© *Proc. Indian natn. Sci. Acad.*, **49**, A, No. 3, 1983, pp. 424-430.
Printed in India.

Solid State and Structural Chemistry

XPS AND AUGER STUDIES OF THE SURFACE OXIDATION OF MANGANESE†

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(*Received on 6 September 1982*)

Surface oxidation of manganese has been investigated by Auger and X-ray photoelectron spectroscopic techniques. The surface oxide formed is MnO. Manganese is found to exhibit an unusually rapid oxidation rate compared to other transition metals. The role of the surface defect oxide in determining oxidation kinetics has been examined.

Keywords : X-ray Photoelectron Spectroscopy; Auger Electron Spectroscopy; Oxidation of Manganese

INTRODUCTION

TECHNIQUES of electron spectroscopy have proved to be most useful for studying the surface oxidation of metals. In particular, Augar electron and X-ray photoelectron spectroscopies have been usefully employed in obtaining quantitative information about oxidation of transition metals (Rao *et al.*, 1980; Sarma *et al.*, 1980; Sen *et al.*, 1982; and Srinivasan *et al.*, 1979). Using electron and X-ray induced Auger spectra, it has been shown (Rao *et al.*, 1980; and Sarma *et al.*, 1980) that not only the chemical shifts of the Auger signals (Castle & Epler, 1975), but the relative intensities of various metal Auger lines are also characteristic of the surface oxidation state and the extent of oxidation of metals. By monitoring the development of the interatomic Auger transition peak in Mn + O_2 system, it has been shown (Rao & Sarma, 1982) that the oxide layer grows rapidly on the surface of Mn, reaching saturation at relatively low oxygen exposures unlike on other transition metals. We thought it to be interesting to study the process of oxidation of Mn quantitatively by employing Auger and x-ray photoelectron spectroscopic techniques.

EXPERIMENTAL

X-ray photoelectron and Auger electron spectra were recorded using an ESCA-3 Mark II spectrometer of V.G. Scientific Ltd., U.K. The spectrometer has a sample preparation chamber fitted with Ar^+ gun for etching, quadrupole mass spectrometer and *in situ* vacuum deposition unit. The sample can be introduced into the spectrometer chamber for analysis from the preparation chamber in high vacuum. Both

†Communication No. 185 from the Solid State and Structural Chemistry Unit.

the preparation and the spectrometer chambers are independently pumped and have a base pressure of $\sim 2 \times 10^{-10}$ torr. The sample temperature can be varied continuously from liquid nitrogen temperature to $\sim$ 900°K.

A small ingot of Mn metal (purity > 99.9%) was cut into proper size and mechanically polished to obtain a smooth surface. The surface was then cleaned under high vacuum by Ar^+ etching. The impurity levels as seen by X-ray photoelectron spectroscopy were negligible. The results reported here are all obtained at room temperature (20°C), unless otherwise stated. Oxygen exposure is measured in terms of Langmuirs (1L = 10^{-6} torr sec.).

Intensities were generally measured by the integrated areas of signals except in the case of the differentiated spectra of electron-induced Auger signals where, peak-to-peak heights were measured. Preceeding the intensity estimation, background contributions were subtracted out of the recorded spectra by an iterative self-consistent method which assumes that the background signal is proportional to the area under the curve starting from the high kinetic energy side. The $Mn(2p_{3/2})$ signal of Mn + O_2 system at each oxygen exposure was decomposed into the component peaks due to those of Mn metal and the metal oxide by a least-square-fit procedure after subtraction of background contribution from the signal.

Results and Discussion

We have shown in Fig. 1 few typical Auger and X-ray photoelectron spectra of Mn + O_2 system to illustrate the variations in the spectral features on oxygen exposure. It can be seen from this figure that even a small exposure to oxygen causes a distinct oxide peak to develop in the X-ray photoelectron spectra. The nature of the oxide on the metal substrate was confirmed by comparing the X-ray photoelectron spectra of various manganese oxides (Rao *et al.*, 1979) with those of

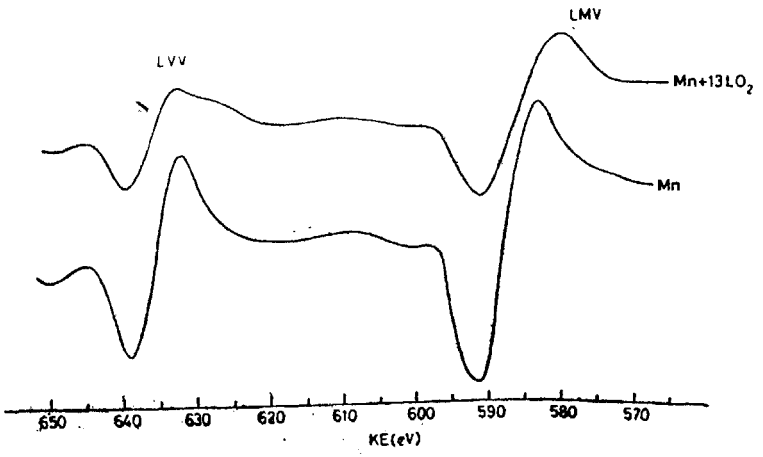

FIG. 1. (a) The electron induced Auger spectra of LVV and LMV regions in the clean metal and the metal exposed to oxygen.

Mn + O_2 system. The chemical shift of the $2p_{3/2}$ signal and the exchange splitting of the 3s level ($\sim$ 6.2 eV) confirmed that only MnO is formed on the surface. A close examination of the Auger spectra (Fig. 1) reveals that the ratio of L_3VV and $L_3M_{23}V$ Auger intensities decrease accompanying the oxide formation as expected (Rao *et al.*, 1980). In Fig. 2(a), we have plotted the variation of the ratio of these two Auger transition intensities of Mn (as measured by the integrated areas) in the X-ray induced Auger spectra with oxygen exposure. Fig. (2b) shows the same ratio as measured by the peak-to-peak heights in electron induced derivative spectra. In

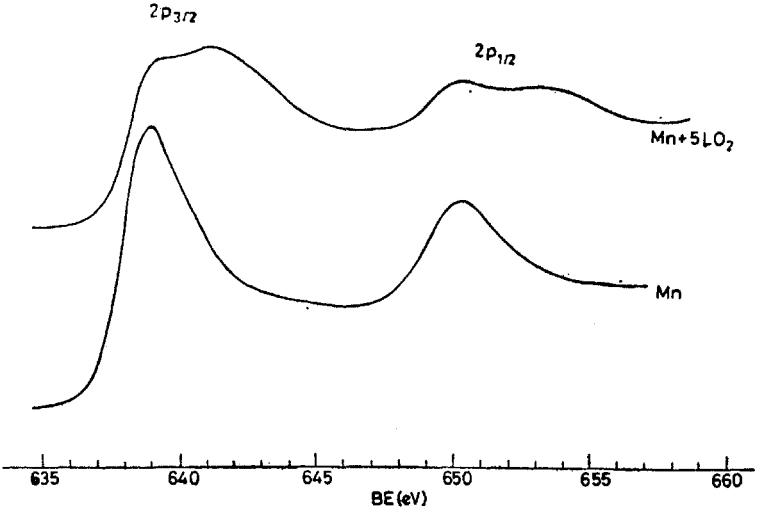

Fig. 1. (b) The x-ray photoelectron spectra of the 2p region of clean metal and the metal exposed to oxygen showing the development of the oxide.

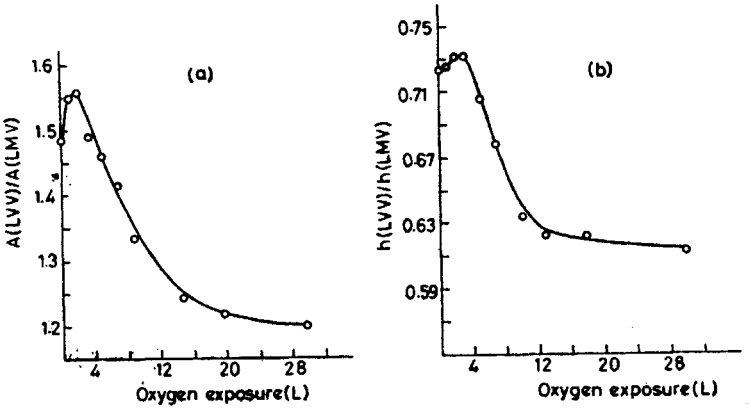

FIG. 2. (a) Plot of the ratio of LVV and LMV Auger intensities (as obtained by integrating the area under the signals) as a function of oxygen exposure.

(b) Plot of the ratio of LVV and LMV Auger intensities (as obtained from peak-to-peak heights in the differentiated signals) as a function of oxygen exposure.

Fig. 3, we have plotted the intensity ratio of the Mn($2p_{3/2}$) signals of the oxide and the metal in X-ray photoelectron spectra.

The oxygen uptake at the Mn surface is shown in Fig. 4 in terms of the variation of the intensity of the O(1*s*) signal with oxygen exposure. Figs. 2, 3 and 4 clearly show three distinct regions of oxidation. Region I consists of little oxidation and the oxygen uptake is due to a dissociative chemisorption process. This is clearly seen in Fig. 4, rapid chemisorption occurs in the low exposure range ($< 2L$) while rapid oxidation sets in at higher exposures ($> 2L$). Accordingly, we find in Fig. 3 that there is very little oxide growth at exposures below 2L. In this exposure range, the Auger intensity ratios (Fig. 2) increase slightly in the values with exposure, if oxidation were to take place, we would expect a rapid decrease of the intensity ratios. The slight rise in the intensity ratios in Fig. 2 at low oxygen exposure is most probably due to an interatomic Auger transition in the chemisorbed state. The chemisorption region at low oxygen exposure has been previously established by following the development of interatomic Auger transiiions in the L_3VV spectra of the Mn + O_2 system (Rao & Sarma, 1982).

In the intermediate exposure range ($2 < L < 15$), oxidation proceeds rapidly as indicated by sharp decrease in the Auger intensity ratios of Fig. 2. Fig. 3. similarly shows a rapid increase in the $2p_{3/2}$ signal due to the oxide layer in this exposure range. These similar results are also supported by the oxyen uptake data in Fig. 4. Beyond this exposure range, oxidation proceeds slowly as indicated in Fig. 4 by the slow oxygen uptake at increasingly higher oxygen exposures.

We have estimated the number of monolayers of the oxide at various exposures from the data plotted in Fig. 3 by assuming the mean free path to be 6 monolayers and that the oxide grows from the surface to the bulk. The results are shown in

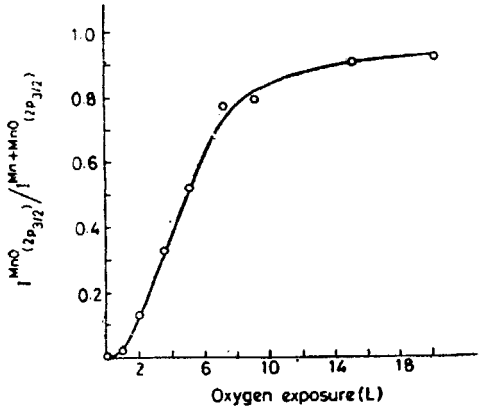

FIG. 3. Plot of the intensity of $2p_{3/2}$ signals from the surface oxide (normalized to the total intensity of $2p_{3/2}$ signal) as a function of oxygen exposure.

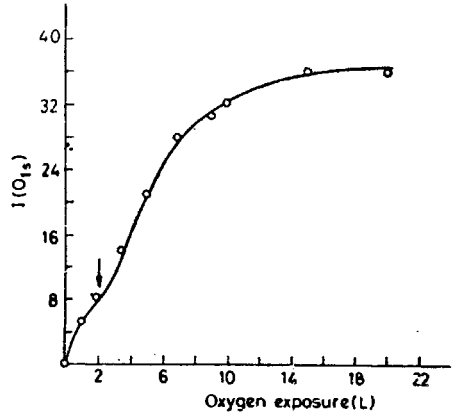

FIG. 4. The plot of intensity of O(1*s*) signal as a function of oxygen exposure. The arrow indicates the stage where chemisorption ends and oxidation begins.

Fig. 5 where we find that the oxidation of Mn at room temperature is very high compared to other transition metals such as Fe, Ni, Cu and Zn. On saturation at room temperature, these metals develop typically 3-5 monolayers of oxides (Rao *et al.*, 1980) as against 13 monolayers of oxide in the case of Mn. We, also find that the oxidation of Mn at room temperature is much more rapid compared to transition metals like Fe, Ni, Cu or Zn, reaching saturation at a comparatively small oxygen exposure (20L). This rapid oxidation of Mn compared to other metals is attributable to two different factors. The heat of adsorption, ΔH, of chemisorbed oxygen on Mn metal is much higher (150 Kcal/mol than those for transition metals like Fe(136 Kcal/mol), Co(100 Kcal/mol) and Ni(107 Kcal/mol) (Lawless, 1974). As the chemisorption is governed by exp ($\Delta H/KT$) (Rao *et al.*, 1980) Mn is expected to show a faster chemisorption kinetics. However, multilayer oxide growth on a metal substrate is limited by the facility with which the cations can move to the surface through the oxide layer by an activated transport mechanism. In this context, it should be remembered that among the oxides of Mn, Fe, Co and Ni, only MnO has a lattice parameter greater than 4.44Å whereas others have lattice parameters less than 4.3Å. We feel that this dilated packing of MnO is responsible for low activation barrier for cation migration leading to faster oxide growth on Mn metal.

It is noteworthy that in an earlier study of the oxidation of Mn, Fuggle *et al.* (1975) reported that the uptake of oxygen varies almost linearly with exposure upto an oxygen exposure $> 10^3$L. This difference, we feel, arises as these workers carried out the investigation with an evaporated thin film of Mn on stainless steel substrate. The structure of evaporated films depends critically on the substrate, and in the extreme case, can be in a highly amorphous state. As it is known that amorphous form of a metal has a slower oxidation rate than that of the crystalline one (Sen

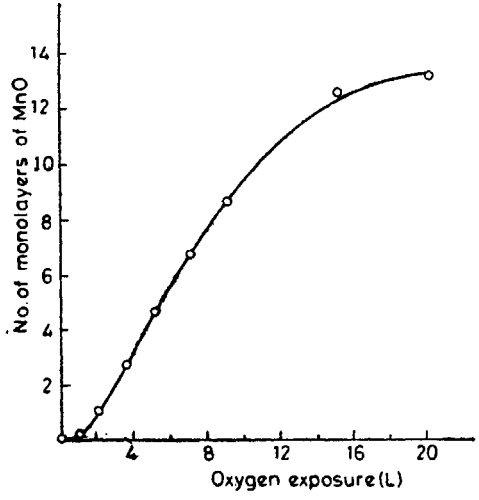

FIG. 5. The number of layers of MnO formed on the surface of Mn (calculated from the data in Fig. 2) as a function of oxygen exposure.

et al., 1982), an evaporated film of Mn can lead to a slower oxidation rate as an artifact of its highly distorted surface structure. A detailed investigation of the O(1*s*) spectra provides us with further support for this interpretation. It was reported by Fuggle *et al.* (1975) that the O(1*s*) signal exhibited a clear doublet structure, the first of the two peaks was attributed to the signal of oxide oxygen, while the second peak (more than 50 per cent in intensity as compared to the main peak) was not assigned. In our O(1*s*) spectra of the Mn + O_2 system at 298 K, we find this peak as a very weak structure (< 10 per cent in intensity of the main peak) (Fig. 6). As this weak peak, appearing at ~532.0 eV, can be due to either a surface defect oxide or a hydroxyl impurity, we exposed Mn to oxygen saturated with water. We find in that case, there is no increase in the intensity of the second peak at 532.0 eV (Fig. 6). This confirms that the weak structure is not due to hydroxyl impurity. We have also found that if dry oxygen is exposed to Mn at higher temperatures (T = 450K) this weak feature is less prominent in the O(1*s*) spectra (Fig. 6). As high temperature is expected to assist surface reconstruction thereby reducing surface defects, we attribute the weak structure at higher binding energy in the O(1*s*) spectra to the formation of a defect oxide at the surface. It appears that the thin film of

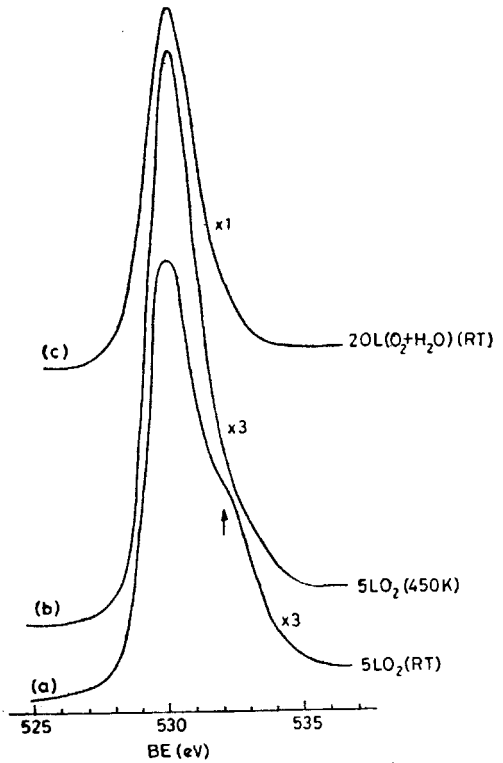

FIG. 6. The O(1*s*) spectra in Mn+O_2 system for (a) 5L exposure at room temperature; (b) 5L exposure at 450K; and (c) 20L exposure of O_2 saturated with moisture at room temperature. The arrow indicates the defect oxide signal at ~532 eV.

Mn used by Fuggle *et al.* (1975) had a high proportion of the defect oxide ($\sim$ 50 per cent) compared to the present study.

ACKNOWLEDGEMENT

The authors are thankful to Professor C. N. R. Rao for suggesting the problem and constant guidance. Financial support from the Department of Science and Technology, Government of India, is gratefully acknowledged.

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