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A Systematic Investigation to Obtain Physical Assets on the Moon through Self-propagating High-temperature Reactions

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Future space missions on the Moon, Mars and near Earth asteroids, etc., are expected to be strongly facilitated and time extended by the possibility of "In-Situ Fabrication and Repair" (ISFR) the required equipments and infrastructures. In addition, the combination of the latter approach with the "In-Situ Resources Utilization" (ISRU) paradigm contributes to overcome drawbacks related to the transportation of the needed material from the Earth. In this regard, various technologies have been recently proposed with the aim of developing suitable structures to be placed on the Moon surface for the protection against cosmic rays, solar wind, meteoroids, etc. Specifically, the possibility of exploiting combustion synthesis-type reactions using Lunar resources for the fabrication of ceramic-based products was considered. Along these lines, by taking advantage of the fact that Lunar soil contains up to 20 wt.% of ilmenite ($FeTiO_3$), the highly exothermic thermite reduction of the latter oxide with Al is systematically investigated in this work. A self-propagating (SHS) behavior is displayed only above a certain Al/$FeTiO_3$ molar ratio (0.9). In addition, as the amount of Al in the mixture is increased, the reactive process proceeds faster and the combustion temperature becomes higher, due to the increased system exothermicity. Correspondingly, the maximum amount of Lunar regolith to be possibly reacted with additional $FeTiO_3$ and Al is identified. The obtained products (a mixture of Al-, Ti-, Mg-, and Ca-oxides, and metallic phases) exhibit satisfactory compressive strength properties (≥ 25.8 MPa) that make them promising as construction materials. Parabolic flight experiments evidenced that SHS process dynamics and product characteristics are barely affected by gravity. The obtained findings allow us to conclude that the optimal conditions identified during terrestrial experiments are still valid for *in-situ* applications in Lunar environment.

1. 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. (cf. Bassler et al., 2006; Hammond et al., 2006; Howell et al., 2008). 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 (cf. Allen et al., 1994; Toutanji et al., 2005; Tucker et al., 2006; Martirosyan and Luss, 2006; Faierson et al., 2010; Faierson and Logan, 2010; White et al., 2011; Cao et al., 2011). For instance, a process where regolith Lunar simulant was sintered at 1100°C by radiant and microwave heating was proposed (Allen et al., 1994). Lunar regolith was also utilized for fabricating a thermo-plastic material (Toutanji et al., 2005) and fiberglass for reinforcing Lunar concrete (Tucker et al., 2006). 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 (Martirosyan and Luss, 2006; Faierson et al., 2010; Faierson and Logan, 2010; White et al., 2011; Cao et al., 2011). For instance, the exothermic chemical reaction $x(Ti + 2B) + (1-x)JSC\text{-}1 \rightarrow x(TiB_2) + (1-x)JSC\text{-}1$, 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 (Martirosyan and Luss, 2006). On the other hand, the direct aluminothermic

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reduction of Lunar regolith was found to produce, after a relatively long preheating stage (7-15 min), a ceramic composite material, mainly consisting of Al_2O_3, Si, $CaAl_4O_7$ and $MgAl_2O_4$. (Faierson et al., 2010; Faierson and Logan, 2010). Along these lines, taking advantage of the presence of significant amounts of iron oxides in Martian soil, the highly exothermic, 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 ($FeTiO_3$), whose presence is up to 20 wt.% on the Moon, by aluminum (Schrunk et al., 2008). Following Faierson et al. (2010) and Faierson and Logan (2010) approaches, 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 (White et al., 2011). In the present work, a recently patented process based on the occurrence of SHS reactions in a mixture made of Lunar regolith simulants with appropriate amounts of $FeTiO_3$ and Al, is described. In this regard, it is important to note that relatively lower gravity levels are encountered in Lunar environment as compared to Earth. Therefore, after systematically investigating the composition of the starting mixture, the influence of gravity conditions on SHS process behaviour and product characteristics is also taken into account in this work.

2. Experimental

The JSC Lunar (R_L) regolith used in the present investigation has been provided by Orbitec (USA). The JSC simulant mainly consists of plagioclase, Ca-rich pyroxene, olivine and ilmenite minerals, as well as other minor phases (Sibille et al., 2005). The original simulant has been preliminarily sieved to produce powders with particle size less than 45μm. 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:

$FeTiO_3 + xAl + y(wt.\%)\ R_L \rightarrow$ Products (1)

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/$FeTiO_3$ molar ratio and R_L# represents the weight percentage (y) of Lunar regolith in the mixture.

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^{-2} g) onboard of the Airbus 300 during the 53rd 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 Ircon Mirage OR 15-990 (Ircon, 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).

3. Results and discussion

Due to low pressure level characterizing Lunar atmosphere and the relatively lower vapour pressure of Al with respect to Mg, the first metal was selected as reducing agent in our experimentation. As pointed out in a recent paper (White et al., 2011), Al could be extracted from Moon soil minerals containing this element or recovered from certain vehicles components utilized in previous space missions. The study regarding the effect of the Al/$FeTiO_3$ ratio on the combustion front velocity and the maximum combustion temperature evidenced that reacting systems display a SHS character only if $x \geq 0.9$, when no regolith was present in the mixtures. In addition, both the velocity and combustion temperature increased as the Al/$FeTiO_3$ is correspondingly augmented. Therefore, the obtained result indicates that the exothermic character of reaction (1) is progressively enhanced as the x value is increased from 0.9 to 3.

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 1(a)-1(b) when x=2 and 3, respectively. Similar results are obtained using the other Al/$FeTiO_3$ 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. It is also possible to observe from Figure 1 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 (Munir and Anselmi-Tamburini, 1989). Therefore, the behaviour displayed in Figure 1 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 $FeTiO_3$ 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 (Schrunk et al., 2008) and that 99,8% pure commercial powders additionally provided. 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. 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.

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 Figures 2(a)-2(d) at the various x values investigated. For the sake of comparison, the XRD spectra related to the starting mixtures are also reported.

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 (R_L=0). It can be generally stated that, except for the case of x=0.9, Al_2O_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 2(a)) to 1 (cf. Figure 2(b)) the formation of Ti_3O_5 is replaced by the relatively less oxidized Ti_2O_3 specie. Nevertheless, the presence of partially reduced iron oxides (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 $FeAl_2$ and $Al_3Ti_{0.75}O_{0.25}$.

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. Figures 2(a)-2(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 $MgAl_2O_4$, $Ca(Al,Fe)_{12}O_{19}$, $Ca_2(Al,Fe)_2O_5$ and $CaAl_4O_7$, 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 $FeTiO_3$, $CaAl_2Si_2O_8$, $CaSiO_3$, and Mg_2SiO_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 (Faierson et al., 2010). 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. According to the XRD results, SEM-EDS analysis of a reaction product synthesized when x=3 and no JSC simulant was added to the reacting mixture indicates that the composite material mainly consists of Al_2O_3 grains and a multiphase metal matrix 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. Specifically, for the case of the S_L_x3_R_L30 system, a complex fibrous microstructure is obtained. In particular, a phase with a filament-like structure is present inside sample pores, while it is found embedded into product matrix throughout the bulk of the SHSed sample. 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 ascribed to be 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 (Faierson and Logan, 2010).
Compressive strength measurements performed on cylindrical shaped S_L_x2_R_L20 and S_L_x3_ R_L30 products provide average values of 27.2 ± 3.6 and 25.8 ± 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 simulant, i.e. about 18 MPa (Faierson et al., 2010). 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 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 3(a)-3(b) when x=2 and 3, respectively, with the values related to the analogous experiments performed in a microgravity environment (~10^{-2} g) during a recent parabolic flight campaign.
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. SEM investigation conducted on SHSed samples obtained under microgravity conditions shows microstructures with Al_2O_3 grains size, metal phase distribution and composition similar to those of analogous products synthesized under terrestrial conditions. Since the gravity level on the Moon is about 1/6 g, on the basis of the experimental results obtained during parabolic flights under relatively more drastic conditions (about$\cdot 10^{-2}$ 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.

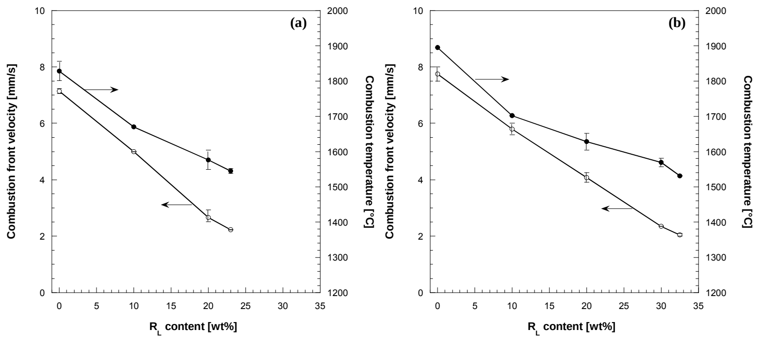

Figure 1. Effect of the presence of Lunar regolith content in the starting mixtures on the front velocity and combustion temperature when (a) x=2 and (b) x=3.

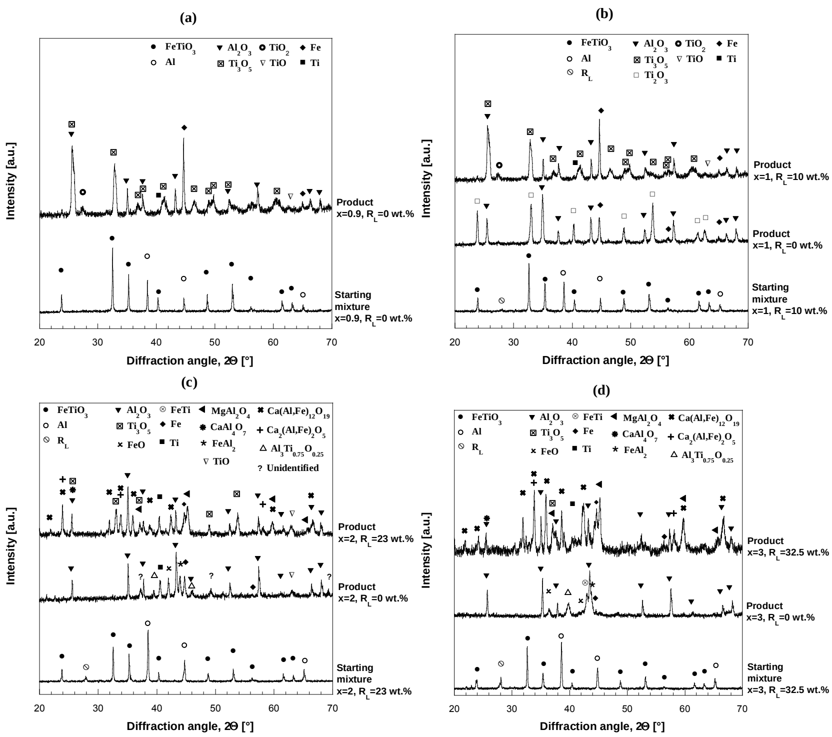

Figure 2. Composition of the starting mixtures and end products obtained in Lunar systems by SHS without or with JSC regolith (maximum allowable content): (a) x=0.9, (b) x=1, (c) x=2, (d) x=3.

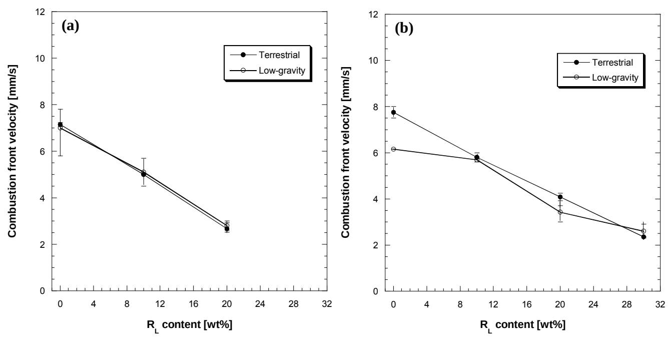

Figure 3. Comparison of the combustion front velocity measured during SHS under terrestrial and parabolic flight (about 10-2 g) conditions for the cases of (a) x=2 and (b) x=3.

4. Concluding remarks

A fabrication process based on the occurrence of SHS reactions for obtaining composite ceramics to be used as construction materials in Lunar environment is described in this work. Following the ISRU and ISFR principles, Lunar regolith simulant is utilized in the mixtures to be reacted, due to the relatively high content of ilmenite on Moon soils. The experiments performed on Lunar 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. It should be noted that an enrichment stage of FeTiO3 already present in Lunar regolith can be foreseen for favoring the in-situ utilization of this process. This and the other technical stages required in the framework of the process for the fabrication by SHS of physical assets for construction applications in Lunar environment are reported elsewhere (Cao et al., 2011). Briefly, the process consists first in the production of solar electric power needed for the different fabrication stages, including the excavation of Lunar regolith. The latter one has to be then enriched in ilmenite 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.

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