Engineering Notes

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Vacuum Reduction of Extraterrestrial Silicates

Douglas R. Sparks*
General Motors Corporation,
Kokomo, Indiana

Nomenclature

A, B, C, D, E = empirical constants
F = Gibbs free energy of transformation
P = oxygen partial pressure
R = gas constant
T = temperature

Introduction

EXPERIMENTAL work done in the electronics industry on the evaporation of metal oxides provides a good data base on the behavior of metal oxides at high temperature under vacuum. Steurer[7] first proposed the use of vapor phase pyrolysis of lunar soil in 1985. Both silicon oxide and iron oxide, two of the major components making up the lunar soil[1,2] and detected from Earth-approaching asteroids,[3-6] have been vacuum reduced at pressures 10 orders of magnitude higher than would be encountered in interplantary space. As will be shown, the vacuum reduction of other silicates found in extraterrestrial soils should also be possible. The presentation also discusses the purification of the metals using such space-compatible techniques as vacuum distillation, slagging, and zone refining.

The utilization of lunar and asteroidal materials for the construction of space habitats, rocket fuel, and satellite solar power systems has been proposed by several authors.[7-12] As is the practice on Earth, the proposed systems to convert metal oxides into metals involve the use of large quantities of gaseous, liquid, or solid chemicals.[7-9] A system based on vacuum reduction would eliminate the need for these chemicals and the associated containment and recycling equipment. Such a mass reduction will substantially reduce the cost of the first lunar or asteroidal soil processing facility.

Thermodynamics

Vapor phase pyrolysis or vacuum reduction occurs, without the addition of chemical reducing agents, when metal oxides are heated in a vacuum. The vacuum reduction of the oxides of silver, mercury, and palladium was studied in the early part of this century.[14-17] For industrial applications this method is impractical on Earth, but in interplanetary space where the atmospheric pressure drops to 10^{-19} atm,[18-19] vacuum reduction may be the most feasible technique available.

Equilibrium thermodynamics can be used to predict the temperatures, for a given oxygen partial pressure, at which metal oxide to metal transformation will occur. Equation (1) represents an ideal metal oxide system

$$M(s) + 1/2O_2(g) = MO(s) \tag{1}$$

where M and MO represent a metallic and oxide species. The Gibbs free energy of transformation with respect to temperature at a constant oxygen partial pressure is expressed in Eq. (2), and with respect to both temperature and oxygen partial pressure in Eq. (3) as follows:

$$F = A + BT\ell n T + CT^2 + DT^{-1} + E \tag{2}$$

$$F = -RT\ell n(1/P)^{1/2} \tag{3}$$

By combining Eqs. (2) and (3), empirical data[20] can be used to determine the regions of temperature and oxygen partial pressure over which the solid phases (metal or oxide) are stable. Figure 1 depicts the phase fields of the primary oxides found in lunar and asteroidal soils. In Fig. 1 the metal phase is to the right of the plotted line and the oxide phase is to the left. As can be seen from the plot, for an oxygen partial pressure of 10^{-19} atm, metallic Fe, Si, Ti, Mg, and Al are all stable phases for temperatures ranging from 900–1800°C.

Both metallic iron and silicon have been produced as the result of attempts to evaporate oxides of each. In the case of Fe_2O_3, the source material was found to decompose upon heating under vacuum into a mixture of metallic iron and Fe_3O_4. Hass[22] found that at 3×10^{-8}atm, above 1250°C silicon was formed when attempting to evaporate SiO. The percentage of silicon in the evaporated films increased as the temperature for a given pressure increased and as the pressure for a given temperature decreased. An extrapolation of these data predicts that pure silicon will be evaporated above 1450–1550°C at 3×10^{-8}atm. Bradford et al.[23] found that as the temperature of the substrate upon which the films were condensed was increased, the percentage Si increased. This

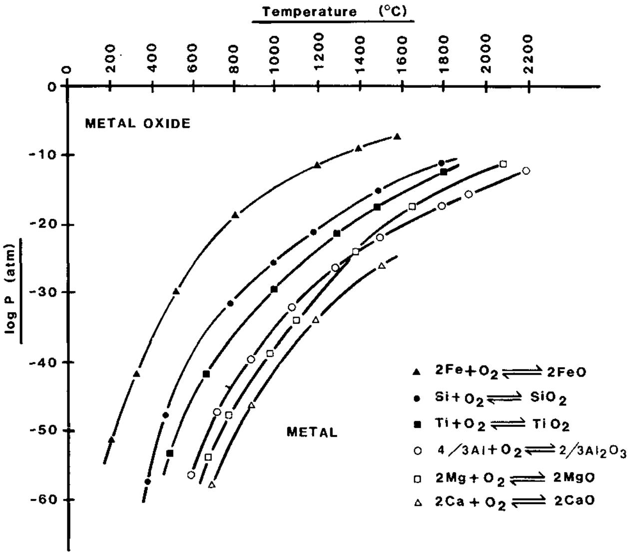

Fig. 1 Temperature vs oxygen partial pressure, solid metal/oxide phase fields for the major lunar and asteroidal soil components.

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*Engineer, Delco Electronics Division.

Table 1 Evaporation data for the major oxides and metals found in the lunar soil

Material	Observed vapor species of oxide (in order of decreasing frequency)	Temp., °C at which v.p. is	
		10^{-5}atm	10^{-3}atm
Al	—	996–1217	1557[33,34]
Al_2O_3	$Al, O, AlO, Al_2O, O_2(AlO)_2$	1800	2150[35,36]
Ca	—	597–605	802[33,34]
CaO	Ca, CaO, O, O_2	2050	2600[35,37]
Fe	—	1477	1857[33]
Mg	—	439–443	605[33,34]
MgO	Mg, MgO, O, O_2	1560	1950[35,36]
Si	—	1343–1632	2057[33,34]
SiO	SiO, (Si, O_2 above 1250°C)	1025	1200[38,39]
SiO_2	SiO, O_2	1250	1500[35]
Ti	—	1546–1737	2177[33,34]
TiO_2	TiO, Ti, TiO_2, O_2	[a]	[a](Refs. 34,41)

[a] Source material decomposition into suboxides upon heating.

was explained on the basis of reduced oxygen sticking coefficients with increasing substrate termperatures. Increasing the substrate temperature then decreases the amount of oxygen absorbed during film deposition that leads to oxidation. Also, as the substrate temperature increases, the mobility of Si atoms increases and Si clusters form that cannot be oxidized easily.

Maisel and Glang[24] have collected a great deal of information on the evaporation of metal oxides. The Table 1 gives evaporation data for the most important lunar oxides. Metals are the most common vapor species found when evaporating Al_2O_3, MgO, and CaO. In all cases oxygen is found. When heated in the ultra-high vacuum of space, the metallic and gaseous oxygen components of the vapor should increase substantially.

From examination of Fig. 1 it is apparent that the temperature at which metallic silicon is produced under vacuum from the vapor phase is much lower than what is predicted for the solid phase. Very little thermodynamic data for gaseous metal oxides exist. If the other metal oxides found in lunar soil behave like SiO, the oxide vapor pressure could be the primary factor determining the minimum reduction temperature and pressures. The rapid evaporation or reduction of useful oxides found in the lunar soil should occur below 1800°C.

System Design

In a batch process silicates could be ball milled to an appropriate size or, as has been used to evaporate metals,[25-27] a rod could be employed to continuously feed material to the heat source. Several methods are available that can obtain temperatures in excess of 2000°C. These include metal and ceramic resistance heating elements, electric arc or electron beam, and a solar concentrator. The electric arc is the only heat souce mentioned that is used to heat large batches of material in industry. The temperature of the electric arc approaches 3400°C, and nonconsumable electric arcs have been constructed.[28] At 3400°C the vapor pressure of all the aforementioned metals and oxides is close to or above 1 atm. Such temperatures under a high vacuum will result in the rapid reduction and evaporation of the soil constituents.

Due to the different vapor pressures of the metals involved, heating the walls or baffles of the chamber into which the material is evaporated will lead to the segregation of the metals. Suboxides, titanium, silicon, and iron will condense at the hotter end of the chamber, with aluminum, calcium, and magnesium condensing at the cooler end of the chamber. Oxygen will be cryogenically trapped at the exhaust end of the retort. The vacuum of space will be used to efficiently insulate the cryogenic trap. This system is similar to the ferrosilicon process[29] used to produce magnesium. In that process MgO is mixed with a SiFe alloy and heated to 1250°C under a low vacuum. Metallic Mg is produced and instantaneously evaporates to condense into crystals at the cool end of the system.

The purification of the metals, like the reduction, must not require the use of bulk chemicals to be economically attractive for space processing. After the metals are reduced, vacuum distillation[30] will be used to separate Mg, Ca, and Al from the rest of the material. Since Ti, Si, and Fe have similar vapor pressures but quite different free energies of formation of their respective oxides, slagging can be used to separate them. To produce high purity metals such as semiconductor grade silicon, zone refining[31] can be used.

Based on the eutectic temperatures found in the phase diagrams of the metal[32] the maximum impurity concentration over which zone refining will be effective can be determined and is given as

Al: 7.6% Ca, 1.9% Fe, 35% Mg, 87.4% Si
Ca: 27% Al, 16.2% Mg
Fe: 41.3% Al, 14.1% Si, 14% Ti
Mg: 32.3% Al, 18.3% Ca
Si: 12.6% Al, 41.2% Fe, 43.5% Mg, 22% Ti
Ti: 32.2% Fe, 8.5% Si

The zone refining process is repeatable with the final purity of the metal limited primarily by the background concentration of impurities in the processing apparatus. Induction heating is typically used, but in space, solar concentrators may provide a viable mass-saving alternative.[13]

Several other possible methods for using vacuum reduction can be envisioned. Oxides could first be separated by vacuum distillation and then reduced. Sequential reduction based on the different free energies of oxide formation could be used to separate the metals while they are being reduced. If it is only assumed that Fe and Si can be vacuum-reduced, the Si can be used to reduce MgO.[29] Based on thermodynamic calculations, the Mg produced could then be mixed with Al_2O_3 and TiO_2 to manufacture Al and Ti at temperatures greaster than 1400°C.

Cost Savings

In an earlier study on the processing of lunar soil[10] the different reduction schemes proposed were silicon reduction of FeO carbothermic reduction of SiO_2, and Al_2O_3 and the silicon reduction of MgO. This system required the importation of reducing agents and the equipment necessary to recycle the water, carbon monoxide, and hydrocarbons produced back into usable material. By using vacuum reduction as the sole means of treating metal oxides, it is estimated that 50% less power will be required. This power reduction is primarily because of the elimination of the electrolysis of water. Approximately 52% less mass will be required for the installation of the initial plant.

Fitting these figures into the lunar manufacturing model proposed by Koelle,[10] the use of vacuum reduction should save 39% on the installed electric power, 38% on the annual power usage, and 14% on the mass imported for the initial installation of the complete manned lunar base. Because of the potential decrease in process complexity, personnel and spare parts required also may be reduced. Since the transportation cost is the main barrier to space manufacturing, a reduction in mass of 14% will reduce the initial investment by a substantial amount.

Recommendations

Most of the research and development for a vacuum reduction system could be done on Earth, with the remainder done in Earth orbit. Research and development work should include the following:

(1) Research into vacuum reduction kinetics. At lower temperatures and higher pressures, such oxides as FeO, SiO, Cr_2O_3, Na_2O, K_2O, P_2O_5, PbO, ZnO, and CoO could be used to study the vacuum reduction behavior of individual oxides as well as oxide mixtures and compounds. The more refractory oxides such as SiO_2, TiO_2, MgO, Al_2O_3, and CaO could be studied at higher temperatures such as those obtained in the electric arc. Both the reduction system and the cryogenic oxygen trap could also be tested on Earth

2) Further metal purification work on vacuum distillation, centrifugal slagging, and zone refining with alloys of lunar or asteroidal compositions.

3)Deployment of a small scale, Earth-proven system in low Earth orbit to investigate the effect of zero gravity on the process and equipment.

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Effects of Cross Section and Nose Geometry on Slender-Body Supersonic Aerodynamics

G. R. Hutt* and A. J. Howe†
University of Southampton,
Hants, England, United Kingdom

Nomenclature

C_D = drag coefficient
C_L = lift coefficient
d_B = cylinder diameter
d_N = blunt-nose diameter
$Re(d_B)$ = Reynolds number based on cylinder diameter
X_{cp} = center-of-pressure location aft of nose-afterbody interface
α = angle of attack
Ψ = angle of roll

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*Lecturer, Aeronautics and Astronautics Department. Member AIAA.

†Undergraduate Student, Aeronautics and Astronautics Department.