Effect of shot blasting on process oxidised stainless steel – morphology, chemistry and pickling performance

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Abstract

The oxide scale created during manufacturing of stainless steel is often removed by a chemical pickling with mixed acid. Various pre-treatments to pickling are also applied to increase the efficiency of the oxide scale removal. Shot blasting is one such pre-treatment, which operates to remove a certain amount of oxide and also to generate cracks and openings for the subsequent pickling. In this work, three materials, AISI 2205, 430 and 304 have been blasted and later exposed to mixed acid. This was conducted to quantify the effect shot blasting has on the subsequent pickling of stainless steel. Three shot products and two blasting parameters were investigated and varied. Shot blasting significantly reduced the oxide scale but was unable to remove the chromium oxide layer closest to the steel surface. No significant difference was observed when comparing the result from the three shot products after blasting. Increasing the particle velocity or the coverage rate further enhanced the pickling but reduced the amount of oxide removed during blasting. These effects are however relative small, so in practise relatively mild conditions seems preferable for economic reasons. Oxide scale containing hematite was difficult to remove by both shot blasting and pickling.
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1. Introduction

The industrial processing of stainless steel includes high temperature operations such as hot working and annealing to gain control over shape and properties of the material. Elevated temperatures however promote an unwanted oxide scale at the surface of the steel [1]. The scale lowers the corrosion resistance and the aesthetic appearance of the product, which is why the scale has to be removed before it reaches the customers. The oxide scale is commonly removed with pickling which removes the scale by dissolution mainly of reducing the underlying metal [2].

There exist numerous variations of the total removal procedure, depending on for example stainless steel grade or facility. However the majority of the methods may be scaled down to two steps: Initially one or several pre-treatment operations and later a subsequent chemical pickling. Chemical pickling is the method that commonly removes the final part of the oxide scale while mechanical operations or electrolytic pickling operates as pre-treatment methods. The pre-treatments are done because the oxides formed on stainless steel are very resistant to pickling [3].

The oxide scale on stainless steel contains high amount of chromium, owing to its high affinity toward oxygen. Cr-rich oxide scales are generally dense and adherent to the steel surface and this result in a more difficult pickling. Furthermore, the diffusion of chromium from the steel to the oxide lead to the formation of a so called “chromium depleted layer” (CDL) directly under the scale. The lack of chromium makes this layer more susceptible to dissolution during pickling, compared to the oxide scale or the rest of the steel with normal chromium concentration [2].

Pickling stainless steel is an occupational safety and health (OSH) issue with its hazardous acids so it would be beneficial if the process could be removed or at least improved. It is well known that the pickling time is reduced if the scale has been roughened up beforehand with high amount of spallation (detachment) or formation of cracks. This will let the acid penetrate the oxide scale, reach the CDL, which will dissolve, and undermine the oxide scale [4]. The efficiency of this total removal varies, which highly depend on the properties of the actual scale. A very porous scale for example can be easily removed.

Shot blasting is a method that may operate as a pre-treatment to pickling and it has been proven to enhance the pickling rate [3]. Shot blasting propels a large number of small steel shots towards the oxide scale, mechanically disrupting it [5]. Information regarding shot blasting of stainless steel is limited so far, however the environmental concern against pickling is rising, which in turn heighten the interest for blasting.

The aim of this project was to investigate the effect of shot blasting on the rate of pickling stainless steel.

Project goals

- Characterise the effect shot blasting generate as a pre-treatment to pickling
  - Which shot blasting parameters has the highest influence on oxide removal?
- Determine by experiment and a literature study oxides resistant to removal.

This report is limited to three stainless steel grades, austenitic AISI 304, duplex AISI 2205 and ferritic AISI 430.
1.1 Chemical Pickling of Stainless Steel

Mixed acid is used for chemical pickling of stainless steel. The mixed acid consists of the oxidising agent nitric acid (HNO₃) and the reducing agent hydrofluoric acid (HF). By varying the concentration of these two, a controlled and efficient pickling can be achieved. The process is fairly quick and produces a relatively good surface quality. It is also one of the few methods that can remove the chromium depleted layer. The HNO₃-concentration normally ranges between 10 to 25 wt% and HF between 1 to 8 wt%. Normal pickling temperatures operate between 50-60°C, increased temperatures results in excessive HF-evaporation and may also lead to nitrogen oxide emissions, which are highly undesired [4].

Nitric acid alone is not capable of dissolving or removing the oxide scale on stainless steel, on the contrary it, promote the corrosion resistant oxide film found on stainless steel [6]. The nitric acid provides stabilisation of the passive film, elevation of the redox potential, oxidising agents for the base metal, dissolving agents for the scale and is a source of H⁺ ions. The hydrofluoric acid provides destabilisation of the passive film, stabilisation of the redox potential and complex agents for metal ions in solution [4].

The oxide removal rate during pickling depends on a couple of factors [2]:

- Degree of spalling and cracking in the oxide.
- The chemical composition of the stainless steel and more important, the properties of the chromium depleted layer.
- Concentration of the dissolved metal, i.e. Fe, Cr and Ni in the acid bath.
- Bath temperature.
- Bath circulation.

A low amount of dissolved metal, increased rate of spalling, bath temperature and circulation will improve the rate of pickling. The effect chemical composition has on pickling is complex, but generally an increased resistance against wet-corrosion by e.g. high Cr lowers the pickling rate [4].

The mixed acid is quite dangerous to both the environment and the steel plant operators. Nitrous gas emissions and nitrate effluents are a result of using the mixed acid during pickling [7]. Great care is preferable when handling HF because of its hazardous effect on humans [6].

1.1.1. Environmental Concern

Pickling requires an extra process to regenerate and handle the spent pickling [4]. Spent pickling liquors (defined as metal enriched acid depleted solution) are considered as hazardous waste and designated as K062 in the Environmental Protection Agency (EPA) hazardous waste list of the USA [8]. In Europe, it is catalogued as hazardous waste number 110105 by the European List of Wastes [9].

Pickling stainless steel gives rise to lots of waste products, such as metal oxide particles, metal containing sludge from waste water and metal enriched acid solutions. All of these should be neutralised and regenerated, it is however impossible due to its complexity. Methods to regenerate spent acid are state of the art but are currently not enough. For example in Europe, year 2012, more than 2500 tonnes of nickel with a value of 40 million euro were deposited and thus irrecoverable lost [10].

Laws and higher demands to improve the environmental and economic aspect of pickling are pushing engineers to come up with a good solution regarding recycling [11]. One solution might be to include shot blasting as an oxide removal step before conducting pickling [12].
1.2 Shot Blasting

Shot blasting is a mechanical method to remove the oxide scale and in some cases to impart a specific surface roughness or texture. The steel surface is blasted by numerous small steel shots, disrupting the oxide scale by impacting on it, see Figure 1[5]. The shots are propelled towards the steel surface by either compressed air or rapidly spinning paddles which throw the shots off their blades with the help of the centrifugal force [13]. The shots are collected and used several times before being discarded. Shot blasting enhance the pickling rate by removing some of the oxides or at least by breaking up the oxide scale. This will enable subsequent pickling to easier penetrate the oxide scale. Various blasting parameters may be changed to optimise the blasted surface:

- Type of abrasive shots.
  - Geometry.
  - Size.
  - Material.
    - Density (mass), hardness, toughness.
- Impact angle.
- Particle velocity .
- Coverage rate, i.e. the impacted area divided by the total surface area.
  - Influenced by the particle velocity, blasting time and size of the shot.

Shot blasting is, compared to pickling, quite an environmental friendly process. However this is only true if the dust, created during the process, is collected and contained. Dust may otherwise come in contact with paint or unprotected steel at the plant, leading to problems with corrosion. Abrasive particles may enter moving parts and can also cause health problems for the operators. The major portion of the dust is however collected and reinserted into the process [5].
1.2.1. Mass and Particle Velocity

If the kinetic energy equation \( E = \frac{mv^2}{2} \) has been taken into consideration, the increase of particle velocity or mass can be seen as beneficial in regard to oxide removal. The equation proves that increasing the mass or velocity will increase the kinetic energy and thus the effect on impact. Figure 2 shows the effects of particle velocity and size on substrate roughness evaluated from \( R_t \). Increasing size or velocity will lead to a deeper impact on the substrate [15].

![Figure 2 Effects of particle impact velocity and particle size on substrate roughness. \( R_t \) is defined as the distance between the highest and the lowest points of the profile within the evaluation length. This was measured on a clean metal surface][15].

It is only natural that an amount of the kinetic energy will be lost by being converted to heat or absorbed into the shot particle. Nevertheless increasing the kinetic energy will contribute to a larger amount of energy into the material as well and this will affect the removal rate. It is however not certain that it will enhance the removal efficiency. The impact of particles on the brittle oxide surface will create patterns of cracks around the impression, both lateral cracks and others that extend radially outward [16].

These cracks, especially the lateral ones, will contribute to the oxide removal if they meet the surface, which can be understood from Figure 3. A plastic zone can be found under the impression, which extends to about twice the radius of the impression. The maximal tensile stress lies at the plastic zone border, with a depth roughly equal to the contact radius between the particle and the oxide. This area is where the lateral cracks originate from, see Figure 4 [16].

Increasing the particle velocity, and thus the kinetic energy, will position the maximum tensile stress further down in the oxide scale or might even go below the oxide scale, into the substrate. Energy meant to remove the oxide will instead be absorbed by the steel, which will decrease the removal rate and there also exist a chance of work hardening [15].
It has been proposed that the oxide scale is sequentially eroded down by a cracking and chipping mechanism during blasting rather than by tearing away large parts of oxide directly from the steel interface. This is due to the high amount of cracks in the scale which is induced from impacts. The pattern of cracks divides the scale into numerous small oxide parts. Figure 5 is illustrating the complex pattern of cracks that may form during impact [15].

Figure 3 Crack pattern formed in the bulk of an oxide layer due to impingement [16].

Figure 4 Contour plot of the residual stress component normal to the lateral crack system [16].

Figure 5 Illustration of the complex pattern of cracks induced from one impact on oxide scale [15].
1.2.2. Hardness, Size and Geometry

Momber states that it is the rate between the abrasive particles hardness and the target material hardness which determine the roughness and thereby the removal rate, not the absolute hardness of only the abrasive particles. Experiments have concluded that abrasive elongated particles with insufficient hardness tend to round up too quickly and lose efficiency during oxide removal. However, there also exists a limit to how hard the particles have to be. After a certain ratio, the increased efficiency gained from increased particle hardness will have reached its limit [15].

Soft material tends to absorb a larger amount of energy than harder materials. Softer particles deform to a larger extent, which absorbs energy, so instead of transferring that energy to the surface, it is lost in the shots [17]. However, these deformed shots will also harden after deformation and as the same shots are used several times, only the initial blasting may give a lower effect. An article proposes that the hardness has no real significance when discussion erosion resistance due to the high amount of cracks formed after impact and furthermore claims that toughness has the dominant role [16]. The truth probably lies somewhere in between.

Another aspect is the effect from geometry, the force is equally divided on the impacted area so a pointy shot with a small impact area will affect the surface with a larger, concentrated force and thus penetrate deeper [15]. Grit shots (uneven, rough shots) are more effective in removal of softer coatings, i.e. rust or paint, whereas spherical shaped shots has the highest removal rate on mill scale. Grit particles tend to remove the scale by a cutting-mechanism while spherical particle remove it by a ploughing-mechanism [15]. This is dependent on the properties of the shot particles and the coating as well. One article concludes that a relationship between the particle embedment and the particle shape exists. Furthermore, it seems that particles with a higher roughness or uneven shape will contribute to an increased embedment in the material [18].

1.2.3. Blasting Time

Blasting time is an important parameter and is one of the factors influencing the coverage rate. Increased blasting time leads to a higher coverage rate. In simple theory, the efficiency of oxide removal should increase with an increased blasting time, however saturation effects exists as well. The effect from blasting may drop after a certain time and an increase in grit and oxide embedment will occur. The abrasive particles and the blasting machine are exposed to wear during every blasting so unnecessary long blasting times are undesired [15].

1.3 Alternative Pre-Treatments

In addition to shot blasting, there exist a couple of accepted pre-treatments which function is to decrease the amount of oxides and/or increase the efficiency of the subsequent pickling.

- Electrolytic pickling.
- Salt bath.
- Mechanical scuffing, wire brushing.

Electrolytic pickling consists of an electrolyte with an added current and may be performed either anodically or cathodically in acidic, salt bath or neutral electrolytes to improve the final, chemical pickling and to condition the oxide scale [7].

Electrolytic acid pickling in H2SO4 was a common treatment prior to chemical pickling. The acid and method is inexpensive and effective, however caution has to be exerted as pitting corrosion may arise as a consequence. Instead the Neolyte Process is extensively used at modern steel plants as an electrolytic neutral pickling with Na2SO4. This process is used
because of better working environment for operators, cheap maintenance, low metal loss, gives a superior surface finish and is easy to control. Salt bath pickling is also effective and the result is usually a smooth, uniform surface, the downside is the difficulties to handle the pickling operation and the high cost to maintain the process [19].

The purpose with salt baths is usually to chemically alter the oxide scale to a more soluble oxide, without attacking the base metal. One such solution consists of molten 85% sodium hydroxide (NaOH), 14% sodium nitrate (NaNO3) and 1% sodium chloride (NaCl) [4].

1.4 The Oxide Scale

There are several areas of interest regarding the oxide scale on stainless steel. Characterisation of the high temperature oxide scale is very complex and information is limited. The focus of most articles concerning oxide scale during processing seems to lie within the annealing procedure, few studies have been performed to characterise the oxidation during hot rolling [20].

The formation and structure of the oxide scale appear to depend on several factors [4,21-23]. There are a couple of, arguably, obvious major factors involved such as temperature, time, environment, oxygen partial pressure and composition of the steel itself [2]. However, studies of factors such as cooling rate, influence of mechanical forces and diffusion at grain boundaries are scarce and deserve more attention.

1.4.1. Structure

The oxide scale on carbon steel during industrial processing can normally be described by three layers, a thick inner FeO layer (Wustite) close to the steel surface, a thin Fe3O4 layer (Magnetite) in the middle and a very thin outer Fe2O3 (Hematite) layer [20]. This depends on environment, time and temperature. FeO is chemically active and will quickly be dissolved during pickling, the others will not [24].

The oxide on stainless steel is more complex. Articles seem to be in agreement that the oxide scale on stainless steels during industrial processing is divided into an adherent layer and one or more outer layer(s). Often an inner corundum-type of oxide (M2O3) and a mixture of corundum- and spinel type of oxide (M2O3 and M3O4) at the outer layer. Furthermore, experiments have shown that the inner layer is usually Cr-rich while the outer layer is Fe-rich [21,25,23]. A small amount of silicon oxides have also been observed close to the steel surface, but only with sensitive analytical techniques, e.g. GDOES or TEM [1,26]. The correct composition highly depends on the stainless steel grade.

Saeki et al states that, for stainless steel grade 304, the inner corundum-type oxide include either Cr or Fe or a combination of both and that the spinel-type is formed from Fe, Cr or Mn. No amount of Ni was observed in the oxide layer [21]. However, IVL Swedish Environmental Research Institute Ltd reports to have found oxides containing Ni but have excluded Mn, see Table 1[2].

<table>
<thead>
<tr>
<th>Grade</th>
<th>Hot rolled</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304</td>
<td>FeCr2O4; NiFe2O4; Fe3O4; Fe2O3</td>
<td>(Fe,Cr)2O3 (Most likely from FeCr2O4)</td>
</tr>
<tr>
<td>AISI 430</td>
<td>FeCr2O4; Fe3O4; Fe2O3</td>
<td>(Fe,Cr)2O3 (Most likely from FeCr2O4)</td>
</tr>
</tbody>
</table>

Table 1 Swedish Environmental Research Institute Ltd reports to have found these oxides on AISI 304 and 430 [2].

Time is important as well, e.g Jepson claim that the oxide scale on grade 304 after 4 hours of oxidation in air at 1200°C may consist of an inner layer of Cr-rich oxides followed by an intermediate layer of Fe and Ni oxides below the outer thin layer of hematite. One hour of
oxidising grade 2205 at 1200°C will lead to a large amount of oxide nodules. These nodules are made up of three layers, outer layer is Fe-rich, intermediate layer is Cr-rich and inner layer is Ni- and Cr-rich [27].

From this uncertainty in the literature it is evident that more work is needed to understand the influence of different alloying elements on the formation of oxide scales.

1.4.2. Growth of the Oxide Scale

The oxide scale may grow inward or outward, usually a combination of both occurs. Inward diffusion of oxide ions and outward diffusion of cationic species usually produce the protective layer Cr₂O₃ on stainless steel at ambient temperatures. At elevated temperatures, the oxide layer follows a parabolic growth until the protective layer fails [20]. Diffusion of metal and oxygen through the Cr₂O₃-layer is low, so the only chance for the scale to rapidly grow is by breakaway oxidation.

Local disruption of the Cr₂O₃ will encourage breakaway oxidation, which is induced by cracks from internal stress, external mechanical force, chemical failure or grain boundaries. Basically, cracks opens up a way for oxygen and metal ions to diffuse faster through the oxide and the result is often a large Fe-rich oxide nodule and/or a Fe-rich layer above a Cr-rich one [28]. The growth of the oxide scale is proposed to be seen as an oxidation cycle pattern with successive layers of protective oxidation, breakaway oxidation and duplex oxidation [20].

Si has the highest affinity towards oxygen of all the alloying elements, however it will most often only be found under the Cr₂O₃ layer as an amorphous SiO₂ sublayer. Mn may diffuse easily through the Cr₂O₃ and it has been reported that a MnCr₂O₄ spinel phase is present above the Cr₂O₃ layer [29]. This depends on the amount of Mn and Si in the steel. The preferred diffusion path for elements is by grain boundaries, where the diffusion rate is much higher. The exact value of the grain boundary diffusion coefficients has not been measured, but one article states that it is five orders of magnitude bigger than the bulk diffusion coefficients in AISI 304 steel [30]. This might lead to a thicker and perhaps a more porous oxide at the grain boundaries.

The important thing to consider is that the oxide may grow inward, creating valleys filled with oxides, which will enhance the difficulties of removing the oxide by mechanical means.
1.4.3. Morphology of Common Oxides Found in the Scale

The oxides represented below in Table 2 have been mentioned in various articles as possible phases present in the oxide scale. As discussed earlier, different combination of these phases may be found in the scale depending on treatment, atmosphere and chemical composition of the base material. Finding all of these oxides together in the same oxide scale is however unlikely.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Formula</th>
<th>Hardness (Mohs)</th>
<th>Density [g/cm³]</th>
<th>Structure-Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>5 - 6</td>
<td>5.3</td>
<td>Corundum</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe²⁺Fe²⁺O₄</td>
<td>5½ - 6½</td>
<td>5.2</td>
<td>Inverse-Spinel</td>
</tr>
<tr>
<td>Trevorite</td>
<td>NiFe₂O₄</td>
<td>5</td>
<td>5.2</td>
<td>Inverse-Spinel</td>
</tr>
<tr>
<td>Jacobsite</td>
<td>MnFe₂O₄</td>
<td>5½ - 6½</td>
<td>4.8</td>
<td>Inverse-Spinel</td>
</tr>
<tr>
<td>Chromite</td>
<td>FeCr₂O₄</td>
<td>5½</td>
<td>4.5 – 4.8</td>
<td>Inverse-Spinel</td>
</tr>
<tr>
<td>Wüstite</td>
<td>FeO</td>
<td>5 – 5½</td>
<td>-</td>
<td>MgO</td>
</tr>
<tr>
<td>Eskolaite/chromia</td>
<td>Cr₂O₃</td>
<td>8 - 8½</td>
<td>5.2</td>
<td>Corundum</td>
</tr>
<tr>
<td></td>
<td>MnCr₂O₄</td>
<td>-</td>
<td>-</td>
<td>Inverse-Spinel</td>
</tr>
</tbody>
</table>

Articles have been found regarding descaling of wire drawn carbon-steel and the existing problems with abrasive oxides on wire rods. A result from these articles is that magnetite, and especially hematite are not desirable for either mechanical descaling or pickling [24,12].

1.4.4. Effect of Hot Rolling and Annealing

It is well known that hot rolling produces a thicker oxide scale (~1-10 µm) compared to annealing of cold rolled steel (~0.1-0.3 µm)[1]. The hot rolling process operates at longer times and at higher temperatures. The morphology of the oxide scale will definitely vary depending on what type of process it goes through. The annealing environment, for example, may significantly differ depending on what kind of furnace and fuel that is used. Humidity is one factor that may vary and experiments have shown that a higher humidity will contribute to a thicker oxide and in some cases promote other oxide phases [43,44]. The tendency for spallation on scale formed during annealing is lesser than on hot rolled scale. This might be because of the greater thermal expansion found at hot rolled scale, induced from higher temperatures and thus faster cooling [42]. Actually, oxide scale produced from annealing is adherent and compact while hot rolled scale have tendency to spall and are slightly crushed from mechanically induced forces.

There are few articles that mention the influence the actual rolls in the hot rolling process has on the scale. One article report that the oxide scale seem to have a high ductility at hot rolling temperatures and shows excellent plastic deformation behaviour during the process and even that the scale show higher reduction compared to the steel, giving the steel a flat and even
oxide [23]. Furthermore, scale created in Steckel mills also have a tendency to form tertiary scale, partly mixed in with the steel [45]. This is examples of why it is difficult to reproduce the oxide scale in a laboratory environment and without a mechanical force, nothing stops the oxide from growing unhindered and it will grow to be slightly more porous [23]. The surface of the rolls are not perfectly polished either and will create small scratches all over the scale and some parts of the scale will on occasion stick to the rolls and thereby tear itself loose from the steel [20].

2. **Experimental procedure**

Various experiments have been conducted to study the effect shot blasting has on the rate of pickling stainless steel and to analyse if there are certain types of oxide that may prove to be more adherent/resistant to blasting or pickling.

2.1 **Material**

Three common commercial stainless steel grades have been studied in this work; austenitic grade AISI 304, ferritic grade AISI 430 and duplex grade AISI 2205, see Table 3.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Supplier*</th>
<th>Condition</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 [46]</td>
<td>SMT</td>
<td>Hot Rolled</td>
<td>.08</td>
<td>.10</td>
<td>18-20</td>
<td>8-10.5</td>
<td>2</td>
<td>-</td>
<td>.75</td>
<td>.045</td>
</tr>
<tr>
<td>430[47]</td>
<td>OSOY</td>
<td>Clean product</td>
<td>.05</td>
<td>-</td>
<td>16.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2205[48]</td>
<td>OSAB</td>
<td>Hot Rolled</td>
<td>.02</td>
<td>.17</td>
<td>22</td>
<td>5.7</td>
<td>1.45</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Sandvik Materials Technology (SMT)
  Outokumpu Oy (OSOY)
  Outokumpu Stainless AB (OSAB)

Steel 430 was laboratory annealed at Swerea KIMAB at 1200°C in air for 30 minutes in the high temperature furnace Entech Eurotherm 2408. The size of the annealed samples was 140x100x4 mm³. The ferritic samples should be treated as a special case because it was proven difficult to reproduce the oxide scale found on industrial oxidised materials.
2.2 Shot Blasting Experiments at Winoa

Shot blasting experiments were conducted at the Winoa facility in Grenoble, France. The intention was to investigate the blasting effect from three different abrasive shot products with different hardness and geometry. The coverage rate and particle velocity were also varied, resulting in a total of 27 different samples, see Table 4. The size of the blasted samples can be found in Table 5. The following parameters were kept constant:

- The impact angle, 45°.
- Median size of 0.1 mm shots.

Table 4 Summary of all 27 samples including blasting parameters.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Oxide Scale</th>
<th>Particle Velocity [m/s]</th>
<th>Particle Shape</th>
<th>Particle Hardness [HRC]</th>
<th>Coverage Rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>A2</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Round</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>A3</td>
<td>Hot rolled at Sandvik</td>
<td>70</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>A4</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>A5</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>A6</td>
<td>Hot rolled at Sandvik</td>
<td>70</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>A7</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
<tr>
<td>A8</td>
<td>Hot rolled at Sandvik</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>100</td>
</tr>
<tr>
<td>A9</td>
<td>Hot rolled at Sandvik</td>
<td>70</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
<tr>
<td>F1</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>F2</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Round</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>F3</td>
<td>Laboratory oxidised</td>
<td>70</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>F4</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>F5</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>F6</td>
<td>Laboratory oxidised</td>
<td>70</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>F7</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
<tr>
<td>F8</td>
<td>Laboratory oxidised</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>100</td>
</tr>
<tr>
<td>F9</td>
<td>Laboratory oxidised</td>
<td>70</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
<tr>
<td>D1</td>
<td>Hot rolled at Outokumpu</td>
<td>70</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>D2</td>
<td>Hot rolled at Outokumpu</td>
<td>55</td>
<td>Round</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>D3</td>
<td>Hot rolled at Outokumpu</td>
<td>70</td>
<td>Round</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>D4</td>
<td>Hot rolled at Outokumpu</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>D5</td>
<td>Hot rolled at Outokumpu</td>
<td>55</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>100</td>
</tr>
<tr>
<td>D6</td>
<td>Hot rolled at Outokumpu</td>
<td>70</td>
<td>Elliptic</td>
<td>48-50HRC</td>
<td>60</td>
</tr>
<tr>
<td>D7</td>
<td>Hot rolled at Outokumpu</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
<tr>
<td>D8</td>
<td>Hot rolled at Outokumpu</td>
<td>55</td>
<td>Round</td>
<td>40-44HRC</td>
<td>100</td>
</tr>
<tr>
<td>D9</td>
<td>Hot rolled at Outokumpu</td>
<td>70</td>
<td>Round</td>
<td>40-44HRC</td>
<td>60</td>
</tr>
</tbody>
</table>
The performed shot blasting experiments were conducted in a Schlick rolling conveyor with two throwing wheels of 5.5kW each. The shot blasting machine is showed in Figure 6. The plates were blasted perpendicular to the rolling direction to illustrate an industrial blasting setup.

Table 5 Size of the blasted sample plates.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Length [mm]</th>
<th>Width [mm]</th>
<th>Height [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>140</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>2205</td>
<td>14</td>
<td>110</td>
<td>8</td>
</tr>
<tr>
<td>304</td>
<td>150</td>
<td>100</td>
<td>4</td>
</tr>
</tbody>
</table>

The sample plates were blasted with a so-called operational mix of the shot product. This mix is found during real industrial processing and consists of work hardened shots, which have already experienced blasting, together with a percentage of new shots. The three applied shot products are made of normal carbon steel however the product with a lower hardness value has less amount of carbon.

The shot blasting machine was cleaned and removed of all shot products before the next product was inserted.

2.2.1. The Coverage Rate

The parameter ‘Coverage rate’ is defined as a sample’s impacted area divided by the total surface area. A method exists to reach the intended coverage rate and was applied during the experiments. These steps were taken to acquire the correct coverage rate:

1. Blast three reference samples while they are traveling at a standard operating speed through the blasting machine, in this case: 3m/min.
2. Inspect the impacted area for each sample by using a portable microscope at the site.
3. Compare the impacted area with reference pictures to determine the initial coverage rate.
4. Table 6 helps the user to achieve the correct coverage rate if the initial was unsatisfied. Two options exist:
   a. Repeat blasting the samples until the desired coverage rate has been achieved.
   b. Recommended: Calculate the required operating speed of the blast machine from Table 6 and blast a new set of test samples with the adjusted speed.
5. Repeat step 2-4 until the correct coverage rate, and consequently the correct operating speed, has been reached.

The operating speed, and thereby the blasting time, can be stated as the controlling factor for obtaining correct coverage rate. Keep in mind that shots may impact on approximately the same area multiple times.
Table 6 Template for attaining the correct coverage rate.

<table>
<thead>
<tr>
<th>Coverage rate after one stick [%]</th>
<th>Coverage rate after n stick [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>64</td>
</tr>
<tr>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>55</td>
<td>80</td>
</tr>
<tr>
<td>60</td>
<td>84</td>
</tr>
<tr>
<td>65</td>
<td>88</td>
</tr>
<tr>
<td>70</td>
<td>91</td>
</tr>
<tr>
<td>75</td>
<td>94</td>
</tr>
<tr>
<td>80</td>
<td>96</td>
</tr>
<tr>
<td>85</td>
<td>98</td>
</tr>
<tr>
<td>90</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 6 is built up from the theoretical equation: 
\[ C_n = 1 - (1 - C_1)^n \]
where \( C \) = Coverage rate and \( n \) = number of passages through the blasting machine [49].

2.3 Pickling with Mixed Acid

Prior to pickling, twelve samples were cut out from each of the 27 blasted plates by water jet cutting, resulting in 324 specimens. The size of each specimen was 25x25\( \text{mm}^2 \), the thickness was not altered.

The company who performed the water jet cutting sent back slightly corroded AISI 430 samples. The influence this might have had on the subsequent pickling is unknown but most likely negligible, since the water jet cutting is performed in ambient temperatures. Corrosion rate is low at room temperature and only small amount of easily dissolved Fe-rich oxide might have been formed.

An industrial reference values for the temperature and concentration of the mixed acid was given to us by the company Sandvik, see Table 7. However, this concentration would have rapidly cleaned the steel. The intention was to completely clean the sample after one hour exposure to mixed acid. Experiments were conducted and lead to a 20% decrease in mixed acid concentration, lowering of temperature from 40\(^\circ\)C to room temperature for austenite and ferrite and from 60\(^\circ\)C to 40\(^\circ\)C for duplex. 3g of iron per litre were also added to lessen the effect of the acid and to simulate an industrial pickling bath.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>2.24 HNO$_3$, 1.6 HF, 3g Fe$^{3+}$/L</td>
<td>Room temperature (~21)</td>
<td>25x25x4</td>
<td>100</td>
<td>10/20/30/40/50/60</td>
</tr>
<tr>
<td>430</td>
<td>2.24 HNO$_3$, 1.6 HF, 3g Fe$^{3+}$/L</td>
<td>Room temperature (~21)</td>
<td>25x25x4</td>
<td>100</td>
<td>10/20/30/40/50/60</td>
</tr>
<tr>
<td>2205</td>
<td>2.24 HNO$_3$, 1.6 HF, 3g Fe$^{3+}$/L</td>
<td>40</td>
<td>25x25x8</td>
<td>100</td>
<td>15/30/45/60/75/90</td>
</tr>
<tr>
<td>Pickling Experiment 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>0.5 HNO$_3$, 0.4 HF, 3g Fe$^{3+}$/L</td>
<td>Room temperature (~21)</td>
<td>25x25x4</td>
<td>100</td>
<td>10/30/60</td>
</tr>
<tr>
<td>430</td>
<td>0.5 HNO$_3$, 0.4 HF, 3g Fe$^{3+}$/L</td>
<td>Room temperature (~21)</td>
<td>25x25x4</td>
<td>100</td>
<td>10/30/60</td>
</tr>
<tr>
<td>2205</td>
<td>0.5 HNO$_3$, 0.4 HF, 3g Fe$^{3+}$/L</td>
<td>40</td>
<td>25x25x8</td>
<td>100</td>
<td>15/30/90</td>
</tr>
</tbody>
</table>

A second pickling experiment was executed after the first one, with even lower acid concentrations, as can be seen in Table 7. Six different pickling times were decided upon for experiment 1; see Table 7. 27 different blasted plates and six pickling times for each plate resulted in a required amount of 162 samples for experiment 1 and 81 samples for Experiment 2, due to half the amount of exposure times. 18 non-blasted samples were also pickled to be used as references.

### 2.3.1. Experimental Setup

The pickling experiments were set up so samples with the same material and exposure time lay together in containers. See Figure 7. The samples lay with the blasted surface facing up. Pouring the mixed acid into all containers took approximately one minute and ten seconds from start to end. This was taken into consideration and accounted for when calculating the

![Figure 7 Containers holding mixed acid and samples.](image)
exposure time. When a group of samples had been exposed for a certain desired time, see Table 7, their container was poured into a bucket with an applied filter, separating the samples and the acid. The samples, lying on the filter, where immediately poured to another bucket filled with distilled water. 36 containers in total containing four or five samples and 100 ml of mixed acid each. The pouring and throwing method took approximately 10-20 seconds to perform. The pickled samples were later hand brushed with a normal dish brush under running water to remove any loose oxide left on the exposed surface.

2.4 Analysing Methods

Analyses of the oxide scale were performed according to the following scheme:

- Measurement of oxide thicknesses and characterisation of its morphology using light optical microscopy (LOM).
- Mapping of elements in the oxide scale using a scanning electron microscope (SEM).
- Weight loss before and after pickling with the help of an analytical scale.
- Measurement of oxide thicknesses and characterisation of its morphology using FIB-SEM on samples influenced by no mechanical grinding or polishing.
- Determination of phases in the oxide scale with XRD.

2.4.1. Sample Preparation

Sample preparation was carried out to appease the various requirements from the analytical methods. Samples were cut into smaller pieces by the cutting tool Buehler Abrasimatic 300. The cross-section analysed in LOM and SEM included the material’s normal direction (ND) as width and transverse direction (TD) as the length, NDxTD. This particular cross-section was of interest due to the higher amount of grains and grain boundaries and it gave the ability to characterise the oxide scale’s thickness, shape and composition.

During sample preparation, the oxide scale is affected by mechanical forces from grinding and polishing, which might lead to disruption or reduction of the oxide scale. As a precaution, the oxidised samples were plated with nickel, which forms a layer on the oxide scale and thereby contain it. The method used may be described by these steps:

1. **Required equipment:**
   a. Sample holder.
   b. Container.
   c. Piece of nickel.
   d. DC power supply.
   e. Electrolyte.
      i. NiSO₄*7H₂O -240 g/L.
      ii. NiCl₂*6H₂O - 45 g/L.
      iii. H₃BO₃ - 30 g/L.
   f. Sample to be plated.
   g. Acetone.
2. Clean the sample in acetone to remove possible grease or lubricants. This will improve the adherence of the Ni-layer.
3. Place the nickel piece in the container and add the electrolyte, the nickel should be partly submerged.
4. Connect the nickel and sample with the power supply, the sample should be negative charged and nickel positive.
5. Place the sample in the sample holder and submerge the part desired to be plated.
6. Turn on the power supply; the desired current density should be ~20 A cm\(^{-2}\).
   If the sample begins to bubble, lower the current until the bubbling stops.
7. Wait until the sample has been fully covered in a thin Ni-layer.

Before grinding could begin, the now Ni-plated samples were mounted in conducting bakelite or resin, the former if the samples were planned to be analysed in SEM. The instrument BUEHLER SimpliMet 2000 was used to mount the samples. For both SEM and LOM, the samples were grinded initially with 80# and up to 2400# fine paper and later polished with 3 µm to 1 µm diamond paste.

The only required preparation for XRD and FIB-SEM was cutting samples into an appropriate size and later clean them.

2.4.2. Documentation and Cleaning

Samples were documented before and after each experiment with the camera NIKON D80 with lens AF Micro-Nikkor 60 mm 1:2.8 D.

Samples were also cleaned in acetone before and after each experiment. Normal procedure was to put the samples into a bath for five minutes, however before pickling the samples were exposed to ultrasonic cleaning for 15 minutes while emerged in acetone. This was conducted to fully remove possible grease or lubricants that may affect the pickling rate. The cleaner used was of model NEY 28B Ultrasonik.

2.4.3. Weight Measurement

An analytical scale, BP211D Sartorius with 0.01 mg readability, was used to measure the weight of all samples before and after pickling. Accuracy: +/- one display resolution.

2.4.4. Light Optical Microscopy

Light Optical Microscopy was used to characterise and measure the oxide thickness and general form. The analysis was performed using the instrument LEICA DM IRM with 1000x magnification. An overall screening was first implemented to gauge the appropriate size and form of the oxide scale. Representing pictures were taken on all samples before pickling.

2.4.5. XRD

The XRD equipment was a Bruker D8, operating on a CuK\(\alpha\) radiation and used for phase identification. The instrument was equipped with a G"obel mirror to produce a parallel beam.

Four ferritic 430 and three duplex 2205 samples were analysed for a better understanding of the existing phases in the oxide scale. A subsequent analysis was also performed on two of the duplex samples to compare the oxide thickness.

2.4.6. SEM-EDS

SEM-EDS was performed using a JSM-7001F from JEOL with the software AZtec from Oxford Instruments. 15 kV acceleration voltage was used with a working distance of 10 mm. Element mapping of the oxide scale and surrounding area were conducted on the AISI 304 and 2205 samples.
2.4.7. FIB-SEM

FIB-SEM was applied to characterise the oxide thickness, morphology and general chemical composition for two cases, for a non-blasted area and for a blasted area. FIB-SEM ensured that the results would be free from mechanical influence.

FIB milling was performed using a QUANTA 3D FEG FIB-SEM from FEI. The ion column was operated at an acceleration voltage of 30 kV with ion probe currents of 30 nA for milling of trenches and later down to 1 nA for cleaning and polishing of cross sections. Ga-ions were used to mill and polish. Before milling could begin a 30x2x4 µm³ sized Pt-layer was applied on the surface to protect it from the harsh ion milling. The dimensions of the non-blasted trench and the blasted trench were 50x30x20 µm³ and 20x30x8 µm³ respectively.

Figure 8 Conducting FIB-SEM on a non-blasted AISI 304.

Figure 8 show six pictures taken while conducting FIB-SEM on a non-blasted area. The dark elongated rectangle seen in the first picture was the Pt-layer applied to protect the surface. The second picture displays the same Pt-layer but the sample have been tilted, observe that the oxide surface was fairly flat. The Pt-layer has increased in thickness in the third picture. The trench had been milled out by Ga-ions in the fourth and fifth pictures, revealing the cross section. Fifth picture display a polished cross-section. Picture number six has been taken inside the SEM to illustrate how the sample was positioned.
The series of images given in Figure 9 shows the same procedure as in Figure 8 but is taken on a blasted sample. The blasted area/crate seen in these pictures are from shot blasting AISI 304 with elliptic shots, 55 m/s particle velocity and 60% coverage rate.

3. Results

3.1 Characterisation of Oxide Scale before and after Blasting

3.1.1 Visual Appearance and Light Optical Microscopy

Figures 10-12 below represent the result for all blasted samples. The surfaces on all samples were still covered with oxides after blasting and it was not possible to visually estimate any change in oxide thickness or roughness caused by the blasting operation. There existed no area where metal could be seen except for the markings. No distinguishable visual difference could be observed when comparing a blasted and a non-blasted sample from the austenitic or duplex plates. A noticeable difference could however be seen on three of the nine ferritic plates. The samples below are representative for each respective material group.
Figure 10 Comparison between AISI 304, non-blasted (to the left) and blasted (to the right).

Figure 11 Comparison between AISI 430, non-blasted (to the left) and blasted (to the right). The top two samples, marked with F4 represent all plates blasted with 60 % coverage rate, 55 m/s particle velocity, regardless of shot product. The F9 samples represent the rest of the ferritic plates and blasting conditions.

Figure 12 Comparison between AISI 2205, non-blasted (to the left) and blasted (to the right).
The blue oxide layer found on AISI 430 was fully removed on only three occasions, F1, F4, F7, see Figure 11. Note that the samples had the same blasting parameters, 55 m/s particle velocity and 60 % coverage rate. However different shot products were applied, see Table 4 for more detailed information. F9 in Figure 11 may represent the visual appearance for the rest of the ferritic samples.

Hot rolled mill scale is heterogeneous with varying oxide thickness, which makes it hard to quantify the oxide thickness. Figure 13 shows how the oxide scale on AISI 2205 and 304 is affected by shot blasting, in terms of thickness. It is evident from the light optical analysis that shot blasting has reduced the oxide scale even though the macroscopic appearance was unchanged.

The thickness of the oxide on non-blasted samples was ~7 µm while the blasted oxide was ~3 µm. There existed some difference in oxide thickness depending on how the material had been blasted. Generally a thicker oxide could be found on samples blasted with 70 m/s particle velocity and also on samples blasted with 100 % coverage rate.

The laboratory oxidation of AISI 430 have to be seen as a special case, the intention was a stable, compact and reproducible oxide performed at similar temperature- and time values as in the industrial process. The oxide created during annealing satisfied all demands but grew too thick to be representable. See Figure 14.

![Image](image1.jpg)

**Figure 13** AISI 2205 cross-section, comparison between blasted sample (to the left) and non-blasted (to the right). The dark area in the middle is bakelite and the white layers between it and the oxide are the Ni-plating. The picture was taken with LOM.

![Image](image2.jpg)

**Figure 14** LOM-picture presenting the oxide scale from the laboratory oxidised ferritic AISI 430. The thickness of the oxide was estimated to ~ 45-70 µm.
3.1.2. SEM-EDS

SEM-EDS element mapping was conducted on AISI 2205 and 304 before and after blasting. The oxide scale was not homogeneous and consisted of two dominant oxide layers. Figure 15 shows a representative example of a non-blasted AISI 2205 oxide. Several observations can be made from the information given by the element mapping:

- The oxide consists of a Fe-rich outer layer and a Cr-rich inner layer. This is in line with the previous observations from literature.
- Existence of a Mo-layer at the steel/oxide interface.
- The oxide scale in this area is approximately 3-4 µm thick.
- Small amount of Ni is present in the inner layer of the oxide scale.

Figure 15 SEM-EDS element mapping of AISI 2205, cross-section of a non-blasted sample.
Figure 16 show a representative example of how the oxide may look on a blasted AISI 2205 sample. Observations:

- The scale is thinner compared to the non-blasted case in Figure 15. The oxide scale is ~1µm but varies substantially along the cross-section.
- The oxide is dominated by a Cr-rich oxide with small amount of Fe and Mn.
- The Fe-rich oxide layer found in the non-blasted oxide is not present.
- The oxide may have grown inward, oxide valleys can be observed.
- Mn is represented in the oxide to a larger degree than in the steel.
- Very small amount of Ni can be observed in the oxide layer.

Figure 16 SEM-EDS element mapping of AISI 2205, cross-section of blasted D7 sample (spherical 40-44 Hrc shots, 55 m/s particle velocity, 60 % coverage rate).
Grinding and especially diamond polishing may influence the oxide scale which makes optical observations very tricky. An example of such a case is given in Figure 17. Some observations can be made:

- The oxide layer was quite thick, ~10 µm.
- A small, compact Cr-rich oxide layer can still be found close to the steel surface.
- Mo-layer can be seen in the steel, close to the steel/oxide interface.

Figure 17 SEM-EDS element mapping of AISI 2205, cross-section of a blasted D6 sample (elliptic shots, 70 m/s particle velocity, 60 % coverage rate).
Figure 18 shows a typical scale, sporting layers of oxide. The scale was observed on AISI 304, blasted with 60 % coverage rate, 70 m/s particle velocity and with elliptic shots. Some observations:

- The oxide scale is dominated by a Cr-rich oxide layer at the inner part of the scale and a outer Fe-rich oxide layer.
- This is probably an area not affected by blasting, since only 60 % of the surface was blasted.
- The oxide scale is porous. Ni from the plating has been able to find ways through parts of the oxide layer and filled the voids between the layers.
- The oxide layer is approximately 7 µm thick.
- Cr and Fe are, to a larger degree, mixed together in the oxide compared to the scale in AISI 2205.

![SEM-EDS element mapping of AISI 304, cross-section of blasted D6 (elliptic shots, 70 m/s particle velocity, 60 % coverage rate).](image)

Figure 18 SEM-EDS element mapping of AISI 304, cross-section of blasted D6 (elliptic shots, 70 m/s particle velocity, 60 % coverage rate).
3.1.3. FIB-SEM

The oxide scale’s thickness, morphology and chemical composition on AISI 304 was observed by FIB-SEM at a non-blasted area and under a crater made from shot blasting. The oxide scale under a non-blasted area is given in Figure 19. Observe the relatively high amount of porosity. This scale has not been grinded or polished by mechanical means. The scale is approximately 4-7 µm thick.

The oxide found under a shot blasting crater was thinner compared to a non-blasted oxide, approximately one to three µm thick. Observe the decreased amount of porosity at the scale in Figure 20.

Figure 19 Two pictures showing the oxide scale under a non-blasted area on AISI 304. The right picture is magnified 15 000 times.

Figure 20 Pictures showing the oxide scale under a crater created from shot blasting AISI 304. The white layer is deposited Pt. The right picture is magnified 35 000 times.
EDS-element mapping was conducted on both the non-blasted and blasted sample. Figure 21 and Figure 22 show the element mapping on the left side and the corresponding electron image on the right side of the figures. The element mapping has focused only on the oxide layer and a small part of the steel, hence the different size of the element maps and electron image. Observations from the non-blasted sample:

- Oxide scale consists of two layers, a Cr-rich oxide at the oxide/steel interface and a Fe-rich oxide layer above. Same observation as the mechanical polished samples shown in 2.4.6 SEM-EDS.
- Ni-rich oxide may be found close to the oxide/steel interface.

Figure 21 SEM-EDS, element mapping on FIB-polished cross-section of AISI 304, non-blasted sample. Pictures on the left side display the element mapping at the oxide seen in the electron image.
Element mapping was performed on the oxides directly under the impinged zone. The results are represented in Figure 22:

- Oxide scale consists of mainly a Cr-rich oxide with a small concentration of Ni present.
- A very small amount of iron is present in the oxide.

Figure 22 SEM-EDS, element mapping of FIB-polished cross-section of AISI 304, directly under a crater generated from shot blasting. The pictures to the left side display the element mapping of the oxide seen in the electron image. The sample was blasted with elliptic shots, 55 m/s particle velocity and 60 % coverage rate (D4).
3.1.4. XRD

XRD were performed on ferritic 430 and duplex 2205 samples.

3.1.4.1. AISI 430

Four ferritic samples were analysed with XRD. The conclusions given were drawn from the results shown in Figure 23.

Non-blasted, blue oxide sample

The non-blasted sample was completely oxidised and covered in a blue-looking oxide, which was of interest to investigate further. The scale was dominated by a $\text{M}_2\text{O}_3$ corundum-type phase which unit cell parameters are close to hematite $\text{Fe}_2\text{O}_3$. However, it also included a small concentration of $\text{M}_3\text{O}_4$ spinel phase with unit cells parameters close to chromite $\text{FeCr}_2\text{O}_4$. The oxide was adherent and thick enough to hinder the x-ray from reaching the steel. These peaks distinguished the non-blasted sample:

- A small chromite-peaks.
- A small BCC-peak.
- Strong hematite-peaks.

Non-blasted, light ground sample

This sample had not been blasted but had instead experienced light grinding. The intention was to remove the first, blue oxide layer and thereafter analyse the oxide closest to the metal-oxide interface. The result after the mechanical oxide removal was a surface containing brown/blue oxide together with the now exposed steel. The scale consisted of mainly two phases. One spinel-type with unit cell parameters close to chromite and one corundum-type with unit cell parameters close to hematite. These peaks distinguished the non-blasted, scraped sample:

- Strong BCC-peak (derived from the steel surface).
- Small chromite peaks.
- Medium strong hematite peaks, slightly shifted to higher $2\theta$ likely due to solid solution with small amounts of Cr.

Blasted F7 (spherical 40-44Hrc, 60% coverage rate, 55m/s velocity), brown/blue oxide sample

The scale consisted of mainly two phases. One spinel-type with unit cell parameters close to chromite and a one corundum-type with unit cell parameters close to chromia. These peaks distinguished the blasted, brown/blue oxide sample:

- Strong BCC-peak.
- Medium strong chromite peaks.
- Medium strong corundum-type peaks, close to chromia.

During blasting, the oxide scale is reduced in thickness, a result from section 3.1.1. This reduction made it possible for the x-ray to penetrate the oxide and reach the steel, hence the large BCC-peak. The oxide covered the whole surface, no islands with bare steel were visible which would otherwise have been one reason for the BCC-peak’s existence.
Blasted F8 (spherical 40-44Hrc, 100% coverage rate, 55m/s velocity), blue oxide sample
The sample belonged to one of the ferritic plates that showed no visual effect from blasting. This sample was dominated by two phases, a corundum-type with unit cell parameters close to hematite and a spinel-type with unit cells close to chromite. It was also thick enough to hinder the x-rays from reaching the steel. This sample was very similar to the non-blasted sample in both appearance and XRD-result. These peaks distinguished the blasted, blue sample:

- Small, non-existent BCC-peak.
- Strong hematite peaks.
- Small Chromite peaks.

Figure 23 XRD results from analysing four different AISI 430 samples.

C=Corundum-type $M_2O_3$
S=Spinel-type $M_3O_4$
BCC=Iron (BCC)

Black line=Non-blasted
Red line=Blasted, non-blue
Blue line=Non-blasted, scraped
Green line=Blasted, blue
3.1.4.2. AISI 2205
Sample D4 and D5 were analysed to reveal the difference between the blasted oxide scales.
- D4: Elliptic shots blasted with 55 m/s particle velocity and 60 % coverage rate.
- D5: Elliptic shots blasted with 55 m/s particle velocity and 100 % coverage rate.

The presence of both austenite and ferrite peaks seen in Figure 24 reveal that the x-ray penetrated the oxide scale and reached the duplex steel. The height of the BCC-peak in D4 is slightly stronger than in D5, which indicates that a larger percentage of the bcc-phase was present in the D4 sample. The oxide scale on D4 can therefore have been thinner, letting the x-ray penetrate further down into the steel. The option that there might be an influence from texture can almost be disregarded since both samples have been devised from the same plate. The oxide scales on both samples were also compact and covered the steel surfaces.

![XRD scan](image)

**Figure 24** XRD-scan on two AISI 2205 samples, D4 and D5.

The phases found in the oxide scale were a corundum-type with unit cell parameters close to chromia and a spinel-type with unit cells close to chromite. D5 seem to have a stronger S-peak, revealing that the shot blasting might not have been able to fully remove the outer oxide layer. Oxides with spinel phase are, according to literature, often placed at the outer layer of the scale.
The sample in Figure 25 was analysed with XRD to gain further knowledge on the remaining resistant and adherent oxide. The sample was a test sample to find the correct acid concentration during pickling. It had been exposed to mixed acid with concentrations of 2.8 M HNO₃ and 2 M HF in 40°C for 30 minutes.

The remaining oxide scale was dominated by one phase, a corundum-type with unit cell parameters close to chromia, as seen in Figure 26. A small amount of a spinel-type phase with unit cells close to chromite was also present.

These peaks distinguished the sample:
- Strong BCC and FCC peaks.
- Strong chromia peaks.
- Small Chromite peaks.

Figure 25 non-blasted duplex test sample exposed to mixed acid.

Figure 26 XRD-scan on a non-blasted duplex 2205 sample with remaining oxide after being exposed to mixed acid.
3.2 Pickling

Experiments with non-blasted samples exposed to mixed acid concentrations were conducted in advanced to gain the correct acid concentration for the blasted samples. Figure 28 shows the result from one of the experiments with 2.8 M HNO₃ / 2 M HF. The right sample shows a large amount of remaining oxide. Nevertheless, it was decided that the mixed acid concentration should be lowered with 20% to include the effect from blasting. However the 1.6 M HF, 2.24 M HNO₃ was proven to be slightly too strong during pickling of blasted samples.

The second experiment with a lower acid concentration was used to document the initial effect from acids on the oxide scale, it was not meant to fully clean the steel.

Visual and weight loss results can be found below. The figures display the visual result from all blasted samples exposed to pickling. Samples are ordered in groups of six, all with different exposure times. The groups are numbered from 1 to 9 with an including letter in front of the number i.e. D stand for duplex, A for austenite and F for ferrite. Each group represent a unique shot blasting setup; see Table 4 in section 2.2 for more detailed information.

Groups exposed to shot blasting:

- Groups 1,4 and 7: 60 % coverage rate and 55 m/s particle velocity.
- Groups 2,5 and 8: 100 % coverage rate and 55 m/s particle velocity.
- Groups 3,6 and 9: 60 % coverage rate and 70 m/s particle velocity.

A group of non-blasted, pickled samples (referred to as reference samples) are also included in the figures below.

General visual result after pickling:

- No real difference can be observed when comparing samples blasted with different shot products.
- It is clear that the oxide scale is undermined from dissolution of the Cr-depleted layer. A good example is shown in Figure 31, the 430 reference sample.
- Resistant, remaining oxides on samples can generally be found as stringers along the rolling direction.
- Samples blasted with mild blasting conditions (groups 1,4,7) display the best pickling result at short exposure times, but show the least cleaned surface at long exposure times. However, the difference is small.
3.2.1. **Duplex 2205**

Figure 29 shows the result from pickling with 1.6 M HF and 2.24 M HNO$_3$ while samples in Figure 32 have been pickled in 0.4 M HF and 0.5 M HNO$_3$. Observations on AISI 2205 exposed to mixed acid:

- A relatively large amount of oxides can be found on the non-blasted samples at low exposure times.
- Sample groups of D1, D4 and D7 display the best result at short exposure times and the least cleaned at long exposure times.
- No difference in result can be seen between the three shot products and only a small difference in result can be observed between the shot blasting conditions.

**Figure 29** Visual result after pickling AISI 2205, samples were exposed to mixed acid with a concentration of 2.24 M HNO$_3$ and 1.6 M HF at 40°C. A reference group of non-blasted samples can be found at the right side.
3.2.2. Austenite 304

No result between the blasted samples could be gained from pickling austenite in 2.24 M HNO₃ and 1.6 M HF. A big difference between blasted and non-blasted samples is however noticed. The effect generated from shot blasting was underestimated and this lead to choosing a too strong acid. There exist no pattern to follow and samples belonging to the same group have, on occasion, reacted differently to the acid. Figure 30 display a too widespread result, which might have come from the hot rolling process or simply bad luck at the shot blasting process. The mechanical influence during hot rolling will contribute to a more unstable oxide scale with varying thickness. Some samples might have a larger area of a thinner or crushed oxide scale. There also exist areas which have been more blasted than others, due to the random spray of shot products on the surface. This means that there will be samples that have a more easily removed oxide scale.

Figure 30 Visual result after pickling AISI 304. Samples were exposed to mixed acid with a concentration of 2.24 M HNO₃ and 1.6 M HF at 21°C. A reference group of non-blasted samples can be found at the right side.

The samples in Figure 33 were expose to low concentration of mixed acid. Nevertheless, no existing pattern can be observed between the different blast setups. Hence, the different blasting conditions do not seem to play such a big role as long as the outer layer is removed or at least cracked so that acid can reach the chromium depleted layer.
3.2.3. Ferrite 430

Mixed acid with 2.24 M HNO₃, 1.6 M HF was too powerful for the ferritic material. Almost all the samples had their oxide removed after 10 minutes of exposure, which can be seen in Figure 31. Samples have also been overpickled, the darker areas on samples with exposure times over 40 minutes are examples of that. Subsequent corrosion has also occurred and tinted the otherwise white surface yellow. This is due to choosing a too strong acid concentration for this type of material. The effect from shot blasting was, again, underestimated.

Observations made on pickled ferritic 430:

- There exist a significant difference between the blasted samples and the non-blasted sample in terms of oxide removal.
- The combination 55 m/s particle speed and 60 % coverage is superior in terms of oxide removal. This can easily be acknowledged in Figure 34 as well as in Figure 31 when comparing oxide removal at 10 minutes exposure time.

![Figure 31 Visual result after pickling AISI 430. Samples were exposed to mixed acid with a concentration of 2.24 M HNO₃ and 1.6 M HF at 21°C. A reference group of non-blasted samples can be found at the right side.](image)
Figure 32 Visual result after pickling AISI 2205. 0.5 M HNO₃ and 0.4 M HF at 40°C.

Figure 33 Visual result after pickling AISI 304. 0.5 M HNO₃ and 0.4 M HF at 21°C.

Figure 34 Visual result after pickling AISI 430. 0.5 M HNO₃ and 0.4 M HF at 21°C.
3.2.4. Weight Loss Measurements

The diagrams below show the weight loss of each specimen after exposure to acid. This can be gained from the diagrams:

- Each samples individual weight loss and direct comparison between samples with the same exposure time.
- Total sum of weight loss for each group of samples blasted with the same setup.
- Comparison between the three shot products.
- Comparison between the different blasting conditions.

Each diagram contains the weight measurement results from 45 samples, divided into nine sample groups. Each sample group contain five samples blasted with the same conditions. Each sample in the group has its own, unique exposure time. The shortest exposure time is 10 minutes while the longest belong to a sample exposed to 50 minutes (See also figures 29-34).

Figure 35, Figure 36 and Figure 37 below display each sample group’s accumulated weight loss for the five samples included in the group. However weight loss for each individual sample can also be obtained. For example, the sample exposed to the acid for 10 minutes in the A1-group lost 0.021 g while the total A1-group with its five samples lost approximately 0.120 g.

The bars display the effect, in terms of weight loss, of the shot blasting conditions:

- Bars 1, 4 and 7: 60 % coverage rate and 55 m/s particle velocity.
- Bars 2, 5 and 8: **100 % coverage rate** and 55 m/s particle velocity.
- Bars 3, 6 and 9: 60 % coverage rate and **70 m/s particle velocity**.
The rate of pickling drastically decreases when the acid has dissolved the chromium depleted layer and reached the corrosion resistant bulk steel. This means that the depleted layer and the oxide scale represent the majority of the weight loss values.

It will be easier to notice if a certain blasting parameter improve the effect of pickling by accumulating the weight loss from all samples blasted with that parameter. The effect from blasting is then enhanced and easier to perceive.

Patterns exists in Figure 35 and Figure 36, the bars with the lowest weight loss values are 1,4,7 while the bars representing a higher particle velocity (3,6,9) show the highest weight loss.

Figure 35 Diagram showing the accumulated weight loss for each respective shot blasting group after pickling. Each group contain five samples with their individual weight loss summerised into one bar. The % and m/s represent coverage rate and particle velocity respectively. This diagram display the result for the austenitic AISI 304 samples.
The combined mass of the oxide scale and chromium depleted layer has been estimated by rough calculation. The scale and Cr-depleted layer weights approximately 0.1455 g for 430, 0.0267 g for 304 and 0.0205 g for 2205. Assuming an average density of 5 g/cm³, average scale thickness of 7 µm, 5 µm and 45 µm for 304, 2205 and 430 respectively. The thickness of the chromium depleted layer was estimated to 1 µm with 7.8 g/cm³ in density. These calculated values seem to be in line with the weight measurements when comparing them to the visual results as well. This can be seen as further evidence that the weight loss values are made up mainly of the oxide scale.

Observe that Figure 37 does not follow the same pattern as the other two diagrams. One explanation might be that the ferritic AISI 430 has been exposed to a too strong acid concentration. This resulted in a continued dissolution of the steel whereas it should have, in normal concentrations, been greatly diminished.

Figure 36 Diagram showing the accumulated weight loss for each respective shot blasting group after pickling. Each group contain five samples with their individual weight loss summerised into one bar. The % and m/s represent coverage rate and particle velocity respectively. This diagram display the result for the duplex AISI 2205 samples.
Figure 37 Diagram showing the accumulated weight loss for each respective shot blasting group after pickling. Each group contain five samples with their individual weight loss summarised into one bar. The % and m/s represent coverage rate and particle velocity respectively. This diagram display the result for the ferritic AISI 430 samples.

Figure 38 and Figure 39 show the same weight loss as the previous diagrams but these line diagrams also demonstrate the performance of each blasting parameter. Each colour represents a certain parameter:

- **Light grey lines**: 55 m/s particle velocity, 60 % coverage rate
- **Dark grey lines**: 55 m/s particle velocity, **100 % coverage rate**
- **Black lines**: 70 m/s particle velocity, 60 % coverage rate

Since no difference could be related to shot blast product the colour of the lines are equal for simplicity.
Figure 38 Line diagram showing the pickling performance in terms of weight loss for each blasting parameter. Light grey represent the mild blasting 55 m/s particle velocity, 60 % coverage rate while dark grey represent an increase in coverage rate to 100 % and black an increase in velocity to 70 m/s. This diagram displays the weight loss for AISI 304 samples.

Figure 39 Line diagram showing the pickling performance in terms of weight loss for each blasting parameter. Light grey represent the mild blasting 55 m/s particle velocity, 60 %
coverage rate while dark grey represent an increase in coverage rate to 100 % and black an increase in velocity to 70 m/s. This diagram displays the weight loss for AISI 2205 samples.

The light grey lines are generally placed under the others. A conclusion can be made that increasing the velocity or the coverage rate will increase the weight loss during pickling.

4. Discussion

4.1 Remaining Oxide after Blasting

Shot blasting had a large effect on reducing the thickness of the oxide scale, as can be seen from the LOM-picture (Figure 13) in section 3.1.1.

It has been proven by FIB-SEM analysis that the scale directly under a blasted surface is dominated by a Cr-rich oxide with small concentrations of Ni. The Fe-rich oxide, which is commonly positioned above the Cr-rich oxide, has been removed during blasting. The underlying reason might be the low adherence between the outer and inner layers, the spinel and the corundum-type. Articles report of spalling of the outer layer during cooling after being hot worked or annealed. This is due to the generated stress from the layers different thermal expansion coefficients [32,36].

Literature further states that the Cr-rich oxide is adherent to the steel and it has been proven in this report as well. This adherence might be explained from the oxides tendency to grow inward as well as outward. Oxides grown inward are out of reach for the shot products as the steel will absorb most of the energy from the impacts. Another reason might be the hardness of the Cr-rich oxide scale. Chromia, in comparison to the other oxides, have a relatively high hardness value. Momber [15] states that for an effective shot blasting, it has to be a certain ratio between the hardness of the shot product and the oxide, the Cr-rich oxide might have been to too hard in this case.

4.2 Blasting Parameters and Shot Products

Experiments have shown that blasting parameters such as particle velocity and coverage rate are more important than choosing the right shot product, in terms of blasting result. Only a small difference may be observed when comparing the result from the three shot products. Visual appearance shows no sign that blasting with elliptic shaped products would enhance the pickling. However, samples blasted with elliptic shots on 2205 seem to have a slightly higher weight loss. Three possibilities should be taken into consideration:

1. The elliptic shots are less effective. High amount of the oxide scale remain and the shots have failed to create cracks or other openings for the acid. The outcome is a higher weight loss during a slow pickling.
2. The elliptic shots are more effective. Removing a high amount of oxide scale and puncturing through the oxide scale, giving the acid plenty of openings to effectively remove the remaining oxide and underlying metal.
3. A combination of the previous two occurs. Elliptic shaped shots disrupt and puncture the oxide scale locally, creating openings but fail to reduce the oxide scale.

Option 1 is the most likely candidate after a comparison of initial weight loss between the samples. The oxide scale blasted by elliptic shaped shots must have a larger amount of oxide scale remaining, as the measured weight loss is dominated by the oxide scale. If the elliptic shots were effective and punctured through the oxide scale, thereby increasing the rate of pickling, a higher weight loss should be revealed at the early stage. This is not the case, comparing weight loss between elliptic samples D4,5,6 with low-carbon D7,8,9 shows a
weight loss for the first 15 min of: 0.008, 0.010, 0.013 g respectively 0.009, 0.011, 0.011 g. Note however that the differences between the products are still very small.

A more interesting aspect is the effect from the two blasting parameters: particle velocity and coverage rate. The visual analysis clearly show that 60% coverage rate and 55m/s particle velocity, which is the mildest blasting condition in this report, is the best alternative when it comes to removing the oxide scale on ferrite. Furthermore, this setup provides the lowest weight loss results in all diagrams for all three materials. This is important because measuring the weight loss before and after pickling is a good method to quantify the effect blasting had on pickling. A high weight loss can mean a rapid rate of pickling.

Shot blasting can blast away a large portion of the oxide scale and/or disrupt and crack open the scale, both options will affect the subsequent pickling positively. The first option seems to be the case for the mildest blasting condition. Compared to the other conditions, a higher percentage of the oxide scale has been removed for samples blasted with the mildest blasting condition and this lead to the reduced values in the weight loss diagram.

The result might initially be confusing with the mildest blasting condition removing the largest amount of oxide. However, as stated in the literature study, increased particle speed might not always be the best option. The position of the maximum tensile stress, created during impact, will vary depending on the velocity, too high and it may be absorbed by the ductile steel substrate. An optimal velocity might exist where the maximum stress can be positioned at a weak area in the oxide scale. The interface between two oxide layers, where the adherence is already low, can be one such place. The removal of one oxide layer has been observed and documented in this report so this notion might not be far from the truth. The position for the maximum stress can possibly be determined using SEM-EBSD and/or XRD.

Even though the mildest blasting condition removes the largest amount of oxide scale, increasing the particle velocity or coverage rate may instead enhance the pickling rate. Visual observations show that slightly cleaner results have been obtained at longer exposure times for samples blasted with increased velocity or coverage rate. Initial larger amount of oxides combined with a cleaner result at longer exposure times, most likely mean an enhanced pickling. Increased particle velocity or coverage have created more openings for the acid but failed to reduce the scale.

4.3 Oxide Scale Containing Hematite

It has been proven that the outer layer of the oxide on ferritic 430 consists of a M₂O₃ corundum-type phase which unit cell parameters close to hematite Fe₂O₃. Oxide scale including hematite should be avoided if an effective removal by pickling is desired. The previous statement is in agreement with literature results and the difficulty with hematite has been noticed in this report as well. Visual observations together with XRD results conducted on AISI 430 conclude that blasted samples without hematite were more easily pickled. The mixed acid appeared to have trouble penetrating the dense outer layer. It was, unfortunately, difficult to remove the oxide by mechanical means as well; a surprising fact was noticed when conducting a more fierce shot blasting, a decrease in oxide removal could be observed. Increasing the particle velocity of the shots and/or raising the coverage rate had no real impact on the blue hematite layer; it remained generally intact and visible. The three cases when the blue hematite layer were blasted away required blasting with the mildest blasting condition, 55 m/s particle velocity instead of 70 m/s and 60 % coverage rate instead of 100 %.

As discussed in 4.2 Blasting Parameters and Shot Products, the mildest blasting condition might position the stress at the interface between the oxide layers and thus spall off the outer hematite layer.
4.4 Optimal Shot Blasting Conditions

The shot blasting machine is more or less a self-destructing machine exposed to high amount of wear from abrasive erosion. Both the shot products and the parts handling these products must be replaced relatively frequently due to wear. Harsher blasting conditions i.e. longer blasting times and higher particle velocity will further increase the wear. The results from the current work conclude that choosing a milder shot blasting with lower particle velocity and coverage rate leads to approximately the same surface finish as the more powerful blasting. Choosing a milder blasting setup would decrease the wear of the blasting machine and the operating time would decrease. It might not be worth to go up to 100% coverage rate as the time to achieve it is so much longer compared to the time it takes to reach 60% coverage rate.

A recommendation to lower the blasting conditions is given due to the presence of the chromium depleted layer and the fact that shot blasting is unable to remove all oxide on stainless steel. Focus should be on removing the outer oxide layer in the scale and possibly to condition the Cr-rich lower layer for the subsequent pickling.

This can be performed by adjusting the particle velocity so the maximum stress is applied at the interface between the layers. This will require several tests as the oxide scale thickness may vary depending on facility, process and steel grade. The benefits may be an even higher pickling rate, less metal loss, cheaper maintenance costs and lower risk for work hardening on the steel surface.
5. **Conclusions**

- No major difference may be observed when comparing the effect induced from the three shot products. Shape and hardness seem to be inferior to particle velocity and coverage rate in terms of effect.
- Increasing velocity or coverage rate slightly enhances the pickling rate.
- The oxide hematite shows strong resistance towards shot blasting and pickling. However, applying a lower particle velocity and coverage rate seems to be effective in this aspect.
- Cr-rich oxide remains after shot blasting along with the chromium depleted layer. Thus, subsequent chemical pickling will always be necessary. Optimizing the shot blasting line should therefore be made with respect to the iron-rich layer.
6. Acknowledgments

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7. References


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[49] Discussion with Joan Samuel at WINOA ABRASIVES facility in Grenoble, France, 12/11-13
### 8. Appendix

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</tr>
<tr>
<td>F7-10min</td>
<td>18.90855</td>
<td>18.72599</td>
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<tr>
<td>F8-10min</td>
<td>18.86369</td>
<td>18.71702</td>
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<td>0.778</td>
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<tr>
<td>F9-10min</td>
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<td>18.6679</td>
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<td>0.722</td>
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<tr>
<td>A1-10min</td>
<td>20.53643</td>
<td>20.51496</td>
<td>0.021</td>
<td>0.105</td>
</tr>
<tr>
<td>A2-10min</td>
<td>20.04866</td>
<td>20.02176</td>
<td>0.027</td>
<td>0.134</td>
</tr>
<tr>
<td>A3-10min</td>
<td>20.50716</td>
<td>20.48324</td>
<td>0.024</td>
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<tr>
<td>A4-10min</td>
<td>20.76092</td>
<td>20.74121</td>
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<td>0.095</td>
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<tr>
<td>A5-10min</td>
<td>20.78399</td>
<td>20.7615</td>
<td>0.022</td>
<td>0.108</td>
</tr>
<tr>
<td>A6-10min</td>
<td>20.64602</td>
<td>20.61133</td>
<td>0.029</td>
<td>0.142</td>
</tr>
<tr>
<td>A7-10min</td>
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<td>20.50624</td>
<td>0.022</td>
<td>0.108</td>
</tr>
<tr>
<td>A8-10min</td>
<td>20.5103</td>
<td>20.48353</td>
<td>0.027</td>
<td>0.131</td>
</tr>
<tr>
<td>A9-10min</td>
<td>20.3043</td>
<td>20.27928</td>
<td>0.025</td>
<td>0.123</td>
</tr>
</tbody>
</table>

### Figure 40 Weight loss result from pickling. These tables represent the first four out of six exposure times for each material.
### Table 1: Weight loss results from pickling

<table>
<thead>
<tr>
<th>Material</th>
<th>Mini</th>
<th>Mafter</th>
<th>Weighloss [g]</th>
<th>Weighloss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1-50min</td>
<td>18.55237</td>
<td>17.98109</td>
<td>0.571</td>
<td>3.079</td>
</tr>
<tr>
<td>F2-50min</td>
<td>18.82727</td>
<td>18.11175</td>
<td>0.716</td>
<td>3.800</td>
</tr>
<tr>
<td>F3-50min</td>
<td>18.82276</td>
<td>17.97898</td>
<td>0.844</td>
<td>4.483</td>
</tr>
<tr>
<td>F4-50min</td>
<td>18.70506</td>
<td>18.20097</td>
<td>0.504</td>
<td>2.695</td>
</tr>
<tr>
<td>F5-50min</td>
<td>18.67312</td>
<td>17.86475</td>
<td>0.808</td>
<td>4.329</td>
</tr>
<tr>
<td>F6-50min</td>
<td>18.93619</td>
<td>17.83612</td>
<td>1.100</td>
<td>5.809</td>
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<tr>
<td>F7-50min</td>
<td>18.97634</td>
<td>17.90887</td>
<td>1.067</td>
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<tr>
<td>F8-50min</td>
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<td>18.34982</td>
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<tr>
<td>F9-50min</td>
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<td>18.1278</td>
<td>0.776</td>
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<td>A1-50min</td>
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<td>20.51726</td>
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<td>20.03247</td>
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<tr>
<td>A3-50min</td>
<td>20.33944</td>
<td>20.30623</td>
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<td>0.163</td>
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<tr>
<td>A4-50min</td>
<td>20.76559</td>
<td>20.73543</td>
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<td>0.145</td>
</tr>
<tr>
<td>A5-50min</td>
<td>20.77625</td>
<td>20.746</td>
<td>0.030</td>
<td>0.146</td>
</tr>
<tr>
<td>A6-50min</td>
<td>20.60838</td>
<td>20.57476</td>
<td>0.034</td>
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<tr>
<td>A7-50min</td>
<td>20.16423</td>
<td>20.13253</td>
<td>0.032</td>
<td>0.157</td>
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<tr>
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<td>20.505</td>
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<tr>
<td>A9-50min</td>
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<td>20.37252</td>
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<td>40.58349</td>
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<td>0.041</td>
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<td>40.50589</td>
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<td>0.045</td>
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<tr>
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<td>40.56163</td>
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<tr>
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<td>40.53207</td>
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<td>40.56862</td>
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<tr>
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<td>40.56657</td>
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<td>0.043</td>
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<tr>
<td>D8-75min</td>
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<td>39.65477</td>
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<tr>
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<td>40.33551</td>
<td>40.31539</td>
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</tbody>
</table>

**Figure 41** Weight loss result from pickling. These tables represent the last two out of six exposure times for each material.