Case study of grate-chain degradation in a Grate-Kiln process

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Abstract. Austenitic stainless steels are often used in high temperature applications due to their resistance to corrosion. Grate-Kiln processes that sinter iron ore pellets use grate-chains which are made of austenitic stainless steel to withstand the severe environment. It has been shown, however, that the grate-chain is affected by several degrading mechanisms in the harsh environment of the sintering process. A grate-chain that has been in service for 8 months was investigated in order to find the mechanisms of degradation.

Results show that slag products are accumulated on the grate-chain and interact with the steel as hot corrosion. The stainless steel is believed to be sensitized against inter-granular attack by carburization followed by inter-granular attack. The resistance towards degradation seems to decrease with time which is suggested to be caused by depletion of chromium.

1. Introduction
Austenitic stainless steels are regularly used in applications for high temperatures and demanding atmospheres due to their chromium oxide forming capabilities and the thermal stability of austenite [1]. An application for these steels is in the Grate-Kiln process which pelletizes iron ore pellets. The pelletizing process, or induration can be seen in figure 1. The grate-chain (A) is made of austenitic stainless steel and transports the green pellets to the rotary kiln indurator (furnace) (B) where the pellets will be sintered. During the transportation the wet green pellets are dried and pre-heated by heated air. Drying and pre-heating of the pellets are performed in four different stages (C-F) with different gas temperatures flowing through slits in the grate-chain and through the bed of pellets. The main problem when investigating and evaluating degradation in industry processes is the irregularity of the environmental properties during the operation. Different quantities of additives in the pellets make both the temperature, type of particles and chemical composition of the gas fluctuate.

The grate-chain consists of several grate-links that are linked together which can be seen in the schematic image of the Grate-Kiln indurator in figure 1. The grate-link has several slits and ribs which allows the gas to flow through the grate-link and heat the pellets. The temperature of the heated air ranges between 200 and 1200°C.
Process case studies have mostly been focusing on the petroleum industry [2-4] or heat exchange applications [5]. To the authors knowledge there are few investigations concerning the degradation of stainless steels in pellet sintering processes. Bani P. Mohanty et al. investigated hot corrosion of grate-bars within taconite indurators [6]. They concluded that degradation of stainless steel grate-bars by sulfuric salts of alkali metals was more severe when mixed together with chlorides of the same alkali metals. The alkali metals were vaporized from the pellets and later condensed as salts onto the grate-bars due to their lower temperature. This mechanism was repeated during each heating cycle and increased the concentration of the alkali salts. It was also stated that the resulting oxides from hot corrosion were more prone to spallation by thermal cycling and thereby significantly reduced the lifetime of the grate-bars [7]. J-Y Liu et al. [8] studied the addition of boron, zirconia and manganese to a stainless steel in order to enhance the lifetime of grate-grids in a Grate-Kiln. The results show that the lifetime was enhanced from 8 months without the additions to 18 month with the additions. However, their study mostly focused on high temperature corrosion without the influence of alkali metals. These different studies show that it is necessary to investigate each environment separately in order to clarify which mechanism that governs the degradation of the material. The present study investigates the degradation mechanism of a grate-link that has been serving in an indurator during 8 months.

2. Material and Method
2.1. Material
The grate-link that was investigated had been in service for 8 months in a Grate-Kiln indurator from Metso Minerals which is operated by the Swedish mining company LKAB. The grate-link is presented in Figure 2. The material of the grate-link is an austenitic castable stainless steel named HH in the ACI standard or A 297 HH in the ASTM standard. The chemical composition of the material as stated by LKAB can be seen in table 1, together with the standard specification for ACI HH. The HH material is the most common austenitic steel for high temperature applications as it has a good resistance to corrosion.
Table 1. Chemical composition of the material in the grate-chain and standard specifications for ACI HH.

| Alloying element | C   | Si  | Mn  | Cr   | Ni   | Mo  | Fe  |
|------------------|-----|-----|-----|------|------|-----|-----|
| Material         | 0,272 | 0,94 | 0,55 | 25,53 | 10,83 | 0,24 | Bal. |
| ACI HH (ASTM A297) | 0,2-0,5 | 2 | 0-2 | 24-28 | 11-14 | 0-0,5 | Bal. |

The chemical composition of the environmental gases inside the indurator have been evaluated by LKAB and contains other than nitrogen; 15-20% of oxygen, 2-5% of carbon dioxide, 20-100ppm of carbon monoxide, 50-100ppm of NOx gases, 2-5ppm of sulfur dioxide and 5-10% of water vapor. An unknown small amount of vaporized Na and K is also assumed to exist in the environmental gas, originating from the coal fuel and the pellets.

2.2. Visual inspection
The grate-chain has been inspected during service by operators and engineers and their observations are taken into account in this study in order to increase the understanding of the degradation of the grate-chain.

2.3. Investigation of deposits
Thick deposits were found on the grate-links. In order to determine if these deposits originated from the material or from the process they were analyzed with Inductively Coupled Plasma – Sector Field Mass Spectroscopy (ICP-SFMS) to give a quantitative estimation of the chemical content.

2.4. Overall degradation
To evaluate the reduction of thickness of the ribs each rib was cut so that the cross section could be measured, see figure 3. Cut A was done first to cut all the ribs loose from the grate-link. The thickness of the ribs were measured and compared to casting specifications at two positions on the rib; in the middle of the rib and close to the slit-edge. The oxide thickness and chemical content of the ribs were of interest so each rib was cut in the middle to get a cross section piece. To avoid any extensive amounts of water soluble oxides to be removed during cutting the ribs were covered in a layer of

Figure 2. A grate-link after being in use for 8 months. The photo to the right shows cracks at the edges of the slits.
Lacquer from METACOAT®. The gradient of chemical elements at the surface of the specimen and inwards was investigated by Energy Dispersive Spectroscopy (EDS).

2.5. Crack investigation at slit-edges
To evaluate the cracks in the slit-edges the grate-link was cut according to figure 3, slice B, C and D. The resulting samples were polished so that the cracks and their propagation characteristics could be evaluated by scanning electron microscopy (SEM). The cracks were investigated by EDS to see possible chromium depletion, signs of carburization and chemical content inside the cracks.

2.6. Instruments
The optical microscope used during the evaluation was a Nikon Eclipse MA 200. SEM imaging and EDS measurements was carried out by a JEOL JSM 6460LV with an Oxford INCA system. Hardness measurements were done by a Matsuzawa MXT-α Vickers micro hardness tester. The chosen load for hardness measurements was 300 gram with a loading time of 15 seconds.

3. Results
3.1. Visual inspection and deposits
Visual inspection of the grate-links during service showed that there is a clear pattern of the degradation that can be divided into three different steps.

1. During the initial period the grate-links get thicker by deposits. Since no apparent degradation is visible underneath the deposits it is concluded that the deposits do not originate from the grate-links but from the induration process.

2. After the initial period the material starts to degrade at an accelerated rate which can be seen by the visual loss of thickness. The deposits are thick and flaky and can easily be removed from the grate-link.

3. Cracks start to arise at stressed locations at the slit-edges and eventually on the ribs, perpendicular to their elongation direction.
Results from the elemental evaluation by ICP-SFMS of the deposits on the grate-link are shown in table 2. A relatively high amount of alkaline metals can be seen together with sulfur.

**Table 2.** Analysis of the elements in the deposits performed by ICP-SFMS.

|   | Si  | Al  | Ca  | Fe  | K   | Mg  | Mn  | Na  | Cr  | Ni  | S   | C   |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| wt%| 1,98| 1,53| 0,68| 50,0| 3,98| 0,35| 0,08| 1,06| 4,85| 1,26| 1,98| 0,10|

3.2. Overall degradation

3.2.1. Relative thickness loss. The thickness of the ribs before and after a service life of 8 months was compared to establish a relative thickness loss in order to see if the grate-link has been evenly degraded. The thickness was measured at two different locations at the ribs, one measurement close to the slit-edge of the grate-link and a second measurement on the middle of the rib. The relative thickness loss can be seen in figure 4. It is clear that the ribs have not been evenly degraded. The center rib (number 6) has the highest loss of relative thickness while ribs 1 and 11 (close to the sides of the grate-link) have the smallest loss of thickness. There is a large difference between the measurements close to the slit-edge of the grate-plate and the middle of the ribs for all positions. The middle part of the ribs suffers a significantly larger degradation than those closer to the slit-edge of the grate-link. Ribs 1 and 11 have an increased thickness due to deposition.

![Rib thickness variation](image)

**Figure 4.** Rib thickness variation with the position of the rib. Rib 1 and 11 are furthest from the center of the grate-chain, while rib 6 is in the center.

3.2.2. Oxide layer investigation of rib cross section. Figure 5 shows back-scattered electron (BSE) images of the cross section of the oxide on the surface of the metal. Depositions on the metal surface and an underlying oxide layer can be seen in figure 5 a). Image b) in figure 5 shows thick grain boundaries beneath a cracked oxide layer. EDS investigation of image b) shows that the carbon and oxygen content is slowly decreasing as a function of distance from the surface while the concentrations of the metals quickly approach the concentrations for the bulk, see figure 6. Carbon,
oxygen and small traces of sulfur are abundant in the surface of the material. The chromium content close to the surface is reduced compared to the normal chromium content in the bulk material.

Figure 5. SEM images in BSE mode for the cross section of the oxide and the surface of the material. Deposits (A) can be seen on the surface of the metal (B) in picture a). A crack (C) is dividing the deposits from the metal. Thick grain boundaries (D) beneath a cracked oxide layer (E) can be seen in image b). The dashed arrows show the position, direction and length of the EDS analysis.

Figure 6. EDS measurements as a function of distance from the surface for image b) in figure 5.

3.2.3. Hardness measurements of rib cross section. Results from hardness measurements as a function of the distance into the material, together with standard deviations, are shown in figure 7. The hardness is decreasing as a function of the distance into the material.
3.2.4. Microstructure of cross section. The cross section of the material was investigated by an optical microscope in dark-field imaging mode. Attacked grain boundaries are present as shown in figure 8 a) and b). The majority of the attacked grain boundaries are found at a distance up to 100 µm beneath the surface. As can be seen in figure 8 b), there are some severely attacked grain boundaries that go around 300 µm below the metal surface.

![Image 8](a) Attacked grain boundaries, (b) Attacked grain boundary, Chill zone.

**Figure 7.** Hardness profile of the cross section of the ribs.

3.3. Crack investigation of slit-edges

3.3.1. SEM and EDS-investigation. The crack propagation of the material can be seen in figure 9. The cracks have been following the grain boundaries which seem to be thickened in front of the crack tip. EDS analyses of the thick grain boundaries show that the carbon, oxygen and chromium content in these grain boundaries are higher than in a normal grain boundary.

EDS measurements of a crevice on the surface show that there is a significant difference in the chemical content in the inner end of the crevice compared to a point closer to the surface, which can be seen in figure 10. The inner end of the crevice contains high amounts of chromium and oxygen indicating a high amount of chromium oxide. The outer part of the crevice contains higher amounts of...
iron and oxygen which indicates iron oxide. EDS analyses also showed that chromium was depleted from the neighboring metal closest to the crevice. Such crevices are believed to be initiation points for crack propagation into the metal.

**Figure 9.** Crack propagation in the material. In a) a crack can be seen that follows a grain-boundary and in b) the crack tip can be seen to consist of an attacked grain-boundary before the actual crack arrives.

| Element | Weight % |
|---------|----------|
| C       |  4,33    |
| O       |  34,16   |
| Cr      |  36,39   |
| Fe      |  18,36   |
| Ni      |  3,43    |

| Element | Weight % |
|---------|----------|
| C       |  3,73    |
| O       |  33,28   |
| Cr      |  10,92   |
| Fe      |  45,59   |
| Ni      |  5,52    |

**Figure 10.** EDS measurements of two positions at a crevice, believed to be initiation points for cracking. The results of the EDS measurements can be seen below each image respectively.
4. Discussion
The inhomogeneity of the relative loss of the thickness of the ribs after exposure could be explained by the thermal differences between the measured positions. The center rib will have a higher temperature than those closer to the sides of the grate-link due to higher exposure rate to hot gas and smaller possibility to conduct the heat away from the rib to the bulk of the grate-link. This is also the reason why the measured positions closer to the slit-edge of the grate-link had a reduced loss of thickness for all the ribs. Another explanation could be that the gas flow is different at different locations on the grate-link which could be caused by clogging of the slits in the grate-link.

EDS shows that carbon, oxygen and sulfur contents decrease with distance from the surface and that carbon reaches normal quantities for the alloy 200 $\mu$m below the surface.

The hardness evaluation shows decreased hardness from the surface and inwards and the hardness reaches normal values of 220 HV [9] around 200 $\mu$m into the material. This suggests an inward diffusion of carbon which forms hard chromium carbides. Also the thickened grain boundaries close to the surface supports this mechanism.

Chromium oxide is a protective oxide layer and does not allow any high diffusion but the study has shown reduced amount of chromium at the surface which implies chromium depletion. There are generally two different mechanisms that could weaken the oxide layer in this case, a chemical or a mechanical mechanism.

Reduction of the effectiveness of the oxide layer by chemical means could be described by the complex chemistry of the environment with alkali metals, sulfur and water vapor. Literature suggests that the alkali metals Na and K with their sulfates, hydroxides and chlorides enhance the corrosion mechanism which is a process known as hot corrosion. These salts generally have a low nominal melting temperature and when they are mixed together their melting temperatures will be even lower. These melted salts dissolve and disperse the protective oxides so that they become porous and less protective. Hot corrosion resembles aqueous corrosion since a liquid increases the ionic transportation of the system [10, 11].

A second possible chemical mechanism that weakens the oxide layer is related to the role of water vapor in the environment since chromium oxide is unstable in hot environments containing high amounts of water vapor. Two different theories have been proposed to understand this mechanism. The first is a process of hydroxide ion uptake of the oxide which renders the oxide more prone to ion transportation which reduces the effectiveness of the protective layer. The second mechanism deals with the stability of chromium as a gaseous phase and studies have shown that chromium evaporates at 600 degrees in an environment with $O_2 +10\%H_2O(g)$ [12, 13][14].

Thermal cycling is a mechanism that could remove the protective layer mechanically. The difference between the highest and lowest temperature of the grate-link makes the protective oxide layer spall from the surface. This is due to the difference in linear thermal expansion of the oxide and the metal which causes stresses at the border between the metal and the oxide. The oxide layer also becomes more brittle when no melt is present as the temperature is decreasing which further increase of the rate of spallation [15].

Hot corrosion is described to have an initiation period where the alkali salts are accumulating on the surface and the material still resists the attack and it is reported that the oxides become thick and flaky after service [7, 16]. The ICP evaluation has confirmed alkali metals inside the cracks and in the oxide of a total of 5 percent.

While these theories explain the degradation of the protective layer they fail to explain the cracks inside the material and the thickened grain boundaries. Sensitization to Inter-Granular Attack (IGA) is a mechanism that arrives from the stability of chromium carbides. Carbon reacts with chromium and depletes the chromium in the material close to the grain boundaries which in turn becomes susceptible to IGA. Sensitization to IGA normally occurs at temperatures above 400 degrees to ensure a high diffusion of carbon but below 800 degrees because carbides are unstable above these temperatures [17].
The carburization is probably responsible for the sensitization which makes the grain boundaries susceptible to IGA. Thickened grain boundaries with an increased amount of carbon seem to support this idea.

Stress concentrations in the slit-edges of the grate-link are likely to form the cracks that are observed there. As the sensitization and IGA progresses into the material along the grain boundaries, the stress widens the grain boundaries and forms a crack. It is suggested to define the cracks as a mechanism of Inter Granular Stress Corrosion Cracking (IGSCC) [18].

5. Conclusions
The degradation of a grate-link in a grate-kiln indurator has been investigated.

The difference in rib thickness is due to the thermal difference, or the gas flow around the ribs.

Alkaline vapor from the warmer zones in the indurator are believed to condensate at the cool grate-link and form chlorides and sulfates together with sulfur and chlorine which continuously accumulate on the grate-link during service.

The alkaline salts cause hot corrosion on the grate-links. The H₂O (g), CO₂ and SO₂ content in the environment together with thermal spallation render the surface susceptible to carburization, sulfidation and internal oxidation. This could lead to sensitization towards IGA and thereby renders the material damaged by IGA. At places where stress concentrations are present it is proposed that IGSCC forms cracks in the grate-link.

6. Acknowledgements
This project is sponsored by the Hjalmar Lundbohm Research Centre (HLRC) and the mining company LKAB. Thanks also to Ragnar Tegman who has been a reliable support during the project.

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