XPS and AES of Beryllium and Beryllium Oxide

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Introduction

Beryllium is a metal with unusual properties that are exploited for certain highly specific applications across a wide range of technologies. Examples are found in the use of copper beryllium alloys, where some 2% gives hardness and a spring function to copper, whilst retaining its good thermal and electrical conductivity[1]. These properties are utilised in tools for mining applications, where the spark free behaviour is of particular value. At low levels in magnesium it can give resistance to high temperature oxidation, as was exploited in the Magnox alloy used to clad uranium in the first series of commercial nuclear power plants in the UK[2]. Its use in unalloyed form is most usually encountered in windows for x-ray detectors, e.g. in EDX energy analysers. As a window it has excellent transmission combined with high strength as required for a vacuum component. Its high rigidity, low density and low coefficient of expansion has made it ideal for components in mirrors intended to operate in space[3]. The Be^{2+} ion is strongly polarising because of its small radius, and thus has a strong influence on the structure of minerals in which it is found. In the silicates, such as beryl, this action stabilises a cyclo-silicate ring structure, a highly strained structure that gives the silicon ion one of the lowest Auger parameter values found in the aluminosilicates[4]. In spite of such a wide range of use, there are almost no published XPS spectra of Be or of BeO[5,6]. While there are AES spectra available describing the oxidation of beryllium[7], there are no published spectra of bulk BeO.

In this work we have attempted to provide this data using commercially available samples of both the metal and the oxide. The metal is contaminated with low levels of impurities that are not thought to have had an impact on the resulting spectra. However, because of its high reactivity Be metal often carries an oxide film ~3 nm thick[8] which is highly significant in XPS analysis. Unfortunately the oxide, particularly in dust form, is highly toxic and thus the surface cannot be repolished under conditions found in a typical metallographic laboratory. We have provided here the *KLL* Auger peaks of both Be and BeO as collected by XPS as well as the Be *KLL* collected from freshly scribed beryllium in vacuum, the native oxide film and bulk beryllium oxide.
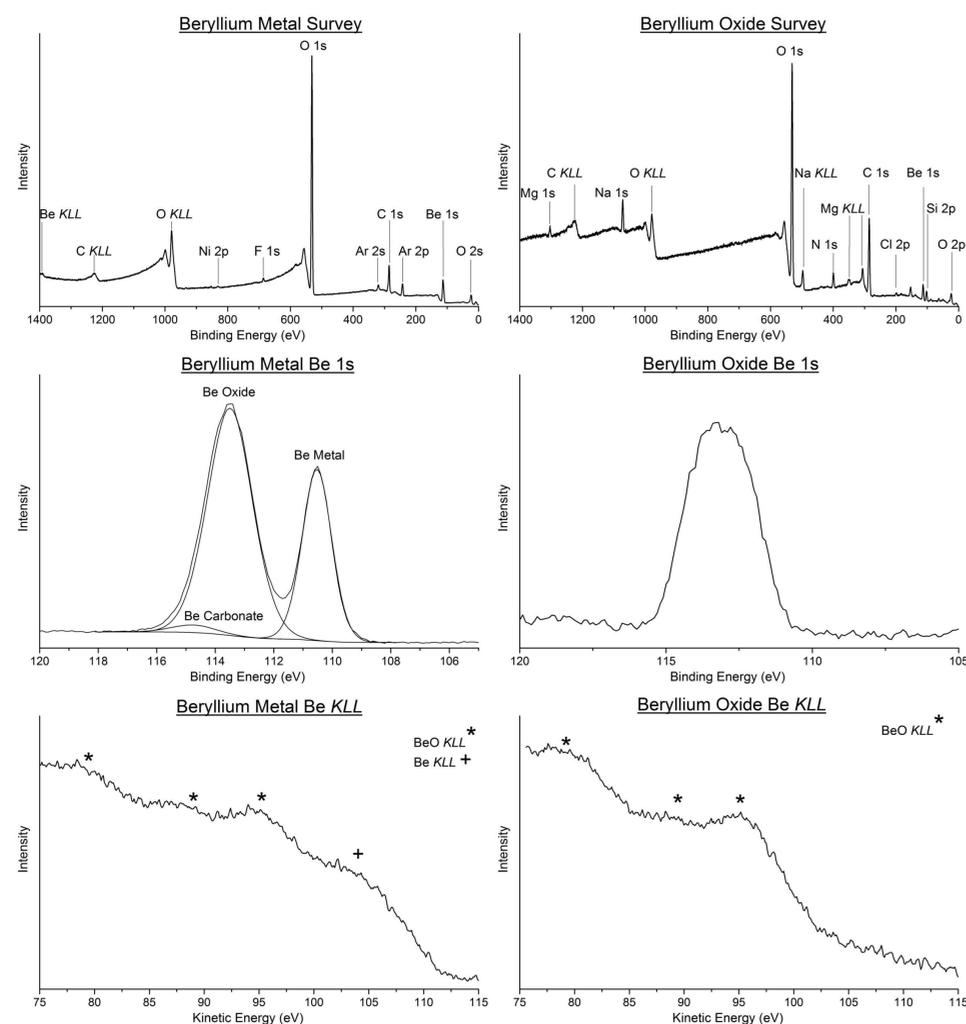
Experimental

25 x 25 x 1 mm samples of beryllium metal (99 %) and beryllium oxide (99.5 %) were purchased from Goodfellows and analysed using X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES).
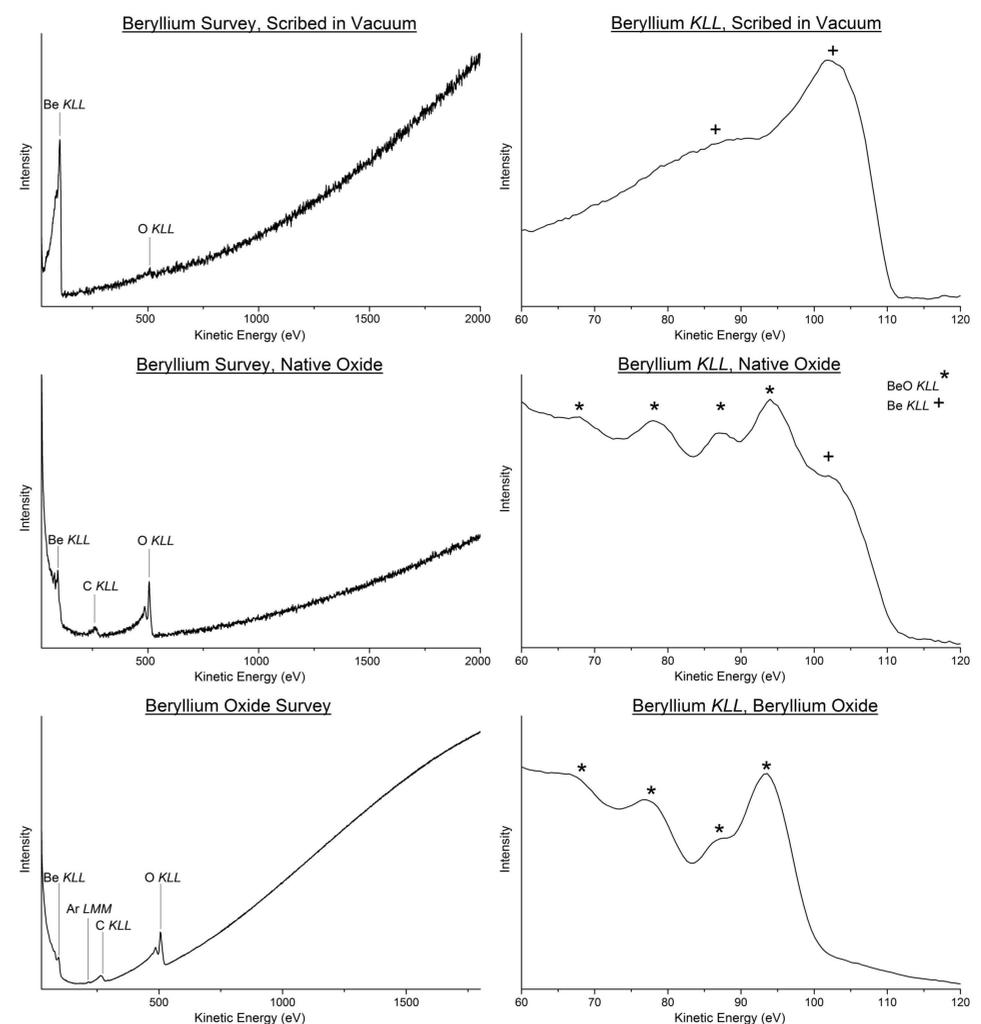
XPS: Survey spectra, as well as high resolution spectra of Be 1s and Be *KLL,* are presented. Spectra were collected on a Thermo Scientific Theta Probe using monochromatic Al Kα radiation. Pass energies of 300 and 80 eV were used for the survey, Be *KLL* and Be 1s spectra respectively. Beryllium oxide was analysed using electron and argon ion charge compensation. A charge shift of -1.3 and +1.1 eV was applied to the metal and oxide respectively, to align adventitious carbon to 285 eV. An energy step size of 0.1 and 0.3 eV for high resolution and survey spectra were used. The electron take of angle was 53° from the sample normal with an acceptance angle of ±30°.

AES: As received beryllium, beryllium scribed in vacuum and bulk beryllium oxide were analysed by AES using a Thermo Scientific Microlab 350. Survey spectra as well as high resolution Be *KLL* spectra have been presented. Spectra from the metal were collected with beam energy of 10 kV, sample current of 1.1 µA, energy step size 0.5 eV and a retard ratio of 4. Spectra from the oxide were acquired by tilting the sample to near vertical (~85°) and reducing the beam energy to 2.5 kV. Tilting to this extreme lowers the electron take-off angle to 35° from the sample normal with an acceptance angle of ±25°.

XPS Spectra

Beryllium Metal Survey

Beryllium Oxide Survey

Beryllium Metal Be 1s

Beryllium Oxide Be 1s

Beryllium Metal Be *KLL*

Beryllium Oxide Be *KLL*

AES Spectra

Beryllium Survey, Scribed in Vacuum

Beryllium *KLL*, Scribed in Vacuum

Beryllium Survey, Native Oxide

Beryllium *KLL*, Native Oxide

Beryllium Oxide Survey

Beryllium *KLL*, Beryllium Oxide

Results and Discussion

As-received beryllium and beryllium oxide were analysed by XPS and AES. Additionally beryllium metal was scribed in vacuum and analysed by AES. Survey spectra together with high resolution spectra were acquired in XPS and AES mode and are presented here. The binding energies of the beryllium and the beryllium oxide Be 1s peaks were found to be 110.5 and 113.4 eV respectively, as collected by XPS. A small beryllium carbonate peak is also present at 114.7 eV. The kinetic energies of the primary metal and oxide *KLL* Auger transitions were found to be 103.0 and 93.6 eV respectively, as collected by AES. Three loss peaks are also observed at 87.1, 78.0 and 67.2 eV in the AES spectrum of beryllium oxide. The oxide layer on beryllium metal could not be reliably removed using argon etching for Auger analysis. Therefore, oxide free spectra were collected by scribing the surface with the end of a wobble stick and performing analysis on the exposed region. During AES analysis gradual oxidation and trace carbon deposition were observed. Together with the an oxide component the metal shows a peak expected for a carbonate and its presence was confirmed by examination of the C 1s peak. This probably originates from air exposure during transport.

Conclusions

Analysis of beryllium and beryllium oxide was completed using XPS and AES. The very low kinetic energy of the Be *KLL* Auger transition requires the surface to be moderately clean. The surface oxide on beryllium heavily influences the structure of the beryllium Auger transition. For the first time bulk beryllium oxide has been successfully analysed using AES. All spectra and raw data from this investigation are to be published in the archival journal Surface Science Spectra.

Further work

Knowledge gained during this work will be used to study chloride induced pitting corrosion in beryllium. The high spatial resolution of AES will be utilised to characterise intermetallic particles and their associated corrosion pits. XPS will be used to identify the possible corrosion products, with the aim of the work to explore the exact corrosion mechanism.

Acknowledgments

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