



The properties of surface oxidation of zirconium by auger electron spectroscopy and secondary ion mass spectroscopy  
by Tair-ji Lee

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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**Abstract:**

Zirconium dioxide is one of the most active isosynthesis catalysts. It has also found application as a construction material for nuclear reactors and high temperature devices.

To develop an improved understanding of the surface oxidation of zirconium, the adsorption of oxygen on polycrystalline zirconium under ultra high vacuum has been studied using Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectroscopy (SIMS). AES measurements have been conducted for zirconium samples with different extents of oxygen exposure over temperatures between 300 K to 673 K. Auger spectra were also recorded for Zr surfaces with the same extents of oxygen exposure but accomplished under different oxygen pressures and exposure times. The process of sputtering an initially 60 L O<sub>2</sub>-exposed Zr sample was studied employing SIMS. AES spectra were recorded at sequential interruptions during sputtering.

Oxygen adsorption seems to follow the reaction sequence of first chemisorption, next rapid oxide nucleation, and finally slow oxide thickening. Diffusion of oxygen onto the bulk of zirconium is negligible at temperatures below 470 K and becomes significant at temperatures between 470 K and 673 K. Oxygen uptake was found to primarily depend on O<sub>2</sub> exposure level and slightly on O<sub>2</sub> exposure pressure (or exposure time). Secondary ion yield of the ZrO<sup>+</sup> SIMS signal is closely related to the oxidation state of the Zr surface.

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APPROVAL  
of a thesis submitted by  
Tair-ji Lee

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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## ABSTRACT

Zirconium dioxide is one of the most active isosynthesis catalysts. It has also found application as a construction material for nuclear reactors and high temperature devices.

To develop an improved understanding of the surface oxidation of zirconium, the adsorption of oxygen on polycrystalline zirconium under ultra high vacuum has been studied using Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectroscopy (SIMS). AES measurements have been conducted for zirconium samples with different extents of oxygen exposure over temperatures between 300 K to 673 K. Auger spectra were also recorded for Zr surfaces with the same extents of oxygen exposure but accomplished under different oxygen pressures and exposure times. The process of sputtering an initially 60 L O<sub>2</sub>-exposed Zr sample was studied employing SIMS. AES spectra were recorded at sequential interruptions during sputtering.

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## INTRODUCTION

Heterogeneous catalysis plays a role of vital importance in a wealth of chemical manufacturing processes. Nevertheless, there still exists quite a bit of uncoordinated information relating to catalysis. Hence, understanding the mechanisms of heterogeneously catalyzed reactions and how catalytic activity relates to properties of the catalyst surface has always been of primary concern to scientific investigators and practicing technologists who want to develop and improve catalysts. During the last decade, the advent of new surface-sensitive analysis techniques has provided improved tools for researchers to execute microscopic investigations of the structure and reactions on the uppermost surface layers of catalytic systems. The application of these surface-sensitive analysis techniques to the studies of the surface of solid catalysts and reactions catalyzed by solids has greatly enhanced the knowledge of the processes occurring at solid/gas interfaces.

Zirconium dioxide ( $ZrO_2$ ) is known to exhibit active catalytic behavior in dehydrogenation, hydrogenation and hydrogen exchange reactions [1]. Studies of the catalytic

chemistry of zirconium dioxide, however, have proceeded mainly on bulk zirconium dioxide [2]. No major studies have been performed on surface oxide formed on zirconium foil. The oxide layer has been shown to have  $ZrO_2$  stoichiometry [3] and to have an activity for the adsorption and exchange of hydrogen and oxygen similar to that of bulk  $ZrO_2$  [4].

The objective of the present study is to develop an improved understanding of the surface oxidation of zirconium utilizing two widely used surface-sensitive analysis techniques, Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectroscopy (SIMS). Auger spectra at different oxygen exposure levels are investigated at room temperature and at several temperatures above room temperature. SIMS and AES are utilized to investigate the chemical state and surface structure of the oxidized Zr. This spectral information is used to identify the effects of temperature and extent of oxygen exposure on the nature of the surface oxide formed. They also provide a basis for identifying the oxidation state of Zr on an oxygen exposed Zr sample.

## BACKGROUND

Zirconium

Bulk zirconium (atomic number 40) is a silver-grey metal similar to steel in appearance. It is an element of the titanium subgroup IV of the periodic system. Natural zirconium consists of five stable isotopes,  $Zr^{90}$  (51.46%),  $Zr^{91}$  (11.23 %),  $Zr^{92}$  (17.11%),  $Zr^{94}$  (17.4%) and  $Zr^{96}$  (2.8%) and it ranks twelfth among the elements in terrestrial abundance. The pure metal exists in two allotropic modifications. The low temperature  $\alpha$ -zirconium exhibits a hexagonal-close-packed (h.c.p.) structure and the high temperature  $\beta$ -zirconium has body-centered-cubic (b.c.c.) structure. The  $\alpha$ - $\beta$  transition temperature is 1135 K ( $\pm 5$  K) [4]. The electronic configuration of zirconium is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^2 5s^2$  (or  $[Kr]4d^2 5s^2$ ). The energy levels of the electrons in zirconium are shown in (a) of Figure 1 with X-ray designation of each energy level [5].

Zirconium reacts readily with oxygen-containing compounds (e.g.  $H_2O$ ,  $CO$ ,  $CO_2$ , ...) to form a cohesive surface oxide film. This thin oxide film protects the surface of bulk zirconium from further oxidation at room



temperature [4].

Zirconium and its alloys show a great affinity for absorbing and/or adsorbing most gases at elevated temperatures, even at very low pressures. This property has led to the use of zirconium as a so called "bulk getter material" in high-vacuum technology. In this respect, zirconium resembles titanium [6] which has been thoroughly studied.

Since zirconium and its alloys have small neutron capture cross sections, outstanding anti-corrosion and mechanical properties, they are widely used as construction materials for nuclear reactors. Thus, there have been many studies of the oxidation of zirconium and its alloys. Most of these studies have been concerned with thick oxide films formed at high temperatures [7]. It has generally been observed that the oxidation of zirconium at high temperature is a process of simultaneous bulk oxygen absorption and oxide film formation [8].

At low concentrations, oxygen dissolves in zirconium, occupying lattice interstices instead of forming stoichiometric oxide compounds. In the h.c.p. Zr lattice, the dissolved atoms may occupy two types of interstitial sites: those which have octahedral symmetry and those which have tetrahedral symmetry. Between the two possible interstitial sites, the dissolved oxygen atoms in zirconium lattices are primarily located in the larger octahedral

sites. The occupation can be up to about 60% of the octahedral sites in an h.c.p. zirconium lattice or up to a concentration of 29 atomic percent oxygen, as indicated by the X-ray diffraction pattern on a zirconium-oxygen system [9].

Experimental results suggest that the absorption of oxygen in bulk zirconium primarily follows a grain-boundary diffusion at temperatures up to between 770 and 970 K and a bulk, or lattice, diffusion at higher temperatures. The diffusion is of minor importance when the temperature is below about 770 K but becomes increasingly important at higher temperatures [9]. The oxygen diffusion coefficient in Zr is approximated by  $D = 0.0661 \exp(-44,000/RT) \text{ cm}^2/\text{s}$  for the temperatures in the range of 560 K to 920 K, and  $D = 16.5 \exp(-54,700/RT) \text{ cm}^2/\text{s}$  for the temperatures in the range of 920 K to 1770 K (R in cal/gmolK), as reported by Ritchie et al. [10] following the analysis of a large number of experimental results. The oxygen diffusivity has been shown by Pemsler [11] to vary by a factor of two depending upon grain orientation.

The rate of diffusion of oxygen in zirconium dioxide is significantly lower than that in the metal [12].

Auger Electron Spectroscopy and  
Auger Transitions of Zirconium

Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a widely used surface-sensitive analytical technique based on the Auger process. An Auger process, or Auger transition, is an adjustment to an inner-shell-vacancy formed in an atom by external energetic excitation, which takes place by having one electron from a less tightly bound orbital fill the hole, while a second electron (Auger electron) is ejected into the continuum with an energy equal to the difference in total energies of the initial and final states of the Auger process (see (b) & (c) of Figure 1). In an AES analysis, the energetic excitation is generally initiated by an impinging electron beam and sometimes by a photon beam.

An Auger transition is generally denoted in terms of X-ray designated energy levels as an XYZ transition when the initial vacancy is in the X shell, a Y shell electron drops to fill the hole in the X shell and the Auger electron is expelled from the Z shell. This is exemplified by the  $M_{v}N_{23}N_{23}$  Auger transition displayed in Figure 1 ((b) & (c)). Auger transitions that involve electrons from the same shells are sometimes not differentiated from each

other. In other words, the levels in each shell are omitted in the designation. As in the case of  $MvN_23N_23$ , it is also denoted as  $MNN$  by some researchers.

The kinetic energy of an Auger electron originated from an  $XYZ$  transition can be estimated by [13]

$$E(\text{Auger}) = E(X) - E(Y) - E(Z)^*$$

where

$E(\text{Auger})$  : the kinetic energy of the ejected Auger electron from the  $Z$  shell.

$E(X)$  : the binding energy of an electron in the initial hole.

$E(Y)$  : the binding energy of the  $Y$  electron that drops in the  $X$  hole.

$E(Z)^*$  : the binding energy of the final state. (i.e. the binding energy of the  $Z$  level in the presence of a hole in the  $Y$  level).

As shown in Figure 2, there are three types of Auger transitions possible. In this Figure,  $C$  stands for a core shell and  $V$  stands for a valence shell. Thus, the  $CCC$  process is an Auger transition that involves only the core level electrons.  $CCV$  and  $CVV$  processes are the Auger transitions that involve one or two valence electrons, respectively, in the Auger processes.

In AES, the signal intensity of an element can be described by an explicit function of the Auger electron

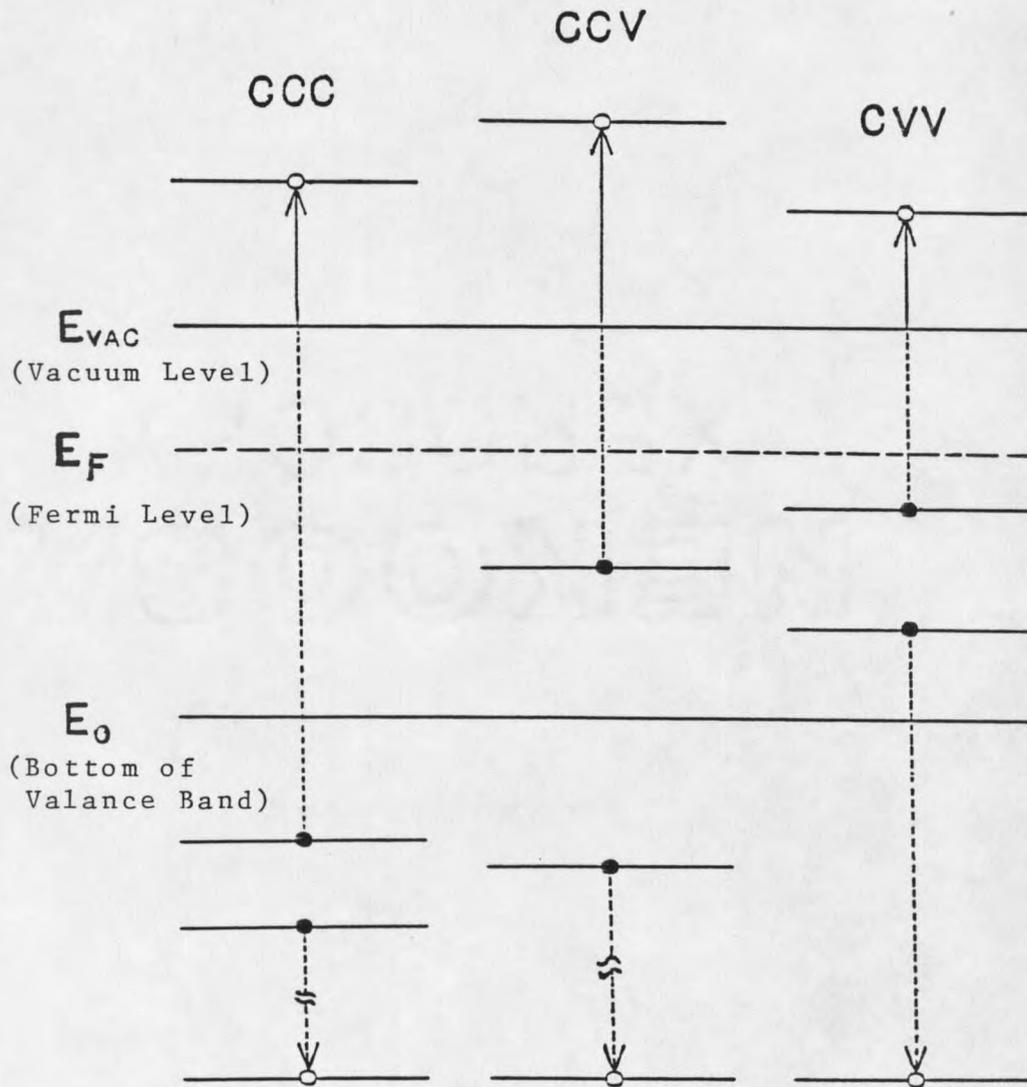


Figure 2. The three possible types of Auger transitions.

- C : core level electrons.
- V : valence level electrons.
- CCC : Auger transition involving only core level electrons.
- CCV : Auger transition involving one valence electron.
- CVV : Auger transition involving two valence electrons.

escape depth, concentration distribution of the element as a function of depth and electron backscattering factors [14].

The utility and popularity of AES is based on its high sensitivity (1% to 5% of a monolayer can be detected), its excellent elemental sensitivity for all atoms except H and He, the availability of energy analyzers with high transmission and the good lateral resolution afforded by electron beam excitation.

#### Auger Transitions of Zirconium

The Auger energies of the principal Auger transitions of Zr lie in the ranges of 80 to 180 eV and 1520 to 1950 eV [15]. The Auger transitions of the lower energy range of 80 to 180 eV are more pronounced than those of the higher energies. These Auger transitions at the lower energy range are therefore widely investigated in the studies of surface oxidation of zirconium. The Auger transitions of zirconium in the range of 80 to 180 eV and the KVV Auger transition of oxygen [5] are associated with the Auger energy levels, as illustrated in Table 1. An example of a differentiated Auger spectrum of a slightly oxidized zirconium is shown in Figure 3 with the Auger peaks designated.

Table 1. Auger Transitions from Oxygen Exposed Zirconium.

Element	Auger (#) Transitions	Symbolic Name	Auger Energy(Ψ) Clean Zirconium
Zr	MNN & MMN	ZR <sub>92</sub>	95, 92
	MNN & MMN	ZR <sub>117</sub>	120, 116
	MMN, MMV & MNV	ZR <sub>126</sub>	126
	MNV & MMV	ZR <sub>148</sub>	145, 147
	MVV	ZR <sub>175</sub>	175
O	KVV	O <sub>509</sub>	509.5 (*)

- (#) Each of these peaks listed in this table is actually a combined result of several Auger transitions. For instance, the primary sources that form ZR<sub>92</sub> include M<sub>3</sub>MvN<sub>1</sub>, MvN<sub>1</sub>N<sub>23</sub>, M<sub>2</sub>M<sub>4</sub>N<sub>1</sub>, M<sub>4</sub>N<sub>1</sub>N<sub>23</sub> and M<sub>2</sub>MvN<sub>1</sub> [5]. These transitions are therefore symbolized as MNN & MMN in this table.
- (Ψ) The Auger peak energy in  $d[N(E)*E]/dE$  is identified in this Table by the maximum negative excursion. The Auger energies of the ZR<sub>126</sub> and the O<sub>509</sub> peaks are taken from the result of this study. The rest of the Auger energies listed in this Table are taken from Axelsson et al. [17].
- (\*) measured from a Zr sample with 100 L O<sub>2</sub> exposure in this research.

### Secondary Ion Mass Spectroscopy

Secondary Ion Mass Spectroscopy (SIMS) has been extensively used as a tool for surface and bulk solid analysis. The SIMS method possesses the following features [16]:

- (1) detection of surface compounds by their fragment ions.

















































































































































