

AN XANES STUDY OF CARBIDES OF MOLYBDENUM AND TUNGSTEN

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Abstract—The X-ray absorption near edge structure (XANES) of molybdenum and tungsten compounds has been studied by using synchrotron radiation. Substantial difference in XANES features between metals and their carbides suggested significant difference in electronic structure between them. The shift in edge position indicated charge transfer from metal to carbon when a carbide is formed. In light of a modern band theory, the larger white line areas for carbides could be interpreted as due to some of the unoccupied d-states which are not measured by x-ray white line area.

INTRODUCTION

Transition metal carbides have received industrial interest as refractory materials due to their extreme hardness and thermal stability [1]. Recently, these materials, especially carbides of molybdenum and tungsten, have also been applied in heterogeneous catalysis [2-7]. Of particular interest is the resemblance of their catalytic properties to those of group 8 metals. Thus tungsten carbide shows Pt-like behavior [8], and molybdenum shows characteristics of Ru [5, 6] in some catalytic reactions.

The properties of carbides must depend on their electronic structure and bonding. Much of the early attention has been paid to the direction of charge transfer between the metal and carbon. Ramqvist et al. [9-12], by means of x-ray photoelectron spectroscopy (XPS) and other x-ray techniques, showed that the metal carried positive charge and that the magnitude of the charge agreed with the value calculated by Pauling's electronegativity scale.

The increased availability of synchrotron radiation has had a profound impact on many spectroscopic techniques including x-ray techniques. The spectral properties of synchrotron radiation improved the quality of data and shorten the collection time remarkably compared to conventional x-ray sources. This paper describes the results of an x-ray absorption near edge

structure (XANES) study on carbides of molybdenum and tungsten. Many reviews are available for the technique itself [13, 14]. It is well known that XANES yields information on the electronic structure of absorbing atoms. The overall shape of XANES features, particularly of K-edges, fingerprints the chemical environment of the absorbing atom. The edge position is related with the binding energy of excited electrons. Threshold peak ("whiteline") areas of L_{II} and L_{III} edges could provide an estimate of d-band vacancy [15-17]. Special attention has been paid to compare the XANES features of carbides with metal counterparts.

EXPERIMENTAL

Foils of molybdenum (25 μm thick) and tungsten (127 μm thick) were purchased from Alfa. Powders of Mo_2C (99.8%), WC (99.9%), and WO_3 (99.998%) were also purchased from Alfa. A cubic molybdenum carbide αMoC_{1-x} was prepared as described elsewhere [18].

The x-ray absorption data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) under a dedicated condition, at 3.0 GeV and ca. 30 mA. Molybdenum L-edge spectra occur at energies of 2500-2900 eV which is experimentally difficult to reach by using hard x-ray beam lines since absorption in the beam lines, detectors and beam paths greatly reduces the available x-ray flux at these low energies. Therefore,

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Table 1. X-ray absorption edge position of Mo and W

Material	K-edge/eV	L _{II} -edge/eV	L _{III} -edge/eV
W	—	11,538.0	10,199.9
WC	—	11,538.7	10,200.7
WO ₃	—	—	10,201.8
Mo	20,003.9	—	2,521.3
Mo ₂ C	20,003.9	—	2,521.5
αMoC _{1-x}	20,003.9	—	2,521.8

a fluorescence ionization chamber detector was used with no filters or slits in front of the detector. Harmonic rejection was accomplished by detuning the Si(111) double crystal monochromator to decrease the incident intensity of x-ray to 40-80%. Powdered sample was positioned in the beam on a piece of Mylar tape fixed on an aluminum holder. Spectra for Mo K-edge and W L-edges which occur near 20 keV and 10 keV, respectively, were collected for self-supporting wafer samples positioned in usual EXAFS set-up with two Si(220) single crystal monochromators and ionization chamber detectors. The K-edge of W cannot be measured because it is located near 70 keV. The X-ray absorption data were analyzed with a standard EXAFS analysis program [19]. Briefly, the reported XANES spectra were subject to background subtraction by fitting a line through the pre-edge, and then normalized to give an each jump (difference between the heights of post-edge and pre-edge) of 1.0.

RESULTS

Table 1 summarizes x-ray absorption edge positions of Mo and W. Edge positions are defined as the energies of the major inflection point in the rise of the edge [19], and assigned with known edge energy values for metallic W or Mo. Hence, the shifts in edge positions of carbides from those of metals are of main concerns rather than absolute values. For both Mo and W, carbides showed absorption L-edges at higher energies than corresponding metals. Tungsten oxide showed a higher edge position than both W and WC. However, K-edge spectra of Mo obtained above 20 keV did not show this difference probably because of poorer energy resolution at this higher energy range.

Detailed features of Mo and W absorption edges are compared in Fig. 1 and 2, respectively. The Mo K-edge spectra did not show any strong threshold peaks. The only noticeable difference between K-edge XANES spectra of Mo and its carbides (Fig. 1a) was a separation of the two broad peaks above the absorption edge. The Mo spectrum showed a larger separa-

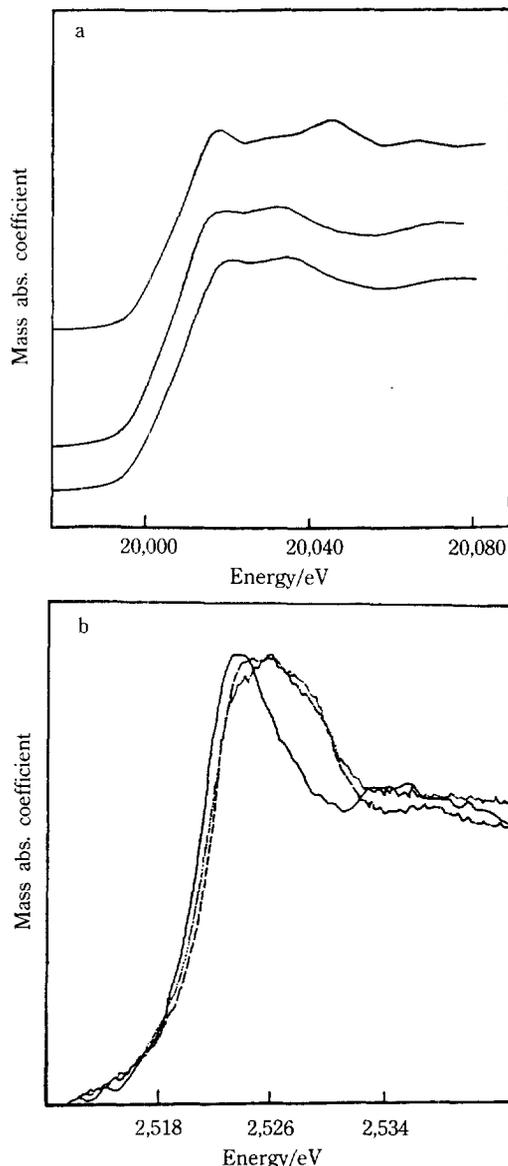


Fig. 1. The XANES spectra for Mo. (a) K-edge spectra of (from top to bottom) Mo, Mo₂C, and αMoC_{1-x}. (b) L_{III}-edge spectra of (from left to right) Mo (—), Mo₂C (---), and αMoC_{1-x} (---).

tion than carbide spectra. In the case of L-edges for both Mo and W, whiteline areas for carbides were larger than those for metals. For W, the difference was greater for L_{II} edges. The whiteline area for the L_{III} edge of WO₃ was smaller than those for W and WC. In all cases, little difference in XANES was observed between Mo₂C and αMoC_{1-x} in spite of their difference in crystal structure (hcp vs. fcc).

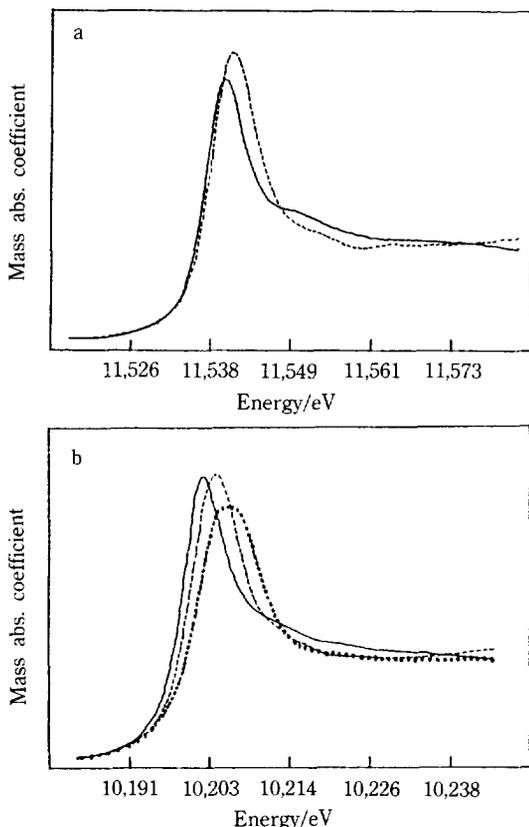


Fig. 2. The XANES spectra for W. (a) L_{II}-edge spectra of W (—) and WC (···). (b) L_{III}-edge spectra of (from left to right) W (—), WC (---), and WO₃ (···).

DISCUSSION

As mentioned, XANES provides information on the electronic structure of the absorbing atom. The K-edge of Mo arises from the excitation of 1s electron. According to the dipole selection rule ($\Delta l = \pm 1$), the final state of the transition must be the lowest-lying unoccupied p-state (5p for Mo) and continuum. Hence the features in Fig. 1a arises from the transitions. The first peak above the edge is thus due to 1s→5p transition. The origin of the second maximum in Mo K-edge is not clear. The interpretation of the XANES spectra in this region of energy is complicated by the presence of the multiple scattering [13]. However, the difference of their position between molybdenum and its carbides provides a useful signature to identify the phase in unknown samples [5]. In contrast, the L_{II} and L_{III} edges arises from transitions from, respectively, the 2p_{1/2} and 2p_{3/2} core levels to mostly unoccu-}}

pled 4d-states in the absorbing atom. Thus whiteline areas of L-edges could measure the extent of unoccupied d-states.

The positive shift of edge position for carbides indicates that oxidation state of the metal is raised by forming carbides. In other words, electrons flow out of the metal to carbon. This direction of charge transfer agrees with the XPS results of Ramqvist et al. [9-12].

Lytie [15] was the first to show that whiteline areas of L-edges could provide an estimate of d-band vacancy, and a number of attempts have been made to refine his semiquantitative interpretation [17]. Hence, it is tempting to understand the positive edge shifts and the increased whiteline areas of carbide XANES as cognate phenomena, namely, d-vacancy of carbides has increased due to charge transfer to carbon. However, this interpretation does not agree with the empirical trend of both bulk and surface properties of transition metal carbides. Thus the variation in hardness and bulk modulus of transition metals and their carbides along the same row of the periodic table [1] and the resemblance of surface reactivity of carbides to noble metals rather than parent metals [2] could be explained by the increased occupancy of the metal d-bands, and therefore by electron transfer from carbon to the metal as carbides are formed.

Recent theoretical works of Siegel [20] and Williams et al. [21] attempted to resolve this apparent contradiction of charge transfer in metal carbides by demonstrating that simultaneous electron donation to carbon and filling of metal d-bands were not mutually exclusive. According to Heine [22], the width of the d-band is inversely proportional to the fifth power of the metal-metal distance. Since the interatomic distance is generally larger for a carbide than for the parent metal, the carbide has a narrower band. Such a band can lose electrons to carbon and yet be filled to a higher extent than the broader band of the parent metal.

If we accept both the band theory and Lytle's interpretation of the whiteline areas, we should expect smaller whiteline areas for XANES of carbide L-edges. However, the simple interpretation of whiteline areas has been experimentally demonstrated only for Pt and its compounds. By comparison between experimental and theoretical whiteline areas, Horsely [23] showed that L-edge resonance of IrO₂ and OsO₂ did not include any transition to empty d-states at the top of the valence band. This makes the relationship between the L-edge whiteline area and the unoccupied d-states in transition metals complicated. The system employ-

ed in this study may be another example for which the relationship is not a simple one. Indeed, the white-line areas for WO_3 are smaller than those for W and WC. This is opposite to what has been observed for Pt and PtO_2 [15]. It is unlikely that tungsten d-band in WO_3 is filled to a higher degree than in W or WC.

The most important finding in this comparative study of x-ray absorption edges is believed to be the significant differences between the XANES features of metals and their carbides. Although not all of these differences could be explained in terms of current theories on XANES interpretation and electronic structure of carbides, one can conclude at least that a systematic change in electronic structure occurs when a metal is transformed to corresponding carbides. The conclusion is not necessarily obvious if one considers that both the current understanding on the electronic structure of carbides and their physical properties indicate that both of them are essentially *metallic* in nature in spite of perturbations induced by interstitial carbon [2]. The XANES features of Mo, W and their carbides may be rich in electronic and chemical information. However, the theoretical basis for the interpretation of these features should be greatly refined before this information helps us understand better the electronic structure of the materials.

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