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Combustion Synthesis Technology for a Sustainable Settlement Overnight

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| Article info | Abstract |
|---------------------------|--|
| Received: | Space technology has been developed for frontier exploration not only in low- |
| 18 July 2017 | earth orbit environment but also beyond the earth orbit to the Moon and Mars, |
| Received in revised form: | where material resources might be strongly restricted and almost impossible to be resupplied from the earth for distant and long-term missions performance toward |
| 27 September 2017 | "long-stays of humans in space". For performing such long-term space explorations, |
| Accepted: | none would be enough to develop technologies with resources only from the earth; |
| 24 November 2017 | it should be required to utilize resources on other places with different nature of |
| | the earth, i.e., <i>in-situ</i> resource utilization. One of important challenges of lunar <i>in-situ</i> resource utilization is thermal control of spacecraft on lunar surface for long- |
| | lunar durations. Such thermal control under "long-term field operation" would be |
| | solved by "thermal wadis" studied as a part of sustainable researches on overnight |
| | survivals such as lunar-night. The resources such as metal oxides that exist on planets or satellites could be refined, and utilized as a supply of heat energy, where |
| | combustion synthesis can stand as a hopeful technology for such requirements. |
| | The combustion synthesis technology is mainly characterized with generation of |
| | high-temperature, spontaneous propagation of reaction, rapid synthesis and high |
| | operability under various influences with centrifugal-force, low-gravity and high vacuum. These concepts, technologies and hardware would be applicable to both |
| | the Moon and Mars, and these capabilities might achieve the maximum benefits |
| | of <i>in-situ</i> resource utilization with the aid of combustion synthesis applications. |
| | The present paper mainly concerns the combustion synthesis technologies for |
| | sustainable lunar overnight survivals by focusing on "potential precursor synthesis and formation", " <i>in-situ</i> resource utilization in extreme environments" and "exergy |
| | loss minimization with efficient energy conversion". |

1. Introduction

Combustion synthesis has gathered reputations as a unique and effective process not only for synthesizing high-temperature materials but also as a quickly super-heating chemical oven. By controlling combustion propagation and consequentially formed high-temperature field, the combustion synthesis technology could make it possible to sinter and form products during its process. The basis of the technology comes from the thermo-chemical concepts used in the field of propellants and explosives, and the reaction releases the maximum energy when the reductive mixture follows its chemical formula. There are a number of reaction parameters which affect combustion synthesis reactions; reactant particle sizes, stoichiometric compositions even with the use of diluents or inert reactants, green densities, thermal conductivities of reactants and products, ignition temperature, heat loss, combustion temperature, heating and cooling rates and phase conditions of reactants in solid, liquid or gas. Many of these parameters are interdependent and have a significant effect on morphologies and properties of final products. 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 combustion synthesis processes, which has been one of the most active research areas on combustion synthesis.

An early application of combustion synthesis was in thermite reactions, which synthesize metal elements and/or alloys with aluminum oxides

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from metal oxide and aluminum powders. In our previous work, combustion synthesis has been applied to in-situ formation of ceramic linings inside metal pipes and vessels under centrifugal force for product densifications and/or directional control of composite formations. Main characteristics of the technology are in a large amount of reaction heat generated by the combustion synthesis process, centrifugal force applied to the reaction products and the behavior of reaction propagation under the influence of centrifugal force which was confirmed through long-sized ceramic lined pipe development [1]; the combustion synthesis process proceeds rapidly along the inner hollow surface of the reactant formed under the centrifugal effect first and then into the reactant layer simultaneously in the radial direction resulting in homogeneous quality in the direction of pipe length under the conditions of proper amount of thermite powders and centrifugal force. The technology reveals unique characteristics on mechanical properties of the produced ceramic-lined pipes; the innermost ceramic layer is compressed by the intermediate metal and outer steel pipe layers and the stress in the outer steel pipe layer graded from tension to compression toward larger radial direction in both pipe circumference and length. By forming the intermediate metal layer with residual tensile stress, the ceramic-lined pipes produced by the process can stand in high potential with residual compression stress on surface compared to those by other conventional ceramic lining techniques. The characteristic performance of the combustion synthesis process under centrifugal force has guided further activities toward combustion synthesis applications in extreme environments of space exploration under microgravity and others.

For performing space technology for frontier exploration, none would be enough to develop only with the resources from the earth. Therefore, it must be investigated to utilize the resources on other places where the nature would be different from that of the earth. It is expected that the resources such as metal oxides that exist on planets or satellites could be refined, and utilized as useful supplies of heat energy, where combustion synthesis technologies can stand as hopeful ones for such requirements, i.e., in-situ resource utilizations (ISRU). By establishing the optimum parameters under fundamental understanding of the controlling reaction mechanisms relating with each combustion reaction system, the combustion synthesis technologies can be simply applied to operate under various conditions of "extreme environments" such as low gravity and high vacuum in space not only for synthesizing high-temperature materials but also for super-heating chemical ovens. Regarding ISRU, key elements of oxygen and nitrogen from in-situ resources in fields would be able to guarantee the flexibility when scheduling and managing future space missions [2].

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 combustion synthesis process can stand as a hopeful technology for such requirements. In order to carry out experiments and make long-stays of human beings on extraterrestrial planets, permanent habitats or settlements are required to shield heat, cold, cosmic rays and meteorite impact. For constructions of settlements on the Moon and Mars, to transport structural elements from Earth and assemble them at the destination is expensive and infeasible for large-scale implementation. 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 specifically lunar overnight ones have been extensively studied with the combustion synthesis technology. Thermal control of spacecraft and material supply on lunar surface for long-lunar durations, which is one of important challenges of lunar ISRU under "long-term field operation", would be solved by the combustion synthesis technologies carried out as a sustainable lunar overnight survival research with lunar regolith utilization as "thermal wadis" [3].

Under such combustion synthesis characteristics in economical and energy saving standing-points, the combustion synthesis technology is recognized as one of typical methods useful in "exergy loss minimization", which might result in highly promising possibility of combustion synthesis and related processes as advanced and respective technologies. Since 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 in the present work; not only "on ground" but also "in space", "underground", "underwater" and "disaster-stricken area", where the approaches with advanced combustion synthesis technologies would work much effectively.

The present paper mainly concerns the applications of combustion synthesis technologies relating with potential precursors formation and exergy loss minimization connecting with the ISRU efficient to sustainable survivals overnight.

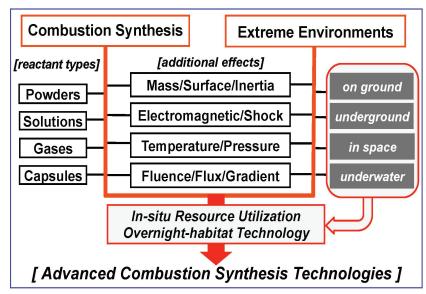


Fig. 1. Schematic design systematically categorized in extreme environments with additional effects and varieties of reactant selections.

2. Potential technology expected in extreme environments

Key features of combustion synthesis are to initiate chemical reactions with partial heating and to provide heat for driving the accomplishment of compound synthesis through the reaction itself and not by an external source. The combustion synthesis technology is advantageously applied to ISRU in space without any oxygen supply, which can initiate chemical reactions with partial heating and to provide heat for driving the accomplishment of compound synthesis through the self-sustaining reaction without any other external source. Since the heat generated by the exothermic reaction is sufficient for applications in heat treatments of various materials, the technology has been world-widely investigated not only in fundamental purpose but also in practical development.

Combustion synthesis has emerged as an economical method for oxygen-free synthesis and power-free processing of high-temperature materials such as carbides, borides, nitrides, oxides, intermetallic compounds, etc. Depending on selections of reactants including natural resources, combustion synthesis can be classified not only in self-propagating high-temperature synthesis of solid-state reaction systems but also in solution, emulsion, low-temperature and gel ones. Such reactant elements and compounds are varied in complex phases with solid, liquid and gas; each nature of exothermic reaction characterizes the process of combustion propagation and high-temperature gradients formation. As technological and practical applications performed in previous R&Ds, various productions have been proposed and investigated as follows; abrasives, cutting tools and polishing powders, resistive heating elements, shape memory alloys, high temperature inter-metallic compounds, electrodes for electrolysis of corrosive media, coatings for containment of liquid metals and corrosive media, powders for further ceramic processing, thin films and coatings, functionally graded materials, composite materials and functional materials. Compared with conventional processes, characteristics of combustion synthesis are in the generation of high temperatures, resulting in higher purity products by volatilizing low boiling point impurities. Since the exothermic nature of the process does not need any expensive processing facilities and equipment, the short reaction time can result in low operating and processing costs, the high thermal gradients and rapid cooling rates can give rise to new non-equilibrium or metastable phases and various materials can be synthesized and consolidated into a final product in one step by utilizing the chemical energy of the reactants.

As shown schematically in Fig. 1, the combustion synthesis technologies have been advantageously applied to high-temperature studies not only in space exploration but also in extreme environments on ground, underground and, even recently, underwater. Since combustion synthesis mainly consists of reaction induction and propagation with product synthesis and its structure formation, thermo-gravitational flows of gas and liquid phases affect the propagation rate and the subsequences.

Based on the process of combustion synthesis with rapid and continuous propagation of exothermic reaction, it is possible to improve the technology more flexibly with the effective aids of external additions and emphasize its potential benefits. Utilizations of natural minerals as the reactants for combustion synthesis can be also evaluated and applied to the production of submicron-sized particles. In view of recent developments on nanotechnology and others, the possibility of combustion synthesis can expand much wider areas and its process can be controlled much precisely in fundamental and practical approaches. By handling the particle sizes of aluminum powders from micrometer to nanometer, for example, the concept of combustion synthesis would cover the following three type reactions of Al-H₂O with the products of Al₂O₃, AlOOH and Al(OH)₃, respectively;

 $2AI + 3H_2O = AI_2O_3 + 3H_2 \dots \dots \dots (1)$

 $2AI + 4H_2O = 2AIOOH + 3H_2 \dots (2)$

 $2AI + 6H_2O = 2AI(OH)_3 + 3H_2 \dots$ (3)

The AlOOH can be obtained by Eq. (2) with nano-sized Al particles and that of Eq. (1) is with submicron-sized ones. The Al(OH)₃ following Eq. (3) would appear mainly with larger Al particles. Researches on aluminum and water mixture have been much attractive recently not only in the field of propellants and explosives [4] but also in the field of hydrogen extraction and storage [5], and a mixture of AlOOH and Al(OH)₃ may be a candidate of BNF(boehmite nanofiber) sol which has been invested as ultra-low density transparent porous bulk materials [6].

In order to evaluate the combustion synthesis process under the balance of energy and materials with useful qualitative changes in energy, exergy analysis based on the second law of thermodynamics can provide an alternative means of assessing and comparing method in system of material production processes alternating the insufficiency of conventional estimation in energy consumption. The concept of exergy has been widely applied to assess various systems in which the qualitative loss of energy in each process. As a time- and energy-consuming procedure, the combustion synthesis technology is deemed highly attractive from the perspectives of minimized operating time and maximized energy savings in comparison with conventional method for heat treatment, pulverization and activation treatment. The conventional estimation of energy consumption that is based on the balance of energy and materials is essentially insufficient for evaluations of material production processes, since the qualitative changes in energy are not considered. Energy is always conserved in the energy flow diagram, and the waste-heat in processes carries large amount of energy into environments as exhaust gases. In the exergy flow diagram, the exergy of exhaust gases is evaluated to be comparable with that of the waste-heat because the temperature of the waste-heat is close to ambient one.

3. R&D achievements with the aids of inertiaforce and excess-heat

Combustion synthesis technologies can make a rapid, versatile and near net shaping process possible without any oxygen supply other than the system, establish high temperature environment by reaction heat generation, and simply operate under various conditions of high and low gravities, high and low pressures even high vacuum, etc. Compared with conventional processes, most of the combustion synthesis technologies can perform highly purified product synthesis through high reaction temperature generation and exothermic nature with steep thermal gradients and rapid cooling rates. These advantages have made researchers proceed actively in exploring the combustion synthesis approach of new and improved materials with specialized mechanical, electrical, optical and chemical properties. The R&Ds have been also devoted to improvement of the final product quality, particularly with respect to porosity reductions. Combustion synthesis has emerged as an important technology for the synthesis and processing of advanced materials. Establishments of the optimum reaction parameters for synthesizing a material, which are interdependent and significant on the final product morphology and properties, are based on obtaining a fundamental understanding of the controlling reaction mechanisms in each combustion reaction system.

The consecutive orders of the basic process in combustion synthesis can give the essential concept for the determination of the synthesis mechanisms with ignition and propagation of reactions. The chemical and physical processes are identified, which affect the structure formation during the combustion synthesis:

(a) heat transfer from the reaction zone to the non-reacting zone,

(b) phase transition of solid reactants to molten dispersed to gas phase,

- (c) chemical reaction propagation,
- (d) crystalline formation of products,
- (e) crystal growth and recrystallization,
- (f) phase transition of products and
- (g) structure ordering of products.

The steps of (a) - (d) occur during heating process and those of (e) - (f) occur during cooling one. Therefore, the control of the combustion propagation process is much important for its performance.

Several R&D studies have been carried out specially with the originally designed aids of additional forces and heat of reaction as shown in Fig. 2. The combustion synthesis and related technologies shown in Fig. 2[I] are performed with the aids of centrifugal force ([I]-<1>) and microgravity ([I]-<2>). High pressure hysteresis derived by phase-transition from liquid to gas and the activation and evaporation of fuel and solution with excess waste-heat are designed as typical applications of combustion synthesis shown in Figs. 2[II] and 2[III], respectively.

TiN combustion synthesis in liquid nitrogen under atmospheric pressure has been performed by

changing the position of reaction induction point; the upward propagation is more effective for getting higher reaction conversion ratio than the downward one. Since both thermal flow and evolved nitrogen gas are considered to propagate upward, TiN conversion ratio is much higher in the case of upward reaction propagation compared to the downward one. In the case of TiN combustion synthesis with Ti powder compact of 0.25 mole (15 mm in diameter and 30 mm in hight) in a closed vessel almost fully filled with liquid N₂ as shown in Fig. 2[II]-<1>. As shown in Fig. 2[II]-<2>, the temperature reached about 2600 K within 2 sec and the pressure increased by more than 20 MPa within 10 sec after the ignition. The sample temperature reached 2600 K within 2 sec and pressure increased by more than 20 MPa within 10 sec. In the case with the Ti powder compact of 1 mole ($25 \text{ mm} \times 43 \text{ mm}$), the pressure of the closed vessel drastically increased by more than 60 MPa (approximately 20 MPa/s). The pressure hysteresis of the process mkes the product shrink and become dense, resulting in its density as 4.96×10^3 kg/m³ (about 99% densified TiN_{0.87}).

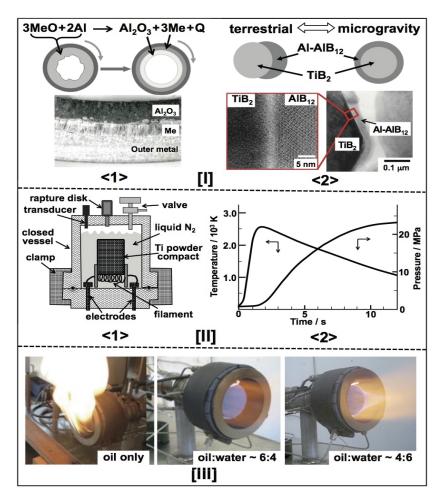


Fig. 2. Typical performances with the aids of inertia-forces and excess-heat. [I] Gravitational composite formations under high-g <1> and μ -g <2>. [II] TiN combustion synthesis with liquid N₂; <1> closed-type apparatus, <2> T and P changes during the process. [III] Self-circulation with activated waste-heat.

4. Unique progresses in precursor synthesis and formation

Influences of temperature changes in product particle sizes are illustrated as shown in Fig. 3[I], in which dependences of crystal nucleation and growth to the product melting point are also explained for the determination of particle size variation. Temperature changes with chemical ovens of Ti-C and Ti-B-Al combustion synthesis systems at the hollow part (10 mm) in cylindrical compact (25 mm \times 30 mm). In the process of its performance, two types of chemical ovens have been used for increasing the conversion ratio as shown in Fig. 3[II]; Ti+B+Al and Ti+C reactant systems for 1000 K- and 1500 K-class ovens, respectively. As shown in Fig. 3[III], graphitic textures and crystalline orders of carbonaceous species are possible directly to transform from sp² carbon to sp³ one, i.e., diamond phase, which could lead potential investigations relating with phase transitions for diamond formation from carbonaceous precursors.

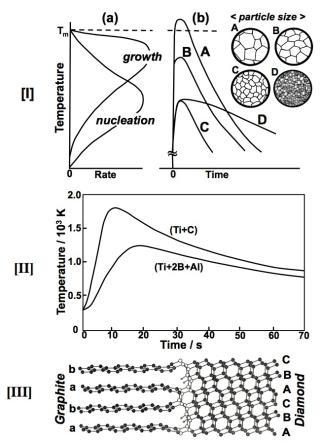


Fig. 3. Precursors supplies followed by nano- and lowdensity compounds synthesis. [I] high-temperature gradients; Ti-B-Al systems, Sr-Al-O systems. [II] chemical oven and waste-heat utilization; B-C systems, Ti-N systems. [III] phase transformation design from graphitic prism to diamond nucleation.

Combustion synthesis has been mainly improved from "compound synthesis" of powders and layered- and wire/needle-shaped composites and "low-density formation" in light, porous and fluff products to "precursor synthesis and formation" for networked and transformed functional materials. Each of these categories is effectively performed with directionally propagating solid-state reaction, solution combustion synthesis, generated reaction heat as heat source and high temperature/pressure gradient with flame or detonation as follows:

1) Ti-B-Al system for TiB_2 -AlB₁₂-Al nano-composite particle synthesis; in the case of the Ti-Al-B system, it could be found fine composite-layered particle of TiB_2 and Al-AlB₁₂ synthesized under microgravity condition, where the Al-AlB₁₂ layer of about 40 nm surrounds TiB_2 particle of about 300 nm [7];

2) Sr-Al-O system for phosphor matrix nano powder synthesis by solution combustion synthesis; nanoparticles were synthesized under precise control of crystalline structure and distribution of sizes from metal nitrate/fuel solutions [8] and laser ablation in liquid [9];

3) B-C system for B_4C formation; with the aid of TiC combustion synthesis as a chemical oven;

4) Ti-N system with liquid nitrogen; the pressure in a closed vessel was drastically increased (~ 20 MPa/s in the case with 1 mole of Ti powder compact) with evaporation of liquid nitrogen during nitride combustion synthesis, then the product was shrunk and densified up to 99% [10, 11];

5) C-allotropes formed with combustion-flame method and detonation technology; a diamond/ gypsum-flower-like carbon deposition process was performed by a combustion flame method using an acetylene/oxygen torch [12, 13];

6) B-N-O-H system as a precursor for BN synthesis [14];

7) metal-C system synthesizing carbides as precursors for functional carbon, e.g., grapheme [15].

Figures 4, 5 and 6 show typical experimental results of the R&Ds on combustion synthesis related with the Ti-B-Al, B-C and C-allotropes systems, respectively.

4.1. TiB₂-AlB₁₂-Al nano-composite synthesis

 TiB_2 and Al base composite powders, which will offer a weight-saving improvement in stiffness, were produced by combustion synthesis of Ti, Al, and B ternary powder mixtures. Finely dispersed TiB_2 has been synthesized by combustion synthesis with a powder mixture of Ti, B and Al

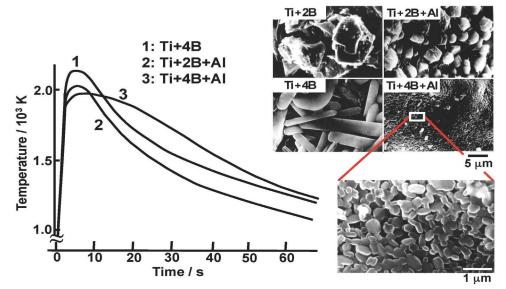


Fig. 4. Typical results obtained on Ti-B-Al system for TiB₂-AlB₁₂-Al nano-composite particle synthesis.

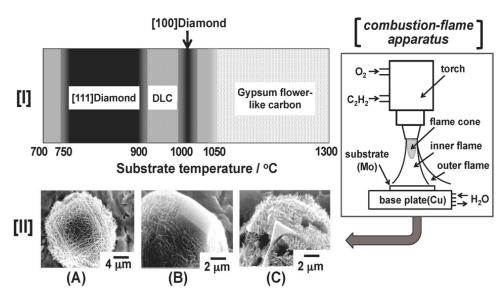


Fig. 5. Typical results obtained in the R&Ds on C-allotropes formed with a combustion-flame method. [I] : Temperature ranges for carbon allotropes formation; [II]: Changes from gypsum flower-like carbon to diamond.

in the molar ratio of 1:4:1, and the grain size of the synthesized TiB₂ is $< 0.5 \mu m$, which is much smaller than that obtained from combustion synthesis with a powder mixture of Ti, B and Al in the molar ratio of 1:(n+2):0 or 1:2:n (n = 0, 1, 2 or 3). The cooling rate in the process of combustion synthesis with the Ti+4B+Al powder mixture is found to be much smaller than that with the Ti+2B+2AIor the Ti+4B one. The heat of formation is a little higher in the former compared to the latter because of A1B₁₂ formations. It is considered that the reaction of Al-B system at high temperature would proceed and supply a little excess heat to the reaction system behind the main combustion front following the reaction of Ti-B system, resulting in the increase of TiB₂ nucleation ratio.

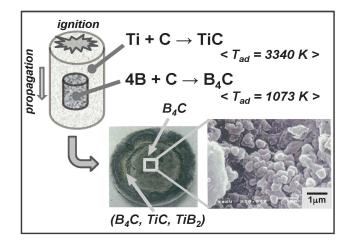


Fig. 6. Typical results obtained in the R&D on B-C system for B_4C formation with the aid of Ti-C combustion synthesis as a chemicall oven.

4.2. C-allotropes formation by a combustion flame method

By operating a method of combustion-flame with the apparatus shown in Fig. 5, the aggregates of peculiar carbonaceous species called gypsumflower-like carbon (GFC) with sp²-bond could be obtained. Diamond phase was revealed to appear on the GFC surface in the process of its growth, which may lead to the possibility of the GFC as precursor for the diamond synthesis. The GFC can be formed in temperature ranges of substrate from 1050 to 1300 °C, and the ordered graphitic sheets of diamond seeds appeared on GFC in the range of 1200-1250 °C. The diamond can nucleate on the GF 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 GFC may play a role as a seed of diamond growth, which should control the acquisition of sp³ diamond from sp²-bonded carbon.

4.3. B-C system for B_4C formation with a Ti-C chemical oven

Combustion of B and C mixtures for the formation of B_4C phase becomes possible if the composition is designed for the addition of more exothermic reactions. The direct combustion synthesis of B and C mixtures has not been completed because less heat of reaction of its system. By covering the powder compact of B and C mixture with that of Ti and C mixture as shown in Fig. 6, the B_4C combustion synthesis can be performed with the aid of the reaction heat of TiC combustion synthesis. The chemical oven designed with a highly exothermic reaction of Ti and C mixture shell has been successfully employed to synthesize B_4C . The present chemical oven has been recently applied to Al_4SiC_4 combustion synthesis.

5. ISRU and lunar overnight survival research

It is important to carry out experiments and live longer durations on extra-terrestrial planets, permanent habitats for shielding heat, coldness, darkness, cosmic rays and meteorite impact. Due to negligible lunar atmosphere or scarce Martian atmosphere, spaceship landing and launching off will cause frozen ice crystal from the fuel and gravels flying at a fast speed far away. High speed flying objects including micrometeorites threaten devices and inhabitants around. With solid landing pads and protective walls, landing and launching off will be much safer. Most proposals for construction on the Moon and Mars are based on transporting structural elements from the earth and assembling them at that place. Such approach is expensive and infeasible for large-scale implementation. For survivals on lunar surface assets during periods of darkness when the lunar environment is very cold, concepts of "thermal wadis" are much attractive when applying the combustion synthesis technologies. Thermal wadis are engineered sources of stored solar energy using modified lunar regolith as a thermal storage mass that can enable the operation of lightweight robotic rovers or other assets in cold, dark environments without incurring potential mass, cost, and risk penalties associated with various onboard sources of thermal energy.

According to "NASA ISRU Capability Roadmap" [16], the NASA initiated developments of three oxygen extraction systems which bound the risk and performance ranges of all of these methods; (1) hydrogen reduction, (2) carbothermal reduction and (3) molten electrolysis. Even though each of these methods are different and extract oxygen from different minerals in the lunar regolith which is made up of greater than 40% of oxygen, they do all share common aspects such as regolith excavation, handling, and sorting, as well as oxygen and reactant cleaning/contaminant removal, recycling, and storage. If humans ever hope to explore and colonize space beyond low-earth orbit, the essential goals of ISRU are to reduce the cost of human missions and to enable the establishment of long-duration manned space bases constructed on the Moon, Mars or others.

Major areas of ISRU which may result great benefit to future robotic and human exploration architectures have been shown as follows; (1) mission consumable production such as propellants, fuel cell reagents, life support consumables, and feedstock for manufacturing & construction, (2) surface construction for radiation shields, landing pads, walls, habitats, etc., (3) manufacturing and repair with in-situ resources with spare parts, wires, trusses, integrated systems etc. and (4) space utilities and power from space resources. Then, the following ISRU capability elements were defined and examined:

- (i) resource extraction;
- (ii) material handling and transport;
- (iii) resource processing;
- (iv) surface manufacturing with in-situ resources;
- (v) surface construction;

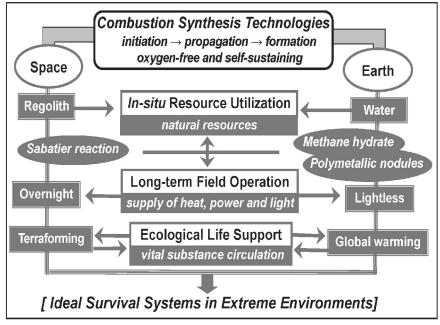


Fig. 7. Schematic illustration of combustion synthesis technologies conceptually designed as the relationships between in space exploration and the Earth environments.

(vi) surface ISRU for product, consumable storage and distribution.

In order to assess the impacts and benefits of ISRU, effects of ISRU on transportation, energy and power, life support, sustainability and commercialization have to be considered. Challenges for achieving extended stays of human in extreme environments have recently proceeded not only in space exploration but also in areas of underwater environment, where combustion synthesis could work practically in fulfilling efficient for the goals of the technological success. The technologies in survival system formation including availabilities of renewable and self-sustaining energy can play a critical role, specially, in the prime of extreme environment developments. As shown in Fig. 7, "long-term field operation" and "ecological life support" as well as the ISRU ones should be also important to overcome sustainable lunar-night (overnight) survival with such CO_2 – reduction and H_2 – extraction reseaches for essential life support system establishment.

One of the top priorities for ISRU is determining the availability of potential water resources on the Moon and Mars. Having a source of readily available water could provide both oxidizer and fuel for propulsion and fuel cell power systems, and can define the degree of self-sufficiency, radiation shielding, and closed-loop life support required to sustain humans in space. If water is not available on the Moon, oxygen extraction from the regolith can be performed. Other ISRU capability priorities include surface construction techniques for dust, debris, and radiation mitigation, in-situ fabrication by metal and silicon extraction from regolith, and in-situ solar power production and storage to enable a power-rich environment. When a sustainable settlement would be established beyond low-earth orbit such as the Moon, energy could be supplied by solar cells on its surface. Since the transportation of complete solar cell arrays to the moon is much difficult with highly-costly efforts, the fabrication scenario with thin film deposition in moonbased ultra-high vacuum has been designed as an ISRU [17]. The starting raw materials for thin film growth of solar cells would be supplied by extracting element materials from the Moon regolith with the aid of the combustion synthesis technology.

As a main goal for lunar robotic and human ISRU missions, such as oxygen production, hydrogen & water extraction and thermal & chemical processing subsystems have been carried out;

(a) excavation and material handling & transport,

(b) oxygen production and hydrogen & water extraction,

(c) thermal & chemical processing subsystems

(d) cryogenic fluid storage & transfer on surface.

To support sustained human presence on the Moon, it is essential to develop and evolve lunar ISRU capabilities that enable new exploration capabilities, such as long-range surface mobility, global science access, power-rich distributed systems, enhanced radiation shielding, etc. Because many ISRU processes are power intensive, the power density of stationary and mobile power systems is important when considering the total benefits and impacts of ISRU on missions and architectures. When a sustainable settlement would be established in space, energy could be mainly supplied by solar cells on its surface and some fabrication scenario with thin film deposition in Moonbased ultra-high vacuum should be designed [17]. For lunar ISRU, the resources on the Moon have been identified and characterized, and some activities have already been performed as early demonstrations of ISRU on the Moon. Through in-situ production of fuel cell reactants, solar energy generation and storage units, and power management, control, and distribution, ISRU can provide longterm products for a power-rich environment and surface power infrastructure growth. The need date for surface nuclear power is highly linked to the start date for large scale ISRU production.

6. Exergy loss minimization with efficient energy conversion

Exergy is a suitable scientific concept in the work towards sustainable development, which can provide important knowledges on effective and balanced environmental situations when accounting for the use of energy and material resources. This knowledge can identify areas in which technical and other improvements should be undertaken, and indicate the priorities, which should be assigned to conservation measures, efficiency improvements and optimizations. Thus, exergy concept and tools are essential to the creation of a new engineering paradigm towards sustainable development. By combining life cycle assessment with exergy anal-

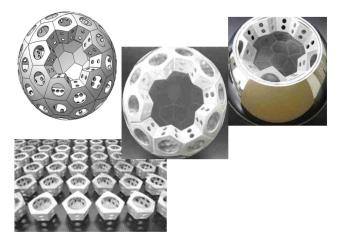


Fig. 8. Stereo fabric model for generating components with complex shape and large size [18] synthesis as a chemical oven.

ysis and distinguishing renewable resources from non-renewable one, the life cycle exergy analysis can offer a unique efficient method to analyze the level of sustainability for energy systems.

The International Space Station has been used not only as an in-orbit research laboratory but also as a training base for deeper space exploration, which will finish its existence around 2020. Although it has still been under discussion to formulate a vision for space exploration beyond lowearth orbit, continuous efforts have been undertaken toward human space activities and presence in space. They include the participation in the ISS and future exploration of Moon with construction of a lunar outpost. Furthermore, under participation in international manned space exploration with construction of lunar base, "extended stays of humans in space" are aimed with necessary steps in realizing such as robotics, nano- and micro-machine technologies, space solar energy, and multiple resource utilizations of which energy and mass loss should be reduced. Specially, the availability of renewable or self-sustaining energy is prime for space exploration and essential for space utilization, and it plays a critical role in the design and implementation for human space access in space exploration beyond low-earth orbit.

Two combustion synthesis-related technologies have been recently developed to fulfill highly efficient space exploration in energy and mass; the combustion synthesis-join-technology applied to "stereo fabrication of large-sized matters with hollow ceramic units assembling" and the combustion synthesis-capsule-formations applied to "largesized light and tough aggregate fabrication with metal and/or ceramic hollow spheres"; the former R&D has been performed as a part of "Innovative Development of Ceramics Production Technology for Energy Saving" project with the Stereo Fabric Research Center and the latter has related with mesoscopic scaled metallic/ceramic hollow spheres fabricated with small sized hierarchic structures such as hollow spheres and capsules.

The main concept of the stereo-fabric is, for example, when a large-sized ceramic container with high thermal insulation and light mass is required by designing the shape in spherical, large-sized spheres can be regarded as an assembly of uniform polygons divided into small units made of ceramic that are hollow as shown in Fig. 8 [18]. Each ceramic unit was fixed and joined using an alumina-based mortar. Flexible alumina-based mortar can cover the stress toward the center of the container.

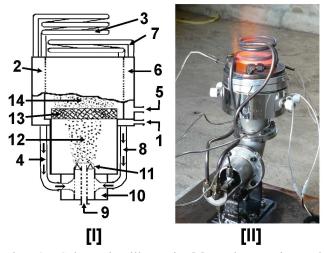


Fig. 9. Schematic illustration[I] and experimental view [II] relating with the self-circulation combustion process aided with waste-heat: 1 – solution circulation with excess-heat; 2 – fuel circulation with excess-heat; 3 – evaporation tube of solution; 4 – fuel evaporation tube; 5 – steam pipe; 6 – high-temperature fuel pipe; 7 – flow mixer; 8 – spray nozzles; 9 – solution inlet; 10 – fuel inlet; 11 – air inlet; 12 – buffle plate (Cu-mesh); 13 – mixing space; 14 – burning space.

The present design was the case for this container as the stress originated from the external metallic shell. The finished large-sized products can be more energy efficient and lighter in weight compared to the conventional ones with the segments manufactured and assembled. In order to fix and join ceramic units, the R&D with alumina-based combustion synthesis joining has been performed successfully as one of in-situ processing methods [19]. Due to low thermal shock resistance of ceramics, the joining process with reactant mixture compacts or powders has been performed in the so-called the mode of volume combustion synthesis, that is, the entire sample is heated uniformly in a controlled manner to keep its thermal gradient distribution less during pre-heating. Since Al has an extremely high affinity to oxygen, it can be used to reduce many oxides to form Al₂O₃ phase. The containing of Al₂O₃ phase in the joining layer could help to decrease the mismatch of thermal expansion between alloy and Al₂O₃ ceramics during the high temperature application. Besides, the existence of Al₂O₃ phase could enhance the wettability of joining layer on Al₂O₃ surface compared to alloys.

Hollow spheres and capsules are attractive owing to their wide applications in low dielectric constant substrates, sensing and labeling, optoelectronics, catalysis, wave scattering, lasing, photonics, etc. The group of the JFE Techno-Research Corp. has developed a sintering process performed mainly with the reduction of iron oxides [20]. Exergy is a suitable scientific concept in the work towards sustainable development, which can be evaluated in various processes with a technique based on the second law of thermodynamics with qualitative change from available energy to unusable energy in the form of work.

7. Sustainable process design for improvements of ISRU

In general, natural resources are evaluated to be useful or non-useful in flowing and storing; useful one is renewable while non-useful be non-renewable. Then, all in flowing, storing and/or re-cycling are recognized as exergy power over time. Renewable energy related are solar irradiation on the earth surface, wind, water flows, waves, geothermal and tidal energies. Biomass is accumulated solar energy and is taken as stores and reserves. Available resources prevail all present primary energy or exergy needs of humans for many hundred times if we take into account only the technologies developed up to day. The first primary exergy source in the system is the solar energy including direct irradiation and all secondary forms of solar exergy: biomass, water, wind and waves. The second source would be planetary energies extracted from such as heat and tidal flow on ground or underground. These exergy sources are inexhaustible and available for human lifetime.

The technology characterized with waste-heat circulating has been originally proposed through the combinational technologies of solution and/or emulsion combustion synthesis, which performs not only fine powders production but also highly efficient resource utilization with the evaporation of solution and fuel in energy saving before/after combustion propagation. The solution combustion synthesis and emulsion combustion synthesis technologies can perform not only fine powders production but also highly efficient ISRU with the aid of water and mineral resources, resulting in system-pressure-controlled energy saving before combustion propagation. As shown in Fig. 9, a concept design for the combustion system of "waste-heat circulating" was modified from the idea of conventional solution combustion with an activating system of reactants. Both fuel and solution are transformed from liquid to gas with the aid of waste-heat, and their gas-flow velocities are

estimated to be proportional to <[volume of evaporated gas] /[tube diameter]>. The scale-up design can be derived with the flow pattern of gas in consideration of linear dispersion of gas in flow direction, where the gas velocity decreases with increasing the dispersing diameters.

Since natural convection is effectively controlled and suppressed by rotating the walls around combustion front, mixtures of gasified fuel and solutions can flow in smooth, uniform and stable manners as a result of the application such as centrifugal and Coriolis forces. Elements at heating-front made of meshed copper plate were corroded with steam water activated with heat of burning, which were changed to non-corrosive, low-expansive, abrasion-resistant and thermally-stable materials like silicon nitride. The process is controlled as follows:

(1) to heat the lines of reactant solution and fuel liquid which are pumped and flown through the separated tubes;

(2) to ignite the steam-mixture of fuel and solution formed during their flow in a proper-sized pipe after flowing through nozzles;

(3) to control the amounts of solution and fuel evaporated with the self-sustaining heating for attaining complete combustion;

(4) to control the reactant stable mixture flow and combustion propagation with proper rotations of fins set inside the tube.

The characteristic merits of the present method are in self-sustaining evaporation system assisted with combustion heat and wall rotation system of reactant flow lines for uniform and stable reaction performance. Since the nozzles are open to the atmospheric pressure before the combustion front, the process can be controlled much in higher reliability compared to conventional emulsion and liquid spray technologies.

The volume of evaporated gas by self-heating is estimated with the liquid volume, molar weights of solution and fuel, gas molar volume and the combustion temperature. The gas velocity is calculated with the data of the evaporated gas volume and the tube diameter. The flow pattern of gas can be designed in consideration of gas diffusion; linear dispersion of gas in the direction of flow with gases around, which makes the gas velocity decreases with increasing the dispersing diameters. The present burner-type combustion technology is combined with a mist combustion process. Since the combustion process is assisted with steamed water generated by heating with the reactant heat during sustaining combustion, fuels such as oil can completely burn without any polluted soot. This technology can attain almost 50% energy saving with water assistance and form finer product powders through the process. When adding water as a solution, the completeness of its combustion could be improved by the extra reaction of residual carbon and water as shown in the following Eq. (4):

$$C + H_2O \rightarrow CO + H_2$$
 (4), and

the consecutive reaction of CO and H_2 of Eq. (4) with air leads to the final components of CO₂ and H_2O . Judging from the data of temperature changes in combustion flame as shown in Table 1, the effect of water addition to the fuel would be more effective with A-fuel oil compared to lamp oil.

The comparison tests have been carried out for the cases of lamp and fuel oils. In the case of lamp oil combustion, the temperature decreases with increasing water addition. On the other hand, the compatibility of A-fuel oil and water seems to be effective until 50% addition of water without any meaningful decrease of temperature. The present technology is considered to stand the combination of solution or emulsion combustion synthesis, which will perform not only fine powders production but also highly efficient resource utilization with the aid of water, resulting in sustainable system-pressure-control in somewhat exergy loss minimization during combustion propagation.

Radioisotope heating units and heat generators had been used for lunar exploration program designed in the 1960s and 70s. The utilization of radioisotopes is much negative nowadays because of

| Table 1 | | | | | | |
|---|--|--|--|--|--|--|
| Combustion temperature changes during the oil/water mist combustion | | | | | | |

| Fuel (100 cc/min) | Combustion temperature (K) with water addition | | | | | |
|----------------------|--|-----------|-----------|-----------|-----------|--|
| | 20 cc/min | 30 cc/min | 40 cc/min | 50 cc/min | 60 cc/min | |
| lamp oil | 1150 | 1120 | 1010 | 1020 | 980 | |
| A-fuel oil | 1550 | 1550 | 1550 | 1500 | 1420 | |

its difficulties in careful handling, human protecting, etc. For surviving on the lunar surface, thermal wad are prospectively admired, which are stored using modified lunar regolith as a thermal storage mass during the lunar night. Combustion synthesis technologies can provide thermal controls for lunar exploration although additional developments are essential. To prove the efficiency of the technology, the feasibility of long-duration sustainable application has to be made clear without any power and resource except in-situ lunar ones.

Concepts of high-temperature "heat-to-electricity" conversion have been recently proposed in consideration of and developed in various fields aided with the waste-heat; thermo-photovoltaic energy conversion, acoustic-to-electric power conversion, thermo-electric tube, etc. Since the present combustion synthesis technologies can provide a high-temperature environment with simple processes, the system related with energy conversion of heat-to-electricity would be combined with combustion synthesis technologies. Such approaches will be one of promising technologies applied in extreme environments. In order to realize heat-to-electricity processes, advanced photonic crystals have been developed as optimum spectral control components useful for a highly effective thermo-photovoltaic system, and a sputter-etching technology has been developed for enhancement of visible light absorbance [21]. By combining the present combustion synthesis technology with these ones for heat-to-electricity energy conversion, approaches toward sustainable overnight survivals would be realized effectively.

As already mentioned, the basic characteristics of combustion synthesis mainly consisted of the following three processes; "ignition", "propagation" and "structure formation". With the technological improvements with the aids of additions affecting in or between each process, combustion synthesis can provide various benefits not only in industries but also in fundamental approaches with challengeable prospects. If phenomenological differences between ignition process and propagation one are taken into consideration, optimum conditions such as reactant composition, temperature, pressure and diluents in process would be different each other rather drastically. Although approaches concerning "propagation threshold" may be less attractive compared to those of "ignition threshold", it would be important to make clear much in details when considering "sustainable" utilizations in various environments.

8. Conclusions

Combustion synthesis technologies applicable to ISRU in extreme environments are discussed in consideration of exergy loss minimization and process control concepts in the technologies relating with differences in ignition and propagation processes. Although ISRU can provide mass, cost, and risk reduction benefits to future human lunar exploration missions, it requires further development and demonstration to convince mission planners to incorporate ISRU capabilities into early missions. A stepwise approach utilizing laboratory, environmental chamber, analog field testing, and robotic precursor experiments with international participation is recommended. Three robotic precursor flight experiments are proposed that may provide the greatest impact and risk reduction aspects for early incorporation of ISRU into lunar architecture plans: (1) characterizing and mapping lunar polar volatiles and water/ice, (2) performing subscale demonstrations of critical oxygen extraction from regolith tasks, and (3) performing a near full-scale system demonstration of ISRU, mobility, power, and cryogenic fluid management technologies.

According to a formulated vision for space exploration onward, many efforts have been continuously undertaken toward human space activities and presence in space. These activities include the participation in future exploration to the Moon and further even with construction of a lunar outpost. The extended stay of humans in space requires multiple resources of which energy and radiation protection are of the utmost, where the availability of electrical energy is much useful for space exploration and essential for space utilization. To develop energy sources utilizing the in-situ resources, for example, of the Moon is also attractive and important. The ultra-high vacuum environment of the lunar surface and the presence of raw material building blocks allow for the fabrication of thin film solar cells directly on the surface of the Moon. By making clear optimum conditions of the combustion synthesis technology for the process controls, one can simply apply and operate the combustion synthesis and related technologies under various conditions applicable in sustainable settlements in extreme environments not only for synthesizing high-temperature materials but also for super-heating chemical ovens. By establishing useful branding of the combustion synthesis technology with ISRU, the scenario of "live off the land" would be realized.

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