

## Self-Propagating High-Temperature Synthesis Reactions for ISRU and ISFR Applications

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### Abstract

In the framework of ISRU (In-Situ Resource Utilization) and ISFR (In-Situ Fabrication and Repair) applications, a novel recently patented process based on the occurrence of Self-propagating High temperature Synthesis (SHS) reactions potentially exploitable for the *in-situ* fabrication of construction materials in Lunar and Martian environments is described in this work. Specifically, the SHS process involves thermite reactions type between Lunar or Martian regolith simulants and aluminum as reducing agent. To overcome the fact that the original content of ilmenite ( $\text{FeTiO}_3$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ) on Moon and Mars soils, respectively, is not enough to make the SHS process possible, suitable amounts of these species have to be added to the starting mixtures.

The dependence of the most important processing parameters, particularly the composition of the starting mixture, evacuation level, and gravity conditions, on SHS process behaviour and product characteristics is specifically examined for the case of Lunar regolith. All the obtained findings allows us to conclude that the optimized results obtained under terrestrial conditions are valid for *in-situ* applications in Lunar environment. In particular, parabolic flight experiments evidenced that neither SHS process dynamics nor product characteristics are significantly influenced in both Lunar and Martian systems when passing from Earth to low gravity conditions.

Finally, the complete scheme involving all stages required for the fabrication of physical assets to be used as protection against solar rays, solar wind and meteoroids, etc., is reported.

### Introduction

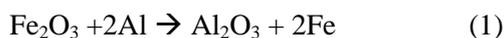
The development of innovative technologies in the framework of the ISFR (In-Situ Fabrication and Repair) and ISRU (In-Situ Resources Utilization) concepts is relevant for facilitating and time extending future human exploration on the Moon, Mars, near Earth asteroids, etc. [1-3]. In this regard, several studies have been recently addressed with the final aim to obtain suitable structures for protection against cosmic rays, solar wind and meteoroids, making use of available *in-situ* Lunar resources [4-11].

For instance, a process where regolith Lunar simulant was sintered at  $1100^\circ\text{C}$  by radiant and microwave heating was proposed [4]. Lunar regolith was also utilized for fabricating a thermoplastic material [5] and fiberglass for reinforcing Lunar concrete [6]. The other investigated methods are mainly based on the exploitation of combustion synthesis-type reactions for the fabrication of ceramic composites using Lunar regolith in the starting mixture [7-12]. For instance, the exothermic chemical reaction  $x(\text{Ti} + 2\text{B}) + (1-x)\text{JSC-1} \rightarrow x(\text{TiB}_2) + (1-x)\text{JSC-1}$ , that displays a SHS behavior when  $x > 0.25$ , was proposed as a possible method for the preparation of Lunar bricks using JSC-1 Lunar regolith simulant [7]. On the other hand, the direct aluminothermic reduction of Lunar regolith was found to produce, after a

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relatively long preheating stage (7-15 min), a ceramic composite material, mainly consisting of  $\text{Al}_2\text{O}_3$ , Si,  $\text{CaAl}_4\text{O}_7$  and  $\text{MgAl}_2\text{O}_4$ . [8-9].

Along these lines, taking advantage of the presence of significant amounts of iron oxides in Martian soil, the highly exothermic, i.e.  $(-\Delta H_r^\circ) = 851.444$  kJ/mol of  $\text{Al}_2\text{O}_3$  [13], self-propagating aluminothermic reduction of hematite:



could be exploited in the framework of the ISRU principle. This statement holds also true when considering the reduction of ilmenite ( $\text{FeTiO}_3$ ), whose presence is up to 20 wt.% on the Moon, by aluminum [14].

Following Faierson et al. [8-9] work, the use of Mg as reducing agent to be reacted with JSC lunar regolith was recently preferred to Al, because of the correspondingly higher adiabatic temperature [11]. In the present work, a recently patented process based on the occurrence of SHS reactions in a mixture made of Lunar or Martian regolith simulants with appropriate amounts of  $\text{FeTiO}_3$  or  $\text{Fe}_2\text{O}_3$ , respectively, and Al, is described. In this regard, it is important to note that relatively lower pressure and gravity levels are encountered in both Lunar and Martian environments as compared to Earth.

Therefore, after systematically investigating the composition of the starting mixture, the dependence of the evacuation level and gravity conditions on SHS process behaviour and product characteristics is also taken into account in this work, particularly for the case of Lunar based-systems.

## Experimental

The JSC Lunar ( $R_L$ ) and Martian ( $R_{M1}$ ) regoliths used in the present investigation have been provided by Orbitec (USA), while Mojave Martian ( $R_{M2}$ ) soil simulant was obtained by Jet Propulsion Laboratory (USA).

The minerals identified in the three different regolith simulants are summarized in Tables 1, 2 and 3. Table 1 indicates that the JSC simulant mainly consists of plagioclase, Ca-rich pyroxene, olivine and ilmenite minerals, as well as other minor phases [15]. Similarly, as reported in Tables 2 and 3, plagioclase feldspar, pyroxene, iron oxides, ilmenite and olivine are the main species found in JSC and Mojave Martian regoliths [16-17].

**Table 1**  
Minerals present in JSC Lunar simulant [15]

Class of Mineral	Chemical species
Ilmenite	$\text{FeTiO}_3$
Plagioclase	$\text{CaAl}_2\text{Si}_2\text{O}_8$ , $\text{NaAlSi}_3\text{O}_8$ , $\text{KAlSi}_3\text{O}_8$
Olivine	$\text{Mg}_2\text{SiO}_4$
Ca-Pyroxene	$\text{CaSiO}_3$
Chromite*	$\text{FeCr}_2\text{O}_4$
Cristobalite*	$\text{SiO}_2$
Iron oxides*	$\text{Fe}_3\text{O}_4$ , $\text{Fe}_2\text{O}_3$

\*Minor phases

**Table 2**  
Minerals present in JSC Martian simulant [16]

Class of Mineral	Chemical species
Iron, Titanium-oxides	$\text{Fe}(\text{Fe},\text{Ti})_2\text{O}_4$
Plagioclase feldspar	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Olivine	$\text{Fe}_2\text{SiO}_4$ , $\text{Mg}_2\text{SiO}_4$
Ca-Pyroxene	$\text{MgSiO}_3$ - $(\text{Mg},\text{Fe})\text{SiO}_3$ , $\text{CaSiO}_3$ , $\text{FeSiO}_3$

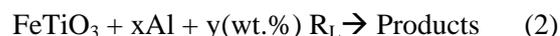
**Table 3**  
Mineral present in Mojave martian simulant [17]

Class of Mineral	Chemical species
Iron oxides	$\text{Fe}_3\text{O}_4$ , $\text{Fe}_2\text{O}_3$
Ilmenite	$\text{FeTiO}_3$
Plagioclase feldspar	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Olivine	$\text{Fe}_2\text{SiO}_4$
Ca-Pyroxene	$\text{Ca}(\text{Cr},\text{Al},\text{Fe})(\text{Si},\text{Al})_2\text{O}_6$
Manganite*	$\text{MnO}(\text{OH})$
Barite*	$\text{BaSO}_4$
Apatite*	$\text{Ca}_5(\text{PO}_4)_3[\text{F}, \text{OH}, \text{Cl}]$

\*Minor phases

The original simulants have been preliminarily sieved to produce powders with particle size less than  $45\mu\text{m}$ .

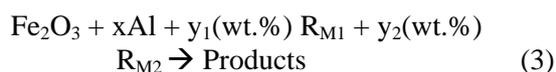
Aluminum (Alfa Aesar, -325 mesh, 99,5% purity) and iron titanate (Alfa Aesar, - 100 mesh, 99,8% + purity) were added to JSC Lunar regolith according to the following general reaction:



where, x was varied in the range 0.9-3, while y was increased from 0 to the maximum allowable weight percentage, depending on the corresponding x

value, able to guarantee the SHS character in the resulting reacting system. The obtained systems are indicated with  $S_{L\_x\#\_R_L\#}$ , where  $x\#$  is the Al/FeTiO<sub>3</sub> molar ratio and  $R_L\#$  represents the weight percentage ( $y$ ) of lunar regolith in the mixture.

Due to the hygroscopic character of Martian regoliths, both  $R_{M1}$  and  $R_{M2}$  have been first desiccated for 2 h at 700°C, before blending them with Al and hematite (Aldrich, < 5µm, 99%+ purity) as follows:



Specifically, the Martian systems investigated in this work are indicated as  $S_{M\_x2.44\_R_{M1}0\_R_{M2}45}$  and  $S_{M\_x2.44\_R_{M1}13\_R_{M2}32}$ . They are both characterized by a Al/Fe<sub>2</sub>O<sub>3</sub> molar ratio equal to 2.44 and total amount of regolith of about 45 wt.%. However,  $R_{M2}$  is the only simulat present in the mixture in one case ( $y_1=45$ ,  $y_2=0$ ), while both of them are combined in the other system ( $y_1=13$ ,  $y_2=32$ ).

Each mixture was compacted using an uniaxial press to provide cylindrical (11 mm diameter and 25 mm height) or parallelepiped (14 mm x 17 mm x 33 mm) shaped pellets to be reacted by SHS.

The experimental set up used in the present investigation, not reported here for the sake of brevity, consisted of a battery of reaction chambers, a power supply (Legrand safety isolating transformer, mod. 642310, primary 230-400V, secondary 12-24V, power 1000 VA) which provides the energy required for reaction ignition, a video camera (Imaging Source CMOS color camera, model DFK 21AUC03, using Pentax lenses, model B1218A) and a computer system connected to a data acquisition board (cDAQ-9174 equipped with NI 9481 high voltage relay module, NI 9213-16ch-24bit thermocouple module and NI 9239-4ch-24bit analog input module, National Instruments) and supported by a software package (LabVIEW, National Instruments). This apparatus was used not only to perform SHS reactions under terrestrial conditions but also for low-gravity experiments (about 10<sup>-2</sup> g) onboard of the Airbus 300 during the 53<sup>rd</sup> ESA Parabolic Flights Campaign held in Bordeaux (France) last October 2010. In this case, the entire SHS apparatus was mounted on an aluminum plate provided of suitable holes to permit its fixation to the airbus rails. A quartz container was used to sustain, during low gravity experiments, the pellet in a stable position.

Thermal levels achieved during the evolution of combustion synthesis reactions were measured using two thermocouples (W-Re, 0.13 mm diameter, Omega Engineering Inc.), 8-10 mm distant each other, embedded in the pellet. A two-colour pyrometer Iacon Mirage OR 15-990 (Iacon, USA) was also used for measuring temperature-time profiles in the sample surface during SHS experiments performed on the ground.

The selected evacuation level inside the reaction chambers, about 25 Torr, was monitored through appropriate vacuum sensors.

The combustion front was generated at one sample end by using of a heated tungsten coil (R.D. Mathis Company, USA), which was immediately turned off as soon as the reaction was initiated.

The obtained SHSed products were characterized in terms of chemical composition and microstructure by X-ray diffraction (XRD) analysis (Philips PW 1830 diffractometer using CuKα Ni-filtered radiation) and Scanning Electron Microscopy (SEM) using a Hitachi S4000 microscope, equipped with an EDS microprobe.

Compressive strength tests on SHSed samples were carried out taking advantage of a METRO COM (mod. 100 MI) press using a 10 kN load cell (METIOR CVS).

The conditions to desiccate both Martian simulants were chosen on the basis of the results obtained by thermogravimetric analysis (TGA) from room temperature to 900°C using a NETZSCH STA 409PC Simultaneous DTA-TGA Instrument.

## Results and discussion

### *Lunar systems*

It was recently reported in the literature that mixtures consisting of JSC lunar regolith and Mg as reducing agent are preferred as SHS systems, in comparison with those involving Al, because of the correspondingly higher adiabatic temperature [11].

On the other hand, Mg is relatively much more volatile [18] so that, unless sufficiently high pressures are applied, noticeable gas expulsion may occur under the typical temperature conditions encountered during SHS process evolution. However, the pressure levels characterizing Lunar and Martian atmospheres are rather low. The direct consequences of excessive gas development are reactants/products loss, sample weight decrease, increasing in product porosity, possible interruption

of combustion front propagation, difficulties in process control, etc.

These considerations have been experimentally confirmed in our study when the SHS process was carried out at 25 Torr using Mg as reductant. Indeed, a significant amount of gases was produced and the resulting product resulted highly porous and did not keep its original shape. In addition, pellet disintegration took place when further decreasing the pressure level. Accordingly, Al was selected as reducing metal in our experimentation. In this context, as pointed out in a recent paper [11], this metal could be extracted from Moon soil minerals containing this element or recovered from certain vehicles components utilized in previous space missions.

The influence of the composition of the Al-based mixtures was then investigated. The effect of the Al/FeTiO<sub>3</sub> ratio on the combustion front velocity and the maximum combustion temperature is reported in Figure 1 for the case when no regolith was present in the reacting mixtures. It is found that all these systems display a SHS character only if  $x \geq 0.9$ . In addition, both the velocity and combustion temperature increased as the Al/FeTiO<sub>3</sub> is correspondingly augmented. Therefore, the obtained result indicates that the exothermic character of reaction (2) is progressively enhanced as the x value is increased from 0.9 to 3.

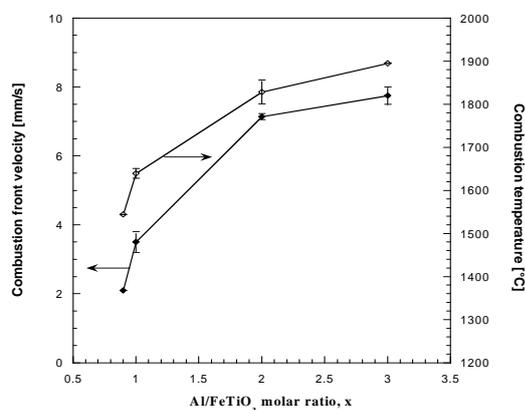


Fig. 1. Effect of the (Al/FeTiO<sub>3</sub>) molar ratio in the starting Lunar mixtures on the front velocity and combustion temperatures measured during the SHS process ( $y=0$ ).

When Lunar regolith simulant is also introduced in the initial mixtures, significant changes in SHS process behaviour of the corresponding reacting systems are produced. For example, the effect of the Lunar regolith content on the average velocity of the combustion front and the maximum

combustion temperature is reported in Figures 2a)-2b) when  $x=2$  and 3, respectively. Similar results are obtained using the other Al/FeTiO<sub>3</sub> ratios considered in this work. It is clearly observed that both these parameters decrease as the y value is augmented. Moreover, a threshold in the amount of regolith present in the mixture, i.e. 23 and 32.5 wt.% for the cases of  $x=2$  and 3, respectively, has not to be overcome for maintaining the SHS character. Such a behaviour clearly depends on the fact that the aluminothermic reduction of iron titanate has to drive less favourable chemical reactions involving the other, apparently less reactive, Lunar regolith constituents.

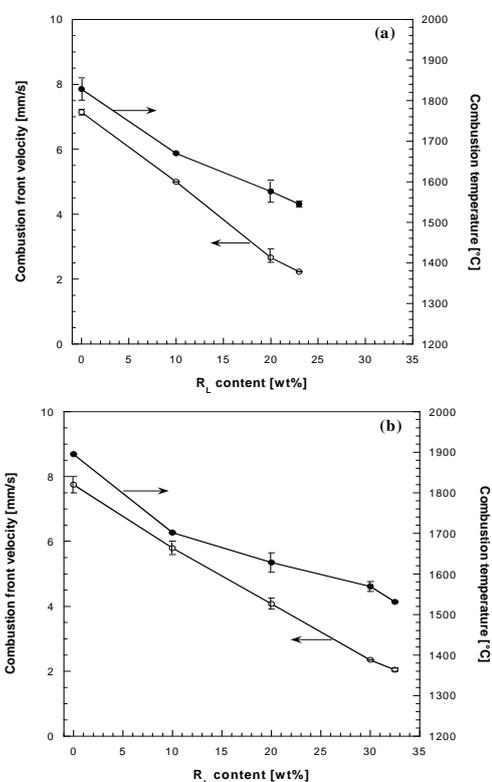


Fig. 2. Effect of the presence of Lunar regolith content in the starting mixtures on the front velocity and combustion temperature when (a)  $x=2$  and (b)  $x=3$ .

It is also possible to observe from Figure 2 that the minimum front velocity and combustion temperature values measured in SHSed systems are approximately 2 mm/s and 1520°C, respectively. The latter condition is well consistent to the interval of 1800-2000 K that represents the empirical requirement for the adiabatic temperature generally reported in the literature for self-sustaining systems [19].

Therefore, the behaviour displayed in Figure 2 suggests that, in order to increase the amount of

Lunar regolith in the mixture to be reacted, the required Al has to be correspondingly augmented for guaranteeing the self-propagating character of the system. Based on these results, it is possible to evaluate the total amount of  $\text{FeTiO}_3$  in the mixture to be reacted with Al by SHS as the sum of two contributions, i.e. the fraction originally present in the Lunar regolith [14] and that 99,8% pure commercial powders additionally provided. As pointed out in a recent paper [10], the situation above can be regarded as a simulation of a SHS system consisting of Al and a “modified” Lunar regolith, obtained after its ilmenite content is enriched up to a prescribed level.

Figure 3 shows an example of final product in the parallelepiped configuration, specifically obtained for the  $S_L\text{-}x_3\text{-}R_L32.5$  system, thus reproducing a possible “Lunar brick” prototype. It should be noted that the original specimen shape is maintained during the course of the reaction process which is an important aspect in view of the exploitation of the SHS process for the fabrication of structural component with defined dimensional characteristics.

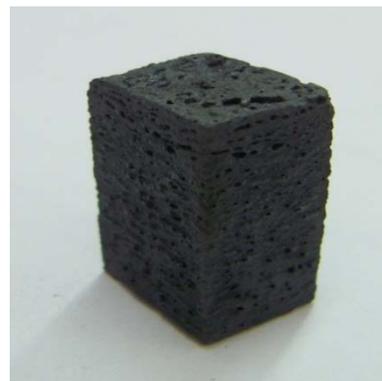


Fig. 3. Example of final parallelepiped sample obtained by SHS for the  $S_L\text{-}x_3\text{-}R_L32.5$  Lunar system.

The XRD patterns of the SHSed products obtained directly reacting Al with only ilmenite ( $y=0$ ) or otherwise produced in presence of the maximum allowable Lunar regolith content in the mixture for maintaining the SHS character in the reacting systems, are shown in Figure 4(a)-4(d) at the various  $x$  values investigated. For the sake of comparison, the XRD spectra related to the starting mixtures are also reported.

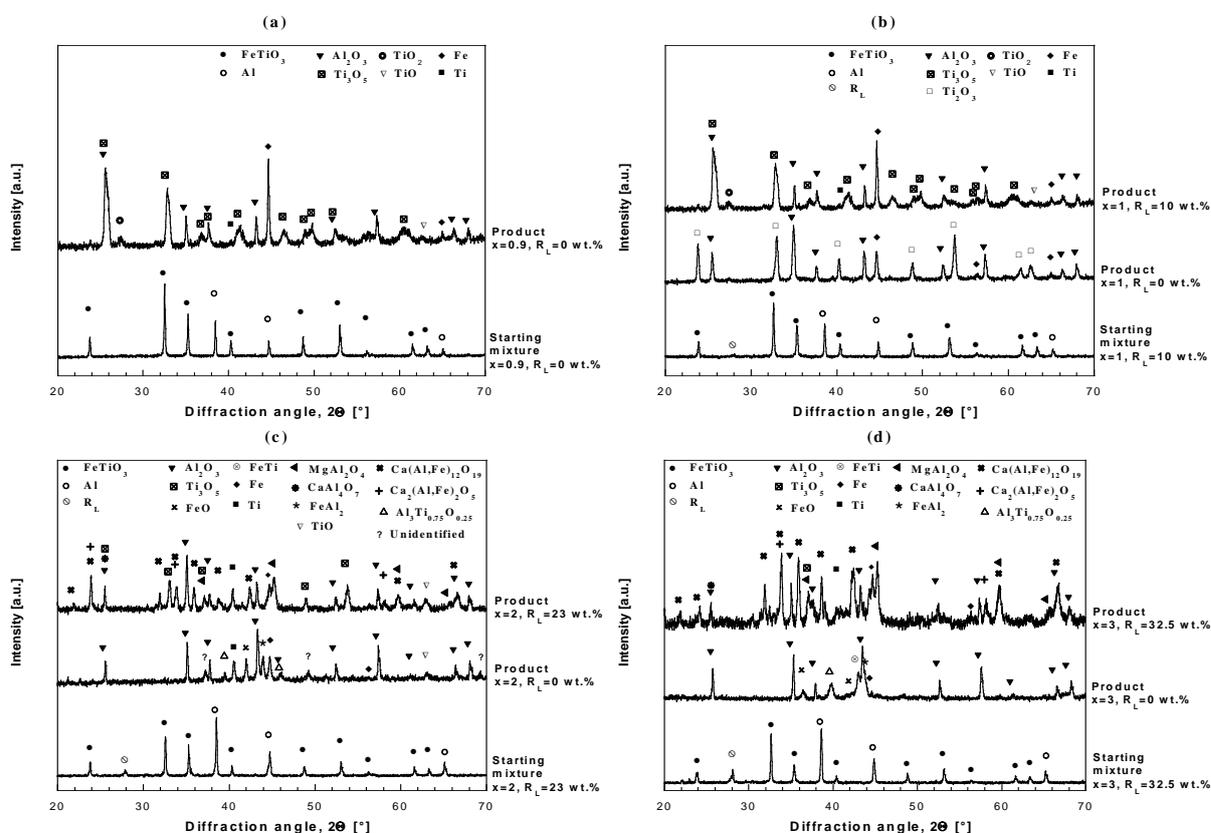


Fig. 4. Composition of the starting mixtures and end products obtained in Lunar systems by SHS without or with JSC regolith (maximum allowable content):

(a)  $x=0.9$ , (b)  $x=1$ , (c)  $x=2$ , (d)  $x=3$ .

It is clearly possible to state that in all the synthesized ceramic-metal composite materials, whose composition depends on the  $x$  value considered, no traces of initial reactants were found.

For the sake of simplicity, let us consider first the systems where Lunar regolith was not involved. Consistently with the obtained product composition, possible global reactions describing the most relevant chemical transformations taking

place during SHS process for the various  $x$  values are summarized in Table 4, where the major and minor phases detected by XRD were also reported.

In this regard, it should be noted that the latter ones are often not considered in the proposed global reactions. Moreover, it is not possible to postulate a certain reaction stoichiometry for the case of  $x=3$ , due to the presence of significant amounts of relatively complex secondary species, like  $\text{Al}_3\text{Ti}_{0.75}\text{O}_{0.25}$ , in end products (cf. Figure 4d).

**Table 4**

Proposed global reactions and related enthalpies [13] for the description of main chemical transformations taking place in Lunar systems during the SHS process for different  $x$  values ( $y=0$ ).

$x$	Main phases	Minor phases	Proposed global reaction	Enthalpy of reaction ( $-\Delta H_r^\circ$ ) [kJ/mol of $\text{FeTiO}_3$ ]
0.9	$\text{Al}_2\text{O}_3$ , Fe, $\text{Ti}_3\text{O}_5$	$\text{TiO}_2$ , $\text{TiO}$	$\text{FeTiO}_3 + 0.9\text{Al} \rightarrow 0.45\text{Al}_2\text{O}_3 + \text{Fe} + 0.33\text{Ti}_3\text{O}_5$	330.044
1	$\text{Al}_2\text{O}_3$ , Fe, $\text{Ti}_2\text{O}_3$	-	$\text{FeTiO}_3 + \text{Al} \rightarrow 0.5\text{Al}_2\text{O}_3 + \text{Fe} + 0.5\text{Ti}_2\text{O}_3$	362.753
2	$\text{Al}_2\text{O}_3$ , Ti, Fe, $\text{FeAl}_2$	$\text{FeO}$ , $\text{Al}_3\text{Ti}_{0.75}\text{O}_{0.25}$ , $\text{TiO}$ , unidentified phase	$\text{FeTiO}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Ti} + \text{Fe}$	440.157

It can be generally stated that, except for the case of  $x=0.9$ ,  $\text{Al}_2\text{O}_3$  always represents the main phase detected by XRD. As expected, the increase in the  $x$  value corresponds to relatively higher reducing environments. For instance, when passing from  $x=0.9$  (cf. Figure 4a) to 1 (cf. Figure 4b) the formation of  $\text{Ti}_3\text{O}_5$  is replaced by the relatively less oxidized  $\text{Ti}_2\text{O}_3$  specie. Nevertheless, the presence of partially reduced iron oxides ( $\text{FeO}$ ) in the end-products obtained when starting from relatively high Al amounts ( $x=2, 3$ ) is likely due to the fact that this metal not only acts as reducing agent but it is also consumed to form  $\text{FeAl}_2$  and  $\text{Al}_3\text{Ti}_{0.75}\text{O}_{0.25}$ . As also reported in Table 4, it is also important to note the increase in the enthalpy of reaction as the  $\text{Al}/\text{FeTiO}_3$  molar ratio is augmented. The enhanced exothermicity of the corresponding reacting systems is in agreement with the front velocity and combustion temperature behaviour shown in Figure 1.

Let us now take into account the XRD results related to SHS systems involving the maximum allowable content of Lunar regolith, which correspond to the optimal mixture compositions in the framework of the ISRU principle.

For the sake of simplicity, peaks reflection corresponding to the crystalline phases present in Lunar regolith are indicated in cumulative manner as  $R_L$ .

Figure 4(a)-(d) clearly shows that, as the  $x$  value is augmented, so that the amount of regolith in the mixture was accordingly increased, several additional phases have been detected by XRD, as compared to systems with  $y=0$ .

Indeed, while the composition of the product synthesized when  $x=1$  and  $y=10$  wt.% is similar to that corresponding to  $x=0.9$  without adding any regolith simulant, when the amount of the latter one is progressively augmented ( $x \geq 2$ ), various mixed oxides such as  $\text{MgAl}_2\text{O}_4$ ,  $\text{Ca}(\text{Al},\text{Fe})_{12}\text{O}_{19}$ ,  $\text{Ca}_2(\text{Al},\text{Fe})_2\text{O}_5$  and  $\text{CaAl}_4\text{O}_7$ , are additionally formed during SHS. Other minor or non-crystalline phases, particularly silicates, are also likely present in final products. The formation of all the species above is consistent with the chemical transformation of the main constituents initially present in Lunar regolith simulant, such as  $\text{FeTiO}_3$ ,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ,  $\text{CaSiO}_3$ , and  $\text{Mg}_2\text{SiO}_4$ , with Al.

It is also worth noting that the SHSed Lunar samples prepared in this work display a

composition qualitatively similar to that recently reported in the literature relatively to products obtained when directly reacting JSC regolith simulant with 33 wt.%Al [8]. As mentioned in the introduction, in the latter investigation the combustion synthesis reaction was activated only after heating the mixture for at least 7 min.

The obtained SHSed products have been characterized also from the microstructural point of view. For instance, the SEM micrograph of a reaction product synthesized when  $x=3$  and no JSC simulant was added to the reacting mixture is shown in Figure 5a. According to the XRD results, EDS analysis clearly indicates that the

composite material mainly consists of  $\text{Al}_2\text{O}_3$  grains (dark phase) and a multiphase metal matrix (lighter region) containing Ti, Fe and Al based alloys.

As expected, the introduction of the Lunar simulant in the starting mixture to be reacted by SHS strongly affect microstructural characteristics of the resulting material, as seen in Figures 5b-5c relatively to the  $S_{L\_x3\_R_{L30}}$  system. A relatively more complex fibrous microstructure is obtained in the latter case. In particular, a phase with a filament-like structure can be clearly distinguished inside sample pores (cf. Figure 5c), while it is found embedded into product matrix throughout the bulk of the SHSed sample (cf. Figure 5b).

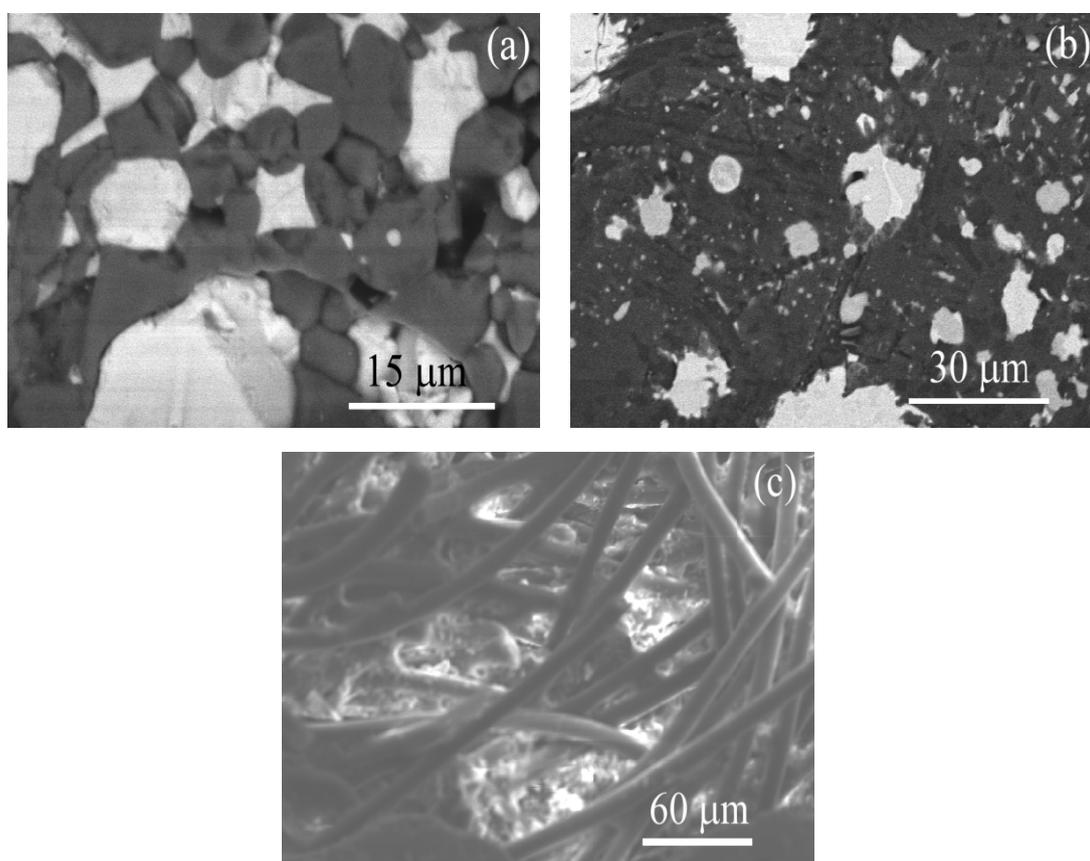


Fig.5. SEM micrographs of end products obtained by SHS for the case of Lunar systems: (a) bulk region of  $S_{L\_x3\_R_{L0}}$  sample, (b) bulk and (c) pore region for the  $S_{L\_x3\_R_{L30}}$  specimen.

The formation of this phase may be associated to the occurrence of a vapor-liquid reaction mechanism, because of Al vaporization taking place during SHS evolution under vacuum (25 Torr) condition. As far as the composition of this phase is concerned, no reliable information was unfortunately available from EDS analysis, probably because we could find isolated

“filaments” only inside the pores where microanalysis signals were highly disturbed. Nevertheless, this phase most probably consists of Al-based oxides, since Al vaporization is likely the origin of their formation.

In this regards, it should be noted that whiskers with diameters down to about 25 nm and reported to be “likely” consisting of Al nitrides and oxides

were formed during the reaction of JSC regolith with Al [9].

Compressive strength measurements performed on cylindrical shaped  $S_Lx2R_L20$  and  $S_Lx3R_L30$  products provide average values of  $27.2 \pm 3.6$  and  $25.8 \pm 3.6$  MPa, respectively. These data evidenced a significant improvement in comparison with the best values reported in the literature relatively to materials produced from the direct aluminothermic reaction of Lunar regolith stimulant, i.e. about 18 MPa [8]. These differences may be ascribed to the different reaction conditions encountered in the two studies. In particular, the relatively higher content of  $FeTiO_3$  in the starting mixture used in the present work increase reacting system exothermicity, so that sintering phenomena among particles are correspondingly enhanced during SHS. This feature certainly produces

beneficial effects towards the obtained material strength.

The results shown and discussed above refer to SHS experiments carried out under terrestrial conditions. However, due to the low gravity level characterizing Lunar environment ( $1.622 \text{ m/s}^2$ ), the influence of gravity on the SHS behaviour and products properties has to be taken into account in view of the possible *in-situ* application of the fabrication process described in this work.

Along these lines, the reaction front velocities measured during SHS under terrestrial conditions are compared in Figures 6(a)-6(b) when  $x=2$  and 3, respectively, with the values related to the analogous experiments performed in a microgravity environment ( $\sim 10^{-2} \text{ g}$ ) during a recent parabolic flight campaign.

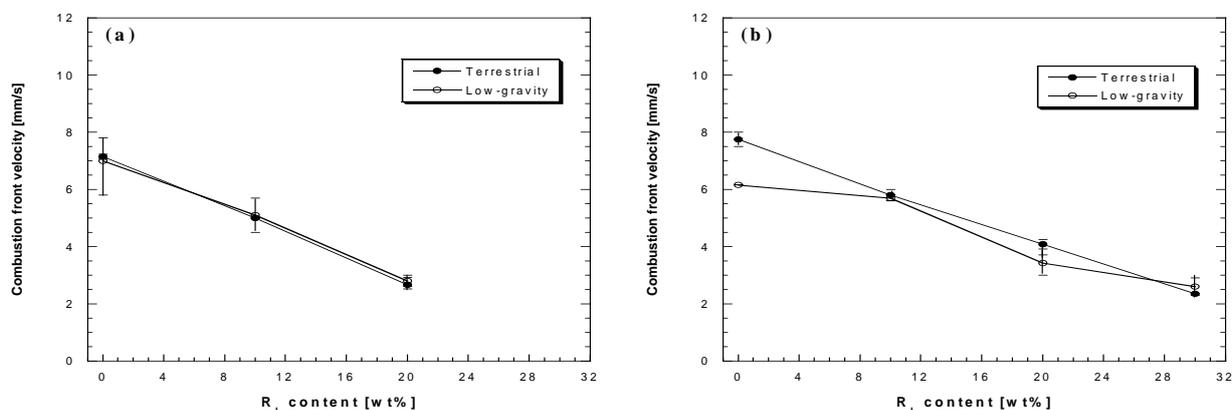


Fig. 6. Comparison of the combustion front velocity measured during SHS under terrestrial and during parabolic flight (about  $10^{-2} \text{ g}$ ) conditions for the cases of (a)  $x=2$  and (b)  $x=3$ .

In this regards, it should be noted that combustion front velocities higher than 2 mm/s are sufficient to guarantee the complete occurrence of the SHS process in 25 mm high samples within the time interval (about 20 s) where the low-gravity condition is established during parabolic flights. Relatively small differences in combustion front velocities are generally observed under the two gravity conditions, particularly when processing highly containing regolith mixtures, that are the most interesting systems from the ISRU point of view. Similar considerations can be made when comparing combustion temperature, although some problems were encountered with thermocouple measurements during parabolic flights experiments, whose signals were disturbed when the more exothermic systems are reacted.

Furthermore, XRD analysis and SEM investigation do not reveal remarkable differences

in the composition and microstructure of products obtained on the ground or during parabolic flights. As an example, Figure 7 shows a SEM micrograph corresponding to the  $S_Lx2R_L0$  system obtained under microgravity conditions. A microstructure with  $Al_2O_3$  grains size, metal phase distribution and composition similar to that of analogous product synthesized under terrestrial conditions (cf. Figure 5a) is obtained. This holds also true for systems containing Lunar regolith in the starting mixture. Since the gravity level on the Moon is about  $1/6 \text{ g}$ , on the basis of the experimental results obtained during parabolic flights under relatively more drastic conditions (about  $10^{-2} \text{ g}$ ), we can assess that the fabrication process investigated in this work is not expected to be significantly affected from the gravitational point of view when performed *in-situ* on Lunar environment.

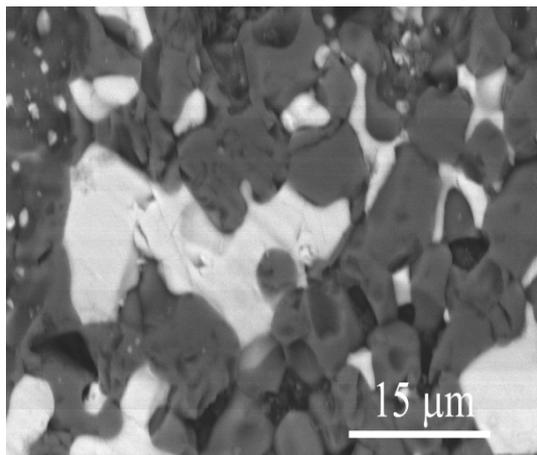


Fig. 7. SEM microstructure of the bulk region of the  $S_{L\_x3\_R_L0}$  end-product obtained by SHS under low gravity conditions (about  $10^{-2}$  g).

### Martian systems

A significant gas expulsion with incomplete reaction and/or pellet disintegration was observed to occur during preliminary SHS tests conducted using as received Martian regoliths, particularly the JSC type. Consistently to the considerations reported in the literature [17], it is possible to assess that these negative features are caused by the excessive presence of water inside the original hygroscopic materials. To identify the experimental conditions required for removing moisture and chemically adsorbed water from the original regolith, TGA analysis consisting of heating the samples up to  $900^{\circ}\text{C}$  has been conducted. Correspondingly, as the temperature was increased from the room value up to  $700^{\circ}\text{C}$ , weight losses of about 5 and 40% were measured when processing  $R_{M2}$  and  $R_{M1}$  materials, respectively, while negligible changes were observed at higher thermal levels. Therefore, the temperature of  $700^{\circ}\text{C}$  was chosen for desiccating both Martian simulants before blending them with the other constituents of the mixture to be reacted by SHS.

Both Martian systems investigated in this work, i.e.  $S_{M\_x2.44\_R_{M1}0\_R_{M2}45}$  and  $S_{M\_x2.44\_R_{M1}13\_R_{M2}32}$ , exhibit a SHS behaviour. The XRD patterns of the obtained products are shown in Figure 8 along with that of the starting mixture.

As for the case of Lunar systems, the crystalline phases related to JSC and Mojave Martian simulants are indicated in cumulative manner in the XRD spectra as  $R_{M1}$  and  $R_{M2}$ , respectively. No evidence of the presence of residual reactants in final products is found by XRD analysis. Moreover,

the identification of product phases is relatively simple, being  $\text{Al}_2\text{O}_3$  and Fe the only crystalline phases present, regardless the type of Martian simulant utilized. The formation of these two phases is perfectly consistent with the occurrence of the base thermite reaction (1) between commercial hematite and Al, but is also the result of the reduction of the various iron oxides present in both Martian regolith simulants (cf. Table 2 and 3). Indeed, these oxides can be chemically reduced by the excess of Al present in the mixture ( $x=2.44$ ), as compared to that consumed ( $x=2$ ) by  $\text{Fe}_2\text{O}_3$  reactant according to reaction (1).

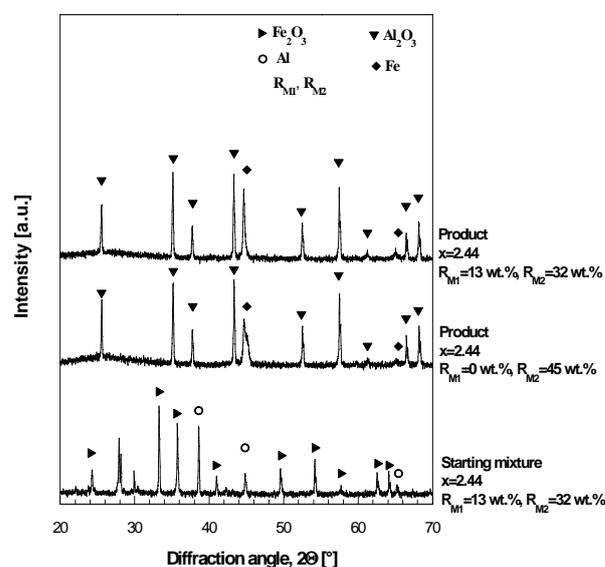


Fig. 8. Composition of the starting mixture ( $x=2.44$ ,  $R_{M1} = 13$  wt.%,  $R_{M2} = 32$  wt.%) and end products obtained in Martian systems by SHS for the cases of  $S_{M\_x2.44\_R_{M1}0\_R_{M2}45}$  and  $S_{M\_x2.44\_R_{M1}13\_R_{M2}32}$  specimens.

The occurrence of the SHS reactions involving Martian systems under low-gravity condition ( $\sim 10^{-2}$  g) did not show, as compared to terrestrial experiments, any significant difference from either the process dynamic or products characteristics. Thus, similar considerations to those already made when examining Lunar systems can be made. Specifically, since the gravity level on Mars' surface is relatively closer (about  $1/3$  g) to that on the Earth, in comparison with the microgravity condition encountered during the 20 s parabolic flights, we can conclude also in this case that the SHS process investigated in this work is not expected to modify its behaviour when evolving under the gravitational Martian environment.

## Conclusion

A fabrication process based on the occurrence of SHS reactions for obtaining composite ceramics to be used as construction materials in Lunar and Martian environments is described in this work. Following the ISRU and ISFR principles, Lunar and Martian regolith simulants are utilized in the mixtures to be reacted, due to the relatively high content of ilmenite and iron oxides on Moon and Mars soils, respectively. Thus, the self-propagating metallothermic reductions of these two oxide species represent the base reactions of the fabrication process.

In this context, the dependence of the composition of the starting mixture, evacuation level, and gravity conditions, on SHS process behaviour and product characteristics is taken into account in a systematic manner. This study was particularly focused to Lunar systems and allows us to identify the optimal composition of the starting mixtures to be reacted by SHS.

Firstly, it is found that, although mixtures involving Mg instead of Al as reductant exhibit relatively superior adiabatic temperatures, the correspondingly higher volatility makes SHS process control very difficult and the resulting products highly porous at the evacuation level (25 Torr) investigated.

Moreover, this study evidenced that the SHS behavior is guaranteed only for mixtures with the Al/FeTiO<sub>3</sub> molar ratio higher than 0.9. In this regard, no additional regolith simulant is allowed to be added to the mixture for maintaining the self-propagating character, unless the Al/FeTiO<sub>3</sub> is correspondingly augmented. Specifically, the minimum amount of Al required in SHSed systems increases from 13.5 wt.% (x=0.9), if the reaction is performed with pure ilmenite, to 23.5 wt.% (x=3), needed when the starting mixture also contained 32.5 wt.% of the original simulant.

The obtained products mainly consist of Al<sub>2</sub>O<sub>3</sub>, Fe and, for the case of Lunar regolith, Ti, and various Ca- and Mg- simple and mixed oxides.

Compressive strength measurements provided average values, in the range of 25.8-27.2 MPa, significantly higher in comparison to that (18 MPa) reported in the literature relatively to products obtained from the direct thermite reaction between Lunar regolith simulant and 33 wt.% Al [9].

This outcome is likely due to the most favorable reaction conditions encountered in our study

because of the presence of the relatively higher ilmenite percentage in the initial mixture. Indeed, the corresponding increase in the exothermicity of the reacting system promotes the interaction among reactant particles towards the obtainment of strongly sintered materials.

The SHS experiments performed on Lunar and Martian systems under low gravity conditions (parabolic flights) indicate that neither SHS process dynamics nor product characteristics are significantly affected by gravity. Therefore, the optimized results obtained under terrestrial conditions can be considered still valid for *in-situ* applications on Moon and Mars.

It should be noted that, while in this study FeTiO<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> were added to promote the self-sustaining character in the original mixtures, an enrichment stage of these two species already present in Lunar and Martian regoliths, respectively, can be foreseen for favoring the *in-situ* utilization of this process. This and all the other technical stages required in the framework of the process for the fabrication by SHS of physical assets for construction applications in Lunar and Martian environments, are schematically represented in Figure 9. Briefly, the process consists first in the production of solar electric power needed for the different fabrication stages, including the excavation of Lunar or Martian regoliths. The latter ones have to be then enriched in ilmenite or iron oxides using suitable techniques, before being mixed and reacted by SHS using optimal amounts of Al. Finally, the desired infrastructures can be obtained by mounting the fabricated structural elements. Further details related to this process are reported elsewhere [12].

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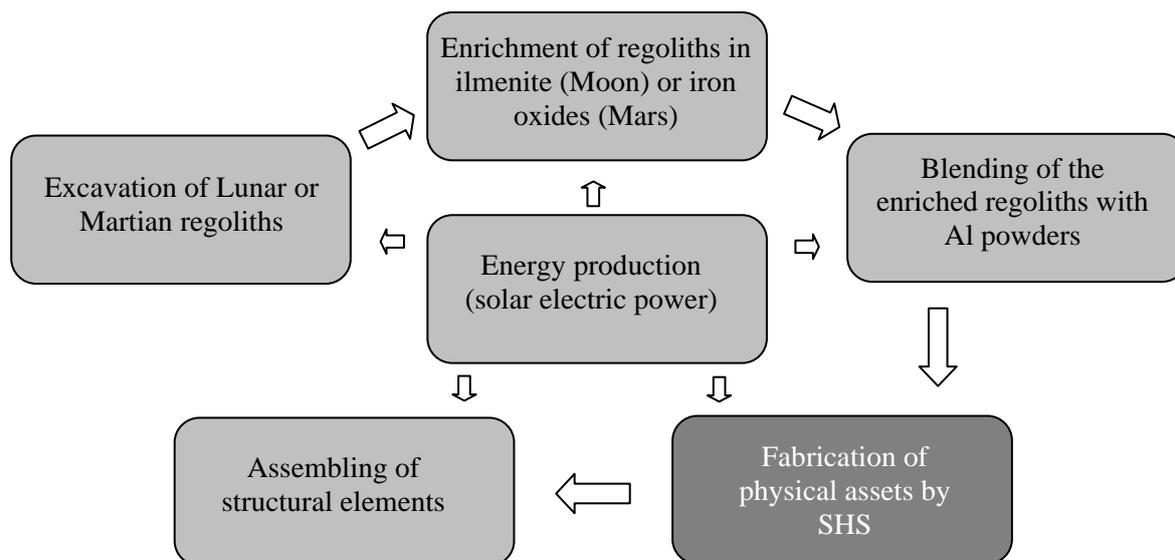


Fig. 9: Main stages involved in the process based on SHS reactions for the fabrication of physical assets on Moon and Mars [12].

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