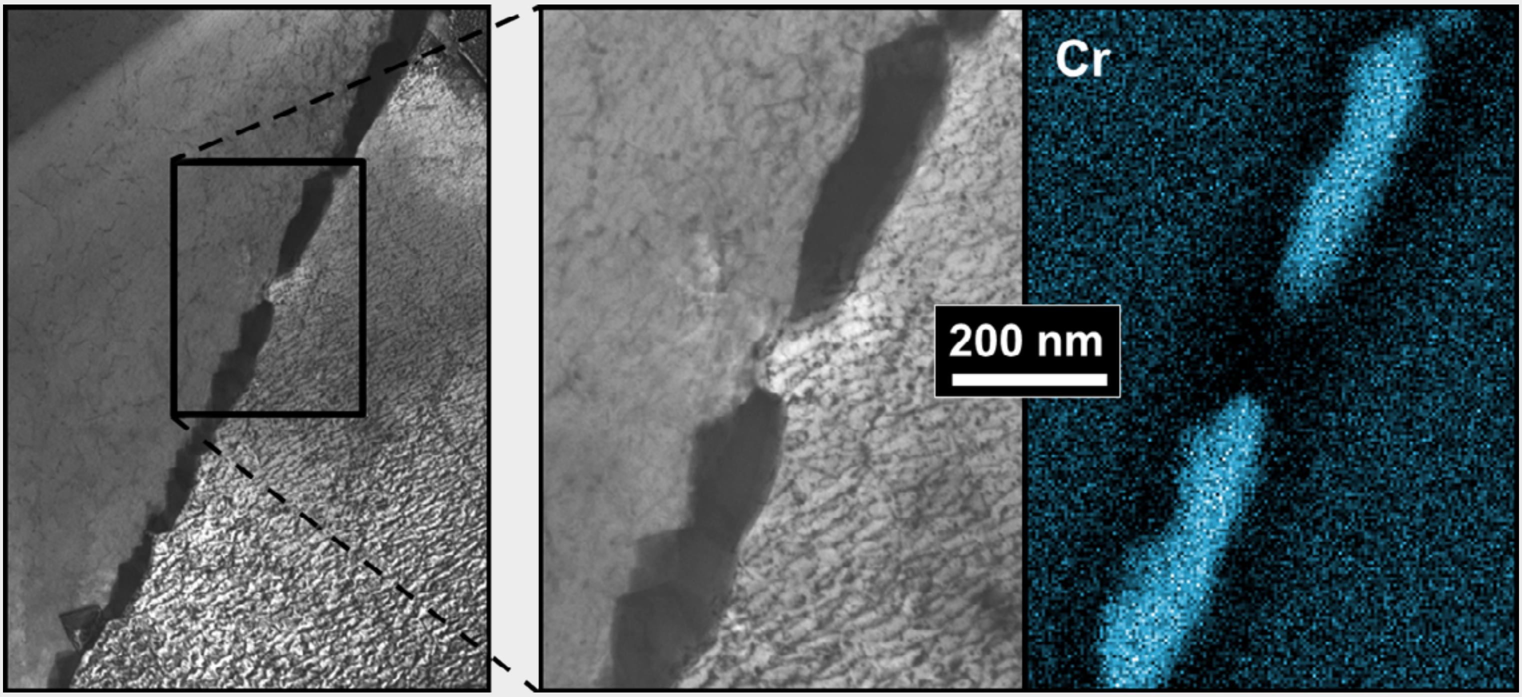

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High Resolution STEM and EDS Study of Chromium Depletion in Stainless Steel

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High Resolution STEM and EDS Study of Chromium Depletion in Stainless Steel

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This Application Note describes a study of heat affected X2CrNi18-10 stainless steel. Small chromium carbide particles form at the grain boundaries of the material, causing chromium depletion of the surrounding matrix and thus promoting corrosion. A thin lamella was prepared at a grain boundary and analyzed with scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) by a ZEISS FIB-SEM instrument. The EDS results obtained on the lamella show a spatial resolution of the order of 10 nm and allow the extent of the chromium depletion to be qualitatively determined.

Introduction

An important application of FIB-SEM instruments is the preparation of thin lamellae for analysis in the TEM [1]. Such thin samples can also be imaged in transmission in the SEM. The advantages of scanning transmission electron microscopy (STEM) in the SEM, compared to conventional SEM on the bulk, are enhanced imaging resolution, complementary contrasts [2], and a dramatic improvement in energy dispersive spectroscopy (EDS) spatial resolution.

This Application Note describes a STEM experiment on a sample from a corroded stainless steel X2CrNi18-10 power plant pipeline. Corrosion was observed happening near a weld. During welding the material is exposed to temperatures around or above 600 °C, the onset temperature for chromium carbide particle formation at grain boundaries [3]. These carbides are highly undesirable as they deplete chromium from the surrounding matrix material. Consequently, the chromium concentration can drop locally below a critical level and corrosion is allowed to happen in the material.

Methods

Figure 1 (a) shows a photograph of the sample holder [4] used for this experiment.

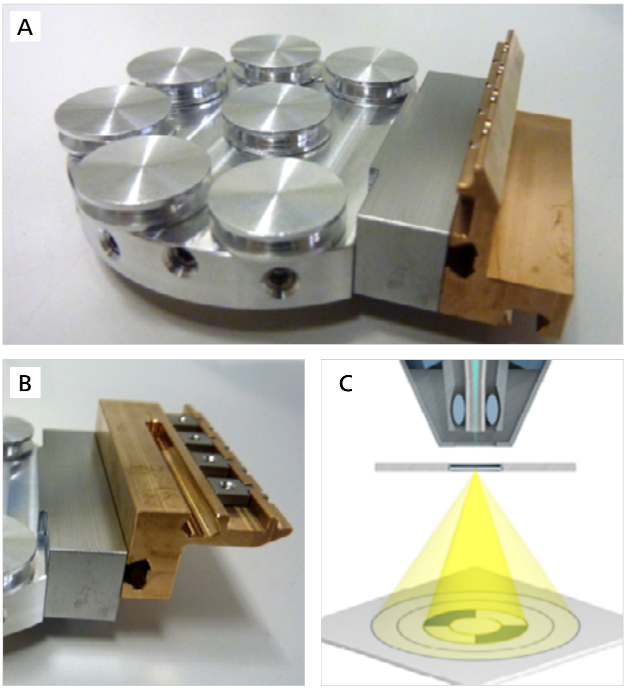

Figure 1 *Photographs of the grid sample holder with the grid rail in (a) FIB thinning and (b) STEM position. (c) Schematic of a sample during STEM observation.*

The rail piece on its right hand side is used to hold up to four standard 3 mm half ring grids [5] aligned along a straight line. The rail piece features two dovetail grooves at an angle of 90° to each other, which allow the device to be mounted in two different positions: a FIB thinning position (Fig. 1(a)) and a STEM position (Fig. 1(b)). The transfer of the specimen between the two positions is easy and fast.

In the FIB thinning position, the grids are oriented perpendicular to the sample holder main plane. Thus, in the Crossbeam, any sample attached to the grid can be accessed from the top for FIB thinning until electron transparency is reached. In this position the grids can be tilted eucentrically.

In the STEM position, the grids lie horizontally. Therefore, the retractable STEM detector can be placed underneath the sample to detect transmitted electrons (see Fig. 1(c)). EDS analysis was performed in STEM position using an EDAX Octane Super (60 mm²) system equipped with a drift correction software option.

A sample of approximately 15 mm x 6 mm x 4 mm was cut from the pipeline with a saw. The sample was extracted from a region near a corroded weld. It was mechanically ground, polished, treated briefly with V2A etchant, and finally glued to a stub with silver paint. The stub was then mounted on one of the seven available stub positions of the sample holder (see inset of Fig. 2).

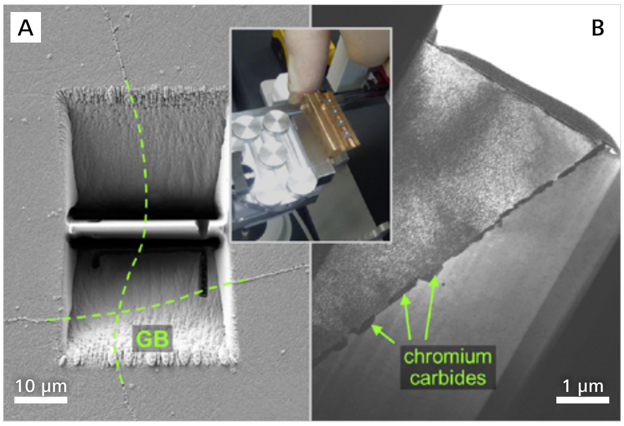

Figure 2 *(a) SEM image of the prepared lamella. The dashed lines show the course of the grain boundaries. The inset shows the transfer of the sample to STEM position in the airlock. (b) STEM overview image of the lamella.*

Experiment

In the SEM image the grain boundaries could be easily detected as they appeared as slight elevations of the sample surface.

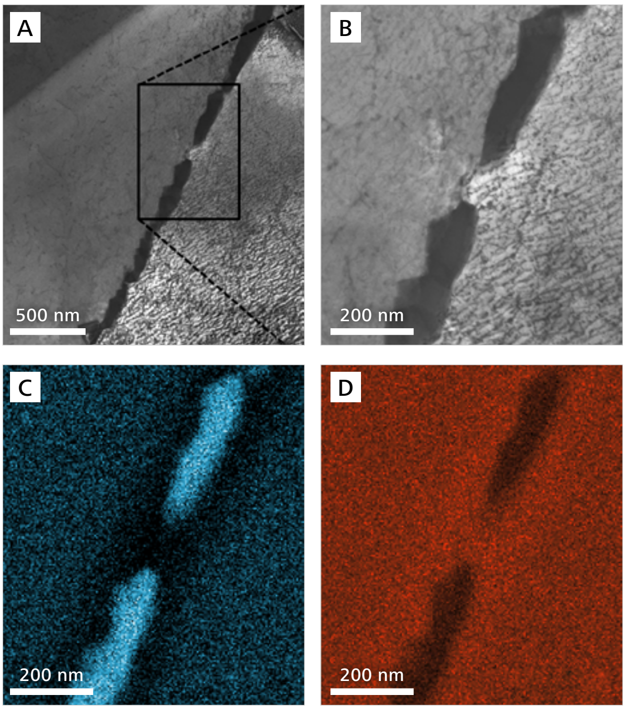

Figure 3 *(a) STEM image showing chromium carbide particles along the grain boundary. (b) STEM close-up of an area analyzed with EDS. (c) and (d) EDS maps of chromium and iron, respectively.*

A lamella was FIB cut roughly perpendicular to one of the grain boundaries as shown in Figure 2 (a), transferred to a grid mounted on the grid rail (in FIB thinning position), and FIB thinned to its final thickness (≤ 100 nm).

In the airlock of the FIB-SEM instrument the grid rail was transferred to STEM position (see inset of Fig. 2) for subsequent STEM imaging and EDS analysis of the thinned lamella. Figure 2 (b) shows an overview brightfield STEM image of the lamella at 30 kV SEM acceleration voltage. Many chromium carbide particles can be observed aligned along the grain boundary. They are elongated in shape with widths in the range of 50 to 150 nm (see also Fig. 3 (a)).

Figure 3 shows EDS map data of an area of the sample containing two carbides separated by a gap of (95 ± 5) nm. The EDS data was acquired at 15 kV acceleration voltage and the K〈 lines of chromium (c) and iron (d) used for element detection. In the chromium map, the chromium depleted area appears as a dark frame completely surrounding the carbides.

An EDS line scan across a chromium carbide particle allows a more quantitative analysis and is shown in Figure 4. The 600 nm long line was scanned with a pixel step size of 5 nm. The shaded area in the plot corresponds to a particle of 70 nm width along the line as can be determined from the brightfield image shown in the inset. The chromium signal (blue curve) features a pronounced maximum and two dips left and right of the particle. On both sides, at a distance of around 150 nm, a plateau in the chromium concentration is reached (blue curve). The lowest chromium concentration – which is proportional to the measured counts – corresponds to (65 ± 10) % of the plateau level.

As expected, the iron and nickel curve shapes are inverted in comparison to the chromium one, i.e. a dip is observed where the carbide is located surrounded by maxima left and right.

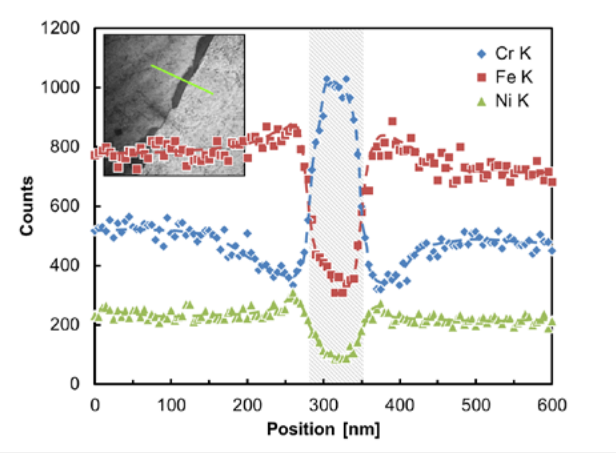

Figure 4 *EDS counts as a function of position along the line shown in the inset (green line) for chromium, iron, and nickel. The dashed lines are guides to the eye.*

Summary

In this Application Note we presented a STEM experiment on a lamella from a heat affected X2CrNi18-10 steel sample. STEM allowed to study the distribution and morphology of chromium carbide particles present at the grain boundaries with great detail. EDS measurements showed a spatial resolution of the order of 10 nm, which is far superior to the achievable resolution on the bulk.

The combination of STEM and high resolution EDS is a powerful tool in materials research as demonstrated by this example.

References:

[1] Introduction to Focused Ion Beams, Eds. L:A: Giannuzzi and Fred A. Stevie, Springer (2005).

[2] G. Pavia, An Annular Detector for ZEISS FE-SEMs and Crossbeams, ZEISS Technology Note (2015).

[3] E. Wendler-Kalsch and H. Gräfen, Korrosionsschadenskunde, p. 154ff, Springer (1998).

[4] The grid sample holder for STEM applications carries the ZEISS part number 348242-8106-100.

[5] See e.g. www.microscopyconsumables.com/category-s/100.htm

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