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Structural characterization of $VC_{0.88}$ using transmission Extended Electron Energy Loss Fine Structure Spectroscopy

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We investigate the feasibility to obtain the local structure of the vanadium carbide system ($VC_{0.88}$)of transmission core ionization electron energy loss spectroscopy. The near edge structure of C K edge and V L_{23} edge are discussed. The structural parameters were found analyzing the extended fine structure associated to the ionization edge in the core loss window. In order to improve the results, the experimental phase shifts were calculated and applied on each interatomic value. The interatomic distance for V - C bond was 0.20 nm and 0.21 nm which is very close to the expected value of 0.205 nm. A second interatomic distance was found and corresponds to the C – C bond with a numerical value of 0.3 nm and 0.33 nm which is also close to the respective expected value of 0.29 nm. These values were obtained by analyzing the fine structure associated to the carbon K-edge and those associated to the vanadium L_{23}-edge. The interatomic distances are in good agreement to the expected values for $VC_{0.88}$ when the experimental phase shifts were applied.

Keywords: EELS; EXEELFS; VC

1. Introduction

The use of synchrotron radiation sources to study x-ray absorption in materials science, has been wide employed and is very well established. But there are a few synchrotrons in the world and its use is really expensive. Fortunately, a similar process occurs in the vicinity of the ionization threshold in electron energy loss spectra and a method known as Extended Electron Energy Loss Fine Structure, (EXEELFS) has been establish to characterize materials. This method in combination with transmission electron microscopy, offers the possibility to analyses nearest neighbors configurations of small particles and clusters. Besides, actually it is very easy to perform Electron Energy Loss Spectroscopy, (EELS) on a wide number of materials as; compared with the difficulty to have access to a synchrotron source

Electron probes have been used successfully during many years as a relatively easy way to investigate surface properties. In fact analysis using electron probes are in good agreement with the results obtained employing the most popular and precise technique, extended X-ray absorption fine structure, (EXAFS). Several techniques involve the electron probe to characterize materials within them we found: Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Electron Energy Loss Spectroscopy (EELS). The EELS technique has been used in reflection and transmission modes of the electron beam, and low or high incident electron energies are used to obtain structural and electronic properties of many materials [1-4].

The EELS technique probes the solid state environment of elements in a sample by analyzing the energy distribution of electrons that have been inelastically scattered during their passage through the material. Analysis of the energy loss spectrum reveals which elements are present in the specimen, as well as afford on the bonding environment (e.g. oxidation state, coordination number, etc.). EELS is particularly sensitive for detecting trace quantities of transition elements, rare-earth elements, and low-Z elements such as Be, B, C, N, and O.

New detection systems have been developed for EELS, in reflection and transmission geometries. For reflection geometries the hemispherical analyzers are the best way to analyze physical properties of surfaces. These analyzers can be operated with electron energies of 0.5-5 KeV and with a typical resolution of $\Delta E/E = 0.1\%$. For transmission geometries the detector is usually placed in the bottom of a transmission electron microscope. These modern systems can acquire data in serial or parallel mode with the second architecture being the most efficient way to obtain good quality spectra. Parallel acquisition systems are known as Parallel Electron Energy Loss Spectrometers or simply PEELS. The most important advantages are; the good signal to noise ratio and the very short time of sample exposition to the electron beam. The problem the energy range of the signal of the fine structure presented in EELS spectrometers with serial acquisition systems is avoided by using the parallel acquisition systems. Actually the use of PEELS is the best way to perform investigations of a wide number of materials, specifically in their structural properties where it achieves an impressive resolution at higher energy losses.

In this work the core ionization electron energy losses of the $VC_{0.88}$ system are examined, in order to perform a full fine structure analysis to obtain the local chemical structure of the system. The corrections by experimental phase shifts are also included in order to improve the results.

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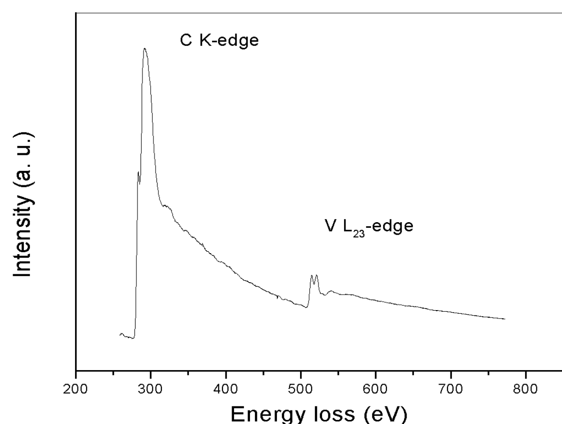

Figure 1. Core loss window of the electron energy loss spectrum for the VC_{0-88}. We note the well defined shapes of C and V ionizations.

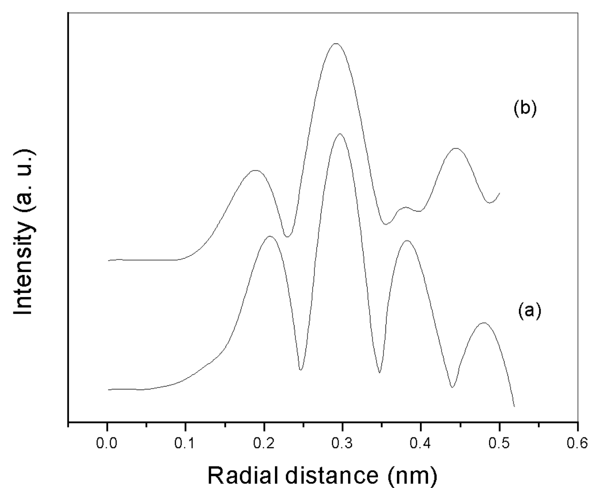

Figure 2. Radial distribution function obtained by applying the Fourier transform to the spectrum of Figure 1.

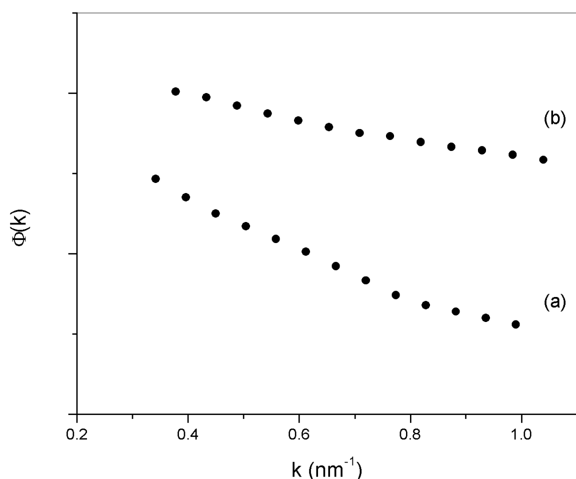

Figure 3. Comparison between the experimental phase shifts for VC_{0-88} and that obtained theoretically for C.

2. Experimental

Vanadium carbide with a stoichiometry $VC_{0.88}$ was purchased as commercial powder from Alfa Aesar with a purity of the 99.5%. The sample was prepared in the standard method for powder observation in a transmission electron microscope (TEM). EELS experiments were carried out in a Phillips CM 200 STEM equipped with a Gatan 766 PEELS spectrometer. The experimental conditions for data acquisition were the following: a spot size of 500 nm, a chamber length of 360 mm and a detector aperture of 3 mm using an energy dispersion of 0.3 eV/channel with a beam energy of 200 KeV. A typical FWHM of 1.18 eV was used. Acquisition time was around 10 mn taking an average of 1000 spectra.

All the EELS spectra were corrected by background subtraction and multiple scattering deconvolution, before the fine structure analysis. The background subtraction has been done applying a polynomial fit at the curve. By other hand the single scattering deconvolution formalism [6], (SSD), was used in order to remove this effect in the spectrum. Special care was taken in order to obtain a good quality spectrum around the ionization edges where the fine structure exists. In order to isolate the oscillations in the fine structure a second derivative was performed on each spectrum. A low pass smoothing was performed in the derivative spectrum before applying the Fourier transform. The fine structure range used for analysis was 200 eV beyond the C-K edge located at an energy loss of 283 eV and the VL_{23}-edge located at an energy loss of 513 eV, respectively.

3. Results and discussion

The EELS spectra around the ionizations edges of C and V appear in Figure 1, where the contributions for background and multiple scattering were removed in order to calculate the atomic concentration. The elemental ratio C/V was estimated using the respective cross section for C and V as follows [5,6]

$$\frac{Nc}{Nv} = \frac{S_C(\Delta\beta)\sigma_V(\Delta\beta)}{S_V(\Delta\beta)\sigma_C(\Delta\beta)} \tag{1}$$

where $\frac{N_c}{N_v}$ is the elemental ratio, $S_V(\Delta,\beta)$ and $S_C(\Delta,\beta)$ are the area under the experimental threshold of V and C, respectively, and $\sigma_V(\Delta,\beta)$, $\sigma_C(\Delta,\beta)$ represent the area under the calculated threshold of V and C. In this case the elemental ratio C/V was 0.878, which corresponds to the $VC_{0.88}$ system.

In Figure 1 we clearly observed a double signals located at 284 eV and 291 eV. These peaks are identified as the π and σ antibonding transitions (π* and σ*) for carbon. These values are slightly shifted depending on the bond characteristics of carbon with the V atoms. However, it

does not affect the extended fine structure and therefore our analysis. Likewise in this Figure appears clearly the V-L_{23} transition showing clearly the L_{23} doublet with peaks located at an energy loss of 513 and 521 eV. From a detailed inspection on this Figure we can appreciate that there is a close similarity in the period of the oscillations of the fine structure beginning approximately 40 eV beyond both ionization edges. These isolated extensions in energy were used to calculate the radial distribution function (RDF) applying the fast Fourier transform to the energy loss spectrum [7].

The radial distribution function may be obtained applying the fast Fourier transform, FFT, to the selected extended fine structure. In the EXAFS case, the oscillations around the absorption edge are given by the equation:

$$\chi(k) \propto \left| \langle \psi_i | \hat{\varepsilon}_q \cdot \vec{r} | \psi_j \rangle \right|^2 \quad (2)$$

Where $\chi(k)$ is the oscillatory part, $\hat{\varepsilon}_q \cdot \vec{r}$ is the dipolar term associated with the polarization of the x-rays and ψ_i and ψ_j the respective initial and final states of the electron. Applying the FFT to this oscillatory function [8] a radial function (real space function) is obtained as follows:

$$F(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} \chi(k) k^{\mu} \varpi(k) e^{-2i\vec{k}\cdot\vec{r}} dk \quad (3)$$

Here k is the wave vector, k^{μ} is a weight factor to avoid any divergences in the integral where μ may take values of 2 or 3. The term $\varpi(k)$ is a selected window function and r is the respective radial distance.

A similar situation occurs with EXEELFS, in this case the oscillatory part depends on the matrix element as follows:

$$\frac{d^2\sigma(E,q)}{dEdq} \propto \left| \langle \psi_i | \vec{q} \cdot \vec{r} | \psi_j \rangle \right|^2 \quad (4)$$

in this case the dipolar term $\vec{q} \cdot \vec{r}$ is associated with the transferred moment. For electrons is needed to change the wave vector k into the energy space through the relation $k = \sqrt{0.263(E_0 - E)}$. Here, E is the energy loss, E_0 in our case is chosen at the inflection point of the carbon K-edge and $E_0 - E$ is their respective energy loss. Then applying the FFT is possible to obtain a similar radial distribution function like in EXAFS.

In EXAFS technique the main peaks in the radial distribution function do not correspond directly to the atomic positions but they should be corrected for the phase shift effect. The values for the phase shifts are tabulated for the different edges and elements [9,10]. However the phase shifts can also be deduced directly from the same experiment using the model compounds [11]. The experimental phase shifts can be used afterwards in all the compounds where the same absorber and backscattered pair is involved, invoking the phase shift transferability principle. In this case the experimental phase shifts were calculated applying the equation (2) to the RDF spectra. In this equation the quantities of $\mathrm{Re}\{FFT^{-1}\}$ and $\mathrm{Im}\{FFT^{-1}\}$ are the real part of the Fourier transform and the imaginary part of the inverse Fourier transform, respectively, $\Phi_j(k)$ the respective experimental phase shifts, k the wave vector and R_j the atomic position of the j th atom.

$$\Phi_j(k) = Tan^{-1}\left[\frac{\mathrm{Re}\{FFT^{-1}\}}{\mathrm{Im}\{FFT^{-1}\}}\right] - 2kR_j \quad (5)$$

Figure 2 shows the comparison between the Fourier transform of the energy loss spectra schematized in the Figure 1, where it is noticeable the good agreement in both, RDF obtained using the fine structure corresponding to (a) the C-K edge and (b) the V-l_{23} edge, respectively.

Figure 3 displays the other comparison between (a) the theoretical phase shifts for carbon extracted from [12] and (b) the respective experimental phase shifts of $VC_{0.88}$.

The absolute main peak positions obtained after analyzing the fine structure associated to the C-Kedge were: 0.2 nm for the first nearest neighbors and 0.3 nm for the second nearest neighbors. On the other hand the main peak positions obtained by processing the respective fine structure associated to the V-L_{23} edge were 0.21 nm for the first nearest neighbors and 0.33 for the second nearest neighbors. As we can see the estimated differences among these positions are 0.01 nm for the first nearest neighbors and 0.03 nm for the second nearest neighbors. These results confirm the known phase transferability argument, which assumes that the phase shifts are independent of the kind of scatter atom.

Table 1 shows the numerical values for the first and second nearest neighbors positions obtained here and their respective known crystallographic values [13]. From this table we can estimate the difference among the values for the first and second nearest neighbors. With respect to the analysis of the fine structure associated with the C edge we have a difference of 0.05 nm for the first nearest neighbors positions and 0.01 nm for the second nearest neighbors. In the same way, for the V edge we have a difference of 0.05 nm for the first nearest neighbors positions and 0.04 nm for the second nearest neighbors positions .

Table 1. Numerical values for the first and second nearest neighbors for $VC_{0.88}$ structure.

	First nearest neighbors distance (nm)	**Second nearest neighbors distance** (nm)
This work (respect to the C Kedge)	0.20 ± 0.03	0.30 ± 0.03
This work (respect to the V L_{23} edge)	0.21 ± 0.03	0.33 ± 0.03
Known crystallographic values [13]	0.205	0.29

4. Conclusions

We have determined the atomic positions of the first and second nearest neighbors of the $VC_{0.88}$ system using the EXEELFS technique making evident the very short time this technique takes as compared with others like XRD. The values obtained here are in good agreement with the known crystallographic values after applying the corrections for experimental phase shifts. The transferability of the phase has been demonstrated when the EXEELFS procedure was applied to the fine structure associated with the C and V, respectively, getting the same values.

Although the electron energy loss spectroscopy is one of the most ancient technique for surface analysis, only in the last years it has proved to give also good structural information of a wide range of materials using modern detection systems, mainly due to the parallel detection.

We want to point out that it is completely necessary to analyze the phase shift effect in all the EXEELFS study of materials.

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