XTrace

Quantification results

Micro-XRF spectrum

Application Note # MXRF-SEM-05

Analysis of molybdenum in alloy steels

The addition of heavy metals is essential for the mechanical and thermal properties of alloy steels. In most cases, the low concentration of these elements can be determined by electron microprobe analysis or by optical analysis methods. In laboratories where only SEM/EDS is available, the analysis becomes challenging due to the

- insufficient detection limit
- line overlapping in the low energy range
- specimen inhomogeneity.

The determination of the molybdenum content in alloy steels is a typical example for this situation. Only if the molybdenum content exceeds 1 mass%, the intensity of the Mo-L line is sufficient for an accurate EDS analysis. To determine lower molybdenum contents other techniques are required.

The aim of this application note is to demonstrate how Micro-X-ray fluorescence spectroscopy (micro-XRF) can considerably improve the determination of the molybdenum content in alloy steel. Bruker's QUANTAX Micro-XRF on SEM system with the micro-focus X-ray source XTrace and an XFlash® energy dispersive detector is an ideal choice for this analytical task.

Sample

This application note presents the results for EDS and micro-XRF analyses of three samples with different molybdenum contents:

- Sample 1 - high alloy steel CRM JK 37
- Sample 2 - high alloy steel 1.4548 (X5CrNiCuNb17-4-4)
- Sample 3 - low-alloy steel 1.7792 (58CrMoV4).

Sample 1 has with 3.55 mass% the highest Mo content, followed by sample 2 with < 0.6 mass% and sample 3 with the lowest molybdenum content of < 0.25 mass%. The certified mass fractions of all determined elements are displayed in Table 1–3.

Measurement conditions

All presented results were obtained using a QUANTAX Micro-XRF system consisting of an SEM equipped with XTrace, the focused X-ray photon source with a Rh anode, and XFlash® 6 | 30, a 30 mm² active area silicon drift detector (SDD) with an energy resolution of 123 eV for Mn Kα.
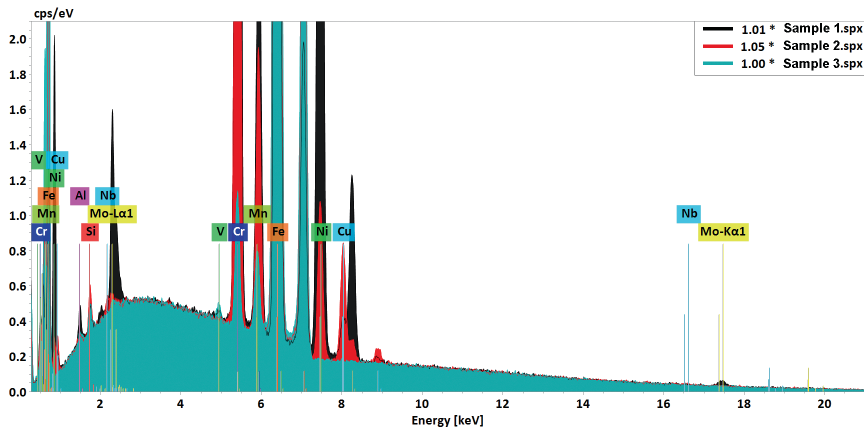
EDS spectra of the alloy steels

Fig. 1 EDS spectra of the three analyzed steel samples. The differences in the intensities of Mo-K and Mo-L lines are visible for each spectrum.

The SEM was used for electron excitation, whereas XTrace was used for photon excitation. The XFlash® 6 I 30 SDD detects X-rays generated by both sources.

The EDS spectra were measured with 30 kV and 200 s real time with an input count rate of ~ 11 kcps. Micro-XRF point analyses were acquired on different sample areas at 50 kV, 600 µA and 25 s real time using the Object mode in the ESPRIT 2 software. The input count rate was ~ 55 kcps.

SEM/EDS characterization

Fig. 1 shows the EDS spectra at 30 kV for the three analyzed alloy steels. Sample 1 has a relatively high molybdenum content of 3.55 mass% and only 0.001 mass% sulfur (Table 1), which is a concentration below the EDS detection limit. Therefore, no deconvolution of the Mo-L and S-K lines is required and the EDS analysis can be performed using the Mo-L line, which has nearly the tenfold intensity of the Mo-K line.

For steels with molybdenum contents below 1 mass% the EDS analysis becomes much more complicated, especially if the alloy steel also contains a significant amount of sulfur like sample 2. The related spectrum in Fig. 1 shows no Mo-K line and only a weak Mo-L line. According to DIN EN 10088-3 the maximum molybdenum concentration in sample 2 is 0.6 mass%. It also contains up to 0.45 mass% niobium and 0.03 mass% sulfur, both Nb-L and S-K line overlap with the Mo-L line. Therefore, an accurate EDS analysis becomes challenging.

Sample 3 has a molybdenum content in the range of 0.15–0.25 mass% and a sulfur content of up to 0.04 mass%. The molybdenum content is close to the EDS detection limit.

Micro-XRF on SEM analysis

Fig. 2a shows the X-ray fluorescence (micro-XRF) spectrum of sample 1 in comparison with the electron beam excited (EDS) spectrum, where the remarkable difference in the molybdenum line intensities becomes evident. Due to distinctions in the ionization probabilities for electrons and photons, the Mo-L line in the electron excited spectrum is more intensive than the Mo-K line. On the other hand, the situation is reverse for the micro-XRF spectrum, which shows almost no background and a very intensive Mo-K line.

The EDS and micro-XRF spectra for sample 2 and 3 are displayed in Fig. 2b and Fig. 2c, respectively. Even for sample 3 a sufficiently strong Mo-K line is visible in the micro-XRF spectrum.

Using a standardless fundamental parameter (FP) quantification method, the mean values of the element concentrations were calculated. Tables 1–3 display the quantification results for all three samples and the comparison with the respective certified values. All standardless measured values are in a good agreement with the certified element concentrations.

However, the analytical results can even be improved using a standard-supported FP quantification method with a standard as reference. This method can be used for the quantification of similar steel samples to increase the quality of the quantification results compared to a standardless quantification.

Sample 1 was used to create a standard-supported FP quantification method in the ESPRIT 2 software. In the method editor an element factor for the specific element was defined and applied to improve the accuracy of the

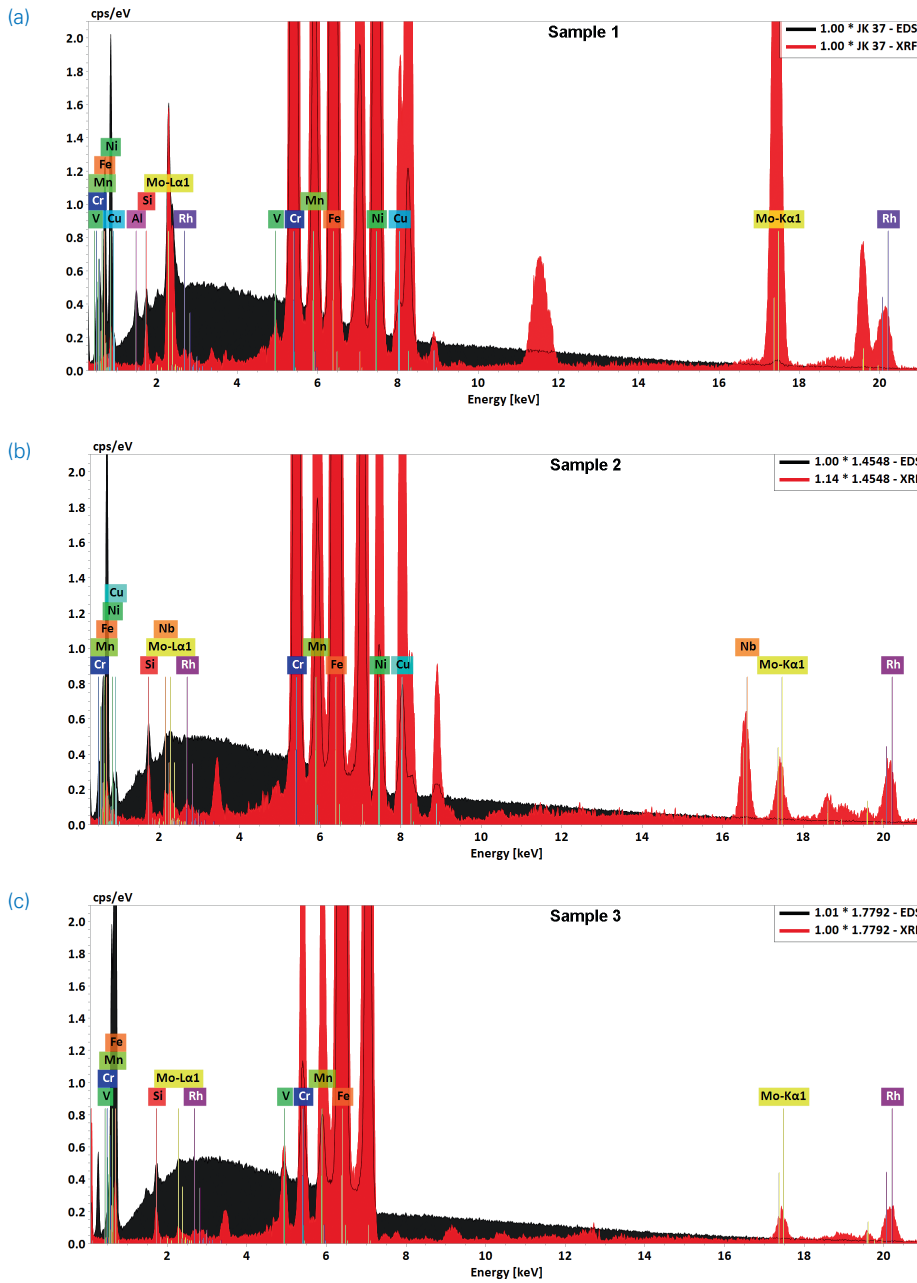**Comparison of Micro-XRF and EDS spectra for the different alloy steels**

Fig. 2 Micro-XRF and EDS spectra of a) sample 1 (CRM JK 37), b) sample 2 (1.4548) and c) sample 3 (1.7792). Unlabelled peaks are diffraction peaks.

quantification results. The element factor has to be changed until a satisfactory result compared to the certified values is achieved. For sample 1 an element factor of 0.9 was applied for Mo-K. Due to the secondary fluorescence of iron, which affects chromium and nickel, another element factor of 0.96 was applied to correct the chromium value.

It has also been considered that the certified Si concentration of 0.14 mass% for sample 1 is close to

the XRF detection limit for silicon in steel. To prevent less precise results, the EDS value for Si of 0.21 mass% was set as a fixed concentration in the standard-supported FP quantification method.

Afterwards, sample 2 and 3 were quantified twice using the standardless and the adapted standard-supported FP method including the applied element factors for Mo and Cr. For Si-K the EDS analysis values of the respective sample was used. The results are displayed in Table 2 and 3.

Table 1 Measured and certified micro-XRF values of sample 1 in mass% normalized.

	Si	V	Cr	Mn	Ni	Cu	Mo
Measured mean value (standardless)	0.50	0.04	27.47	1.71	30.00	0.93	3.79
Measured mean value (standard-supported FP)*	0.21**	0.04	26.75	1.74	30.75	0.96	3.51
Certified value	0.141	0.075	26.72	1.73	30.82	0.936	3.55

Table 2 Measured micro-XRF values of sample 2 and certified element concentration ranges according to EN 10088-3 in mass% normalized.

	Si	Cr	Mn	Ni	Cu	Nb	Mo
Measured mean value (standardless)	0.7	16.59	0.91	3.61	3.26	0.37	0.19
Measured mean value (standard-supported FP)*	0.47**	16.04	0.92	3.67	3.31	0.38	0.17
Certified value min / max	0 / 0.7	15 / 17	0 / 1.5	3 / 5	3 / 5	0 / 0.45	0 / 0.6

Table 3 Measured micro-XRF values of sample 3 and certified element concentration ranges according to EN 10088-3 in mass% normalized.

	Si	V	Cr	Mn	Mo
Measured mean value (standardless)	0.50	0.16	0.96	0.79	0.16
Measured mean value (standard-supported FP)*	0.28**	0.16	0.96	0.79	0.15
Certified value min / max	0.14 / 0.4	0.05 / 0.12	0.9 / 1.2	0.7 / 1.1	0.15 / 0.25

* The standard-supported FP method was created on the high-alloy steel sample 1 with an element factor of 0.96 for Cr and 0.9 for Mo.

** Si value from EDS analysis

Conclusion

Micro-XRF provides good quantification results even for steels with low molybdenum concentrations (< 1 mass%), since the excitation of the Mo-K lines by X-rays is much more efficient than the excitation by electrons.

Using a standardless quantification method good quantification results were achieved. Standards can be applied in order to enhance precision: a standard-supported FP method must be created which can be applied to quantify samples with a similar elemental composition.

A combination of both analysis methods EDS and micro-XRF delivers more precise results instead of using only one of the methods.

Acknowledgements

Author

Birgit Hansen, Application Scientist EDS & Micro-XRF/SEM, Bruker Nano GmbH, Berlin, Germany

● Bruker Nano GmbH

Berlin · Germany
Phone +49 (30) 670990-0
Fax +49 (30) 670990-30
info.bna@bruker.com

www.bruker.com/quantax-micro-xrf