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CHEMICAL REDUCTION OF REFRACTORY OXIDES BY ATOMIC HYDROGEN

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Refractory oxides are utilized for a number of electrically insulating components in controlled thermonuclear reactors (1). These components are subjected to bulk radiation damage by high energy particles and, like graphite (2), may be susceptible to surface chemical attack by deuterium and tritium. The nature of the chemical attack of UO_2 and Al_2O_3 by thermal energy atomic hydrogen has been investigated by the modulated molecular beam-mass spectrometer technique (3,4). The experiment is conducted in the high vacuum system shown in Fig. 1. The reactant atomic hydrogen beam is produced by effusion from a hot (2500°K) dissociation oven. This beam is modulated by a mechanical chopper prior to striking the solid surface. Desorbed reaction products (water vapor and perhaps lower oxides or the metallic component of the target) and scattered atomic hydrogen are detected in flight by a quadrupole mass spectrometer. The main quantity which is measured is the reaction probability, which is defined as the rate of desorption of a reaction product divided by the rate of impingement of the reactant. The reaction probabilities reported here refer to the signal ratio of water to atomic hydrogen detected by the mass spectrometer. The modulated aspect of the experimental technique serves to enhance the signal-to-noise ratio of the method and also provides information on surface residence times which is very valuable in deducing a detailed mechanism of the surface reaction. The two model oxides selected for this investigation, UO_2 and Al_2O_3, are the best characterized of any oxides; their physical and thermochemical properties are reasonably well known and there have been many investigations of their vacuum vaporization behavior and their reactivity with other gases. The basic difference between

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the two oxides is the possibility of formation of nonstoichiometric compounds. Urania contains a cation which exhibits multiple valence states and thus can form a wide range of solid solutions of the $UO_{2\pm x}$ type which retain the basic fluorite structure of UO_2. The aluminum ions in alumina, however, possess only +3 valence, so aluminia is essentially a line compound with practically no deviation from the formula Al_2O_3 whether the environment is oxidizing or reducing.

Results of the UO_2/H investigation indicates that reduction of UO_2 by atomic hydrogen proceeds by the production of water vapor and hypostoichiometric urania:

$$\frac{1}{x} UO_2 + 2H \rightarrow \frac{1}{x} UO_{2-x} + H_2O(g) \qquad (1)$$

The reaction probability for water production as a function of UO_2 temperature was measured at a fixed H atom beam intensity and modulation frequency. The reaction probability increased from the noise level at low temperatures to a high temperature plateau at about 1300°C. At the plateau, approximately one H atom out of seven striking the surface undergoes reaction and returns to the gas phase as water.

Contrary to UO_2, the range of deviation from stoichiometry of Al_2O_{3-x} is probably so small that even slight reduction of Al_2O_3 requires production of the metal. Because alumina cannot be rendered hypostoichiometric, its reduction by atomic hydrogen results in production of aluminum metal:

$$\frac{1}{3} Al_2O_3 + 2H \rightarrow \frac{2}{3} Al + H_2O(g) \qquad (2)$$

The results of our study of the Al_2O_3/H system indicate that the reaction does indeed proceed according to Eq(2). However, the observed reaction probability for water production remains too low to be detected (i.e., $< 10^{-3}$) until the temperature is greater than 1300°C. At higher temperatures, both H_2O and aluminum are detected by the mass spectrometer as gaseous reaction products. Other products, such as AlO, AlH, AlOH, Al_2O and Al_2OH were sought but not found. The reaction probability increases with temperature, but remains two orders of magnitude below the maximum value for the UO_2/H reaction.

The relative ease which UO_2 is reduced by atomic hydrogen compared with Al_2O_3 is due to two factors. The first is related to the thermochemistry of reactions (1) and (2). Although thermodynamics cannot be invoked to predict chemical kinetics, one can at least expect that thermochemically favored reactions should be the most readily observed.

A rough estimate of the ease of reducing Al_2O_3 by atomic hydrogen can be obtained from the standard free energy change of reaction (2), which is:

$$\Delta G^\circ_{(2)} = -\frac{1}{2}\Delta G^\circ_{Al_2O_3} - 2\Delta G^\circ_H + \Delta G^\circ_{H_2O}$$

where ΔG°_H and $\Delta G^\circ_{H_2O}$ are the standard free energies of formation of atomic hydrogen and water, respectively, and $\Delta G^\circ_{Al_2O_3}$ is the free energy of formation of alumina (per mole of O_2). The equilibrium oxygen pressure over the Al/Al_2O_3 couple is given by: $\Delta G^\circ_{Al_2O_3} = RT\ln p_{O_2}$ where R is the gas constant. The comparable quantity of UO_2 is the oxygen potential $\overline{\Delta G}_{O_2}$. Hence, the standard free energy change for reaction (1) for small x is:

$$\Delta G^\circ_{(1)} = -\frac{1}{2}\overline{\Delta G}_{O_2} - 2\Delta G^\circ_H + \Delta G^\circ_{H_2O}$$

The free energy change of reaction (1) at 1000 K is -310 kJ/mole, whereas that of reaction (2) is -71 kJ/mole. The fact that both of these free energy changes are substantially negative suggest that, barring kinetic restrictions, reduction of the oxides should proceed in atomic hydrogen. However, urania should be easier to reduce than alumina because removal of oxygen from UO_2 does not require production of the metal.

The second feature which favors efficient reduction of UO_2 but not of Al_2O_3 is the oxygen diffusivity. As the reduction reaction proceeds at the surface, oxygen depletion of the surface layers will quickly stop the reaction unless oxygen can be transported to the surface from the bulk solid. The self-diffusion coefficient of oxygen in hypostoichiometric urania has not been measured, but is probably very large (5), whereas oxygen migration in alumina is smaller, probably by many orders of magnitude (6). Consequently, oxygen transport from the interior of the solid to the reacting surface takes place easily in UO_2 but in alumina, evaporation of the aluminum metal reaction product appears to be necessary to prevent a protective scale of Al from halting the surface reduction process.

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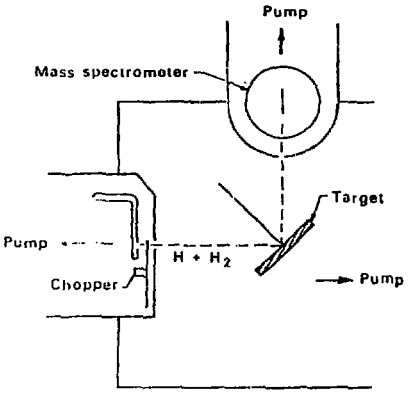

Fig. 1.