The chemical state plot for beryllium compounds

Christopher F. Mallinson^{*1}, James E. Castle¹, John F. Watts¹

¹*The Surface Analysis Laboratory, Department of Mechanical Engineering Sciences,
University of Surrey, Guildford, Surrey, GU2 7XH, UK,*

**c.mallinson@surrey.ac.uk*

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Abstract: Herein we report the construction of a Wagner chemical state plot for beryllium containing the: metallic, oxide, nitride and carbide forms of beryllium by combining electron beam induced AES and XPS data. AES and XPS values were collected from metallic beryllium mechanically abraded in vacuum, bulk and native beryllium oxide and homogeneous secondary-phase beryllium nitride and beryllium carbide inclusions. XPS data for beryllium nitride and carbide were obtained from the literature.

The concept of the Auger parameter was introduced by Wagner [1] in order to extract further information from the Auger and photoelectron transitions present in the XPS spectrum. The Auger parameter, α , was originally defined as shown in Equation 1:

$$\alpha = E_K(jkl) + E_K(i) \quad (1)$$

Where $E_K(jkl)$ is the kinetic energy of the Auger transition and $E_K(i)$ is the kinetic energy of the photoelectron line. This occasionally led to negative values and so a modified Auger parameter, α^* , was introduced, which is shown in Equation 2:

$$\alpha^* = \alpha + hv = E_K(jkl) + E_B(i) \quad (2)$$

Where hv is the kinetic energy of the exciting x-ray photon and $E_B(i)$ is the binding energy of the photoelectron.

By combining the binding energy of the photoelectron transition and the kinetic energy of the Auger transition, in the form of the modified Auger parameter, an empirical measurement is made that is unique for each chemical state. The modified Auger parameter is combined with the kinetic and binding energy values in a graph known as a Wagner chemical state plot. The Auger parameter can be particularly helpful in the analysis of insulating samples as the peak separation is constant and independent of charging.

Previous surface analysis investigations have been carried out on thin films of beryllium nitride and beryllium carbide grown in vacuum. While these have not reported Auger kinetic energies they have reported photoelectron binding energies. The XPS carried out on nitride films showed Be1s binding energies of: 114 eV Be₃N₂ and 113.7 eV BeO [2]. XPS on the carbide films reported binding energy values of: 112.1 eV Be₂C and 111.3 eV for Be [3].

The Be1s literature values for Be₂C and Be₃N₂ were then referenced to metallic beryllium and beryllium oxide at 110.5 and 113.5 with shifts of -0.2 and -0.8 eV respectively, resulting in Be₃N₂ and Be₂C Be1s binding energy values of 113.8 and 111.3 eV respectively. In turn the Be and BeO 1s values were charge referenced to carbon at 285.0 eV [4].

AES data was collected from beryllium carbide and beryllium nitride inclusions [5]. Beryllium carbide is a good insulator and so the sample was tilted to a near vertical 80° from its usual horizontal analysis position, the primary beam energy was also reduced from 10 kV to 3 kV. The same analysis conditions have been used for the study of bulk beryllium oxide [6]. Beryllium nitride inclusions were found to be good conductors showing no signs of charging during imaging and so the spectra were believed to be free from sample charging. The signal to noise for the oxide and carbide spectra is significantly improved compared to the metal and the nitride spectra. This is a consequence of the increased electron beam spot size at the sample surface when the sample is tilted and the lower beam energy bringing the electron cascade closer to the sample surface.

By combining the previously collected AES and XPS data, as well as the Be 1s binding energy values for beryllium nitride and carbide from the literature, it is possible to construct Wagner chemical state plot for beryllium and its compounds; this is shown in Figure 1. The data used to calculate the values in the plot are shown in Table 1.

Figure 1 Wagner chemical state plot for beryllium.

In addition to the Wagner chemical state plot the shift in the kinetic energy of the Be *KLL* Auger transition with changing chemical state is highlighted in Figure 2 which shows the high resolution Auger spectra from the four beryllium forms.

Figure 2 High resolution AES spectra from all forms of beryllium investigated.

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Table 1 Auger and photoelectron peak energy values for the four beryllium materials

Material	Be KLL (KE, eV)	Be 1s (BE, eV)	Modified Auger parameter α^* (eV)
Be	103.0	110.5	213.5
Be ₂ C	100.4	111.3	211.7
Be ₃ N ₂	96.7	113.8	210.5
BeO	93.7	113.5	207.2