DEVELOPMENT OF A FERRITIC DUCTILE CAST IRON FOR INCREASED LIFE IN EXHAUST APPLICATIONS

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The ship is safest when it is in port, but that’s not what ships were built for.
Paulo Coelho
ABSTRACT

Due to coming emission legislations, the temperature is expected to increase in heavy-duty diesel engines, specifically in the hot-end of the exhaust system affecting components, such as exhaust- and turbo manifolds. Since the current material in the turbo manifold, a ductile cast iron named SiMo51, is operating close to its limits there is a need for material development in order to maintain a high durability of these components. When designing for increased life, many material properties need to be considered, for example, creep-, corrosion- and fatigue resistance. Among these, the present work focuses on the latter two up to 800°C improving the current material by additions of Cr, for corrosion resistance, and Ni, for mechanical properties. The results show improved high-temperature corrosion resistance in air from 0.5 and 1 wt% Cr additions resulting in improved barrier layer at the oxide/metal interface. However, during oxidation in exhaust-gases, which is a much more demanding environment compared to air, such improvement could not be observed. Addition of 1 wt% Ni was found to increase the fatigue life up to 250°C, resulting from solution strengthening of the ferritic matrix. However, Ni was also found to increase the oxidation rates, as no continuous SiO₂-barrier layers were formed in the presence of Ni. Since none of the tested alloys showed improved material properties in exhaust gases at high temperature, it is suggested that the way of improving performance of exhaust manifolds is to move towards austenitic ductile cast irons or cast stainless steels. One alloy showing good high-temperature oxidation properties in exhaust atmospheres is an austenitic cast stainless steel named HK30. This alloy formed adherent oxide scales during oxidation at 900°C in gas mixtures of 5%O₂-10%H₂O-85%N₂ and 5%CO₂-10%H₂O-85%N₂ and in air. In the two latter atmospheres, compact scales of (Cr, Mn)-spinel and Cr₂O₃ were formed whereas in the atmosphere containing 5%O₂ and 10%H₂O, the scales were more porous due to increased Fe-oxide formation. Despite the formation of a protective, i.e. compact and adherent, oxide scale on HK30, exposure to exhaust-gas condensate showed a detrimental effect in form of oxide spallation and metal release. Thus, proving the importance of taking exhaust-gas condensation, which may occur during cold-start or upon cooling of the engine, into account when selecting a new material for exhaust manifolds.

Keywords: SiMo51, HK30, material development, exhaust manifolds, high-temperature corrosion, high-temperature low-cycle fatigue.
PREFACE

This thesis is based on research performed at the Department of Materials Science and Engineering, Royal Institute of Technology, in collaboration with the Departments of Materials Technology and Engine Development, Scania CV AB. The work was supervised by Prof. Stefan Jonsson and the project was lead by Dr. Baohua Zhu, Scania CV AB. The project was granted by VINNOVA (Vehicle Development). The thesis includes the following papers:

1. M. Ekström, P. Szakalos, S. Jonsson; Influence of Cr and Ni on the high-temperature corrosion behavior of ferritic ductile cast iron in air and in exhaust gases. *Published in Oxidation of Metals, 2013.*

2. M. Ekström, S. Jonsson; The influence of Cr and Ni on the high-temperature low-cycle fatigue behavior of a ferritic cast ductile iron. *Submitted as conference proceeding for 7th International Conference on Low Cycle Fatigue, Aachen Sep 2012*

AUTHOR CONTRIBUTION TO APPENDED PAPERS

Paper 1

The author participated in the process of developing alloys for the study and was active in a patent application (international application number: PCT/SE2012/050307).

The author performed oxidation experiments in air, including sample preparation, exposures, collection of data and oxide scale analysis (SEM, EDX). For oxidation experiments in diesel exhaust-gas, the author planned the experiments, collected data and performed oxide scale analysis (SEM, EDX). The author developed a successful sample preparation method for EBSD studies on oxide scales and was also active during the analysis part. Additionally, the author made all Thermo-Calc calculations. The paper was written in whole by the author.

Paper 2

The author performed tensile test experiments, evaluated data and studied fracture surfaces using stereo microscope and SEM. The author planned the low-cycle fatigue testing, evaluated data and performed fractographic examinations. The author also studied microstructures using LOM and SEM and made Thermo-Calc calculations. The paper was written in whole by the author.

Paper 3

The author performed the oxidation experiments in air and planned the experiments in O₂-H₂O and CO₂-H₂O. The author performed sample preparation prior to all oxidation tests, collected data and studied oxide scale structures using SEM, EDX and GDOES. Moreover, the author made the EIS experiments and performed immersion studies in exhaust-gas condensate prior to ICP analysis. The paper was written in whole by the author.
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PAPERS I-III
1 INTRODUCTION

1.1 Background

The temperature in heavy-duty diesel engines is expected to increase in the near future, creating a need for material development of hot components, such as exhaust manifolds. The industry is facing coming emission legislations, demanding cleaner and more efficient engines. Also, there is a wish to increase the power while maintaining low fuel consumption. Ways of meeting these demands include increasing the combustion pressure, minimizing heat losses and changing to new fuels. All of these actions will result in increased exhaust-gas temperature, specifically affecting the exhaust- and turbo manifolds in the hot-end of the exhaust system. The material used today in the turbo manifold is a Si- and Mo alloyed, ferritic, ductile cast iron named SiMo51. This alloy is operating close to its limits regarding its corrosion resistance and mechanical properties. Thus, in an ongoing project, new materials are developed in order to maintain a high durability and reliability of the components. The aim of that project is to provide the industry with a guideline for material selection in exhaust-gas temperatures ranging from 700 up to 1000°C.

1.2 Aim of this work

This thesis comprises a part of the material development project, focusing on improvement of SiMo51 for increased high-temperature corrosion- and fatigue life in exhaust-gas temperatures up to 800°C, corresponding to a material temperature of 700 to 720°C. Additionally, this thesis also includes a general overview of material selection for exhaust manifolds as well as a study of the performance of an austenitic cast stainless steel, named HK30, oxidized in exhaust environments and subjected to exposure of exhaust-gas condensate.
1.3 Challenges of the components

The components in the exhaust system of a diesel engine are exposed to a demanding environment during its operation including hot and corrosive exhaust gases combined with both thermal- and strain cycling. A schematic description of the system is presented in Fig. 1, showing a set-up of exhaust manifolds connected to a turbo manifold that is attached to the cylinders of the engine in one end and to a turbo charger in the other.

**Figure 1.** Schematic description of the hot end of an exhaust system of a 6-cylinder diesel engine, showing the exhaust manifolds connected to a turbo manifold, attached to a turbo charger.

The turbo manifold, which is a double-channel compound, is subjected to highest loads, partly due to the increased mass flow of exhaust-gases and also to the additional load from the weight of the turbo charger, putting higher demands on the material in this component compared to the material in the exhaust manifolds. However, throughout this thesis, these two types of components will be referred to only as exhaust manifolds.

When designing for high durability of these components, many material properties need to be considered, for example, creep-, corrosion- and fatigue properties. This thesis focuses on the latter two.

When corrosive exhaust gases passes through the manifolds, an oxide scale will be formed on the inner surfaces. During thermal cycling, stresses will
be formed in these scales, increasing the probability of oxide spallation. A rupture of the protective oxide scale does not only increase the oxidation rate but can also be detrimental if the spalled oxide flakes enters the turbo charger with the gas flow at a high speed. A continuously oxidized material will result in depletion of oxide forming elements and consumption of the metal, resulting in degradation of the mechanical properties. It is therefore important that the formed oxide scale is protective and adherent.

Furthermore, thermal cycling also affects the fatigue life of the components, the other important issue in this thesis. The required design and construction of the exhaust manifolds put high demands on the fatigue properties since the manifolds are clamped by bolts to the engine block and the turbo charger and also have varying sections creating stress concentrations induced by thermal cycling. By selecting a material with a low thermal expansion coefficient and high thermal conductivity, the internal stresses formed during the heating and cooling stages can be reduced. The fatigue life can also be improved by fundamental material properties, such as high strength and ductility, inhibiting crack initiation and growth during thermal-and strain cycling.

1.4 Material trends
Depending on the exhaust-gas temperature and design of the components, the material selection for exhaust manifolds includes ferritic- or austenitic ductile cast irons as well as cast stainless steels. From market analysis and literature review, a relationship between exhaust temperature and material selection has been made and is presented in Fig. 2.

The current maximum temperature of diesel exhaust gases in heavy-duty diesel engines is approximately 750°C. Up to this temperature, the most widely used material is a ferritic ductile cast iron named SiMo51. This material has been improved over the years by increasing its Si- and Mo contents up to 5 and 1wt%, respectively, resulting in improved oxidation resistance and high-temperature strength.¹,²

When the exhaust-gas temperature is increased, this alloy shows limitations and many manufacturers therefore turn to an expensive, austenitic cast ductile iron named Ni-resist D5S, commonly found in exhaust manifold in
gasoline engines. This alloy has a higher strength compared to SiMo51 but has in experiments, not presented in this work, shown limitations regarding its corrosion resistance at temperatures below 900°C.

Due to the high cost of Ni-resist D5S, the interest in cast stainless steels has increased, leading to development of both ferritic- and austenitic cast alloys. These are known for both high strength and corrosion resistance at high temperatures, coming from their high Ni- and Cr-contents, which make them a suitable choice in exhaust components. However, compared to the ductile cast irons, cast stainless steels show decreased castability due to their lower carbon content, resulting in higher melting temperatures. Additionally, the lack of graphite in the microstructure makes them more prone to solidification shrinkage. The combination of a high melting temperature, putting higher demands on sand moulds in the production, and increased cost of alloying elements raises the cost of the components significantly compared to those produced from SiMo51.

**Figure 2.** Illustration of the relationship between material selection and fuel condition.
1.5 Ductile cast irons

Cast irons are a group of ferrous alloys containing more than 2wt% carbon. The high carbon content gives the alloys a low melting point and high fluidity, which provides them with good castability.

1.5.1 Solidification

Graphitic cast irons are formed by solidification according to the stable system in the Fe-C phase diagram, allowing graphite precipitates to form. This type of solidification is controlled by a low cooling rate, large number of nucleating sites and addition of graphitizing elements, such as C, Si, Cu and Ni. There are generally three types of such cast irons: grey irons, compacted graphite irons and ductile irons, classified according to their graphite shape, see Fig. 3. Grey irons contain graphite with flaky morphology and is commonly found in applications where thermal conductivity is of high importance, such as in brake discs. In exhaust applications, where strength and ductility are of high importance, ductile cast irons, containing spheroidal graphite, are preferred. The nodular graphite shape is achieved by adding Mg to the melt. Compacted graphite iron has graphite shapes intermediate between flake and spheroidal.

If the cooling rate during solidification is high, if the number of nucleating sites are low or if the melt contains carbide stabilizing elements, such as V, Cr, Mo and Mn, the solidification can occur according to the metastable system, allowing cementite, Fe₃C, instead of graphite to be formed. However, for exhaust gas components, primary carbides are generally of the M₆C-type, whose formation is not so dependent on cooling rate.

Secondary carbides are formed at lower temperatures during the decomposition of austenite, forming ferrite grains surrounding the graphite nodules and filling the intercellular regions with pearlite and isolated carbides of Cr, Mo or Si. Pearlite itself, is a lamellar structure of Fe₃C and α-ferrite, and contributes to strength of the material. However, it is not desirable in exhaust manifolds as its cementite component decomposes to graphite at elevated temperatures resulting in a volume expansion. Carbides also add strength to the material but may contribute to detrimental brittleness if they are present in excessive amounts.
By adding high amounts of nickel, a fully austenitic material can be received at all temperatures. Elements, such as Mn, Cu and N also have the effect of stabilizing the austenitic phase. Similarly, the ferritic phase can be stabilized by adding Cr, Ti, Mo, W, Si or Al. With stabilizing, it means that the thermodynamically stable temperature range of the phase is being extended, i.e. the transformation temperature, at which ferrite is transformed into austenite on heating (or vice versa on cooling) is changed. This temperature is referred to as the $A_1$-temperature.

**Figure 3.** Illustration of different graphite morphologies of graphitic cast irons, such as grey iron, compacted graphite iron and ductile iron.

The ferritic cast irons have a higher thermal conductivity and lower coefficient of thermal expansion compared to austenitic alloys, which is an advantage for alloys used in exhaust applications as it enhances the fatigue life. The austenitic alloys, on the other hand, have other advantages in form of higher strength at high temperatures, making them a better choice for high-temperature applications. The reason for the higher strength of the austenite structure is that it has fewer slip systems compared to the ferritic structure, making it harder for deformations to occur. Another factor contributing to the higher strength of austenite is that its fcc (face-centered cubic) structure allows a higher level of interstitial carbon in the structure.
compared to ferrite, which has a bcc (body-centered cubic) structure, resulting in a higher solid solution strengthening effect in austenite.

1.5.2 SiMo ductile irons

SiMo is a group of ferritic ductile cast irons alloyed with Si and Mo. The alloy studied in this work is designated SiMo51 and has a chemical composition as given in Table 1. As can be seen in Fig. 4, the microstructure of SiMo51 consists of graphite nodules distributed in the ferritic matrix and stable M₆C carbides (M=Fe, Mo, Si) in the intercellular regions. The silicon content contributes with oxidation resistance, derived from formation of an SiO₂-barrier layer at the oxide/metal interface. Si also forms carbides together with Mo and Fe, which contribute to mechanical strength. This alloy is commonly used in exhaust manifolds but, as already mentioned, it shows limitations regarding corrosion- and fatigue resistance at temperatures above 750°C.

In order to improve the mechanical properties of SiMo51, different approaches can be used. To strengthen the ferritic matrix, elements entering the substitutional sites in ferrite can be added, resulting in solid solution strengthening. Elements commonly used for this purpose include Si, Mo, P, Mn, Ni and Cu. Another method of strengthening the material is to add elements forming carbides, such as Cr, V and Mo. However, improving the strength by increasing the carbide content normally results in an adverse effect on ductility. Adding Cr to the alloy can also have the effect of improving oxidation resistance.
Figure 4. Etched (Nital 2%) microstructure of SiMo51, showing graphite nodules dispersed in ferrite (white) with carbides of M₆C-type (M=Fe, Mo, Si), formed in the intercellular regions.

Table 1. Chemical composition of SiMo51, given in wt% (Fe bal.).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>P</th>
<th>S</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMo51</td>
<td>3.17</td>
<td>4.15</td>
<td>0.4</td>
<td>0.1</td>
<td>0.04</td>
<td>0.86</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>

1.5.3 Ni-resist ductile irons

Ni-resist ductile irons belong to a group of austenitic ductile cast irons. Due to their austenitic structure, the alloys show improved high-temperature strength compared to the ferritic SiMo alloys. According to ASTM A439 standard, there are 9 different grades, specified according to the contents of Ni, Si and Cr, as shown in Table 2. The alloy commonly used in exhaust manifolds is the D5S grade, containing the highest Ni-content, 34-37%, and increased amounts of Si and Cr, 4.90-5.50% and 1.75-2.25%, respectively, providing the alloy with high-temperature strength and corrosion resistance. According to literature, the maximum operating temperature is 850°C for the D5S grade⁶. The alloy can be used in conditions with short peaks at temperatures up to 900-1000°C. However, for prolonged exposure, a lower temperature is preferred.
Table 2. Chemical composition of Ni-resist alloys, given in wt% (Fe bal.).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-2</td>
<td>3.00</td>
<td>1.50-3.00</td>
<td>0.7-1.25</td>
<td>0.08</td>
<td>18-22</td>
<td>1.75-2.75</td>
</tr>
<tr>
<td>D-2B</td>
<td>3.00</td>
<td>1.50-3.00</td>
<td>0.7-1.25</td>
<td>0.08</td>
<td>18-22</td>
<td>2.75-4.00</td>
</tr>
<tr>
<td>D-2C</td>
<td>2.90</td>
<td>1.00-3.00</td>
<td>1.8-2.40</td>
<td>0.08</td>
<td>21-24</td>
<td>0.5max</td>
</tr>
<tr>
<td>D-3</td>
<td>2.60</td>
<td>1.00-2.80</td>
<td>1.00max</td>
<td>0.08</td>
<td>28-32</td>
<td>2.50-3.50</td>
</tr>
<tr>
<td>D-3A</td>
<td>2.60</td>
<td>1.00-2.80</td>
<td>1.00max</td>
<td>0.08</td>
<td>28-32</td>
<td>1.00-1.50</td>
</tr>
<tr>
<td>D-4</td>
<td>2.60</td>
<td>5.00-6.00</td>
<td>1.00max</td>
<td>0.08</td>
<td>28-32</td>
<td>4.50-5.50</td>
</tr>
<tr>
<td>D-5</td>
<td>2.40</td>
<td>1.00-2.80</td>
<td>1.00max</td>
<td>0.08</td>
<td>34-36</td>
<td>0.10max</td>
</tr>
<tr>
<td>D-5B</td>
<td>2.40</td>
<td>1.00-2.80</td>
<td>1.00max</td>
<td>0.08</td>
<td>34-36</td>
<td>2.00-3.00</td>
</tr>
<tr>
<td>D-5S</td>
<td>2.30</td>
<td>4.90-5.50</td>
<td>1.00max</td>
<td>0.08</td>
<td>34-37</td>
<td>1.75-2.25</td>
</tr>
</tbody>
</table>

1.5.4 Effects of alloying elements

*Carbon* improves the fluidity of the iron melt and thereby also the castability. The carbon content, together with inoculation practice and solidification rate, affects the amount and size of graphite nodules in the matrix. Increased number of nodules will counteract formation of carbides and increase ferrite formation, which in turn will reduce hardness and brittleness. Graphite is formed by the precipitation of carbon during the solidification process. Since the density of graphite is lower than that of iron, the graphite precipitation leads to expansion, counteracting the solidification shrinkage.

*Silicon* is an important alloying element as it promotes graphite formation and stabilizes ferrite. By increasing the silicon content, the A1-temperature is increased. For a fully ferritic cast iron, increased silicon content contributes to improved strength by solution hardening of the ferrite. A side effect is, however, reduced ductility. Additions up to 4wt% have shown a great increase in the thermal fatigue resistance whereas elevated amounts (>5%) have shown negative effects such as increased brittleness. Silicon is
also an oxide former and contributes to increased oxidation resistance by the formation of a thin and compact silicon oxide film at the oxide/metal interface.

*Molybdenum* stabilizes pearlite and is commonly added to cast iron to improve the mechanical properties, such as tensile strength and creep resistance, at high temperatures. However, the amount of molybdenum must be controlled since it has a tendency to form stable carbides in the intercellular regions, which can cause embrittlement.

*Manganese* stabilizes pearlite and is added to ductile iron to improve mechanical properties, such as strength. Negative effects of manganese in ductile iron are reduced ductility and machinability.

*Nickel* is an austenite stabilizer and improves strength at high temperatures.

*Chromium* improves the high-temperature oxidation resistance by the formation of a protective oxide on the alloy surface. It is also a strong carbide former and stabilizer of pearlite. Small amounts of chromium improve tensile strength and hardness, but when excessively added, negative effects, such as increased brittleness may arise.

*Copper* increases tensile strength and hardness by promoting pearlite formation. Copper has a graphitizing effect and suppresses carbide formation.

*Titanium* is a very strong carbide former and its content is therefore recommended to be held as low as possible. Also, titanium promotes vermicular (compacted) graphite.

*Aluminum* raises the $\text{A}_1$-temperature and improves the oxidation resistance at high temperatures. However, aluminum also acts as anti-spheroidizer and the maximum amount in ductile cast irons is therefore limited to 0.05wt%.

*Vanadium* is a strong carbide former and contributes to increased tensile strength and hardness but excessive additions may cause brittleness. Vanadium is a ferrite stabilizer.
Cobalt has been found to reduce the thermal expansion coefficient in austenitic cast irons (eg. Ni-resist)\textsuperscript{11}.

### 1.6 Cast stainless steels

#### 1.6.1 Ferritic cast stainless steels

Ferritic cast steels show a lower high-temperature strength compared to the austenitic steels but show benefits in form of lower cost, owing to a lower nickel content, and better thermal fatigue resistance, due to their lower thermal expansion coefficient and higher thermal conductivity\textsuperscript{12}.

Disadvantage of ferritic cast steels is that the carbon content is generally low, resulting in a high melting point and poor castability. Low carbon content may also result in a microstructure containing large grains, resulting in decreased ductility and fatigue life. The reason for this is that at very low carbon contents ferrite forms directly from the melt, removing the grain size reduction obtained from the austenite-to-ferrite phase transformation. Consequently, ferritic steels are commonly found in exhaust manifolds made of sheet metal obtaining grain size reduction by metal forming.

However, Daido Steel Co. has developed a ferritic cast stainless steel alloy named StarCast DCR3, used as replacement for Ni-resist D5S in gasoline turbine housing, with temperature reaching 900°C\textsuperscript{3}. The castability of the DCR3 alloy was improved by increasing the C-content, effectively decreasing the melting temperature, and compensating the austenite stabilizing effect from carbon by adding the ferrite stabilizing elements Nb and W (see Table 3).

**Table 3.** Chemical composition of the ferritic cast stainless steel; DCR3, given in wt% (Fe bal.).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCR3</td>
<td>0.35</td>
<td>19</td>
<td>...</td>
<td>1.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>
1.6.2 Austenitic cast stainless steels

Austenitic cast stainless steels are normally applied in the most demanding conditions where ferritic alloys show limitations. One commercially used austenitic alloy is a 25Cr/20Ni alloy, designated HK30 (ASTM specification A 351). This material is commonly found in exhaust manifolds in high-power gasoline engines, where the gas temperatures may reach 1000°C. Other, less expensive alloys, developed for exhaust applications are the two 19Cr/10Ni alloys named CF8C-plus\(^4\), developed by Oak Ridge National Laboratory and Caterpillar, and NSHR-A3N, developed by Hitachi Metals.

As can be seen from their chemical compositions, given in Table 4, these alloys contain a lower Ni-content, compared to HK30, but also additions of Nb, W and Mo, improving their mechanical properties by solid solution strengthening and increased carbide formation.

### Table 4. Chemical composition of austenitic cast stainless steels, given in wt\% (Fe bal.).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSHR-A3N</td>
<td>0.45</td>
<td>0.5</td>
<td>1.0</td>
<td>20</td>
<td>10</td>
<td>2.0</td>
<td>3.0W</td>
</tr>
<tr>
<td>CF8C-Plus</td>
<td>0.1</td>
<td>0.5</td>
<td>4.0</td>
<td>19</td>
<td>12.5</td>
<td>0.8</td>
<td>0.3Mo</td>
</tr>
<tr>
<td>HK30</td>
<td>0.25-0.35</td>
<td>1.75</td>
<td>1.5</td>
<td>23-27</td>
<td>19-22</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>

1.7 High-temperature corrosion

Exhaust gases form a demanding environment for the manifolds, including high temperatures, many oxidative species and high gas flows resulting in increased oxidation rates. High-temperature corrosion is a complex process where the metal reacts with gaseous species to form an oxide scale on the metal surface. In addition, the process may also involve evaporation of oxides, modification of surface properties (eg. from carburization or nitridation) and condensation.

1.7.1 General

The oxidation of metals at high temperatures commonly follow a parabolic time dependence, where the reaction rate is controlled by diffusion through
the oxide scale, i.e. outward diffusion of metal ions or inward diffusion of gaseous reactants\textsuperscript{13}. If a compact oxide scale is formed on a metal surface, it may act as a protective barrier layer, reducing the inward and outward diffusion and thereby decreasing the oxidation rate. However, if the oxide scale has a high defect density, i.e. containing pores, channels and cracks, the oxidation reactions can continue to proceed with the consequence of alloy depletion combined with formation of thick oxide scales that are prone to cracking and to spallation.

The thermodynamic driving force for oxide formation according to Eq. 1 (where M is a metal) is expressed by Gibbs free energy change according to Eq. 2.

\[ M + O_2 = MO_2 \] (1)

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{a_{MO_2}}{a_M \cdot p_{O_2}} \right) \] (2)

Plotting \( \Delta G^\circ \) as function of T, the partial pressure of oxygen, in equilibrium with a metal oxide at a given temperature, can be estimated. This allows for interpretation of oxide scale structures when adding oxide-forming elements to an alloy. When adding, for example, Si and Cr to the alloys, SiO\textsubscript{2} and Cr\textsubscript{2}O\textsubscript{3} are expected to be formed at lower oxygen partial pressures compared to the iron oxides, i.e. they will be formed closer to the metal surface.

1.7.2 Corrosion of ductile cast irons

The oxide scale formed on ductile cast irons is normally built up of two oxide layers, where the inner layer is formed by inward transportation of oxygen, resulting in an inward growing oxide encapsulating graphite nodules and carbides, and the outer oxide layer is formed by outward diffusion of Fe. During oxidation of SiMo51 in O\textsubscript{2} (g) at 700 and 800\textdegree{}C, calculations using Thermo-Calc suggest formation of wüstite, FeO, and fayalite, Fe\textsubscript{2}SiO\textsubscript{4}, in the inner layer whereas magnetite, Fe\textsubscript{3}O\textsubscript{4}, and hematite, Fe\textsubscript{2}O\textsubscript{3}, are formed in the outer layer. The calculated oxide scale structure of SiMo51 is illustrated in Fig. 5.
The addition of Si (approx. 4wt%) results in formation of an SiO$_2$ barrier layer at the oxide/metal interface. The $\beta$-SiO$_2$-phase shown in Fig. 5 is the high-temperature form of silica and transforms to $\alpha$-SiO$_2$ at lower temperatures. SiO$_2$ is more compact compared to the Fe-oxides and decreases the oxidation rate by reducing the outward diffusion of Fe and inward transportation of oxidative species. The higher porosity of Fe$_2$O$_3$ compared to an Si-rich oxide, both formed on SiMo51 at high temperature, is clearly seen in the topographical SEM images shown in Fig. 6.

Figure 5. Fraction of phases vs. oxygen partial pressure calculated with Thermo-Calc in O$_2$ (g) at 700°C for SiMo51.

A cross section of an oxide scale formed on SiMo51, after oxidation in air at 800°C for 96h, is shown in Fig. 7, illustrating the described oxide scale structure with a thin SiO$_2$ layer at the metal/oxide interface. In order to enhance the oxidation resistance of SiMo51 further, the properties of this barrier layer can be modified. Paper 1 summarizes work of improving the barrier layer by adding different amounts of Cr (0.3 to 1wt%) to form a layer of Cr$_2$O$_3$. 
**Figure 6.** SEM images presenting different morphologies of oxides: **a)** Fe$_2$O$_3$ and **b)** Si-rich oxide, clearly showing a higher porosity in a.

**Figure 7.** EDS mapping images of an oxide scale formed on SiMo51 in air at 800°C after 96h of oxidation, showing a scale structure of an outer Fe-oxide (a), inner Fe-Si-oxide (b) and a SiO$_2$ barrier layer at the oxide/metal interface (c).
1.7.3 Corrosion in exhaust gases

The combustion of diesel results in an exhaust gas containing mostly water vapor, oxygen, carbon dioxide, nitrogen and smaller amounts of sulfur- and nitrogen oxides, providing an environment containing a high amount of oxidative species. The corrosion behavior of ductile cast irons and cast stainless steels, intended for use in exhaust components, in exhaust gases of diesel and gasoline fuel has been studied by Tholence\textsuperscript{14,15}. His studies showed a clear reduction in oxidation resistance in these atmospheres, linked to the presence of water vapor, sulfur- and nitrogen oxides.

Water vapor

High-temperature oxidation of Fe-based alloys in water vapor-containing atmospheres has been widely studied and is observed to result in formation of poorly protective oxide scales\textsuperscript{16,17,18}. The increased oxidation rate of chromia-forming alloys is generally attributed to the evaporation of chromium oxide hydroxide, formed according to Eq.3, leading to Cr-depletion in the alloy.

$$\frac{1}{2} Cr_2O_3(s) + \frac{3}{4} O_2(g) + H_2O(g) \rightarrow CrO_2(OH)_2(g) \quad (3)$$

This evaporation phenomenon has been studied by Asteman\textsuperscript{19,20,21} at temperatures from 500°C up to 800°C in atmospheres containing 10% and 40% water vapor. In his work, it was observed that the formation of the volatile CrO$_2$(OH)$_2$(g) could be linked to a conversion from an initially formed, protective Cr$_2$O$_3$ oxide into a poorly protective Fe-rich oxide. Asteman observed that CrO$_2$(OH)$_2$(g) was formed, not only at high temperatures (>1000°C), but also at lower temperatures (600°C). Additionally, a connection between increased gas flow rate and increased chromium oxide hydroxide evaporation was identified. This means that low water vapor content in the gas can still degrade the protective properties of the scale if the gas flow is high enough. Since the gas velocity in the exhaust system may reach values as high as 100m/s, it forms a very demanding environment for the manifolds regarding its corrosion resistance.
Another observed effect of water vapor, also resulting in reduced oxidation resistance, is a change in physical properties of the oxide scales, in form of swelling, cracking and spallation\textsuperscript{22}.

**Carbon dioxide**

The combined presence of water vapor and carbon dioxide has been studied by Rahmel and Tobolski\textsuperscript{23}, who observed a significant increase in oxidation rate of Fe-based alloys. In their study, it is proposed that H\textsubscript{2}O(g) and CO\textsubscript{2}(g) transfer oxygen across pores in the oxide scale by setting up redox systems of H\textsubscript{2}-H\textsubscript{2}O and CO-CO\textsubscript{2} according to the reactions given in Eq. 4 and Eq. 5, resulting in faster inward transport of oxygen across the pores.

\begin{equation}
CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)
\end{equation}

\begin{equation}
H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)
\end{equation}

Another aspect of CO\textsubscript{2} in the gas is a modification of the metal surface properties in the case of carburization (i.e. carbon pick up) or decarburization (i.e. carbon loss). These processes depend on the carbon activity gradient. If the carbon activity is higher in the gas compared to that of the metal, carburization will be promoted. Carbon uptake in the metal may degrade the oxidation resistance by carbide formation of elements that would otherwise form a protective oxide.

**Sulfur oxides**

In the exhaust gas, sulfur is present either as SO\textsubscript{2} or, by reaction with O\textsubscript{2}, as SO\textsubscript{3}. For elements commonly found in cast irons and stainless steels; Fe, Cr, Ni and Mn, the oxidation rate in gases containing SO\textsubscript{2} and O\textsubscript{2} has been found to exceed the oxidation rates in pure O\textsubscript{2}\textsuperscript{24,25,26,27}. This is derived from a simultaneous formation of oxides and sulfides. In a study by Gilewicz-Wolter\textsuperscript{28}, where oxidation of pure Fe in SO\textsubscript{2} and O\textsubscript{2} at temperatures between 500°C and 900°C was examined, the reaction was found to occur mainly by outward diffusion of Fe. Sulfur was found to penetrate the scale through defects, such as fissures and micro-channels, forming iron sulfide, FeS,
the oxide/metal interface. The diffusion of iron in FeS was found to be fast, resulting in accelerated oxidation in the presence of SO₂ compared to oxidation in dry O₂. The stability of sulfides is dependent on temperature and partial pressure of SO₂ or SO₃. Thus, in certain temperature ranges and at sufficiently low SO₂/SO₃ pressures, the sulfide formation is inhibited and only oxides are formed.

*Nitrogen oxides*

The presence of NO₂ or NO₃ in the gas may result in formation of nitrides, changing the surface properties of an alloy. Excessive formation of nitrides at the surface may result in depletion of oxide forming elements, such as Cr and Si, and increased brittleness, which reduce both oxidation resistance and mechanical properties.

Tholence²⁹ studied the behavior of SiMo51 in normal and clean (no NOₓ) synthetic petrol- and diesel exhaust-gases. In his study, the nitride formation occurred only in the presence of NOₓ and was not linked to reactions with N₂. The nitridation was found to be extensive in an exhaust gas containing no water vapor showing formation of course Si₃N₄, resulting in depletion of Si. In exposures to normal gasoline and diesel, containing water vapor, the nitride formation was found to be lower, showing micro-sized MgSiN₂ in cell boundaries.

1.7.4 **Thermal cycling**

During operation of an engine, the manifolds are exposed to thermal cycling, which may induce stresses causing elastic or plastic deformation of the oxide scale. With time, this may cause fracture and oxide spallation leading to both further oxidation of the alloy and also to transferring of oxide flakes of high velocity into the turbo charger. The detrimental effect of the thermally induced stress is dependent on the ratio of the thermal expansion coefficient of the alloy and the oxide scale and also on the magnitude of the temperature change. As can be seen in Table 5, the Fe-oxides; FeO and Fe₂O₃, show a lower ratio compared to Cr₂O₃, indicating a higher tendency for oxide spallation of the Cr-oxide. Similarly, austenitic alloys (eg. HK and Ni-resist in Table 5) point at higher spallation ability, showing a larger difference in thermal expansion compared to that of the
ferritic alloys (eg. HC and SiMo in Table 5). However, kinetic effects must also be considered as thicker oxide scales have higher tendency for spalling. Generally Cr form thinner scales compared to Fe and may thus be favorable even if their thermal expansion coefficient is deviating more from the base material.

**Table 5.** Mean coefficients of linear thermal expansion ($\alpha$) of some oxides, ferritic- (SiMo) and austenitic (Ni-resist D5S) ductile cast irons, ferritic- (HC) and austenitic (HK) cast stainless steels and ratio between various metal/oxide systems.$^{30,31,32}$

<table>
<thead>
<tr>
<th>System</th>
<th>Metal $10^6 \alpha$, K$^{-1}$</th>
<th>Oxide $10^6 \alpha$, K$^{-1}$</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMo/FeO</td>
<td>13.7</td>
<td>12.2</td>
<td>1.12</td>
</tr>
<tr>
<td>SiMo/Fe$_2$O$_3$</td>
<td>13.7</td>
<td>14.9</td>
<td>0.92</td>
</tr>
<tr>
<td>Ni-resist/ Fe$_2$O$_3$</td>
<td>15.7</td>
<td>14.9</td>
<td>1.05</td>
</tr>
<tr>
<td>Ni-resist/Cr$_2$O$_3$</td>
<td>15.7</td>
<td>7.3</td>
<td>2.15</td>
</tr>
<tr>
<td>HC/ Fe$_2$O$_3$</td>
<td>13.9</td>
<td>14.9</td>
<td>0.93</td>
</tr>
<tr>
<td>HC/ Cr$_2$O$_3$</td>
<td>13.9</td>
<td>7.3</td>
<td>1.90</td>
</tr>
<tr>
<td>HK/ Fe$_2$O$_3$</td>
<td>18.7</td>
<td>14.9</td>
<td>1.26</td>
</tr>
<tr>
<td>HK/ Cr$_2$O$_3$</td>
<td>18.7</td>
<td>7.3</td>
<td>2.56</td>
</tr>
</tbody>
</table>

### 1.7.5 Exhaust-gas condensation

Corrosion due to condensation is an important aspect for material selection for the components in the after-treatment step, such as the EGR-system, where the exhaust gas temperature is close to the acidic dew point. However, condensation of exhaust gases may also occur in the hot part of the exhaust system, for example during cold start or during cooling of the engine. This may result in acidic liquids covering the inner surfaces of the manifolds, affecting both the oxide scale as well as the metal underneath (paper 3). The condensed liquid can penetrate the oxide scale through pores and cracks, reaching the metal surface, where it can participate in corrosion reactions, either at low temperature or at high-temperature when the engine is back in operation. If the metal is consumed by the corrosion reactions, it may not only result in depletion of the alloy and reduced protective properties but also to degradation of the sealing properties between the manifolds.
The corrosive environment during condensation is formed when the sulfur- and nitrogen oxides react with water vapor forming sulfuric acid, H$_2$SO$_4$ and nitric acid, HNO$_3$. These acids may also be formed from dissolution in condensed water vapor. The presence of nitric- and sulfuric acid results in a condensate having a low pH, in the order of 2.5, producing an aggressive environment for the oxide scales and the metal. Additionally, from the inlet air, chlorides may also be present in the condensate increasing the corrosive effect further.

1.8 High-temperature fatigue

1.8.1 Fatigue in exhaust manifolds

During operation of the engine, the exhaust manifolds are subjected to thermal cycling causing fatigue damage. Depending on position in the component, the loading is either in-phase (load and temperature increase at the same time) or out-of-phase. By in-phase loading, tensile stresses form during heating and compressive stresses during cooling. On the contrary, by out-of-phase loading compressive stresses form during heating and tensile stresses during cooling.

Low-cycle fatigue data is generally used for dimensioning and fatigue life prediction of components exposed to a constant high temperature and an external load cycling. This is not the case for exhaust manifolds where the loading is mainly formed by thermal stresses. However, by using Chaboche transient model$^{33}$, LCF data can be converted to TMF data, thus of interest for dimensioning of exhaust manifolds.

During the LCF process, the isothermal mechanical strain cycling causes fatigue damage due to straining in the plastic deformation regime. If the applied stress is lower, reducing the plastic deformation, the material can withstand a higher number of load cycles causing high-cycle fatigue (HCF). This may occur in exhaust manifolds due to vibrations. The term very high-cycle fatigue is used when the stress amplitude is at a level where no fatigue failure is observed during testing, commonly referred to as the endurance limit (σ$_D$). The different fatigue modes with approximate number of load cycles are illustrated in Fig. 8.
1.8.2 Crack initiation and growth

Fatigue emerges due to plastic deformation and the fatigue resistance depends on the applied cyclic stress amplitude ($\sigma_{\text{amp}}$ or $S$). The fatigue life is commonly presented using an S-N curve of the type shown in Fig 8, also called a Wöhler diagram.

To characterize the fatigue in a material, different phases in the process can be identified\(^{34}\). First, there is an activation of a cyclic hardening- or softening process, which is dependent on the dislocation density in the material. For a soft material, in which the initial dislocation density is low, the plastic deformation occurring during straining will increase the number of dislocations, resulting in a hardening of the material. For a hard material, where the dislocation density is high, plastic straining will instead rearrange the dislocations resulting in cyclic softening. As the process proceeds, submicroscopic pores and cracks will be formed and coalesce to microscopic cracks, which with time forms macroscopic cracks. The fatigue process continues by growth of the macroscopic cracks until failure is reached.
1.8.3 Micro-structural aspects

Fatigue cracks are nucleated at sites where the stress concentration is highest. This normally occurs at the surface due to load conditions (bending moments), formation of slip bands or to the presence of inclusions or secondary phases\textsuperscript{35}. For this reason, the surface finish is of high importance when discussing fatigue. Microscopic cracks may also be formed at grain boundaries since they are harder and more rigid than the grains, making accommodation to deformation more difficult in these regions resulting in increased stresses. This type of crack nucleation becomes more pronounced at higher temperatures when the grain becomes even softer. The presence of carbides in grain boundaries may both increase and decrease the fatigue life depending on their size. Generally coarse carbides and carbide networks should be avoided. Moreover, the grain size itself plays an important role on fatigue life. Larger grains allow longer dislocation pile-ups forming higher stress concentrations than in smaller ones.

1.8.4 Influence of temperature

Since low-cycle fatigue is related to plastic deformation, which occurs more easily at higher temperatures, it can be assumed that the fatigue growth rate increases with the temperature. At high temperatures, cracks may also nucleate easier in sub-surface regions due to decohesion of inclusions and secondary phases from the surrounding matrix.

Fatigue at elevated temperatures is a very complex phenomenon since it also includes creep, temperature-induced changes of the microstructure and environmental effects, such as oxidation. Studies by Coffin\textsuperscript{36} show a large impact of the atmosphere on the fatigue resistance. For example, LCF testing of an austenitic stainless steel (AISI A286) showed the same fatigue life at 593°C as at 20°C when tested in vacuum, whereas during testing in air, the fatigue life readily decreased with increasing temperature. The reduced fatigue life in air is an effect of mechanical crack growth combined with oxidation.
2 EXPERIMENTAL

2.1 Materials

The alloys were cast in ingots with geometry as shown in Fig. 9. The ingots were designed to avoid poor formation in the test materials by adding cylindrical bars along the test plate. The cylinders as well as 75mm of the flat ends of the plate were cut off, leaving a plate of size 220x150x20mm for experimental use. The ductile cast irons alloys were cast by Casting P.L.C and the cast stainless steel by Smålands Stålgiuteri AB.

![Figure 9. Geometry of ingots, values in mm.](image)

To increase the operating temperature range of SiMo51, modifications of this alloy, by addition of alloying elements improving its high-temperature strength and oxidation resistance, is examined. In this work, the addition of 1wt% Ni was selected to improve mechanical properties. Furthermore, to improve the oxidation resistance, additions of 0.3 to 1 wt% Cr were examined. The chemical composition of the studied alloys is given in Table 6. The effect of these alloying additions on the high-temperature oxidation resistance is described in paper 1, whereas the effect on high-temperature mechanical properties is described in paper 2.

Also, the austenitic cast stainless steel HK30, commonly used at temperatures above 800°C, was included in the study. See Table 7 for chemical composition. For this alloy, the thesis comprises the results from
oxidation testing in exhaust atmospheres and exposure to exhaust-gas condensate (paper 3).

**Table 6.** Chemical composition of ductile cast irons, given in wt% (Fe bal.). All alloys contain 0.04-0.06% Mg, 0.02% P and 0.01% S.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMo51</td>
<td>3.17</td>
<td>4.15</td>
<td>0.4</td>
<td>0.1</td>
<td>0.04</td>
<td>0.86</td>
</tr>
<tr>
<td>SiMo51+0.5Cr</td>
<td>3.28</td>
<td>4.23</td>
<td>0.35</td>
<td>0.52</td>
<td>0.06</td>
<td>0.78</td>
</tr>
<tr>
<td>SiMo51+1Cr</td>
<td>3.28</td>
<td>4.19</td>
<td>0.36</td>
<td>0.94</td>
<td>0.52</td>
<td>0.86</td>
</tr>
<tr>
<td>SiMo51+0.3Cr1Ni</td>
<td>3.19</td>
<td>4.20</td>
<td>0.31</td>
<td>0.33</td>
<td>1.23</td>
<td>0.83</td>
</tr>
<tr>
<td>SiMo51+0.6Cr1Ni</td>
<td>3.23</td>
<td>4.08</td>
<td>0.30</td>
<td>0.72</td>
<td>1.27</td>
<td>0.78</td>
</tr>
<tr>
<td>SiMo51+1Ni</td>
<td>3.06</td>
<td>4.19</td>
<td>0.38</td>
<td>0.07</td>
<td>1.29</td>
<td>0.86</td>
</tr>
</tbody>
</table>

**Table 7.** Chemical composition of the austenitic cast stainless steel, HK30, given in wt% (Fe bal.).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK30</td>
<td>0.51</td>
<td>1.50</td>
<td>1.45</td>
<td>25.4</td>
<td>18.7</td>
<td>0.02</td>
<td>0.02</td>
<td>0.005</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### 2.2 High-temperature testing

#### 2.2.1 Tensile testing

High-temperature tensile testing was performed using a MTS 810 Material Test System (100kN) equipped with a two heating-zone furnace (model MTS 653.02). The geometry of the test specimen is shown in Fig. 10a. The temperature of the test specimen was controlled using two thermo couples (Pentronic Inc600, ø 0.5mm, type K), attached on the upper and lower part of the test specimen neck using thin, stainless steel wires. The experiments were conducted with a fixed displacement rate of 0.004mm/s (0.00008 s⁻¹) at temperatures from 20°C up to 800°C (+/- 10°C). An MTS extensometer with ceramic contact rods (model MTS 632.54F-11) was employed to
measure the strain amplitudes. Stress and strain data were collected using MPT (Multiple Purpose Testware) software.

2.2.2 Low-cycle fatigue testing

Low-cycle fatigue testing (LCF) was performed on a Schenk tensile test machine (100kN) equipped with a MTS control system, using test specimens with geometry shown in Fig. 10b. Since the equipment required threaded specimen ends, special adapters were applied, preventing movement of the specimens inside the threads during testing. For heating the test specimen, the test machine was equipped with a three heating-zone furnace (model MTS 653.04). A similar extensometer- and thermo- couple arrangement, as used for the tensile testing, was adopted. The isothermal fatigue tests were conducted symmetrically (R= -1) in air with a constant strain rate of $10^{-3}\text{s}^{-1}$. Six different temperatures, ranging from 20°C up to 700°C, were tested. For each combination of material and temperature, five strain amplitudes in the range 0.2 to 0.9% were applied, generating a lifetime range between 300 and 30,000 cycles.

![Figure 10. Test specimen geometries employed during a) tensile testing and b) LCF-testing. Dimensions in mm.](image)

\[\text{Dimensions in mm.}\]
2.2.3 Oxidation testing

The oxidation behavior of the alloys was studied by exposure to exhaust atmospheres at high temperatures. Prior to oxidation, test coupons with size 20x20x5mm were cut from as-cast ingots, ground with SiC paper down to a finish of 1200 grit, ultrasonically cleaned in acetone for 15min and finally washed with ethanol and deionized water. Reproducible results were received using double test samples.

The cast ductile irons were first oxidized in air at 700°C and 800°C, using a chamber furnace (model Naber N60/HR) (paper 1). Additionally, a method for oxidation testing in exhaust gases of a diesel test-engine was developed (paper 1). As illustrated in Fig. 11, this test was carried out by mounting test specimens in form of screws in an exhaust manifold of an engine, exposing flat, circular ground ends (ø 9mm) of the screws, to the exhaust gases. The engine was run to produce two test series, one for isothermal exhaust temperatures of 700°C up to 740°C for 50h and one for thermal cycling between 240°C and 730°C for 700h. The exhaust gas composition is given in Table 8. During the tests, the exhaust gas flow during full load was 1775kg/h, which is estimated to a gas velocity of more than 100m/s.

Since the cast stainless steel is intended for use at higher temperatures than can be reached in the engine test cell, this alloy was instead tested in two synthetic atmospheres with gas mixture compositions given in Table 8. The oxidation tests were performed at 900°C in a tubular furnace (Elite 12/100/750-2416) with a gas flow rate of 220ml/min (approx. 0.3cm/s). Water vapor was added to the gas using a peristaltic pump (Watson Marlow). Additional oxidation tests were performed in the chamber furnace (previously described) in air at 900°C.
Figure 11. Description of oxidation test procedure in an engine test-cell, showing attachment of screws in an exhaust manifold exposing the flat end surface (diameter 9mm) to the exhaust gases inside the manifolds.

Table 8. Composition of gas mixtures used in the high-temperature oxidation tests, given in mol %. \( \text{N}_2 \) bal.

<table>
<thead>
<tr>
<th>Gas atmosphere</th>
<th>( \text{O}_2 )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{CO}_2 )</th>
<th>( \text{CO} )</th>
<th>( \text{NO}_x )</th>
<th>( \text{SO}_x ) ppm</th>
<th>( \text{HC}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel exhaust-gas(^1,2)</td>
<td>4</td>
<td>4</td>
<td>9</td>
<td>0.01</td>
<td>0.03</td>
<td>0.4</td>
<td>0.004</td>
</tr>
<tr>
<td>Gas mixture 1</td>
<td>5</td>
<td>10</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Gas mixture 2</td>
<td>…</td>
<td>10</td>
<td>5</td>
<td>…</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
</tbody>
</table>

\(^1\)Measured at 650°C during full load (1900rpm) with an air-to-fuel ratio of 1.6.  
\(^2\)Containing 10ppm S and 7% biodiesel  
\(^3\)Unburned fuel
2.3 Analysis and sample preparation

2.3.1 Microscopy
High-resolution micrographs were taken using a Field Emission Gun Scanning Electron Microscope, FEG-SEM (Zeiss Sigma VP with Gemini field emission column) and element analysis were made using an Energy Dispersive Spectrometer, EDS (INCA, Oxford Instruments). Additionally, Light Optical Microscope, LOM (Zeiss Axio) was used for micrographs whereas a stereo microscope (Zeiss Discovery V12) was utilized for macrograph imaging.

2.3.2 EBSD
Characterization of crystalline oxide phases and their defect structures were made using SEM (LEO 1530 with Gemini field emission column) equipped with an Electron Backscatter Diffraction, EBSD, detector. The analysis was performed by inserting a flat and polished sample, tilted by 70°, in the SEM. When an electron beam is applied, electrons are diffracted forming a Kikuchi pattern, characteristic of the crystal structure and orientation from which it was generated, on a fluorescent screen and is recorded by a CCD camera. Phases are then identified by matching with theoretical data.

2.3.3 XRD
X-ray Diffraction (D8, Bruker AXS) were ran directly on the oxidized surfaces using Cu-Kα X-Rays with energy dispersive detector (SolX Bruker) to characterize crystalline phases in the oxide scale. Response from the underlying metal confirmed a total penetration of the x-rays through the scale.

2.3.4 GDOES
Element depth profiles through the oxide scales were received using Glow Discharge Optical Emission Spectroscopy, GDOES (Spectruma GDA750 glow discharge spectrometer). The measured area was 5mm².

2.3.5 Hardness measurement
Brinell hardness measurement was performed according to ISO standard 6506-1:2005 using a KB3000 hardness testing machine (ball diameter of
2.5mm, force-diameter ratio of 30N/mm² and nominal value of test force of 1.839kN).

2.3.6 ICP-OES
Metal release from the oxide scale into the exhaust-gas condensate was studied by immersing oxidized samples in glass vessels containing 10ml synthetic exhaust-gas condensate, giving a sample surface area to solution volume ratio of 0.5cm⁻¹. The test procedure included immersion of oxidized samples for different times and changing to new condensate for each exposure time, in order to study the time dependence of the metal release. Samples oxidized in air at 900°C for 24h were examined. Reproducible results were received using double samples. Prior to analyzing, the condensate solutions were filtered to remove particles larger than 0.2μm. Trace element analysis was performed using inductively coupled plasma optical-emission spectroscopy (Thermo Scientific iCAP 6000 series ICP spectrometer (ICP-OES)). The analysis was performed at the wavelengths of 238.2nm, 273.0nm and 371.9nm for Fe, 216.5nm, 230.3nm and 231.6nm for Ni, 266.6nm, 267.7nm and 360.5nm for Cr and 279.4nm and 403.0nm for Mn using ICP multi element standard IV from Merck.

2.3.7 Electrochemical impedance spectroscopy
Electrochemical impedance spectroscopy was applied to examine the effect of an acidic exhaust-gas condensate formed on metal surface of HK30, oxidized in different environments: air, 5%O₂-10%H₂O (N₂ bal.) and 5%CO₂-10%H₂O (N₂ bal.) at 900°C.

The electrochemical instrument set-up consisted of a Solartron 1287 potentiostat, a Solartron 1260 frequency response analyzer (FRA) and a three-electrode electrochemical cell, shown in Fig. 12, with platinum as counter electrode and Ag/AgCl (3M KCl) as reference electrode. The experiments were conducted at 60°C in an electrolyte of synthetic condensate of pH 2.4 with a composition of 200ppm H₂SO₄, 110ppm HNO₃ and 50ppm NaCl, deionized water bal.

A small single-sine AC wave of 30 mV was applied to the working electrode vs. the Pt-electrode, an AC current measurement was then made. This process was repeated by scanning the frequency and the data
acquisition of impedances from the ac voltage and current (ΔE/ΔI) using ZPlot/ZView software package.

![Diagram of three-electrode cell set-up](image)

**Figure 12.** Schematic description of the three-electrode cell set-up with Ag/AgCl reference electrode (RE), Pt counter electrode (CE) and oxidized specimen, functioning as working electrode (WE).

### 2.3.8 Sample preparation

Depending on analysis technique, different methods of sample preparation were applied. For cross-sectional examinations, specimens were mounted in conductive Bakelite followed by grinding and polishing. For surfaces sensitive to spallation, such as in the case of some oxide scales, two surfaces were attached to each other using conductive epoxy before grinding. This method was also applied for samples studied with EBSD, where the application of epoxy contributed to more planar oxide surfaces. Furthermore, for etching of microstructures, Nital 2% was used for ductile cast irons whereas etching with Kallings etchant (5g copper chloride, 100ml hydrochloric acid, 100ml ethanol, 100ml water), was used for cast stainless steels.

### 2.4 Thermo-Calc

Thermodynamic equilibrium calculations for oxide- and alloy microstructures were conducted using the Thermo-Calc Software\(^ {37} \). In the calculation of the oxide scale structures, two databases were combined: TCFE6 for the metal matrix and SSUB4 for the oxides. In the calculation of alloy microstructures, only the TCFE6 data base was used.
3 RESULTS AND DISCUSSION

3.1 Microstructural characterization

As can be seen in Fig. 13, the microstructure of the studied SiMo alloys are showing nodular graphite distributed in a ferritic matrix. All alloys fulfill material requirements of 80% of the graphite being of nodule type V or VI, according to ISO standard 945-1975. However, at 1% Cr intercellular graphite is formed. As expected, stable M$_6$C carbides and small amounts of spheroidized pearlite are precipitated in the intercellular regions in SiMo51.

When adding Cr to the alloys, the amount of pearlite increase as well as the formation of stable Cr-carbides. From EDX analysis and Thermo-Calc calculations, the carbides are suggested to be of types M$_6$C (M=Mo, Si and Fe) and M$_7$C$_3$ (M=Cr). In the phase diagram, shown in Fig. 14a, a precipitation of M$_7$C$_3$ is calculated to occur at 620°C for 0.5% Cr and at 770°C for 1% Cr. The latter alloy also shows formation of cementite at 830°C. A comparison of the carbide morphology in SiMo51, with and without, addition of Cr is shown in Figs. 15 and 16, respectively.

When adding Ni to the alloy, the microstructure is not observed to be changed. However, despite the small amount of Ni added, the A$_1$-temperature is reduced by 20°C for 1 wt% Ni (see Fig. 14b), reducing the maximum allowed operating temperature of the alloy with the same magnitude. In the phase diagram, it can be noted that, when adding Ni, graphite precipitates earlier in the melt. This could result in increased graphite formation, which however, was not observed in this work.
Figure 13. Micrograph images showing the etched (Nital 2%) microstructure of SiMo51 with additions of a) none, b) 0.5wt% Cr, c) 1wt% Cr, d) 0.3wt% Cr, 1wt% Ni, e) 0.6wt% Cr, 1wt% Ni and f) 1wt% Ni. Scale bars indicate 200μm.
Figure 14. Phase diagrams calculated using Thermo-Calc for SiMo51 with additions of a) Cr and b) Ni.
Figure 15. Intercellular region of SiMo51 showing a) micrograph image of M₆C carbides and spheroidized pearlite in a ferritic matrix and b) SEM image of an M₆C carbide.
**Figure 16.** Intercellular region of SiMo51 with additions of 0.6Cr and 1Ni showing **a)** micrograph image of M₆C and Cr-rich carbides and spheroidized pearlite in a ferritic matrix and **b)** SEM image of a mixed carbide of M₆C and a Cr-rich phase.
3.2 High-temperature oxidation

3.2.1 SiMo51
The oxidation behavior of SiMo51 in air at 700 and 800°C is characterized by formation of a multi-layered oxide scale with layers of hematite and magnetite growing outwards and a subscale of magnetite and spinel phases growing inwards. The addition of 4wt% Si to the alloy results in formation of a continuous SiO₂ barrier layer at the oxide/metal interface. From oxidation testing in diesel exhaust-gases at 700 to 740°C for 50h, it was found that the oxidation rate increases with increasing temperature. The high gas flow combined with the high amount of oxidative gas species, such as H₂O, O₂, CO₂, NOₓ and SOₓ, give rise to a more demanding environment in the exhaust gases compared to oxidation in air, where the increased temperature did not show a significant influence on the oxidation rate. The increased oxidation rate in exhaust gases could also be revealed from formation of continuous iron oxide scales already after 7.5h in exhaust gases whereas during exposure in air, Fe-oxides nucleated at graphite/ferrite interfaces forming oxide islands that gradually grew to cover the entire surface. One important observation during oxidation of SiMo51 in exhaust gases is the suppressed formation of the SiO₂ barrier layer. The alloy did form a continuous barrier layer during thermal cycling between 240°C and 730°C for 700h and in the isothermal tests at 700 to 740°C for 50h, however, these were much thinner than those formed in air. This suppressed silica formation during oxidation in diesel exhaust gases has also been observed in the work by Tholence Tai5.

3.2.2 Influence of Cr- and Ni additions
Addition of Cr to SiMo51 was found to increase the oxidation resistance in air at both 700 and 800°C, derived from formation of an oxide layer at the oxide/metal interface containing both SiO₂ and a Cr-oxide. The weight gain curves at 800°C is shown in Fig. 17. The phases in the thin Cr-oxide layer could not be characterized using XRD and EDX, but are suggested to be Cr₂FeO₄ according to Thermo-Calc calculations. During exposure in exhaust gases, no Cr-oxide was detected in the alloy containing 1wt%Cr. The high gas flow and the presence of water vapor in the gas are suggested to have induced Cr-evaporation from the alloy. The alloy showed similar
oxidation behavior as SiMo51 during thermal cycling but required higher temperatures (>720°C) to form continuous SiO$_2$ layers during the isothermal exposures.

Figure 17. Weight gain curves after exposure in air at 800°C, showing a non-protective behavior of the alloys containing Ni whereas additions of Cr improve the oxidation resistance.

Addition of Ni showed reduction in oxidation resistance in air, particularly significant during oxidation at 800°C, see Fig. 17. This behavior was linked to an absence of a continuous SiO$_2$ layer at this temperature, resulting in increased oxidation rates. A breakdown of the silica layer is suggested to be linked either to a ferrite-to-austenite phase transformation or to stresses formed during rapid oxide growth. The reduced oxidation resistance in the presence of Ni was also observed during isothermal testing in exhaust gases where the alloy formed isolated Si-precipitates at all temperatures instead of a continuous barrier layer.
3.3 High-temperature low-cycle fatigue

3.3.1 SiMo51
LCF-testing of SiMo51 was observed to produce transgranular crack growth followed by a final ductile fracture. In no specimen, striations were found. The crack growth resulted in both cleavage of graphite nodules as well as crack growth along the graphite/ferrite interface. As temperature increased, the percentage of brittle fracture decreased and at 700°C, only a ductile fracture could be seen. As expected, the fatigue life decreased with increased temperature.

3.3.2 Influence of Cr- and Ni additions
From examination of microstructures, it is observed that additions of Cr to SiMo51 resulted in increased pearlite and carbide formation, producing alloys of lower ductility and increased hardness compared to the original alloy. Due to the reduction in ductility, only a moderate Cr-addition can be accepted. The addition of 0.5wt% Cr shows no negative effect on the fatigue life, despite the reduction in elongation from 9.8% to approximately 4.5%. On the contrary, this alloy shows an increased fatigue life at room-temperature but shows similar results as SiMo51 at higher temperatures.

When adding 1wt% Ni to SiMo51 a solution hardening effect is received. This results in a small reduction in ductility, giving an average elongation value of 7.8%. The Ni- addition increases the fatigue life up to 250°C. Above this temperature, no further improvement is noted.

3.4 High-temperature oxidation of HK30
The oxidation of the austenitic cast steel, HK30, in the three different environments: air, 5%O₂-10%H₂O and 5% CO₂-10% H₂O at 900°C for 6, 24 and 96h resulted in formation of adherent oxide scales of varying thickness.

During oxidation in air at 900°C for 96h, the alloy mainly developed a 5μm thick oxide scale of an outer (Cr, Mn)-spinel, an inner layer of Cr₂O₃ and a non-continuous zone of Si-oxide precipitates at the oxide/metal interface. Similar results were received from oxidation in the 5%CO₂-10%H₂O gas mixture. However, during oxidation in the 5%O₂-10%H₂O gas mixture, increased formation of porous Fe-oxide was observed, showing an outer,
dendrite-shaped Fe$_2$O$_3$ oxide growing on top of a layer of (Cr, Mn)-spinel already after 6h of exposure. During continuous growth, the oxide layers of (Cr, Mn)-spinel and Cr$_2$O$_3$ were gradually embedded by porous layers of Fe$_3$O$_4$ and Fe$_2$O$_3$. After 96h of oxidation, the scale thickness was measured to 10μm.

### 3.4.1 Characterization of oxide scales using EIS

Using the EIS method for characterization of oxide scales, a significant higher impedance response for oxide scales formed in O$_2$-H$_2$O, compared to those formed in the other atmospheres, was measured during immersion in exhaust-gas condensate. Fitting parameters showed lower resistance- and higher capacitance values for oxide scales formed in air and in CO$_2$-H$_2$O, compared to oxide scales formed in O$_2$-H$_2$O, revealing a higher conductivity, which, from oxide scale analysis, could be coupled to thinner and less defective oxide scales.

### 3.4.2 Interaction between condensate and oxide scales

Immersion of the oxidized samples in exhaust-gas condensate resulted in flaking of the oxide scale with sulfur precipitating in the spalled areas after longer immersion times (24h). EIS measurements in the low frequency range indicated acidic corrosion. This was confirmed by trace element analysis of the condensate, in which a sample oxidized in air at 900°C for 24h was immersed. As can be seen in Fig. 18, the analysis shows an increasing release rate of Fe, Ni and Cr, up to an immersion time of 60min, and thereafter a reduction. Fe and Ni shows the highest release rates. Moreover, Mn is found to be released into the condensate only during the first 5min. A repassivation of the metal surface could not be confirmed and the reduction in release rate is believed to be due to precipitation of corrosion products on the surface. Since the amount of Fe and Ni in the oxide scale was low for the examined samples, it is suggested that most Fe and Ni are released from the bulk material.
Figure 18. Release rates of Fe, Ni, Cr and Mn during immersion of oxidized specimen (air at 900°C for 24h) in exhaust-gas condensate at 60°C, exposure times ranging from 5 min up to 1280 min.
4 CONCLUSIONS

A moderate addition of 0.5wt% Cr to SiMo51 shows positive effects in forms of improved oxidation resistance in air up to 800°C, linked to formation of a Cr-oxide at the oxide/metal interface, and improved fatigue life at room-temperature, derived from increased carbide formation.

Addition of 1wt% Ni results in solid solution strengthening of the ferritic matrix improving the fatigue life up to 250°C. However, adding Ni also results in a decreased $A_1$-temperature, reducing the maximum allowed operating temperature. Moreover, Ni also reduces the oxidation resistance, due to a disrupted SiO$_2$ barrier layer in the presence of Ni.

The addition of Cr and Ni to SiMo51 does not seem to improve the life of SiMo51 in exhaust environments including corrosive exhaust-gases with temperatures of 700°C. Thus, in order to maintain a high durability of the components, materials of higher strength and oxidation resistance needs to be investigated.

From oxidation testing of the austenitic cast stainless steel HK30, it is shown that the alloy forms compact oxide scales of an inner Cr$_2$O$_3$ and an outer Cr-Mn-spinel with Si-precipitates at the oxide/metal interface in air and in 5%CO$_2$-10%H$_2$O gas mixture at 900°C. Oxidation in 5%O$_2$-10%H$_2$O gas mixture at 900°C results in a thicker oxide with a high amount of outer, porous Fe-oxides. However, the alloy shows good oxidation properties in forms of adherent oxide scales in all of the tested atmospheres.

Finally, exhaust-gas condensate was shown to have a detrimental effect on the compact oxide scale formed on HK30 in air at 900°C showing spallation and metal release. Thus, the presence of exhaust-gas condensate must be taken into account when selecting a new material for exhaust-system components.
5 FUTURE WORK

The additions of Cr and Ni to SiMo51 did not show the desired improvements in corrosion resistance and mechanical properties at high temperature. Thus, the performance of Ni-resist D5S and a selection of cast stainless steels will be studied.

For improving oxidation resistance of SiMo51 and also reducing the material temperature, thermal barrier coatings will be studied.

Additionally, since the atmosphere is known to affect the fatigue life, LCF testing in exhaust gases at high temperature will be performed in a new project, also granted by Vinnova. The purpose of this project is to increase the understanding of the fatigue behavior of cast alloys in exhaust gases. Also, these results will give an indication of the accuracy of using LCF-data from testing in air for dimensioning and strength calculations of exhaust components.

Moreover, the thermal cycling behavior of SiMo51 will be calculated using Chaboche transient model. The results will be verified by performing TMF testing.
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