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CERAMICS IN FISSION AND FUSION TECHNOLOGY

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CERAMICS IN FISSION AND FUSION TECHNOLOGY

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SUMMARY

The role of ceramic components in fission and fusion reactors is described. Almost all of the functions normally performed by ceramics, except mechanical, are required of nuclear ceramics. The oxides of uranium and plutonium are of predominant importance in nuclear applications, but a number of other ceramics play peripheral roles. The unique service conditions under which nuclear ceramics must operate include intense radiation fields, high temperatures and large temperature gradients, and aggressive chemical environments. Examples of laboratory research designed to broaden understanding of the behavior of uranium dioxide in such conditions are given. The programs described include high temperature vaporization, diffusional processes, and interaction with hydrogen.

INTRODUCTION

The distinguishing feature of the usage of ceramics in fission and fusion technology is the radiation environment in which they must function. Of the many types of radiation generated in nuclear reactors, those with the most significant effects on ceramics are thermal neutrons and fission fragments in the fuel material of fission reactors and energetic neutrons and high-energy ions in fusion systems. These radiations interact with the atoms of the ceramic in a number of ways: stopping of the radiation by the solid produces heat, which is the principal reason for these systems; direct collisions of the energetic nuclear particles with atoms of the solid lattice cause displacements (i.e., vacancy-interstitial pairs) which then agglomerate into macroscopic defects which affect mechanical, physical and chemical properties; nuclear reactions with neutrons transmute constituent atoms into elements with different and usually deleterious properties.

A number of monographs review the effects of radiation on both metals and ceramics (1 - 4). A complete recent summary of the behavior of all types of ceramic nuclear fuels is available (5). The remainder of this section is devoted to brief summaries of irradiation effects in fission and fusion technology. Following this introduction, several research programs in nuclear ceramics are reviewed.

Ceramics in Fission Reactors

The material which comprises the core of a fission reactor must function in the most inhospitable environment that any technological device has ever had to withstand. Temperatures high enough to melt all but a few substances require that nuclear fuel elements be constructed of the most refractory materials and be designed with Spartan simplicity.

In fast breeder reactors the nuclear fuel is a ceramic oxide containing the uranium and plutonium needed for the nuclear reactions; plutonium-239 fissions upon neutron capture to produce the heat which is ultimately converted into electricity. The uranium-238 in the fuel serves to regenerate plutonium by neutron-absorption and subsequent radioactive decay. The solid-solid solution mixed oxide (U,Pu) O₂ is employed because the oxide has a sufficiently high melting point and structural stability to survive the designated lifetime in the reactor. The ceramic fuel is contained in a close-fitting stainless steel tube. These two components, ceramic fuel pellets and a metal cladding tube, constitute the fuel element.

The fuel elements for the present generation of light-water reactors differ from those used in fast breeder reactors in the materials of construction; the fuel in a light-water reactor is pure uranium dioxide (enriched in fissionable ²³⁵U) and the cladding is an alloy containing primarily zirconium.

Other types of ceramics have been investigated as potential nuclear fuels. Uranium-plutonium carbide or nitride maintain the refractory features of oxides (high melting point, low chemical reactivity) but possess thermal conductivities closer to those of metals, which greatly reduces operating temperatures. The compound (U,Pu)N is to be the fuel for the space nuclear power reactor in the U.S.

The high temperatures and large temperature gradients experienced by oxide fuels during operation, when superimposed upon the fission process, produce novel phenomena such as gross restructuring of the ceramic, radial redistribution of its component chemical elements and substantial swelling due primarily to precipitation of insoluble fission gases. Economics demands a fuel burnup (fraction of heavy metal fissioned) approaching 10% for fast breeder reactors, compared to the 3% burnup characteristic of light-water reactors.

Nuclear transmutations convert uranium and plutonium atoms into fission-product elements. Some fission products are gaseous and either escape from the fuel to cause pressure buildup in the cladding or precipitate into bubbles which swell the fuel and bring it into mechanical contact with the cladding. Chemically, fission is an oxidizing process. When a uranium or plutonium atom in an oxide nuclear fuel fissions, two changes occur. First, two fission-product atoms appear in place of the heavy-metal atom, and second, the two oxygen atoms that were associated with the original heavy-metal atom (in the solid UO₂ or

PuO_2) are liberated. The fission products can be any one of the 30-odd elements in the middle of the periodic table. If one of the two products of fission has a strong affinity for oxygen (zirconium, for example), this element can re-immobilize the liberated oxygen. However, if neither of the fission products form stable oxides (ruthenium or iodine, as examples), the liberated oxygen is free to leave the fuel and to chemically attack the cladding.

Perhaps the single most important physical property of ceramic fuel materials is its thermal conductivity. When the fuel element is operated at a specified power density, the thermal conductivity determines the temperature of the fuel. The fuel temperature directly controls the kinetics and thermodynamics of a host of processes which affect fuel performance, such as fission gas swelling and release, defect mobility, sintering, and creep.

The morphology of the as-fabricated fuel form, which is a pellet about 1 cm in diameter by 1 cm in height, is carefully controlled. Grain size and the quantity and diameter of the closed porosity influence processes such as irradiation sintering, swelling and fission gas release. The fuel fabrication process is designed to tailor the morphology of the fuel and to control its chemical reactivity. In oxide fuels, the oxygen-to-metal ratio must be as low as possible in order to prevent corrosion of the metal cladding by the fuel.

The diameter of the fuel pellets is specified to tolerances measured in microns because the size of the initial gap between the fuel and the cladding is critical to subsequent in-reactor performance. If the gap is too large, the insulating gas layer between the fuel and the cladding causes excessive fuel temperatures during irradiation; if the gap is too small, swelling of the fuel by fission products causes premature fuel-cladding mechanical interaction which risks cladding rupture.

As a result of the 1979 accident at the Three Mile Island nuclear reactor, renewed attention has been directed at the behavior of oxide fuels when protection of the cladding tube is lost. Additional phenomena which arise in this situation include oxidation by steam and accelerated fission product release. The effect of hydrogen in the steam (H_2 is produced during an accident by oxidation of the zirconium cladding) may also be important. If temperatures during the accident exceed the melting point of the zirconium-based cladding alloy ($\sim 1750^\circ\text{C}$), a low-melting eutectic of Zr and UO_2 can be formed, thereby increasing the possibility of a core melt.

Ceramics in Fusion Reactors

One of the most demanding applications of ceramics is in fusion reactors. Clinard (6) has summarized the unique problems that ceramics face in such an environment. Common ceramic fusion reactor components are insulators and dielectrics, where alumina and beryllia are commonly specified. When exposure

to the plasma is required, the ceramic must consist of low atomic weight elements to avoid degradation of plasma performance by sputtering of heavy atoms. Typical materials for this application are SiC, Si₃N₄ and graphite.

The 14-MeV neutron flux to which these ceramics are exposed creates volume swelling as large as several percent, with the attendant possibility of mechanical interaction with nearby structures. When high energy neutrons collide with atoms of the lattice, sufficient energy is transferred to the latter to permanently displace the atom from its lattice site, creating a "displacement" or a vacancy-interstitial pair. Radiation effects generally depend upon the dose, which is commonly measured in displacements per atom. This quantity denotes the number of times that a given atom is displaced from its lattice site during the period of neutron bombardment. An atom can be displaced more than once because recombination processes occurring during irradiation continually return interstitial atoms to vacant lattice sites.

Swelling of ceramics begins at doses of ~0.2 dpa. At low temperature, the magnitude of swelling is consistent with assignment of one atomic volume per displacement. At high temperature, swelling may involve clustering of the point defects into voids and interstitial disks, phenomena which are common irradiation effects in metals.

Aside from the dimensional change caused by swelling, anisotropic swelling (in noncubic ceramics) or differential swelling (due to dose variation over a component) can generate internal stresses which result in loss of strength by microcracking.

Chemically, the plasma is principally atomic hydrogen, which is an exceedingly reactive species. A generic ceramic MO₂ which is stable in H₂ by virtue of the positive free energy of the reaction $MO_2 + 2H_2 = M + 2H_2O$ may become easily reducible in the presence of atomic hydrogen because of the large negative free energy contributed by the reaction $2H = H_2$. Were the reaction $MO_2 + 4H = M + 2H_2O$ to occur in operation, the ceramic would suffer degradation of electrical properties by partial conversion to the metal and the plasma would become contaminated by water. A similar problem of chemical stability exists for graphite or carbide ceramics exposed to the plasma, where H-atom attack can produce methane.

The breeder is a fusion reactor component whose function is to absorb neutrons and produce tritium. This nuclear reaction is only possible with lithium so ceramics containing this element, such as Li₂O and LiAlO₂, must be used. The principal consideration in selecting ceramic breeder materials is retention of tritium and the form in which it is released. Strong retention is undesirable because the bred tritium needs to be continuously recycled as fuel into the plasma, not accumulated in the ceramic. The temperature at which release occurs affects the structural stability of the breeder and its containing

structures and the chemical form of the liberated tritium is important in design of subsequent processing to recover the fuel.

CURRENT RESEARCH ON NUCLEAR CERAMICS

High Temperature Vaporization

In off-normal or accident situations, components of nuclear power systems can be driven to very high temperatures, where, in addition to melting, vaporization may be important. In fast breeder reactors operating with the mixed U-Pu oxide fuel, knowledge of the vapor pressure is needed to determine the consequences of a severe accident(7). In a core melt accident in a light water reactor, the rate of production of aerosols is in part determined by vaporization of the UO_2 fuel. In both of these cases, temperatures up to 4000 K can be involved.

In fusion reactors, certain components are subject to intense radiation and particle fluxes. To prevent loss of structural integrity and plasma contamination by the evaporated vapor, refractory materials are used as protective armor(8).

To predict evaporation rates in the situations described above, the vapor pressure of the material must be known. Because of the high temperatures required and the lack of suitable containers, conventional techniques for vapor pressure measurement are not applicable. A promising alternative is rapid heating of just the surface of the material held in vacuum by a short (<1 ms) laser pulse. Temperatures during the heating transient are measured by a fast optical pyrometer and the vaporizing species is detected by a mass spectrometer directly viewing the irradiated surface. This technique has been applied to graphite by Lincoln and Covington(9) and to uranium dioxide by Tsai and Olander(10) and by Ohse et al.(11). The apparatus is shown in Fig. 1 and typical mass spectrometer time-response curves are given in Fig. 2. Excellent agreement between the measured and theoretical time-of-arrival curves of UO_2 following pulsing with a Nd-glass laser is seen. In these tests, the temperatures achieved in the transient were in the range where the vapor pressure is known, so the comparison demonstrates the accuracy of the method. The width of the curves is due to the Maxwell-Boltzmann distribution of velocities of the evaporated molecules and the magnitude of the curves is determined by the vapor pressure-temperature relationship of the solid which is employed in the Hertz-Langmuir formula relating the vaporization rate to the vapor pressure. The theoretical time-dependent number density of evaporated molecules in the mass spectrometer based upon the model described above is:

$$n(t) = \frac{\alpha A_s}{k} \left(\frac{m}{2\pi k} \right)^{3/2} \int_0^t \frac{P(T_s)}{T_s^{3/2} (t-\tau)} \exp \left[-\frac{mL^2}{2kT_s(t-\tau)^2} \right] d\tau$$

- where α = evaporation coefficient
 A_s = laser-irradiated area
 P = vapor pressure at surface temperature
 T_s = time-dependent surface temperature (measured)
 m = molecular mass
 k = Boltzmann's constant
 L = distance from surface to detector

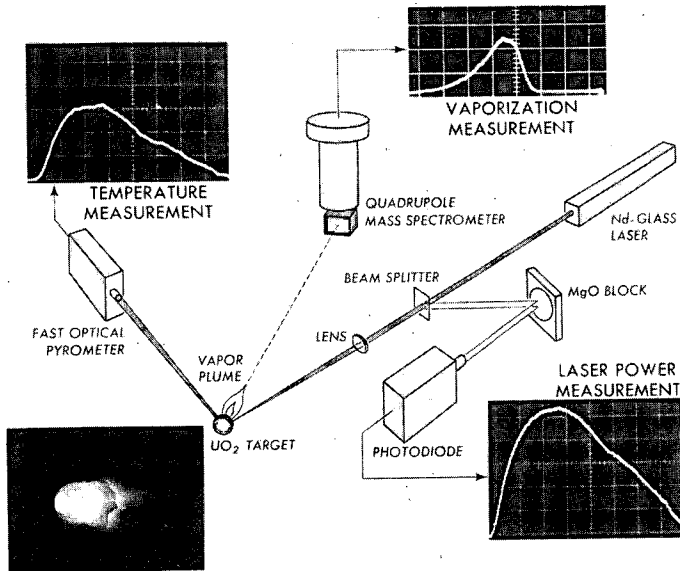


Fig. 1. Apparatus for studying high temperature vaporization of refractory ceramics by laser pulse heating.

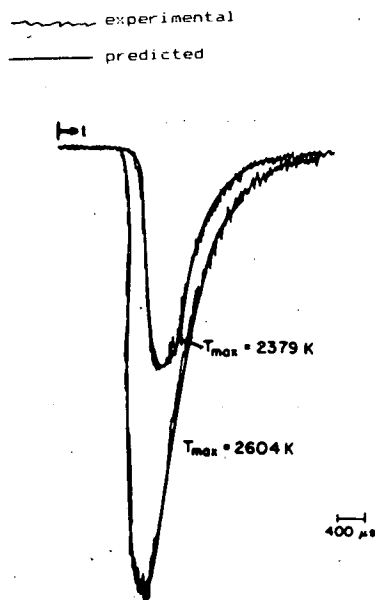


Fig. 2. Time-of-arrival signals for laser pulsing of UO_2 .

Diffusion in Uranium Dioxide

The in-reactor performance of oxide fuel depends upon the mobility of a variety of constituents along surfaces and grain boundaries, and in the lattice

Measurement of the diffusivities of the host ions in the heavy metal oxides is a long-standing problem which has recently been reviewed by Matzke(12). Tracer(self) and chemical diffusion coefficients of both oxygen and the cations (U^{4+} , Pu^{4+} , and Th^{4+}) have been measured as functions of temperature, O/M ratio and cation composition. The chemical diffusion coefficient of oxygen in these materials is nearly composition-independent and very much larger than cation diffusion. The latter is quite sensitive to the oxygen-to-metal ratio, achieving a minimum near exact stoichiometry.

In common with host ion diffusion, the mobility of the fission product xenon in UO_2 has been intensively studied for three decades, primarily because of the drastic effects that this noble gas has on the behavior of the fuel(4). The review of xenon diffusivity in UO_2 by Matzke(13) reveals that there still remains order-of-magnitude disagreement among investigations concerning the diffusion coefficient, which is apparently very sensitive to composition and microstructural details of the oxide. The atomic mechanism appears to be motion of a xenon atom as part of a complex consisting of two oxygen vacancies and one uranium vacancy. There is also sound evidence of irradiation-induced diffusion in UO_2 at low temperatures.

The accident at the Three Mile Island nuclear reactor in 1979 demonstrated the need to better understand the mobilities in UO_2 of fission products other than the rare gases. Tellurium, iodine and cesium are of special concern because of their volatility and biological hazard.

Fission product diffusion can be studied by in-reactor experiments, which are complex and expensive, or by simpler out-of-reactor experiments called postirradiation anneals. In the latter method, a specimen of oxide fuel material is subjected to a short irradiation in a research reactor to build up a quantity of fission products sufficient to measure by radiation detection devices. The specimen is then annealed in a furnace under a controlled oxygen potential for a specified time period at a constant temperature between $1000^{\circ}C$ and $2000^{\circ}C$. The anneal releases a fraction of the initial fission product content of the irradiated specimen. In the case of rare gases, the released fission product can be trapped (on refrigerated charcoal) and measured with a radiation detector in order to determine the diffusion coefficient.

This procedure cannot be easily applied to chemically reactive or low-volatility fission products. For these species, the gamma-ray spectrum of the specimen is measured before and after annealing, and the reduction in intensity of the gamma ray lines of particular fission product nuclides is used to deduce the fraction released and from this the diffusion coefficient. In results

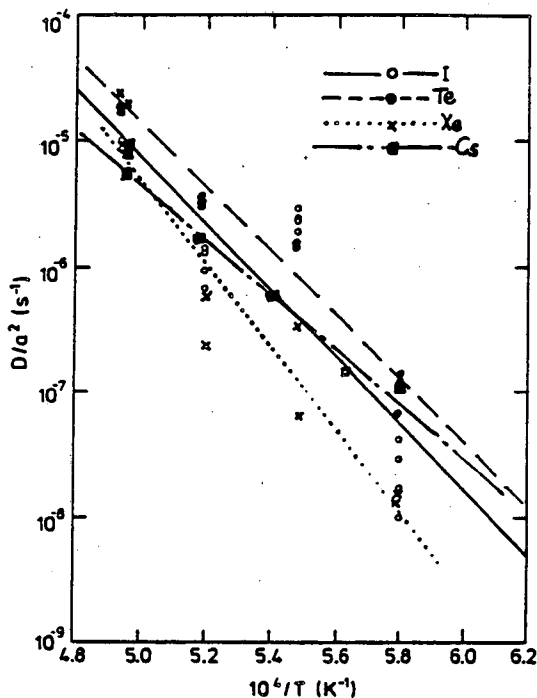


Fig. 3. Effective diffusion coefficients of volatile fission products in UO_2 measured by the postirradiation annealing method (Ref. 14).

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obtained to date with this method (Fig. 3), tellurium exhibits the largest diffusivity, nearly an order of magnitude larger than that of xenon at low temperatures.

It has long been observed that the mobility of fission products in polycrystalline UO_2 with a grain size of $\sim 10 \mu m$ is an order of magnitude or so larger than that in single crystal specimens. To account for this effect, Booth(15) proposed modeling the polycrystal as a collection of independent "equivalent" spheres of unknown radius. The release properties of the polycrystal are represented by simple diffusion from the spheres. What is measured by the experiment is an "effective" diffusion coefficient, which is the ratio of the true diffusion coefficient to the square of the radius of the equivalent sphere (this is the ordinate in Fig. 3).

While the Booth model is a convenient means of correlating data on fission product migration, it has no fundamental basis, and at least one untenable consequence. It predicts that the concentration distribution in a polycrystalline body following release should be spatially uniform, since all of the equivalent spheres are assumed to release the same quantity of gas whether they are near the surface or at the center of the specimen. Figure 4, which gives the distribution of iodine in a UO_2 slab from which 50% has been released, demonstrates that this consequence of the Booth model is incorrect.

To avoid the inconsistencies of the Booth picture, a model of combined grain

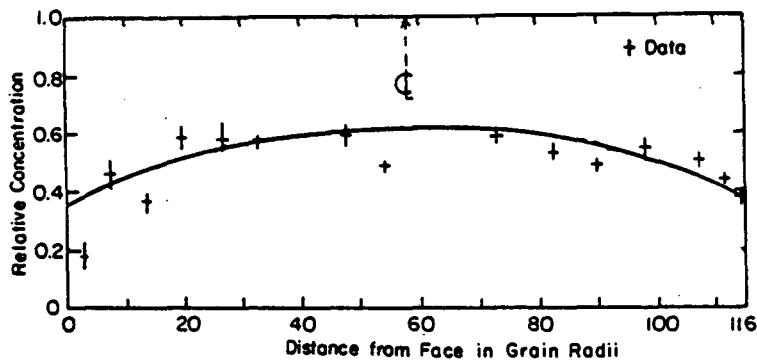


Fig. 4. Concentration distribution of radioiodine in trace-irradiated UO_2 following an 8 h anneal at $1650^{\circ}C$.

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boundary and volume diffusion in fine-grained polycrystalline bodies was developed(16). The model depicted in Fig. 5 treats two release paths from the interior: the first is by direct volume diffusion, ignoring the presence of grain boundaries (this is the only mechanism available in single crystals); the second is lattice diffusion from the grain interior to the grain boundaries, followed by migration in the latter to a free surface. The two physical properties controlling the release process are the diffusion coefficient in the lattice and the product of the grain boundary diffusivity and the solute segregation coefficient between the lattice and the grain boundaries. The relative importance of the two pathways depends on these transport properties and on the grain size. The curve in Fig. 4 represents the fit of this model to the iodine distribution data. The fitting process results in values of both the volume and the grain boundary diffusion coefficients and provides good agreement with the experimental points.

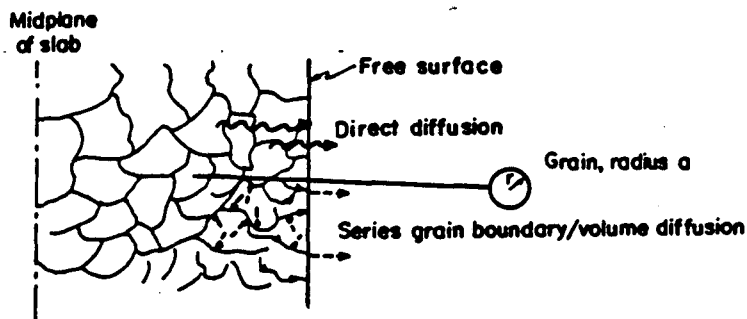


Fig. 5. Multigrain grain boundary/volume diffusion model.

The mobility of UO_2 on its own surface controls the rate of the important in-reactor process of fission gas bubble migration in the temperature gradient of an operating fuel element(4). This property has been measured by a tracer

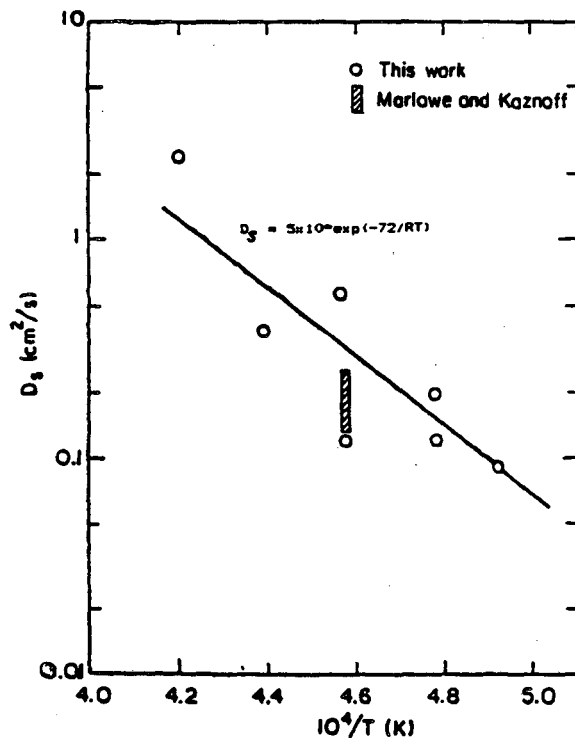


Fig. 6. Surface diffusion coefficient on UO_2 .

spreading experiment in which a wafer of $^{235}\text{UO}_2$ is bonded to a similar wafer of $^{238}\text{UO}_2$ by a layer of liquid uranium metal(17). After annealing, the radio-activity from ^{235}U decay measured on the surface of the $^{238}\text{UO}_2$ wafer is utilized to determine the surface diffusion coefficient. The results shown in Fig. 6 reveal an extraordinarily high surface mobility on UO_2 , which appears to behave as a two-dimensional ideal gas.

Interaction of Hydrogen with Oxides

Hydrogen interaction with ceramic nuclear oxides has many practical ramifications. As was discussed in the Introduction, the kinetics and release behavior of the tritium isotope of hydrogen from lithium oxides and the reduction of oxide insulators are important aspects of the functioning of fusion reactor components. In fission reactor technology, there is evidence that the H_2 product of zirconium oxidation by steam can decelerate the rate of corrosion during a core-damaging accident. Additionally, hydrogen reduction of UO_2 and $(\text{U,Pu})\text{O}_2$ is the principal step in the fabrication of fission reactor fuels.

Hydrogen can interact with ceramic oxides in two ways. In common with metals, ceramics can dissolve hydrogen, either in atomic or molecular form, and hydrogen migration through the ceramic is controlled by its diffusion coefficient. Figure 7 shows the two-part apparatus used to measure solubilities and release kinetics of hydrogen in oxide ceramics(18). In the vessel on the left, the specimen is saturated with hydrogen by long exposure at high pressure

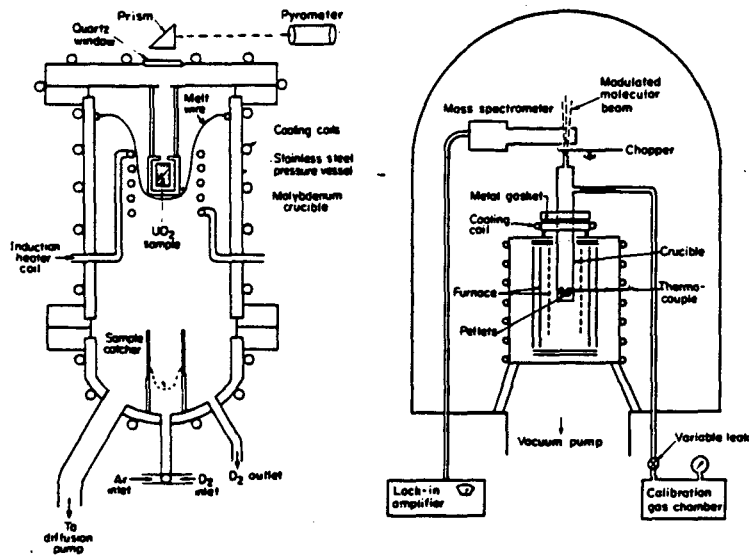


Fig. 7. Hydrogen solubility apparatus infusion furnace (left); vacuum outgassing furnace (right).

(to 30 bars) and high temperature (up to 1600°C). Provision is made for rapidly dropping the saturated sample from the hot zone in order to retain the infused hydrogen. The specimen is then transferred to the vacuum outgassing apparatus shown on the right of Fig. 7. Here the sample is subjected to a linear temperature ramp inside a molybdenum crucible and the released hydrogen detected in direct flight by a mass spectrometer situated just above the exit capillary. The efflux is modulated mechanically to permit detection by lock-in amplification, which greatly improves the signal-to-noise ratio. The technique can detect ~20 ng of hydrogen, or ~1 ppm atomic in an oxide specimen.

Figure 8 is an example of the desorption spectra of hydrogen emitted from UO₂ in a linear temperature ramp. The most remarkable feature of this result is the appearance of multiple peaks, which indicates that the interaction is not one of simple interstitial dissolution and release by ordinary diffusion; rather, hydrogen appears to be bound in a number of discrete trapping sites in the oxide, each of which has a distinct binding energy. The most likely trapping sites are dislocations, grain boundaries and pores. It is noteworthy

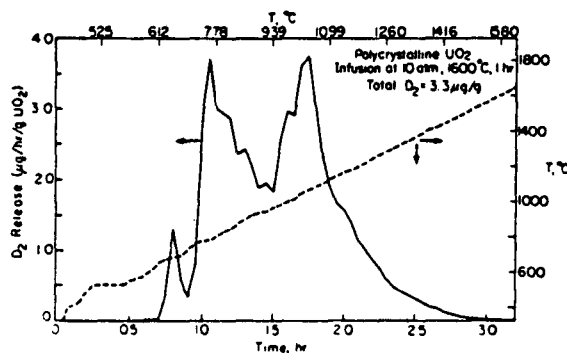


Fig. 8. Typical hydrogen desorption rate spectrum in a linear temperature ramp.

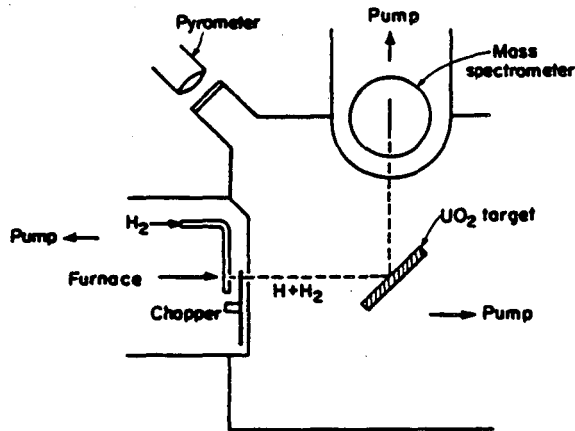
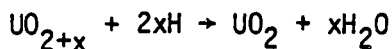


Fig. 9. Apparatus for studying the reactions of atomic hydrogen with ceramic oxides.

that sorbed hydrogen is released as H_2 and not in the form of water.

In addition to the predominantly physical interactions such as diffusion and trapping, hydrogen can alter the composition of oxides by reaction which removes oxygen and produces water. Although uranium dioxide of near exact stoichiometry is too stable to be chemically affected by hydrogen, the hyperstoichiometric oxide is readily reduced. This process is an important step in the fabrication of nuclear fuel elements.

The fundamental reactions and transport mechanisms during reduction of ceramic oxides by atomic hydrogen have been studied in the atomic beam apparatus shown in Fig. 9(19). Hydrogen gas is dissociated into the reactive atomic form (for reasons of detector sensitivity) in a tungsten oven and collimated into a thin beam which strikes the oxide surface in a small spot. The reaction



takes place on the surface in this spot and the scattered reactant atoms and desorbed product H_2O are detected by a mass spectrometer viewing the reaction spot. The measure of the extent of reaction is the reaction probability, defined as the rate of H_2O production divided by the rate of H atom impingement on the surface. When the oxide is near exact stoichiometry, the reaction probability increases rapidly with temperature and levels off at about $1300^\circ C$, indicating that the rate is limited by the supply of atomic hydrogen to the surface. The reaction rate is a strong function of initial oxide stoichiometry. For $UO_{2.036}$, for example, the reaction probability initially attained at $600^\circ C$ is the maximum possible value of 0.5. However, oxygen transport from the interior of the specimen to the reacting spot very quickly becomes the rate-limiting step. Shown in Fig. 10 is the temporal behavior of the reaction probability for a specimen with an initial O/U ratio of 2.015. The decrease in the reaction probability with time is due to the progressive depletion of oxygen in the solid near the reaction spot on the surface. This interpretation was confirmed by

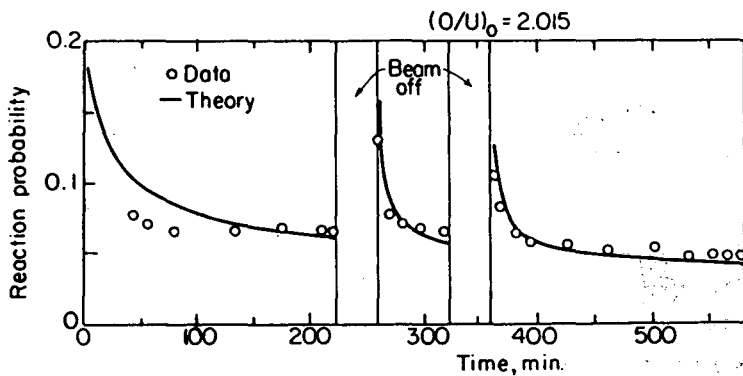


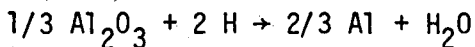
Fig. 10. Variation of the reaction probability of atomic hydrogen on hyperstoichiometric urania with time.

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shutting off the H-atom beam for 30 min. periods during the experiment. The reaction probability on restarting was significantly higher than just prior to shutting off the beam. This behavior is due to resupply of oxygen to the region around the beam spot by diffusional processes during the beam-off period. The curves in Fig. 10 are the results of a model which includes rate limitation due to surface reaction, bulk oxygen transport, and surface diffusion of oxygen(20).

In contrast to the very high reactivity of hyperstoichiometric urania towards atomic hydrogen, no reaction was detectable with stoichiometric UO_2 . The reason for this inertness is the thermodynamic instability of hypostoichiometric urania at temperatures below $1200^{\circ}C$. Although a powerful reducing agent, atomic hydrogen is incapable of reducing UO_2 to uranium metal.

However, it is possible to reduce alumina in atomic hydrogen. Because alumina cannot be rendered hypostoichiometric to any measurable extent, reduction by atomic hydrogen proceeds according to the reaction:



The results of a study of alumina reduction by atomic hydrogen in the apparatus of Fig. 9 confirm the existence of the products Al and H_2O of the above reaction at temperatures above $1300^{\circ}C$ at hydrogen atom impingement rates equivalent to pressures of this species of $\sim 10^{-4}$ Torr(19).

Several general conclusions can be drawn from the atomic hydrogen-ceramic oxide reactions studied to date. First, the reducibility (as measured by the reaction probability) in the highly nonequilibrium conditions of the atomic beam apparatus parallels the thermodynamic stability of the oxide indicated by its standard free energy of formation. Second, reduction of oxides in which deviations from stoichiometry are small proceeds slowly and by production of the metal and water vapor. Third, in easily reduced oxides, the rate of reduction is likely to be limited by oxygen transport in the solid as well as by reaction of the atomic hydrogen at the surface.

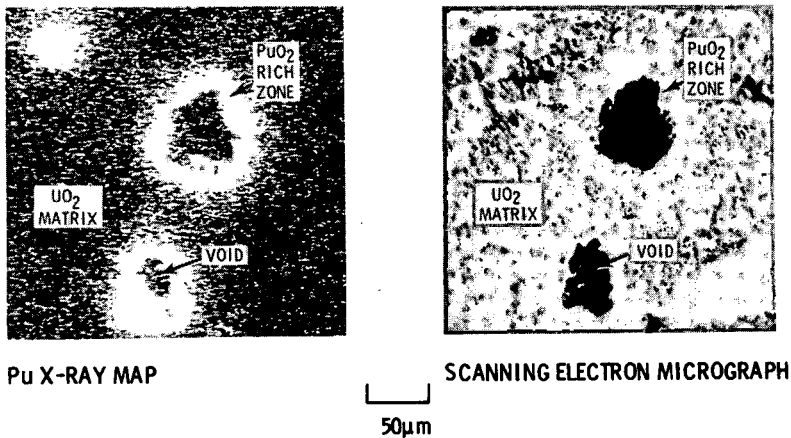


Fig. 11. Void formation and plutonium distribution in sintered mixed oxide fuel material (from Ref. 21).

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In contrast to UO_2 , the stoichiometric oxide PuO_2 is quite easily reduced to PuO_{2-x} because of the stability of the Pu(III) oxidation state, the analog of which in uranium is very unstable, if existent. The mixed oxide nuclear fuel for fast breeder reactors is prepared by blending the constituent oxide powders and sintering. The result is a microstructure comprised of a UO_2 matrix with PuO_2 present as small ($\sim 50 \mu m$) embedded particles. The oxygen-to-metal ratio of this material must be reduced to ~ 1.96 for use as a reactor fuel. Reduction is accomplished in an atmosphere of hydrogen gas at about $1700^\circ C$. Analysis of the resulting microstructure (Fig. 11) shows that the previously solid PuO_2 particles have developed sizeable cavities in their centers. This phenomenon suggests the reduction mechanism depicted in Fig. 12 (21). Hydrogen in UO_2 has a small (several ppm atomic) solubility and a high diffusion coefficient(22). Thus, H_2 permeates the UO_2 matrix without reaction, but upon reaching a plutonia particle, undergoes reaction to produce Pu^{3+} and water vapor. The latter, having negligible mobility or solubility in the ceramic oxide, is trapped, and forms high-pressure bubbles visible as the cavities surrounded by a rim of reduced plutonia. Recent work has revealed a very similar water-vapor-bubble-formation phenomenon due to oxidation of UO_2 which had previously been sintered in hydrogen(23).

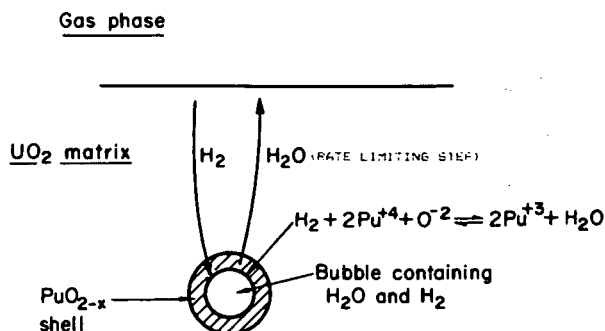


Fig. 12. Mechanism of the reduction of mixed uranium-plutonium oxides in hydrogen.

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