Cyclic oxidation to high temperature of ASTM - A53 grade B

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Abstract. Samples of ASTM A53 steel grade B underwent 500 oxidation cycles at 600°C. Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD) were performed to study the morphology, composition and phase structure of Fe₂O₃ and Fe₃O₄ layers on oxidation surface. Such layers were homogenous and poorly adhesive. Mass loss was significant due to absence of protective oxides and inevitable flaking, leaving the substrate exposed to corrosive environment.

1. Introduction
Industrial processes at high temperature, under corrosive and erosive conditions, not only affect life cycle of materials but also increase maintenance costs. Since carbon steel alloys are recurrently used, it is important to analyse their behaviour when integrity of parts is compromised to such an extent that a complete degradation might take place, thus the manufacturing process must cease leading to economic losses [1-3].

The usage of steel alloys (ASTM A53 grade B) requires heating and cooling cycles, as in the case with boilers and airplane turbines. During cooling, the most resistant alloys give rise to slow formation of oxide layers that retard the mechanical failure. The difference between thermal expansion coefficients of the metallic substrate and the oxides lead to several phenomena, namely: increase of compressive strength of substrate, as well as cracking, delamination and flaking of the oxide layers. Finally, substrate surface become exposed to the action of oxide gases and oxidation rate increases [4,5].

Cyclic Oxidation Tests (COT) are frequently used to assess materials employed under high-temperature conditions. COT usually consist in subjecting materials to heating and cooling cycles to create testing conditions shorter and more severe than actual working conditions. The most relevant indicator in COT is mass variation of the substrate. Samples are also exposed to thermal tensions that may produce some effects observable through SEM; such as cracking, blistering or flaking of oxide layer [2,6,7].

2. Experimental procedure
ASTM A53 grade B specimens (10cm×7cm×5cm) underwent cyclic oxidation in an automated convection oven. Each cycle had a heating stage at 600°C during 50 minutes followed by a cooling stage during 10 minutes, where samples were placed 30 cm away from the oven. Specimens mass was measured with an analytical balance (10⁻³g accuracy) to monitor changes; measurements were taken before introducing samples in the oven and after cycles 5, 10, 25, 50, 100, 150, 200 and 500. Chemical composition of oxides formed was reported by means of EDS, additionally SEM was carried out to obtain surface and cross section images, topography, porosity and homogeneity of oxide layers.
3. Results and analyses

Figure 1 summarizes the mass variation of specimens in accordance with measurements of the analytical balance. The first 50 cycles exhibited the largest amount of oxides generated, and thus the highest oxidation rates. SEM topography explains such mass gain by reporting the emergence of oxide spinels until 5th cycle and the subsequent formation of the protective oxide layer after the 10th cycle. From the 50th cycle on, oxides generation and oxidation rates decrease; until the 150th cycle where samples begin to lose mass due to iron oxides flaking off the surface [8-10].

![Figure 1](image1.png)

**Figure 1.** Mass variation during cyclic oxidation.

Cross section of a sample after the 10th cycle based on SEM topography (Figure 2) reveals three zones: the resin corresponding to the darkest zone, the substrate (point 1) whose chemical composition is 99.2% iron and 0.8% oxygen; and finally, a 100-µm-thick protective oxide layer (points 2, 3, 4) with good adherence to substrate, although exhibiting high porosity that will result in cracking. The respective EDS attests to the presence of protective compounds Fe₂O₃ and Fe₃O₄ in the oxide layer, given its results reported 80.4% iron and 19.6% oxygen.

![Figure 2](image2.png)

**Figure 2.** Cross section of sample after the 10th oxidation cycle.
Magnified view illustrated in Figure 3 confirms the good adherence between substrate (point 1) and protective oxide layer (points 2 to 9). However, Figure 3 also details the little homogeneity on points 8 and 9 of the oxide layer due to constant thermal expansion, which in turn induces flaking on upper surface of the oxide layer. These conditions make easier the oxygen penetration and/or the inter-diffusion of the oxide layer with Fe. This phenomenon occurred due to iron has two energy levels, where oxide structure determines the physical-chemical properties of surface [11-14]. For this magnified zone, EDS yielded the following percentages 82.3% iron and 17.7% oxygen.

The oxide layer reached the greatest thickness (450µm) after the 50th cycle, as seen in Figure 4. The preview is in accordance with the highest oxidation rates described in Figure 1. Nevertheless, a first horizontally oriented crack separating points 1 and 2 can be considered as the precursor of the
subsequent flaking. Chemical composition at this point for the oxide layer presents 21.8% oxygen and 78.2% iron.

Figure 5. Magnified view on protective oxide layer after 50th oxidation cycle.

Figure 5 provides further details on the zone surrounding the first reported crack. As far as the porosity is concerned; whereas pores appearing after the 10th cycle had an average size of 7µm, those appearing after the 50th cycle were nearly 13µm in average. EDS found the following chemical compositions: 22.1% oxygen and 77.9% iron for points (1, 2, 4 and 5), as well as 75.5% oxygen, 14% calcium and 10.5% iron for the crack (point 3).

Figure 6. Cross section of sample after the 150th oxidation cycle.

Cross section of sample (Figure 6) points out that the oxide layer has become thinner (200µm), as result of flaking due to some severe horizontally oriented cracks. Having said that, cracking from this point on will develop vertical orientation leading to the inevitable exposure of the substrate to corrosive environment. There is not presence of pores nor cracks in the interphase between substrate
and oxide layer according to Figure 6. The chemical compositions corresponding to this Figure are: for oxide layer (75.9% iron and 24.1% oxygen) and for the substrate (98.9% iron and 1.1% oxygen).

![Figure 7](image)

**Figure 7.** Magnified view on protective oxide layer after 150th oxidation cycle.

Magnified view illustrated in Figure 7 allows to see that the vertically oriented crack is about to come in contact with the substrate. The chemical composition corresponding to this magnified area revealed the highest percentage of oxygen (29.3%), while iron decreases to 70.7%. Experimental results are in strong agreement with literature stating that iron oxides increase with exposure time to corrosive environment at 600°C [10-17]. EDS analysis corresponding to the substrate after the 150th cycle still reports percentages of iron above 98.2% with low percentage of oxygen (1.8%).

4. Conclusions

ASTM A53 grade B steel was subjected to cyclic oxidation at 600°C to simulate shorter and more severe than actual working conditions. Oxides produced begin to lose their protective properties after 50 cycles, when the first significant cracking takes place. Eventually, the oxide layer flakes off the surface leaving the substrate exposed to the corrosive environment (after 150 cycles).

Fe$_2$O$_3$ and Fe$_3$O$_4$ were the predominant oxides during the entire cyclic oxidation, their precursor spinels started to form after the 5th cycles.

Findings in the experimental tests concur with similar studies on thermal expansion of materials concerning high porosity and cracking.

References

[1] X Cheng, L Fan, H Yin, L Liu, K Du, D Wang 2016 High-temperature oxidation behaviour of Ni-11Fe-10Cu alloy: Growth of a protective oxide scale *Corrosion Science* **112** 54-62

[2] Huabing Li, Bindin Zhang, Zhouhua Jiang, Shucai Zhang, Hao Feng, Peide Han 2016 A new insight into high-temperature oxidation mechanism of super-austenitic stainless steel S32654 *Journal of Alloys and Compounds* **686** 326-338

[3] Bradford S A 2001 *High temperature corrosion, Handbook A* vol 2, ed John E Bringas (Alberta: CASTI Publishing Inc) pp 62-76

[4] Marulanda Jose L, Castañeda SaáI, Pérez Francisco J 2013 Study microstrucuture and compositions of oxidation in steam at 700 and 750°C of austenitic steels AISI 304, 316 and 317 *Revista Facultad de Ingeniería Universidad de Antioquia* **67** 98-111

[5] B Pujilaksono, T Jonsson, M Halvarsson, J Svensson, L Johansson 2010 Oxidation of iron at 400–600 C in dry and wet O$_2$ *Corrosion Science* **52** 1560–1569
[6] Norinsam K Othman, Jianquiang Zhang, David J Young 2010 Temperature and water vapour effect on the cyclic oxidation behavior of Fe-Cr alloy Corrosion Science 52(9) 2827-2836

[7] E Dokumaci, I Özkan, B Önay 2013 Effect to boronizing on the cyclic oxidation of stainless steel Surface & Coatings Technology 232 22-25

[8] Li Dong-Sheng, Dai Qi-xun, Cheng Xiao-nong, Wang Rong-rong, Huang Yan 2012 High- Temperature oxidation resistance of austenitic stainless steel Cr18Ni11Cu3Al3MnNb Journal of Iron and Steel Research, International 19(5) 74-78

[9] Balaji Raman, Derek M Hall, Stephen J Shulder, Michael F Caravaggio, Serguei N Lvov 2016 An experimental study of deposition of suspended magnetite in high temperature- high pressure boiler type environments Colloids and surfaces A: Physicochemical and Engineering Aspects 508 48-56

[10] Xiao-jiang Liu, Yong-quan He, Guang-ming Cao, Tao Jia, Teng-zhiu Wu, Zhen-yu Liu 2015 Effect to Si content and temperature on oxidation resistance of Fe-Si alloys Journal of Iron and Steel Research, International 22(3) 238-244

[11] Kamel Makhlouf, J W Jones 1993 Effects of temperature and frequency on fatigue crack growth in 18% Cr ferritic stainless steel International Journal of Fatigue 15(3) 163-171

[12] D Pérez, J L Marulanda, J M Meza 2015 Mechanical characterization by CVD-FBR aluminum Coatings on austenitic stainless steel and the steam oxidation resistance Revista Facultad de Ingeniería 24(40) 9-16

[13] N K Othman, J Zhang, D J Young 2010 Temperature and water vapour effects on the cyclic oxidation behaviour of Fe–Cr alloys Corrosion Science 52(9) 2827-2836

[14] Shreir L S, Jarmon R A, Burstein G T 2000 Corrosion, Metal/Environmen Reactions vol 1 (Oxford: British Library Cataloguing In Publicatin Data) pp 1:55-1:117

[15] Zurek J, Wessel E, Niewolak L, Schmitz F, Kern T, Singheiser L, Quadakkers W 2004 Anomalous temperature dependence of oxidation kinetics during steam oxidation of ferritic steels in the temperature range 550–650°C Corrosion Science 46(9) pp 2301–2317

[16] Hirobumi Okabe 1981 High temperature oxidation of Fe-14Cr-4Al Alloy Japanese Journal of Applied Physics 20(3) pp 165-241

[17] Michael Mueller, Klaus Hilper, Lorenz Singheiser 2005 High temperature corrosion of MoSi2-HfO2 composites in coal slag Journal of Physics and Chemistry of Solid 624 pp 270-278