Identification and 3D Reconstruction of Cr$_5$S$_6$ Precipitates Along Grain Boundaries in Fe13Cr

KATHRIN NÜTZMANN, NICOLE WOLLSCHLÄGER, CHRISTIAN ROCKENHAUSER, AXEL KRANZMANN, and CHRISTIANE STEPHAN-SCHERB

1.—Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany. 2.—Freie Universität Berlin, Fachbereich Geowissenschaften, Malteserstraße 74-100, 12249 Berlin, Germany. 3.—e-mail: kathrin.nuetzmann@bam.de

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% SO$_2$ 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 Cr$_5$S$_6$ 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 H$_2$O/steam inside the tube and flue gas containing CO$_2$, SO$_2$, H$_2$O, NO$_x$, and O$_2$ 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 SO$_2$ and SO$_3$ are known to increase corrosion rates and material loss of high-temperature iron-based alloys. 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. Sulfide precipitates in grain boundaries of the base metal are described in literature only occasionally and mostly for oxygen-free atmospheres. Newly formed precipitates in grain boundaries due to corrosion might also have a significant influence on the mechanical properties of the component. Sulfide precipitates mentioned in literature mostly refer to CrS; 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. Sulfide precipitates within the base material were noticed in 9Cr-1Mo steels under sulfurous environments in the refinery industry. In all the mentioned previous studies, 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 SO$_2$ 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. 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 × 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 furnace with a gas mixture of 0.5% SO2 and 99.5% Ar [see Electronic Supplementary Material (ESM) for further details]. The Ar/SO2 gas mixture was not equilibrated to minimize the SO3 content or reach the gas composition of oxyfuel combustion processes.

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 4.3.431U2015 by Stadelmann.

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 SO2 treatment, exemplarily. The grains are still visible with grown oxide islands in the grain center consisting of FeCr2O4, Fe3O4, and Fe2O3.15 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
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 \( \mu \)m. The number of precipitates along 1 \( \mu \)m of surface grain boundary increased linearly with time (Fig. 2d). After 12 h ageing time, 2.3 precipitates were formed along 1 \( \mu \)m 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 \( \mu \)m\(^3\) chromium sulfides was formed in the sliced volume along 1 \( \mu \)m 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 \( \mu \)m\(^3\) per particle. After 6 h, the average particle volume was about 1.4 \( \mu \)m\(^3\). Compared with the average volume per particle of 0.08 \( \mu \)m\(^3\) 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 \( \mu \)m. 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 \( \mu \)m and 6 \( \mu \)m 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 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 \( \pm \) 0.6 at.% S and 46.9 \( \pm \) 0.6 at.% Cr, indexing a composition of murchisite (Cr\(_5\)S\(_6\)), which contains 54.44 at.% S and 45.45 at.% Cr at nominal composition. To confirm the crystal structure of the Cr\(_5\)S\(_6\) precipitate, SAED along the [3 1 0]
Σ 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 Vanlaar 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 7.0 for the same system, this Cr-rich oxide is most likely chromite FeCr$_2$O$_4$. 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. 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$_2$O$_3$ and Fe$_3$O$_4$ in the outer corrosion zone and FeCr$_2$O$_4$ in the inner corrosion zone, while S diffuses continuously through the oxide. 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, 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, can nucleate Cr$_5$S$_6$ 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. Formation of Cr$_5$S$_6$ precipitates requires sulfur partial pressure of $p_{SO_2} = 10^{-1}$ Pa and oxygen partial pressure of $p_{O_2} = 10^{-21}$ Pa (Supplementary Fig. S5). The main driving force for formation of Cr$_5$S$_6$ precipitates is therefore supersaturation through constant S diffusion. TEM–EDX/SAED as well as EBSD analysis identified metal sulfide grain boundary precipitates as Cr$_5$S$_6$ (murchisite). The precipitates at the grain boundary with the greatest possible distance to the surface were used for analysis by TEM-SAED 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...
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 Cr$_5$S$_6$ (murchisite) for a Fe$_{13}$Cr 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.

OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

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.

REFERENCES

1. P. Kofstad, High Temperature Corrosion, 1st ed. (London/New York: Elsevier Applied Science, 1988), pp. 437–464.
2. M. Kutz, Handbook of Environmental Degradation of Materials, 1st ed. (Norwich: William Andrew Pub, 2005), pp. 132–142.
3. S. Mrowec, Oxid. Met. 44, 177 (1995).
4. H.J. Grabke, E. Reese, and M. Spiegel, Corros. Sci. 37, 1023 (1995).
5. A. Jalowicka, W. Nowak, D. Naumenko, L. Singheiser, and W.J. Quadakkers, Mater. Corros. 65, 178 (2014).
6. T. Flatley and N. Birks, J. Trans. Iron Steel Inst. 209, 523 (1971).
7. S.H. Choi and J. Stringer, Mater. Sci. Eng. 87, 237 (1987).
8. M. Loudjiani, J.C. Pyvin, C. Roquescarmes, P. Lacombe, and J.H. Davidson, Metall. Trans. A 13, 1299 (1982).
9. T. Narita, W.W. Smeltzer, and K. Nishida, Oxid. Met. 17, 299 (1982).
10. H.J. Mai er, T. Niendorf, and R. Bürgel, Handbuch Hochtemperatur-Werkstofftechnik, 5th ed. (Wiesbaden: Springer Fachmedien, 2015), pp. 60–70.
11. J. Hucińska, Adv. Mater. Res.-Switz. 6, 16 (2006).
12. A. Kranzmann, T. Neddemeyer, A.S. Ruhl, H. Huenert, D. Betitso, G. Oder, and R.S. Neumann, Int. J. Greenh. Gas Control 5, 168 (2011).
13. C. Duhamel, J. Caballero, T. Couvant, J. Crepin, F. Ga- slain, C. Guerre, H.T. Le, and M. Wehbi, Oxid. Met. 88, 447 (2017).
14. S.S. Singh, J.J. Loza, A.P. Merlde, and N. Chawla, Mater. Charact. 118, 102 (2016).
15. K. Nützmann, A. Kranzmann, and C. Stephan-Scherb, Mater. High Temp. (2018). https://doi.org/10.1080/09603409.2018.1446705.
Identification and 3D Reconstruction of Cr\textsubscript{5}S\textsubscript{6} Precipitates Along Grain Boundaries in Fe\textsubscript{13}Cr

16. T. Wall, Y.H. Liu, C. Spero, L. Elliott, S. Khare, R. Rathnam, F. Zeenathal, B. Moghtaderi, B. Buhre, C.D. Sheng, R. Gupta, T. Yamada, K. Makino, and J.L. Yu, Chem. Eng. Res. Des. 87, 1003 (2009).
17. D. Fleig, F. Normann, K. Andersson, F. Johnsson, and B. Leckner, Energy Proc. 1, 383 (2009).
18. P.A. Stadelmann, Ultramicroscopy 21, 131 (1987).
19. B. Vanlaar, Phys. Rev. 156, 654 (1967).
20. E.B.C.W. Bale, P. Chartrand, S.A. Dectereov, G. Eriksson, K. Hack, I.H. Jung, Y.B. Kang, J. Melancon, A.D. Pelton, C. Robelin, and S. Petersen, Calphad 33, 295 (2009).
21. C. Stephan-Scherb, K. Nützmann, A. Kranzmann, M. Klaus, and C. Genzel, Mater. Corros. (2018). https://doi.org/10.1002/maco.201709892.
22. K. Chandra, A. Kranzmann, R. Saliwan Neumann, G. Oder, and P. Rizzo, Oxid. Met. 83, 291 (2015).
23. J.-H. Kim, B.K. Kim, D.-I. Kim, P.-P. Choi, D. Raabe, and K.-W. Yi, Corros. Sci. 96, 52 (2015).
24. D.J. Young, High Temperature Oxidation and Corrosion of Metals, 2nd ed. (Amsterdam: Elsevier, 2016), p. 399.