Microstructural Aspects during the Preparation of $Y_3Al_5O_{12}$ by Combustion Synthesis and Temperature Field Simulation

Yuepeng Song^{1,2}, Jiangtao Li³, Yixiang Chen³, Wenwen Ji²,
Chong Soo Lee¹ and Hyoung Seop Kim^{1,*}

¹Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

²Mechanical and Electronic Engineering College, Shandong Agricultural University, Tai'an Shandong 271018, P. R. China

³Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

The combustion front quenching method (CFQM) combined with the temperature field simulated using the finite element method was used to investigate the microstructural aspects of the fabrication of transparent $Y_3Al_5O_{12}$ via combustion synthesis. The simulated results indicate that there are three regions corresponding with the temperature distribution whose microstructural aspects were studied. The composite mixtures of the products cannot be separated depending only on their gravities. The filamentous profile of aluminum along with many aluminous intermediate products are detected by XRD, SEM and EDS analysis in the preheat region, which indicates that the heat-transfer can affect the mass-transfer process and the subsequent reaction process. The microstructural aspects show that the combustion reaction of the Al/NiO/ Y_2O_3 powder mixture was initiated by the melting of Al particles. [doi:10.2320/matertrans.M2010295]

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1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is a promising material due to its high melting point, absence of polymorphous transitions, good electrophysical indices, stability in alkali metal plasmas, and elevated thermal stability. Due to its high light transmission indices in the visible region of the spectrum, this ceramic can replace glass in instruments that operate in conditions of night vision requirements, high temperatures, and/or aggressive media.¹⁻⁷⁾ The research on transparent YAG ceramics reported thus far has focused mostly on pulverization and sintering technologies. However, most pulverization and sintering approaches are associated with time-consuming procedures, require complicated equipment or call for costly starting materials.^{1,4,5)} On account of its importance, promising prospects in industry fields, and the defects associated with the traditional preparation of this material, it is generally recognized that low-cost and rapid fabrication methods should be developed.

As is known, combustion synthesis technology, having unique advantages such as simple processing, short reaction times, low energy consumption, and the use of pure synthesized products, is utilized in the preparation of a variety of materials, including carbides, borides, nitrides, intermetallics, and composites.⁸⁻¹⁰⁾ There have been several successful examples of its use. Song *et al.*¹¹⁾ established the thermodynamic basis of YAG fabrication by combustion synthesis through a study of the adiabatic temperature of many aluminothermic systems. Recently, Pei *et al.*¹²⁾ designed a new apparatus that can be used for combustion synthesis under ultra-high gravity (UHG). In their study, considering all kinds of factors (higher adiabatic temperature of system, more different density between ceramics and

metallic products, lower cost and so on), the Al/NiO/ Y_2O_3 is utilized. The combustion reaction of an Al/NiO/ Y_2O_3 mixture was ignited and a molten mixture of YAG and Ni was then generated. Solidification of the pure YAG melt was realized under ultra-high-gravity fields due to the different densities of YAG and Ni melts, and the maximum relative density of a YAG ceramic ingot reached 99.30%. The range of the grain size distribution was 30–50 μm , and the polished as-fabricated ceramic sample was translucent. However, due to the lack of sufficient microstructural detail regarding the fabricated samples, information pertaining to microstructural evolution during the combustion synthesis process remains unclear.

The combustion front quenching method (CFQM) is a powerful technique that has been widely used to investigate the mechanism of combustion synthesis.^{9,13-16)} By investigating the structure of a specimen in the regions in which the front is quenched, it becomes possible to obtain information about the structural aspects of the sample and thus the process mechanism. For quenching, the burning specimens were immersed in water or a mixture of the combustion synthesis system was burned on a massive copper tray.¹⁷⁾ Rogachev^{18,19)} studied the structural transitions in a gasless combustion of Ti-C and Ti-B systems by quenching with a copper tray. Fan *et al.*^{13,15)} improved the CFQM and obtained a cylinder-shaped quenched compact to study the process mechanisms of the SHS of a TiC-Fe composite, a TiC-Al cermet, and a TiC-Ti cermet. On the other hand, Maksimov *et al.*¹⁷⁾ estimated the water quenching of the specimens to investigate the macrokinetics of structural changes upon a gas-free combustion of powder mixtures.

In this paper, we investigate the microstructural features of transparent $Y_3Al_5O_{12}$ fabrication by combustion synthesis using the combustion front quenching method (CFQM)

*Corresponding author, E-mail: hskim@postech.ac.kr

Fig. 1 The reliability of the temperature distribution simulation by ANSYS of compact.

combined with the temperature field simulated using the finite element method. Based on these experimental results combined with temperature field simulations during the burning of the compacts, a mechanism of the combustion reaction is proposed. These results of stable states will provide a good reference model to explore the mechanism of microstructural aspects during the YAG bulk preparation by combustion synthesis under a UHG field.

2. Experimental Procedures

Al powders (purity 99.9%, particulate size 60~70 μm), NiO powders (purity 99.99%, particulate size 44 μm) and Y₂O₃ powders (purity 99.98%, particulate size 2~3 μm) were used for the combustion synthesis system. The reaction is as follows:

The reactant powders were mixed by ball milling in ethanol at a mol ratio of Al : NiO : Y₂O₃ = 10 : 15 : 3. The homogenized reactant powders were fully dried for 24 h, and the powder mixtures were then cold-pressed into a cylindrical compact with a diameter of 30 mm and a height of 20 mm. The density of this powder compact was nearly 60% of the theoretical value. This thermite compact was ignited by a W coil by passing an electric current through it. After burning for 2 s, the specimen was quickly immersed in water and the combustion was therefore quenched, freezing the intermediate and final products of the reaction. The extinguished compact was taken out of the water immediately and dried for 24 h at 200°C.

It is known that the microstructural aspects during the formation of YAG are related to the temperature distribution of the burnt compact. However, this has seldom been investigated to the best of the authors' knowledge. The reliability of temperature field simulated by the commercial finite element method software ANSYS has been proved in many studies.^{20–22} Chae *et al.*²⁰ used the ANSYS software to predict the effect of the Si phase on melting in the combustion synthesis of MoSi₂. In more recent work,²² the ANSYS-CFX software was used to simulate the heat-transfer and the temperature distribution of compacts.

The dried quenched compact was cut longitudinally and inspected by X-ray diffraction (XRD) with Cu Kα to study

the phase constituents. The microstructural aspects in the specimen were analyzed using scanning electron microscopy (SEM) and an energy dispersive spectrometer (EDS). Combined with the temperature distribution simulation results, the mechanism of the microstructural aspects during the YAG bulk preparation process by combustion synthesis was explored.

3. Results and Discussion

3.1 Temperature simulation and verification

The reliability of the predicted temperature distribution and heat-transfer simulation by the ANSYS software was initially verified. A schematic of testing apparatus is shown in Fig. 1(a). The testing procedures were as follows: a low electrical current passes through a tungsten coil ignition for about 20 s, and the coil was withdrawn from the top of the compact where a temperature of 300°C was measured by an infrared thermometer. The temperature-time history at the points 5 mm away from the compact top was obtained by a temperature sensor.

The physical parameters of the compact were sourced from the literature.^{23–25} The density is 3100 kg·m⁻³, the thermal conductivity is 0.55 W·m⁻¹·°C⁻¹, the specific heat is 300 J·kg⁻¹·°C⁻¹, and the heat convection of air is 2.5 W·m⁻¹·°C⁻¹. The temperature-time history results of the simulation compared to those of the experiment are shown in Fig. 1(b). It is easy to draw the conclusion that the simulation results agree very well with the experimental results. Hence, the high reliability of the temperature distribution and heat-transfer simulation by the ANSYS software was verified. The following simulations results are reliable in accordance with the step of this simulation method, including selection of the physical parameters, the simulating step, and so on.

3.2 Temperature distribution of the burning compact

The compact was water-quenched after burning for 2 s. Due to the great stress that developed during the quenching process, the products of the combustion synthesis were broken into many fragments and stripped from the matrix. The longitudinally cut sectional macro-photography of the dried quenched-compact can be clearly divided into three regions according to the temperature distribution during the

burning process. They are i) the burnt zone, ii) the preheating zone, and iii) the original zone, which can be clearly distinguished based on the color of the cross-section of the compact. These three zones were observed previously in earlier reports.^{13,15,16} In the simulation process, the temperature reached 2600°C on the compact top because the adiabatic temperature of aluminothermic systems is 2619°C .¹¹ The other simulation conditions followed the former simulation step. The temperature distribution simulation and a practice cross-section of the compact are displayed in Fig. 2.

There is a close corresponding relationship between the three regions existing in both the experimental specimen section and the simulation section. The burnt zone was broken and stripped from the matrix. The thickness of the

preheat zone where the temperature ranges from 660°C to 1741°C in the compact-cross section is about $3\sim 5\text{ mm}$ in the experimental section and 4.5 mm in the simulation section.

Frankly, simulation error will exist because the temperature range for verification simulation (20°C to 80°C) is more narrow and lower than that for simulating the temperature of burning compact ($20\sim 2600^\circ\text{C}$). Considering the compact of aluminothermic systems burns very quickly as soon as been ignited and the time of experimental combustion and computer simulation is very short (only 2 s), the high temperature zone of burning compact is considerable narrow. Most of the compact is in the low temperature range as shown in Fig. 2. The simulation error can be acceptable in engineering.

3.3 Microstructural aspects

The region under 660°C temperature (the melting point of Al) is known as the original zone where the particles retain their original formation. Song *et al.*²⁶ studied the microstructures of original compacts with different densities. Aluminum particles in the region over 660°C will melt, which changes the microstructure of the compact. Figure 3 shows SEM photographs of this region (over 660°C), where the temperature ranges from 660°C to 1455°C . There are many cracks in this region, as arrow shown in Figs. 3(c) and 3(d), owing to the great stress that develops during the quenching process. After the melting of the Al particles, the other powders (NiO and Y_2O_3) are held together by Al liquid, forming many mostly spherical mixtures of approximately

Fig. 2 The temperature distribution simulation and practical cross section of compact.

Fig. 3 SEM photographs in the preheat region of low temperature ($660\sim 1455^\circ\text{C}$).

Fig. 4 EDS results for preheat region at low temperature (660~1455°C).

Fig. 5 Profile of filamentous material in preheat zone at high temperature (over 1455°C).

50~70 μm in size. This matches the original size of the Al particles, as observed in the EDS results for this region in Fig. 4.

A SEM photograph and EDS analysis in the preheat region over 1455°C are shown in Fig. 5. The shape of the mixtures is more spherical and the size is larger. The diameter of these materials is approximately 100 μm. There are many filament shaped materials, as confirmed by only the presence of the Al element in the EDS analysis. The temperature in the high temperature zone exceeds the melting point of Al. The viscosity of the Al melt decreases with the temperature, and the Al melt easily infiltrates into the low temperature region of the compact by its own gravity. A previous report²³⁾ showed that in the compact there were many porous structures that acted as a sieve and enhanced the osmosis of the Al melt. This is a mass transfer process that stems from the heat transfer in the compact as it combusts. Therefore, the heat transfer affects the mass transfer during the burning process, which induces extremely heterogeneous components. This heterogeneity of micro-area in compact will even affect the products. Further examinations indicate that only the shape and size and not the phases of the particles in these regions change.

It is difficult to define the reaction region of the burning compact. Until now, there is no relevant report on solving the difficulty according to the latest literatures. From the simulation results (Fig. 2), the temperature near the pit surface of water-quenched compact is in the range of

2050°C~2200°C. In the high temperature region (over 2000°C, above the melt point of YAG), a number of new phases were detected. These results are shown in Fig. 6. Spherical Al_2O_3 intermediate products of reaction (1) were detected in Fig. 6(a). One of the products, Ni powder, is spherical and coated by Y_2O_3 , as shown in Fig. 6(b). This result clearly indicates that reaction (1) occurred gradually, which was also verified by a thermokinetics analysis.¹¹⁾ The XRD detection in Fig. 7 shows that there are complex phase components in this region. The results of different points in this region are shown in Figs. 7(a) and 7(b). Figure 7 indicates that there are many aluminous intermediate products in this region, which is related to the inhomogeneous components because of the mass transfer in the compact during the burning process as the former conclusions. However, because the mol ratio of reactants is $\text{Al} : \text{NiO} : \text{Y}_2\text{O}_3 = 10 : 15 : 3$ which matches eq. (1), when the combustion synthesis completely finished, there are only two phases in the products mixture: Ni and YAG, although many aluminous intermediate products ever existed. As in the former analysis, the heat transfer can so affect the mass transfer process and the products proceed during combustion. Due to the low melting point of Al compared to the other components in the compact, overdosing of Al melt can occur in the micro region, which induces extremely heterogeneous micro-components. Regarding the burnt zone, there are only two product phases of the Al/NiO/ Y_2O_3 thermit system: Ni and YAG according to

Fig. 6 SEM photographs and EDS spectrum of high temperature (over 2000°C) region of the quenched compact.

Fig. 7 XRD detection results of the different points in high temperature (over 2000°C) region.

the results of XRD detection results. Macro-inspection indicated that the ceramic and metal products mixed together and become a porous bulk solid. In the SEM and EDS analyses of Fig. 8, the product mixtures cannot be separated by their own gravity. The literature²⁶⁾ has also obtained such conclusions.

3.4 Discussion

The microstructural aspects in the quenched sample, as mentioned above, showed that the combustion reaction of the $\text{Al}/\text{NiO}/\text{Y}_2\text{O}_3$ powder mixture was initiated by the melting of the Al particles. The Al liquid will come into contact with the NiO particles and the thermit will react, which generates a considerable quantity of heat, with the temperature reaching 2891 K .¹¹⁾ The melt product of Al_2O_3 and the Y_2O_3 powders will be heated, the reaction $5\text{Al}_2\text{O}_3 +$

$3\text{Y}_2\text{O}_3 = 2\text{Y}_3\text{Al}_5\text{O}_{12}$ occurs, and the $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) material is thus obtained.

The heat and mass transfer processes will then occur along with the reaction development. In the preheat region of the compact in conjunction with the reaction area, because the temperature exceeds the melting point of Al , the particles of Al melt and infiltrate into the raw materials region. Given the characteristics of the screens, which are made of the different particles compressed into the compact, the liquid Al takes on a filamentous profile, which changes the components in the micro-area in the compact. Owing to the excess of the Al element, the reaction cannot occur following the normal ratio of reactants, which produces many aluminous intermediate products, such as Ni_3Al , Al_2O_3 , and YAlO_3 . Finally, these intermediate phases will further react into the last products: Ni and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG).

Fig. 8 SEM and XRD detection results of the burn zone in the compact.

In the region far from the reaction area, the temperature is low but over the melting point of Al. The Al particles melt and become mostly spherical drops coated with Y_2O_3 powders. Alternatively, they are immersed with the Ni particles.

4. Conclusions

A CFQM was performed to explore the microstructural aspects of $\text{Y}_3\text{Al}_5\text{O}_{12}$ fabricated by combustion synthesis. Three regions resulted from the sectional macro-photography of quenched compacts: a burnt zone, a preheating zone and the original zone. Compared with the simulation results, the area division is closely associated with the temperature field.

The composite mixtures of Ni and YAG are the main profile in the burnt zone; i.e., the mixtures cannot be separated depending only on their own gravity. Therefore, transparent YAG cannot be obtained in a stable state by combustion synthesis. The quantity of heat generated by the reaction preheats the raw materials, which reach a high temperature that exceeds the melting point of the Al particles. The Al melt infiltrates into the underside of the compact through the pores established by many particles and takes on a filamentous profile. This causes the micro area components to become extremely heterogeneous, producing many aluminous intermediate products. The heat transfer affects the mass transfer process as well as the subsequent reactions. In the preheating region, far from the reaction area, the Al particles melt into spherical drops and are coated by Y_2O_3 powders or immersed in the Ni particles.

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