Overcoming Quantitative Challenges Presented By X-ray Line Interferences in EDS and WDS

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Key Words

Compass Software, Elemental Mapping, Energy-Dispersive X-ray Spectroscopy, Interfering X-ray Lines, Peak Deconvolution, Spectral Imaging, Spectral Phase Mapping, Standardless Quantitative Analysis, Ti-V-Al-Fe Metal, Wavelength-Dispersive X-ray Spectroscopy

Introduction

Quantitative analysis using Energy-Dispersive X-ray Spectroscopy (EDS) or Wavelength-Dispersive X-ray Spectroscopy (WDS) of materials that contain elements which exhibit interfering X-ray lines presents challenges to the microanalyst. Although electron-probe microanalysis (EPMA) software commonly includes rigorous interference corrections for WDS, such corrections are typically not available to the SEM user. To illustrate some of these challenges, quantitative analysis of a Ti-V-Al-Fe sample consisting of two phases with only small differences in vanadium and iron content was done.

EDS and WDS Quantitative Analysis

The sample of Ti-V-Al-Fe metal was mounted, uncoated, in thick section and examined in an FESEM. EDS spectra and spectral images were collected using a Thermo Scientific™ UltraDry™ EDS detector and the Thermo Scientific™ NORAN™ System 7 microanalysis system (NS7). WDS spectra were collected and measurements were made using the Thermo Scientific™ MagnaRay™ WDS spectrometer. EDS and WDS data were both processed with NORAN System 7 software. EDS and WDS quantitative analysis was performed at a 15 kV accelerating voltage and EDS spectral imaging was done at a 10 kV accelerating voltage in order to mitigate the interaction volume. The subtle differences in phase composition rendered elemental mapping impractical.

Therefore, phases were identified using the Thermo Scientific™ COMPASS™ spectral phase mapping software, which identifies unique phases based on the principle component analysis of the EDS spectrum at each pixel.[1]

Results

Two Ti-V-Al phases (Figures 1 and 2) were identified. Small, typically ~5 µm, V-rich (~13 wt% V) grains occur along the boundaries of larger, typically ~10 µm, V-poor (~3 wt% V) grains. Additionally, the V-rich grains contain ~1.6 wt% Fe. EDS (standardless and standards-based) and WDS quantitative results are in Table 1.
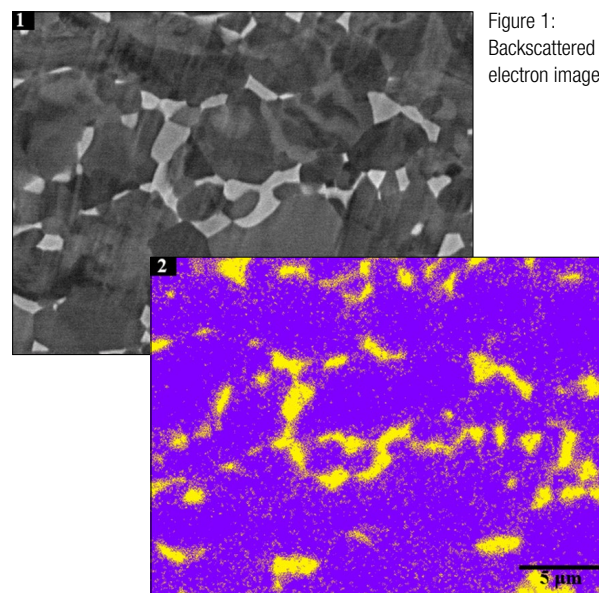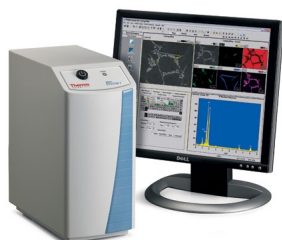

Figure 1: Backscattered electron image

Figure 2: COMPASS phase map: V-poor phase is purple; V-rich phase is yellow

UltraDry EDS Detector

NORAN System 7

MagnaRay WDS

Thermo
S C I E N T I F I C

The Ti Kβ line (4.931 keV) is only separated from V Kα line (4.948 keV) by 17 eV; these X-ray lines are indistinguishable by EDS and are distinguishable, but poorly resolved, by WDS (Figure 3).
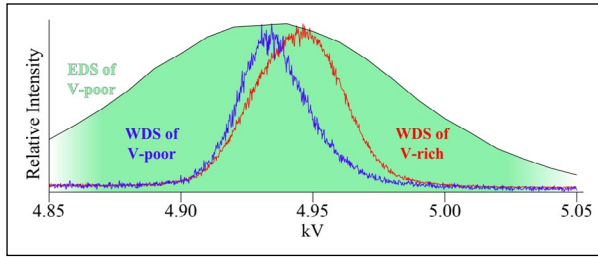

Figure 3: WDS energy scans over V Kα of V-poor and -rich grains overlaid on EDS spectrum of same spectral region

Table 1:
Quantitative analyses of a Ti-Al-V alloy

		EDS		WDS	
		Standardless	Standards-based	Standards-based	
		Filter	Filter	$V_{Meas.}$	$V_{Diff.}$
V-rich Grains	Al	3.46	3.63	3.29	3.29
	Ti	81.2	83.4	78.3	78.3
	V	13.8	13.2	15.8	16.9
	Fe	1.61	1.55	1.54	1.54
	Total	100.0	101.8	98.9	100.0
V-poor Grains	Al	6.42	6.77	5.23	5.22
	Ti	90.7	93.4	90.0	90.0
	V	2.87	2.75	6.49	4.49
	Fe	0.07	0.06	0.26	0.26
	Total	100.0	103.0	102.0	100.0

In this table the "Standardless" column refers to standardless quantitative analysis. "Standards-based" refers to analysis done using Al, Ti, V, and Fe metal standards (both for EDS and WDS). The "Filter" column indicates that the background was subtracted using a digital top hat filter. "$V_{Meas.}$" refers to analyses in which the V concentration was determined by counting on V Kα ($V_{Meas.}$; contains a contribution from interfering Ti Kβ). "$V_{Diff.}$" refers to analyses in which the V concentration is the difference between 100 and measured concentrations of Al, Ti, and Fe.

The effect of this interference in the WDS quantitative analyses, in which V is counted on the Kα line, of these phases is the over-estimate of the V concentration. This effect is greater in magnitude in the analyses of the V-poor grains because fewer of the counts represent V Kα X-rays. WDS analyses of both grain types, without rigorous interference corrections, do not produce accurate results.

There are three methods by which this shortcoming may be overcome. First, the V Kβ line is an appealing peak on which to count because there is no interfering energy line in this sample. However, greatly (>10×) extended acquisition times are required for counting the V Kβ line in the V-rich grains. In the V-poor grains, the V concentrations are low (~3 wt%) and the V Kβ line cannot be distinguished from the background. Second, a difference method can be utilized. This method subtracts the wt% of the other elements from 100% with the remainder representing the V concentration. This method requires that only one line is confounding and that the measurement of the remaining elements is done with perfect accuracy. The third method is to perform EDS quantitative analysis with standards, It is typically assumed that WDS is more accurate than EDS. However, EDS has the advantage of well-developed peak deconvolution methodologies with both standards based and standardless EDS quantitative analysis, thereby providing more accurate results than WDS in this scenario.

Conclusions

WDS is a necessary technique for confirming the presence or absence of interfering elements. However, unless the WDS spectrometer is able to completely resolve interfering X-ray lines, it cannot be used for accurate quantitative analysis without interference corrections. In addition, these interfering energy lines confound the concept of phase mapping with WDS element maps. The peak deconvolution methods involved in modern EDS quantitative analysis provide accurate results when WDS is unable to do so. Furthermore, COMPASS software distinguishes between phases with only subtle compositional differences. The result is a complete phase map with accurate quantitative analysis of each phase.

References

1. P. Camus, Thermo Scientific (2009) White Paper 51782.

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