PRELIMINAR RESULTS ON HIGH TEMPERATURE PROCESS OF ILMENITE REDUCTION BY AMMONIA

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On the basis of our previous studies on the reduction of ilmenite at high temperature by hydrogen and methane, we have carried out some experiments on the ilmenite ammonia reduction process in a thermobalance coupled with a mass spectrometer.
The aim of the work has been to investigate the process of interaction between ilmenite and NH_3 at high temperature according to the following reaction:

$$FeTiO_3(s)+2/3NH_3(g) \rightarrow Fe(s)+TiO_2(s)+H_2O(g)+1/3N_2(g) \quad (1)$$

The reduction process of this reaction has been investigated in a range of temperature up to 1200 K by varying the values of ammonia flow rates .
The first results obtained regards the gas phase investigation by using mass-spectrometric analysis directly on the reaction products.

INTRODUCTION

There is a growing interest in some NASA milieu to reconsider plans for return to Moon after completion of the ISS[1]. In this contest the exploitation of lunar resources would receive new lymph for further developments.
A number of studies were carried out in the past on the subject[2] mostly concerning in situ oxygen production from ilmenite and some others lunar soil components.
Subsequently over twenty different chemical and physical processes have been proposed for the oxygen production from lunar materials[2-6]. They can be grouped into major categories characterized by solid-gas interaction, pyrolisis, silicate-oxide melt, aqueous solution and coproduct recovery. Among these processes the reduction of ilmenite with hydrogen occupies a prominent place[7-9].
Our group has carried out experiments on ilmenite, H_2 reduction process in a sound assisted fluidized bed[10] heating the reactor with solar energy[11]. More recently satisfactory results have been obtained by using methane as reducing agent[12]. The same procedures used in these previous investigations are here employed to verify the possibility to get ilmenite reduction by ammonia. The importance of this new approach is to carried out scientific data on the possible obtainment of nitrogen, other than metallic iron and water as principal products.

RESULTS

A commercial thermobalance, Ugine Eyraud. Setaram B 60 with a vertical furnace constituted by an alumina tube (25 mm in diameter and 600 mm long) inserted in a graphite heater has been used. An alumina cell is suspended in the isothermal zone of the furnace trough a tungsten wire. A thermocouple (Pt/PT,Rh), under the cell, allows the temperature measurements, while a steel capillary has been inserted on the top of the alumina tube, to sampling gas to be analyzed by a quadrupole mass-spectrometer (Balzers QMA 410) coupled with the thermobalance.
The ammonia flux is settled by a mass-flow controller in order to have a laminar flux in the alumina tube. In this way, the gas collected in the mass spectrometer is representative of the gas produced in the cell.
Samples of Canadian ilmenite, powder (90-105 μm), with weight 285 mg, were made interact with ammonia gas at different pressure values, ranging from room pressure to – 5 kPa at temperatures varying up to 1200 K and a superficial velocity ranging from 7–20 cm/min Figg. 1,2, 3 are reported the behavior of the H_2O^+, N_2^+, H_2^+, mass peak intensity respectively, during the reduction process in comparison with the loss mass variation, bold line.

Error! Not a valid link. Fig. 1. Typical behavior of the intensity H_2O^+ (mass=18) mass peak during the reduction process in comparison with the loss mass variation, bold line

Error! Not a valid link. Fig.2.Typical behavior of the intensity N_2^+ (mass=28) mass peak during the reduction process in comparison with the loss mass variation, bold line.

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Fig. 3. Typical behavior of the intensity H_2^+ (mass=2) mass peak during the reduction process in comparison with the loss mass variation bold line .

The increasing of the mass peak intensity of water and nitrogen, in correspondence with the sample weight loss leading us to define the equation (1) as probable mechanism of the reduction process. One observation can be made, while the water peak intensity decreases after the complete iron reduction, the signals of hydrogen and nitrogen do not decrease in same way. This effect can be suggest the hypothesis of a secondary reaction iron catalyzed interesting the ammonia decomposition according to the scheme:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (2)$$

By considering the thermobalance results, show in Figg.1,2,3 as bold line, it is possible to observe that the quantitative transformation of the iron oxide in iron and water is achieved.

The application of the thermogravimetry and mass spectrometry to the interaction of ilmenite with ammonia, has made possible to elucidate informations concerning the development of the reduction process. The results obtained will be utilized to perform the process in a solar energy sound assisted fluidized bed system as before tested for ilmenite/hydrogen reduction. As it is well known nitrogen is not present on the lunar soil and has to be brought from the earth to make possible a human habitation of our satellite.

One can foresee the utility of transporting in the form of NH_3 the nitrogen, by utilizing the process here described, could give rice to N_2 H_2 and water besides other not less important subproducts as metallic iron and titanium dioxide.

REFERENCES

1. G. De Maria Proceed. of the Space Resources Round-table II, Colorado School of Mines – Duke M. Editor. - Nov. 2000
2. A. H. Cutler, P. A. Krag "Lunar Bases and Space Activities in the 21st Century" –W. Mendell, . Editor – LPI – Houston – 1985, 559-569.
3. A. R. Martin and W. E. F. Moulford, Lunar Resources Exploitation Study - ESA Contract No.11196/94/JG (1966)
4. F. Shadman. Y.Zhao " Production of Oxygen from Lunar Ilmenite" Annual Process Report; NASA/University of Arizona Center for Utilization of Local Planetary Resources, (1989 -1990)
5. L.A. Taylor and W.D. Carrier III, "The feasibility of processes for the producttion of oxygen on the Moon", in Engineering, Construction, and Operations in Space III, pp 752-62, American Society of Civil Engineers, NY 1992
6. M.A.Gibson, C. W.Knudsen, D. J. Brueneman, C.C. Allen, H. Kanamori and D.S. McKay, J. of Geophys.Research 99(E5) (1994)10,887-97
7. S. K. Tarby, Ph.D Thesis, Carnegie Insitute of technology Pittsburg,PA,(1962)
8. K. Sun, Rare Metals, 16(1) (1997) 59-62
9. G. Bardi, D. Gozzi and S. Stranges , Mater. Chem. And Phys. 17(1987) 325-341
10. De Maria G., Brunetti B., Trionfetti G. and Ferro D. Proceed. of 30th International Conference on Environmental Systems (ICES) – Toulouse July 2000.
11. De Maria G., Brunetti B., Trionfetti G. and Ferro D. Proceed. of 31th International Conference on Environmental Systems (ICES) – Orlando, Florida, August 2001.
13. De Maria G., Brunetti B., Trionfetti G. and Ferro D., AIAA - Albuquerque - August 2001, 4579