JOURNAL OF MATERIALS SCIENCE 27 (1992) 2731–2733

Valence determination of titanium and iron using electron energy loss spectroscopy

M. SANKARARAMAN, D. PERRY
School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA

A method of determining the valence state of titanium and iron in ceramic materials using the electron energy loss spectroscopy is given. In this method the $L_{2,3}$ loss edges of a standard are determined and the unknown valence state is determined by observing its spectrum and comparing it to the established standard.

1. Introduction

Traditional methods, such as volumetric titrations and Mössbauer spectroscopic methods, have serious limitations in determining the valence state of an element in a ceramic compound. Determining the valence states in ceramic compounds by volumetric titrations requires dissolving the compounds. Finding a suitable solvent is usually very difficult, if not impossible. The Mössbauer spectroscopic method is model dependent; further, only magnetic ions can be studied and hence it is not universal. In this report we provide an alternative method to determine the valence states using electron energy loss spectroscopy (EELS).

When an electron beam passes through a thin crystal, some of the energy is lost in exciting the inner core electron to an unfilled state. The study of energy loss of the electron beam provides a means to identify the elements and their valence states. In the case of 3d transition metal ions, the L_2 and L_3 loss edges (due to the transition from $2p^{1/2}$ and $2p^{3/2}$, respectively, to the unbound states) are characteristic of the valence states of these ions [1, 2]. Our method of determining the valence state using EELS proves to be straightforward and can be extended to other elements such as chromium, etc. This method can also be utilized in determining the mixed valence state such as the coexistence of Fe^{2+} and Fe^{3+} in Fe_3O_4 [3]. More detailed discussion of EELS is given elsewhere [4].

2. Experimental procedure

The spectrometer consists of a Jeol 2000FX analytical electron microscope, a Gatan 666 PEELS and a Link System analyser version AN 10 000. This spectrometer has an energy resolution of 0.7 eV for an entrance aperture of 1 mm with 100 kV incident electrons. All the reported spectra were smoothed using a three-point smoothing routine of the AN 10 000. Even though this routine improves the appearance of a spectrum, it does not alter the statistics. Background intensity was not subtracted in any of the spectra reported here. The spectra were acquired using Gatan 666 parallel detection system capable of recording all the 1024 channels simultaneously. A primary voltage of 200 kV is used for all spectra shown here.

2.1. Determination of valence states of titanium and iron

Determination of valence states of these elements first requires the accurate determination of the position of the $L_{2,3}$ loss edges of Ti^{2+}, Ti^{3+} and Ti^{4+} and Fe^{2+} and Fe^{3+}. Once the standard values for these states have been established, an unknown valence state can be determined by observing its spectrum and comparing it to the established standards. We took (99.9% pure) TiO, Ti_2O_3, TiO_2, FeO and Fe_2O_3 powders as our standards. Samples for EELS studies were prepared by crushing the powders with acetone in an agate mortar and depositing a small amount on a 3 mm diameter carbon micro-grid. To avoid multiple scattering within the sample, very thin samples were selected using low magnification.

Usually, the EELS edges drift due to small shifts in the zero loss peak and we could not stabilize the zero loss peak even after stabilizing the beam current for over an hour. In order to determine the position of the $L_{2,3}$ loss edges accurately, we took the oxygen K loss edge at 532 eV as an internal standard for our calibration because the position of this loss edge is well established. Further, as most of the ceramics are oxides, the O K edge as an internal standard will provide measurements that are compatible with other oxides. As is customary in EELS work, we took the inflection point of the spectrum rather than the peak itself. This is due to the fact that the position of the peak is not as reproducible as the inflection point.

Fig. 1 shows a comparison of the spectra due to the three valence states of titanium. The values given in Fig. 1 are averages after several repeated measurements. The chemical shifts in L_3 loss edges between Ti^{2+} and Ti^{3+} and that between Ti^{3+} and Ti^{4+} are 1.0 and 2.0 eV, respectively. Further, one would expect the ratio of L_3 to L_2 to be of the order of 2/1 because there are four electrons in $2p^{3/2}$ and two electrons in $2p^{1/2}$ [5]. But in practice, these vary not only with the atomic number but, as we found out, also with the valence state. Fig. 2 shows $L_{2,3}$ loss edges for Fe^{2+} and Fe^{3+} valence states.

In order to determine the valence state of titanium in a compound, we just have to compare the position L_3 and $\Delta L_{2,3}$ and the shape of the $L_{2,3}$ loss edges of

0022-2461 © *1992 Chapman & Hall*

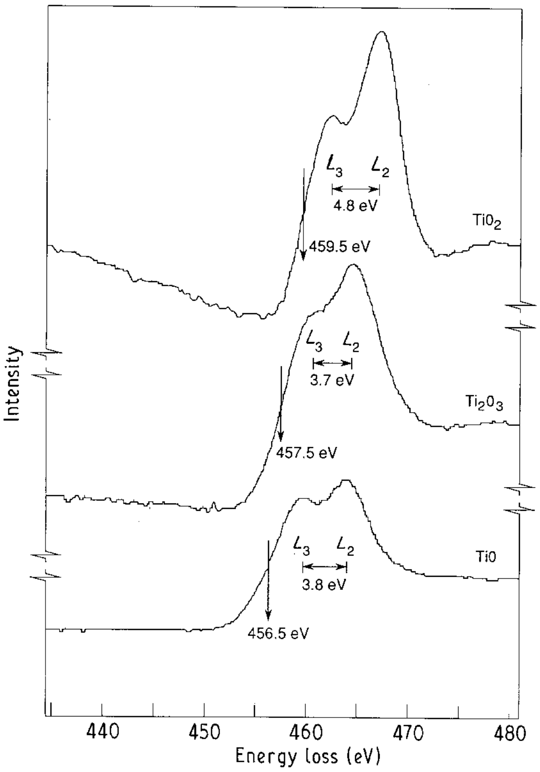

Figure 1 $L_{2,3}$ loss edges of Ti^{2+} in TiO, Ti^{3+} in Ti_2O_3 and Ti^{4+} in TiO_2.

titanium in this compound with the corresponding features of the spectra given in Fig. 1. A similar comparison for the iron loss edges can also be done with Fig. 2. In order to check our standardization methods, we took two samples in which the valence states of the constituting elements have been well established. The first one, Ulvospinel ($Fe^{2+}[Ti^{4+}Fe^{2+}]O_4$), has an inverse spinel structure in which Fe^{2+} occupies both tetrahedral and octahedral sites and Ti^{4+} occupies the octahedral sites [6]. The second one, the zinc ferrite ($ZnFe_2O_4$), has a normal spinel structure with iron occupying the octahedral sites in the Fe^{3+} state.

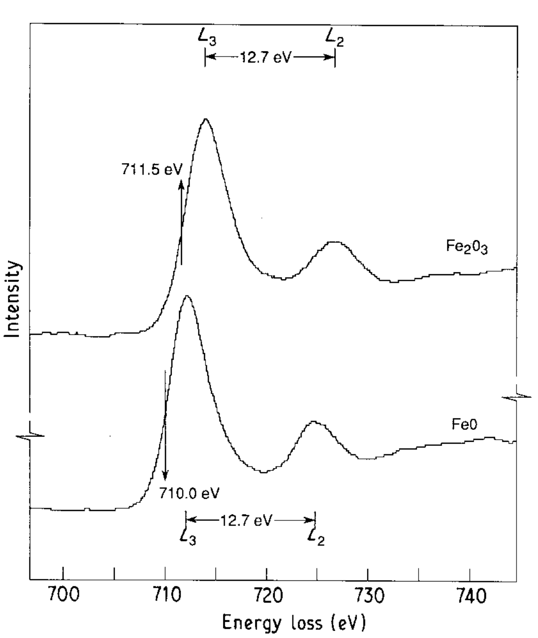

Figure 2 $L_{2,3}$ loss edges of Fe^{2+} in FeO and Fe^{3+} in Fe_2O_3.

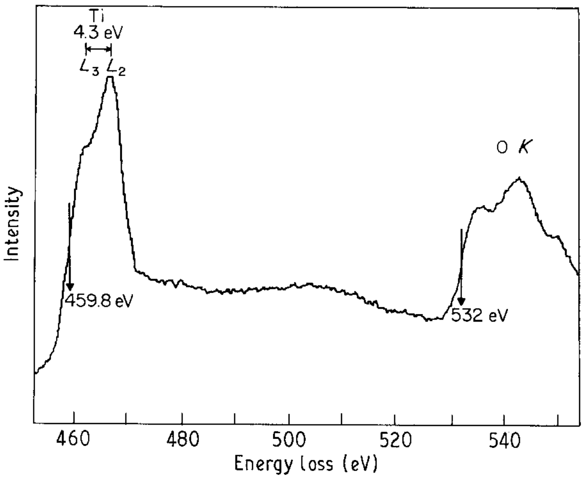

Figure 3 Ti^{4+} $L_{2,3}$ and O K loss edges in Fe_2TiO_4.

The Ti $L_{2,3}$ along with O K loss edges of Fe_2TiO_4 are shown in Fig. 3. The position of the titanium loss edge is calibrated by taking the O K peak at 532 eV as an internal standard, as mentioned earlier. Similarly the Fe $L_{2,3}$ loss edge in Fe_2TiO_4 is also determined and the results are given in Table I. The comparison of the results do, in fact, indicate that the valence state of titanium is 4 and that of iron is 2. Similar conclusions can be drawn for Fe^{3+} in $ZnFe_2O_4$ as shown in Table II.

3. Conclusion

A procedure is given above to determine the valence states of titanium and iron using EELS which is a good alternative method of establishing the valence states. This method, in general, can be extended to the other elements and can be very useful for ceramic materials. Quantitative information can also be obtained by comparing the integrated intensities of the $L_{2,3}$ loss edges of the element whose composition and valence state are known, with those of the unknown, provided the spectra are obtained under identical conditions.

TABLE I Comparison of the results for Ti^{4+} and Fe^{2+} in Fe_2TiO_4 with those of Ti^{4+} in TiO_2 and Fe^{2+} in FeO

	Ti^{4+} in Fe_2TiO_4	Ti^{4+} in TiO_2	Fe^{2+} in Fe_2TiO_4	Fe^{2+} in FeO
L_3 (eV)	459.8	459.5	709.5	710.0
$\Delta L_{2,3}$ (eV)	4.3	4.8	12.8	12.7

TABLE II Comparison of the results for Fe^{3+} in $ZnFe_2O_4$ with those of Fe^{3+} in Fe_2O_3

	Fe^{3+} in $ZnFe_2O_4$	Fe^{3+} in Fe_2O_3
L_3 (eV)	711.5	711.5
$\Delta L_{2,3}$ (eV)	13.1	12.7

Acknowledgement

The authors thank Professor H. Sato, School of Materials Engineering, Purdue University, for many helpful discussions throughout this project, and Dr Z. Kakol, Department of Chemistry, Purdue University, for providing Fe_2TiO_4 single crystals. M. Sankararaman thanks the Purdue Research Foundation for the financial assistance through the David Ross Fellowship.

References

1. R. D. LEAPMAN, L. A. GRUNES and F. J. FEJES, *Phys. Rev. B* **26** (1982) 614.
2. M. T. OTTEN, B. MINER, J. H. RASK and P. R. BUSECK, *Ultramicroscopy* **18** (1985) 285.
3. R. F. EGERTON, in "Electron Energy-Loss Spectroscopy in the Electron Microscope" (Plenum Press, New York, 1986).
4. J. TAFTO and O. L. KRIVANEK, *Phys. Rev. Lett.* **48** (1982) 560.
5. D. H. PEARSON, B. FULTZ and C. C. AHN, *Appl. Phys. Lett.* **53** (1988) 1405.
6. R. H. FOSTER and E. O. HALL, *Acta. Crystallogr.* **18** (1965) 859.

Received 22 January
and accepted 7 June 1991