Supplementary Material for:

Identification and 3D-Reconstruction of Cr_5S_6 Precipitates along Grain Boundaries in Fe13Cr

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Materials and Methods

FIB serial slicing

Using FIB serial slicing the whole dimension (shape) of each particle can be visualized at once using multiple slices per precipitate.

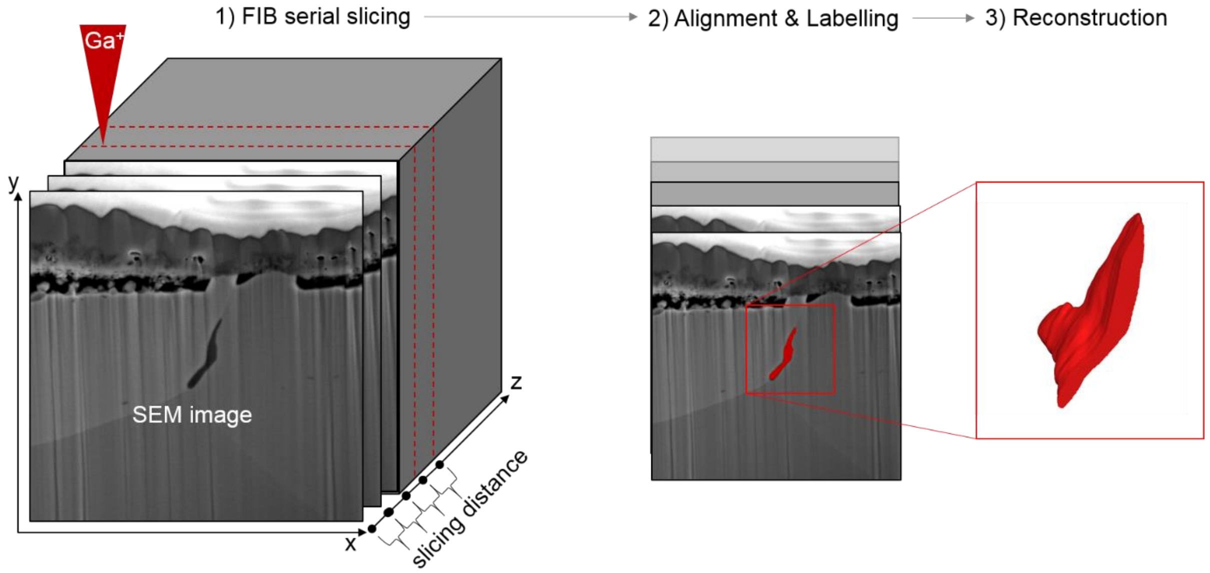

Fig. S-1 Scheme of the 3D slicing process using FIB/SEM showing one 3D precipitate of Fe13Cr aged for 6 h extracted and modelled from a number of aligned images.

Ageing experiments

The infra-red light furnace consists of a gas flow system inside a steel container with four infrared radiators. A gas mixture of 0.5 % SO_2 and 99.5 % Ar was used with a constant flow rate of 1.1 l*min^{-1}. The gas flow was parallel to the samples and a thermocouple was placed inside each metal sheet to control the samples temperature and to regulate the power of the IR-radiators to a constant sample temperature of 650 °C. Heating and cooling procedure were performed under pure Ar-flow.

TEM sample preparation

After 3D slicing, a lamella with large sulfide precipitates within a grain boundary of the 12 h sample was prepared for transmission electron microscopy (TEM) using the FIB to determine the exact phase of the precipitates. Thinning of the lamella started with 30 kV and was decreased to 2 kV as a final polishing step. The JEOL JEM-2200FS (Jeol, Japan) microscope is equipped with an in-column energy filter, a scanning unit with bright field a high-angle annular dark field detector, and an energy dispersive X-ray spectroscopy (EDX) system with an energy resolution 138 eV (Jeol, Japan).

Results and Discussion

TEM Results

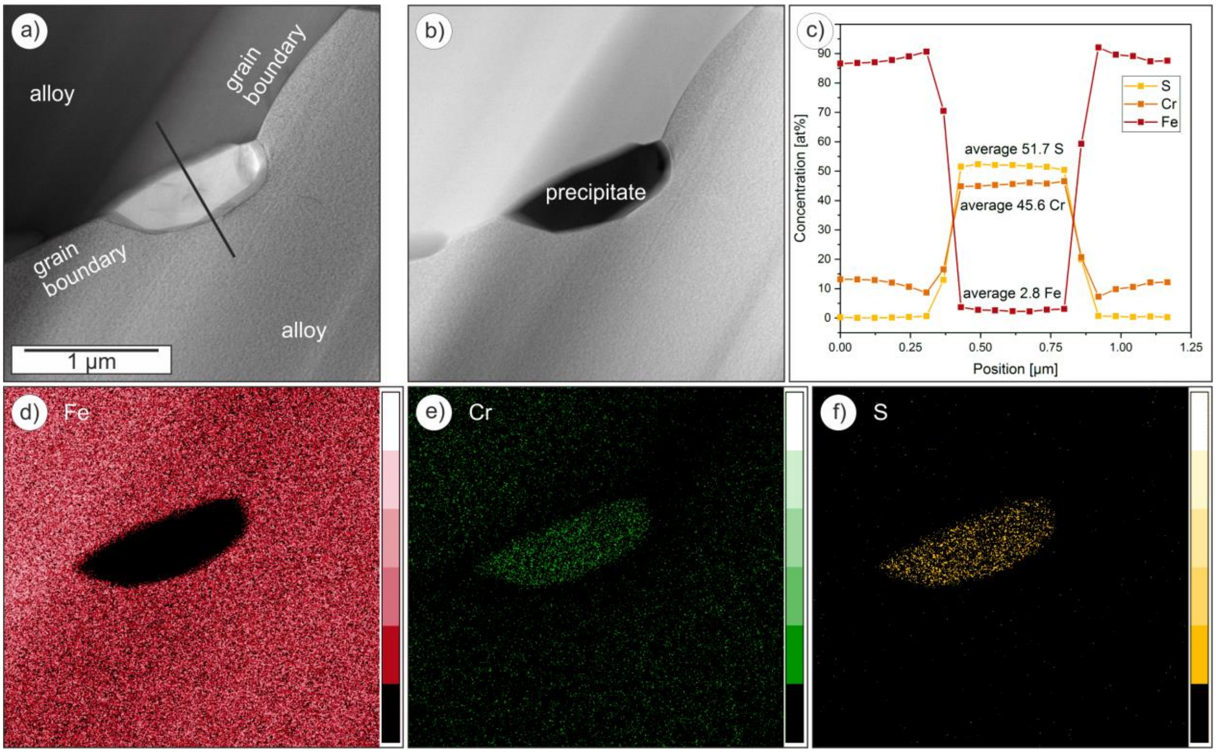

Fig. S-2 STEM micrographs (a) bright field and b) dark field) of the precipitate, c) STEM/EDX line scan across the precipitate (black line in a), and corresponding elemental maps of d) Fe, e) Cr, and f) S, where white color corresponds to the highest amount of the respective element.

To obtain precise compositional information scanning TEM (STEM) was performed in combination with energy-dispersive X-ray spectroscopy (EDXS). A STEM bright field image and the corresponding dark field image of a grain boundary precipitate are shown in Fig. S-2 a) and b). The brighter contrast of the precipitate suggests that the particle is lighter than the surrounding material and it was formed at a grain boundary of the alloy. To acquire detailed elemental distributions, EDX spectra were measured at each position of the image and accumulated over multiple scans of the same area. The intensity of one pixel in an elemental map (Fig. S-2 d-f) corresponds to the integrated peak intensity of element specific K_α X-ray emission lines (2.307 keV for S, 5.411 keV for Cr, 6.398 keV for Fe, and the 9.441 L_α emission line for Pt) of the accumulated spectra without background corrections. The elemental maps show (Figs. S-2 d-f)) that the matrix consists of Fe and Cr whereas the precipitate contains Cr and S solely. A depletion of Cr in the alloy is observed around the particle and along the grain boundary (Fig. S-2 e)).

An EDX line scan across the precipitate was performed to determine the precise composition of the particle. The position of the line scan is denoted by the black line in Fig. S-2 a). The quantified compositions are shown in Fig. S-2 c). The precipitate consists mainly of S and Cr with homogenous composition across the precipitate. Mean concentrations of 45.6 ± 0.7 % in atoms Cr, 51.7 ± 0.6 % in atoms S, and a low Fe concentration of 2.8 ±0.5 % in atoms were calculated from the data. The observed Fe content is assumed to be an artefact by re-deposition of Fe from the matrix during preparation of the sample. To verify this assumption, a line scan of the protective Pt layer deposited before thinning the lamella was acquired. Quantification leads to an average concentration of 2 % in atoms Fe within the initially pure Pt layer, which is at the sample surface and therefore further away from the base metal than the sulfide precipitate located within the base metal. This confirms re-deposition of Fe during sample preparation. Hence, the precipitate line scan was again quantified neglecting Fe. This results in average concentrations of 53.1 ± 0.6 % S in atoms and 46.9 ± 0.6 % in atoms Cr. These concentrations fit very well to the composition of murchisite (Cr_5S_6) which contains 54.44 % in atoms S and 45.45 % in atoms Cr at nominal composition.

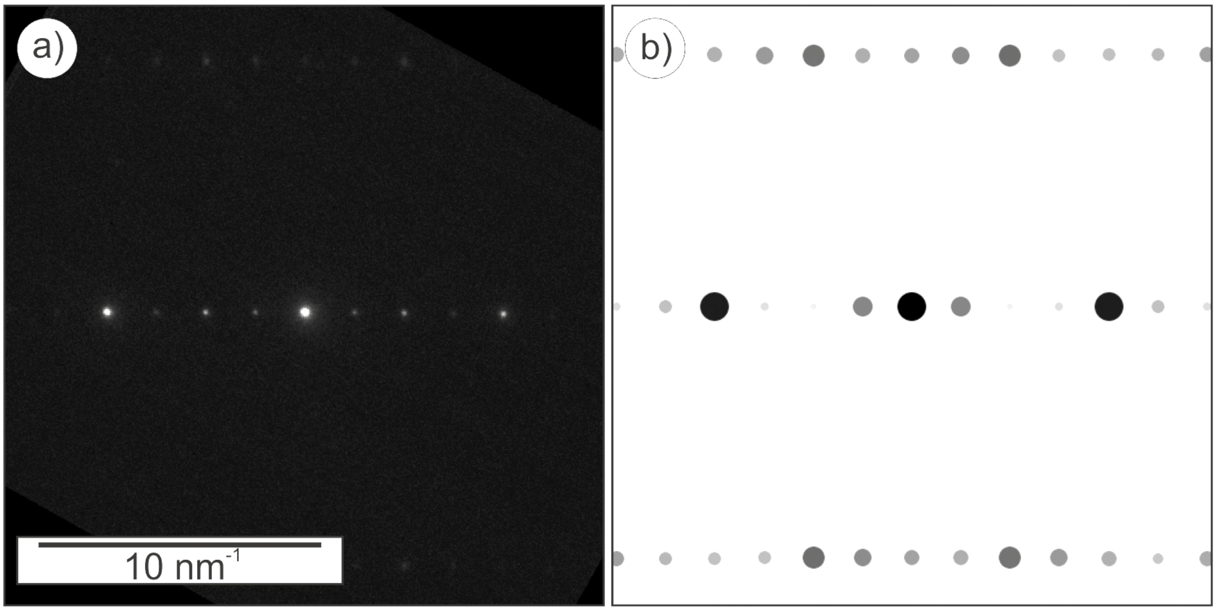

Fig. S-3 Diffraction Image along the [3 $\bar{1}$ $\bar{2}$ 0] zone axis of the sulfide precipitation within lamella: a) Experimental diffraction image, b) Simulated diffraction image of Cr_5S_6 murchisite.

SAED along the [3 $\bar{1}$ $\bar{2}$ 0] zone axis was performed for the particle shown in Fig. S-2. An experimental diffraction pattern of the particle is shown together with a simulated one in Fig. S-3. The simulation in Fig. S-3 b) shows a simulated diffraction pattern of hexagonal Cr_5S_6 murchisite with space group P$\bar{3}$1c oriented along the [3 $\bar{1}$ $\bar{2}$ 0] zone axis according to the crystal structure given by Vanlaar [19]. The reflection positions of the experimental diffraction pattern in Fig. S-3 a) match the reflections positions of the simulated diffraction pattern in Fig. S-3 b) very well and confirm the hexagonal structure expected for a murchisite particle.

EBSD

Fe13Cr aged for 24 h at 700 °C under the same gas atmosphere also show sulfide metal grain boundary precipitates. Using EBSD these precipitates were identified as murchisite (Cr5S6). Precipitates in this sample were deeper compared to precipitates formed in the 12 h sample aged at 650 °C.

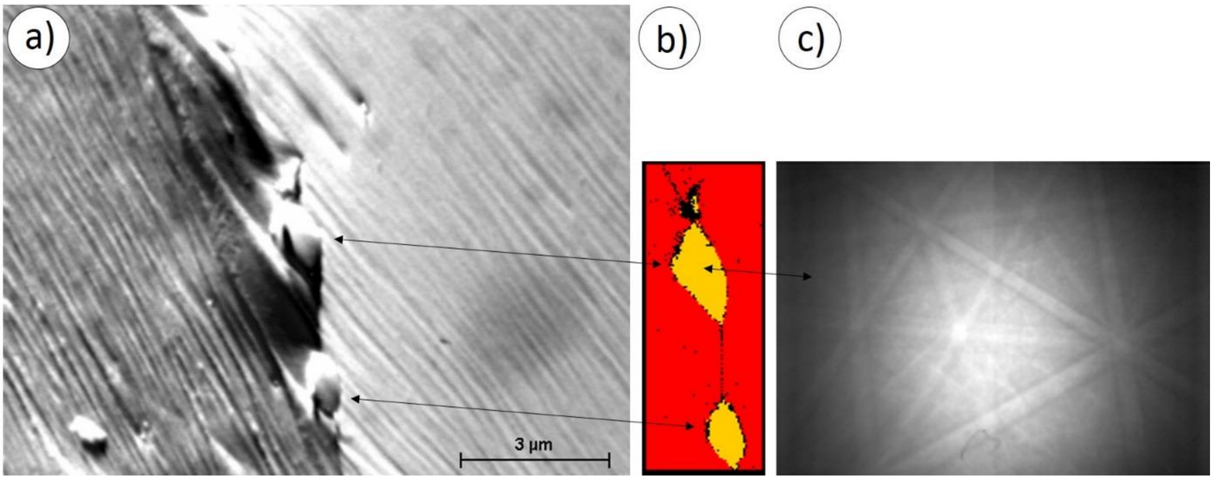

Fig. S-4 a) EBSD SEM image of Cr_5S_6 precipitates in Fe13Cr aged for 24 h at 700 °C under 99.5 % Ar and 0.5 % SO_2, sample stage was tilted 70°, (b) with corresponding phase map and c) Kikuchi pattern of the larger precipitate confirming murchisite – Cr_5S_6 structure

Formation Model

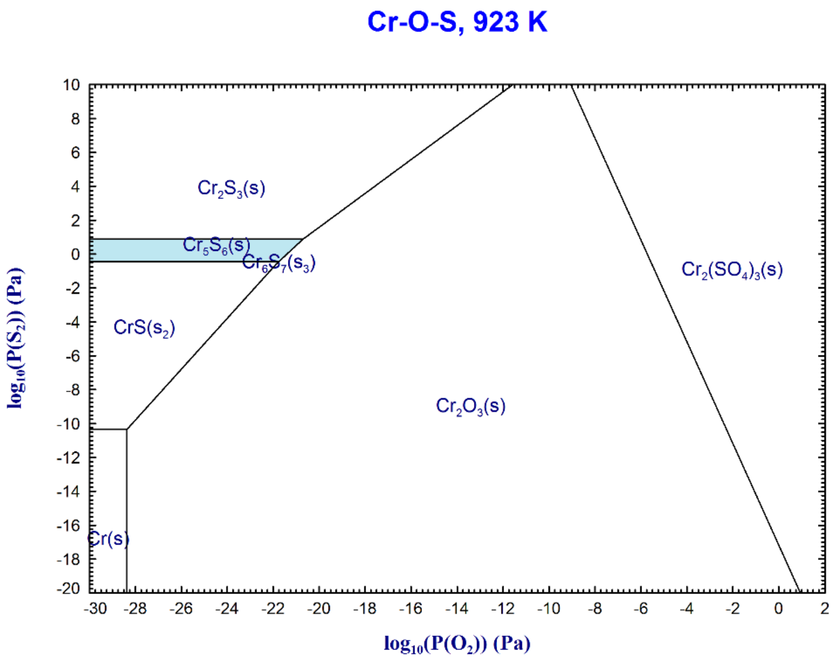

Fig. S-5 Stability diagram for the system Cr-O-S at 650 °C calculated by FactSage 7.0. Blue area marks the stability field for Cr_5S_6.