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Metal-CO_2 Propulsion for Mars Missions: Current Status and Opportunities

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I. Introduction

IN SITU resource utilization (ISRU) is recognized as an enabling technology for exploration of Mars, which can significantly reduce the mass, cost, and risk of robotic and human missions. The critical element in future missions is the large mass of propellant for a Mars ascent vehicle, although power and propellant to accommodate a long stay and mobility on Mars are also important. Transportation of propellant from Earth to Mars requires a tremendous increase in the initial mass of hardware in low Earth orbit (and hence mission cost) as compared to prior *no-return* missions. Fortunately, Mars possesses resources that can be used for propellant production. The Martian atmosphere consisting of 95% CO_2 is the obvious and most promising in situ resource.

Two methodologies for production of propellants on Mars received the most attention for nearly three decades after pioneering research by Ash et al. [1]. One of them postulates production of CO and O_2 by electrolysis of the Martian CO_2 in a zirconia cell for use as a liquid bipropellant in rocket engines [1–6]. Because CO/O_2 propellant provides relatively low performance [5], generation of only liquid oxygen on Mars for use with better (hydrocarbon) fuel transported from Earth was also considered. A major problem in the technologies based on CO_2 electrolysis is that zirconia electrolyzers are fragile and require high operating temperatures (>1000 K). This drawback is eliminated in the second methodology [7–11], which brings liquid hydrogen to Mars and then uses it with the Martian CO_2 in a chemical plant to produce hydrocarbon fuel (e.g., methane, methanol, ethylene) and oxygen. The chemical plant includes a Sabatier reactor, a water electrolyzer, and may also include a reverse water–gas shift reactor. The attractive features of this concept are the relatively simple technology and high-performance characteristics of the produced propellants, but the long-term storage of liquid H_2 is a significant problem. Recently, the two methodologies were, in fact, converged in a new architecture for an in situ propellant production plant, which uses the Sabatier process and combined H_2O/CO_2 solid oxide electrolysis [12]. Although this technology promises some benefits, it has both major problems of the two main methodologies, i.e., it needs hydrogen and uses fragile electrolysis cells, operating at high temperatures. The hydrogen transportation from Earth can be avoided if it is extracted from H-rich, near-surface deposits discovered in some locations on Mars [13–15], or water is adsorbed from the Martian atmosphere [16] (0.03% H_2O), but these options require additional operations and energy. The common drawback of all aforementioned Mars ISRU scenarios is the significant power required to produce, liquefy, and store cryogenic propellants [17].

An alternative approach in the Mars ISRU suggests using the Martian CO_2 directly as an oxidizer in a jet or rocket engine. This approach is based on the unique ability of some metals and compounds to burn with CO_2. The idea to burn metals in atmospheres of planets for propulsion appeared long ago. In the 1960s, Rhein [18] studied ignition of several metals in CO_2 and N_2 environments for propulsion on Venus and Mars, respectively (it was thought then that the Mars atmosphere consists of nitrogen). Historically, the direct use of Martian CO_2 as an oxidizer has received less attention than its conversion to propellants, possibly due to the fact that CO_2 is usually considered an extinguishing agent. Nevertheless, a number of contributions to this area have been made.

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In early developments by Golaido et al. [19] and Yuasa and Isoda [20], "CO_2-breathing" jet engines were considered. This is quite understandable as no CO_2 processing is required and the propulsion system is the only element that needs to be developed in this case. For sample return and human missions, however, rocket engines are required. Fortunately, the low temperature of the Mars atmosphere favors CO_2 liquefaction, thus allowing relatively easy accumulation of liquid CO_2 at pressure $\sim$10 bar for subsequent use in rocket engines. On the other hand, the low atmospheric pressure of Mars (7–9 mbar), being a major problem for jet engines, is perfect for rockets (no need for pressure higher than 10 bar in the combustion chamber to obtain high nozzle expansion ratio). These favorable circumstances were noted by Shafirovich et al. [21], who first conducted thermodynamic calculations of performance characteristics for rocket engines using metal-CO_2 propellants and made ballistic estimates.

Subsequent publications have demonstrated the feasibility of this approach and further advanced the concept of metal-CO_2 propulsion on Mars. This includes tests of simplified engines using CO_2 as an oxidizer by Wickman [22] and Zubrin et al. [23]. Also, successful design solutions were developed for engines using powdered metal fuel with air or steam, which could be used in metal-CO_2 propulsion systems. Fundamental studies of metals combustion have improved significantly understanding of Mg and Al particle combustion in CO_2 atmosphere. Noticeable progress was made in development of methods for CO_2 acquisition on Mars, and new ideas appeared for production of metal fuel on Mars. Finally, mission analyses have identified scenarios in which metal-CO_2 propulsion promises greater advantages. The purpose of the present paper is to review the current status of the metal-CO_2 propulsion concept, including all relevant aspects, such as scientific data on metals combustion in CO_2, engine types and characteristics, production of liquid CO_2 and metal fuel on Mars, and potential missions.

II. Combustion of Magnesium and Aluminum in CO_2

It is well known that some metals (e.g., magnesium) burn in CO_2 atmosphere. In fact, reactions of metals with CO_2 have been used in rocket propulsion and pyrotechnics for many years. For example, in solid rocket engines, aluminum particles burn in gaseous products of ammonium perchlorate/hydrocarbon binder combustion, where CO_2 and H_2O are the main oxidizers [24]. It should be noted that H_2O was previously considered to be a stronger oxidizer for Al than CO_2, but recent particle burning time measurements [25] suggest that this is not always correct. The solid rocket motor applications and the potential of metal-CO_2 propulsion on Mars inspired researchers to study combustion of metals (mainly Al and Mg) in CO_2. Since the first systematic experiments by Mellor and Glassman [26] and Rhein [18] in the 1960s, a significant volume of data on Mg [27–45] and Al [25,46–68] combustion in CO_2 has been acquired. Based on the obtained results, we can state that Mg and Al particles burn rapidly in a CO_2 environment, producing metal oxide, CO, and a relatively small amount of carbon. More specific, but brief, information is summarized next.

A. Ignition and Combustion of Magnesium Particles in CO_2 Atmosphere

1. *Experimental Results*

Magnesium particles ignite easily in a CO_2 environment. When a 2 mm Mg particle is introduced into a high-temperature CO_2 gas, ignition occurs if the gas temperature is higher than the Mg melting point (923 K) [31–33]. Thermogravimetric analysis [40] revealed a slow heterogeneous combustion regime at the ambient temperature range of 923–965 K. At higher temperatures, ignition leads to fast vapor-phase combustion which involves a well-developed flame, with the temperature being much higher than on the particle surface [31–33]. Experiments with heating by radiation or contact methods in a room-temperature gas environment showed that the particle ignites at 1000–1100 K and burns in the vapor phase [39,42,43].

Combustion of Mg particles in CO_2 results in formation of a porous solid shell, which is about the same size as the initial particle and consists of MgO and carbon [31–33]. Also, submicron MgO particles form in flame and agglomerate. Formation of carbon near the particle surface and its absence in the gas phase are caused by thermodynamics and temperature distribution in the vapor-phase combustion flame. More specifically, thermodynamics of an Mg-CO_2 system allows carbon to be formed by reaction of Mg with CO (produced in flame) at sufficiently low temperatures, occurring at the particle surface. Note that according to experiments [32], smaller Mg particles can be overheated much above the boiling point of Mg, thus hindering the reaction of Mg with CO and formation of carbon.

The obtained dependence of burning time on the initial particle size fits well with the square law $t_b = k \cdot d^2$. Similar values of the constant k (0.5, 1, and 0.63 $\mathrm{s/mm^2}$ from [39,42,43], respectively) were obtained in experiments involving different experimental methods, such as electrodynamic levitation and microgravity. The square dependence indicates that combustion is controlled by diffusion in the gas phase over the size range from 50 μm to 4 mm.

Dilution of CO_2 by Ar decreases the burning rate, as expected for diffusion-controlled combustion [33]. On the other hand, dilution by CO, which is one of the products, results in pulsations of combustion [33,36,38,41]. Pulsations were also observed in pure CO_2 for particles heated by contact methods in a room-temperature gas environment [27,43]. Note that the pulsating regime is undesirable for applications, as it makes the total process time longer than for stable combustion. It is believed, however, that the pulsating regime occurs either at CO concentrations as high as 50% in a CO_2/CO gas mixture, or at near-room temperatures in a CO_2 environment. The latter is obviously impossible in engines, whereas high CO concentrations are expected for stoichiometric Mg/CO_2 mixtures. Fortunately, mixtures with higher CO_2 concentrations will likely be used, thus decreasing the probability of the pulsating regime.

Most experiments on combustion of Mg in CO_2 and CO_2/CO mixtures were conducted at a pressure of 1 atm. Increasing pressure decreases the flame size and increases the density of the MgO/C shell but does not prevent stable combustion of Mg particles in CO_2 owing to observed ejection of fragments [32]. On the other hand, decreasing pressure from 1 atm to some level also does not interrupt the process; ignition of Mg particles in CO_2 was observed at pressures as low as 5.3 mbar [34].

2. *Modeling*

Specific features of Mg combustion in CO_2 were taken into account in several models. Shafirovich and Filonenko [29] have developed a quasi-steady diffusion-controlled model for Mg particle burning in CO_2. Based on thermodynamics, they postulated two infinitely fast reactions: between Mg vapor and CO_2 in the gas phase ($Mg + CO_2 \rightarrow MgO + CO$) and between Mg and formed CO near the particle surface ($Mg + CO \rightarrow MgO + C$). The predicted burning times ($k = 0.55\ \mathrm{s/mm^2}$), the influences of Ar and low CO concentrations, as well as the quantities of product carbon are in a good agreement with experimental data [31–33,39–43]. The model shows that only a small fraction of Mg reacts near the surface (with CO), which explains to some extent why the formed MgO and carbon do not prevent diffusion of Mg vapor. The reaction of Mg with CO, however, influences significantly the burning rate because it is highly exothermic and located near the surface.

The two-reaction scheme, described also in [31,33], was later adopted by Valov et al. [35] and Yuasa and Fukuchi [36] to qualitatively explain their experimental results on Mg combustion in CO_2. More recently, the model [29] was further advanced by King [45], who considered finite kinetics for the near-surface reaction of Mg with CO. His calculations predict $k = 0.83\ \mathrm{s/mm^2}$ for diffusion-controlled reaction on the surface and 3.0–3.2 $\mathrm{s/mm^2}$ for the case with no reaction occurring on the surface.

Abbud-Madrid et al. [42] also used the two-reaction scheme in a numerical finite kinetics quasi-steady model for Mg particle combustion in CO_2. The model shows that the overall burning process appears to be diffusion controlled. An ambient temperature of 1000 K is necessary for convergence of the simulation, which agrees with the aforementioned experimental data on ignition and pulsations. The model provides more detailed information on the flame structure but does not include an adequate description of product condensation, radiation heat loss, and heterogeneous surface reactions, and suffers from the lack of kinetic parameters.

Formation of MgO particles was analyzed by Lukin and Stepanov [28] in a nonsteady numerical model for combustion of a single Mg particle in air or CO_2, using Becker–Doring equations to describe homogeneous condensation of supersaturated MgO vapor. Although only the reaction $Mg + CO_2 \rightarrow MgO + CO$ was considered for combustion in CO_2 environments, the approach appears to be fruitful and can be used in future models if the goal is to obtain information on oxide particle sizes.

Combustion of Mg in CO_2 was also considered by Liu et al. [44] with the purpose of studying, via activation energy asymptotics, the effect of product condensation on droplet combustion. This model assumes that Mg vapor reacts with CO_2 in a detached flame zone, producing condensed magnesia and carbon ($2Mg + CO_2 \rightarrow 2MgO + C$). This scheme contradicts the experimental observations described previously, but the conducted analysis is interesting and could be accounted for in future developments.

B. Ignition and Combustion of Aluminum Particles in CO_2 Atmosphere

1. Experimental Results

Despite the extensive use of Al particles in rocket propellants, their combustion mechanisms in oxidizing gases, including CO_2, are less understood than for Mg. This situation is partially explained by more complicated chemistry. The final product of aluminum oxidation, alumina (Al_2O_3), does not exist in the gas phase but there are several gaseous suboxides of Al. Thus, combustion of an Al particle (droplet) and formation of alumina involves numerous reactions in the gas phase, on the droplet surface, and possibly on the surface of growing oxide particles. Further, a liquid oxide cap forms on the Al surface during combustion.

The CO_2 environment adds additional complexities and makes combustion of Al different from that in oxygen or air. For an Al-O_2 system, the maximum adiabatic flame temperature at any pressure is much higher than the Al boiling point (at the same pressure), which results in a vapor-phase flame detached from the particle surface. For an Al-CO_2 system, if both reactants are initially at 298 K, the adiabatic flame temperature is comparable with the Al boiling point at a pressure of 1 atm and is less than the boiling point at a pressure of more than 5 atm [59]. This leads to a larger role of surface reactions and a thinner flame zone, adjacent to the surface [54,55,59].

During combustion of an Al particle in CO_2, carbon forms on the particle surface and dissolves in liquid Al [60]. Because the droplet size decreases, the carbon concentration inevitably reaches the saturation limit, upon which either a carbon or aluminum oxycarbide layer covers the surface, hindering Al vaporization [66]. It should be noted that the second burning regime reported in [66], leading to the disappearance of carbon through the gasification reaction $C + CO_2 \rightarrow 2CO$, was observed under continued laser heating of 3 mm Al droplets and may not occur during self-sustained combustion of smaller Al particles.

As mentioned earlier, there exists discussion in the literature on relative "strengths" of CO_2 and H_2O as oxidizers for Al particles. The results on the burning times are contradictory: similar values [46], longer in CO_2 [53,63,65] and in H_2O [25]. This is likely related to different experimental conditions, which include the ranges of particle sizes from 10 μm [25] to 3 mm [65] and temperatures from 298 [65] to 2650 K [25].

The particle size is an important parameter influencing combustion behavior. A decrease in the initial size leads to the transition from a diffusion- to kinetic-controlled regime. As noted previously, the diffusion-controlled regime is observed for Mg particles in CO_2 over the range of sizes from 50 μm to 4 mm. For Al particles in CO_2, analysis of combustion behavior and characteristics (e.g., flame structure, pressure effect) indicates that combustion is controlled by diffusion for particle sizes more than 200 μm (e.g., no pressure influence observed) [56–58], whereas for sizes less than 80 μm, the limiting step is possibly kinetics of reactions on particle surface [59,68]. Experiments with nanoparticles (average size 80 nm) in CO_2 environments also indicate that combustion is kinetic-controlled and has some features that distinguish it from that in O_2 atmospheres, including only slight increase of the particle temperature above the ambient temperature during combustion [67,68]. Note that the 80 nm particles ignite at 1200 K [67], the lowest temperature investigated.

The high ignition temperature, unless nanoparticles are used, is a major drawback of Al. Whereas Mg usually ignites in CO_2 at temperatures of 1000–1100 K, micron-scale and larger Al particles must be heated above 2000 K, close to the melting point of Al_2O_3 (2327 K). This is not critical in solid rocket motors, where combustion of Al occurs at temperatures of 2700–3000 K [25], but is important for metal-CO_2 engines. Because their chamber temperatures for Al/CO_2 mixtures with high CO_2 fraction (which may be useful for Mars propulsion) are expected to be 2000–2500 K [21], stable ignition will likely need a permanent igniter which adds weight and power consumption. Thus, to use Al particles in metal-CO_2 propulsion, their ignition must be improved.

One obvious idea is to use Al-Mg alloys. Unfortunately, ignition of 50% Al–50% Mg alloy particles levitated in CO_2 was not observed in all ranges of tested pressures from 1 to 20 bar [39]. A possible reason for this is the high protective properties of the surface oxide film for these particles. Note that in earlier experiments [27] magnesium burned out of Al-Mg alloy particles ignited by a contact method in CO_2 atmosphere, but aluminum did not. There is a possibility, however, that metastable Al-Mg (5–50 at.% Mg) mechanical alloy particles [69–72] may burn well in a CO_2 environment. It was shown that such particles ignite in air at 950–1060 K [69], as well as exhibit higher combustion rates and more complete oxidation than equilibrium alloy particles [71]. Qualitatively similar effects were reported for Al-Ti (10–25 at.% Ti) mechanical alloy particles in air [73], but Ti provides worse performance than Mg for metal-CO_2 propulsion [21]. Thus, it would be interesting to conduct experiments with metastable Al-Mg mechanical alloy particles in a CO_2 atmosphere.

Another promising method for the improvement of Al particle ignition is coating by another metal, such as nickel, which reacts with Al at high temperatures. The noticeable exothermic reaction between the Ni shell and Al core starts after melting of Al (melting point 933 K) and triggers the ignition [74–79]. Experiments with single Ni-coated Al particles levitated in air have shown that as little as 3 wt % Ni is required to achieve the maximum (by a factor of $\sim$4) decrease in ignition delay time [77]. In CO_2 environments, Ni-coated Al particles ignite after several consecutive phase transformations in the surface layer, at a temperature $\sim$1600 K [78], i.e., at significantly lower temperature than original, oxide-coated Al particles. Very recently, experiments with iron-coated Al particles have shown that such particles ignite at a surface temperature 1600–1700 K and hence could also be used for propulsion applications [79]. Finally, it is worthwhile to investigate nonmetal coatings, such as fluorine-containing polymers [80–82] and complex fluorides [83], as methods to facilitate ignition of Al particles in CO_2 atmosphere.

2. Modeling

Numerous models have been developed for Al particle combustion. Here, we give a brief review of only those developments where CO_2 was considered.

Gremyachkin et al. [48] have developed a quasi-steady model where the surface reaction between Al and gaseous oxidizer plays the main role, and the rate of this reaction (i.e., the particle burning rate) is controlled by diffusion of the oxidizer to the surface. Aluminum vapor, gaseous suboxide Al_2O, and CO (when the oxidizer is CO_2) diffuse from the particle surface toward the oxidizer. It is assumed that reactions of Al(g) and Al_2O with the oxidizer occur on the surface of condensation nuclei, far away from the particle surface, and do not influence the process. This model is valid if diffusion is, on one hand, much slower than reactions on the Al particle surface and, on the other, much faster than reactions on condensation nuclei in the gas phase. According to experimental data on the pressure dependence of the burning time [56–58], the former inequality may occur in CO_2 at particle sizes larger than 200 μm. Experimental studies of flame structure for 230 μm Al particles in CO_2 [54] indicate, however, that condensation reactions in the gas phase effect the process.

King [50] has developed a quasi-steady model for Al droplet burning in CO_2 with the following reaction scheme: the gas-phase reaction $Al + CO_2 \rightarrow AlO + CO$, vaporization $Al(l) \rightarrow Al(g)$, surface reaction $AlO + Al(l) \rightarrow Al_2O$ (and, as a variant, $2Al(l) + CO_2 \rightarrow Al_2O + CO$), and condensation reactions of Al, AlO, and Al_2O with CO_2 to produce CO and liquid Al_2O_3. The condensation reactions occurred in a thin zone whose location was determined by specification of a condensation temperature. Experimental kinetic data [49] were used for the gas-phase reaction, and all other reactions were assumed to be infinitely fast. It was shown that the use of finite kinetics leads to the lower than 2 exponent in a power law for the particle-size dependence of the burning time, observed for Al by many authors [63]. Note, however, that the significant temperature maximum in the gas phase (where the condensation zone is located) appears to contradict the flame observations for 40–80 μm particles discussed previously.

Bucher et al. [54] have conducted numerical calculations for Al particle burning in various atmospheres, including CO_2. For Al-containing species, local equilibrium was assumed at each nodal position above the particle surface, whereas for all other species, finite rate chemistry was used. No surface reactions were considered and the final condensed product Al_2O_3 was treated like a gas-phase species with a low diffusivity. A classical diffusion flame was reported for combustion in CO_2 atmosphere, in contrast to experimental data.

Beckstead et al. [64] have developed a two-dimensional, unsteady-state, numerical model for Al particle combustion in various atmospheres, including CO_2. The particle was considered in free fall after ignition. The reaction scheme for CO_2 included kinetic-controlled gas-phase reactions of Al and AlO with CO_2 and O_2, vaporization of Al and diffusion-controlled surface reaction $AlO + Al(l) \rightarrow Al_2O$, kinetic-controlled dissociation of liquid Al_2O_3 to AlO and O_2, and, finally, condensation reactions of Al suboxides with CO_2 and O_2 to produce CO, O_2, and liquid Al_2O_3. To describe the condensation process, a two-step mechanism was proposed, where the first step is the gas-phase reaction that yields a gaseous Al_2O_3 and the second step is its homogeneous condensation. Although gaseous Al_2O_3 was never observed experimentally, it can be considered as an intermediate product with a short lifetime, and this approach appears to be acceptable. Further, the model described deposition of the condensed product onto the particle surface and formation of the oxide cap. The flame structure for an Al particle in CO_2, predicted by this model, does not contain the sharp temperature maximum (in contrast to the results for O_2 and H_2O) and looks similar to those observed in experiments. The modeling results also demonstrate that the exponent of the particle-diameter dependence of the burning time is less than two and decreases with decreasing the particle size. This model appears to be the most comprehensive development for Al particle combustion in CO_2 environments, though it does not describe experimental observations such as carbon dissolution in liquid Al and formation of an oxycarbide layer, as noted previously.

C. Combustion of Metal Particle Clouds in CO_2 Atmosphere

The preceding review shows that a good level of understanding has been reached for combustion of single Mg and Al particles in CO_2. Much less has been reported, however, on flame propagation in metal particle clouds in CO_2. To our knowledge, the only research publication on this topic is by Goroshin et al. [84] who investigated flame stabilization and measured the laminar flame velocity in the flowing Mg powder/CO_2 gas mixture at 1 atm. Self-sustained Mg/CO_2 flame propagation was obtained, with a laminar flame velocity ~1 m/s (close to the results for Al/air mixtures under the same conditions). Although conditions in a rocket engine differ significantly from this experiment, the results are interesting and encouraging.

III. CO_2-Breathing Jet Propulsion

Performance characteristics of ramjet engines in the Martian (CO_2) atmosphere were calculated for use of aluminum [19] or magnesium [20,85] as fuel. Unfortunately, low atmospheric pressure on Mars leads to either low thrust [19], or large specific fuel consumption and large inlet and exhaust nozzle sizes [20]. Note that ramjets require supersonic vehicle speeds and hence cannot be used for takeoff from the Martian surface. They could be used, however, for thrust augmentation of rocket engines, as retroengines for vehicles entering the atmosphere, and for survey missions [85]. Experiments [34] show that Mg particles ignite in CO_2 even at pressures as low as 5.3 mbar, which makes feasible the operation of ramjet engines on Mars.

Performance characteristics of turbojet engines in the Mars atmosphere were also calculated [20,86]. It was reported that they are better than for ramjets but the engines still have large inlet and nozzle sizes; further, the compressor and turbine additionally increase the engine weight. Tests of a small (thrust 1.9 N) turbojet engine using Mg/CO_2 propellant have shown that deposition of solid combustion products on the turbine blades prevents stable operation; specifically, the engine could be operated for only a few seconds before the turbine blades became clogged by carbon deposits [22].

IV. Performance Characteristics of Rocket Engines Using CO_2

Thermodynamic calculations of the CO_2-using rocket engine performance characteristics for Li, Be, B, Mg, Al, Si, Ca, Ti, Zr, BeH_2, MgH_2, and mixtures of Be and Mg with N_2H_4, were reported by Shafirovich et al. [21]. The calculations were made for a wide range of CO_2/fuel mass ratios. The results indicated that the highest theoretical specific impulse I_{sp} could be reached with Be or BeH_2. Accounting for toxicity, ignitability, and other issues, the authors concluded, however, that the most practical fuel is Mg. Aluminum exhibits a higher I_{sp} but lower ignitability in CO_2. It was also shown that replacement of pure Mg or Al by a hydride of the metal increases the maximum I_{sp}, but does not influence (for Al) or decreases (for Mg) I_{sp} at oxidizer/fuel ratios higher than stoichiometric (see Fig. 1) [87]. Also, the specific impulse can be increased by addition of hydrogen gas [22] but the hydrogen storage and transportation is a significant problem. It should be noted that the addition of hydrogen in the form of hydride or, to a lesser extent, as a gaseous component

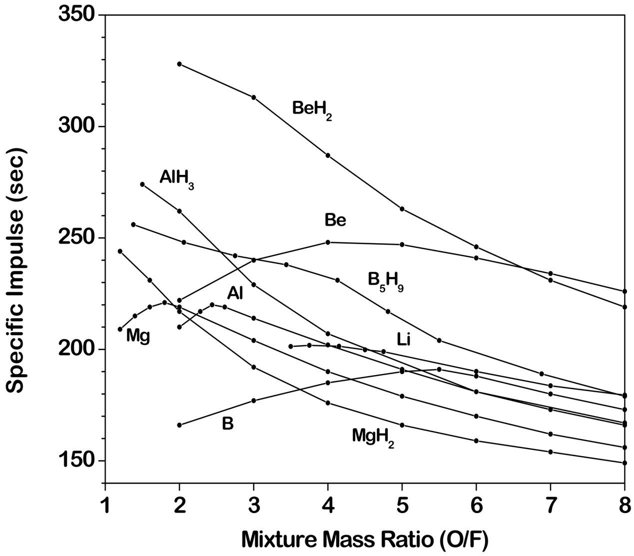

Fig. 1 Ideal specific impulse of a rocket using CO_2 as an oxidizer vs mixture ratio for some fuels; chamber pressure 10 atm, exit pressure 0.01 atm, ambient pressure 0.01 atm [87].

decreases the combustion temperature, which can prevent stable ignition and combustion in the engine.

Later, Zubrin [88] proposed diborane (B_2H_6) as a candidate fuel for burning with CO_2. Diborane is a cryogenic liquid (boiling point 181 K at 1 atm) and, although extremely toxic, could be used in a liquid bipropellant engine. For stoichiometric mixtures with CO_2, diborane promises higher I_{sp} than Mg or Al (though lower than for Be or BeH_2). The author, however, did not report the condensed mass fraction in combustion products, which may decrease I_{sp} significantly. Shafirovich and Goldshleger [89] have shown that the condensed mass fraction is much higher for diborane and pentaborane-9 (B_5H_9) than for Mg and BeH_2. Further, previous experience in attempts to use boron compounds as rocket and jet fuels indicates that boron oxide deposition in nozzles would be a serious problem. Obviously, the low melting point of B_2O_3 (723 K) increases adhesion and thus promotes deposition. On the other hand, MgO and Al_2O_3 melt at 3100 and 2327 K, respectively. This eliminates the possibility of sticking liquid oxide to the nozzle walls for Mg at any, and for Al at sufficiently high, CO_2-fuel ratios.

Silane (SiH_4) and aluminum borohydride [$Al(BH_4)_3$] were also considered by Shafirovich and Goldshleger [89]. These fuels show higher I_{sp} but also higher condensed mass fraction than Mg or Al. Because silane is a cryogenic liquid (boiling point 161 K at 1 atm) and could be used in a liquid bipropellant engine, it was recommended to investigate ignition and combustion of SiH_4/CO_2 mixtures. Later tests of small (diameter 2.5 cm, length 7.6 cm) silane/CO_2 engines by Zubrin et al. [23] have shown that combustion of these mixtures is possible but the deposition of silica in the combustion chamber is a major problem.

It should be noted that Zubrin et al. [23] also reported thermodynamic values of specific impulse for other compounds, such as $LiBH_4$, $NaBH_4$, $Al(BH_4)_3$, Si_2H_6, $MgAl_2H_8$, and $LiAlH_4$. Without consideration of condensed phase fraction and two-phase losses, all of them promise higher I_{sp} than Mg for stoichiometric mixtures with CO_2. We believe, however, that metal borohydrides and Si_2H_6 would likely have the same problems with condensed product deposition as boranes and silane. Lithium aluminum hydride may deserve further consideration, but the relatively low melting point of Li_2O (1726 K) also indicates potential problems with oxide deposition. As for $MgAl_2H_8$, this compound looks promising in terms of specific impulse and oxide deposition but, as compared with Mg and Al, will exhibit a much lower combustion temperature (see data in [21] for MgH_2), which may became critical for engine operation.

Based on thermodynamic calculations, analysis of properties (including toxicity), and ignition/combustion characteristics, the conclusion can be made that Mg is the main candidate fuel for rocket engines using CO_2. Aluminum can also be used, provided its ignition is improved.

V. Design of Metal-CO_2 Rocket Propulsion System

To our knowledge, the first tests of Mg/CO_2 rocket engines were carried out by Wickman [22]. Gaseous CO_2 and magnesium powder in a carrier nitrogen gas were fed to a combustion chamber and ignited using an electric arc. In final tests, chamber pressure corresponding to the desirable thrust 180 N was maintained for about 3 s. Later, tests of an even smaller Mg/CO_2 rocket engine were conducted by Zubrin et al [23]. The powder-fed system design was adapted from [84] and included a vertical cylinder with the powder and a piston driven by an electric motor, which moved the powder upward to an axial gap through which a carrier gas (CO_2) flowed. The Mg/CO_2 mixture was ignited in a combustion chamber by an oxygen/propane burner, which was shut down after ignition of the mixture. The engine operated in a steady manner for about 10 s at CO_2/Mg mass ratio 4.2:1. The systems [22,23] were, however, too simplified.

Several alternative design concepts for the metal/CO_2 rocket propulsion system have been discussed [21,84,87,90]. Among them, the direct injection of powdered metal and liquid CO_2 in a bipropellant engine appears to be the most promising option. Available experience in development of engines and reactors using powdered metal fuel [91–97] can be effectively applied to the metal-CO_2 propulsion system. This experience includes pneumatic feed systems for metal powders based on fluidization techniques. In such a system, metal powder is contained in a pneumatic cylinder with a porous piston. Carrier gas is supplied into the cylinder and through the porous piston into the powder. The powder/gas mixture then flows out of the cylinder through a ball valve. The piston is used to maintain uniform powder density at the feed line inlet as powder is removed. Previous experience indicates that this type of system can provide a stable feed of powdered metal to a combustion chamber. The fuel system can be shut down and restarted by opening or closing the ball valve in the fuel line and also has throttling capabilities.

Experiments on combustion of metal powders with steam were conducted for underwater propulsion applications [94,95]. Miller and Herr [95] reported the difference in oxide deposition on the combustor walls for Al and Mg. The deposition was negligible for Mg and significant for Al. This was explained by comparison of the combustion temperatures with melting points of magnesia and alumina. The formed oxide was in a solid state for Mg and in a liquid state for Al; thus, better adhesion of liquid Al_2O_3 droplets as compared with solid MgO particles caused the observed effect. As mentioned before (see Sec. IV), the similar difference between Mg and Al in oxide deposition is expected for stoichiometric mixtures with CO_2, but may not occur for mixtures with higher CO_2 fractions.

Figure 2 shows a schematic diagram of a pressurized reactor for Al powder combustion in air, developed by Malinin et al. [96]. The metal powder feed system was based on the porous piston concept described previously. Nitrogen was used as the carrier gas (its mass flow rate was less than 1.5% of the powder flow rate). A solid propellant igniter initiated combustion in a prechamber where the air-to-fuel ratio was 0.04–1.8, whereas the secondary air-to-fuel ratio was from 1 to 10. It was reported that the facility successfully operated at 0.1–2 kg Al per second and 1–10 kg air per second with a pressure of 0.1–1.5 MPa and a temperature of 1000–3500 K in the combustion chamber. The cold airflow velocity was in the range from 1 to 50 m/s in the prechamber, whereas the high-temperature flow velocity in the main combustion chamber was from 50 to 500 m/s. The facility included a system for collecting the produced alumina.

The metal-CO_2 propulsion system could be designed based on the described engineering solutions. Obviously, a major change would be the addition of a liquid CO_2 storage and feed system. A part of liquid CO_2 could be vaporized and used as the carrier gas instead of the additional gaseous component, which would decrease the mass that would need to be transported from Earth. The liquid CO_2 could also be used for regenerative cooling. Note that the cooling does not appear to be a difficult problem at high CO_2-metal ratios, due to relatively low temperatures in the combustion chamber [21].

Finally, it should be emphasized that the described engine configuration (powdered metal fuel–liquid CO_2) would have an important advantage as compared with alternatives: no processing of the metal fuel on Mars is required and the engine is ready to operate as soon as liquid CO_2 is acquired.

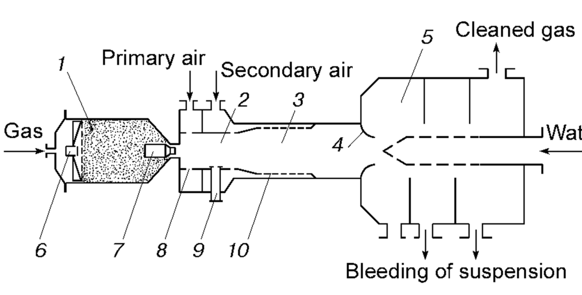

Fig. 2 Schematic diagram of the experimental reactor: 1) metal powder feed system, 2) prechamber, 3) nozzle combustion chamber, 4–5) sampler for collecting dispersed oxides from two-phase high-temperature flow, 6) piston valve, 7) locking and regulating valve, 8) primary air distributor, 9) igniter, 10) secondary air distributor [96].

VI. Acquisition of CO_2 and Production of Metal Fuel on Mars

As mentioned previously, low temperature near the Mars surface (mean temperature 227 K) favors liquefaction of CO_2 from the atmosphere. Because CO_2 acquisition is an integral part of propellant production in most ISRU technologies, significant progress has been made in development of methods for CO_2 collection on Mars.

According to the CO_2 phase diagram (see Fig. 3) and atmospheric conditions on Mars, to liquefy CO_2 gas near the Mars surface, its pressure should be increased from ~8 mbar to ~10 bar. This can be achieved by different methods, such as mechanical compression, adsorption pumping, and freezing. Mechanical compression uses a multistage device, which means large mass and poor efficiency; also, the presence of rotating parts limits operating lifetimes. In the adsorption method [98], a sorbent bed adsorbs low-pressure CO_2 gas at low temperatures during the Martian night, and then desorbs high pressure CO_2 gas during the day, when the temperature increases. The CO_2 liquefaction, however, will require additional compression. Sorption pumps for CO_2 acquisition on Mars have been demonstrated, but require large sorbent bed volumes. Note that the entire mass of sorbent, gas, and pressure vessel must be heated and cooled in the sorption cycle. In the freezing method, solid CO_2 is collected on a heat exchanger that is cooled to the freezing temperature (~150 K at the atmospheric pressure of Mars) with a cryocooler. The heat exchanger is inside a pressure vessel, the heating of which during the Martian day results in accumulation of liquid, self-pressurized CO_2. A freezing device for collecting atmospheric CO_2 on Mars, constructed by Clark et al. [99–101], exhibits an effective compression ratio of over 10,000, a value that would require several stages of mechanical compressors. Another feature of the process is the purity of the CO_2 product (other gases in the atmosphere need much lower temperatures for freezing than CO_2). The collection rate as high as 120 g of CO_2 per hour at a cooling power of ~32 W was reported [101]. The concept is readily scaled to greater quantities with a linear relationship of cooling power to acquisition rate.

For the metal fuel, two options are possible. The easier one is to transport the metal fuel from Earth to Mars. In this case, the in situ propellant production system (ISPPS) is reduced to the CO_2 acquisition system, decreasing both power consumption and mass of ISPPS by about 80% [88]. As compared with conventional (non-ISRU) scenarios of Mars missions, the use of Martian oxidizer (CO_2) in a rocket engine will allow significant reduction of propellant mass transported from Earth, especially in missions with several flights on Mars when CO_2 is acquired before every takeoff [21,87,102] (see Sec. VII).

The second option is to produce the metal fuel on Mars. One possibility is to recycle metal parts of the lander or other materials that are no longer needed. Interestingly, in 1924, Russian engineer F.A. Tsander proposed a launcher that would take off from the Earth's surface like an airplane and then burn the wings as fuel in a rocket engine [103]. More recently, transforming structural aluminum to powdered fuel for $Al/H_2/O_2$ rocket engines was discussed for recycling the space shuttle's external tank on the orbit [104]. It was suggested that aluminum would be cut and fed into an induction furnace for melting and powdering. Recently, an interesting idea was proposed by M. Lang,[‡] who suggested using metal hydrides (e.g., MgH_2, AlH_3) for hydrogen storage in a fuel cell power system, and, after all hydrogen has been used, using the remaining metal as a fuel for metal-CO_2 propulsion. Another possibility is to recover the metal fuel from Martian soil and rocks. Analyses of their chemical compositions by two Viking landers, Sojourner, Spirit, and Opportunity rovers, as well as analyses of Martian meteorites, have shown a relatively high content of Mg [105–108]. There exists voluminous literature on methods for extraction of metals from lunar and Martian minerals. Recently, a new method for recovery of Mg from Martian regolith, based on dissolving in supercritical CO_2, was proposed by Debelak et al. [109]. This method appears to be particularly attractive for use with metal-CO_2 rocket engines, as it needs liquid CO_2 which will be obtained in large amounts anyway for propulsion.

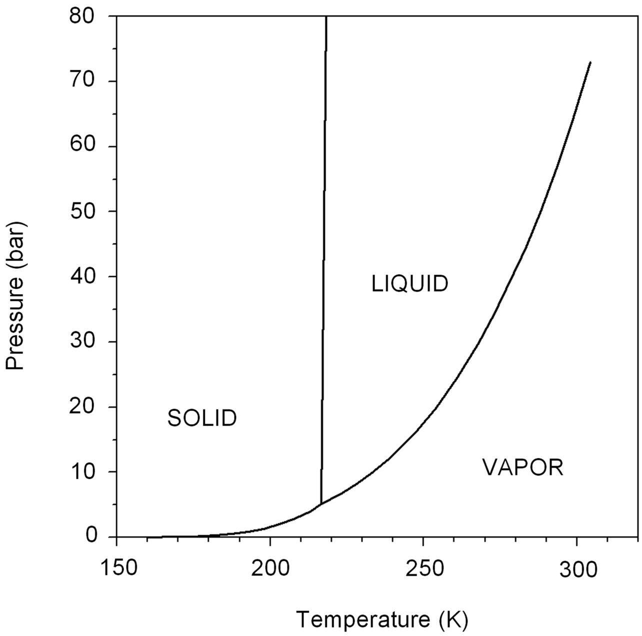

Fig. 3 CO_2 phase diagram.

VII. Potential Mars Missions Using Metal-CO_2 Rocket Propulsion

Some concern was expressed [88] that the specific impulse of the rocket engine using Mg/CO_2 propellant is too low. Conventional stereotypes, however, may not apply to ISRU approaches. The decrease in propellant mass transported from Earth makes the metal/CO_2 rocket engine advantageous even despite the relatively low I_{sp} (see its typical values in Fig. 1). Analysis for "Martian CO_2–Earth-borne metal fuel" demonstrated that, in a Mars sample return mission, the proposed rocket propulsion system is advantageous when used as the first stage of vehicle for ascent to low Mars orbit [97]. Significant benefits of metal/CO_2 propulsion are expected in missions with visiting several sites on Mars (e.g., ballistic hopper, multisample return), when the oxidizer (liquid CO_2) is taken from the atmosphere before each hop [21,87,102].

The most applicable analysis was made recently for a small hopper mission, which could be used instead of a rover for visiting several sites on the Mars surface [110]. The idea of this work was to estimate the number of hops and the total range that the hopper can travel, assuming that the initial hopper mass (without CO_2) and available electric power are the same as for the rover. Basically, the hopper should carry the same scientific and communication equipment as the rover but, instead of chassis, be equipped with metal-CO_2 rocket propulsion and CO_2 acquisition systems. The main problem in the mission analysis was the fact that both these systems were not available yet, and it was difficult to predict their masses precisely. For this reason, it was decided to seek solutions as a function of two parameters: the mass of the propulsion system without propellant m_{eng} and the mass of acquisition system m_{acq}. For propellant, different oxidizer-fuel ratios were tested and the mass of tanks was assumed to be a fixed fraction (10%) of propellant mass. In calculations of the range, active landing was assumed. For CO_2 acquisition, the adsorption method was selected, with power coming from solar arrays. The generated power was proportional to the mass of solar arrays and, on the other hand, determined the mass of the CO_2 acquisition system which, in turn, determined the CO_2 acquisition rate. Time between two consecutive hops consisted of scientific (two days) and CO_2 acquisition periods. The latter and the CO_2 acquisition rate determined the amount of acquired CO_2 and thus the

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[‡] Lang, M., ESA, private communication, 2003.

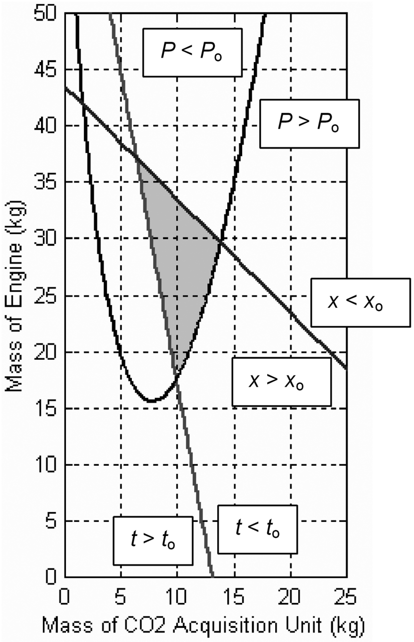

Fig. 4 Design domain for the mission with 10 hops, $x_0 = 10$ km, $t_0 = 180$ days, $P_0 = 300$ W, $I_{sp} = 190$ s, $O/F = 4$ [110].

range of the next hop. Finally, decay of solar array efficiency due to dust deposition was taken into account.

The solution of the equation system for fixed total range x_0, mission duration t_0, and power P_0 was represented as three curves in the space of parameters m_{acq} and m_{eng}. Intersections of these curves formed (or did not) the domain where $x > x_0$, $t < t_0$, and $P < P_0$, which was defined as the *design domain* of the mission. Using special software, the design domains were determined for different sets of parameters. For example, Fig. 4 shows the results obtained for the mission with 10 hops, total range 10 km, total mission time 180 Martian days, power 300 W, at the CO_2-fuel mass ratio 4, and specific impulse 190 s (Mg fuel). The design domain (highlighted in Fig. 4) indicates that the mission is possible with, for example, a 10 kg CO_2 acquisition system and a 30 kg propulsion system.

Variation of parameters has demonstrated that the selection of optimum CO_2/metal mass ratio is a difficult problem for Martian CO_2–Earth-borne fuel missions, which is understandable. Indeed, increasing the CO_2/metal ratio decreases specific impulse but also decreases the Earth-borne fraction of propellant. On the other hand, the increase in the CO_2 fraction requires more energy for CO_2 acquisition, which results in either higher power consumed by the acquisition system, or longer mission duration. Thus, the optimum CO_2/metal ratio depends on the mission scenario, and this fact should be taken into account in future mission analyses.

The obtained results show that the hopper using metal-CO_2 propulsion is competitive with a rover, while offering the benefit of terrain independence. For comparison, a hopper mission with a conventional (non-ISRU) propulsion system using NTO/MMH bipropellant ($I_{sp} = 320$ s) was considered. In this case, an additional amount of propellant can be brought from Earth instead of the CO_2 acquisition system. As compared with Mg-CO_2 propulsion, these calculations have shown a significantly shorter total range for the same number of hops, despite the higher specific impulse of NTO/MMH propellant.

To our knowledge, the mission analysis "Martian CO_2–Martian fuel" option has never been made, apparently because production of metal fuel on Mars was considered unrealistic in the near future. In this context, the supercritical CO_2 process for recovery of Mg from Martian soils [109], mentioned previously, provides a potentially attractive alternative and unique application of available resources.

In general, we believe that the metal-CO_2 propulsion system using Martian CO_2 and Earth-borne metal fuel could be advantageous in forthcoming robotic missions, whereas the production of both CO_2 and metal fuel on Mars could play a significant role in more advanced, including human, missions.

VIII. Conclusions

Fundamental studies have provided voluminous qualitative and quantitative information on ignition and combustion of Mg and Al in CO_2. For Mg, combustion mechanisms have been established and conditions for stable combustion determined. For Al, significant progress in modeling combustion has been achieved and methods have been proposed to improve ignition.

It has been shown that CO_2-breathing ramjet and turbojet engines using Mg or Al are theoretically feasible. Despite some problems (e.g., low pressure, large inlet and nozzle sizes, high fuel consumption), ramjets could be used for thrust augmentation, as retroengines for vehicles entering the atmosphere, and for survey missions. CO_2-breathing turbojet engines, however, do not appear feasible because of product deposition on turbine blades.

Performance characteristics of rocket engines using liquid CO_2 have been calculated for a variety of potential fuels. The main candidate fuels are Mg powder and Al with improved ignition characteristics. Small, simplified prototypes of Mg-CO_2 rocket engines have been tested successfully. Available experience in the development of engines and reactors with pneumatic feed systems for metal powdered fuel could be effectively used for the design and construction of metal-CO_2 propulsion systems. Metal-CO_2 rocket propulsion takes advantage of the low temperature on Mars, which favors liquefaction of CO_2 from the atmosphere. Methods for collecting and compressing atmospheric carbon dioxide on Mars have been developed and demonstration units constructed.

Mission analysis has shown that the rocket propulsion system using Martian CO_2 and Earth-borne metal fuel could be used as the first stage of a Mars ascent vehicle for return to low Mars orbit. As compared with non-ISRU propulsion, the metal/CO_2 rocket engines would have significant advantages in missions with visiting several sites on Mars. Ballistic hoppers with metal-CO_2 propulsion could be used instead of long-range rovers. Note that comparison of the metal-CO_2 propulsion concept with other Mars ISRU approaches should be conducted with consideration of energy consumption in all operations on the Mars surface. Mission analysis for Martian CO_2 – Martian fuel has not been performed yet. New methods for production of metal fuel on Mars, however, have been proposed and need further investigation.

As Mars exploration continues, ISRU approaches will be required and the proposed metal-CO_2 rocket engines will progressively become more attractive. With the developments described in this paper, we believe that the concept of metal-CO_2 propulsion on Mars has reached a sufficiently high technology readiness level to initiate serious engineering work in this area.

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