MICRO-XRF ON SEM

Analysis of a certified copper alloy with micro-XRF on SEM

Application Note # MXRF-SEM-03

Introduction

Copper alloys have found widespread application in various fields. The elemental composition determines the properties of the alloys and consequently their application. Therefore, knowing the composition of a copper alloy is very important.

Metrological institutes like the BAM (German Federal Institute for Materials Research and Testing) offer reference materials that can be used to prove the accuracy of the applied analysis method.

The aim of this application note is to demonstrate how Micro-X-ray fluorescence spectroscopy (micro-XRF) expediently supplements the analysis of copper alloys by using Bruker's micro-focus X-ray source XTrace attached to a scanning electron microscope (SEM) and operating with an energy dispersive spectrometer.

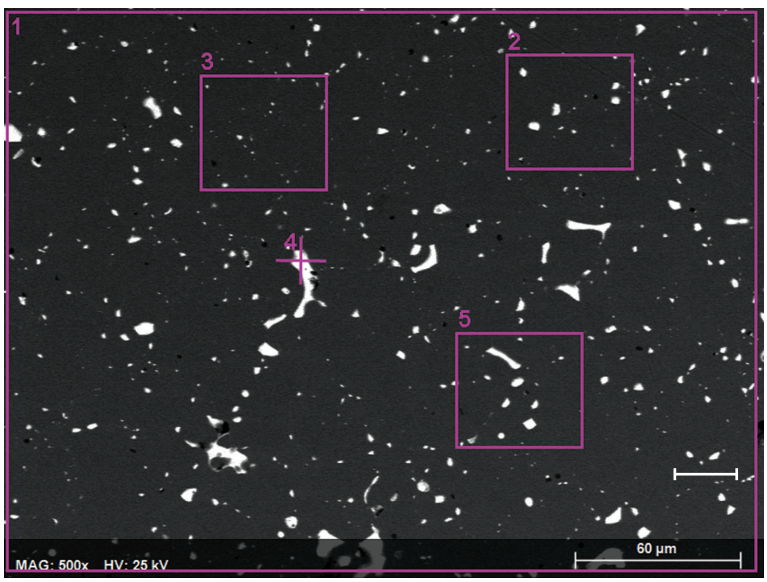

Figure 1
SEM image (BSE) of the polished ERM® -EB375 specimen. The pink squares and the crosshair display the areas analyzed with EDS.

Sample

This application note presents the micro-XRF results achieved for the CuZn39Pb3 alloy (ERM®-EB375, BAM). Certified mass fractions are shown in Table 1. Additionally, the certificate gives further 10 elements in the 100 ppm (mg/kg) mass fraction range.

Measurement conditions

For the analysis, a SEM was equipped with a Bruker QUANTAX system consisting of XTrace, a focused X-ray photon source with a Rh anode, and a 30 mm² active area silicon drift detector XFlash® 6I30 with an energy resolution of 123 eV for Mn Kα.

The SEM was used for electron excitation, whereas the XTrace was used for photon excitation. The XFlash® SDD detects X-rays generated by both sources, electron and photon excitation.

EDS spectra were measured with 25 kV and 300 s live time. Micro-XRF spectra were acquired at 50 kV, 600 µA and 10 s real time and 300 s live time.

Results

SEM/EDS characterization

Figure 1 shows a BSE image of the polished specimen. The sample is inhomogeneous and does not fulfill the requirements for an EPMA (electron probe micro analysis) reference material which are defined in the standard ISO 14595.

Figure 2 shows the EDS spectra of the highlighted areas in Figure 1. The inhomogeneity of the sample results in disparities of acquired spectra and quantification. Besides the three main elements Cu, Zn and Pb; Ni, Fe, and Sn were detected as low concentration elements.

Micro-XRF analysis

Due to the inhomogeneity of the specimen, XRF is more appropriate to determine the alloy's mean composition than EDS, since XRF considers a larger volume of the specimen. Figure 3 shows the spectra measured with 300 s live time at different specimen tilt angles to change refracting lattice planes.

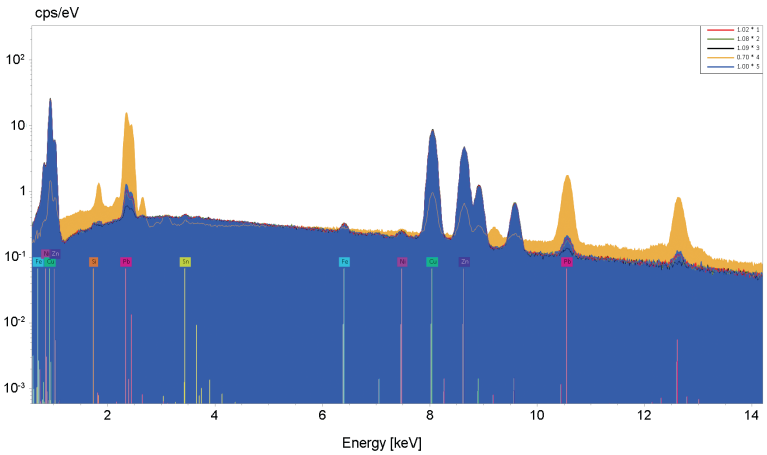

Figure 2
Logarithmically plotted EDS spectra of the 5 analyzed positions shown in Figure 1. The difference in the intensities is visible.

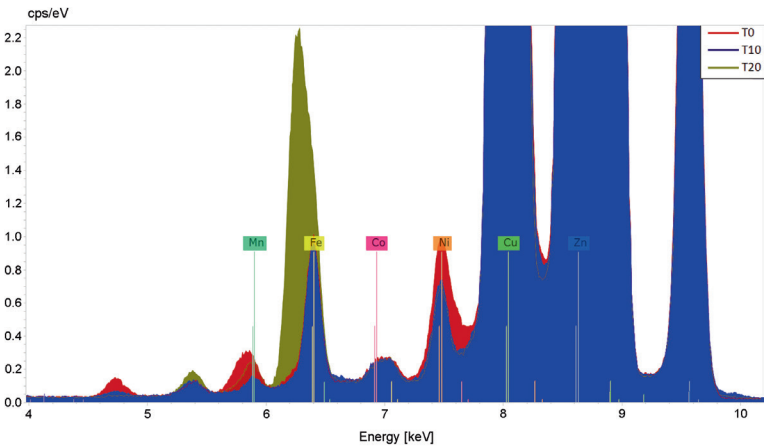

Figure 3
Micro-XRF spectrum of ERM® -EB375 measured at tilt angles of 0°, 10°, and 20°. Unlabeled peaks are diffraction peaks.

The crystalline nature of the specimen causes diffraction reflexes in the spectrum that overlap the characteristic X-ray lines. These diffraction reflexes do not allow to determine the intensity of Mn, Fe, Co and Ni-K lines.

XTrace provides a filter wheel that contains three primary filters made of metal foils. They are placed between X-ray source and sample to suppress diffraction peaks. A 15 µm thin Ti filter was used to suppress the diffraction reflexes above the Ti-K edge at 4.964 keV. The corresponding spectrum is shown in Figure 4. The peak deconvolution result of this spectrum given in Figure 5 shows how easy it is to detect elements without diffraction peaks.

	Cu	Zn	Pb	Fe	Ni	Sn	Mn	Co
Measured mean value	59.306 ± 0.528	37.790 ± 0.267	2.394 ± 0.599	0.202 ± 0.018	0.111 ± 0.010	0.185 ± 0.073	0.007 ± 0.004	0.006 ± 0.004
Certified value	58.32 ± 0.050	38.02 ± 0.080	2.90 ± 0.030	0.207 ± 0.004	0.1053 ± 0.0015	0.20932 ± 0.00240	0.0222 ± 0.0002	0.01964 ± 0.00028

Table 1
Measured and certified values in mass% normalized with standard deviations for the elemental composition of ERM®-EB375. The 30 spectra were acquired on different sample areas using the ESPRIT 2 object mode with image extension.

	Cu	Zn	Pb	Fe	Ni	Sn	Mn	Co
Analysis 1	58.758	37.812	2.938	0.210	0.111	0.158	0.008	0.005
Analysis 2	59.018	38.198	2.210	0.206	0.126	0.231	0.007	0.004
Analysis 13	60.353	37.837	1.328	0.207	0.099	0.167	0.005	0.004
Analysis 25	58.441	37.342	3.756	0.192	0.122	0.129	0.012	0.0.006

Table 2
Measured values in mass% normalized of four exemplary micro-XRF analyses for the elemental composition of ERM®-EB375.

Taking into account the sample's inhomogeneity, 30 micro-XRF point spectra were acquired on various sample areas using the ESPRIT 2 object mode with image extension to cover a large area. The acquisition time for each spectrum was 10 seconds. A standardless fundamental parameter method was used for quantification.

Table 1 displays mean value and standard deviation of the quantification results for these point spectra in comparison to the certified values. The quantification results are in agreement for most elements. Co and Mn could only be identified by using micro-XRF, since its concentration is below the limit of detection (LOD) of EDS. Even for micro-XRF, an inhomogeneity of the element Pb was determined. The quantification result of Pb varies between 1.328 and 3.756 mass% and, therefore, also the Cu and Zn content is variable.

Table 2 shows the quantification results of four spectra out of 30, which have been obtained on different sample positions. These four spectra show the broad variation in the concentrations of Pb, Cu and Zn.

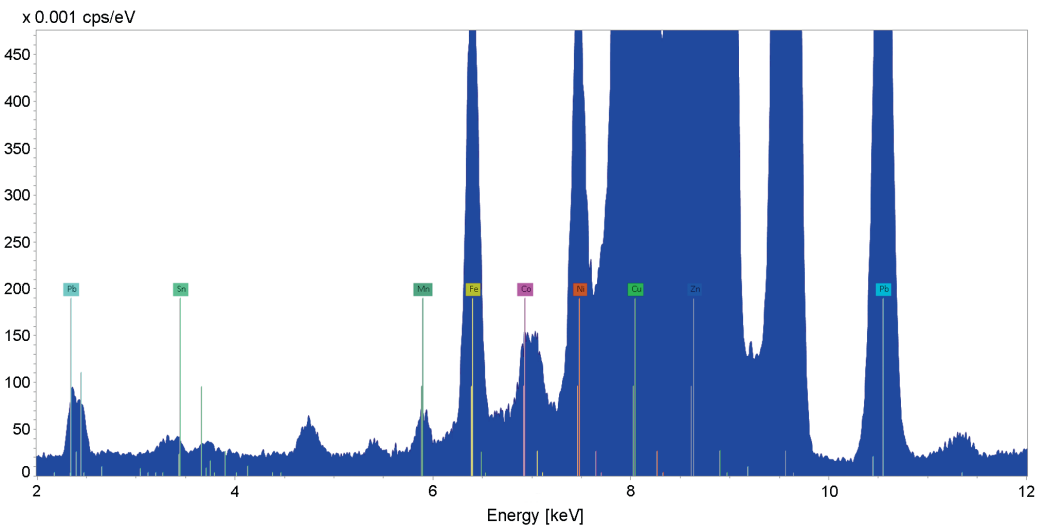

Figure 4
Micro-XRF sum spectrum calculated out of 30 spectra measured with a 15 µm Ti filter.

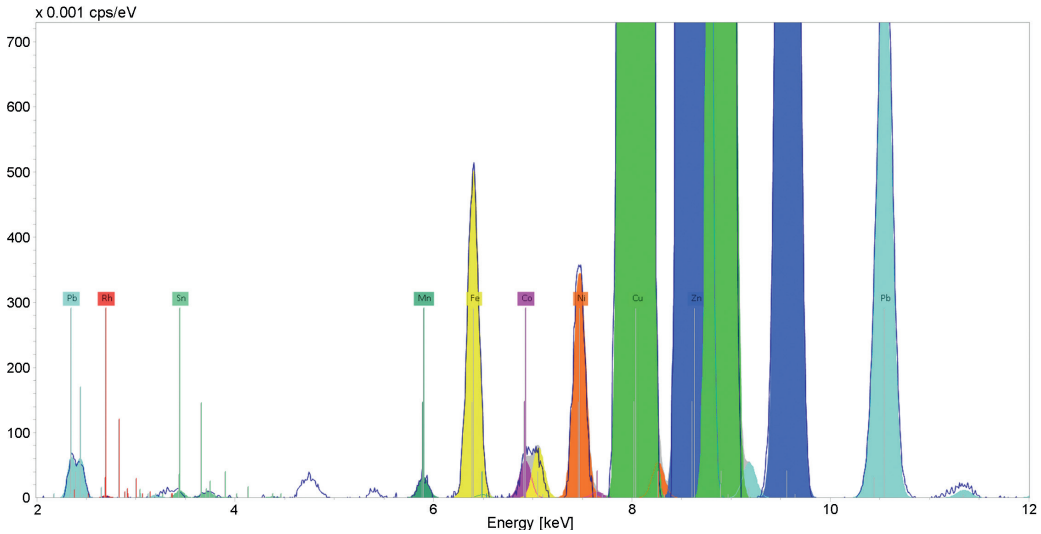

Figure 5
Deconvolution result of the micro-XRF spectrum in Figure 4. Unlabeled peaks are diffraction peaks.

Conclusion

The accuracy of micro-XRF analysis with XTrace has been proven for the copper alloy ERM®-EB375 (CuZn39Pb3). The results for the elements Mn, Co, Ni, and Sn show only a small deviation from the certificated values, which is acceptable for most applications. Despite the large variation in the Pb content of the single analyses, its mean value is close to the certified value. The elements Co and Mn could only be detected by using micro-XRF. Their concentrations are below the LOD of EDS, which is 1000 ppm (0.1 mass%).

The application of primary filters helps suppress diffraction reflexes in X-ray fluorescence spectra and allows to determine the intensity of elements, whose peaks would be otherwise overlapped by diffraction peaks.

The new ESPRIT 2 software function Image extension was very helpful when analyzing the inhomogeneous copper alloy sample by acquiring different point spectra over a large area.

Using the low detection limit of micro-XRF with the high spatial resolution of electron excitation proved to be a very powerful combination to characterize the specimen.

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