

Porous Ceramic/Glass Composite Body by Microwave Assisted Substitutional Combustion Synthesis and Sponge Replica Technique

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Abstract

Porous composite body from Fe_3O_4/Al and SiO_2-RO/SUS system was synthesized by microwave (MW) heating and sponge replica method respectively. A reaction between Fe_3O_4 and Al was used to fabricate the porous ceramic composite through substitutional combustion synthesis by adequately control of the MW ignition condition. On the other hand, the porous glass composite was made from polyurethane (PU) precursor. Regardless of the mixture systems and processing conditions, both the ceramic and glass composite body revealed the formation of microstructure consisting of micron sized metal particles, uniformly dispersed and distributed in the ceramic/glass matrix. Heating behavior study was performed to evaluate the MW heating ability of the fabricated porous composite body. MW heating selectivity allows the samples to be heated up easily and rapidly owing their resulting morphology and phases.

Keywords: Fe_3O_4/Al , SiO_2-RO/SUS , porous composite, microwave heating, PU precursor

1 Introduction

Materials containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Therefore, porous materials have attracted a great attention as new kinds of materials with a wide range of technical and engineering applications. Porous materials exhibit various unique physical and mechanical properties, such as low apparent density, low thermal conductivity, high surface stiffness, gas permeability and high strain energy adsorbing capacity [1]. Besides that, there is strong demand for practical usage of porous composites that can endure severe environments such as high temperature and highly corrosive atmospheres [2, 3]. Such applications include, for example, high temperature thermal insulation, support for catalytic reactions, filtration of particulates from diesel engine exhaust gases, and filtration of hot corrosive gases in various industrial processes [4].

Various process routes have been applied to fabricate the porous ceramic composites, including the combustion synthesis (CS) method [5-7], sponge replica method (SRM) [8-10], foaming agent [11] or space holder method [12]. Out of these, CS and sponge replica method are two of most attractive techniques. The CS method uses the exothermic reaction of a starting compound, ignited to its ignition temperature to spontaneously transform into product. Independent of the ignition method, reaction ignited by conventional heating techniques usually present an inversion of heat flow before and after the synthesis occurs. As soon as the reaction occurs, it is no longer possible for the conventional heating to continue to transfer heat from external heating source to the reaction zone. Instead, the selective heating of microwave is expected to lead to rapid temperature increase of the whole reaction zone, continuing to transfer energy during and after the ignition [13]. In

addition to the above advantage, continuity of the propagation wave front can be controlled by manipulating the microwave input power. According to Clark et al. [14], the rate of propagation of the wave front also can be controlled by the incident power. Turning off the power can terminate the propagation, whereas pulsing the incident power will give more control on the velocity of the propagation of the combustion wave front. This is not possible in conventional synthesis. This method is simple and time saving. However, it was difficult to control the porosity level of the final products and the control of the propagation is possible only for those CS systems of low exothermic heat, but not for the main exotherm.

Polyurethane (PU) sponge replica method is a simple and inexpensive method and was patented in 1963 by Schwartzwalder and Somers [15]. The first step in the fabrication route involves impregnation of a polymeric sponge in ceramic slurry, squeezing out the excess slurry and drying the coated foam. Afterward, the polymeric template is burnt out followed by sintering of the ceramic skeleton at an elevated temperature. This methodology allows to obtain open cell porous ceramic structures with a controllable pore size, interconnected pores and desired geometry [16]. PU sponge selection is an important issue for the fabrication of ceramic foam as the physicochemical properties of these polymers may influence the sinterization of the ceramic during calcining step [17]. These sponges may differ in terms of density and porosity. In addition, it may differ chemically due to various additives that incorporated into the polymer mixture, such as blowing agents, anti-oxidants, pigments etc. Usually, porous ceramic fabricated by the polymeric sponge method show high porosity (70 – 95%) and high permeability ($> 10^3$ D) [18]. Zirconia, silicon carbide and alumina are the most usual among a wide range of ceramics fabricated through this method.

Although the fabrication of porous composite of various materials have been widely reported in the literature, resources on fabricating of porous composite consisting of well distributed metal particle within the ceramic and/ or glass matrix which can be heated up easily by utilizing microwave power was very limited. In the present work, the fabrication of porous ceramic and glass composite consisting of well dispersed and distributed metal particles employing the CS and polyurethane sponge replica method are reported. Additionally,

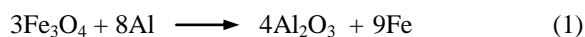
microwave heating ability of the fabricated porous composite was also investigated.

2 Experimental

2.1 Preparation of porous ceramic composite body by CS

Magnetite (~500nm) and aluminium (200-300µm) powders were used to compound the thermite mixtures. Both solids were mixed in an agitate mortar to obtain a homogeneous mixing. The mixed powder was then weighted and uni-axially pressed into cylindrical green compact (Ø6.76mm x 5mm thick). The green compact was put into a glass tube and placed at the H and/or E maximum field position in a TE₁₀ 2 kW, 2.45 GHz, single mode applicator. The details of the single mode microwave system are given elsewhere [19]. Sample temperature was measured using an optical pyrometer through a sapphire rod. During the experiments, atmospheric pressure N₂ gas was passed through the quartz tube to avoid oxidation of the samples.

Based on the results obtained from previous study [19], green compacts correspond to stoichiometric reaction as expressed in reaction (1) was ignited by microwave heating at the H maximum field.



Samples were heated rapidly to a temperature corresponding to the exothermic peak obtained in DTA analysis. Two heating temperatures namely, 1300°C and 1380°C were carried out at the low and high temperature exotherm to determine the controllability of microwave ignition and combustion.

2.2 Preparation of porous glass composite body by sponge replica method

Commercial polyurethane (PU) sponge, with a cell size ~ 45 ppi (pore per inch), were chosen in this study. SiO₂-RO glass powder (D50 = 5 µm) from AGC (Asahi Glass, Japan) and 303L stainless steel powder (140 mesh) from Alfa Aesar (Wall Hill, MA, United State) were used as the raw materials. PU sponges are cut into cylindrical shape with an approximate diameter of 25 mm. SiO₂-RO glass powder was blended with 10 – 30 vol% stainless steel powder in an agitate mortar to obtain a homogeneous mixture.

The slurries are prepared by dispersing the powder mixtures with distilled water without any further additives to give a suspension with approximately 40 wt% solids loading. According to Sifontes et al. [17], this weight allowed obtaining adequate viscosities of slurries and proper mechanical strength for ceramic foam. PU sponge which had been cut into cylinder was immersed into this suspension and was compressed while submerged in order to fill all the pores. At the same time, stirring was carrying out to avoid segregation in the slurries due to powder mixtures density different. After a minute, the impregnated sponge was removed from the slurries and excess slurries were removing by blowing with air followed by drying at 60°C for 12 h in a convection oven. Finally, the coated cylinder was heat-treated to burn out the sponge and sintered at 940°C with a heating rate of 1°C/ min for 1.5 hrs holding time in air.

2.3 Thermal analysis, phases and microstructural characterization

Difference thermal analysis (DTA) was performed in an EXSTAR SII analyzer under the flowing of N₂, with Pt holders, using a heating rate of 20°C/min and samples of approximately 15 mg. Phase composition of the fabricated porous bodies were analyzed by X-ray diffraction (XRD), using a RINT diffractometer with CuK α radiation at 40 kV and 100mA ($\lambda = 0.154\text{nm}$). In order to study the microstructure of the porous bodies, a scanning electron microscope equipped with a Field-Emission Gun (FEG-SEM), Philips XL-30FEG was used. Samples are prepared by attaching the polished porous body to an aluminum sample holder with conductive tape. Carbon coating was performed to prevent charging of the samples. Energy dispersion X-ray (EDX) was performed to quantify the composition of the selected area on the samples.

2.4 Microwave heating behaviour of the porous body

Effect of MW input power and samples morphology on the heating rate was carrying out by heating the fabricated porous bodies in the H maximum field using a 2.45 GHz, 2 kW, TM₁₀ single mode applicator. Heating temperature of the samples was measured by an optical pyrometer (minimum temperature measured = 350°C) and was recorded using a PC. The heating temperature was targeted at

600°C. This temperature was selected based on the soot particulate matter combustion temperature.

3 Results and Discussion

3.1 Microwave assisted substitutional combustion synthesized porous ceramic composite body

Figure 1 shows the DTA curve of the stoichiometric mixture as expressed in reaction (1). At 660°C, an endotherm was observed, attributed to the melting of Al. Two exotherm peaks were observed, at approximately 1310°C and 1380°C respectively. The smaller peak, i.e. the low temperature exotherm, signified the initiation and propagation of combustion by supply of microwave power, on another hand revealed suppression of combustion wave self-propagating by reducing the power. At this point, material with porous structure can be obtained by MW heating. The second peak, i.e. the high temperature exotherm, was much bigger and showed the characteristic of sharp rise. It corresponded to the main combustion reaction, coincided with the melting of reaction products and destroying of porous structure. At the low temperature exotherm, heat generated in the system was insufficient for the combustion wave front to be self-propagate, thus the spontaneous reaction progress is not possible. Constant dissipation of microwave energy to the sample is needed to force the combustion wave front to propagate.

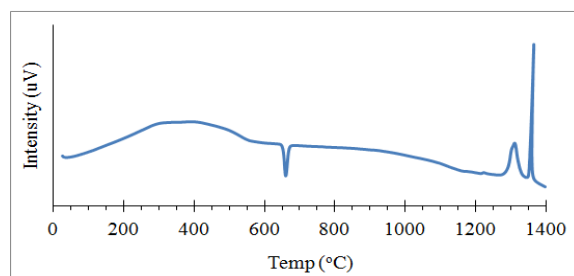


Figure 1: Thermograms of Fe₃O₄/Al mixtures using a heating rate of 20°C/min

X-ray diffractometry in Figure 2 shows the change of products formed by the reaction heated to 1300°C and 1380°C. Samples heated at 1300°C revealed the formation of Fe and spinel hercynite as main phases. Low concentration of Al₂O₃ was also observed. Whereas, sample heated at 1380°C revealed the presence of Al₂O₃ and Fe as main phases and low concentration of non-stoichiometry hercynite originated by some substitution of Al with the Fe

atoms, in the type $\text{Fe}[\text{Al}_x\text{Fe}_{2-x}\text{O}_4]$, with $0 \leq x \leq 2$ as secondary phase. Hercynite was widely recognized as the intermediate product in the thermite reaction. Formation of this intermediate phase was mainly dependent on the ratio of $\text{Fe}_3\text{O}_4/\text{Al}$ and FeO/Al . The reaction mechanism is as follow:

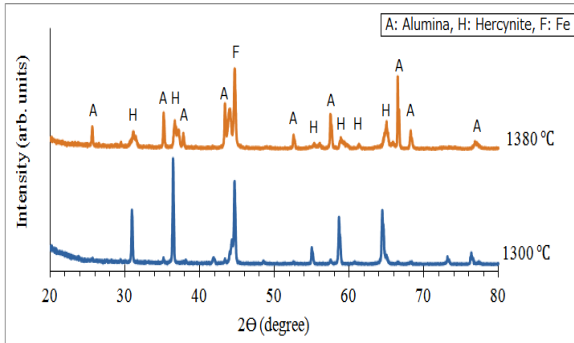
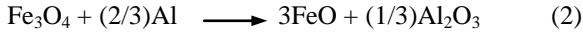


Figure 2: X-ray diffractograms of the samples heated up to 1300°C and 1380°C in a microwave applicator

When heating the mixture compact at 1300°C, it showed a plateau signifying the initiation of ignition and a small rise of temperature (Figure 3a). At this state, it is impossible to hold the heating temperature. Propagation of the ignited combustion wave front can be terminated by turning off the microwave power due to the low velocity of combustion wave. Porous structure materials consisting of micron sized iron particles well distributed and embedded in the hercynite matrix can be obtained (Figure 4a). In contrast, commencement of main combustion occurs when heating the mixture compact up to 1380°C (the high temperature exotherm). Initiation of ignition and a sharp rise to the peak of combustion (T_c) which surpassed the melting point of reaction products was observed (Figure 3b). Control of the combustion wave propagation was impossible, even though the microwave power has been cut off. The combustion wave front propagated rapidly in a self-sustained manner and the combustion reaction was completed in less than a second. Mixture compact underwent melting of products due to high combustion temperature (Figure 4b). Porous multiphase structure sample can be obtained by controlling the reaction progress at the low temperature exotherm to avoid the commencement of main combustion. The mentioned criteria of multiphase porous microstructure formation was also observed by

Biswas et al. [20] in the fabrication of porous NiTi by thermal explosion mode of self-propagating high temperature synthesis (SHS).

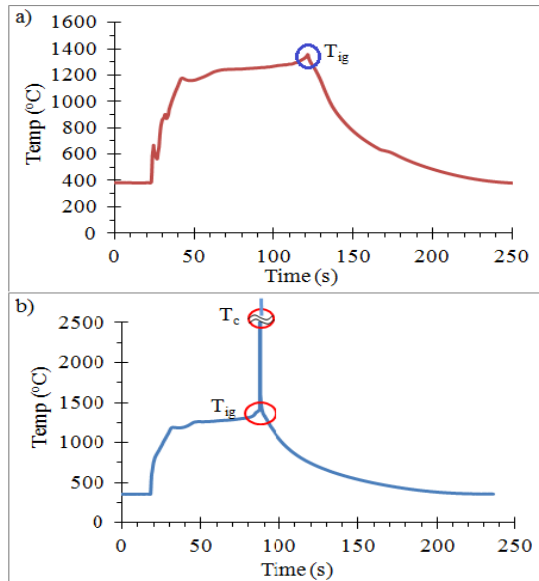


Figure 3: Temperature-time plot for sample heated to: a) 1300°C, b) 1380°C

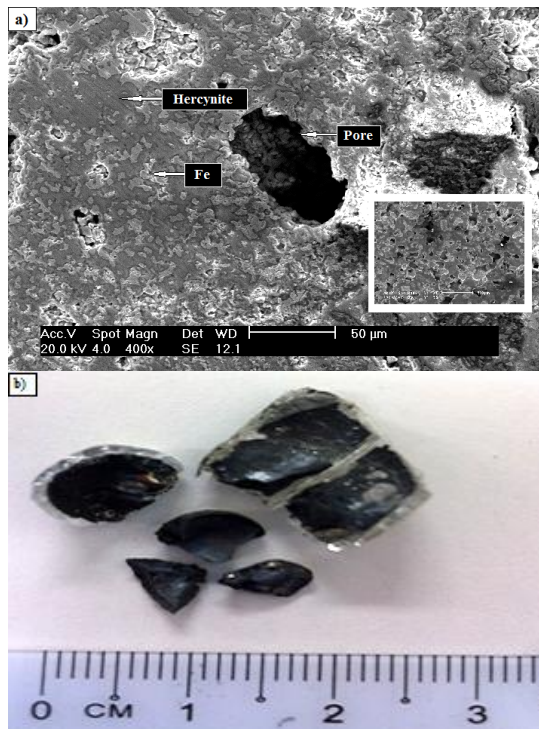


Figure 4: Image of sample heated at different temperature: a) 1300°C, obtaining porous structure b) 1380°C, melting and destroying of porous structure

3.2 Porous glass composite body from sponge replica method

XRD analysis of the green compact and sintered porous sample is shown in Figure 5. It can be observed that both the green compact and sintered porous sample depicted a same pattern. Hence, it looks no reaction occurred between the $\text{SiO}_2\text{-RO}$ and 303L stainless steel mixture after sintering. This is important to ensure the chemical resistance of the fabricated materials.

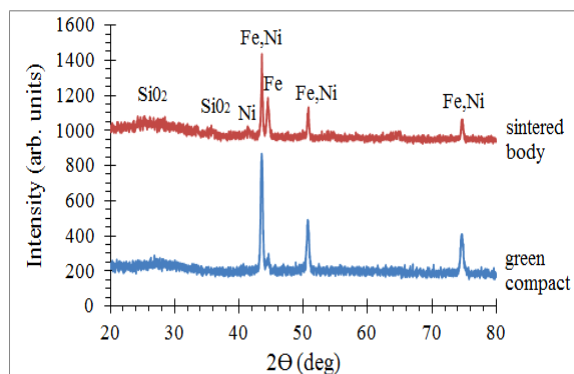


Figure 5: X-ray diffractograms of $\text{SiO}_2\text{-RO/SUS}$ green compact, and sintered sample

Scanning electron microscope (SEM) micrographs of the sintered porous glass-stainless steel composite is shown in Figure 6. It can be observed that the sintered composite sample maintained the pore structure of the original PU template. The skeletons of cells are uniform and free of defects. The pores are mostly interconnected, some macrospores on the skeletons surface can also be observed. Porosity around 65-70% can be obtained.

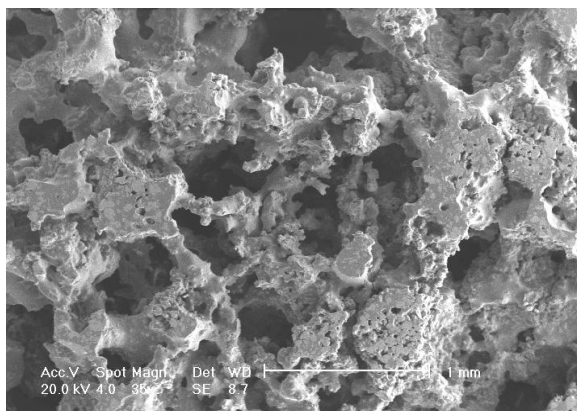


Figure 6: SEM micrograph of the sintered glass-stainless steel porous composite

Figure 7 shows the microstructure of the skeleton surface with different stainless steel fraction. The $\text{SiO}_2\text{-RO}$ matrix had a grey appearance whereas the stainless steel particles were in light grey. No obvious remnants of the PU sponge were detectable. Stainless steel particles were well dispersed and distributed within the glass matrix, increasing with the increased of stainless steel fraction in the mixtures. This microstructure effect was generated during the impregnation process. Since the stainless steel powder has a higher density compared to $\text{SiO}_2\text{-RO}$ glass powder, segregation might occur in the slurries which could draw in non-homogeneity that will influence the uniformity of the stainless steel particle distribution within the glass matrix. Hence, uninterrupted stirring is needed during the impregnation step, to minimize the occurrence of segregation.

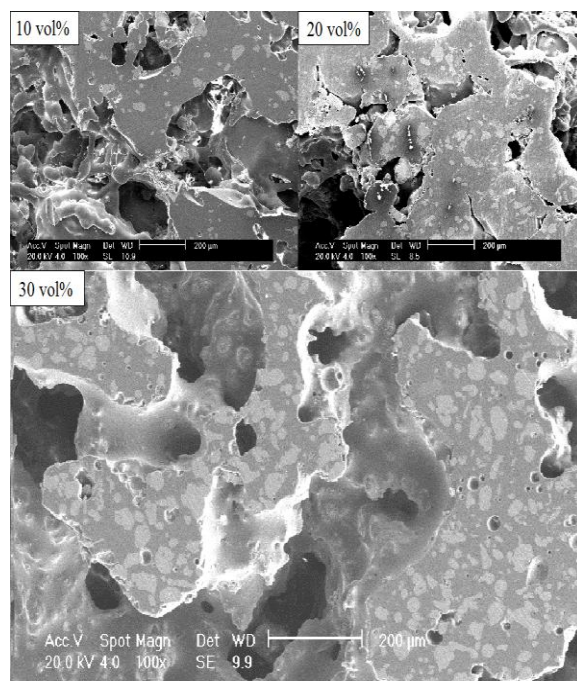


Figure 7: SEM micrograph of sintered glass-stainless steel porous composite with different stainless steel fraction

It is clearly shown in Figure 7, increased in the stainless steel fraction led to higher allocation of stainless steel particles at the skeleton. Some particles were interconnected to form a cluster, but most of the particles were well distributed and isolated within the skeleton. This microstructure feature is very important especially when couple with

microwave heating. Owing different in microwave absorbability and heating selectivity, these allow the microwave to penetrate through the glass matrix, heat up the metal part and subsequently transferred the heat energy throughout the whole samples. Thus uniformity in the stainless steel particles distribution is highly desired to avoid any possibility of non-uniform heating, on the other hand, enhanced the heating ability.

3.3 Microwave heating behaviour

Microwave heating ability of the fabricated porous composite bodies was studied using a 2.45 GHz, 2 kW, single mode applicator. Microwave input power was set at 400 W for all samples. Heating profile of the samples was measured by an optical pyrometer and is illustrated in Figure 8. Heating rate of these porous composites was fully associated with the samples morphology and amount of metal particles in the samples.

To compare the heating ability of the CS porous body, heating behavior of sample fabricated at lower temperature (1200°C) was included. As shown in Figure 8, porous body fabricated at 1300°C (CS-13C) can be heated up to 600°C easily as compared to that fabricated at 1200°C (CS-12C). Product SC-13C took only about 13 s to reach 600°C, whilst product CS-12C needs about 24 s. Since these two products were fabricated at a different temperature, thus it depicts a different in microstructure and phase composition. Product fabricated at 1300°C (CS-13C) was porous and contained uniformly distributed metal particles (bright grey color) in the alumina and/or hercynite matrix structure (Figure 4a), on the other hand, product fabricated at 1200°C (CS-12C) was nearly dense and mainly composed of FeO phase with very little dispersed metallic phase (Figure 9). Microwave heating selectivity allows the microwave to penetrate through the ceramic matrix, heat up the metal part and subsequently transferred the heat energy throughout the whole samples. Owing different in microwave absorbability and separated field heating behavior, sample with well distributed metal particles is easier to be heated up compared to nearly dense sample which composed mainly FeO phase.

For the porous composite body fabricated utilizing sponge replica method (SRM), as the fraction of stainless steel in the mixtures increased, the heating rate also increased. Samples with higher metal fraction can be heated up rapidly compared with those of lower metal fraction. It took only ~13 s for

the sample with 30 vol% stainless steel to reach 600°C. Whereas sample with 20 vol% stainless steel took double the time to reach the target temperature, and the lowest fraction sample took about 70 s. Heating ability of sample with higher metal loading (40 vol%) also been carrying out. Even though the heating rate was faster than sample with 30 vol% stainless steel, but the different was not too large. Thus, it is not included in the figure for the sake of simplicity. Heating rate of these porous composites was fully coupled with the amount of stainless steel particle in the sample. As the fraction of stainless steel in the mixtures increased, the heating rate also increased.

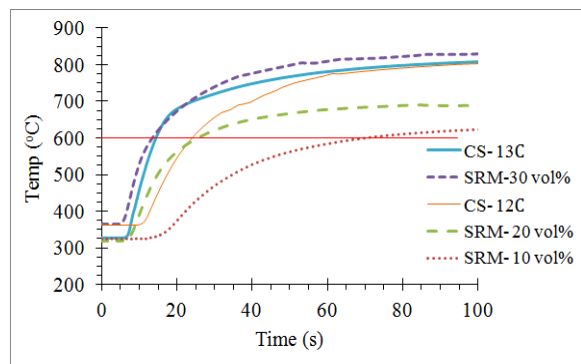


Figure 8: Heating curve of porous composite bodies fabricated by utilizing combustion synthesis (CS- 12C and CS- 13C) and sponge replica method with different stainless steel fraction (SRM-10 vol% - 30 vol%)

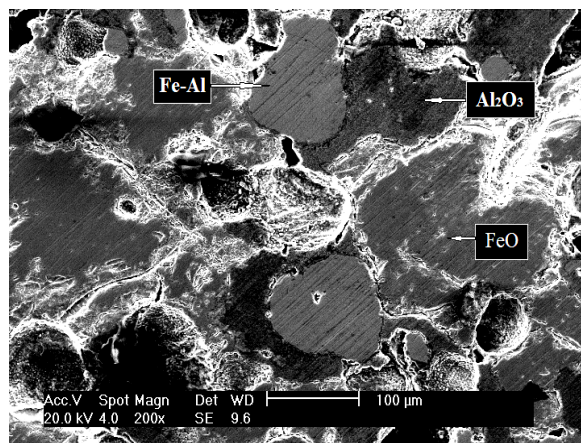


Figure 9: SEM image of microwave-induced substitutional combustion reaction products fabricated at 1200°C

Regardless of the starting materials system and fabrication method, it is clearly shown that both the substitutional combustion reaction and sponge replica method synthesized porous composite bodies can be heated up to the target temperature easily and rapidly, except for the sponge replica method sample with 10 vol% stainless steel, which took longer time. For a 2.45 GHz microwave, SiO₂ is generally considered transparent. Thus, stainless steel particles in the sponge replica method samples played an important role as the absorber of microwave. Microwave was firstly absorbed by the stainless steel particles and subsequently transferred the heat energy throughout the whole sample. Hence, considerable amount of stainless steel particles are needed to achieve a higher heating rate. 600°C was chosen to be the target temperature as referring to the combustion temperature of diesel soot. As reported by Xu et al. [21] and R.D. Nixdorf [22], soot ignition temperature should be > 550°C without a catalyst.

4 Conclusions

- Substitutional combustion synthesis can be carried out utilizing microwave energy. Progress of the combustion wave front can be control when heat generated in the system was insufficient for self-propagation.
- Porous glass-stainless steel composites (SiO₂-RO/SUS) with interconnected pores and high porosity (65-70%) were obtained by the sponge replica method.
- Regardless of the mixture systems and processing conditions, both the ceramic and glass composite body revealed the formation of microstructure consisting of micron sized metal particles, uniformly dispersed and distributed in the ceramic/glass matrix.
- Combustion synthesized sample with porous structure and sponge replica method sample of higher stainless steel volume fraction shows a better and faster heating by microwave.

Acknowledgements

The author wish to thank the Grant-in-Aid of Ministry of Education, Sports, Culture, Science and Technology, Japan, Priority Area on Science and Technology of Microwave- Induced, Thermally Non-Equilibrium Reaction Field (2006–2010) for the financial support given for the realization of this study.

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