 0.8 mm thick, to be present vertically in the centrifugal direction. Combined with the SEM micrograph and EDS micro-area chemical analysis, the XRD results indicate that there is only one phase (YAG) in this material. The results of the transparency, SEM micrograph, and phase-chemical testing of this chip are shown in Fig. 5.

The results from the adiabatic temperature calculation and the experiments verify the feasibility fabricating YAG via combustion synthesis under a UHG field. This study provides a new method for preparing promising YAG materials.

4. Conclusions

Based on thermodynamic theory and a computer calculation technique, the adiabatic temperature of transparent YAG prepared via combustion synthesis under a UHG was calculated. The kinetics of a NiO/Y₂O₃/Al aluminothermic system was investigated by analyzing the calculation results. The procedure of this system is gradual as follows: first, the reaction 2Al + 3NiO = Al₂O₃ + 3Ni starts when the thermit begins, which generates a significant quantity of heat and liquid Al₂O₃ products. Next, the yttria (Y₂O₃) reactants are heated and the following reaction 5Al₂O₃ + 3Y₂O₃ = 2Y₃Al₅O₁₂ occurs. The relationship between the adiabatic temperature and preheating temperature of the NiO/Y₂O₃/Al aluminothermic system indicates that the adiabatic temperature increases from 2891.9 K to 3156 K with increasing the quantities of Ni gas and does not affect the adiabatic temperature of the system. Directed by these results, the bulk transparent YAG was fabricated using a simple method of processing and integrating the combustion synthesis technique with the UHG technique. The theoretical analyses and experimental results prove the effectiveness and establish the theoretical basis of this new method.

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