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Copper-assisted stress-corrosion cracking of stainless steel steam mesh

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Abstract

The study deals with an interesting case of a stainless-steel steam mesh brittle fracturing in a coal power station. The material was studied using scanning electron microscopy (SEM), metallography, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and glow discharge optical emission spectroscopy (GD-OES). The analyses showed an elevated content of copper in the material. Copper was notably enriched in an oxide layer where it occurs mostly in an oxide form, although metallic copper was also detected. Copper oxidation and reduction cause defects within the oxide layer and, in connection with mechanical stress, result in intergranular cracking of steel.

Key words: stainless steel, oxidation, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), glow discharge optical emission spectroscopy (GD-OES)

1. Introduction

An elevated content of copper in stainless steel has recently become a largely discussed topic. With typical scrap metal processing, it is impossible to remove the copper from steel and it thus accumulates in the material. Should the content of copper exceed 0.3 wt.%, it may cause serious problems in certain applications in terms of corrosion. Copper generated at grain boundaries first became an issue in processes involving nitric acid, including the production of HNO_3 and in nuclear fuel reprocessing [1, 2].

Copper is usually added to stainless steel to reduce hydrogen overvoltage and to facilitate material passivability in acidic environments [3]. Precipitation of copper as ε-phase is used to strengthen all structural types of stainless steel [4, 5]. High-alloyed austenitic steels with a copper content of approx. 3 wt.%, which provide excellent creep resistance due to the ε-phase precipitation, are used for superheaters in the power industry [6]. The elevated content of copper increases the fracturing of oxide layers and the rate of high-temperature oxidation [7]. However, this phenomenon does not dramatically shorten the service-life of superheaters, because they operate under lower temperatures.

Fig. 1. An image of the damaged separator.

This study deals with a relatively new case of steam mesh (separator) cracking. Five cases of steam separator cracking (Fig. 1) and one case of cracked steam turbine baffle plate were reported. All defects occurred

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*Corresponding author: e-mail address: jan.stoulil@vscht.cz within 4,000 and 7,000 h of operation under the conditions of 540 ℃ and 9.6 MPa. The material from one of the separators was delivered for analysis and further testing.

2. Experimental

The specimens for metallographic analysis were embedded in acrylate resin and subsequently ground by emery paper to a roughness of P1200. Subsequently, they were polished using a 3 μm diamond paste. The specimens were etched for 30 s in a solution of 10 wt.% oxalic acid under a voltage of 6 V. A platinum wire was used as a counter-electrode.

Other specimens were analysed by the SEM method (VEGA 3, *TESCAN*), XRD (X'Pert PRO, *PANalytical*), XPS (ESCAProbeP, *Omicron Nanotechnology*) and GD-OES (GD-Profiler 2, *Horiba Jobin Yvon*).

Model exposures were performed at 600 ℃ in an argon environment and saturated with steam at 40 ℃; the resulting steam concentration in argon is approximately 4 %, which is a model environment for supercritical water [8]. Two types of material were exposed. One of them had a similar composition as the cracked separator (FeCr18Ni10Cu0.4) and the other had an elevated content of copper (FeCr18Ni10Cu3). The specimens were exposed for a period of 5, 50 and 500 h. Morphology of the oxide layer and element profiles on the oxide layer and in the mass of the material were evaluated on the specimens after the exposure using SEM and GD-OES, respectively.

3. Results

In all cases, GD-OES detected an elevated content of copper exceeding a level of 0.4 wt.% in the damaged equipment, which although was normal in other aspects, used the material FeCr18Ni10 (EN 1.4301; AISI 304). The material analysis of steel meshes that had been in operation for more than 70,000 h showed that the copper content was always lower than 0.1 wt.% in these cases.

The fracture surface and the surface oxide morphology were studied first by SEM. The fracture surface corresponded to an intergranular fracture (Fig. 2), and the crack visibly copies borderlines of the material grains. When compared with energy dispersive X-ray analysis (EDS), the fracture surface did not contain any statistically more notable content of copper than the remaining surface. The surface morphology of the oxide layer is very rough (Fig. 3). However, oxides in the inner layer are compact and no massive oxidation was observed along the grain boundaries going inside the material, as can be seen on the metallographic section in Fig. 4. The thickness of the oxide layer is approximately 14 μm.

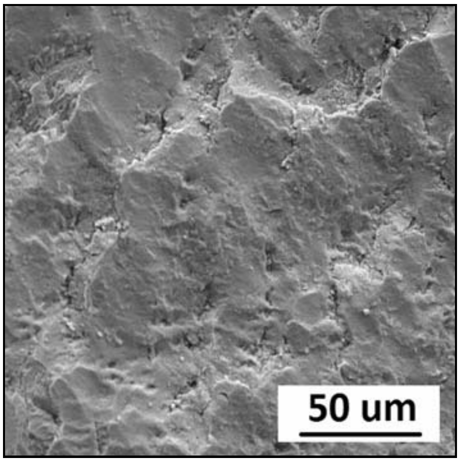

Fig. 2. SEM image of the fracture area.

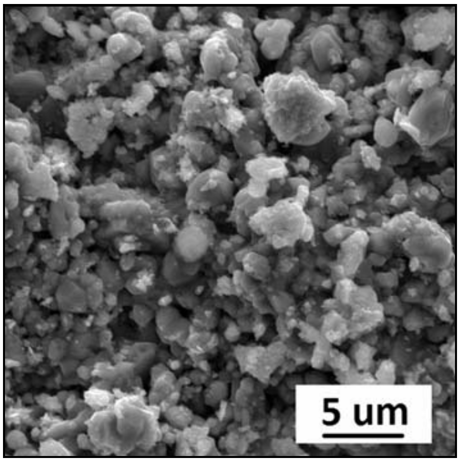

Fig. 3. SEM image of the surface oxide morphology.

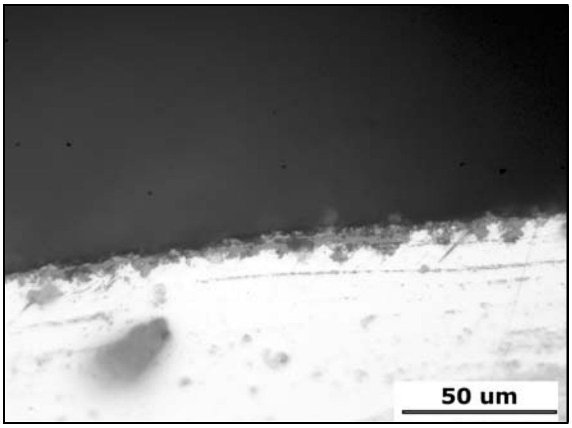

Fig. 4. Metallographic section of the specimen cross-cut.

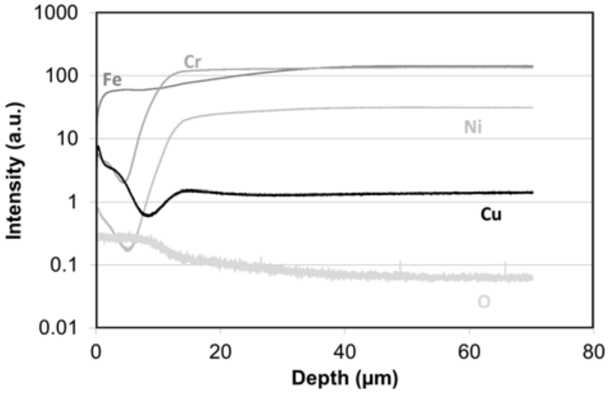

Fig. 5. GD-OES profile of chemical composition of the surface.

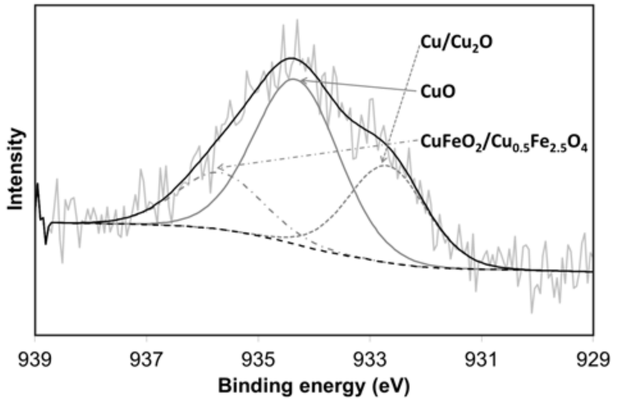

Fig. 6. The specimen's XPS spectrum at a depth of 2 μm.

Table 1. X-ray diffraction analysis of the surface layer composition

Compound	Content
Fe_2O_3, $Cr_{1.6}Fe_{0.4}O_3$, Fe_3O_4	~ 95 vol.%
$CuFeO_2$, $Cu_{0.5}Fe_{2.5}O_4$, metallic Cu	~ 5 vol.%

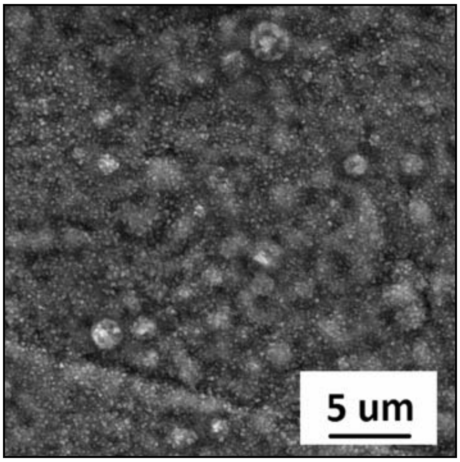

Fig. 7. SEM image of the sample FeCr18Ni10Cu0.4 exposed in a model environment for 500 h.

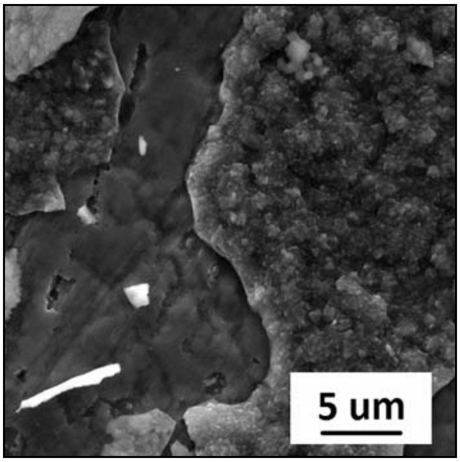

Fig. 8. SEM image of the sample FeCr18Ni10Cu3 exposed in a model environment for 500 h.

Glow discharge optical emission spectroscopy (GD-OES) was used in order to identify the in-depth element profile (Fig. 5). In contrast to other elements, copper is significantly enriched in the layer of oxides. When compared to the content in steel, the enrichment is already apparent at the metal/oxide interface, and is even more significant in the layer of oxides.

Oxidation states of copper were studied by X-ray photoelectron spectroscopy (XPS). An argon beam was used to sputter 2 μm from the oxide layer. The Cu $2p_{3/2}$ peak spectrum is shown in Fig. 6. The spectrum was fitted with the estimated full width at half the maximum level of 1.5 eV. There are three obvious peaks in the spectrum: 932.6 eV – metallic copper and cuprite (Cu_2O), 934.3 eV – tenorite (CuO), and 935.7 eV – mixture of Cu oxides with other metals.

X-ray diffraction (XRD) detected the presence of copper in the oxide layer (Table 1). In addition to hematite (Fe_2O_3) and magnetite (Fe_3O_4) substituted by chromium, substituted magnetite $Cu_{0.5}Fe_{2.5}O_4$, delafossite ($CuFeO_2$) and metallic copper were also detected. Metallic copper may come from:

– Cu oxide reduction to the detriment of Fe and Cr oxidation;

– disproportionation of Cu^+ ion [9];

– or as a remainder after the matrix oxidation.

A thin layer of the oxide FeCr18Ni10Cu0.4 after the 500 h exposure is seen in Fig. 7. The oxides after the 'model' exposure have a finer structure compared to after the 'real conditions' exposure. When the content of copper in the material is elevated (FeCr18Ni10Cu3), delamination of the oxide layer oc-

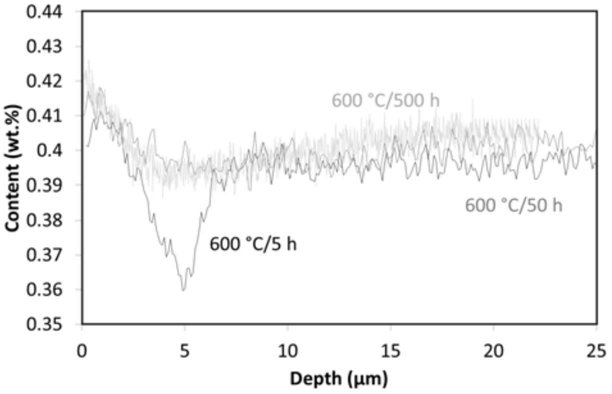

Fig. 9. GD-OES profile of copper under the oxide/metal interface.

curs during the 500 h model exposure (Fig. 8). The copper concentration profile in the material beneath the oxide layer is shown in Fig. 9. A copper-depleted zone can be found below the oxide/metal interface after the 5 h exposure. After 50 h, the concentration is balanced and corresponds to the 'real conditions' exposure after 5000 h at 540 ℃. In all cases, copper enrichment in the oxide layer was notably lower than in the 'real conditions' exposure. No significant copper segregation at the oxide/metal interface was detected in any of the model cases.

4. Discussion

The material contains an elevated mass of copper. A defective layer of oxides with a significant content of copper oxides and metallic copper was detected on the material surface. Mixtures of oxides (substituted magnetite and delafossite) were also seen. Common oxides, such as cuprite and tenorite, may also be present in the layer in a low crystallinity form. It is likely that the deficiency of the outer oxide layer is caused by the presence of copper oxides and their reversal reduction to metallic copper. These defects may work as stress risers and facilitate local damages to the oxide layer.

The character of the damage is intergranular but it is not caused by direct oxidation along grain boundaries. Considering the common trouble-free use of materials with an elevated content of copper for the production of superheaters, it is likely that the defects are associated with the mechanical stresses that are commonly associated with separators or steam turbine baffle plates.

The temperature is too low; therefore the impact of liquid metal embrittlement is very unlikely. The most probable corrosion mechanism is localised cracking of the defective oxide layer as a result of mechanical stress. Even though no elevated content of copper was identified on the fracture area, the negative impact of copper oxide reduction to the detriment of Fe and Cr oxidation cannot be excluded.

Model exposures show that an elevated content of copper in metal and oxide may lead to oxide defectiveness and eventually to the layer delamination. A higher concentration of copper was not seen on the oxide/metal interface, copper segregation on the oxide/metal interface does not affect oxidization and the mechanism of preferential oxidization of Fe and Cr and subsequent enrichment of the surface with Cu was also found to be improbable. It was reported that the material was depleted of copper in close vicinity of the oxide/metal interface in the early phase of oxidization. Copper probably turns into oxide at the start of oxidization in a period of time by an order of magnitude shorter than that during which the material is damaged.

5. Conclusions

The analyses proved the enrichment of copper in the oxide layer. The oxide formed is much more defective and susceptible to damage as a result of the separator's mechanical stress. Localised acceleration of oxidation as a result of Cu oxide reduction by elements with a higher affinity to oxygen, namely chromium, is also possible.

Acknowledgement

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References

[1] Kain, V., Chandra, K., Kumar, M. K., Rhode, S., Gupta, R.: In: Proceedings of Eurocorr 2010. New York, Curran Associates 2011, p. 674. ISBN 9781617824029.
[2] Kapoor, K., Kain, V., Gopalkrishna, T., Sanyal, T., De, P. K.: Journal of Nuclear Materials, *322*, 2003, p. 36. doi:10.1016/S0022-3115(03)00302-7
[3] Itzhak, D., Peled, P.: Corrosion Science, *26*, 1986, p. 49. doi:10.1016/0010-938X(86)90122-8
[4] Isheim, D., Vaynman, S., Fine, M., Seidman, D.: Scripta Materialia, *59*, 2008, p. 1235. doi:10.1016/j.scriptamat.2008.07.045
[5] Ku, B. S., Yu, J.: Scripta Materialia, *45*, 2001, p. 205. doi:10.1016/S1359-6462(01)01019-3
[6] Cheng, S. C., Liu, Z. D., Yang, G., Yang, Y., Wang, L. M., Sun, X. J., Dong, H.: In: Proceedings of the 1st International Conference "Super High Strength Steel". Milano, Italy, Associazione Italiana di Metallurgia 2005, ISBN 8885298567.
[7] Le May, I., McDonald Schetky, L.: Copper in Iron and Steel. New York, Wiley 1982.

[8] Żurek, J., Michalik, M., Schmitz, F., Kern, T. U., Singheiser, L., Quadakkers, W. J.: Oxidation of Metals, *63*, 2005, p. 401. doi:10.1007/s11085-005-4394-1

[9] Hargrave, R. E.: Corrosion, *47*, 1991, p. 555. doi:10.5006/1.3585292