Effects of tempering on corrosion properties of high nitrogen alloyed tooling steels in pyrolysis oil

Ashkan Reza Gholi

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Abstract

Nowadays biofuels are becoming a good alternative for petroleum fuels due to environmental issues like high carbon dioxide emission and increasing vehicles population, together with the high price and fast depletion of petroleum oils. This project aims to investigate the corrosive effects of wood Pyrolysis oil on a special grade of nitrogen alloyed tooling steels to be used for injector nozzles in Diesel engines, where high stress and strain encounter high acidity and corrosivity of the Pyrolysis oil and cause breakdown over short periods. Vanax 35 and Vanax 75 manufactured in Uddeholm are two types of powder metallurgy high nitrogen alloyed martensitic stainless steel with a high combination of hardness (over 56HRC), low friction properties, wear resistance, anti-galling and corrosion properties. In this work, the newly developed Vanax material together with the tool steels Elmax and AISI O1 were tempered at various temperatures from 200°C to 500°C. The tempered steels were then exposed in pyrolysis oil at 4 different temperatures, 20°C, 70°C, 95°C and 130°C. The materials were investigated by means of corrosion rate measurements, microscopy (LOM, SEM, confocal) and Thermo-Calc calculations. The corrosion rate measurement proved that Vanax tempered at lower ranges (200°C, 400°C and 450°C) showed the best corrosion resistance while higher tempering temperatures such as 500°C, Elmax and AISI O1 tempered at 200°C suffered a great deal of general corrosion attack. Thermo-Calc calculations showed the formation of a hard phase, VN as primary nitrides instead of primary chromium carbides at austenizing temperature for the Vanax group. Higher amount of chromium is dissolved in solid solution in Vanax at austenizing temperature hence the martensite matrix has, after quenching, a higher chromium content that helps passivation. The loss in corrosion properties at higher tempering temperatures was due to the formation of CrN secondary phase at around 400°C which reduces the chromium content of the martensite matrix. The results of light optical and confocal microscopy showed the presence of pits when tempering at 400°C and 450°C. No pits were observed at 200°C. Elmax was not passivated at all which resulted in general corrosion attacks, due to a high chromium loss from the austenite solid solution at the austenizing procedure temperature and also the tempering temperatures. The chromium depletion from the austenite can be explained by a high carbon and a low nitrogen content in the composition which resulted in formation of a high amount of Cr₇C₃.

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# Table of contents

1. INTRODUCTION ......................................... 1

AIMS ........................................................................ 3

2. THEORETICAL BACKGROUND .......... 5
   2.1 BIOFUELS AND PYROLYSIS PROCESS .... 5
      2.1.1 Pyrolysis process.......................... 6
      2.1.2 Corrosion in bio-fuels .................. 7
   2.2 STAINLESS STEEL.............................. 8
      2.2.1 Stainless steel grades ................. 8
   2.3 BASICS OF CORROSION .................... 10
      2.3.1 Uniform (general) corrosion ......... 10
      2.3.2 Galvanic corrosion ...................... 10
      2.3.3 Localized corrosion ..................... 11
      2.3.4 Intergranular corrosion .............. 13
   2.4 EFFECTS OF HEAT TREATMENT ON CORROSION PROPERTIES OF MARTENISTIC STAINLESS STEEL ........................................ 13
      2.4.1 Tempering of stainless steel ...... 13
      2.4.2 The effect of austenizing and tempering temperature range on the mechanical properties ......................... 14
   2.5 CORROSION CHARACTERISTICS OF TOOLING STEELS ........................................ 15
   2.6 COMPARISON BETWEEN HIGH NITROGEN ALLOYED STAINLESS TOOLING STEEL AND ORDINARY TOOLING STEEL................................. 16

3. EXPERIMENTAL WORK ................. 17
   3.1 MATERIALS ........................................ 17
      Vanax.............................................. 17
      Elmax.............................................. 18
      AISI O1 ............................................ 18
   3.2 SAMPLE PREPARATION .................... 19
   3.3 OIL CHARACTERIZATION .................... 20
      3.3.1 Water content ............................. 20
      3.3.2 pH measurements ....................... 20
   3.4 EXPOSURE SET UP ............................ 20
      3.4.1 Exposures at 20°C and 70°C ......... 21
      3.4.2 Exposures at 95°C and 130°C ...... 21
   3.5 PICKLING ........................................ 23
   3.6 EVALUATION METHODS .................... 24
      3.6.1 Microstructure analytical methods 24

4. RESULTS .............................................. 25
   4.1 WATER CONTENT AND pH MEASUREMENT .............................................. 25
   4.2 CORROSION MEASUREMENTS ............... 25
      4.2.1 Vanax ....................................... 25
      4.2.2 Elmax and AISI O1 ...................... 27
      4.2.3 Comparison between corrosion rates of Vanax, Elmax and AISI O1 at different temperatures of exposure ........... 27
   4.3 MICROSTRUCTURE OBSERVATIONS ....... 29
      4.3.1 Vanax ....................................... 29
      4.3.2 Elmax ....................................... 31
      4.3.3 AISI O1 ..................................... 32

5. DISCUSSION ........................................... 39
   5.1 VANAX ............................................. 39
   5.2 ELMAX ............................................ 41
   5.3 AISI O1 ........................................... 42

6. CONCLUSION ......................................... 43

7. ACKNOWLEDGEMENTS ............................. 45

8. REFERENCES ......................................... 47

4.4 THERMO-CALC CALCULATIONS ........ 33
   4.4.1 Phase volume fraction at austenizing temperature ........................................... 33
   4.4.2 Austenite composition at austenizing temperature ........................................... 34
   4.4.3 PRE number at austenizing temperature ........................................... 36
   4.4.4 Phase fractions at tempering temperatures ........................................... 36
   4.4.5 Matrix composition at tempering temperatures ........................................... 37
1. Introduction

Nowadays environmental issues like high carbon dioxide emission and increasing vehicles population, together with the high price and fast depletion of petroleum oils have led to an increased interest in using biofuels. Biofuels provide less CO\textsubscript{2} emissions and have low sulphur content. Fast pyrolysis is a process that converts biomass to biofuel by rapid heating at elevated temperatures (about 400°C) in the absence of oxygen. The products are mainly gases, aerosols and charcoal which are generated from biomass decomposition.

There is a wide range of fuel applications for pyrolysis oil. With little modifications in the engine, the pyrolysis oil proves useful as the properties (thermal efficiency, etc) are close to that of diesel. However, high water content, low pH and the presence of metal ions and chlorides make the pyrolysis oil highly corrosive.

Many components in automobile engine such as nozzles, fuel filters, valve bodies and pump rings are made of stainless steel or aluminium alloys. Several works have been done in order to study the effects of biofuels on stainless steels, aluminium and copper [1,2]. However, the compatibility between the materials currently used in the automotive industry and the new biofuels that appears on the market is in many cases not yet properly tested. This paper aims to study the corrosive effects of the wood pyrolysis oil on a special grade of stainless tooling steel, called Vanax, and to compare the results with those of two other grades of ordinary tooling steels called Elmax and AISI O1. Vanax is a specific grade of high nitrogen alloyed martensitic tooling steel produced by powder metallurgy, which will be used in the production of injector nozzles in Diesel engines run by pyrolysis oil. Injector nozzle is an engine part where high corrosion and wear limits the use of conventional materials.

In this work, Vanax, Elmax and AISI O1 were exposed to pyrolysis oil at several temperatures; 20°C, 70°C, 95°C and 130°C. The temperature of Injectors in diesel engines is usually as high as 130°C, while the piping system is normally heated up to 70°-100°C. In addition, it is also interesting to investigate the corrosion attack at ambient temperature, since some parts of engine work at ambient temperature.

Vanax shows a high combination of hardness (over 56HRC), low friction, wear resistance, anti-galling and at the same time high corrosion properties, while these characteristics are not attainable all in one place for ordinary tooling steel grades where hardness is based on carbide precipitates. In order to increase ductility and relieve internal stresses which exist in martensitic, tooling steel is usually tempered. However for stainless tooling steels there is a risk of chromium precipitates and loss of corrosion properties at high tempering temperatures. For this reason there is a need to find an optimized tempering range where the alloy shows good corrosion properties and at the same time ductility, toughness and hardness.
Aims

- The aim of the work is to study the compatibility of high nitrogen alloyed tooling steel to be used as diesel engine material in pyrolysis oil applications. The study includes:
  
  - Comparison between the corrosion resistance of high nitrogen alloyed and ordinary tooling steels in exposures to pyrolysis oil at several temperatures.
  
  - Investigation of the effects of tempering at different temperatures on corrosion properties of high nitrogen alloyed tooling steel exposed in pyrolysis oil.
2. Theoretical background

2.1 Biofuels and Pyrolysis process

Environmental issues like high carbon dioxide emission and increasing vehicles population, together with the high price and fast depletion of petroleum oils have led to an increase interest in biofuels. Biofuels introduce a number of advantages: the plant growth needed for the production of biomass feedstock consumes CO$_2$ in the photosynthesis. In addition, biomass contains low amounts of sulphur and has a high energy efficiency compared to traditional biomass fuels like hog fuel and black liquor. On the other hand there are considerable drawbacks with applications of biofuels; cost (10-100% more than fossil fuels), availability, need of fuel handling due to their incompatibility with normal fossil fuels, environmental safety and health issues, poor volatility, high corrosivity due to high water content and low pH and high viscosity [3].

Bio-oils are free-flowing liquids with a distinctive dark-brown colour and odor of smoke. There are three main groups of biomass used to process bio-oils: Cellulose, Hemicellulose and Lignin. The bio-oil is a product of depolymerisation and fragmentation of biomass. Table 1 shows a comparison between physical properties of bio-oils and conventional petroleum fuels.

Table 1. Typical properties of Wood Pyrolysis Bio-oil and of conventional petroleum oil [3]

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content wt%</td>
<td>15-30</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Specific gravity (ρ$<em>{oil}$/ρ$</em>{water}$)</td>
<td>1.2</td>
<td>0.94</td>
</tr>
</tbody>
</table>

**Elemental composition (wt%)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54-58</td>
<td>85</td>
</tr>
<tr>
<td>H</td>
<td>5.5-7.0</td>
<td>11</td>
</tr>
<tr>
<td>O</td>
<td>35-40</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>0-0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0-0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest Heating Value (MJ/Kg)</td>
<td>16-19</td>
<td>40</td>
</tr>
<tr>
<td>Viscosity at 50°C (centipoise or cP)</td>
<td>40-100</td>
<td>180</td>
</tr>
<tr>
<td>Distillation residue wt%</td>
<td>Up to 50%</td>
<td>1</td>
</tr>
</tbody>
</table>

**Water content, viscosity, volatility and corrosivity**

The oxygen content is normally 35-40%. Lower values result in a lower heating value. High water content is a result of initial moisture in the feedstock. A high water content can negatively affect the properties, decreasing the heating value and the combustion rate, and increasing the ignition delay and flame temperature. On the other hand, a high water content might help in increasing the fluidity, lower NO$_x$
emissions and also contribute to a more uniform temperature profile in the Diesel engine.

The oil usually starts to boil below 100˚C and leaves a residue of 40-50% of the initial material at 250-300˚C. Due to a high content of non volatile components, the oil needs a rather high amount of energy to ignite for the flame to be stable and self-sustaining [4]. The oil is considered to be combustible. The presence of organic acids results in a low pH (2.5-3), which makes the oil highly corrosive. Its corrosive properties increase with elevated temperature and increased water content.

2.1.1 Pyrolysis process
Fast pyrolysis is the process of converting biomass to biofuel by rapid heating at elevated temperatures (about 400˚C) in the absence of oxygen. The products are mainly gases, aerosols and charcoal generated from biomass decomposition [5]. Based on the heating method, pyrolysis process can be divided in three categories:
- Ablative pyrolysis: the oil is produced while biomass is pressed against a heated surface which moves rapidly.
- Fluid bed pyrolysis: a heat source provides the necessary heat which transfers to the biomass by convection and conduction (figure 1).
- Vacuum pyrolysis: costly and slower heating rate, but faster removal of pyrolysis by-products.

![Fluid bed pyrolysis process](image)

Vacuum pyrolysis of scrap tyres into oil resulted in 55% oil, 25% carbon black, 9% steel, 5% fibre and 6% gas. The properties of the tyre pyrolysis oil showed to be close to that of diesel, and with a little simplification on engine design, it can serve as an alternative fuel [6].

**Application in diesel engines**
There is a wide range of fuel applications for pyrolysis oil. Combustion in burner/furnace or burner/boiler system, diesel engines, turbines and stirling engines are typical examples. Diesel engines prove to be highly efficient in power generation. They are also adaptable to combine heat and power generation at the same time. Nowadays there is an increasing trend in using a new type of BCO (bio-crude oil)/
diesel emulsion pyrolysis oil for which there is no need for modifications and adaptation of the engine [7].

Figure 2. Modified fuel feeding system [7]

Figure 2 shows a schematic view of a diesel engine. Usually the hottest parts are the injector nozzles where the temperature could rise up to 130˚C. The pipes (recirculation, de-aeration) could heat up to 70˚-90˚C. Due to the high corrosivity of pyrolysis oil, the main concern is to select a material with good corrosion and wear properties, especially for the nozzles where the condition is most critical as high wear encounters high corrosivity.

2.1.2 Corrosion in bio-fuels

One of the concerns in using biofuels in practice is their corrosivity. The corrosive nature of the biodiesel increases with the presence of water and fatty acids. The absorbed water by biofuel can cause corrosion on the surface of the metal. Moreover, auto oxidation of the biofuel increases its corrosivity and degrades its properties. It should be noted that oxidation of biofuel re-converts esters into mono-carboxylic acids such as formic acid, acetic acid etc, which count for its high corrosivity. This could also give rise to the free water content which enhances microbial growth and could lead to microbiological influenced corrosion attack [8]. The presence of microorganisms and unsaturated acidic components are other factors which might cause problems such as interactions with metal surfaces and oil degradation. It is also proved that the type of feed stock for biofuel also affects its corrosive properties. Palm biofuel seems to be slightly more corrosive that fat biofuel [8].

According to the experiments by Darmstadt et al [1], corrosive effects of vacuum pyrolysis oil from softwood bark residues were high on aluminum and less on copper corrosion attack was observed on stainless steel.

Another aspect is the possibility of galvanic corrosion in connection with the engine material. During the pyrolysis process there is a risk of the increase of iron, lead or copper in the oil due to leaching from the reactors and other installations such as ring
seals. When using the biofuel in the engine, these metal contaminants can cause a galvanic cell with the engine material and initiate a corrosion process.

Many components in automotive engines such as nozzles, fuel filters, valve bodies and pump rings are made of stainless steel. This makes it very important to investigate the corrosive effects of biofuel on stainless steel in order to test the feasibility of the material for this purpose. According to the manufacturers, stainless steel has a good resistance against corrosion in bio-fuels, while aluminium has lower corrosion resistance. Copper has the lowest corrosion resistance compared to aluminium and stainless steel. Limited studies exist that investigate the corrosive effects of bio-fuels on tooling steels. This master thesis aims to study the compatibility of high nitrogen alloyed stainless tooling steel to be used as diesel engine material in Pyrolysis oil applications. These engines are being used in remote areas such as forests where there is low accessibility to petroleum fuel stations. Pyrolysis oil could potentially be a good alternative.

2.2 Stainless steel

Stainless steels refer to a particular class of steels which are mainly used for their high corrosion resistance. They all have a minimum of 10.5 wt% amount of chromium. Stainless steels could also often contain other elements like nickel and molybdenum. The iron content is usually more than 62 wt%. The unique advantage of stainless steels is that they form a passive surface oxide which protects the rest of the metal from corrosion. The chromium content should be at least 12% in order to form a dense protective oxide layer [9]. This chromium oxide, with a thickness of approximately 130 Angstroms, forms due to the high affinity of chromium to oxygen. In most cases this layer "repassivates" if damaged, by reforming the surface oxide. Usually there are enough oxidants in air and in aqueous environments to help "repassivation". However, some special circumstances may lead to the permanent breakdown of the layer, causing corrosion, which might differ in nature and appearance.

The protective chromium oxide does not react with other metals and is replaced by more chromium oxide when damaged or removed, often denoted “repassivity”, “tenaciousity” and “self-renewing” properties [9]. A high chromium and nickel content help this repassivation. Molybdenum usually improves repassivation and copper has desirable effects in reducing environments. All these unique characteristics give stainless steel a wide range of applications from applications in the food industry to pumping and oil containments and nuclear power applications [9].

2.2.1 Stainless steel grades

Figure 3 illustrates an iron-carbon phase diagram. It shows different phases that form at various temperatures when iron and carbon combine to form Fe-Fe₃C. Depending on their alloying elements and the microstructure, all stainless steels can be divided into four categories with different characteristics.
Austenitic grades
Nickel changes the microstructure to austenite, which is a solid solution of iron with other alloying elements. It usually exists at temperatures above 720°C. Austenitic grades are the most common types of stainless steel which counts for 70% of all stainless steel applications. AISI304 (18% chromium, 8% nickel) is probably the most familiar grade in this category. Stainless steels normally have good corrosion properties, weldability, formability and ductility and low temperature properties. Some special grades of austenitic stainless steels i.e. AISI 321, AISI 310, AISI 904L are commonly used in heat resisting applications i.e. automotive and furnace parts [10].

Ferritic grades
These steels contain lower amounts of chromium (10-18%) and show less formability and corrosion resistance. They are typically used in automotive trim and exhaust [10].

Martensitic grades
Martensitic stainless steels have a high carbon content (0.1-1.2%) with 12-18% chromium. Martensitic stainless steels can be hardened and tempered to increase their strength and toughness and are widely used as cutlery and surgical steels, though they have lower corrosion properties than that of the austenitic group. Martensitic stainless steels are widely used in cutlery and tooling applications due to their possibility of being hardened to achieve optimal strength, toughness and corrosion properties. The corrosion resistance of martensitic stainless steel is highly dependent on the amount of chromium dissolved in the matrix and on chromium precipitation during tempering. Thus corrosion properties are highly sensitive to heat treatment for martensitic stainless steel [11].
**Duplex grades**

Duplex stainless steels have a combined structure of ferrite and austenite. They have a high amount of chromium (18-28%) and a moderate amount of nickel (4.5-8%). They show better properties comparing to ferritic and austenitic groups with higher tensile and yield strength and improved resistance to stress corrosion cracking [10].

### 2.3 Basics of corrosion

Based on nature and appearance, there are several types of corrosion on stainless steel.

#### 2.3.1 Uniform (general) corrosion

General corrosion occurs due to destruction of the passive layer. The destruction of the passive layer often occurs in acidic or hot alkaline environments. Stainless steel is proven to be more resistant in oxidizing acids, and more susceptible to corrosion in non-oxidizing acids. In some cases, very strong oxidizing acidic environments (i.e. nitric acid) causes the layer to oxidize into soluble species, so called "transpassive" corrosion.

Uniform corrosion is often measured as the loss of thickness per time unit (e.g. mm/year). Stainless steel are resistant to uniform corrosion in an environment where the corrosion rate do not exceed 0.1 mm/y [12]. Uniform corrosion tests usually include weight loss measurement and microscopic investigations which ensures the absence of pitting and other localized corrosion phenomena.

#### 2.3.2 Galvanic corrosion

Galvanic corrosion occurs when two different metals are connected electrically in a conductive solution called "electrolyte". As a result, the material with less potential (less noble) in the galvanic series corrodes while the material with higher potential (more noble) resists the corrosion attack better. Conductivity of the solution, difference in nobility (driving force for galvanic attack) and the surface area ratio between the two metals are defining factors for the severity of the corrosion attack. Stainless steels are normally the more noble material (cathode) in connection with mild steel, galvanized steel, copper and brass. Coatings and paint systems on metals/alloys with higher potential (noble) are proven to be a good way to prevent galvanic corrosion [12].
2.3.3 Localized corrosion

Localized corrosion counts for the majority of failures of stainless steel applications. Localized corrosion attack occurs when a small area in the passive layer fails and results in corrosion initiation. There are two types of localized corrosion attack:

Pitting corrosion

Non-metallic inclusions such as sulphides and slag deposits might result in a passive layer breakage. A small galvanic cell may form where the bulk metal becomes the anode and corrodes, while a large part of the surrounding area on the surface becomes the cathode. The reactions at the anode and the cathode, respectively, can be written as:

\[ \text{M} \rightarrow \text{M}^{2+} + 2e^- \]  \hspace{1cm} \text{(anodic reaction, oxidation at negative pole)}

\[ \text{H}_2\text{O} + \text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \]  \hspace{1cm} \text{(cathodic reaction, reduction at positive pole)}

A pit forms due to the mass loss from the bulk metal. Negative chloride ions make their way into the pit to balance the positive charge of the dissolved metal. Consequently the inside of the pit becomes highly aggressive and results in failure, if not discovered.
**Crevice corrosion**

crevice refers to the areas in the structure where the penetration of the liquid is unavoidable. Due to the lack of oxygen to maintain the passive layer, and the oxidants in the solution a “concentration cell” forms where the composition of the stagnant solution differs from that of the bulk solution, hence the repassivation process fails. As a combined effect of dissolved metal ions and chlorides, the pH is lowered in the pit and the metal surface is activated, causing the formation of a galvanic cell with the bare metal in the crevice working as the anode resulting in a rapid corrosion rate. The mechanism is similar to that of pitting corrosion. There are different ways to test the resistant of stainless steel to pitting and crevice corrosion. Generally, CPT (critical pitting temperature) refers to the lowest critical temperature at which pitting starts.

The resistance of austenitic and duplex stainless steel towards pitting and crevice corrosion increases with increasing chromium, molybdenum and nitrogen content [11]. The PRE number is a way to indicate the resistance of stainless steel to the pitting corrosion. The PRE number is for instance given by:

\[
\text{PRE} = \%\text{Cr} + 3.3\%\text{Ni} + 16\%\text{Mo}
\]

A higher PRE number indicates a higher resistance to pitting corrosion.

**Stress corrosion cracking**

Stress corrosion cracking is a combination effect of corrosion and tensile stresses, usually in chloride solutions at high temperatures (above 50°C) usually combined with low pH. The attack is usually in the form of thin propagating cracks [11]. An increasing chromium and nickel content is useful to prevent the risk of stress corrosion cracking.
2.3.4 Intergranular corrosion

The main reason for intergranular corrosion is the precipitation of carbides (i.e. $\text{Cr}_7\text{C}_6$) in the grain boundaries of stainless steel due to high temperature heat treatments ($500-800^\circ\text{C}$). Considering the low diffusion rate of chromium in austenite, the depletion of chromium in the area surrounding the grain boundaries leads to depassivation and consequently to the corrosion initiation. This type of corrosion attack is most probable in oxidizing environments where the alloy matrix is passive. Under such condition stainless steels are “sensitized”, which means the grain boundaries, become susceptible to attack.

A lower carbon content is a good way to prevent carbide formation [11]. Niobium, titanium, vanadium and nitrogen form carbides that precipitate in the grain boundaries. This could facilitate chromium to stay in the solid solution and lower the risk of intergranular attack. The new martensitic stainless steel grade alloyed with nitrogen manufactured at Uddeholm, Sweden, contains a significant amount of nitrogen which replaces carbon and tends to eliminate the presence of carbides. The nitrogen indirectly improves the corrosion resistance and favours formation of a new hard phase, MN (i.e. VN), which improves the wear resistance [13]. However, long exposures at high temperatures, could result in precipitation of hard phases which might tend to give rise to localized corrosion. Duplex and austenitic stainless steel shows a good resistance to intergranular corrosion at high temperatures due to their low chromium content.

2.4 Effects of heat treatment on corrosion properties of martensitic stainless steel

2.4.1 Tempering of stainless steel

There are several reasons why ordinary annealed stainless steels are not useful practically. Annealed stainless steels normally contain ferrite and $\text{M}_7\text{C}_6$ carbides (with M representing the metallic constituent of the phase i.e. Cr or Mo). These phases are comparably soft and of low strength. Heat treatment of stainless steels aims to improve mechanical properties such as strength and hardness. Tempering is a heat treatment process which helps to induce ductility and impedes dimensional changes which might occur in the matrix under working condition. Martensitic stainless steel is usually tempered in order to improve the ductility and relieve internal stresses which exist in the martensitic matrix after rapid quenching.

Austenization of stainless steels is a solution treatment of the alloy at a specific temperature in the austenitic region for a period of time to help dissolution of preliminary carbides and chromium in the solid solution. This step is followed by rapid cooling in water, oil or air. After the cooling process the combined structure of austenite-martensite tends to undergo undesired dimensional changes due to the possible transformation of retained austenite. Retained austenite affects mechanical properties such as hardness and strength. Presence of residual stresses from quenching could negatively affect corrosion and other mechanical properties. Furthermore, martensite is a brittle phase susceptible to quench cracks. In order to deal with this problem, a simple heat treatment called tempering could be helpful. During tempering the steel is heated at a temperature below the eutectoid point (i.e. $200-500^\circ\text{C}$) at a fixed length of time, allowing the diffusion process to decompose
the undissolved primary carbides, relieve the stresses and produce a less brittle and more stable structure [14].

**Deep cooling (zero treatment)**

Deep cooling is a rapid cooling process in which the material is chilled at temperatures as low as -196°C in liquid nitrogen. In this process retained austenite decomposes and a reduced structure is obtained. For steel applications a complete martensite structure is desired to obtain the highest possible hardness, wear resistance and strength. Deep cooling has proven to be a good quenching method to cope with this issue. Tooling steels are mainly used for their high wear resistance and hardness. Deep cooling was the quenching method for the Vanax grade used in this project.

The presence of retained austenite after quenching can affect mechanical properties negatively, because austenite is a soft phase. It is been shown that for carbon steels with less than 0.2% carbon, there will be no retained austenite formation after quenching [14]. As a matter of fact, with higher carbon content in the alloy there is a higher possibility of retained austenite formation after quenching. This is due to the fact that martensite has a lower ability to dissolve in carbon compared to austenite. Thus in the case of high carbon steels, it is possible that after quenching austenite do not completely transform to martensite and is left as retained austenite.

**2.4.2 The effect of austenizing and tempering temperature range on the mechanical properties**

**Hardness and strength**

After annealing, stainless steels normally contain ferrite and intermetallic phases like $\text{M}_{23}\text{C}_6$ (i.e. $\text{Cr}_{23}\text{C}_6$). Austenizing helps in dissolving carbon, chromium and carbides in the solid solution. With higher austenizing temperature and time, hardness will be higher. This is due to the fact that a higher amount of carbon and chromium will dissolve in the solid solution, giving a carbon supersaturation and increased lattice distortion and homogeneity in the formed martensite after quenching. On the other hand there will be a risk of retained austenite formation in the lath martensite too. As a consequence, the optimized austenizing temperature is around 1050°C. Moreover, an increased impact strength as a result of higher austenizing temperature could be due to the reduction of carbides fraction and their homogeneous distribution in the martensitic matrix [15].

Increasing the tempering temperature in Cr16Ni5Mo martensitic stainless steel has almost no effect on hardness until 400°C, when due to the formation of coarse $\text{Cr}_3\text{C}_7$ carbides the hardness increases. These carbides transform to softer $\text{Cr}_{23}\text{C}_6$ and reduce the hardness [16].

It is been shown that aging at 550-600°C for 4h results in the best combination of ductility, hardness and strength in test specimens of precipitating hardening martensitic stainless steel [18].
Corrosion

After austenizing a high fraction of carbides, chromium and other alloying elements are dissolved in the austenite solid solution. As was mentioned earlier, the tempering process is used to relieve the internal stresses which form in the martensite due to rapid cooling, and increase its ductility by dissolving the hard primary carbides. Apart from that, tempering could affect corrosion properties of the material negatively. Higher temperature tempering could result in secondary carbides formation. This causes chromium depletion from the martensitic matrix and failure to passivate. Depending on the composition of the alloy, secondary carbide precipitation usually starts at 500-600°C which decreases the corrosion resistance in the case chromium is involved [15, 16, 18, 19].

Changing the austenizing temperature can influence the corrosion resistance significantly. The secondary carbide formation can vary by changing the austenizing range from 900-1100°C and oil quenching. Candelaria et al [19] have investigated AISI4290 stainless steel and showed that with increasing austenizing temperature (up to 1075°C) the corrosion resistance decreased before tempering. This is explained by the fact that a higher austenizing temperature results in more chromium dissolution in the matrix. Hence the martensite matrix has a better ability to passivate itself. According to Candelaria et al [19], the best corrosion resistance is obtained at austenizing temperatures up to 1025°C. They also showed that tempering at higher temperatures promotes secondary carbide precipitation. This causes chromium depletion from the martensitic matrix. The possibility of secondary chromium carbides precipitation increases with the amount of carbon. According to corrosion mass loss test on AISI 420 stainless steel quenched from 1100°C, tempering at 200°C for 2h promoted the lowest amount of secondary chromium carbide precipitation and resulted in a good corrosion resistance, while tempering at 200°C for 48h and 500°C causes a lot of carbide precipitations and affects corrosion properties negatively.

2.5 Corrosion characteristics of tooling steels

The main concern in alloy design for cold work tool steels is to attain a high wear resistance and a good corrosion resistance at the same time. While a high carbon content of tool steels is favourable from a wear resistance perspective, it also influences affects corrosion properties negatively due to the formation of chromium-rich carbides. There are several ways to deal with these problems. One way is a higher chromium. Chromium is a ferrite stabilizer, and high amounts could affect the hardening capacity of the alloy in a negative sense. Another way is to add carbide forming elements which have a higher affinity to carbon than chromium, such as vanadium. Formation of super hard VN phases could help to retain more chromium in the matrix, and hence improve the corrosion resistance. There have been also attempts to replace vanadium with niobium. Niobium has a high affinity to carbon, and a low solubility for chromium. The NbC has almost no chromium content resulting in a high chromium content in the matrix which enables the highest chromium content in the matrix. On the other hand, there could still be 5-15% chromium present in VN hard phases [17].

Another alternative in order to improve the corrosion resistance of tooling steels in aggressive environments (i.e. NaCl) is to use plasma nitriding. During this process nitrogen diffuses into the surface and reacts with steel constituents and forms an iron
nitride layer which improves wear resistance and hardness and corrosion resistance. It has been shown that the pitting corrosion resistance of nitrocarburized AISI H13 tool steels considerably increased due to the formation of iron nitride layers on the surface. However, formation of CrN at higher temperatures of nitriding can lead to chromium loss from the matrix and reduced corrosion properties [20].

Chromium has a higher affinity to nitrogen at high temperatures (i.e. above 420°C). Ordinary martensitic stainless tooling steels contain a low amount of chromium and high amount of carbon. This promotes the formation of iron nitrides. On the other hand, with more chromium present in the matrix, there is a stronger possibility of chromium nitride precipitation at high temperatures and a loss in corrosion resistance.

2.6 Comparison between high nitrogen alloyed stainless tooling steel and ordinary tooling steel

The idea behind adding nitrogen to stainless steel is to replace carbides with high-dispersive nitrides with improved wear resistance and low friction properties, and also help to improve the corrosion properties in some special grades by lowering the possibility of chromium carbide precipitation. A lower content of carbon in stainless steels results in less primary and secondary chromium carbides precipitation, and with more chromium in the matrix, there is improved passivation ability. Moreover, addition of nitrogen to the alloy promotes the formation of nitrides, which improves wear resistance and hardness. It should be noted that the addition of nitrogen for austenite stabilization is problematic in high chromium stainless steels due to the fact that chromium is a ferrite stabilizer and also that the solubility of nitrogen in austenite is limited. The structure of the alloy after quenching is highly dependent of the heating temperature and the amount of nitrogen. Quenching from higher temperatures (i.e. 1200°C) for alloys which contain a high amount of nitrogen (i.e. 0.9%) results in an austenite structure. Quenching from lower temperatures for the same alloys generates an austenite+nitride or ferrite+nitride structure [21].
3. Experimental work

3.1 Materials

Three grades of tooling steels were tested in this project.

Vanax
In stainless steels grades where the wear resistance and hardness is based on carbides, it is hard to obtain a high corrosion resistance and at the same time a good wear resistance because it is difficult to maintain a high amount of chromium, nickel and molybdenum in the solid solution. For conventional wear resistant and corrosion tool steels (i.e. AISI440C) the chromium content in solid solution can not increase more than 11-13% at the austenizing temperature due to the formation of Cr7C3. A useful method is to add carbide forming elements such as vanadium or niobium to the alloy and increase the austenizing temperature up to 1150˚C. Addition of vanadium and niobium promotes the formation of MC carbides. MC (M representing vanadium, niobium etc) primary carbides replace primary chromium carbides and help to have more chromium in the austenite solid solution. But the drawback is the risk of quench cracking and dimensional changes and formation of retained austenite due to the high austenizing temperature. Moreover, soft Cr7C3 would still be present which could affect corrosion properties.

A better concept is to replace most of carbon with nitrogen. This promotes formation of a primary MN hard phase instead of primary M7C3. The MN hard phase embedded in the martensitic matrix increases the hardness and results in low friction properties. Vanax 35 and Vanax 75 manufactured in Uddeholm are two types of powder metallurgy high nitrogen alloyed martensitic stainless steel. They show a high combination of hardness (over 56HRC), low friction properties, wear resistance, anti-galling and good corrosion properties [13].

The characteristic features of this group are:
- High chromium, molybdenum and nitrogen in the solid solution and high PRE number
- Possibility to dimensional readjustment after heat treatment
- No need for surface coating due to the presence of low friction particles (VN) in the bulk matrix. Cold welding and adhesion of work material to the surface can hence be avoided.

Table 2 shows the composition of the alloying elements in Vanax group.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanax 35</td>
<td>0.2</td>
<td>1.9</td>
<td>20</td>
<td>2.5</td>
<td>2.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Vanax 75</td>
<td>0.2</td>
<td>4.2</td>
<td>21.2</td>
<td>1.3</td>
<td>9</td>
<td>0.05</td>
</tr>
</tbody>
</table>
**Elmax**
Elmax is a high chromium, vanadium, molybdenum stainless steel with very good corrosion and wear resistance, dimensional stability and compressive strength. A hardness of 58 HRC can be obtained after hardening and tempering. Elmax is made by powder metallurgy which gives it good corrosion and wear resistance at the same time, one feature which is usually not possible for other conventional stainless steel alloys [22].

*Table 3. The composition of Elmax in wt% [22]*

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elmax</td>
<td>1.7</td>
<td>0.8</td>
<td>18</td>
<td>1</td>
<td>3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**AISI O1**
AISI O1 is a manganese-chromium-tungsten oil hardening tool steel with good machinability, dimensional stability, surface hardness and toughness after hardening and tempering. It has a wide range of applications in tooling manufacturing such as cutting and forming. It can be hardened and tempered to 62 HRC [23].

*Table 4. The composition of AISI O1 in wt% [23]*

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>W</th>
<th>Cr</th>
<th>V</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI O1</td>
<td>0.95</td>
<td>0.6</td>
<td>0.6</td>
<td>0.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>
3.2 Sample preparation

Samples were cut in 18mm×44mm×1mm and sent to Uddeholm for heat treatment. Table 5 shows the heat treatment process for each test group.

Table 5. Heat treatment process for each test group

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Heat treatment Process</th>
<th>Exposure at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanax 35</td>
<td>group1) 1080˚C/30min+200˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C, 130˚C</td>
</tr>
<tr>
<td></td>
<td>group2) 1080˚C/30min+400˚C/2x2h</td>
<td>130˚C</td>
</tr>
<tr>
<td></td>
<td>group3) 1080˚C/30min+450˚C/2x2h</td>
<td>130˚C</td>
</tr>
<tr>
<td></td>
<td>group4) 1080˚C/30min+500˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C</td>
</tr>
<tr>
<td>Vanax75</td>
<td>group1) 1080˚C/30min+200˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C, 130˚C</td>
</tr>
<tr>
<td></td>
<td>group2) 1080˚C/30min+400˚C/2x2h</td>
<td>130˚C</td>
</tr>
<tr>
<td></td>
<td>group3) 1080˚C/30min+450˚C/2x2h</td>
<td>130˚C</td>
</tr>
<tr>
<td></td>
<td>group4) 1080˚C/30min+500˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C</td>
</tr>
<tr>
<td>Elmax</td>
<td>group1) 1080˚C/30min+200˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C, 130˚C</td>
</tr>
<tr>
<td>AISI O1</td>
<td>group1) 850˚C/30min+200˚C/2x2h</td>
<td>20˚C, 70˚C, 95˚C</td>
</tr>
</tbody>
</table>

The austenizing temperature for Vanax group was 1080˚C for 30 min followed by deep cooling at -196˚C. A low quenching temperature helps to achieve a martensitic structure with the highest possible hardness. In order to improve toughness and ductility after quenching, the samples were tempered. Tempering was done at three different temperatures to compare the corrosion resistance and find the optimized tempering condition, giving the best combination of hardness, toughness and corrosion resistance. These three different tempering conditions were 200˚C, 400˚C and 450˚C, and 500˚C twice for 2 hours, with intermediate cooling to room temperature. Elmax and AISI O1 were only tempered at one temperature 200˚C.

After the heat treatment samples were drilled with a Carbide stub Drill. The hole was on the upper half and 3.50 mm in diameter. The samples were then grinded down to 1200 grit with SiC paper on both sides using an automatic grinding machine. Three replica samples were investigated in each test group. In order to clean the surface before exposure, samples were rinsed with water followed by ultrasonic cleaning in ethanol for 1min. The samples were then dried in a desiccator filled with silica gel over night and the initial weight was recorded with a scale (0.00001g accuracy) the following day.
3.3 Oil characterization

3.3.1 Water content

Karl Fischer method
The Karl Fischer coulometric method is based on a classical water determination method. The basis of the water determination is a chemical relation according to equation 1, which summarizes a few reactions in titration of a water containing sample.

\[
\text{H}_2\text{O} + \text{I}_2 + [\text{RNH}]\text{SO}_3\text{CH}_3 + 2\text{RN} \leftrightarrow [\text{RN}]\text{SO}_4\text{CH}_3 + 2[\text{RN}]\text{I} \quad \text{Eq}1
\]

According to the equation, iodine reacts with water, which is the base of water determination. The necessary iodine is generated in the electrode electrochemically [24].

![Figure 6. Karl Fischer coulometer [24]](image)

3.3.2 pH measurements
An Orion™ 250A pH meter was used to measure the pH of the oil.

3.4 Exposure set up

There were three replicas for each test group. Each group of samples was placed in a glass container, where they were immersed in the oil with the help of nylon holders and screws (figure 7). Nylon is resistant in high temperatures and oxidizing environments and it was also used to avoid any type of galvanic coupling.
### 3.4.1 Exposures at 20°C and 70°C

The glass containers were placed in a desiccator. The whole set up was placed in a normal oven (Barden™) and the temperatures set at 20°C and 70°C respectively for the two different exposures. The duration of the exposures was 168 hours (figure 7).

![Figure 7. Exposures set up for 20°C and 70°C](image)

### 3.4.2 Exposures at 95°C and 130°C

According to the oil standards and a simple test which was done to find the flame point, the oil starts to lose its water content around 95°C, when small bubbles appear every few minutes that quickens at higher temperatures up to 120°C. If the oil cools down from this temperature a hard, gel-like substance remains at room temperature due to the loss of water content (figure 8).
For a safe test condition and prevention of any possible ignition at high temperatures and pressures, autoclaves were used for each test group. Glass containers carrying the samples were used. The autoclave was sealed at both ends to prevent leakage of gases. The autoclaves were put inside an explosive safe climate chamber and the temperature was set for 168 hours at 95°C and 130°C, respectively (figure 9). The climate chamber simulates the test temperature in which the materials would work in practice. Moreover, a ventilation system removes any hazardous gases which might be produced inside the chamber.

Figure 8. Pyrolysis oil remnants after it lost its water content

Figure 9. Set up for exposures at 95°C and 130°C: a) set up for autoclaves b) glass containers with samples filled with pyrolysis oil
3.5 Pickling

After exposures at 20°C and 70°C, the samples were removed from the oven and the set up de-assembled. Water and tissue paper were used for oil removal followed by ethanol cleaning in ultrasonic bath. At exposure temperatures of 95°C and 130°C, the oil was more firmly attached to the surface, however the oil could be removed using ethanol and terpentine.

Pickling was used to remove the corrosion products, while the base metal remained intact. The pickling process includes repeated immersion of test specimen in the pickling solution followed by weight loss measurements after each pickling cycle.

Pickling solutions for stainless steels mainly consist of nitric and hydrochloric acids. In this work, the solution “Superclarks” was used. In order to prepare 1 liter of pickling solution, 500 mL of hydrochloric acid (HCl, \( \rho = 1.19 \) g/mL) was mixed with 5g of 1.3-di-n-butyl-2-thiourea and distilled water to make it 1000 mL [25]. The Superclarks solution is useful for almost all grades of stainless steel, and the mass loss of the base metal is moderate. Pickling was performed at ambient temperature.
3.6 Evaluation methods

3.6.1 Microstructure analytical methods

Light Optical Microscope
An ALEICIA light optical microscope was used in this work to investigate the initial microstructure of the samples after etching and also on the corrosion attack initiation after the exposures. The main goal was to investigate the microstructure of the base metal and the presence of carbides/nitrides after the tempering process, and also to identify the type of corrosion attack which might have taken place on the surface.

Scanning Electron Microscopy
LEO 1520 Field Emission Gun Scanning Electron Microscopy was used to study the carbide/nitride formation. Using SEM, it was also possible to have a rough estimation on the amount of the precipitations in microstructure.

Confocal Microscope
An Olympus LEXT Laser Scanning Confocal microscope was used to investigate surface topography of the surface, 3D views of the corrosion attack and oxides, and also the depths of pits. The maximum magnification of the LEXT microscope was 14400x.

Thermo-Calc calculations
Thermo-Calc was used to study the phase transformation and precipitation of carbides and nitrides, the elemental composition of the solid solution and the precipitations at various temperatures.

Thermo-Calc uses a flexible database to calculate all kinds of phase equilibrium, phase diagram and phase transformations. Thermo-Calc applications can be found in chemistry, metallurgy, materials science etc. The software uses a general algorithm in order to calculate the equilibrium condition of a system. The base of Thermo-Calc calculations is “to minimize the free Gibbs energy of a system” to reach equilibrium state. A wide range of values can be set as conditions for Thermo-Calc calculations, including temperature, pressure, overall composition in total number of moles or mass fraction, chemical potential, volume, enthalpy, entropy etc. The Thermo-Calc software makes use of several modules, each for a specific purpose. For example, in order to plot phase diagrams for different binary and ternary systems, it uses BIN and TERN modules [26]. Thermo-Calc also incorporates various thermodynamic models and validated databases for specific systems.

In this work Thermo-Calc calculations were used to generate phase diagrams, which show the type and amount of solid solutions and precipitations at different tempering temperatures for Vanax, Elmax and AISI O1.

Furthermore, the amount of alloying elements (i.e. Cr, Mo etc) and PRE number (directly related to the amount of alloying elements) in the solid solution at austenizing temperature and in the martensite matrix at tempering temperatures calculated and the corresponding graphs were generated. Using Thermo-Calc, it is also possible to calculate the elemental composition of individual phases that form at each temperature.
4. **Results**

4.1 **Water content and pH measurement**

The results from Karl Fisher method showed a water content of 48% (average value) for the Pyrolysis oil. This is higher than the water content from the oil specifications that were received from the manufacturer, claiming a water content of 30%. The pH was measured to be approximately 2.6.

4.2 **Corrosion measurements**

The results of the corrosion rate measurements at different temperatures of exposure in Pyrolysis oil for Vanax, Elmax and AISI O1 are presented in the following paragraphs:

4.2.1 **Vanax**

Figures 11 and 12 show the corrosion rate for Vanax 35 and 75 tempered at 200°C, 400°C, 450°C and 500°C for different temperatures of exposure in Pyrolysis oil.

From figures 11 and 12 it can be seen that the corrosion rate increased with increasing exposure temperature. It is also clear that tempering at 500°C had a drastic effect on the corrosion properties of each grade, an effect more noticeable at higher exposure temperatures. The results at 130°C showed that tempering at 200°C and 400°C gives the best corrosion properties. Furthermore, for both Vanax 35 and Vanax 75, tempering at 450°C showed higher corrosion rates compared to lower tempering ranges such as 200°C and 400°C. When comparing the two diagrams it is clear that Vanax 35 had slightly improved corrosion properties compared with Vanax 75 at all exposure temperatures.
Figure 11. Corrosion rates of Vanax 35 tempered in various temperatures for different exposure temperatures in Pyrolysis oil

Figure 12. Corrosion rates of Vanax 75 tempered in various temperatures for different exposure temperatures in Pyrolysis oil
4.2.2 Elmax and AISI O1

Figure 13 shows corrosion rates determined for Elmax and AISI O1, both tempered at 200°C at different exposure temperatures in pyrolysis oil.

![Figure 13. Corrosion rates of Elmax and AISI O1 for different exposure temperature in pyrolysis oil](image)

The results show that Elmax has a high corrosion rate at all exposure temperatures. The corrosion rate increases with increasing the temperature. This was also true for AISI O1. Furthermore, AISI O1 alloy showed higher corrosion rates at 95°C compared to Elmax, although it did not follow this trend at 20°C.

4.2.3 Comparison between corrosion rates of Vanax, Elmax and AISI O1 at different temperatures of exposure

Figure 14 shows a comparison between determined corrosion rates of Vanax, Elmax and AISI O1 for different exposure temperatures. The Vanax group had a much better corrosion resistance in general, although tempering at 500°C caused a considerable loss in corrosion resistance especially at elevated exposure temperatures i.e. 95°C, 130°C, making this grade almost as susceptible to corrosion attack as AISI O1 and Elmax at 95°C. On the other hand, in general Vanax group showed the best corrosion resistance of all when tempered at lower temperatures i.e. 200°C, 400°C and 450°C. As mentioned before, with a higher temperature of tempering higher corrosion rates were determined for the Vanax group, a fact which was seen at all temperatures of exposures.
Figure 14. Comparison between corrosion rates of Vanax, Elmax and AISI O1 for different exposure temperatures in Pyrolysis oil
4.3 Microstructure observations

Microstructural observations conducted by using SEM, Confocal and LOM in order to investigate carbide/nitride precipitates from the tempering process, corrosion attack initiation and the type of corrosion phenomena.

4.3.1 Vanax

Figure 15 and 16 shows the microstructure of Vanax 35 and Vanax 75 tempered at 200°C. The dark particles are preliminary hard phase (MN).

![SEM image of Vanax 35 200°C 2×2h before exposure](image)

Figure 15. SEM image of Vanax 35 200°C 2×2h before exposure

Figure 17 shows a Confocal image from Vanax 75 tempered at 450°C after 168h exposure at 130°C in Pyrolysis oil. The presence of pits can be seen in the image. The Confocal profile shows the surface profile along the red line marked in figure 17. The vertical axis on the profile corresponds to the depth, while the horizontal indicates the distance. Pits depth can be measured from the profile. Pit number 1 and 2 are approximately sized 0.5 and 0.4 µm, respectively.
Figure 16. SEM image of Vanax 75 200°C 2×2h before exposure

Figure 17. Top) Confocal image from pits observed on Vanax 75 450°C 2×2h
Bottom) surface roughness profile along the red line on the image
Figure 18 shows a Confocal image from Vanax 75 tempered at 500°C after exposure at 130°C in pyrolysis oil. The image shows high general corrosion attack on the sample. The surface was destroyed, and some parts suffered by a significantly higher general corrosion attack while other parts of the surface remained less affected. The Confocal profile indicates a high mass loss from the surface, up to 40 µm in regions which suffered the most severe corrosion attack.

![Confocal image showing general corrosion on Vanax 75](image)

**Figure 18.** Top) Confocal image showing general corrosion on Vanax 75 500°C 2×2h, Bottom) surface roughness profile along the red line in the image

### 4.3.2 Elmax

Figure 19 shows general corrosion on Elmax tempered at 200°C after 168h exposure at 130°C in pyrolysis oil. The profile shows the surface roughness along the red line on the image. As can be seen in the figure the corrosion attack was spread all over the investigated surface, i.e. general corrosion attack was taking place on the Elmax alloy exposed at 130°C.
Figure 20 shows an image from AISI O1 tempered at 200°C after 168h of exposure at 130°C in pyrolysis oil. As can be seen in figure 20 the whole surface was attacked by corrosion. The corrosion is of a general type. The same type of corrosion attack could be observed on the Elmax samples. Significant carbide precipitates in the microstructure was also evident. These carbides are mainly cementite and tungsten carbides.

4.3.3 AISI O1

Figure 20 shows an image from AISI O1 tempered at 200°C after 168h of exposure at 130°C in pyrolysis oil. As can be seen in figure 20 the whole surface was attacked by corrosion. The corrosion is of a general type. The same type of corrosion attack could be observed on the Elmax samples. Significant carbide precipitates in the microstructure was also evident. These carbides are mainly cementite and tungsten carbides.
4.4 Thermo-Calc calculations

Thermo-Calc measurements were conducted in order to study the phase fractions, the chromium content, preliminary and secondary carbide/nitride precipitations to determine PRE number at austenizing and tempering temperatures.

4.4.1 Phase volume fraction at austenizing temperature

Figure 21. Volume fraction at austenizing temperatures for Vanax 35 (left) and Vanax 75 (right)
Figure 21 describes the phase fraction of Vanax at austenizing temperatures. At the temperature of interest (1080°C), Vanax 35 consists of almost 91% austenite and 9% vanadium nitride phase, while Vanax 75 consists of about 77% austenitic phase and 23% vanadium nitride phase. No preliminary carbides or cementite would form at this temperature according to the Thermo-Calc calculations. It can also be seen from the figures that Cr$_2$N and M$_2$(N,C) carbides (i.e. Cr$_2$N) had already completely dissolved in the austenite before reaching 1050°C.

The same type of data is shown in figure 22 for Elmax and AISI O1. It is clear from the figure that Elmax contains around 82% austenite, 15% Cr$_7$C$_3$ and almost 3% primary MC (i.e. VC) at 1080°C. AISI O1, which was austenitized at 850°C, on the other hand, has a solid solution that almost exclusively consists of the austenitic phase in equilibrium condition. According to figure 22, almost no primary precipitations were left at temperatures above 900°C, and all alloying elements and carbides were dissolved in solid solution.

4.4.2 Austenite composition at austenizing temperature

The amount of chromium and molybdenum in austenite at austeniting temperature could be a good indication for passivation ability of stainless steel. Figure 23 shows the alloying elements compositions in austenite at austenizing temperature for Vanax in wt%. The results show that for both Vanax grades the amount of dissolved chromium increased in the solid solution with austenizing temperature until 1080°C, where it remained constant with further increase in temperature. Vanax 35 and 75 consisted of approximately 18.2% and 18.4% chromium, respectively, in solid solution at the temperature of interest (1080°C). The amount of dissolved molybdenum was almost 2.5% and 1.3% for Vanax 35 and 75, respectively.
Figure 24 shows the weight percentage of alloying elements in austenite at austenizing temperature for Elmax and AISI O1. It can be seen that the chromium content in solid solution was low (<12%) for Elmax. This is due to a high precipitation of Cr$_7$C$_3$. AISI O1 had a small amount of chromium dissolved in the solid solution at austenizing temperature.

![Graph showing weight percentage of alloying elements in austenite at austenizing temperature for Elmax and AISI O1.](image)

**Figure 23. Weight percentage of alloying elements in austenite at austenizing temperature for Vanax 35 (left) and Vanax 75 (right)**

![Graph showing weight percentage of alloying elements in austenite at austenizing temperature for Elmax and AISI O1.](image)

**Figure 24. Weight percentage of alloying elements in austenite at austenizing temperature for Elmax (left) and AISI O1 (right)**
4.4.3 PRE number at austenizing temperature

The PRE number at austenizing temperature was calculated for Vanax, Elmax and Arne, based on Thermo-Calc calculations (table 6).

Table 6. PRE number at austenizing temperature

<table>
<thead>
<tr>
<th>Alloy</th>
<th>PRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanax35</td>
<td>35</td>
</tr>
<tr>
<td>Vanax75</td>
<td>30</td>
</tr>
<tr>
<td>Elmax</td>
<td>15</td>
</tr>
<tr>
<td>AISI O1</td>
<td>1</td>
</tr>
</tbody>
</table>

4.4.4 Phase fractions at tempering temperatures

Thermo-Calc calculations showed formation of secondary carbide/nitride precipitations at higher tempering ranges (400°C, 450°C and 500°C) in Vanax group. According to the diagrams (figure 25, left), these secondary precipitates were mostly Cr$_2$N. Cr$_{23}$C$_6$ was also seen at temperatures above 400°C. On the other hand, rather high amount of Cr$_{23}$C$_6$ precipitations were observed on Elmax at tempering (figure 25, right). In addition, a small amount of MC (i.e. VC) was also seen. AISI O1 had a considerable amount of cementite in the martensite matrix at temperatures above 200°C, together with low fractions of primary MC (i.e. WC or VC), (figure 26).

Figure 25. Volume fraction at tempering temperatures for Vanax 35 (left) and Elmax (right)
4.4.5 Matrix composition at tempering temperatures

The "Matrix composition at tempering temperatures" diagrams show chromium depletion from the martensitic matrix at high tempering temperatures (400°C, 450°C and 500°C) for Vanax. The calculations show that the maximum amount of chromium in martensite at tempering temperatures above 400°C for Vanax 35 was 13%, which is much less than that of austenizing temperature and tempering at 200°C (which is almost 18.2%). According to Thermo-Calc calculations, the maximum amount of molybdenum at tempering temperatures above 400°C decreased to less than 1% for Vanax, which was less than the amount of molybdenum dissolved in the austenite solid solution at austenizing temperature.

Thermo-Calc calculations also show that the maximum amount of chromium in the martensite matrix for Elmax was around 9% at 200°C. Also very small amount of molybdenum was seen, which was less than 1%. AISI O1 had very little amount of chromium (<1%) in the matrix at 200°C tempering.

Figure 26. Volume fraction at tempering temperatures for AISI O1
5. Discussion

5.1 Vanax

Generally, with higher exposure temperatures i.e. 95°C and 130°C there was a higher rate of corrosion on the samples. This is due to the fact that at high temperatures there is a higher rate of reactions, "oxidation and reduction". Hence, ion transfer in the electrolyte (pyrolysis oil) is much faster and the corrosion rate increases.

The Vanax group clearly showed good corrosion properties in Pyrolysis oil in general. This can be explained by the high amount of chromium (18.2% and 18.4% for Vanax 35 and 75, respectively) in the solid solution at austenizing temperature, 1080°C. This austenization temperature is high hence higher chromium is dissolved in the matrix (figure 23) which increases the passivation ability of Vanax. High austenization temperatures might increase the risk of internal stresses and dimensional changes in the martensitic matrix after quenching. However, this was not a large concern in the Vanax material because the material was tempered after quenching in order to relieve possible internal stresses which might had formed. It is well known that austenite is a soft phase. Therefore, the presence of retained austenite after quenching is not desirable for tooling steels where high hardness and wear resistance are required. Vanax was quenched at a temperature as low as -196°C; furthermore it has a low carbon and very low nickel content in the composition. Hence, there was a small risk of retained austenite formation and the structure was almost completely martensitic after quenching. Apart from high chromium content in solid solution at austenizing temperature, Vanax contains a large amount of molybdenum as well. This increases the passivation ability of the grade considerably.

The Thermo-Calc calculations (figure 21) showed that the indirect cause for good corrosion properties of the Vanax material can be found in the presence of a special type of preliminary precipitates, i.e. the vanadium nitride (VN) phases, instead of primary chromium carbides (i.e. Cr7C3 from solidification process) at the austenizing temperature. With less primary chromium carbide precipitates a higher amount of chromium dissolves in the solid solution increasing the passivation ability of Vanax 35 and Vanax 75 material. On the other hand, VN is a hard phase which increases the wear resistance and hardness of Vanax. According to figure 21, a high amount of chromium, primary Cr2N and Cr23C7 phase was completely dissolved in the solution before temperature reached 1080°C, preventing the possibility of chromium carbide precipitations. The presence of a low amount of primary chromium precipitates in Vanax at austenizing temperature can be explained by its low carbon content (0.2%), as more carbon in composition tend to form a higher amount of carbides. Instead, the presence of nitrogen favours formation of VN hard phases, a phase which replaces chromium carbide precipitates.

The PRE number is directly related to the amount of chromium and molybdenum dissolved in the matrix. The high PRE number at austenitization temperature for Vanax is due to the high amount of chromium and molybdenum dissolved in solid solution, leading to good passivation ability.
Secondary precipitates may form during the tempering procedure; that will have an effect on the corrosion properties. This can be seen in the confocal microscopy results (figure 17 and 18) where the higher tempering temperatures of 450°C and 500°C give deterioration in the corrosion resistance of Vanax alloys. As was the case for primary precipitates, with more secondary chromium precipitates, there will be a less amount of chromium in the matrix to sustain the passivity of the Vanax alloys. On the other hand, quenching and tempering have no effect on primary precipitations. Hence, directly after quenching the composition of the alloy will be similar to that of austenization at 1080°C, shown in figure 23. Tempering at 200°C for 2 hours is too short for any secondary precipitation. Therefore the corrosion resistance of Vanax 35 and Vanax 75 tempered at 200°C for 2 hours is very satisfactory, since the microstructure is more or less similar to that of austenizing temperature. With a high chromium content in matrix, secondary chromium precipitates (Cr$_2$N) start to form at 400°C (figure 25, left). These intermetallic particles are in the sub-micron level and not viewable in the ordinary SEM. Instead these particles need to be investigated in a Transmission Electron Microscopy (TEM), not within the scope of this master thesis. It should be noted that Thermo-Calc diagrams show the equilibrium condition calculations. In reality thermodynamic equilibrium is not obtained during the tempering process. During tempering, the material is not usually heated enough to reach equilibrium (which might take hundreds of hours). Hence, the thermographic graphs do not provide accurate quantitative data on the amount of each phase at each tempering temperature. However the diagram presents useful information about phases that will form at each tempering temperature. According to corrosion rate measurements for Vanax, the corrosion attack was slightly higher on 400°C and 450°C, and a dramatic increase in corrosion attack was observed from 450°C to 500°C. This can be explained by an increase in secondary Cr$_2$N precipitates at higher temperatures, and consequently significant chromium depletion from matrix. Confocal investigations showed the presence of pits on samples which were tempered at 400°C and 450°C (figure 17 and table 7) and a high general corrosion on samples which were tempered at 500°C (figure 18). Hence the matrix had still enough chromium to help passivation at 400°C and 450°C, but as a result of higher Cr$_2$N precipitation, a low amount of chromium remained in solid solution at 500°C (less than 8%) which caused failure in passivation and consequently led to a high general corrosion.

In addition to chromium, molybdenum also plays an important role in the passivation of the metal. Comparing matrix composition diagrams at austenizing and tempering temperatures (figure 23), there is a considerable decrease in the amount of dissolved molybdenum in the matrix at higher tempering temperatures (400°C, 450°C and 500°C). This leads to the conclusion that secondary molybdenum precipitation could be also present at high tempering temperatures as well.
Table 7. Corrosion types on Vanax, Elmax and AISI O1

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Temperatures</th>
<th>20°C</th>
<th>70°C</th>
<th>95°C</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tempered at</td>
<td>200°C</td>
<td>500°C</td>
<td>200°C</td>
<td>500°C</td>
</tr>
<tr>
<td>Vanax 35</td>
<td>NO</td>
<td>GENERAL</td>
<td>NO</td>
<td>GENERAL</td>
<td>NO</td>
</tr>
<tr>
<td>Vanax 75</td>
<td>NO</td>
<td>GENERAL</td>
<td>NO</td>
<td>GENERAL</td>
<td>NO</td>
</tr>
<tr>
<td>Elmax</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
</tr>
<tr>
<td>AISI O1</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
<td>GENERAL</td>
</tr>
</tbody>
</table>

According to corrosion rate measurements, Vanax 35 had slightly better corrosion properties than Vanax 75. The PRE number at austenizing and tempering temperatures implied a higher resistance to pitting corrosion in case of Vanax 35. The reason is related to the amount of molybdenum in solid solution at austenizing temperature and in the matrix at tempering temperatures. Vanax 35 had 2.5% while Vanax 75 has 1.3% Mo at austenizing temperature. A higher amount of molybdenum results in a higher resistance against pitting corrosion.

5.2 Elmax

The corrosion rate measurements showed significant amount of corrosion on Elmax at each exposure temperature. This was not expected from the beginning because Elmax is a stainless tooling steel grade with a chromium content as high as 18% at annealed conditions. However, the Thermo-Calc calculations could explain the reason for its failure in passivation.

According to the diagrams (figure 22, left), Elmax had around 15% primary $M_7C_3$ (i.e. $Cr_7C_3$) at 1080°C. The material has a high carbon content (1.7%). A high carbon content results in a high tendency to form chromium carbides and causes low chromium dissolution in the solid solution. Only 12% chromium dissolved in the austenite solid solution (figure 24, left). This is not enough for the surface to passivate. The PRE number at austenizing temperature was as low as 16. This is significantly lower than the calculated value for Vanax. In addition, volume fractions at tempering temperature (figure 25, right) showed the presence of a considerable amount of secondary $Cr_23C_6$ when tempering above 200°C. However, the presence of $Cr_23C_6$ is a good indication that chromium is depleted from the martensitic matrix during tempering, and the chromium content decreased to less than 9%. This chromium loss from the martensite matrix causes a high general corrosion attack on Elmax.

Microstructural investigations on the samples exposed at 130°C showed a uniform corrosion attack on the surface (table 7). Corrosion seemed to occur the whole area for Elmax, unlike Vanax 75 tempered at 500°C, where there was a higher general corrosion attack on some specific regions on the surface, while some parts remained...
less corroded. However, the total mass loss was significantly higher in the case of Elmax at the same exposure temperature (130°C).

5.3 AISI O1

On AISI O1 there was a high amount of corrosion at every temperature of exposure. Compared with Vanax and Elmax, AISI O1 was austenized at a lower temperature (850°C) in order to minimize formation of retained austenite after quenching. The equilibrium volume fraction diagrams at austenizing temperature (figure 22, right) showed that the structure contained almost 100% austenite. This material is not a stainless steel grade since the austenite solid solution contained less than 1% chromium (figure 24, right). Volume fraction at tempering temperature diagram (figure 26) shows the presence of a considerable amount of cementite when tempering above 200°C. It is not clear from the Thermo-Calc diagrams whether cementite forms during tempering or it was a primary precipitation. However, at temperatures above 200°C the alloy contained around 88% martensite matrix and 12% cementite. WC and VC carbides were also present at these temperatures. The surface does not passivate at all. Hence, only general corrosion attack could be seen. Microstructural investigations on AISI O1 showed a high uniform corrosion attack and the presence of cracks on the surface (figure 20). A low PRE number (<1) calculated with Thermo-Calc software indicates that surface was unable to passivate.
6. Conclusion

- Vanax showed a high corrosion resistance in Pyrolysis oil in general, due to a low carbon, high chromium and molybdenum content in solid solution at austenizing temperature.

- The main concept for adding nitrogen to the alloy was to replace primary chromium carbides (i.e. \( \text{Cr}_2\text{C}_6 \), \( \text{Cr}_7\text{C}_3 \)) with a new hard phase MN i.e. VN which is densely distributed in the matrix. This indirectly improves the passivation ability, because more chromium is dissolved in solid solution.

- Corrosion rate measurements showed that there was a higher rate of corrosion with increasing temperature of exposure. This was due to the fact that the rate of ion transfer and “reduction and oxidation” reactions is higher at higher temperatures.

- Vanax has a very good resistance to pitting corrosion at austenizing temperature. This is because of a high amount of chromium and molybdenum dissolved in the solid solution. Quenching and tempering have no effect on primary and secondary precipitations; hence the microstructure directly after quenching is similar to that of austenizing temperature.

- Tempering at 200°C for 2h is too short for any secondary precipitations, this explains for a high corrosion resistance at 200°C. No corrosion pits were observed at this temperature.

- Corrosion pits were seen on Vanax samples which were tempered at 400°C and 450°C, with slightly more corrosion attack on 450°C. A decreased corrosion resistance of the material at these temperatures was explained by chromium depletion from the matrix as a result of secondary chromium nitride precipitations.

- At 500°C Vanax failed to passivate due to a high chromium loss from the matrix. There were a lot of secondary chromium nitride precipitations at 500°C. The rate of general corrosion attack on the samples which tempered at 500°C was high at all temperatures of exposure.

- Elmax tempered at 200°C suffered a lot of general corrosion attack at all of exposure temperatures. The alloy contains a high amount of carbon which increases the risk of primary and secondary chromium carbide precipitations and hence chromium depletion from the matrix. Since the chromium content after tempering at 200°C was as low as 9% the surface could not passivate.

- AISI O1 tempered at 200°C suffered from extensive general corrosion attacks at all exposure temperatures. The alloy consisted of almost 100% austenite at austenizing temperature, and there was less than 1% chromium dissolved in the solid solution.
7. Acknowledgements

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Stockholm, May 2011
Ashkan Reza Gholi
8. References


Future work

To complete the experimental work, there will be a few more exposures of the Vanax group in the pyrolysis oil. Vanax tempered at 400°C and 450°C will be exposed at 20°C, 70°C and 95°C. Also Vanax tempered at 500°C will be exposed at 130°C.

In order to study the formation of secondary Cr$_2$N during tempering process, TEM investigations will be carried.

These exposures and TEM investigations will be carried at swerea/KIMAB.
Title: Effects of tempering on corrosion properties of high nitrogen alloyed tooling steel in pyrolysis oil

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