

Introduction

AutoPhaseMap software in **AZtecEnergy** automatically finds areas of different characteristic composition from X-ray map data, and determines the distribution, area, constituent elements and composition of each of these areas or phases. This application note examines how this can be used to investigate the chemistry and distribution of nanoscale intermetallic phases in a Ni-based alloy which are on the scale of 150-1000 nm.

Automatic phase mapping and phase identification

The sample is a Ni-based alloy from a spinner bowl used in the manufacture of fibre glass. In this alloy, intermetallic precipitates provide strength to the alloy at high temperatures. The distribution of the precipitates (Fig. 1a) is on the nano-scale, down to approximately 100 nm. Due to the small size of the precipitates, the data was collected on a FEG-SEM at 5 kV to minimise beam diameter and X-ray interaction volume. The accelerating voltage was sufficient to excite the L lines of the transition metals (Cr, Fe and Ni), and also lines from the precipitate-forming elements (Nb L, Mo L and W M), as seen in the spectrum collected from the entire field of view (Fig. 1b).

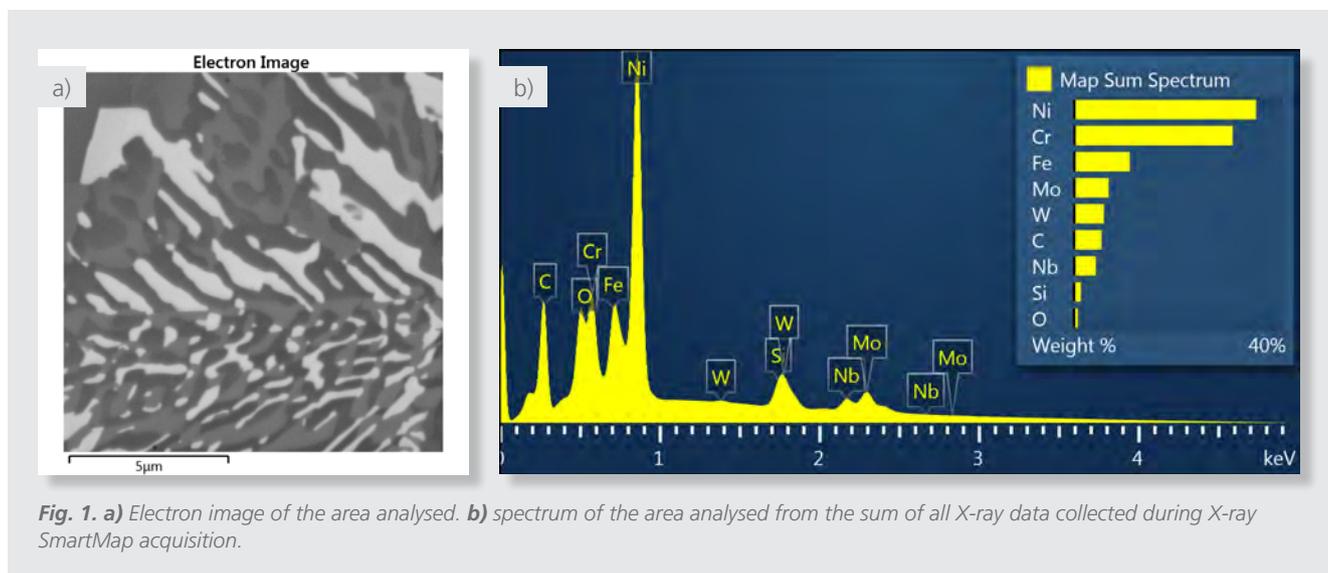


Fig. 1. a) Electron image of the area analysed. b) spectrum of the area analysed from the sum of all X-ray data collected during X-ray SmartMap acquisition.

To investigate the chemistry and distribution of the precipitates, an X-ray SmartMap (spectrum per pixel) was collected from an area of the sample under the conditions shown in Table 1 below. A high map resolution and low accelerating voltage were chosen to suit the scale of the smallest precipitates.

SEM Type	FEG Gun
Acquisition time (mins)	50
Acquisition Rate (cps)	5500
Accelerating Voltage (kV)	5
Map resolution	512x512
No of pixels	262144
Counts per pixel	63

Table 1. Parameters for SmartMap Acquisition.

X-ray maps (Fig. 2) calculated from the SmartMap data suggest the presence of three phases, as shown by different grey levels in the electron image. The maps have been coloured R, G, B according to which of the three phases the element has highest concentration.

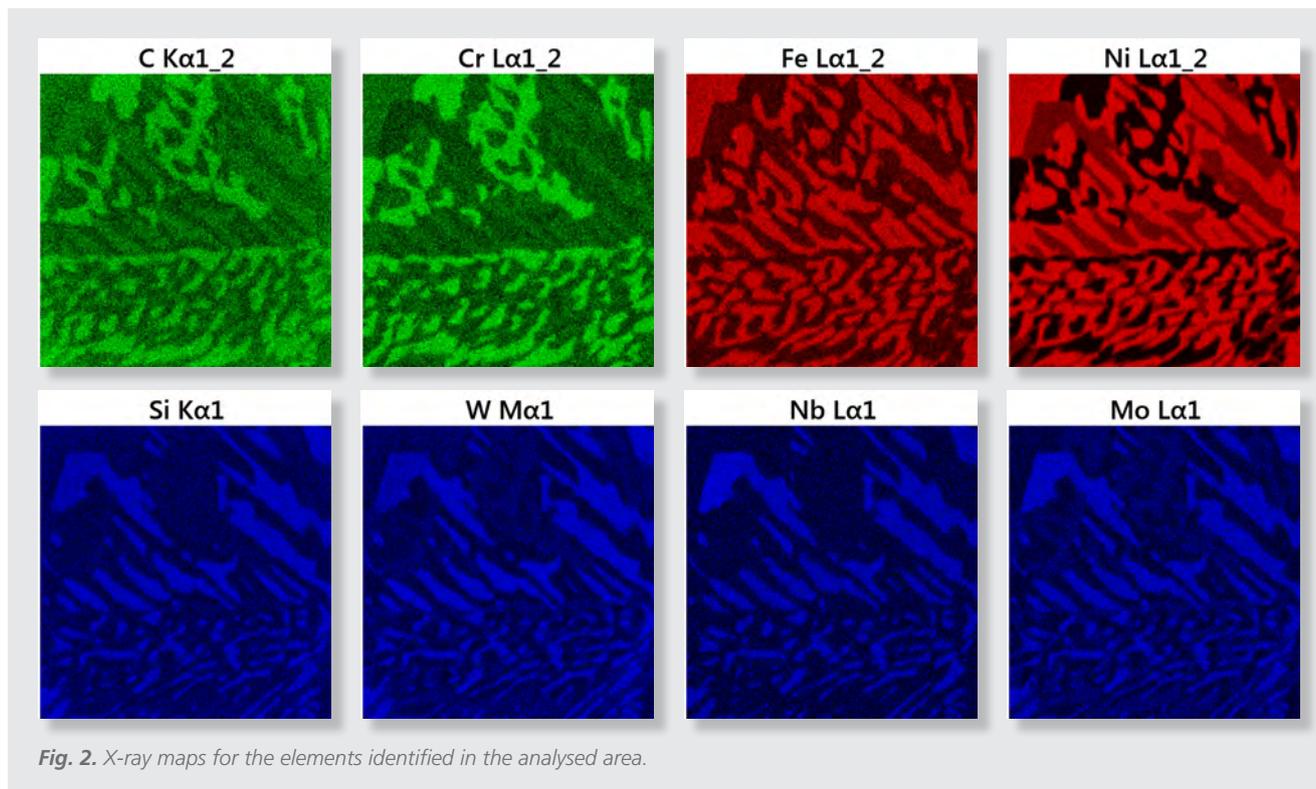
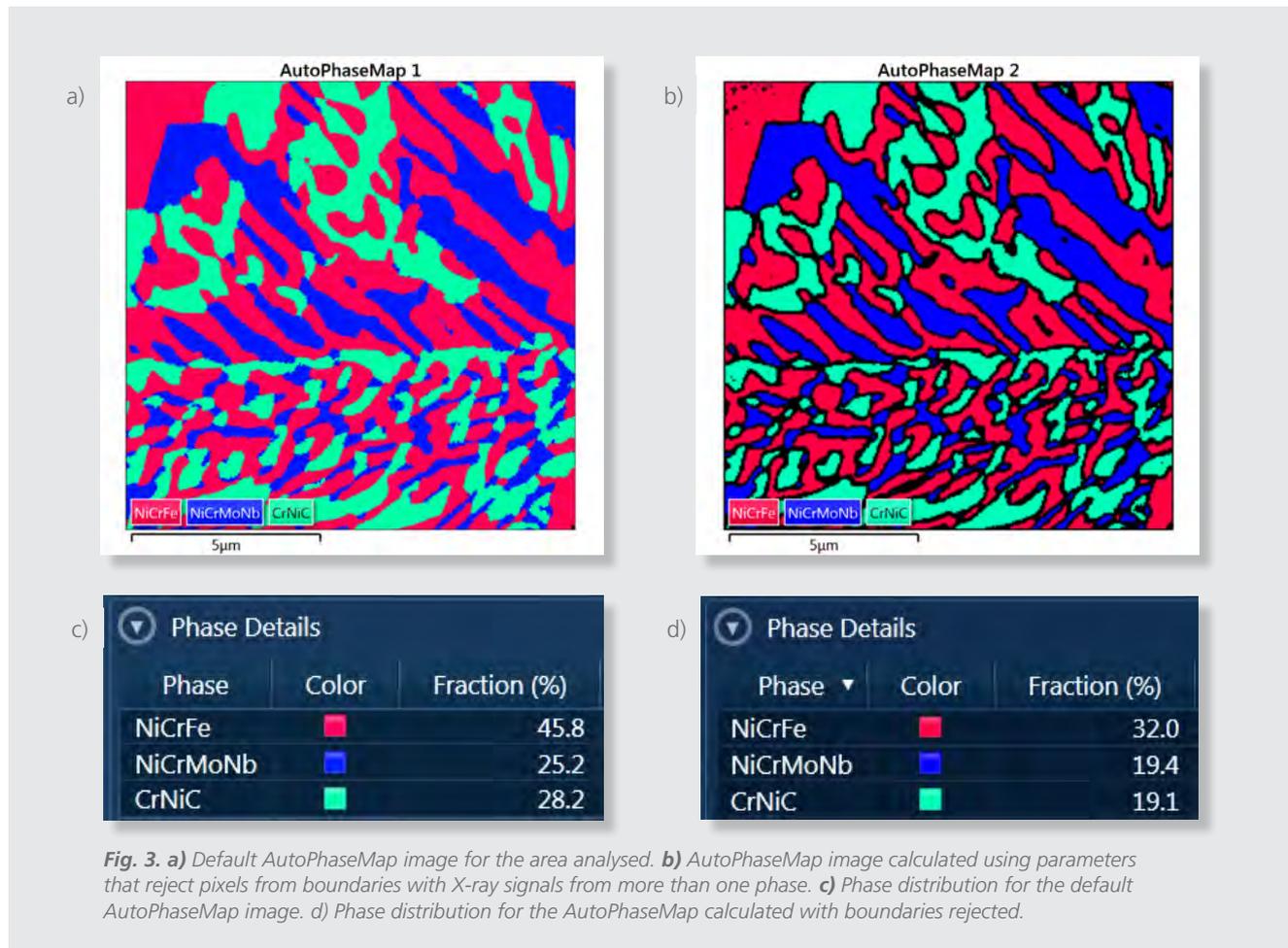


Fig. 2. X-ray maps for the elements identified in the analysed area.

The AutoPhaseMap is calculated from the mapping data during acquisition, and confirms the presence of three phases (Fig. 3a.). These phases are identified by the software as NiCrFe, NiCrMoNb and CrNiC. The relative abundances of these phases in the

area analysed is shown in Fig. 3c. NiCrFe represents the bulk of the sample, a Ni based alloy, and the spectrum and composition calculated for this phase is shown in Fig. 4a. NiCrMoNb is the strengthening precipitate phase where the molybdenum and niobium are concentrated (Fig. 4b). CrNiC has a larger concentration of carbon (Fig. 4c) than the other phases corresponding to over 20 atomic %, and therefore is consistent with chromium carbide.



Testing the accuracy of the phase composition of nano-precipitates determined by AutoPhaseMap

The dataset collected for this sample has an acquisition pixel approximately every 25 nm. This means data is being collected at a spatial resolution that is less than the volume of interaction from which X-rays are being generated in this sample, which is invariably greater than 100nm and can approach 200 nm (Fig. 5). The smallest precipitates are about 100-150 nm, therefore it is inevitable that the X-ray information collected at some pixels will contain X-rays from more than one phase.

AutoPhaseMap has more advanced functions to enable the more detailed study of nano-materials where spatial resolution of X-ray generation is a potential issue. Using the default settings, the software has included pixels that have contribution from more than one phase to give the best possible picture of the distribution of phases in the sample. The settings can be changed

to reject these pixels near boundaries, in order to collect only the information from single phases and therefore to produce more accurate spectral, chemical and compositional information for the phases. Fig. 3b shows an alternative AutoPhaseMap where the boundaries have been rejected. The boundaries in black show where the algorithm has detected significant contribution of X-rays from more than one phase. The fraction of each phase (Fig. 3d), shows decreases in the areas for each phase due to these rejected pixels.

A comparison of the spectra and composition calculated between the two results can be seen in Fig. 4, where a), b) and c) are from the default result, and d), e) and f) from the boundary-corrected result.

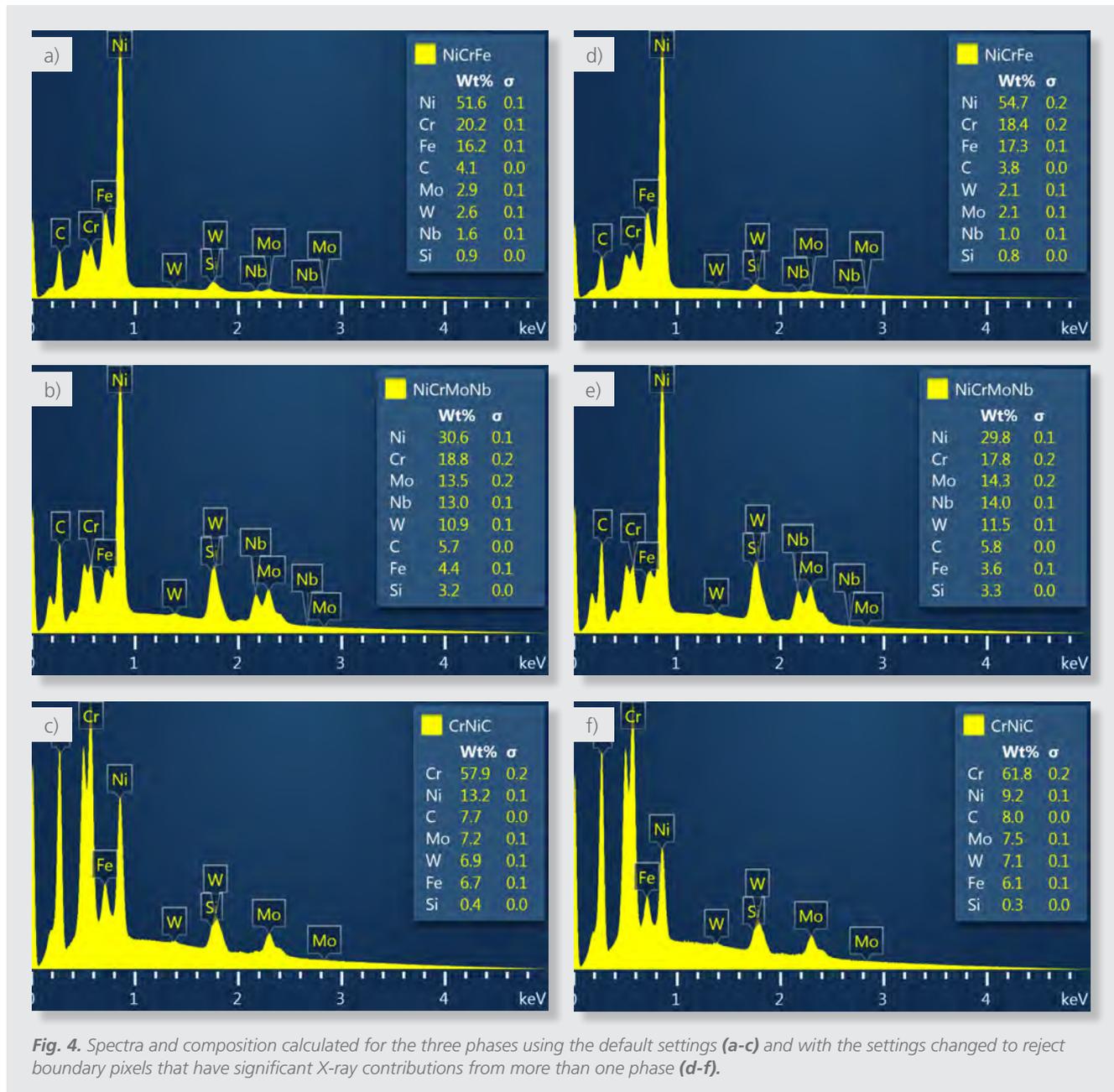


Fig. 4. Spectra and composition calculated for the three phases using the default settings (a-c) and with the settings changed to reject boundary pixels that have significant X-ray contributions from more than one phase (d-f).

Comparing the two results shows that there is no change in the constituent elements identified in the two results. Some compositional differences are seen which are due to the rejection of the boundary pixels. NiCrFe has more nickel and iron and less constituents from the NiCrMoNb (e.g. molybdenum and niobium) and from the CrNiC (chromium). NiCrMoNb has slightly more of the hardening elements (molybdenum, niobium and tungsten). CrNiC has more chromium and carbon and less nickel.

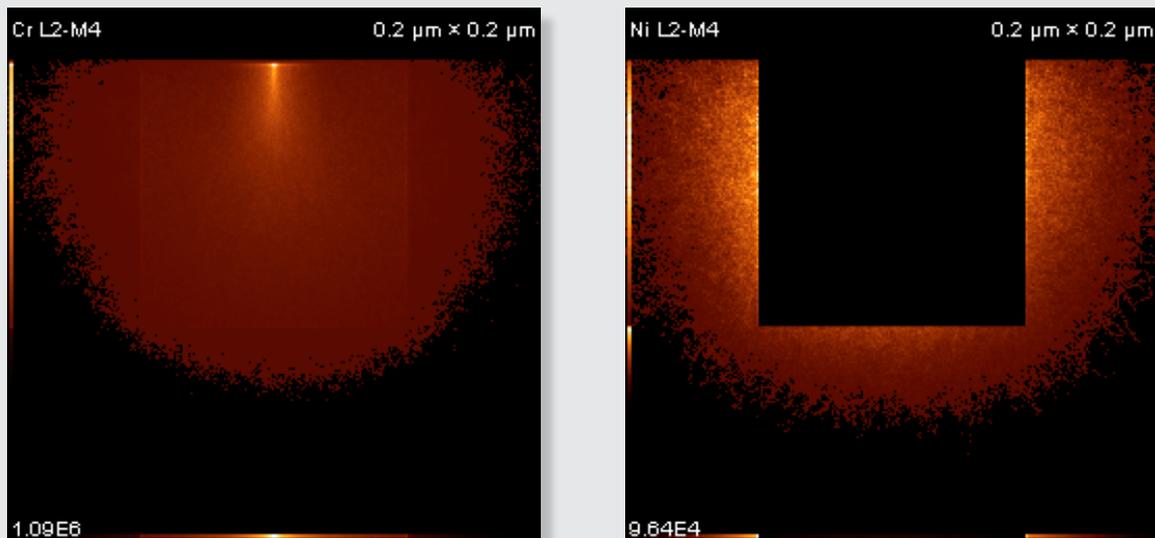


Fig. 5. Monte Carlo simulations calculated using NIST Monte for a 100 nm square-shaped chromium carbide precipitate in a nickel/chromium/iron matrix, where a 5 kV electron beam is analysing the centre of the precipitate. **a)** region from which Cr L X-rays are emitted. **b)** region from which Ni L X-rays are emitted. No NiL X-rays are emitted from the chromium carbide because nickel is only present in the matrix for this simulation.

Because the exclusion of boundary pixels does make a difference, it raises a concern that there may still be mixing of signals between the phases near boundaries. If so, phase composition results would be different if X-rays were collected only from the centre of the phases. This is investigated in Fig. 6, where the compositions calculated for the phases from the two AutoPhaseMap results are compared to spectra reconstructed from pixels well away from the boundaries and in the largest precipitates possible. These results suggest that

the matrix phase NiCrFe does not contain any appreciable niobium or molybdenum (Fig. 6a), and the minor amounts of these elements seen in the AutoPhaseMap results are due to interaction volume effects. The NiCrMoNb, has a slightly different composition calculated from the reconstructed phase, again suggesting some additional nickel, chromium, and iron are in the AutoPhaseMap spectra. There is little difference in the CrNiC phase results.

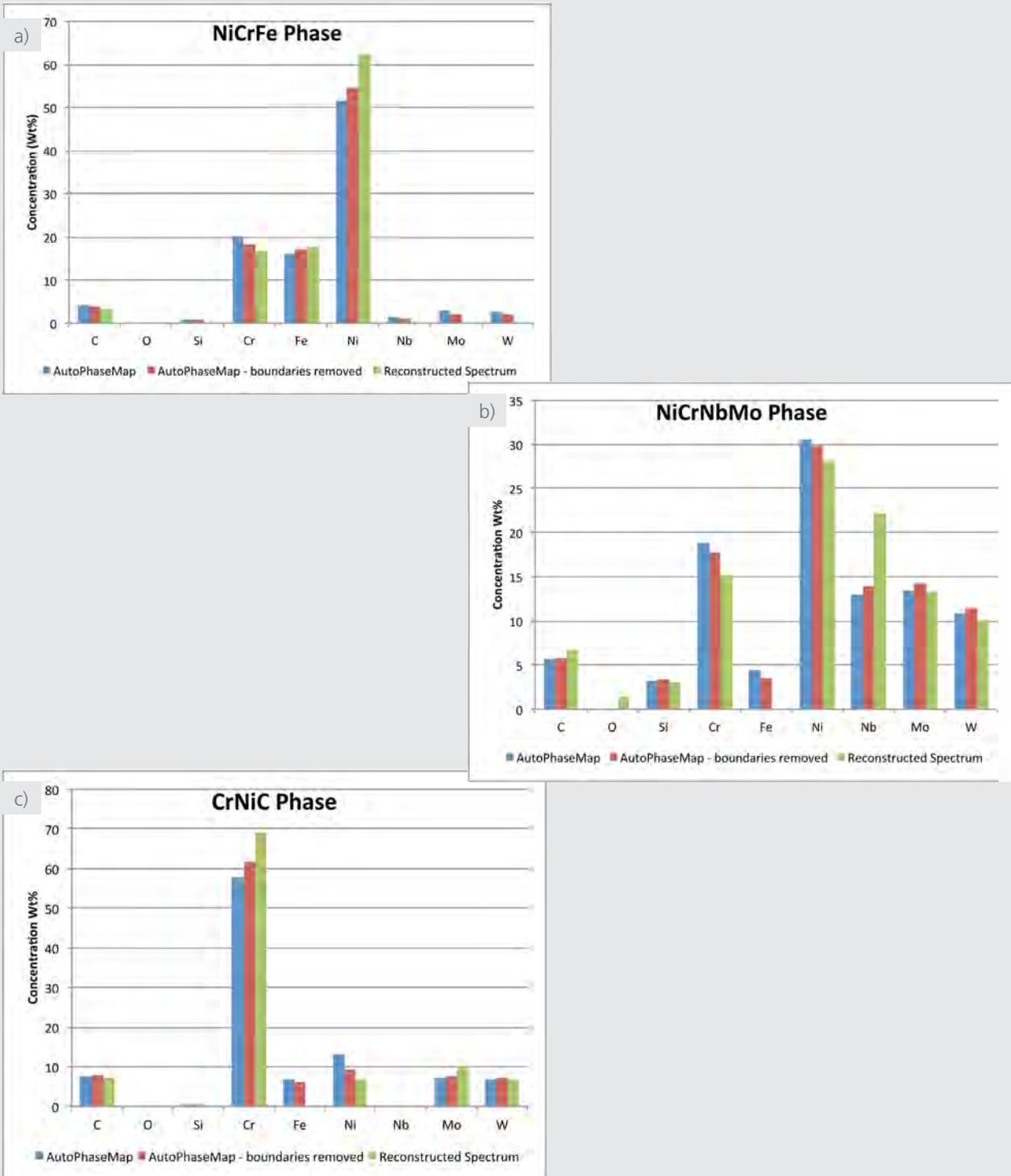


Fig. 6. Comparison of compositions calculated for the three phases using a) AutoPhaseMap with default settings b) AutoPhaseMap with boundaries rejected and c) reconstructed spectra from the 'centre' of large precipitates.

Conclusion

AutoPhaseMap is a powerful tool for investigating the composition and distribution of nanoscale precipitates in materials. The AutoPhaseMap result gives a clear indication of chemical constituents and spatial information. AutoPhaseMap can also be used to check for issues with interaction volume on sub 250 nm areas in 5kV data. Care should be taken at this scale to check for mixing of X-ray signals between phases, however this effect has been shown to be relatively small in this example. The main issue brought into question here is whether X-rays from minor constituent elements are actually generated from other phases which contain these elements. Careful reconstruction of spectra from areas where the interaction volume is wholly contained within a phase can be used to confirm this point and phase compositions may be calculated accordingly.

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