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Magnesium and Carbon Dioxide: A Rocket Propellant for Mars Missions

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In this article a rocket engine for Mars missions is proposed that could utilize CO_2 accumulated from the Martian atmosphere as an oxidizer. For use as possible fuel, various metals, their hydrides, and mixtures with hydrogen compounds are considered. Thermodynamic calculations show that beryllium fuels ensure the most impulse but poor inflammability of Be, and high toxicity of its compounds put obstacles to their applications. Analysis of the engine performance for other metals together with the parameters of ignition and combustion show that magnesium seems to be the most promising fuel. Ballistic estimates imply that a hopper with the chemical rocket engine on Mg + CO_2 propellant could be readily developed. This vehicle would be able to carry out 2–3 ballistic flights on Mars before the final ascent to orbit. The data of an experimental study on ignition and combustion of Mg particles in CO_2 and CO_2/CO mixtures are presented. Analysis of the combustion parameters and mechanism gives grounds to expect high combustion efficiency of Mg + CO_2 propellant in a rocket engine. Several alternative designs of the engine are considered.

Nomenclature

d = particle size
g = acceleration of gravity
g_0 = acceleration of Earth gravity on sea level
H = enthalpy of combustion products
I_{sp} = specific impulse
M_t, M_f = takeoff and final masses of vehicle
M_p^E, M_p^M = masses of propellant transported from Earth and that accumulated on Mars
n = takeoff number of hopper
p = pressure
R = radius of planet
S = flying range of rocket
T = temperature
t_b = burning time
u = velocity of combustion products
v = end-of-boost velocity of vehicle
z = mass fraction of condensed phase
χ = oxidizer-to-fuel ratio (by mass)

Subscripts
a = ambient conditions
c = combustion chamber
e = exit section of nozzle

Superscripts
con = conventional
eff = effective
min = minimum

Introduction

A PERSPECTIVE of a manned Mars mission in the beginning of the 21st century stimulates studies on the feasibility of using Martian resources for propellant production.

Considered is the Martian atmosphere that contains 95% carbon dioxide. For example, it was proposed to build a chemical plant on Mars for manufacturing oxygen and methane from CO_2 and Martian water (Ash et al.[1]) or hydrogen transported from Earth (Zubrin and Baker[2]). Zubrin[3] also proposed to use CO_2 or other gases produced on Mars as a propellant in a nuclear thermal engine. Advantages and disadvantages of various concepts were recently discussed by French.[4]

Little attention was paid to an alternative way; the direct use of CO_2 as an oxidizer in a chemical engine. This may perhaps be explained by the idea that CO_2 does not support combustion. However, this idea does not work when some metals are used as fuel. It was the oxidative capability of CO_2 that stimulated studies of metal combustion in CO_2 and on the feasibility of using such a propellant in engines.

In the sixties, Rhein[5] investigated ignition of a number of powdered metals in CO_2 for this purpose. In the early eighties Kapanadze et al.[6] proposed to develop a ramjet engine for Venus that could use a metal fuel.

Recently Yuasa and Isoda[7] proposed to develop CO_2-breathing ramjet and turbojet engines for a Mars airplane. They studied ignition and the combustion of aluminum, magnesium, lithium, and boron in CO_2 and came to the conclusion that Mg is the most attractive fuel for this purpose. The performance of CO_2-breathing ramjet and turbojet engines on Mg + CO_2 propellant was calculated. It was found that the performance is quite acceptable, but extremely large inlet and exhaust nozzle are required because of the small atmospheric pressure of Mars (6 mb). It seems that the development of the turbojet engine seems to be rather problematic, since its turbine must work under conditions of the two-phase flow with high concentration of MgO solid particles. The variant of an airplane with the ramjet engine seems to be much more realistic if the feasibility of its operation at low pressures of about 10 mb in a combustion chamber will be demonstrated.

A Mars sample return mission is a key aim of the Mars unmanned exploration program. The collection of samples from different regions of Mars is of course desirable. For this to be done, a few ascent-descent vehicles or a rover which can go hundreds of kilometers should be anticipated. However, the use of Mars in-situ propellant allows one to realize another scenario. In the above-mentioned paper,[3] Zubrin proposes to develop a ballistic ascent-descent vehicle (hopper) with a nuclear thermal engine that would utilize CO_2 from the Martian atmosphere as a propellant. Filling liquid CO_2 after every hop will allow the hopper to visit a few regions of the planet and then to propel a returned module into a low Mars orbit for a rendezvous with an orbital transfer vehicle or directly into a minimum energy orbit to Earth.

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A hopper with a chemical engine on ordinary propellant is not realistic because of the great amount of propellant transported from Earth. However, a hopper with a chemical engine on metal + CO_2 propellant may turn out to be promising. In such a case, only fuel has to be transported from Earth, whereas, oxidizer (i.e., CO_2) could be accumulated in a tank after every hop as proposed in the project.[3] In this case, the fuel mass transported from Earth may appear to be less than the mass of a nuclear reactor with radiation shielding.

Therefore, the present study on the feasibility of rocket engine development with CO_2 as an oxidizer seems to be rather urgent and interesting.

Performance Characteristics of a Rocket Engine with the Martian CO_2 as an Oxidizer

Efficiency of CO_2 as an oxidizer or another propellant for a rocket engine can be estimated by performing thermodynamic calculations. In spite of some limitations of such an approach (real kinetics of propellant and processes of heat and mass transfer in a combustion chamber are not taken into account), the thermodynamic calculations enable the evaluation of the most important performance characteristics of a rocket engine. Simplicity of parameter variation, such as the oxidizer and fuel compositions and their mass ratio, allows one to find out the optimal combustion conditions for the given propellant, and therefore, to carry out a comparative analysis of various propellants.

It should be noted that apart from the specific impulse, the oxidizer-fuel ratio is a very important characteristic for an engine which uses the indigenous oxidizer, since this magnitude shows which part of propellant can be produced on the planet and which one must be transported from Earth.

We calculated the performance of the CO_2-utilizing rocket engine using a computer program which is based on the principle of thermodynamic potential minimization and allows the calculation combustion of systems with a high content of condensed phase.[8] Li, Be, B, Mg, Al, Si, Ca, Ti, and Zr were analyzed as fuel. The calculations were performed under the assumption of equilibrium flow in an exhaust nozzle at the chamber pressure of 10 bar and nozzle exit pressure of 10 mb. The specific impulse was assumed to be equal to the calculated exhaust velocity divided by $g_0 = 9.80665$ m/s²:

$$I_{sp} = u_e/g_0 = [2(H_c - H_e)]^{0.5}/g_0$$

Figure 1 shows the obtained values of I_{sp} as a function of χ. Table 1 presents the values of the chamber temperature, the exit temperature, and the condensed phase fraction at the nozzle exit section for $\chi = 2$, 5, and 8.

As seen in Fig. 1, Be ensures the most specific impulse, 250 s, among the considered fuels. Of course, this value of I_{sp} is small as compared to specific impulses for the conventional propellants. However, this value is obtained for CO_2-to-fuel ratio of 5, and therefore, only $\frac{1}{6}$ of the propellant mass has to be transported from Earth.

It should be noted that the maximum of I_{sp} corresponds to the very high exit temperature (see Table 1) as well as to the great content of condensed phase. The engine parameters for $\chi = 8$ seem to be more acceptable; $T_c = 2851$ K, $T_e = 1456$ K, $z_e = 0.31$. A further increase in χ leads to a decrease in the chamber temperature. This is an undesirable factor, since for ignition of beryllium particles in CO_2, the ambient gas temperature has to be at least not lower than the value of 2600 K (Maček[9]). As a result, the acceptable range of χ is narrow.

For Li, Mg, Al, and Si, values of specific impulse are similar and close to about 200 s over the wide range of χ. Large values of χ ensure acceptable values of the condensed phase fraction at the nozzle exit section, $z_e = 0.2$–0.3 and good parameters of the process, $T_c = 2000$–2500 K, $T_e = 700$–1200 K. For the values of χ larger than the stoichiometric ratio, the combustion products contain CO_2, CO, and oxide of the burned metal. For $\chi > 6$ the combustion products of Mg, Al, and Si also contain carbon, and that of Li contain lithium carbonate.

Ca, Ti, and Zr provide worse performance. For B, at $\chi > 4$ we obtained the relatively high specific impulse but with large values of z_e.

Therefore, the calculations show that Be ensures the most specific impulse of a rocket engine using CO_2 as an oxidizer. However, the high toxicity of Be compounds is a great obstacle to its application. Moreover, ignition and combustion of Be in CO_2 has not been studied so far.

Among other fuels, Mg may be outlined. Though Al, Li, and B show higher specific impulse than Mg at large values

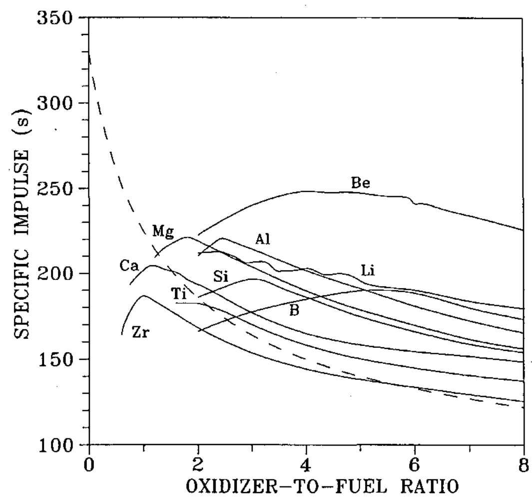

Fig. 1 Specific impulse of a rocket engine using CO_2 as an oxidizer and metals as fuel vs oxidizer-fuel mass ratio. Dashed line shows the minimum specific impulse that the CO_2-using engine must have to propel the same payload into orbit as the N_2O_4 + $(CH_3)_2N_2H_2$ engine can propel, at the same mass of propellant transported from Earth.

Table 1 T_c and T_e in K, and z_e of a rocket engine using metals as fuel and CO_2 as an oxidizer for various CO_2-fuel mass ratios χ

	$\chi = 2$			$\chi = 5$			$\chi = 8$		
	T_c	T_e	z_e	T_c	T_e	z_e	T_c	T_e	z_e
Li	2210	1458	0.58	2096	1403	0.35	2155	1215	0.36
Be	2969	2070	0.71	3001	2281	0.46	2851	1456	0.31
B	2153	1564	0.65	2101	1471	0.55	1802	828	0.36
Mg	3100	1975	0.55	2073	894	0.28	1533	703	0.19
Al	2730	1851	0.52	2327	1022	0.31	1726	735	0.21
Si	2266	1622	0.59	1996	848	0.36	1479	737	0.25
Ca	2869	1384	0.47	1606	905	0.33	1322	704	0.28
Ti	2257	1334	0.56	1504	733	0.29	1123	631	0.21
Zr	2314	989	0.45	1263	643	0.24	951	417	0.16

of χ, they should be rejected because of poor ignitability and low combustion rate in CO_2. Yuasa and Isoda[10] have experimentally found that ignition of B does not occur in the CO_2 stream up to the theoretical stoichiometric flame temperature. They could ignite Al sample in CO_2 only by direct contact with an incandescent tungsten heater. Moreover, Maltsev et al.[11] reported that only Mg burns out Al/Mg alloy particle during its combustion in the CO_2 atmosphere. According to Ref. 10, Li is readily ignited in CO_2, but after the short-lived combustion in vapor phase, the stage of slow heterogeneous combustion occurs and the total duration of combustion is extremely long. In contrast to these metals, Mg combines the low-ignition temperature and the high rate of vapor-phase combustion. Si, Ti, and Zr have worse performance parameters and poor characteristics of combustion (they do not burn in vapor phase[12]).

For these reasons, we consider Mg to be the most promising fuel for a rocket engine utilizing CO_2 as an oxidizer. The optimal parameters of the engine process for Mg are obtained at χ = 4–6; I_{sp} = 190–170 s, T_c = 2388–1845 K, T_e = 1090–760 K, z_e = 0.33–0.24.

Increasing the content of hydrogen in metal propellants is known to increase the specific impulse. For this reason, we studied the feasibility of improving the engine performance of metal + CO_2 propellant by replacing the metal for its hydride or by addition of various hydrogen compounds. As the additives, the well-known rocket fuels, ammonia, hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, kerosene, ethyl alcohol, and also water, were analyzed. In the case under consideration, the use of hydrogen would lead to an unexcusable complexity of the propulsion system design.

The calculations have shown that hydrazine is the best of the considered additives. Figure 2 and Table 2 present the results obtained for mixtures of Mg and Be with N_2H_4 as well as for hydrides of these metals. As is seen, the replacement of Be for BeH_2 makes it possible to noticeably increase the specific impulse with simultaneous improvement in the parameters T_e and z_e. The optimal parameters are obtained for χ = 4; I_{sp} = 287 s, T_c = 2807 K, T_e = 1155 K, z_e = 0.45. With addition of hydrazine to Be, the optimal parameters are obtained for the fuel 70% Be/30% N_2H_4 at χ = 5; I_{sp} = 240 s, T_c = 2851 K, T_e = 1340 K, z_e = 0.32, and for the fuel 50% Be/50% N_2H_4 at χ = 3; I_{sp} = 259 s, T_c = 2851 K, T_e = 1228 K, z_e = 0.35.

The known data on gelled propellants[13] make it possible to expect the development of storable beryllium suspension in hydrazine, which would be attractive for operation of a fuel feed system. However, due to the narrow range of acceptable χ, the development of the engine on Be fuel seems to be rather problematic, even if good parameters of Be combustion in CO_2 are obtained and the problem of toxicity is solved.

As for magnesium, all the considered additives as well as the replacement for hydride make the engine performance worse.

Therefore, the calculations make it possible to conclude that pure magnesium is the most promising fuel for a rocket engine using CO_2 as an oxidizer.

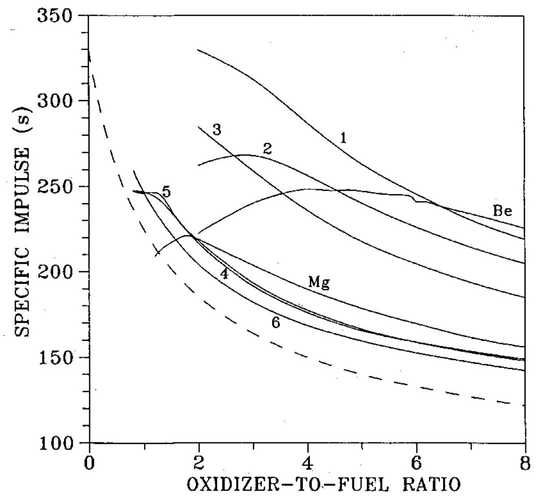

Fig. 2 Specific impulse of a rocket engine using CO_2 as an oxidizer and Be, BeH_2 (1), 70% Be + 30% N_2H_4 (2), 50% Be + 50% N_2H_4 (3), Mg, MgH_2 (4), 70% Mg + 30% N_2H_4 (5), and 50% Mg + 50% N_2H_4 (6) as fuel vs oxidizer-fuel mass ratio. Dashed line shows the minimum specific impulse that the CO_2-using engine must have to propel the same payload into orbit as the N_2O_4 + $(CH_3)_2N_2H_2$ engine can propel, at the same mass of propellant transported from Earth.

Comparison of Mg + CO_2 Rocket Propulsion and Conventional Chemical Rocket Propulsion for Mars Missions

Efficiency of the CO_2-utilizing rocket engine can be briefly estimated by so-called "effective specific impulse" which is the thrust divided by only the fuel mass or the actual specific impulse multiplied by propellant leveraging

$$I_{sp}^{eff} = I_{sp}(\chi + 1)$$

The effective I_{sp} of the Mg + CO_2 rocket engine is equal to 950 s for χ = 4 and 1190 s for χ = 6. These values are much higher than the maximum I_{sp} of a chemical rocket engine and even higher than the one of a solid core nuclear rocket on hydrogen propellant.

A more accurate estimate of the engine efficiency can be made in the following way. Let us evaluate the fuel mass that has to be transported from Earth to carry out a certain program on Mars, and this value is to be compared with the mass of propellant (a fuel + an oxidizer) that has to be transported from Earth for fulfillment of the same task by using a conventional engine. A rocket engine on N_2O_4 + $(CH_3)_2N_2H_2$ liquid propellant (I_{sp} = 330 s) was considered to be "conventional," since such an engine was proposed in the Soviet program of Mars exploration. The task for a rocket engine

Table 2 T_c and T_e in K, z_e of a rocket engine using Mg, Be, their hydrides, and their mixtures with N_2H_4 as fuel and CO_2 as an oxidizer for various CO_2-fuel mass ratios χ

	$\chi = 2$			$\chi = 5$			$\chi = 8$		
	T_c	T_e	z_e	T_c	T_e	z_e	T_c	T_e	z_e
Be	2969	2070	0.73	3001	2281	0.46	2851	1456	0.31
BeH_2	2744	1922	0.84	2581	1027	0.38	2049	803	0.25
Be/N_2H_4 [a]	2851	2187	0.59	2851	1340	0.32	2243	947	0.22
Be/N_2H_4 [b]	2823	1869	0.50	2259	906	0.23	1750	735	0.16
Mg	3100	1975	0.55	2073	894	0.28	1533	703	0.19
MgH_2	2166	846	0.51	1354	718	0.28	1063	635	0.20
Mg/N_2H_4 [a]	2459	982	0.39	1512	707	0.21	1160	610	0.15
Mg/N_2H_4 [b]	1830	747	0.29	1170	633	0.17	945	480	0.12

[a]30% N_2H_4. [b]50% N_2H_4.

was formulated starting from the two above-mentioned scenarios of the Mars sample return mission. The first scenario includes travel of a rover and a single takeoff of an ascent vehicle, the second one proposes to use a ballistic hopper.

In the first scenario, ascent of a payload from the Martian surface into low Mars orbit is the main problem for a rocket engine to solve. The takeoff mass of a vehicle was calculated by the formula

$$M_t/M_f = \exp(v/g_0/I_{sp})$$

The final mass of a vehicle comprises the masses of payload, engine, empty propellant tanks, and rocket body. An engine with the lower specific impulse will require the larger mass of propellant. This may lead to an increase in masses of the empty tanks and rocket body. Calculation of this increase as well as the engine mass require that specific design parameters be known. That is why it was assumed in the estimates of efficiency that the final mass of a vehicle is the same for the different engines and does not depend on the identity of propellant.

It should be noted that the mass of equipment for CO_2 liquefaction is included into the final mass of the hopper with the CO_2-utilizing engine. Of course, this equipment can be left on the surface of Mars before the final takeoff. The mass of this equipment was not taken into account in the estimates since only a small power compressor is needed for manufacturing liquid CO_2 under the Martian conditions. Zubrin[3] calculated that only 84 kWh of energy are needed to produce 1 metric ton of liquid CO_2 at a typical Martian temperature of 233 K.

The end-of-boost velocity of the vehicle was assumed to be equal to Mars circular velocity, 3.5 km/s. Of course, the velocity increment for a real rocket must be somewhat higher due to mostly gravity losses. However, depending on thrust-to-weight ratio and flight trajectory, the losses could be accurately predicted only in a more detailed development of the concept. Here we assume that the losses will be compensated by the second-stage engines on conventional propellant that are necessary for orbital maneuvers and rendezvous with an orbiting vehicle.

Assuming the mass of propellant transported from Earth for the "conventional" engine to be equal to the mass of fuel transported for the CO_2-utilizing engine, we get a formula for the minimum specific impulse I_{sp}^{min} that the CO_2-using engine must have to propel the same payload into low Mars orbit as the conventional engine with the specific impulse I_{sp}^{con} can propel

$$I_{sp}^{min} = v/g_0/\ln\{1 + (\chi + 1)[\exp(v/g_0/I_{sp}^{con}) - 1]\}$$

where χ is the CO_2 fuel mass ratio for the proposed engine.

The dependence of I_{sp}^{min} on χ is represented by a dashed line in Figs. 1 and 2. Calculated values of the specific impulse for the propellants based on metals, except Zr, lay above this curve. This implies that by using these metals one may transport smaller mass of propellant from Earth than for the conventional engine with the specific impulse of 330 s.

Calculations show that about 2 ton of N_2O_4 + $(CH_3)_2N_2H_2$ propellant must be transported from Earth for one surface-to-orbit ascent of a vehicle with the final mass of 1 ton. 5.55 ton of propellant will be needed if the Mg + CO_2 engine (I_{sp} = 190 s, χ = 4) is used, but only 1.11 ton of them (fuel) must be transported from Earth. Of course, the real gain may turn out to be less because of increasing mass of the vehicle; 5.55 ton of propellant must be placed into the tanks instead of 2 ton (densities of liquid CO_2, Mg, N_2O_4, and $(CH_3)_2N_2H_2$ are equal to 1.1, 1.74, 1.44, and 0.79 g/cm^3, respectively).

Now consider the second scenario of the Mars sample return mission, according to which a vehicle makes a few ballistic flights before the final ascent to low Mars orbit.

At first, let us make estimates for the vehicle with a CO_2-utilizing engine. For the sake of simplicity, consider a modification where the mass of CO_2 consumed in every flight is the same and equal to the mass of CO_2 needed for surface-to-orbit ascent (the full oxidizer tank before every takeoff). Knowing the rocket mass and the specific impulse, we can calculate the mass of fuel to be consumed, the end-of-boost velocity and then calculate the distance of every hop.

Now consider the vehicle with a chemical engine on a conventional propellant. Assuming the end-of-boost velocity in every hop is equal to the respective velocity of the vehicle with a CO_2-using engine, we may evaluate the mass of the vehicle before every takeoff and compare it to that for the vehicle with a CO_2-using engine.

Table 3 represents the calculated values of the takeoff mass and the final mass of vehicle in every flight for both types of engine. Moreover, the values of propellant mass accumulated on Mars and of that transported from Earth are represented in the same table. The final ascent to orbit has the number n, since the calculations are performed from the end, i.e., starting from the conditions of the final ascent. The mass of vehicle without propellant was assumed to be equal to 1 ton for both engines.

Table 3 also represents values of the end-of-boost velocity and the range of every hop. The range was estimated by the formula[14]

$$S = 2R \arcsin[v^2/(2gR - v^2)]$$

where R is 3400 km for Mars, and g is 3.7 m/s^2 for Mars (the formula gives a lower estimate).

As is seen, the mass of hopper with the engine on propellant transported from Earth drastically increases with increasing number of hops. For instance, for two hops the mass of propellant must be 10 times and for three hops 17 (!) times larger than the final mass of vehicle. Of course, this makes a hopper essentially unrealistic.

The mass of a CO_2-accumulating hopper does not so drastically depend on the number of hops. For example, in the scenario with three hops, the mass of the hopper with full tanks is equal to 9.9 ton, whereas, the takeoff mass before the ascent to orbit is equal to 6.6 ton.

Advantages of the proposed engine are becoming still more pronounced when compared with the mass of propellant transported from Earth. Figure 3 pictorially represents the mass of propellant transported from Earth as a function of hop number $n - 1$ for both the engines. As is seen, at the same mass of the conventional propellant and that of magnesium, a vehicle is capable of making one and four hops, respectively.

Table 3 Takeoff M_t and final M_f masses of hopper, propellant mass accumulated on Mars M_p^M and that transported from Earth M_p^E in ton, v in km/s and S in km for every flight in the course of Mars mission

Takeoff	M_t[a]	M_t[b]	M_f[a]	M_f[b]	M_p^M[a]	M_p^M[b]	M_p^E[a]	M_p^E[b]	v	S
n	6.55	2.95	1	1	4.44	0	1.11	1.95	3.5	orbit
n-1	7.66	6.19	2.11	2.95	4.44	0	2.22	5.19	2.40	2050
n-2	8.77	11.03	3.22	6.19	4.44	0	3.33	10.03	1.87	1100
n-3	9.88	17.75	4.33	11.03	4.44	0	4.44	16.75	1.54	710
n-4	10.99	26.61	5.44	17.75	4.44	0	5.55	25.61	1.31	500

[a]Mg + CO_2. [b]N_2O_4 + $(CH_3)_2N_2H_2$.

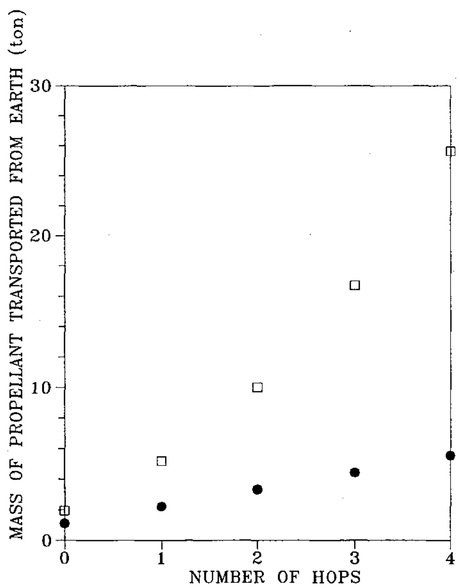

Fig. 3 Mass of propellant transported from Earth vs the number of ballistic flights on Mars for engines on N_2O_4 + $(CH_3)_2N_2H_2$ (□) and Mg + CO_2 (●) propellants.

Therefore, the calculations show that in the scenario with a hopper, in spite of the relatively small specific impulse, the engine on Mg-CO_2 propellant ensures the good gain in the mass of propellant transported from Earth to Mars. The values obtained for the takeoff mass of the vehicle and for the mass of fuel transported from Earth seem to be acceptable for the realization of 2–3 ballistic flights on Mars before the final ascent to orbit. The vehicle would travel the total range of about 4000 km by 3 hops (the distance from equator to pole is equal to 5300 km).

Ignition and Combustion of Magnesium Particles in CO_2 and CO_2/CO Mixtures

Realization of the proposed concept of engine for Mars missions requires the knowledge of mechanism and characteristics of propellant combustion.

Ignition and combustion of magnesium particles in CO_2 and CO_2/CO mixtures was investigated in detail by the authors of Refs. 15–18. Here we represent the basic data of this study together with their analysis from the viewpoint of the utmost combustion efficiency in a rocket engine.

An experimental setup for studies on magnesium particles combustion was developed. The Mg sample of 1–2 mm was introduced by a spring-pneumatic mechanism into an electric furnace that was placed in a steel bomb. In the experiments, the temperature of both the sample and gas were measured by thermocouples and the intensity of light emission was measured by means of a photodiode. High-speed cinematography and spectral analysis of flame were used. The condensed products of combustion were subject to chemical and x-ray diffraction analyses.

The experiments and thermodynamic calculations of the adiabatic combustion temperatures and equilibrium product compositions for a Mg/CO_2 (CO) system at various reactant ratios allowed us to elucidate the mechanism and characteristic features of magnesium particle combustion in CO_2 and to propose an appropriate model for this process. Figure 4 shows schematic representation of Mg particle combustion in CO_2.

According to the proposed model, two spatially separated chemical reactions occur simultaneously in the course of Mg particle combustion in CO_2. The gas-phase reaction Mg + CO_2 = MgO + CO occurs at some distance from the surface of vaporized metal drop, while the reaction Mg + CO = MgO + C occurs near the surface, practically heterogeneously. The reactions are coupled by means of the CO mass transfer. Heat release in both the reactions play an important role in the process of metal drop evaporation.

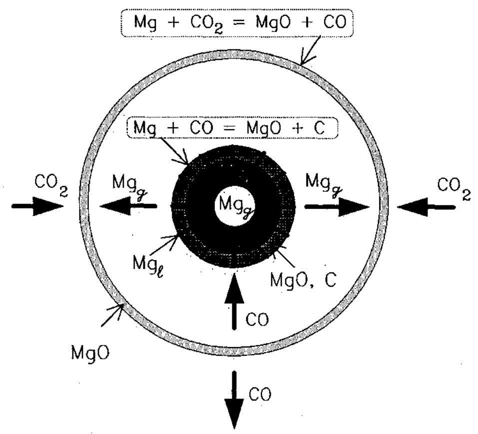

Fig. 4 Schematic representation of Mg particle combustion in CO_2.

A thermodynamic limitation is the reason for separation of these reactions. The second reaction can occur only when the temperature is lower than 2000 K, i.e., near the drop surface. The experimental results confirm this prediction. During Mg particle combustion in CO_2, the shell consisting of MgO/C mixture is formed on its surface, carbon was not found in other zones.

The experimental study on magnesium particle combustion was carried out not only in the atmosphere of CO_2 but also in that of CO. This enabled us to study the combustion mechanism in more detail. The effect of CO on the combustion characteristics is also of interest from the practical viewpoint, since some amount of CO is always present in a combustion chamber.

The experiments showed that the minimum ambient temperature necessary for Mg ignition in CO_2, as well as in CO_2/CO mixtures, is close to the melting point of Mg (923 K). The metal melting leads to the breakdown of a protective film, and therefore, to sharp acceleration of the heterogeneous chemical reaction. This reaction ensures heating of the particle up to the temperature of about 1100 K when the gas-phase reaction is "switched on." In the atmosphere with a high content of CO_2, the gas-phase reaction quickly moves away from the particle surface and the diffusion-controlled combustion front is stabilized.

It should be noted that Yuasa and Isoda[7,10] obtained the higher critical ignition temperature (1124 K) that is close to the values obtained in our experiments for the sample temperature when the gas-phase reaction begins to "work."

The experiments showed that Mg is not only readily ignited but also burns perfectly well in the atmosphere of CO_2. The burning rate for Mg in CO_2 is even several times higher than that for Mg in air. This is due to the fact that a decrease in heat release of the gas-phase reaction with CO_2 instead of oxygen is compensated by the reaction of Mg with CO, which occurs at the drop surface. An empirical formula was obtained for the burning time

$$t_b = 0.25d^{2.7}$$

where d is the particle size in mm and t_b is expressed in seconds.

Upon dilution of CO_2 with an inert gas (Ar), the significant decrease in the burning rate was observed in the experiments (about three times at CO_2 concentration of 25%). This decrease is even and accompanied by gradual weakening of the vapor-phase flame. Addition of small amounts of CO to CO_2 (when CO concentration is less than 25%) does not practically influence the burning rate. A larger content of CO in the atmosphere leads to a sharp decrease in the burning rate.

When CO concentration is more than 50% the combustion behavior is changed; there is no gas-phase flame zone and the combustion becomes heterogeneous. The rate of the heterogeneous combustion is about three times smaller than the burning rate in pure CO_2. Incomplete burnout of magnesium is observed in this combustion mode, since a dense layer of combustion products is formed on the particle surface. Combustion in pure CO is unstable, with repeated flashes, and no steady flame is observed.

The study on Mg combustion in CO_2/CO mixtures implies that CO concentration in a chamber should not exceed 25% to ensure stable combustion of particles and a high extent of combustion. Fulfillment of this requirement is obviously guaranteed at $\chi = 4$. It is interesting to note that the value of $\chi = 4$ also ensures the optimal thermodynamic characteristics of the rocket engine on the Mg + CO_2 propellant, i.e., a lucky coincidence of the conclusions of thermodynamic calculations with those of experimental studies takes place in this case.

In the course of study on Mg combustion in CO_2, the burning particle temperature was found to increase with decreasing initial size and becomes significantly higher than the boiling point of magnesium. Superheat makes a value of 300–400 K for particles about 1 mm in size. Nevertheless, combustion of the superheated metal drop is stable due to the formation of a solid porous shell on its surface (see Fig. 4).

Extrapolation of the dependence obtained to the particle size smaller than 100 μm (that could be used in the engine) shows that the burning particle temperature will be higher than 2000 K. According to thermodynamic calculations, this may suppress Mg reaction with CO, and hence, the carbon formation. This conclusion is confirmed by experiments conducted by the authors on simultaneous combustion of single particles 300 and 100 μm in size that were placed on a quartz plate into a furnace. Carbon was not found in the combustion products of smaller particles.

It is of great interest from the practical viewpoint to study the effect of pressure on the combustion process. In particular, it is known that vapor-phase combustion of magnesium ribbons (Brzustowski and Glassman[19]) or spherical 6-mm samples (Derevyaga[20]) in the oxygen/inert atmospheres under high pressures is ceased before the complete burnout because of the formation of impenetrable oxide shell in the flame. One could be afraid that analogous phenomenon in combustion of small particles will lead to a decrease in combustion efficiency in the engine. However, the combustion of a Mg 2-mm sample in CO_2 atmosphere under pressure up to 20 bar has shown that the premature cessation does not occur. Fragment ejection of the flame is observed in high-speed movies of the combustion process at high pressures. This phenomenon is related to the particle superheating which leads to a sharp increase in the pressure of metal vapor inside the shell and to its local destruction. It is the fragment ejection phenomenon that ensures complete combustion of magnesium particles in CO_2 atmosphere under high pressure.

In general, the study on the Mg particle ignition and combustion in CO_2 and CO_2/CO mixtures gives grounds for expectations of the high combustion efficiency of Mg + CO_2 propellant in a rocket engine.

Problems of Practical Realization of a Rocket Engine Using CO_2

The obtained values of takeoff to final mass ratio for a vehicle with an engine on Mg + CO_2 propellant are 6.6 for a single surface-to-orbit ascent and 9.9 for the scenario with three previous hops that impose strict requirements to the mass of the propulsion system.

Consider some structural features of the engine.

The rocket engine on a solid propellant Mg + CO_2 could hardly be realistic. Apart from the obvious complexity of solid propellant production on Mars, one should mention the difficulty of the propellant homogenization in view of significant difference in volumes for Mg and solid CO_2 at the optimal oxidizer-fuel ratio ($\chi = 4$).

The propulsion system will obviously include a tank with liquid CO_2. Pressure in this tank has to exceed the value of 5.2 bar (the pressure at the triple point of CO_2). The strength calculation for a tank with 4.44 ton of liquid CO_2 (see Table 3) under pressure of 10 bar shows that the thickness of its walls does not exceed the so-called technological thickness and the mass of the tank is relatively small.

Low atmospheric pressure near the Martian surface (p_a = 6 mb) even allows one for $p_c/p_e = 1000$ to obtain the nozzle regime $p_e = p_a$ at the chamber pressure as low as 6 bar. Owing to a favorable combination of pressure at the CO_2 triple point and atmospheric pressure of Mars, one can organize the engine process without turbopump or expulsion system. The state of CO_2 in the tank corresponds to a saturation curve and an ordinary valve will ensure an uniform feed of gaseous carbon dioxide into a combustion chamber.

The fuel feed is much more complicated. At present, rocket engines with metal powder fed by gas stream are unknown to us. According to the data of Alemasov et al.,[21] the development of such engines (so-called "engines on pseudoliquid propellant") is in a stage of experimental studies and test of models. However, the work practice of various technological and energy apparatuses with powder transport by gas stream allows us to hope for the development of the rocket engine with Mg powder fed by gaseous CO_2.

Agosto and Wickman[22] analyzed the feasibility of rocket fuel production from indigenous Lunar and asteroidal metals and proposed, in particular, to mix the metal powder with liquid oxygen. Linne and Meyer[23] have experimentally demonstrated that liquid oxygen/Al mixture can be handled safely. It is not excluded that the analogous modification may be applied for the CO_2-using engine.

There is no fuel feed problem in a hybrid rocket engine where liquid or gaseous CO_2 is fed into a combustion chamber filled with a solid fuel. The fuel in this engine may consist of powdered magnesium with a small additive of a binding material. Complexity of the fuel ignition in multiple starts of the engine can put obstacles to the realization of this scheme.

It should be noted that in the two first schemes of the engine, the ignition of propellant (Mg powder suspension in gaseous or liquid CO_2) may be quite a serious problem; a powerful ignition source might be necessary. However, after initial ignition, fresh propellants entering the rocket chamber will always be readily ignited by the combustion products recirculating in the chamber, since for Mg + CO_2 the ignition temperature is much lower than the combustion temperature.

At present we prefer none of the considered schemes. The optimal scheme of the engine should be selected only after careful experimental studies.

Now return to the problem of the propulsion system mass. Estimates show that the mass of fuel tank in the scenario with three hops is close to that of CO_2 tank, ignition and combustion times are small for Mg particles of about 10 μm in size and a long chamber is not necessary for their complete combustion.

Therefore, the mass of propusion system using CO_2 will hardly be much bigger than that of conventional ones.

Our proposal to develop a rocket engine on propellant Mg + CO_2 is oriented first of all on the problem of unmanned Mars exploration which aims, as mentioned above, at the delivery of Mars samples to Earth. Of course, a hopper with such an engine could also be used in manned Mars missions. Moreover, combination of the rocket engine with a ramjet engine using Mg fuel would also provide a possibility to develop a Mars winged aircraft capable to takeoff and land itself. After construction of a system of permanent bases on Mars, such an aircraft could become an efficient transport for communication between the bases.

The propellant Mg + CO_2 could be used not only in engines but in other power plants as well that may be needed in Mars missions. Various combustion modes can be realized in these plants, e.g., filtrational combustion, fluidized bed combustion, combustion in cyclone chambers, etc. It may be possible that in the future magnesium will be produced directly on Mars (according to the data of the Viking Landers, the Martian soil contains 5% Mg[24]), and Mg combustion in CO_2 will become the main source of energy on the Red Planet.

Conclusions

The thermodynamic calculations of a rocket engine that uses metals as fuel and CO_2 as an oxidizer show that Be, BeH_2, and Be/N_2H_4 mixture ensure the most specific impulse. However, due to the narrow range of acceptable oxidizer-fuel ratios, the toxicity of Be compounds, and a lack of data on Be ignition and combustion in CO_2, the development of the engine on Be fuel seems to be rather problematic. Among other metals, Mg is the most promising fuel owing to the relatively high specific impulse and the easy inflammability in CO_2.

Ballistic estimates show that the use of a rocket engine on $Mg + CO_2$ propellant for a Mars hopper leads to a significant decrease in the mass of propellant transported from Earth as compared with an engine on $N_2O_4 + (CH_3)_2N_2H_2$ propellant. A hopper with the proposed engine could perform 2–3 ballistic flights before the final ascent to low Mars orbit.

The experimental study on the Mg combustion in CO_2 and CO_2/CO mixtures confirms the conclusion that Mg fuel is promising. The characteristics and mechanism of Mg particle ignition and combustion in CO_2 have been elucidated. It has been shown that the concentration of CO in combustion chamber does not have to exceed 25% in order to guarantee fast vapor-phase combustion. The observed superheating phenomenon promotes decreasing content of carbon in the combustion products and increasing combustion efficiency of Mg.

Analysis of various schemes for oxidizer and fuel feed shows that the mass of propulsion system on propellant $Mg + CO_2$ will not differ significantly from those using conventional propellants.

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References

[1]Ash, R. L., Dowler, W. L., and Varsi, G., "Feasibility of Rocket Propellant Production on Mars," *Acta Astronautica*, Vol. 5, No. 9, 1978, pp. 705–724.

[2]Zubrin, R. M., and Baker, D., "Humans to Mars in 1999," *Aerospace America*, Vol. 28, No. 8, 1990, pp. 30–32, 41; see also "Mars Direct," *Ad Astra*, Vol. 2, No. 11, 1990, pp. 33, 34.

[3]Zubrin, R. M., "Indigenous Martian Propellant," *Aerospace America*, Vol. 27, No. 8, 1989, pp. 48–51.

[4]French, J. R., "Some Unconventional Approaches to the Exploration of Mars," *Spaceflight*, Vol. 33, No. 2, 1991, pp. 62–66.

[5]Rhein, R. A., "The Combustion of Powdered Metals in Nitrogen and Carbon Dioxide," *Pyrodynamics*, Vol. 3, No. 2, 1965, pp. 161–168.

[6]Kapanadze, S. A., Mazing, G. Yu., and Prudnikov, N. E., "Feasibilities of Using Planetary Atmosphere for a Takeoff from a Descent Vehicle to Earth" (in Russian), *Nauchnye Chteniya po Aviatsii i Kosmonavtike, 1980*, Nauka, Moscow, 1981, pp. 230, 231.

[7]Yuasa, S., and Isoda, H., "Carbon Dioxide Breathing Propulsion for a Mars Airplane," AIAA Paper 89-2863, July 1989.

[8]Merzhanov, A. G., Kitain, M. M., Goldshleger, U. I., and Shteinberg, A. S., "Thermodynamic Analysis of Iron Oxide Interaction with a Methane/Oxygen Mixture" (in Russian), *Doklady Akademii Nauk SSSR*, Vol. 237, No. 2, 1977, pp. 391–394.

[9]Maček, A., "Fundamentals of Combustion of Single Aluminum and Beryllium Particles," *Eleventh Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1967, pp. 203–214.

[10]Yuasa, S., and Isoda, H., "Ignition and Combustion of Metals in a Carbon Dioxide Stream," *Twenty-Second Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1988, pp. 1635–1641.

[11]Maltsev, V. M., Maltsev, M. I., and Kashporov, L. Ya., *Fundamental Characteristics of Combustion* (in Russian), Khimiya, Moscow, 1977.

[12]Glassman, I., "Combustion of Metals—Physical Consideration," *Progress in Astronautics and Rocketry, Vol. 1. Solid Propellant Rocket Research*, edited by M. Summerfield, Academic Press, New York, 1960, pp. 253–258.

[13]Smal, F. V., and Chulkov, A. Z., "Compositions and Properties of Gelled Propellants" (in Russian), *Rocket Propulsion*, edited by Ya. M. Paushkin and A. Z. Chulkov, Mir, Moscow, 1975, pp. 114–146.

[14]Sarner, S. F., *Propellant Chemistry*, Reinhold, New York, 1966.

[15]Shafirovich, E. Ya., and Goldshleger, U. I., "Some Features of Combustion of Volatile Metal Particles," *Heat and Mass Transfer in Chemical Systems: Proceedings of the International School-Seminar* (in Russian), Vol. 1, Lykov Inst. of Heat and Mass Transfer, Minsk, 1988, pp. 37–46.

[16]Shafirovich, E. Ya., and Goldshleger, U. I., "Ignition and Combustion of Magnesium Particles in Carbon Dioxide" (in Russian), *Fizika Goreniya i Vzryva*, Vol. 26, No. 1, 1990, pp. 3–10.

[17]Shafirovich, E. Ya., and Goldshleger, U. I., "Combustion of Magnesium Particles in CO_2/CO Mixture," *Combustion Science and Technology*, Vol. 84, Nos. 1–6, 1992, pp. 33–43.

[18]Shafirovich, E. Ya., and Goldshleger, U. I., "The Superheat Phenomenon in the Combustion of Magnesium Particles," *Combustion and Flame*, Vol. 88, No. 4, 1992, pp. 425–432.

[19]Brzustowski, T. A., and Glassman, I., "Vapor-Phase Diffusion Flames in the Combustion of Magnesium and Aluminum: II. Experimental Observations in Oxygen Atmospheres," *Progress in Astronautics and Aeronautics, Vol. 15. Heterogeneous Combustion*, edited by H. G. Wolfhard, I. Glassman, and L. Green, Jr., Academic Press, New York, 1964, pp. 117–158.

[20]Derevyaga, M. E., "The Effect of Pressure on Combustion of Magnesium" (in Russian), *Fizika Goreniya i Vzryva*, Vol. 19, No. 1, 1983, pp. 34–39.

[21]Alemasov, V. E., Dregalin, A. F., and Tishin, A. P., *Theory of Rocket Engines* (in Russian), 4th ed., Mashinostroenie, Moscow, 1989.

[22]Agosto, W. N., and Wickman, J. H., "Propulsion Fuels from Indigenous Lunar and Asteroidal Metals," *Symposium on Lunar Bases and Space Activity of the 21st Century*, Houston, TX, 1988, p. 3.

[23]Linne, D., and Meyer, M., "Technical Prospects for Utilizing Extraterrestrial Propellants for Space Exploration," *42nd Congress of the IAF, Montreal, Canada*, IAA-91-669, Oct. 1991.

[24]Moroz, V. I., *Physics of Planet Mars* (in Russian), Nauka, Moscow, 1978.