

Analysis of Ni/Co/Mn alloy using an automated monochromated Ag L α X-ray source

Keywords

Ag monochromator, dual anode, high energy X-rays

Application Note MO405(1)

Further application/technical notes are available online at: www.kratos.com

Overview

Overlapping photoelectron lines and Auger features are a common problem in analysis of complex materials. The standard approach of switching to an achromatic Mg X-ray source is sometimes undesirable due to the introduction of X-ray satellites into the spectrum. In this example we show how Kratos' automatic monochromated Ag L α X-ray source may be used to excite a satellite free spectrum and allow unambiguous determination of the oxidation state of a Ni/Co/Mn alloy.

Introduction

XPS is widely used for the analysis of complex materials, allowing the quantitative determination of surface chemical species. Surface analysis of metal compounds and alloys is an important applications area. One of the most useful aspects of XPS analysis of these materials is the opportunity to quantify the surface species and investigate the oxidation state of the metals. Unfortunately this type of analysis is often compromised by the presence of overlapping photoelectron lines and Auger features in the spectrum, a relatively common occurrence when the alloy has several different metallic components.

One such example is the XPS analysis of a Ni/Co/Mn alloy. The Al K α monochromatic high resolution Co 2p and Mn 2p spectra are displayed in Figures 1 and 2. These spectra are unfortunately complicated by Co and Ni Auger lines which overlap strongly with the photoelectron peaks. The Auger features make accurate quantification of the surface composition difficult. Furthermore, the presence of the Auger lines may lead to an erroneous assignment of the Co and Mn surface oxidation state.

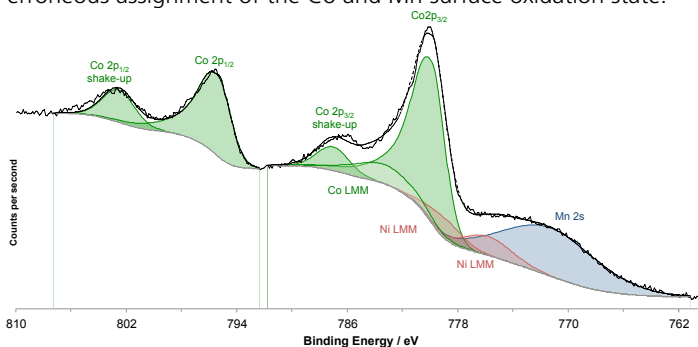


Figure 1: Co 2p Spectrum recorded using the Al monochromatic X-ray source.

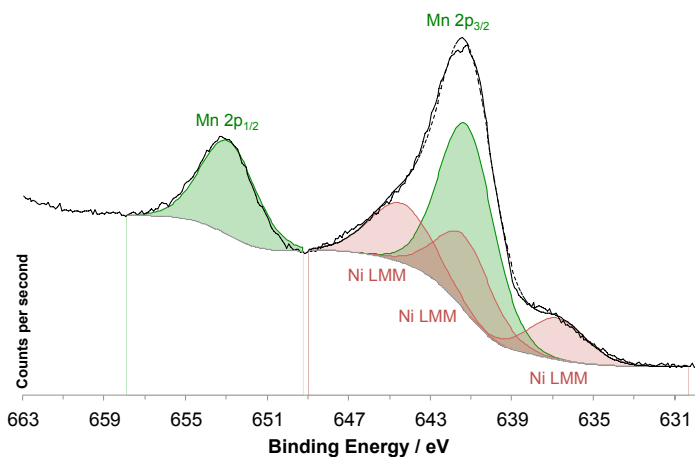


Figure 2: Mn 2p Spectrum recorded using the Al monochromatic X-ray source

The standard method to alleviating the problem of overlapping Auger and photoelectron lines is to change to a different X-ray source. Many instruments are fitted with achromatic Al and Mg dual anode X-ray sources in addition to the Al monochromatic source. It is a simple matter to switch from the Al monochromatic X-ray source (1486.6 eV) to the Mg achromatic X-ray source (1253.3 eV). This will move the Auger lines 233 eV relative to the photoelectron lines. However, a major drawback to this approach is the introduction of X-ray satellites which are intrinsic to all achromatic sources.

Mg $K\alpha_3$ and Mg $K\alpha_4$ X-ray satellites are 8.4 and 10.1 eV respectively lower in binding energy than Mg $K\alpha_{1,2}$. Together they produce a peak with approximately 12% of the intensity of the Mg $K\alpha_{1,2}$ peak. Unfortunately this magnitude of splitting ensures that Mg $K\alpha_{3,4}$ satellites from many $2p_{1/2}$ lines overlay with $2p_{3/2}$ lines. For example, the Mn 2p splitting is 11.7 eV which is low enough to place the Mg $K\alpha_{3,4}$ satellites from the Mn $2p_{1/2}$ line under the Mn $2p_{3/2}$ peak envelope.

Experimental

A solution to these problems is to record the spectra using Kratos' Ag monochromatic X-ray anode. This source generates monochromated Ag L α X-rays at 2984.2 eV. The Ag $3d_{5/2}$ line recorded using Al and Ag X-rays is shown below, Figure 3.

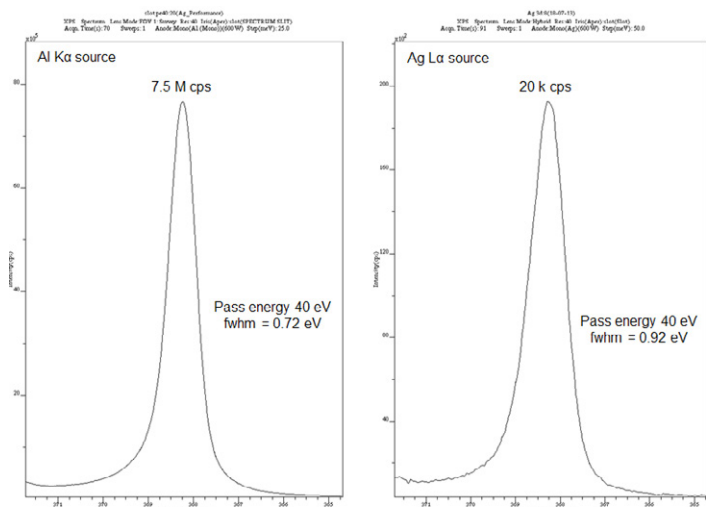


Figure 3: Comparison of the Ag $3d_{5/2}$ spectrum recorded using the Al (left) and Ag (right) monochromatic X-ray source.

The Co 2p and Mn 2p spectra recorded using the Ag monochromatic X-ray source are displayed in Figures 4 and 5.

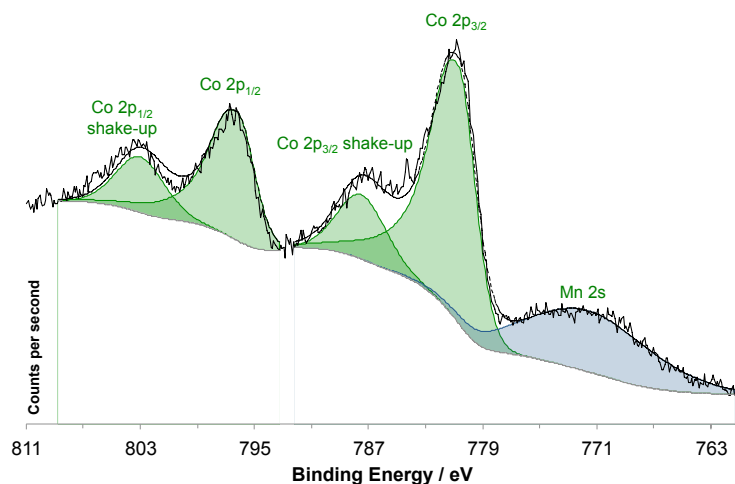


Figure 4: Co 2p Spectrum recorded using the Ag monochromatic X-ray source.

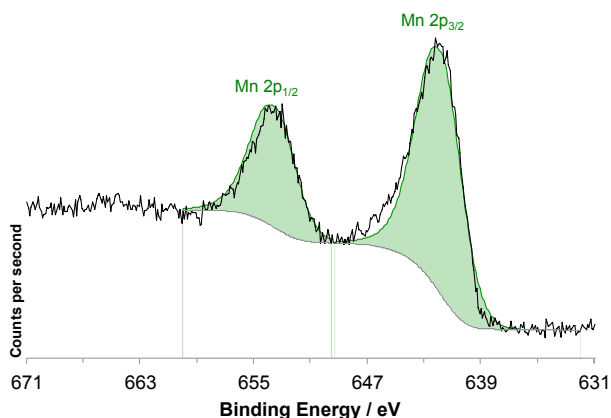


Figure 5: Mn 2p Spectrum recorded using the Ag monochromatic X-ray source.

These spectra are significantly less complex when excited by Ag L α X-rays due to the displacement of the Auger lines. This is illustrated by direct side by side comparison of the Mn 2p spectra recorded with Al and Ag monochromatic sources, Figure 6. This is achieved without the introduction of X-ray satellites. Auger removal leads to spectra which are easier to interpret.

The Mn 2p spectrum now obviously consists of a single chemical component with a Mn $2p_{3/2}$ peak position of 641.0 eV. This is characteristic of MnO with Mn in the +2 oxidation state. Analysis of the Ag mono excited Co 2p spectrum also reveals a single Co chemical component with a Co $2p_{3/2}$ peak position of 780.5 eV. This is characteristic of CoO with Co also in the +2 oxidation state.

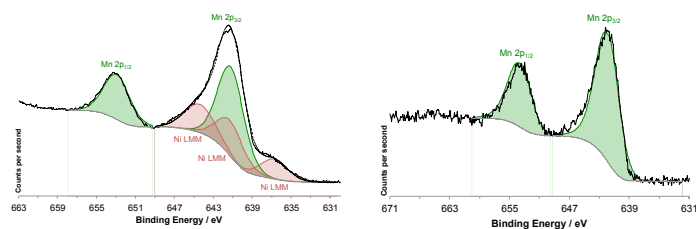


Figure 6: Comparison of the Mn 2p Spectrum recorded using the Al (left) and Ag (right) monochromatic X-ray source.

Selecting the appropriate X-ray anode is simple. The AXIS Supra instrument switches between Al and Ag X-ray lines simply at the click of a mouse. The process is fully automated using the Supra's motorised X-ray monochromator (WX-631) and optional motorised dual anode (Al/Ag) X-ray source (WX-635).

The motorised X-ray source is fitted with an anode which is 2/3 coated with Al and 1/3 coated with Ag. When changing from Al K α to Ag L α excitation motors move the anode relative to the filament such that X-rays are generated from the Ag portion of the anode.

As previously mentioned, Ag L α X-rays have an energy of 2984.2 eV which corresponds to a wavelength of 4.1544 Å. This is approximately half the wavelength of Al K α X-rays. Therefore the same quartz crystal used to monochromate Al K α X-rays may also be used for Ag L α via a 2nd order diffraction after appropriate adjustment of the anode and X-ray mirror position. The AXIS Supra's motorised X-ray mirror is automatically driven to the optimum position for the Ag L α X-rays by the ESCAPE data-system.

Conclusion

In conclusion the complex spectra recorded from the surface of the Ni/Co/Mn alloy using Al monochromatic excitation may be greatly simplified by switching to Ag monochromatic X-rays. This is achieved without the addition of unwanted X-ray satellite lines produced by all achromatic sources. The recorded spectra now allow correct interpretation of the surface chemistry of the alloy.

The dual Al/Ag X-ray source provides an easy to use additional monochromated X-ray line for routine analysis. This higher energy line can excite core levels which cannot be reached with Al, such as Si and Al 1s (see figure 9 for more examples), or, as in this example, used to simplify spectra for easy quantification of surface species.

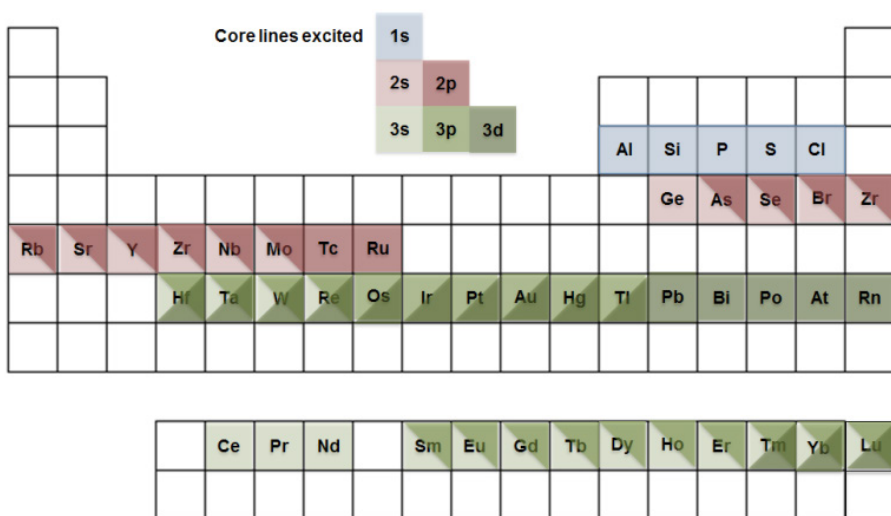
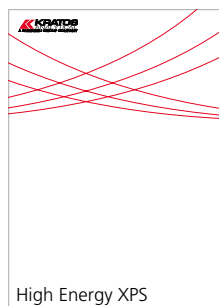


Figure 7: Additional core levels excited using Ag L α X-ray lines which are not accessible using Al K α .

Related documents available online:



[Click to download](#)