Advances on Self-propagating High-temperature Synthesis for Efficient Improvements of Underground and Space Environments Utilizations

Osamu Odawara\textsuperscript{a,b,*}, Anna V. Gubarevich\textsuperscript{b}, Hiroyuki Wada\textsuperscript{a}
\textsuperscript{a}PROSAP Inc., Tokyo, Japan; \textsuperscript{b}Laboratory for Advanced Nuclear Energy, Tokyo Institute of Technology, Tokyo, Japan; \textsuperscript{c}Department of Chemical Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan

In order to maintain and extend sustainable activities of humans, the availability of renewable energies or high efficient energy systems is essential and plays an important role in the design and implementation for further developments forwards. Self-propagation high-temperature synthesis (SHS) which features oxygen-free heat release and high-performance materials synthesis is an economical and energy saving technology effective in exergy loss minimization. The SHS process has been successfully applied to super high heat supplies and high-temperature materials formations under the conditions of inertia forces and steep gradients of pressure and temperature. With such technological merits, various SHS related technologies have been widely performed for in-situ resource utilizations in space exploration and geothermal developments toward space and underground environments utilizations. By validating the experimental conditions and the achievements obtained from the studies on (1) inertia forced composite formations, (2) nitride synthesis with liquid nitrogen and (3) carbon allotropes formation with oxygen deficient flame and plasma spraying, the SHS related technologies would work efficiently even in the environments of low gravity and atmospheric carbon dioxide and nitrogen like Mars. The establishment of the SHS related technologies performed in space and underground environments utilizations would be able to promote further technological progresses exerting actively and flexibly also in other extreme environments such as underwater and disaster-area.

Keywords: \textit{in-situ} resource utilizations, exergy loss, geothermal energy, high performance materials, extreme environments.

1. Introduction

Self-propagating high-temperature synthesis (SHS) is mainly characterized in (1) self-sustainable heating without any oxygen supply and high-temperature furnace, (2) much less energy consumption during its process and (3) highly-pure product synthesized in short time. Compared with conventional processes, the process of SHS can perform high performance materials synthesis and sintering through high reaction temperature generation and exothermic nature with steep thermal gradients and rapid cooling rates. There are a number of reaction parameters which affect the reactions; e.g., reactant particle size, stoichiometry including the use of diluents or inert reactants, ignition temperature, heat loss, reaction temperature, heating and cooling rates and physical conditions of reactants. Depending on selections of characteristic reactants, the SHS technology can be classified for each exothermic reaction nature in reaction propagation and system temperatures by varying the reactants of elements and/or compounds in solid, liquid, gas or mixed phase. The technologies combined with additional techniques on such a joining method and a capsule formation could expand as “stereo fabrication of large-sized matters with hollow ceramic units assembling” [1] and “large-sized light and tough aggregate fabrication with metal and/or ceramic hollow spheres” [2], respectively.

From 1980s, the long metal-ceramic composite-layered pipes and nano-sized metal-ceramic composite-layered particles have been successfully performed under inertia forces of centrifugal force and microgravity with the technologies named as “centrifugal-thermite process” [3] and “micro-gravitational combustion synthesis” [4], respectively. The results obtained under the conditions of inertia forces have nowadays broadened their goals toward casing pipe productions for geothermal development in underground environments and human space access in space exploration beyond low-earth orbit, and various SHS related technologies have been widely performed for space exploration and geothermal developments toward space and underground environments utilizations; for example, additives in propellants, in-situ welding, down-hole sealing [5], drilling technology of flame-jet spallation [6], lunar regolith utilization as “thermal wadis” [7], hybrid thermal protection systems for space probe [8], etc. With such SHS characteristics in economical and energy saving standing-points, the SHS related technologies are recognized to be effective in exergy loss minimization resulting in highly promising possibility of SHS related processes as advanced and respective technologies. The minimization of exergy loss can be attained from the difference between the input and the output with less or limited supplies in extreme environments as concerned.

The approaches relating with the SHS process can work advantageously in extreme environments not only “in space” and “underground” but also “underwater”, “in disaster areas” and others where resources and facilities for life activities would

* Corresponding author  
E-mail address: odawara@justsap-me.org

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be strongly restricted to be resupplied for distant and long-term missions performance. Therefore, none would be enough to develop technologies only with resources used conventionally, so it should be required to utilize resources on other places with different conditions, i.e., in-situ resource utilizations (ISRU) [9]. In order to proceed toward efficient human life support activities in extreme environments, safe and secure bases are required to shield heat, cold, radio-active rays and disaster impacts. With the approaches based on the use of in-situ resources and digital fabrication techniques to construct the infrastructure elements, intense research has been carried out in ISRU and extensively studied with the SHS related technologies. Thermal control of the base and material supply would be one of important challenges for long-term field operations solved by the SHS related technologies. By applying such as inertia force, self-pressure/self-heat control and reactant phase/shape design to SHS processes, the technological qualities in exergy loss minimization would make clear their potentials in extreme environment utilizations and promoting their applicability would make further steps of the challenging missions advance forward. In the present work, the SHS related technologies are mainly focused on the effects of inertia forces and steep gradients in pressure and temperature, and validated with the achievements obtained from the studies on (1) inertia forced SHS, (2) metal nitride SHS with liquid nitrogen and (3) carbon allotropes formation with oxygen deficient flame and plasma spraying.

2. SHS Related Technologies under Inertia Forced Conditions

Since a transportation and fluctuation caused by mass disturbance and heat convection, the SHS process is restrained under inertia forced environments and the reaction propagation features are much changed by the inertia forced conditions. The research and development on simultaneous synthesis and sintering has actively been progressed by applying inertia forces on the SHS process; metal-ceramic composite pipes formed under centrifugal forces on thermite reactions, TiB2-Al composites particles formed under microgravity environment and gas evaporation nano-sized particle synthesis under gas chamber swirling condition as shown in Fig. 1.

The centrifugal-thermite (C-T) process for metal-ceramic composite layered pipes has proposed by applying centrifugal force on thermite reactions and the R&D work on the C-T process have been successfully progressed and achieved the production of long metal-ceramic composite layered pipes [3]. The TiB2-Al composites SHS has also been carried out under microgravity conditions, and it was confirmed that the lack of mass migration and the improvement of wetting between TiB2 and Al under microgravity environment affect the formation of nano-sized composite layered particles [4]. The gas evaporation synthesis of metalofullerene has been conducted by swirling the chamber in which the thermal convection of buffer gas is reduced. The technology has been expected to be a possible ground experimental tool for microgravity experiments [10].

In order to establish the suitable assessment for the utilization of deeper geothermal resources, the C-T pipes have been recently revalidated by reviewing the field tests under much severe conditions at the geothermal power plant in details [11]. As a result of the erosion-corrosion tests of the C-T pipes have been carried out in the conditions of high velocities up to 100 m/s and acidities from pH 2.0 to pH 4.0 of two-phase flows, the erosion-corrosion resistance was superior to the noble stainless steels. The C-T process performed with SiO2 and AlN additives was found to be useful for decreasing the porosity and the FeO content in the ceramic layer basically formed with the reaction system of FeO2 and Al, respectively. Since the nitrides added would play a role as diluent for thermite reaction propagation and the reducing element at high temperatures, the reaction propagates stably and the decomposition of AlN would generate successive reaction after thermite one as “cascade”-like process.

The fine and uniformly distributed composites of TiB2-Al-AlB12 can be performed by the SHS technology with the powder mixtures of Ti (~50 μm), B (~0.6 μm) and Al (~80 μm) blended to comply with the reaction given by:

\[
\text{6 Ti} + \text{24 B} + \text{6 Al} \rightarrow \text{6TiB}_2 + \text{5 Al} + \text{AlB}_{12}
\] (1)

Compared to the products obtained in the terrestrial condition, the particle distribution seemed to be more uniform when synthesized under the microgravity condition. The particle size of the products is almost the same as that obtained on ground except that of the product from Ti + 4B powder compact which is longer in its needle-like structure than that on ground. In the case of the Ti-Al-B system, it could be found fine composite-layered particle of TiB2 and Al-AlB12 synthesized under the microgravity condition, where the Al-AlB12 layer of about 40nm surrounds TiB2 particle of about 0.3 μm. The investigation on SHS as an ISRU in Space exploration has been carried out with the system of Zr-Al-Fe2O3 to make the oxide component of ZrO2-Al2O3. The samples were prepared by packing the above powder mixtures in Ta tubes and setting the tubes in the Ti+4B+Al and Ti+C powder mixture compacts (60% of packing density), respectively. Since the induction temperature of the present thermite reaction, Zr+3.25Al+2.29Fe2O3, was about 700 K, the thermite reaction could be also induced under microgravity conditions by heating with Ti+4B+Al combustion reaction [12]. The convective heat and mass transfer has a considerable influence on the products of materials synthesis in gas and liquid phases. By applying centrifugal and Coriolis force to gas in a chamber with a central heater, the convection reduction was confirmed to be effective in gas evaporation synthesis and chemical vapor deposition processes. The yield of C60 fullerene synthesized by the gas evaporation was compared between the chamber swirling and microgravity condition formed in a dropping capsule. As a

![Figure 1](image-url)

Figure 1. SHS related technologies applied under various inertia force conditions. [I]: Centrifugal-thermite process, [II]: Microgravitational SHS, [III]: Swirling chamber method.
result, almost the same values were obtained at lower pressure up to about half of the atmospheric pressure. In higher pressure condition, the yields obtained in microgravity decreased more rapidly with pressure than those with the chamber swirling. The difference in the yields between under microgravity and chamber swirling would be caused by some effect of natural convection because the natural convection became stronger with gas pressure.

3. SHS Related Technologies under Steep Gradients of Pressure and Temperature

It is important to make clear the mechanism of ignition and propagation in reaction because the micro-reaction of reactant leads to the macro-reactions of the formed zone propagation in the SHS process. Therefore, it is the main key point for the SHS performance to control the optimum conditions of reaction ignition and propagation under proper system temperature, pressure and others. The basis of the technology comes from the thermo-chemical concepts used in the field of propellants and explosives. The reaction releases the maximum energy when the reductive mixture follows its chemical formula. The extrapolation of this concept to ceramic compounds synthesis means that metals should also be considered as reducing elements with the valences they have in the corresponding products. Experimentally, the chemical balance is used to calculate the appropriate amounts of the selected starting materials following its chemical formula designed for expected product composition. This concept is particularly useful when thermodynamic calculations are difficult to carry out for lack of the relevant parameters and it has been shown that there is a direct correlation between the results derived from the valence balance and those based on heat of formation or bond energies. Establishing the optimum reaction parameters for synthesizing a material is based on obtaining a fundamental understanding of the mechanism how to control each reaction of SHS related processes, which has been one of the most active research areas. The SHS related technologies are mainly focused on the effects of steep gradients in pressure and temperature as follows:

1) metal nitrides synthesis and sintering with liquid nitrogen; the pressure in a closed vessel was drastically increased (~2MPa/s) with evaporation of liquid nitrogen during titanium nitride SHS process, then the product was self-sintered [13, 14], and

2) carbon-allotropes formation with oxygen deficient flame and plasma spraying: a diamond/gypsum-flower-like carbon deposition process was performed by oxygen deficient flame using an acetylene/oxygen torch [15, 16] and electromagnetically accelerated plasma spraying [17].

3.1. Metal nitrides synthesis and sintering with liquid nitrogen

Titanium nitride synthesis has been also investigated by sustaining the nitride SHS process of titanium powder compacts set in a closed vessel filled with liquid nitrogen [14]. The characteristic features of the present SHS related technology are the accelerating pressure in the vessel following sample heating through the reaction propagation of Ti-N system, which results in a specific structure formation of the products. It has been confirmed that the pressure in the closed vessel was drastically increased through the reaction propagation, resulting in the product self-sintered. Figure 2 shows typical experimental results of temperature and pressure changes of the sample powder compact placed in the closed vessel filled with liquid nitrogen. In the case of TiN combustion synthesis with Ti powder compact of 0.25 mole (15mm in diameter and 30mm in height) in a closed vessel almost fully filled with liquid N₂, the temperature reached about 2600 K within 2 seconds and the pressure increased by more than 20 MPa within 10 seconds after the ignition. The sample temperature reached 2600 K within 2 seconds and pressure increased by more than 20 MPa within 10 seconds.

Figure 2. Typical experimental results of sample temperature and pressure inside the vessel during the TiN SHS experiment in the closed vessel filled with liquid nitrogen.

Figure 3. SEM micrographs of product fracture surfaces obtained by TiN SHS with liquid nitrogen. (A): under closed condition, (B): under atmospheric condition.

Figure 4. SEM micrographs of diamond and GF-like carbon synthesized by changing the substrate temperature and reactant ration of O₂/C₂H₂. (A): diamond at 1123 K and 0.90, (B): GF-like carbon at 1423 K and 0.80.
In vacuum. MoS2 powders have been used as superior lubricates [18]. Tribology plays an important role to secure the machines and control the acquisition of sp3 diamond from sp2-bonded carbon. After the deposition with high density, and the diamond film could nucleate on the carbon surface in the process of its growth, which may lead to the possibility of the GF-like carbon as precursor for the diamond synthesis. The GF-like carbon can be formed in temperature ranges of substrate from 1323 K to 1573 K, and the ordered graphitic sheets of diamond seeds appeared on GF-like carbon in the range of 1473 K-1523 K. The diamond can nucleate on the GF-like carbon surface along the edge of graphitic sheets soon after the deposition with high density, and the diamond film could be formed after a few minutes deposition. The GF-like carbon may play a role as a seed of diamond growth, which should control the acquisition of sp3 diamond from sp2-bonded carbon. The friction tests of detonation nanodiamonds have been also carried out in order to judge the lubricative and abrasive potentials [18]. Tribology plays an important role to secure the machines and apparatuses for long term and maintenance-free operations in vacuum. MoS2 powders have been used as superior lubricants for exposure components in vacuum such as remote manipulator system and equipment exchange unit for their maintenance-free operation more than 10 years. It was confirmed that the nanodiamonds with average aggregate size of 75 nm formed a uniform lubricating layer with sliding against SiC balls and showed quite low friction coefficient of 0.03 under moderate conditions of 0.5 N as applied load and 3.5 mm/s sliding speed.

### 3.2. Carbon allotropes formation with oxygen deficient flame and plasma spraying

By operating an oxyacetylene combustion flame at O2/C2O2 ratio of less than 1.0, the aggregates of peculiar carbonaceous species called gypsum-flower (GF)-like carbon with sp2-bond could be obtained. The micrograph of diamond synthesized at 1123 K of the substrate temperature and 0.90 of O2/C2O2 ratio is shown in Fig. 4(A), and that of GF-like carbon at 1423 K and 0.80 is in Fig. 4(B). Diamond phase was revealed to appear on the GF-like carbon surface in the process of its growth, which may lead to the possibility of the GF-like carbon as precursor for the diamond synthesis. The GF-like carbon can be formed in temperature ranges of substrate from 1323 K to 1573 K, and the ordered graphitic sheets of diamond seeds appeared on GF-like carbon in the range of 1473 K-1523 K. The diamond can nucleate on the GF-like carbon surface along the edge of graphitic sheets soon after the deposition with high density, and the diamond film could be formed after a few minutes deposition. The GF-like carbon may play a role as a seed of diamond growth, which should control the acquisition of sp3 diamond from sp2-bonded carbon. The friction tests of detonation nanodiamonds have been also carried out in order to judge the lubricative and abrasive potentials [18]. Tribology plays an important role to secure the machines and apparatuses for long term and maintenance-free operations in vacuum. MoS2 powders have been used as superior lubricants for exposure components in vacuum such as remote manipulator system and equipment exchange unit for their maintenance-free operation more than 10 years. It was confirmed that the nanodiamonds with average aggregate size of 75 nm formed a uniform lubricating layer with sliding against SiC balls and showed quite low friction coefficient of 0.03 under moderate conditions of 0.5 N as applied load and 3.5 mm/s sliding speed.

### 4. Extreme Environment Utilizations Promoted by the SHS-Related Technologies

Many efforts have been continuously undertaken toward human space activities and presence in space exploration. These activities include the participation in future exploration to planets and satellites far from the earth and further even with construction of the outpost there. The extended stay of humans in space requires multiple resources of which energy and radiation protection are essential, and the availability of electrical energy and high performance materials is much useful in space exploration and essential for space utilization. The technologies of survival system formations including the availability of renewable and/or self-sustaining energy also play a critical role in the extreme environment utilizations as well as ISRU for long-term field operation such as sustainable lunar-night [19] and longer duration power generation missions [20]. The R&D targets for strengthening life support systems can expand not only in space but also underwater, underground and even disaster-area extreme environments, and the SHS related technologies can work practically in fulfilling efficient for the goal of the technological success. The resources such as metal oxides that exist on planets or satellites could be refined, and utilized as a supply of heat energy, where the SHS related technologies would stand as a hopeful technology for such requirements.

The investigation carried out on “natural volcanic occurrence of H2 fuel production from magma” [21] as an underground environment utilization has led the SHS related technologies advance to a new development on H2 extraction and carbon dioxide reduction and also guided to underwater environment utilization, especially in the fields of undersea resources such as submarine hydrothermal ore and methane hydrate [22]. The magma reaction with H2 extraction principally proceed on the reducing action of basaltic magma on injected water under high-pressure condition, which chemical interaction causes the oxidation of ferrous components in the basalt and the production of H2:

\[ 2 \text{FeO (magma)} + \text{H}_2\text{O (fluid)} \rightarrow \text{Fe}_2\text{O}_3 (\text{magma}) + \text{H}_2 (\text{fluid}) \]  

(2)

Fresh basaltic lava contains on the order of 10wt% FeO and 1 to 2wt% Fe2O3. These components are present as dissolved constituents within the silicate melt and in minerals (e.g., olivine, pyroxene, magnetite) suspended in the magma. The predominance of ferrous over ferric oxide in basaltic magma is in part responsible for the reported concentrations of H2 and carbon monoxide observed in the above volcanic gas collections. As the technologies applied to life-support technologies concentrating on air and water recycling, the Closed Ecology Experimental Facilities with “Sabatier reaction” system has already been established on the International Space Station (ISS) [23]. The Sabatier reaction, which converts CO2 to useful products with H2 generates CH4 and H2O over efficient catalysts, is a key technology for establishing the closed circulatory system in space exploration. The atmospheric CO2 is separated and concentrated with zeolite and mixed with H2 in the presence of a ruthenium catalyst at temperature less than 600 K, then the mixture reacts to produce H2 and CH4 by the Sabatier reaction shown as follows:

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]  

(3)

The Sabatier reaction is highly exothermic (ΔH = -165 kJ/mol). The H2 for this reaction is supplied from the process of water electrolysis:

\[ 2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2 \]  

(4)

The O2 obtained from the reaction (4) has been used for atmospheric regeneration on the ISS. The H2 can be recycled back by the application of the Sabatier reaction. Any effective utilization of CH4 synthesized in the Sabatier reaction has not been done, however, if appropriate methods of methane utilization could be developed, limited resources will be used more effectively. For establishing further closed circulatory system, the present work has been carried out specially to focus on more efficient environments of closed-loop CH4 utilization; not only combustion but also steam reforming, thermal pyrolysis, dry reforming, and so on. The first primary exergy source in the system is the solar energy including direct irradiation and all secondary forms such as biomass, water, wind and waves. The second source would be the energies extracted from such as heat and tidal flow on ground or underground. These exergy sources might be inexhaustible and available for human lifetime. In recent years, power cycles with supercritical fluids of CO2 and H2O have been actively investigated for efficient improvements in exchange of thermal energy to electrical energy. The 1 MW-class facility with closed circulating loop of supercritical CO2 has been built, and it was...
anticipated that there is not any major problem in machinery design and operation efficiency with the turbine and combustor for scaling up the technology up to higher power levels (24, 25). The closed circulating loop geothermal power has been also designed to produce a few MW of existing non-productive wells. If such a closed-circulating loop system is established, it would be possible to prevent the loss of refrigerant and keep the refrigerant stream from interacting with water and minerals with less scaling and corrosion. Concepts of high-temperature heat to electricity conversion have been proposed in various fields aimed with the waste-heat; thermo-photovoltaic energy conversion, acoustic-to-electric power conversion, thermo-electric tube, etc. The present SHS related technologies can provide a high-temperature environment with simple processes, and it is meaningful to merge the combination with the system related to effective energy conversion. Such approaches will be one of promising technologies applicable in extreme environments utilizing toward improvements of sustainable human activities.

5. Conclusions

The SHS related technologies have been successfully performed not only for high-performance powders production but also as highly efficient resource utilization in energy saving with highly efficient ISRU with the aid of mineral resources. With the achievements obtained from the studies on the SHS related technologies on inertia force influences, the potentials of the SHS related technologies have been evaluated through nitride SHS process with liquid nitrogen and carbon allotropes formation with oxygen deficient flame and plasma spraying. The SHS related technologies are expected to work efficiently even in the environments of low gravity and atmospheric carbon dioxide and nitrogen, which can promote further technological progresses exerting actively and flexibly also in other extreme environments such as underwater and disaster-area.

For the establishment of sustainable life support system, it is important to advance the R&Ds for providing reuse systems of waste-heat and efficient heat sink. The SHS related technologies would sufficiently respond to such thermal problems and provide effective supplies for various situations of extreme environments although additional developments are essential. To prove the efficiency of the technology, the feasibility of long-duration sustainable application has to be made clear with in-situ power and resource utilization design.

References