Identification and 3D Reconstruction of Cr₅S₆ Precipitates Along Grain Boundaries in Fe13Cr

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Metal sulfide grain boundary precipitates of a ferrous model alloy with 13 wt.% chromium formed at 650°C under a gas atmosphere containing 0.5% SO₂ and 99.5% Ar were investigated after ageing for 3 h, 6 h, and 12 h. The precipitates formed along grain boundaries were identified as Cr₅S₆ using energy-dispersive x-ray spectroscopy in transmission electron microscopy and electron backscatter diffraction analysis. Serial focused ion beam slicing was conducted followed by three-dimensional reconstruction to determine the number, size, and penetration depth of the precipitates evolved at the different time steps. There was a linear increase in the number of precipitates with time, while their average size increased only for the initial aging time but became constant after 6 h. Based on these results, a model for grain boundary sulfidation of ferritic alloys is discussed.

INTRODUCTION

Ferritic high-temperature alloys with Cr content up to 16 wt.% are used as components of different energy systems, such as coal- and biomass-fired power plants. These materials, especially VM12-SHC (12 wt.% to 13 wt.% Cr), are used as superheater tubes and are exposed to different temperatures, process pressures, and reactive atmospheres, such as H₂O/steam inside the tube and flue gas containing CO₂, SO₂, H₂O, NO_x, and O₂ on the fireside. High temperatures in combination with reactive atmospheres cause massive corrosion, which leads to a change of security-related properties. In particular, sulfurous gases such as SO₂ and SO₃ are known to increase corrosion rates and material loss of high-temperature iron-based alloys.^{1–5} The role of sulfur in combustion gases in corrosion of device materials and sulfidation of grain boundaries is still under discussion. Usually, sulfurous corrosion proceeds by formation of sulfide crystals within corrosion scale, resulting in faster diffusion of Fe cations and faster material loss.⁶ Sulfide precipitates in grain boundaries of the base metal are described in literature only occasionally⁷ and mostly for oxygen-free atmospheres.^{8,9} Newly

formed precipitates in grain boundaries due to corrosion might also have a significant influence on the mechanical properties of the component.¹⁰ Sulfide precipitates mentioned in literature mostly refer to CrS,^{7–9,11} no deeper consideration regarding phase composition and penetration depth is given but is essential to understand formation processes and conditions. Sulfur phases in contact with the base material of VM12 SHC have already been observed.¹² Sulfide precipitates within the base material were noticed in 9Cr-1Mo steels under sulfurous environments in the refinery industry.¹¹ In all the mentioned previous studies,^{7–9,11} the influence of different alloying elements and gas components on formation of grain boundary sulfides cannot be clearly distinguished. This work uses a model alloy of Fe with 13 wt.% Cr and SO₂ as reactive gas to study formation of sulfide precipitates along grain boundaries. The objectives are to identify grain boundary sulfides precisely and obtain information about the formation process by analyzing the size, density, and location of precipitates.

Focused ion beam (FIB) serial slicing was conducted site-specifically at grain boundaries to capture the shape and size of precipitates. Several

approaches in literature underline the potential of FIB slicing to study local reaction mechanisms in engineering materials.^{13,14} Transmission electron microscopy (TEM) analysis at one of the formed precipitates provided chemical information. The results support a formation model of grain-boundary sulfides in thermodynamic and microstructural aspects.

EXPERIMENTAL PROCEDURES

An iron-based model alloy with 13 wt.% Cr (Fe13Cr) was cut into 15 mm $\times$ 20 mm rectangular coupons of 3 mm thickness. The sides of each specimen were ground to 1200 grade using SiC paper and polished to 1 μm using diamond suspension. Ageing experiments for 3 h, 6 h, and 12 h time were performed at 650°C in an infrared light furnace¹⁵ with a gas mixture of 0.5% SO_2 and 99.5% Ar [see Electronic Supplementary Material (ESM) for further details]. The Ar/ SO_2 gas mixture was not equilibrated to minimize the SO_3 content or reach the gas composition of oxyfuel combustion processes.^{16,17}

For each sample, semiautomatic serial slicing was performed using a FIB/scanning electron microscopy (SEM) system (Quanta 3D FEG, FEI Company) equipped with gallium source and energy-dispersive x-ray (EDX) detection system. After localizing the region of interest along the grain-boundary path of the bulk material, a protective and smoothing platinum layer was deposited on the surface using an in situ chemical vapor deposition system. A surrounding volume material of 20 μm /20 μm /10 μm ($x/y/z$) was excavated, and a fiducial structure was generated for beam alignment. Subsequently, the volume was cut slice per slice using acceleration voltage of 30 kV, aperture of 0.5 nA, and slicing distance of 50 nm. After each cutting step, an SEM image was recorded. The resulting image stack was postprocessed using Amira 5.3 software (Thermo Fisher Scientific) for alignment of

images, labeling of precipitates, and generation of 3D figures using triangular approximation (Supplementary Fig. S1).

A lamella with large sulfide precipitates within a grain boundary of the 12-h sample was prepared for TEM (see sample preparation in ESM). TEM investigations were performed using a JEOL JEM-2200FS (JEOL, Japan) microscope with field-emission gun operating at 200 kV. Phase identification was performed by combining scanning transmission electron microscopy (STEM), EDX (energy resolution of 138 eV, JEOL, Japan), and selected-area electron diffraction (SAED) analysis. Diffraction patterns were simulated using the software package JAVA Electron Microscopy simulations version 4.3431U2015 by Stadelmann.¹⁸

RESULTS AND DISCUSSION

FIB Tomography Results

FIB 3D slicing confirmed sulfide precipitates within grain boundaries solely. The precipitates had disc-like shape with widest dimension parallel to the grain boundary. Figure 1a shows the reconstructed 3D figure of the 6-h sample with precipitates colored in red, oxide top layer in green, and porosity in blue. The volume fraction of precipitates was determined from the 3D figure. The correlation of microstructure and precipitates formed in the 3-h sample is shown in Fig. 1c.

The analyzed volume of each sample contained different grain boundary areas. To show the evolution of precipitates quantitatively, their number and total volume were normalized to the grain boundary length on the surface. Figure 2a shows a surface after 6 h of SO_2 treatment, exemplarily. The grains are still visible with grown oxide islands in the grain center consisting of FeCr_2O_4 , Fe_3O_4 , and Fe_2O_3 .¹⁵ The white framed area was chosen for slicing. Figure 2b shows the remodeled sample surface obtained from the sliced x - y images after alignment to display the surface grain boundary shape. The

Fig. 1. Exemplarily reconstructed volume of Fe13Cr after 6 h of SO_2 treatment. (a) x - y view showing precipitates (red) on grain boundaries (transparent) with pores (blue) in the oxide scale at the surface (green). (b) x - z view showing larger pores (yellow arrows) along the grain boundary. (c) Precipitates formed after 3 h of SO_2 treatment correlate with the microstructure of the Fe13Cr base metal.

Fig. 2. Evolution of precipitates as a function of time. (a) Fe13Cr surface after 6 h ageing; marked area was sliced in (b) top view (x - z) directly under the surface with visible grain boundaries (picture remodeled from x - y images). (c) Length of the grain boundary was measured as 31 μm in this example. (d) Correlation between number of precipitates normalized to 1 μm of surface grain boundary and time. (e) Correlation between total volume of all precipitates normalized to 1 μm of surface grain boundary.

grain boundary directly under the thin oxide layer is clearly visible. For the 6-h sample shown in Fig. 2c, this grain boundary length is determined to be 31 μm . The number of precipitates along 1 μm of surface grain boundary increased linearly with time (Fig. 2d). After 12 h ageing time, 2.3 precipitates were formed along 1 μm surface grain boundary, statistically, compared with 1 precipitate after 3 h ageing time. Longer ageing time leads to a higher number of precipitates, and larger precipitates. After 12 h ageing time, a total volume of 3.7 μm^3 chromium sulfides was formed in the sliced volume along 1 μm surface grain boundary (Fig. 2e). According to Fig. 2d, this volume is divided by 2.3 precipitates, resulting in an average volume of 1.6 μm^3 per particle. After 6 h, the average particle volume was about 1.4 μm^3 . Compared with the average volume per particle of 0.08 μm^3 after 3 h, the deviation between 6 h and 12 h is not significant. The precipitates grew in number and volume until 6 h ageing time, but thereafter only in number. Since the number of precipitates increased linearly, a constant nucleation rate is assumed. Therefore, the diffusion of S atoms along the grain boundary must be constant, too. Under the assumption that S atoms diffuse constantly per time unit through the grain boundary and more and more precipitates consume S atoms, precipitates grow slower because less S is left for each particle.

Figure 3a shows the distance from each precipitate to the surface along the grain boundary for each sample. The volumes of the 3-h precipitates were

clearly smaller, while the volume distribution for 6 h and 12 h ageing time seemed to be similar. No statement is made about the absolute precipitate depth in our case. Only in the case of 3 h ageing time was the last particle found at depth of around 6 μm . The maximum penetration depth of the 6-h and 12-h samples exceeded the depth possible using the 3D slicing method.

For each ageing time, the largest precipitates were concentrated in a region between 2 μm and 6 μm depth. With increasing penetration depth, their size decreased again. Very small grains could be found at each depth. Directly under the surface, only small grains were found. Figure 3b shows the correlation of the distance, volume, and number of precipitates for the 12-h sample, exemplarily. Sulfur diffusion along grain boundaries is not limited to the near surface, consequently.

TEM Results

TEM-EDX results verified an alloy composition of Fe and Cr, whereas the precipitate contained Cr and S solely. Cr depletion in the alloy was observed around the particle and along the grain boundary (Supplementary Fig. S2 and details). An EDX line scan across the precipitate showed average concentrations of 53.1 ± 0.6 at.% S and 46.9 ± 0.6 at.% Cr, indexing a composition of murchisite (Cr_5S_6), which contains 54.44 at.% S and 45.45 at.% Cr at nominal composition. To confirm the crystal structure of the Cr_5S_6 precipitate, SAED along the $[3 \bar{1}$

Fig. 3. Penetration depth of sulfur correlated with time: (a) dependence of volume of chromium sulfide precipitates along grain boundaries with time. (b) Volume and number of chromium sulfide precipitates versus their distance along the grain boundary after 12 h of SO_2 treatment.

$\bar{2} \ 0]$ zone axis was performed. The reflection positions of the experimental diffraction pattern matched the reflection positions of the simulated diffraction pattern according to the crystal structure given by Vanlaar¹⁹ very well, confirming the hexagonal structure expected for murchisite (Supplementary Fig. S3 and details).

Metal sulfide grain boundary precipitates formed in Fe13Cr aged for 24 h at 700°C under the same gas atmosphere were also identified as murchisite using electron backscatter diffraction (EBSD) (Supplementary Fig. S4 and details).

Formation Model

The presented results show distinct sulfidation of grain boundaries in Fe13Cr even at an early stage of corrosion. The number and size of precipitates increased with time, leading to the assumption of continuous sulfur diffusion along grain boundaries during the ageing experiment. At the surface, formation of a Cr-rich oxide in the beginning is thermodynamically preferred. According to a phase diagram calculated using FactSage 7.0²⁰ for the same system,²¹ this Cr-rich oxide is most likely chromite FeCr_2O_4 . Chromite consumes a high amount of Cr from the alloy, in this case 2 μm under the original surface, which agrees with the common oxidation model of Fe-Cr alloys.⁷ The formation of the largest Cr sulfide particles is observed between penetration depth of 2 μm and 6 μm . It is assumed that SO_2 decomposes at the oxide surface layer, and oxygen is consumed to form further oxides such as Fe_2O_3 and Fe_3O_4 in the outer corrosion zone and FeCr_2O_4 in the inner corrosion

zone, while S diffuses continuously through the oxide.^{15,21} One part of S is consumed by (Fe,Cr)S sulfide growth in the inner corrosion zone below the external oxide layer at the scale-alloy interface,²² while another part accumulates in pores above the grain boundary. The increased sulfur partial pressure triggers S inward diffusion along the grain boundary. The reconstructed 3D figure shows a high number of pores elongated along the grain boundary below the oxide layer (Fig. 2b). S together with Cr from the alloy, diffusing faster outwards at the grain boundaries than within the grains,²³ can nucleate Cr_5S_6 at the grain boundaries. Due to the higher amount of Cr below 2 μm distance from the original alloy surface, the precipitates in this region become larger. Cr is consumed to form oxides on top and precipitates within the grain boundary, which creates a depletion zone (Fig. 4a).

Formation of Cr sulfides is thermodynamically preferred compared with Fe sulfide formation.²⁴ Formation of Cr_5S_6 precipitates requires sulfur partial pressure of $p_{\text{S}_2} = 10^{-1}$ Pa and oxygen partial pressure of $p_{\text{O}_2} = 10^{-21}$ Pa (Supplementary Fig. S5). The main driving force for formation of Cr_5S_6 precipitates is therefore supersaturation through constant S diffusion. TEM-EDX/SAED as well as EBSD analysis identified metal sulfide grain boundary precipitates as Cr_5S_6 (murchisite). The precipitates at the grain boundary with the greatest possible distance to the surface were used for analysis by TEM-EDX and EBSD. However, the transition to CrS, as suggested in the phase diagram (Supplementary Fig. S5), in deeper regions or after longer ageing time, cannot be excluded. In the 6-h and 12-h samples, more sulfur could diffuse into

Fig. 4. (a) Elemental distribution at a cross-section after 12 h ageing time measured using EDX spectroscopy. (b) Schematic formation model of sulfide precipitates based on experimentally found relations here and in former studies.²² Arrows mark the direction of diffusion.

the metal to form larger precipitates compared with the 3-h sample. The question then arises of why the particle size is not significantly larger in case of 12 h compared with 6 h ageing time. In fact, the 12-h sample has higher total volume and higher number of precipitates. The loss of growth is more likely due to more particles that consume S and Cr. If sufficient Cr is no longer present at one location, S must diffuse further into the material to form new precipitates.

CONCLUSION

Grain boundary sulfidation is a prominent phenomenon in alloys used for superheater tubes in power plants, impacting the service lifetime of construction devices. This work identified and reconstructed grain boundary sulfides as Cr₅S₆ (murchisite) for a Fe13Cr model alloy, already being present at an early stage of corrosion. The number and volume of precipitates increased with time. The particle size was nearly constant after 6 h ageing time due to constant diffusion of S into the grain boundary together with a constant nucleation rate. Diffusion of sulfur along grain boundaries was faster than within the metal lattice, since no sulfide precipitates were found within the alloy grains at similar penetration depth. Furthermore, the penetration depth increased with increasing ageing time, particularly from 3 h onwards. The formation mechanism of grain boundary sulfides is strongly correlated to pore formation during the corrosion process. The sulfur partial pressure within the pores is assumed to increase dramatically to further support sulfur inward diffusion and grain boundary sulfidation.

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ELECTRONIC SUPPLEMENTARY MATERIAL

The online version of this article (<https://doi.org/10.1007/s11837-018-2940-y>) contains supplementary material, which is available to authorized users.

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