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COMPLEX DEFECTS IN THE OXIDATION OF URANIUM

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INTRODUCTION

The oxidation of uranium in oxygen, water vapor, and oxygen/water vapor mixtures has been studied extensively,^{1,2,3} but details of its kinetics and mechanism have not been completely elucidated. Thermogravimetric studies of the reaction pressure dependence^{3,4} suggested that oxygen vacancy rich clusters of the type $2(V_O^a O_i^b)$ control the oxidation of uranium in air with water vapor in the range of 6 to 17 kPa, and oxygen interstitial rich defects such as $2(O_i^a V_O^b)$ in air with lower water vapor pressures, pure oxygen, and pure water vapor. The existence of an oxygen interstitial rich complex $2(O_i^a V_O^b)$ for UO_{2+x} was first proposed by Willis⁵ based on his neutron diffraction work (2:2:2 model). Electrical conductivity measurements on UO_{2+x} and U_4O_9 by Matsui and Naito⁶ were interpreted using defect-cluster theory; a 2:2:2 interstitial cluster model was invoked to explain the oxygen-pressure dependence of the electrical conductivity for UO_{2+x} , and an oxygen vacancy rich model ($2V_O^a O_i^b$) for U_4O_9 . Allen et al.⁷ have recently shown that the x-ray photoelectron spectra of satellites of the $U4f$ peaks can be related to a 2:2:2 chain cluster in the oxygen sublattice (interstitial-rich complex). The linear ordering of oxygen clusters in hyperstoichiometric uranium dioxide has been discussed by Allen and Tempest⁸, and a coordinative model for the defect structure of UO_{2+x} and U_4O_9 has been proposed by Allen et al.⁹ A current summary of the work on the defect structure of UO_{2+x} can be found in a review of Colmenares.³ Even though the 2:2:2 cluster appears to be the most favored configuration of defects used to explain many experimental results, other configurations have also been suggested.¹⁰

The existence of well defined oxidation regimes and unique defect structures in uranium oxides was confirmed by Howell et al.¹¹ by positron lifetime

studies of oxidized uranium samples. Positron lifetimes of ~ 350 ps were associated with a vacancy rich defect state and lifetimes of ~ 400 ps with an interstitial rich defect. Confirmation of the existence of distinct defects, for the various oxidizing conditions defined in references 3 and 4, was obtained by Colmenares et al.¹² with electron paramagnetic resonance on the same type of samples used for positron annihilation spectroscopy (PAS).¹¹

We are reporting EPR results obtained with uranium powder samples fully oxidized in dry air, water vapor, and air/water vapor mixtures. The results reported previously¹² are confirmed and additional paramagnetic centers, associated with chemisorbed species, have been identified. The temperature dependence of the g-value for these centers from room temperature to 10K is also reported.

EXPERIMENTAL

Depleted uranium powder, consisting of spheres ~ 170 μm in diameter, was used for the EPR measurements. The total metallic impurities in uranium powder were ~ 900 ppm by weight, and the main impurities were magnesium and iron at a level of ~ 400 and ~ 300 ppm, respectively. The natural oxide on the uranium powder was removed by treatment with a 50-50 vol % solution of $\text{HNO}_3 + \text{H}_2\text{O}$. The clean powder was dried first with absolute ethanol and dry argon followed by overnight evacuation at room temperature. The powder temperature was then gradually increased to 100°C under vacuum ($\sim 10^{-9}$ Pa) over a period of 8 h to remove adsorbed water. Samples of this powder were oxidized in dry oxygen (< 5 ppm H_2O), oxygen-free water vapor, and mixtures of air/water vapor.

Clean uranium powder samples were oxidized completely in a thermogravimetric multispecimen "flow system" (N_2 or air carrier gas) described in a separate publication.¹³ Table 1 gives the oxidation conditions for the EPR samples. The purity of the gases used in the experiments were: research

grade oxygen (99.99 mole %) selected to have < 5 ppm H_2O ; high purity nitrogen selected to have < 4 ppm O_2 ; air containing typically 1-2 ppm H_2O .

The EPR cell used in this work consisted of a high purity silica tube (~ 25 cm long) attached to a metal-gasketed stainless steel fitting by a graded-glass seal, which in turn was fitted to an all-metal valve. This arrangement permitted the evacuation ($\sim 10^{-8}$ Pa) and outgassing of samples at temperatures up to 500°C . Oxidized samples were transferred from the oxidation apparatus into the EPR cells in an argon-filled glove box (~ 10 ppm H_2O and O_2). Thus, adsorbed and chemisorbed species from a given gaseous environment were preserved on the uranium oxide powder in the EPR cell ("as received" condition).

Magnetic resonance experiments were performed using a homodyne spectrometer operating in the x-band (~ 9.5 GHz) at ambient and low temperatures. These could be set $\pm 0.2\text{K}$ over the temperature range 10-300K.

The lattice parameter of the oxides produced was determined by powder x-ray diffraction techniques. The EPR spectra of these oxides were determined over a wide temperature range.

RESULTS AND DISCUSSION

The EPR spectrum of each oxide contained a substantial $g=2$ component, as expected. The spectrum of the sample grown with 13.3 kPa $\text{H}_2\text{O}(\text{v})$ in N_2 is shown in Fig. 1. The relative intensity of this $g=2$ resonance determined at 10K is shown plotted as a function of the lattice parameter a_0 in Fig. 2. As can be seen, the relation between the two shows that the $g=2$ line is related to the hyperstoichiometry of the system, i.e., either to the amount of U_4O_9 present and/or the concentration of the defects present in the UO_2 and/or U_4O_9 .

That the resonance arises from a possible ferrimagnetic phase associated with U_4O_9 may be ruled out on several grounds. First, the line position and width of ferrimagnetic resonance are dependent on the anisotropy constants

K and the external geometrical shape through the demagnetising factors. For random shaped particles, a reasonable assumption here, both effects will contribute to the line width and position. Usually, for ferrimagnetic resonance, significant shifts from $g=2$ occur with line widths of several hundred oersted. In this case, the position of the line in question, $g=2$, and its relatively narrow line width of 10 oersted is not in accord with ferrimagnetic resonance. Second, any ferrimagnetic resonance will show wild shifts in g -value as the Néel temperature is approached from below, with accompanying severe line broadening. Above the Néel temperature, the ferrimagnetic resonance disappears. The $g=2$ resonance here displays none of these features. Third, ferrimagnetic resonance is only weakly dependent on temperature. In our case, the line observed shows decreasing intensity with temperature from 10K to 300K; i.e., paramagnetic behavior. It is also unlikely that any Néel temperature associated with U_4O_9 is above 300K. Magnetic transitions in the urania system are observed at 30K in UO_2 , 5.9K in $UO_{2.1}$, U_4O_9 and U_3O_7 .^{14,15}

Intensity relations over a limited range such as shown in Fig. 2 cannot be used to determine in which phase the defect center is present. If present in UO_{2+x} , the intensity will pass through the hyperstoichiometric range as the volume fraction of UO_{2+x} decreases but the non-stoichiometry increases. The same is true for U_4O_9-y as we cross the hyper-stoichiometric range in the opposite direction.

Further, very careful quantitative studies of the oxygen pressure dependence of the defect concentration may indicate in which phase the defect centers are located. The independence of the resonance line width of the paramagnetic defect over the range of stoichiometry studied suggest that the defect concentration is "dilute", and therefore contained in non-stoichiometric UO_{2+x} . An analysis of the site symmetries in the two phases may also be useful in identifying the origin. At present, a paramagnetic 2:2:2 defect in UO_{2+x}

seems reasonable.

Depending upon the oxidizing conditions, the EPR spectrum of the urania is also characterized by a number of other broad resonances several hundred oersteds wide with g values between 2.0 and 3.6. A particularly rich spectrum is shown in Fig. 3. These broad resonances could also be introduced by exposing the urania oxidized in dry air to $H_2O(v)$, and also to $H_2O(v)+O_2$, at room temperature. We describe below our efforts to identify the magnetic species responsible.

Fig. 4a shows the EPR spectrum of specimen oxidized in pure air. Fig. 4b shows the EPR spectrum after the specimen was exposed to 4.3 KPa $H_2O(v)$ at room temperature, and Fig. 4c that of a similar sample exposed, also at room temperature, to 101 KPa O_2 and 4.3 KPa $H_2O(v)$ simultaneously. The very broad resonance with an average g , $\langle g \rangle$, of ~ 2.6 appears after exposure to $H_2O(v)$ and to O_2 and $H_2O(v)$ simultaneously. The species responsible for this resonance can be almost completely removed by heating at $500^\circ C$ under a pressure of 10^{-5} Pa.

An attractive explanation of the above EPR data is through reactions of the type $H_2O + O^{2-}$ (lattice or interstitial)

We suggest at this time that the broad $\langle g \rangle = 2.6$ resonances shown in Figs. 4b and 4c are the O^- species present on the surface of the urania. To some extent this suggestion is based on our work on alumina and the similarities of the observed behavior of this material when plasma sprayed into water. (Plasma spraying is a process in which small particles are exposed to a very high temperature $\sim 10^6^\circ C$ plasma for a very short time, $\sim 10^{-5}$ sec, before being ejected at supersonic velocities onto a substrate or as, in this case, into water. The small particles melt, but do not vaporize completely, so that metastable phases and novel chemistry may be realized).

First, let us consider the UO_2 exposed to an $\text{O}_2\text{-H}_2\text{O}$ atmosphere. The $\langle g \rangle$ value of the resonance in Fig. 4 is a marked function of temperature, where the resonance field is observed to decrease with decreasing temperature. The temperature variation of g determined from such measurements is shown in Fig. 5. As far as we are aware, this resonance has not been previously observed.

Let us now consider the EPR of alumina particles that have been plasma sprayed into water. A representative EPR spectrum of alumina particles prepared this way is shown in Fig. 6, while the temperature dependence of the g value is shown in Fig. 7. The g value observed in urania, as well as the temperature dependence is very similar to that observed for alumina powder which has been plasma sprayed into water.

The similarity between the $\langle g \rangle = 2.6$ resonance of the urania exposed to water and oxygen is so similar to that of alumina exposed (at very high temperature) to water and oxygen that we suggest they are in fact of the same origin, namely an exchange coupled magnetic system of 0^- moments on the surface. (In the case of the alumina, Al^{+2} or Al^{+4} ions are unlikely, and bulk oxygen vacancies would not show a temperature dependent g -value; moreover the value of g would be close to 2.00).

For a strongly coupled system, the resonance condition can be written as (Morrish¹⁶):

$$\omega^2 = \gamma^2 H(H + KM) \quad (1)$$

where ω is the angular velocity ($\omega = 2\pi f$, f being the frequency), γ is the gyromagnetic ratio, H is the magnetic field, M is the magnetisation per unit area and K is a "catch all" parameter involving demagnetising fields and anisotropy constants. For small K , this equation reduces to:

$$H_{\text{res}} = \frac{\omega}{\gamma} - \frac{KM}{2} \left[1 - \frac{KM}{4\omega} \right] \quad (2)$$

where H_{res} is the applied field at which resonance condition (1) is satisfied.

Casting this equation into the form:

$$h\nu = g_{obs} \beta H_{res} \quad (3)$$

where g_{obs} is the splitting factor, g_{obs} can be calculated from (2) and (3) as

$$g_{obs} = g \left[1 + \frac{KM_T}{2\omega} \left(1 - \frac{KM_T}{4\omega} \right) \right] \quad (4)$$

where g is the free electron splitting factor with a value of 2.00.

This expression shows that, in this case the observed g values are greater than 2.0; alternatively that the resonance occurs at lower magnetic fields compared to those required for spin-only resonance. Interpreted this way, the increase in the splitting factor, g_{obs} , with decreasing temperature below about 70K comes about from the supposed increase in the resultant magnetization that occurs with decreasing temperature. Moreover, the inferred temperature dependence of $M(T)$ below the Néel temperature is in qualitative agreement with that expected from a magnetically ordered system, e.g., a simple ferrite. Above 80K, i.e., above the supposed Néel temperature, a severely dipole-dipole broadened EPR line is expected with the splitting factor equal to the average of the constituent magnetic species. For urania, the g value of the resonance is about 2.3 at the highest temperature that it can be observed, 80K. For plasma sprayed alumina, the high temperature g -values are indicated by arrows, namely ≈ 2.25 . Similar g -values have been observed for O_2^- and O^- adsorbed on oxide surfaces, Lunsford¹⁷.

CONCLUSION

EPR has revealed a well defined paramagnetic defect center in hyperstoichiometric UO_{2+x}/U_4O_9-y . It is found that the number of these defects increase with x and the evidence favors a center associated with the 2:2:2 defect of Willis.

The surface of UO_2 has been shown to be highly reactive with water. The most likely reaction is the hydrolysis of water to form O^- (or O_2^-) chemisorbed on the surface and H_2 . The magnetic resonance data can be explained on

this basis only by assuming a strong coupling between these ions. This implies that the density on the surface of the paramagnetic species is very large with almost complete coverage.

Further work is in progress to characterize and understand this system more completely.

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Table 1. Oxidation conditions for uranium powder

Oxidant (gas flow = 1 L/min; Total P = 101 kPa)	Temperature °C	Time to complete oxidation, n
Dry air	180	196
13.3 kPa H ₂ O (v) in N ₂	100	170
13.3 kPa H ₂ O (v) in air	100	742

Figure Captions

- Fig. 1 EPR spectrum at 10K showing $g=2$ resonance for the urania produced by oxidizing uranium in 13.3 kPa $H_2O(v)$ at $100^\circ C$.
- Fig. 2 Dependence of $g=2$ resonance intensity on lattice parameter of the urania.
- Fig. 3 EPR spectrum at 40K of urania obtained by oxidizing uranium with 13.3 kPa $H_2O(v)$ in air at $100^\circ C$.
- Fig. 4 EPR spectrum of sample produced by oxidation in dry air.
(a) as oxidized
(b) exposed to 4.3 kPa $H_2O(v)$ at room temperature
(c) exposed to 4.3 kPa $H_2O(v)$ +101 kPa O_2 at room temperature.
- Fig. 5 Temperature dependence of the g -value of resonance shown in Fig. 4.
- Fig. 6 EPR spectrum of plasma sprayed alumina at 60K.
- Fig. 7 Temperature dependence of the g -value of resonance shown in Fig. 6, (top) as sprayed (bottom) treated with dimethylantracene (DMAN).

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Fig. 1

Fig. 2

Fig. 3

Fig. 4a

Fig. 4b

Fig. 4c

Fig. 5

Fig. 6

Fig. 7