

REDUCTION OF TRANSITION METAL OXIDES IN
A HYDROGEN PLASMA

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The possibility of using plasmas for the direct reduction of oxides of valuable metals holds considerable interest. In the present work "active hydrogen", produced in a "Large Volume Microwave Plasma Generator" (LMP)⁽¹⁾ has been used to study the reactions of several transition metal oxides including Nb_2O_5 , V_2O_5 , TiO_2 , and ZrO_2 . In earlier work of this type McTaggart⁽²⁾ had observed the formation of surface layers of protonated "golden oxides", or of lower oxides. However, numerous questions remained open including, in several instances, the exact compositions of the reaction products and the degree of conversion.

In this work, several analytical techniques including X-ray diffraction and differential thermal analysis have been used, but Auger electron spectroscopy, combined with ion etching, and scanning electron microscopy have proven most valuable in providing answers to some of these questions.

The most detailed data presently available pertain to the reduction of Nb_2O_5 , but these results appear to typify reactions of several other oxides: When white α - Nb_2O_5 powder is exposed to the "active hydrogen", a gray-black, electrically conducting product is formed. It is found that only a thin (few tenths of a micro-meter) layer adjacent to the surface is reduced to NbO_x ($1.8 \leq x \leq 2$), the remaining Nb_2O_5 remaining unaffected.

(1) R.G. Bosisio, M.R. Wertheimer and C.F. Weissfloch, J. Phys. E 6, 628 (1973).

(2) F.K. McTaggart, Nature 199, 339 (1963).

REDUCTION OF TRANSITION METAL OXIDES IN

A "COLD" HYDROGEN PLASMA

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The possibility of using plasmas for the direct reduction of oxides of valuable metals holds considerable interest. In the present work "active hydrogen" produced in a microwave discharge has been used to study the reactions of several transition metal oxides including Nb_2O_5 , V_2O_5 , and TiO_2 . In earlier work of this type McTaggart⁽¹⁾ had observed the formation of surface layers of lower oxides or of protonated "golden oxides". However, numerous questions remained open including, in several instances, the exact compositions of the reaction products and the degree of conversion.

In this work, several analytical techniques including X-ray diffraction and electron microprobe analysis have been used, but Auger electron spectroscopy, combined with inert gas ion sputter etching, and scanning electron microscopy have proven most valuable in providing answers to these questions.

The products of reaction between the above-named oxides and "active hydrogen" were found to be NbO_2 , $\text{VO}_{1.75}$ and Ti_3O_5 , respectively, the reduction taking place in a thin ($\sim \mu\text{m}$) surface layer.

(1) F.K. McTaggart, Nature 199, 339 (1963).

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1. INTRODUCTION

The possibility of using plasmas for the direct reduction of oxides of valuable metals holds much interest, and considerable effort has been devoted to this field in recent years⁽¹⁻³⁾. Among the studies reported in the literature one can distinguish between those using high-temperature plasma jets on the one hand⁽³⁾, and "cold" thermodynamically nonequilibrium plasmas on the other^(1,2). The latter are generally produced by high frequency electrodeless discharges at low pressures⁽¹⁾.

Among the oxides for which reduction in hydrogen (or hydrogen-containing) plasmas have been attempted are WO_3 , FeO , Ta_2O_5 , Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , HfO_2 , ThO_2 , CeO_2 , MoO_3 , Nb_2O_5 and V_2O_5 . Whereas complete reductions to the elemental metals have been achieved for the first five oxides in the above list, lower oxides or protonated "golden oxides" were obtained for the others: Using a microwave (2.45 GHz) discharge in hydrogen, McTaggart⁽²⁾ obtained "black electrically conducting lower oxides of metallic appearance" in the case of Nb_2O_5 , V_2O_5 and Ta_2O_5 , whereas for TiO_2 he found a hydrogen-containing compound ($\text{H}_{0.2}\text{Ti}_{1.00}\text{O}_{1.3}$) also displaying metal-like electrical properties. It is interesting to note McTaggart's observation that "active hydrogen" produced in lower frequency discharges was not always as effective as that generated in a microwave discharge.

At the time of the above mentioned studies many of today's advanced analytical techniques (in particular, those used for surface analyses) were not yet available, so that definitive characterizations of the reaction products could not be carried out. In the present work we have reexamined this question, and have used a variety of modern analytical techniques to study the reaction products resulting from exposure of Nb_2O_5 , V_2O_5 and TiO_2 to "active hydrogen" from a microwave discharge.

2. EXPERIMENTAL PROCEDURE

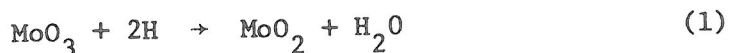
High purity (99.9% +) powders of the starting materials (Nb_2O_5 : white, British Drug Houses; V_2O_5 : mustard yellow, TiO_2 : white, A.D. MacKay Inc.) were used throughout this study.

Two types of sample preparations were used for plasma treatment experiments :

- (i) As-received powder samples (approximately 5 g quantities).
- (ii) Wafers produced by compression molding the powder at 20 000 psi and ambient temperature.

Plasma treatments were conducted in an LMP (large volume microwave plasma generator) apparatus. This apparatus, described in detail elsewhere⁽⁴⁾, consists of a 2.45 GHz microwave source which can supply up to 2.5 kW of power to a 90 cm long strapped bar slow wave applicator. The plasma is generated in a 15 mm diam. quartz reactor tube adjacent to the microwave applicator; samples were placed in an enlarged section at the exit of this reactor tube where the concentration of active hydrogen species is presumably highest.

A flow of ~ 0.5 l (STP)/min. of commercial grade hydrogen gas at approximately 1 torr (~ 133 Pa) was partly dissociated by 1500 W of applied microwave power. A sample of yellowish MoO_3 turned blue according to the reaction⁽¹⁾



indicating the presence of substantial concentrations of atomic hydrogen in the discharge.

As also observed by McTaggart, the other oxide samples rapidly changed color when exposed to the flow of active hydrogen, acquiring a black, metallic aspect after a few tens of seconds at most. Plasma treatment was usually carried out for 5-10 min., much longer than the duration required for complete blackening of the surface. The purpose of this was to ensure saturation conditions for any chemical changes taking place.

Although no attempts have been made to measure the temperature of the powder during plasma treatment, a substantial temperature rise (possibly up

to several hundred °C) occurred during treatment. This was manifested by localized melting in the case of the V_2O_5 sample, and is due firstly to surface recombination of hydrogen atoms⁽⁵⁾ and, presumably to a lesser extent, due to dielectric heating of the lossy oxides in the microwave field.

In our earliest experiments⁽⁶⁾ the reaction product of the Nb_2O_5 /"active hydrogen" reaction was examined by Debye Scherrer X-ray diffraction, and by electron microprobe analysis; since these analyses revealed only the presence of Nb_2O_5 , it was concluded that the black reaction product must form a surface layer which is substantially thinner than the micron-thick region sampled by these techniques. Subsequent analytical work therefore was based exclusively on Auger Electron Spectroscopy (AES), coupled with Scanning Electron Microscopy (SEM).

2.1 Auger Electron Spectroscopy.

AES is ideally suited for this situation since, unlike the X-ray and electron microprobe techniques, a very thin ($\leq 20 \text{ \AA}$) layer is probed. Furthermore, the Auger method is very sensitive to low-atomic-number elements which are characterized by sharp transitions and high Auger electron yield.

Once a surface has been analysed, inert gas ion sputter etching may be used to expose deeper layers of the sample, and by a sequence of such analysis/etching steps one may obtain complete composition profiles for a given sample material. In the present apparatus (Varian) etching was carried out at a total pressure of $4-5 \times 10^{-5}$ torr (6.7×10^{-3} Pa) using a 1-keV argon ion beam having a current density of about $80 \mu\text{A cm}^{-2}$ in the case of Nb_2O_5 , and $400 \mu\text{A cm}^{-2}$ in the other cases. The etch rate R (\AA min^{-1}) may be calculated if one knows the sputtering yield S (atoms per incident ion). For the present oxide systems we estimate

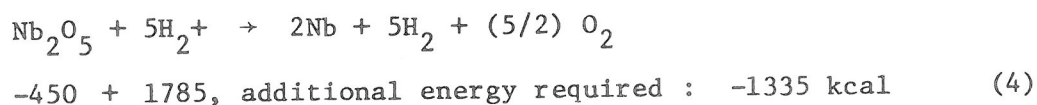
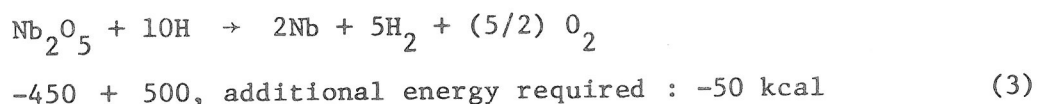
$$\begin{aligned} 30 \leq R \leq 90 & \text{ (Nb oxides)} \\ 100 \leq R \leq 400 & \text{ (Ti, V oxides)} \end{aligned} \quad (2)$$

It should be emphasized that all our Auger work was carried out using low incident electron beam currents (1-10 μA) so as to minimize the possibility of sample surface modification which has variously been reported in the literature.

3. EXPERIMENTAL RESULTS

3.1 Nb₂O₅

According to McTaggart⁽²⁾ hydrogen atoms and H₂⁺ ions are the species in "active hydrogen" most likely to participate significantly in the reduction of metal oxides, and in a reaction of this kind the gaseous reaction products are hydrogen and oxygen rather than water. On the basis of this information we can examine the relationships :



The energy referred to in (3) and (4) is the heat of formation at STP, based on the formation of 2 moles of Nb.

These relationships indicate that the direct reduction of Nb₂O₅ to Nb metal (and certainly to lower oxides) is thermodynamically possible.

Figures 1(a) and (b) show typical scanning electron micrographs of a Nb₂O₅ powder sample, and of a compacted sample, respectively, both untreated. We note that the powder particles consist of agglomerates of needlelike crystallites which are typically of the order of a few tens of micrometers long and 5 μm or less in diameter. During compression molding, many of the crystallites are broken down into smaller fragments, at least near the surface, these fragments being typically 1 μm or less in diameter, although some of them tend to remain intact. Plasma treatment did not modify the structural appearance significantly.

Figure 2(a) shows the surface Auger spectrum of a plasma treated compacted sample; figure 2(b) represents the same sample after 90 minutes of sputter etching, that is, at a depth of approximately 3000 Å from the original surface.

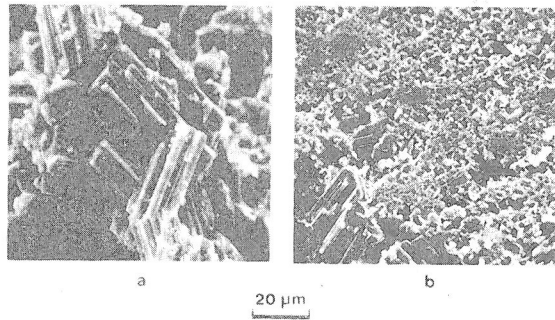
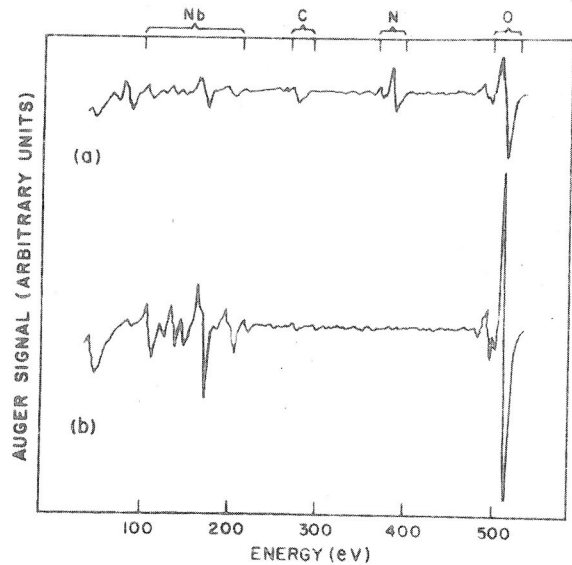


Fig. 1. Scanning electron micrographs of (a) virgin Nb_2O_5 powder, and (b) a typical section of a compacted, untreated sample.

Fig. 2. Auger electron spectra excited by 8-keV primary electron beam. The location of lines identifies the presence of elements indicated at the top. (a) Surface spectrum of plasma treated compacted sample. (b) Same sample after 90 min. of sputter etching.



As described elsewhere⁽⁶⁾ we have used the ratio

$$r_{\text{Nb}} \equiv \frac{h(0503)}{h(\text{Nb}_{166})} \quad (5)$$

in order to obtain composition profiles, where $h(0503)$ and $h(\text{Nb}_{166})$ are the peak-to-peak heights of the main Auger lines for oxygen (at 503 eV) and for niobium (at 166 eV), respectively.

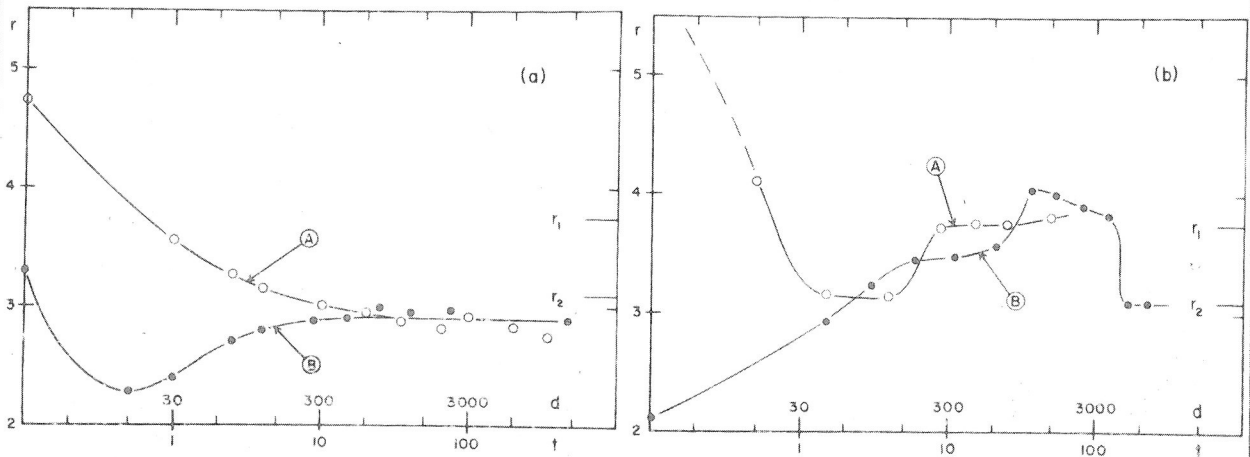


Fig. 3. Composition profiles ($r \equiv h(0503)/h(\text{Nb}_{166})$, see text; t is in minutes, d in Angstroms). Plasma treated, compacted sample; four different locations on the sample surface.

Figures 3(a) and (b) show composition profiles for four different locations on a plasma treated compacted powder sample, illustrating the different types of effects observed. r_1 and r_2 are values of r_{Nb} obtained for standard samples of known stoichiometries :

$$\begin{aligned} r_1 &\equiv r(Nb_2O_5) = 3.75 \\ r_2 &\equiv r(NbO_2) = 3.10 \end{aligned} \quad (6)$$

The abscissa represents the duration of sputter etching t or, using relationship (2), the depth of the layer analysed, d .

3.2 TiO_2 and V_2O_5

On the basis of thermodynamic relationships similar to (3) and (4), the reduction of TiO_2 to Ti metal by H atoms is not possible; a partial reduction to any of the lower oxides TiO , Ti_2O_3 , Ti_3O_5 , Ti_4O_7 , Ti_5O_9 , however, would be possible. We have used a series of samples of these compositions to obtain the "calibration curve" of Auger peak heights, figure 4(a), in which $r_{Ti} \equiv h(O_{503})/h(Ti_{417})$ is plotted against α_{Ti} , the O/Ti atomic ratio.

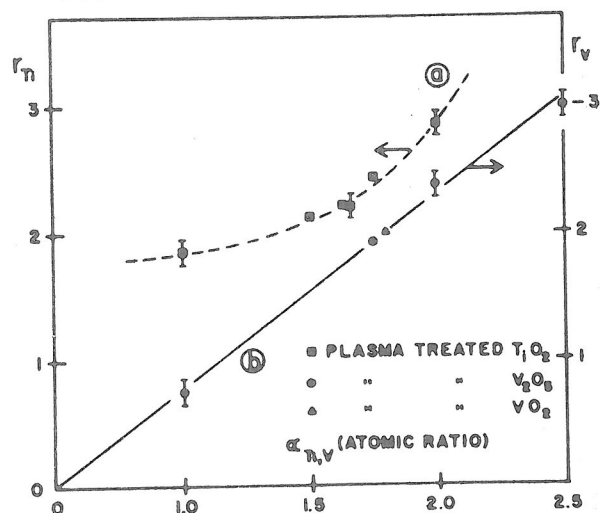


Fig. 4. "Calibration curves" of Auger peak height ratios r_{Ti} , r_V versus α , the atomic ratio. (a) TiO_α , (b) VO_α . Open symbols : standard samples of known α ; full symbols : plasma-treated samples.

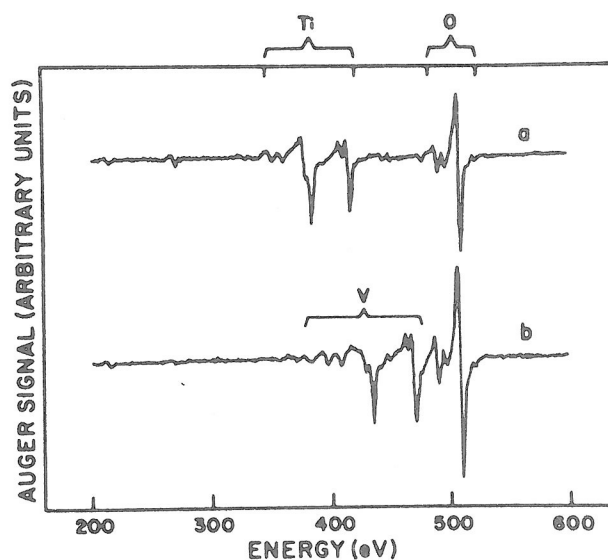


Fig. 5. Auger electron spectra of plasma treated, compacted samples after 5000 sec sputter etch. (a) " TiO_2 ", (b) " V_2O_5 ".

Figure 4(b), where $r_V \equiv h(0503)/h(V470)$ is plotted versus α_V , the O/V atomic ratio, has been obtained from a series of vanadium oxide samples of known stoichiometries. It is interesting to note a linear relationship in the latter case, whereas the r_{Ti} versus α_{Ti} relationship is quite nonlinear.

Figures 5(a) and (b) respectively show Auger spectra of plasma-treated compacted TiO_2 and V_2O_5 samples which had been sputter etched for 5000 seconds ($d \sim 1.3 \mu m$). We find $r_{Ti} = 2.22$ and $r_V = 1.88$, and from figure 4 we note that these values correspond to Ti_3O_5 and $VO_{1.75}$ stoichiometries, respectively (full symbols). $VO_{1.75}$ is also obtained from the reduction of VO_2 (see figure 4(b)).

4. DISCUSSION

For the sake of brevity, only the most salient results of section 3 can be discussed here; the case of Nb_2O_5 has already been elaborated in some detail in reference 6.

It appears certain that complete reductions to the elemental metals do not take place for Nb_2O_5 , V_2O_5 and TiO_2 in a "cold" hydrogen plasma, although such reactions would appear to be thermodynamically feasible. Instead, lower oxides NbO_2 , $VO_{1.75}$ and Ti_3O_5 are obtained, respectively, but only a thin surface layer is reduced. The Auger micro-analysis technique employed is therefore particularly appropriate under the present conditions. In view of the strong tendency of these metals and some of their lower oxides to oxidize to more stable forms⁽⁷⁾ one should, however, not exclude the possibility that the present reaction conditions may lead to unstable products which subsequently oxidize to the observed stoichiometries upon exposure to the atmosphere.

Composition profiles of varying shapes have been shown for the case of Nb_2O_5 (figure 3) : the profile may either be smooth down to a depth of several thousand angstroms (e.g. figure 3(a)) or it may fluctuate between two "allowed" stoichiometries, as noted in figure 3(b). These variations are almost certainly governed by the microstructure of the sample region being analysed, the former corresponding to a coarse crystallite and the latter to fine-grained powder as seen in figures 1(a) and (b), respectively.

As implied by equations (3) and (4), the "active hydrogen" species in a microwave discharge most likely to be responsible for the present reduction reactions are primarily ground-state atomic hydrogen⁽⁸⁾, to a lesser extent H_2^+ ions, and possibly even electronically or vibrationally excited H_2^* . The observed products, and the reduction to only a shallow depth are, however, not likely to help identify the dominating species or the precise reaction mechanisms: Heterogeneous reactions of dissociated gases and refractory materials, recently reviewed by Rosner and Allendorf⁽⁸⁾, form a complex field of study which, in turn, is further complicated by elevated substrate temperatures⁽⁹⁾.

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