High Temperature Resistant Exhaust Valve Spindle

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by

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Preface

The present thesis is submitted in candidacy for a Ph.D.-degree from the Technical University of Denmark. The work was carried out under supervision of Professor Marcel A. J. Somers and Dr. Kristian V. Dahl (Section of Materials and Surface Engineering, Department of Mechanical Engineering), and Harro A. Hoeg (MAN Diesel & Turbo A/S). The project was initiated the first of July 2010 and finished December 2013.

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Uffe Ditlev Bihlet

Lyngby, 9th of December 2013
Publications

Paper I

Paper II

Paper III
U. Bihlet, T. B. Sonne, K. V. Dahl, M. A. J. Somers, $V_2O_5$ induced hot corrosion of Ni base alloys containing 35-45 % Cr and 3.5-6% Nb, (Manuscript).

Paper IV

Paper V

Paper VI

Patent (not appended)
“An exhaust valve spindle for an exhaust valve in an internal combustion engine” (PA 2012 70414).
Abstract

Transport by ship remains the most economical and environmentally friendly mode of transport with a very low weight specific CO$_2$ footprint. Further increase of the fuel efficiency of large ships will result in a higher internal engine temperature. To allow this without compromising the reliability of the engine, new high temperature alloys are required for a specific engine component, the exhaust valve spindle.

Two alloys are used for an exhaust valve spindle; one for the bottom of the spindle, and one for the spindle seat. Being placed in the exhaust gas stream, combustion products such as $V_2O_5$ and $Na_2SO_4$ condense on the spindle, causing hot corrosion. Current industry standards can withstand service temperatures of up to 500°C for the spindle seat and 700°C for the spindle bottom. This project was tasked with increasing these temperatures 50°C each.

Literature review as well as an in-situ corrosion test revealed that the most resistant alloy in such an environment is Alloy 657 (Ni-based, 49 wt% Cr, 1.5 wt% Nb). This alloy is suitable for the spindle bottom, but not for the spindle seat, as it is too weak.

Thermodynamic calculations suggested that it was possible to modify the chemistry of the current valve seat alloy, Alloy 718 (Ni-based, 19 wt% Cr, 18 wt% Fe, 5.1 wt% Nb, 3 wt% Mo, 1 wt% Ti and 0.6 wt% Al), and thereby to obtain a more hot corrosion resistant alloy. To validate these calculations, 16 Ni-based alloys, containing 40 wt% Cr and Nb, Ta and Ti in varying levels, were produced by experimental laser cladding. Heat treatments proved that these alloys were precipitation hardenable, and that some of them reached high levels of hardness. Based on these results, five Ni-based alloys containing 35-45 wt% Cr and 4-6 wt% Nb were ordered, to narrow down the feasible alloy compositions. During the alloy development work, extensive microstructure quantification was performed, the results of which validated the predictive thermodynamical calculations.

The heat treatment results showed that a relation exists between the solution treated microstructure and the mechanical properties. This lead to the design of the alloy Ni40Cr3.5Nb (Ni-based, 3.5 wt% Nb and 0.5 wt% Ti). This alloy is precipitation hardenable to the same level of hardness as Alloy 718, and laboratory testing suggests that it is suitable for application at service temperatures of 550°C.
**Resumé**

Skibstransport er fortsat den mest økonomiske og miljøvenlige transportform med et meget lille vægtspecifikt CO₂-udslip. En yderligere forøgelse af denne effektivitet vil forårsage en højere intern motortemperatur. For at tillade dette uden at kompromittere pålideligheden af motoren, er det nødvendigt med nye højtemperaturlegeringer til brug på en specifik motorkomponent, udstødningsventilspindlen.

To legeringer bruges til en udstødningsventilspindel; en legering til spindelbunden, og en til spindelsædet. Da spindlen er placeret i udstødsgasstrømmen, kondenserer forbrændingsprodukter såsom V₂O₅ og Na₂SO₄ på overfladen, hvor de forårsager en aggressiv form for højtemperaturkorrosion. For at tillade dette uden at kompromittere pålideligheden af motoren, er det nødvendigt med nye højtemperaturlegeringer til brug på en specifik motorkomponent, udstødningsventilspindlen.

Litteratursøgning og en in-situ korrosionstest viste at den mest korrosionsbestandige legering i dette miljø er Legering 657 (Ni-baseret, 49% Cr, 1.5% Nb). Denne legering kan opfylde kravet om en driftstemperatur på 750°C for spindelbunden, men er uegnet til spindelsædet, da den er for svag.

Termodynamiske beregninger antydede at det var muligt at modificere sammensætningen af den nuværende spindelsædelegering, Legering 718 (Ni-baseret, 19% Cr, 18% Fe, 5.1% Nb, 3% Mo, 1% Ti og 0.6% Al), og derved at opnå en mere korrosionsbestandig legering. For at validere beregningerne blev 16 Ni-baserede legeringer med 40% Cr, og et varierende indhold af Nb, Ta og Ti, produceret ved eksperimentiel lasercladding. Varmebehandlinger viste at disse legeringer var udskilningshærdbare, og at enkelte af dem opnåede høje hårdheder. Baseret på resultaterne blev fem Ni-baserede legeringer med 35-45% Cr og 4-6% Nb bestilt for at identificere brugbare legeringssammensætninger. Omfattende mikrostrukturkvantificering af legeringerne fastslog en generel overeenstemmelse mellem de termodynamiske beregninger og den faktiske fasesammensætning.

Resultaterne fra varmebehandlingerne viste en sammenhæng mellem den opløsningsglødede mikrostruktur og de mekaniske egenskaber. Dette ledte til design af Ni40Cr3.5Nb, som er Ni-baseret med 40% Cr og 3.5% Nb. Denne legering er udskilningshærdbar til samme hårdhed som Legering 718, og laboratorieforsøg tyder på at den er egnet til anvendelse ved en servicetemperatur på 550°C.
Acknowledgements

In this project, I have been so lucky to have three dedicated supervisors.

Harro Hoeg is an allround oustading human being with a frightening energy level, and I must thank him for keeping my project on track, especially during my paternity leaves. I must also thank Harro for supporting my alloy composition suggestions.

Kristian Dahl has always been forthcoming when I needed help and feedback, even when he had to do it in his own time, and has on many occasions gone out of his way to help me.

Marcel Somers has always delivered relevant input during our meetings and his feedback on papers is rightfully known for being thourough and to the point.

Besides my supervisors, I must thank several people:

The technical staff at the Section of Materials and Surface Engineering for all their kind assistance.

My co-workers at MAN Diesel & Turbo for accepting my university disappearances without any need for explanation.

The vibrant Phd community at MTU for being awesome.

Finally I must thank my wife Sine for her support in the periods where my activities reduced to sleeping and working.
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Introduction

On the 2nd of July 2013 the container vessel Mærsk Mc-Kinney Møller shown in Fig. 1.1 entered service, and thereby set another high-water mark on the size of container vessels. With a load capacity of 18,000 20-foot containers, this behemoth of the seas represents the most fuel efficient type of bulk cargo transport presently available. To move 1 ton of cargo 1 km by train produces 18 g of CO2. To accomplish the same feat, the Mærsk Mc-Kinney Møller produces just 3 g CO2.

![Figure 1.1. Size of the container vessel Mærsk Mc-Kinney Møller. Image courtesy of Maersk A/S.](image)

A main contributor to the high efficiency of Mærsk Mc-Kinney Møller and large ships in general is the use of two-stroke engines for propulsion, one such shown in Fig. 1.2. The optimal engine rotational speed (typically 80-110 rpm) is matched with the propeller design, so that no gearbox is required, and as the combustion cycle is long, slow burning and thereby low cost fuels can be used.
Figure 1.2. A 12 cylinder MAN Diesel & Turbo two-stroke engine, which produces 74 MW of energy, roughly comparable to the amount of energy required to make a fully loaded 400 ton 747 jet airborne.

MAN Diesel & Turbo A/S (MDT), that designed the engines powering Mærsk Mc-Kinney Møller, has been developing two stroke diesel engines for sea-going vessels since the 1930’s. Fig. 1.3 shows the relation between fuel burned and the size of the combustion chamber. The historical trend has been to increase the compression ratio to gain higher efficiency of the engine, basically increasing not only the amount of fuel burned per engine revolution, but also the efficiency of the process.

Figure 1.3. The historical trend for MDT engines with cylinder bore size of 60 cm. The quantity on the y-axis represents the amount of burned fuel per second relative to the combustion chamber volume.

Converting more fuel to heat results in a higher combustion chamber temperature, something which has been mitigated by water cooling the combustion chamber wall internally. However, active cooling is currently not an economically feasible method to protect the exhaust valve spindle, shown in Fig. 1.4.
With the use of commercially available alloys as spindle materials, the temperature of the spindle has historically not been a major issue for MDT, and prolonged service has been possible with spindle bottom metal temperatures of up to 700°C, and spindle seat temperatures of up to 500°C. Recent operating experience with exhaust valve spindles operating at higher temperatures have however revealed two direct consequences: 1) A highly increased material loss rate for the spindle bottom, increasing from the accepted maximum value of 0.1 mm / 1000 hours, to as high as 1 mm / 1000 hours. 2) An increased risk of localized corrosion of the spindle seat, in the form of a blow-by (Fig. 1.5), which can form if the gas tight seal is broken by particles caught between the spindle and the cylinder cover.
**Objectives of the present project**

The primary objective of this project is to design materials that allow a significant temperature increase of future exhaust valve spindles, with desired values being 750°C on the spindle bottom and 550°C on the spindle seat. As such each goal represents a substantial 50°C increase compared to the current high temperature standard. In order to accomplish this, a range of superalloys with desirable properties must be designed, produced, and evaluated with the aid of literature studies, thermodynamic modeling, kinetic exposure studies and state of the art characterization methods.
The engine cycle and the exhaust valve

The two-stroke engine cycle is shown in Fig. 2.1. During operation, the exhaust valve is subjected to a dynamic situation with fluctuating pressures and temperatures.

Figure 2.1. The two-stroke engine cycle shown at illustrative stages. During (a), the piston compresses the cylinder air, and at (b) fuel is injected, which auto-ignites. Fuel continues to be injected into the flame during step (c), driving the piston downwards with combustion chamber pressures of up to 200 bar. At (d), the cylinder is purged with clean compressed air which enters the cylinder from the scavenging ports placed near the bottom of the cylinder, flushing the exhaust gas through the open exhaust valve.

Heat enters the spindle through the bottom, which forms the combustion chamber ceiling. During stage (c) in Fig. 2.1, the temperature of the spindle bottom surface is most likely momentarily higher than 700°C. The spindle seat is cooled during stages (a) through (c) by firm contact with the water cooled cylinder cover seat and during (d) by the fresh air purging the cylinder. A temperature gradient forms, where the temperature of the spindle bottom can be 200°C above that of the spindle seat, as shown in Fig. 2.2. The only appreciable cooling taking place for the bottom of the spindle is when the cylinder is air purged with high air speed at stage (d) in Fig 2.1.
During fuel combustion, local compressive stress of up to 700 MPa is imposed on the spindle seat, as the cylinder pressure climbs towards 200 bar. Fig. 2.3 shows the “W-seat” configuration of the cylinder cover seat which establishes a gas tight seal by concentrating the load on the spindle seat in two concentric contact lines.

To ensure an even wear of the exhaust valve spindle, vane wheels are installed on the shaft (Fig. 2.4). When the exhaust valve is opened at the end of the combustion cycle, the high speed exhaust gas causes the spindle to rotate 2-3° for every engine cycle.
Figure 2.4. Three exhaust valves ready for installation. The vane wheel (arrows) on the shaft causes the spindle to rotate 2-3° for every engine cycle.

The chemical environment of the spindle

When gasoline and other high grade products have been distilled out from a batch of crude oil, the remainder is termed residual or heavy fuel, a sample of which is shown in Fig. 2.5.

Figure 2.5. Heated heavy fuel. At room temperature it behaves like a viscous grease and cannot be pumped.

Due to the fossile origin, it contains not only combustible hydrocarbons, but also water, sediment and trace amounts of S, O, N, P, V, Ni, Co, Fe, Na, K, Ca, Mg, Al, Si, Cu, etc. Historically, the hydrocarbon/impurity ratio of residual fuel has been declining due to increasing oil prices. The only regulation currently imposed is the ISO8217 standard, which among other things, states a maximum V content of 450 ppm. There is
regional variation in the allowable S content, with 3 wt% being the current maximum. As a result of the impurities of heavy fuel, the exhaust valve spindle is covered by combustion products during service, as shown in Fig. 2.6.

Figure 2.6. The appearance of a spindle after 6000 hours of service.

Considering the tribological situation of the exhaust valve seat and the cylinder cover seat, the two of which are forced together at high temperatures and pressures, the combustion products are believed to have a beneficial effect by preventing micro-welding of the metallic surfaces. As a downside, the brittle non-compressible scales cause dent marks on the exhaust valve seat, as shown in Fig. 2.7. This plastic deformation is possible due to the high metal temperature, which leads to a reduced yield strength of the spindle seat. During service, the amount of dent marks reach a constant level, and as the spindle is rotated 2-3° for every engine cycle, they become evenly distributed. In this way the spindle seat is plastically deformed dynamically. Service experience has shown that the dent marks are harmless. However, a very deep dent could lead to a blow-by if the gas tight seal is broken. In that case, the high temperature corrosion resistance of the spindle seat material is put to the test by hot gasses escaping at supersonic speeds through the tiny hole. If both contact lines formed by the W-seat are breached, a catastrophic blow-by as that shown in Fig. 2.7 is inevitable. If the general temperature of the spindle seat is below a certain material specific level, a deep dent mark does not necessarily lead to a blow-by. As a result of the spindle
rotation, a deep dent may be formed in one engine cycle and closed in the next, as a result of the change in the exact fit of the spindle seat and the cylinder cover seat after spindle rotation.

Figure 2.7. An exhaust valve spindle disk with a severe blow by.

The current spindle materials

Historically, the entire spindle was made entirely from the Ni-based alloy Nimonic 80A (Table 2.1). Due to the increasing price of Ni, this is however a costly solution, and MDT has consequently developed a more cost-efficient solution, the *DuraSpindle*. The differences between the spindles are shown in Fig. 2.8. Due to the much reduced use of Ni, a *DuraSpindle* represents a cost saving of 50% compared to a Nimonic 80A spindle.

Figure 2.8. (Left) the fully forged Nimonic 80A exhaust valve spindle. (Right) The DuraSpindle, which employs multiple welded coatings on a forged bulk.
The weld overlays used on the *DuraSpindle* are well known commercial Ni-based alloys, with nominal compositions shown in Table 2.1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nimonic 80A</td>
<td>3</td>
<td>bal</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Alloy 718</td>
<td>18</td>
<td>bal</td>
<td>19</td>
<td>3</td>
<td>5.2</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>Alloy 625</td>
<td>1</td>
<td>bal</td>
<td>22</td>
<td>9</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

To ensure a high wear resistance and a high resistance towards deeper dent marks, the seat area of the *DuraSpindle* is deformation hardened by a rolling operation, which is shown in Fig. 2.9. A disc with a tip radius of 2.5 mm is forced into the seat with a load of up to 10 tons while the spindle rotates, creating a groove with a depth of 2.2 mm below the original surface level. Depending on the size of the spindle, up to four grooves are created this way, fully covering the seat area. This creates a highly deformation hardened zone in the seat, and ensures a high level of compressive stress which prevents weld cracks from propagating.

Following the rolling operation, the spindle is precipitation hardened, which for the *DuraSpindle* gives the hardness distribution in the seat shown in Fig. 2.10. The maximum hardness is in the range of 550 HV. The seat of a Nimonic spindle is not rolled prior to precipitation hardening, and is therefore softer, approximately 400 HV. After precipitation hardening, the spindle is machined to the final dimensions at a depth of 2.5 mm from the pre-rolled surface. Thereby the rolling grooves are removed.
Service experience with current spindles

MDT describes the Nimonic 80A spindle as a rather costly spindle with satisfactory all-round high temperature properties for service temperatures up to 700°C on the disk bottom and 500°C on the seat.

Common material loss on the spindle bottom is approximately 0.1 mm / 1000 hours. The material loss of the spindle seat is normally negligible due to the lower metal temperature. For the spindle seat the corrosion hazard is formed by the risk of blow-by which increases with temperature. With regard to the two existing spindle material solutions and their performance, the DuraSpindle matches the Nimonic 80A spindle with the exception of the Alloy 718 seat, which cannot be used at seat temperatures above 470°C due to limited high temperature corrosion resistance of Alloy 718.

An exhaust valve spindle for the future

A prior MDT project, focused on increasing the high temperature corrosion resistance of the bottom of the DuraSpindle, has resulted in a novel spindle concept where the Alloy 625 spindle bottom weld overlay is replaced by the relatively simple, but extremely corrosion resistant Ni49Cr1.5Nb alloy (also known as Alloy 657). This high Cr alloy is not weldable by conventional methods, so the spindle has been produced by the rather costly Hot Isostatic Pressing (HIP) production method, by which a forged substrate of stainless steel
is bonded to Ni49Cr1.5Nb metal powder particles at high pressure and temperature. The spindle concept has been named the *HIP compound spindle* (Fig. 2.11). The Ni49Cr1.5Nb alloy has performed well on the spindle bottom, but the alloy 718 seat remains vulnerable to blow by.

![HIP compound spindle](image)

*Figure 2.11. The HIP compound spindle concept.*

**Requirements for the spindle materials of the future**

A high degree of material selection freedom is gained by using the HIP process, as it makes non-weldable alternatives to Alloy 718 available. Therefore the HIP process will be used in the present project for the development of a spindle for the future. The demands for the spindle alloys are divided by their application area. For the spindle bottom, hot corrosion resistance is the single most important feature.

The requirements for an exhaust valve spindle bottom alloy can be summed up to:

1. A maximum corrosion rate of 0.1 mm / 1000 hrs with a service temperature of 750°C.
2. The alloy should not become brittle during service.

For the spindle seat, Alloy 718 has a unique mix of properties, which is the original reason for its application. Should the seat be made out of an alternative alloy, this alloy should not only have a
significantly higher corrosion resistance than Alloy 718, it should also retain the desirable properties of its predecessor. The demands for the spindle seat alloy are collected below:

1. The as produced ductility of the seat alloy should allow work hardening by rolling.
2. Precipitation hardenable to the same hardness level as Alloy 718.
3. Alloy should not become brittle during service.
4. Be resistant towards blow-by at a service temperature of 550°C.
5. Nice to have: An alternative to the HIP production method is desirable, but not crucial.
Corrosion of the exhaust valve spindle

The exhaust valve spindle experiences high temperature corrosion in service. The present chapter seeks to identify the corrosion mechanism and to formulate recommendations for the development of spindle alloys.

Fundamentals: Pure oxidation

When exposed to air at ambient conditions, most metallic elements react with $O_2$ to form metal oxides according to Eq. (3.1),

$$\frac{2x}{y}M + O_2 = \frac{2}{y}M_xO_y$$

where $M$ is a metallic element. Oxide formation is thermodynamically favourable because it lowers the Gibbs energy of the system. How much the energy is lowered depends on the oxide composition and type. A clearly defined minimum $O_2$ partial pressure exists below which a given metal oxide will not form (if already formed it will be reduced to metal and $O_2$ below this pressure). This is given by Eq. (3.2),

$$P_{O_2}^{\text{diss}} = \exp\left(\frac{\Delta G^o}{RT}\right)$$

where $\Delta G^o$ is the standard Gibbs energy of formation of the oxide at absolute temperature $T$ and $R$ is the gas constant. $P_{O_2}^{\text{diss}}$ values for a selection of common metal oxides can be found as a function of temperature in the Ellingham diagram in Fig. 3.1. The lower the line is in the diagram, the more stable the oxide is.
Figure 3.1. Stability of metal oxides. For a given oxide formation reaction at a given temperature, the $P_{O_2}^{\text{diss}}$ value described by Eq. (3.2) can be found by drawing a line from point 'O' on the upper left hand of the diagram through the intersection of the oxide formation reaction and the relevant temperature line. $P_{O_2}^{\text{diss}}$ in atm is then found by extending the resulting line to the $pO_2$ scale.

For illustration this has been done with a dashed line, showing the $P_{O_2}^{\text{diss}}$ for Cr$_2$O$_3$ at 1000°C is $\approx 10^{-21}$ atm.

Considering a metal-air interface in atmospheric air, the $O_2$ partial pressure increases moving outwards from the metal, going from a value very close to zero inside the bulk metal, to 0.2 atm in air. With Fig. 3.1 in
mind, the oxide formed closest to the metal will be the one that is stabilized by the lowest $P_{O_2}^{\text{diss}}$. The resulting oxide can be porous and thereby gas transparent. Depending on the non-stoichiometry of the oxide, it can act as an ionic conductor. In a corrosion resistance context this is harmful, as it allows oxygen transport through the oxide. Two important oxides with low non-stoichiometry which are dense and which form efficient diffusion barriers, are $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$, both of which effectively prevent further oxidation of the substrate. Depending on temperature, these oxides act protectively for NiCr alloys at 500-800°C, and for NiAl from 900°C and upwards. This self-sealing effect is the foundation on which most engineering materials used in oxidizing environments, be it high or low temperature, rests. This is also the case for exhaust valve spindles, which are made from Fe- or Ni-based alloys with Cr, Al and Ti additions. Due to the type of fuel used, the working environment in the combustion chamber contains not only $\text{O}_2$, but also compounds such as $\text{V}_2\text{O}_5$ and $\text{Na}_2\text{SO}_4$, which in combination form eutectic mixtures with relatively low melting points, as shown in Fig. 3.2, where a melting point down to 500°C for a mixed salt of $\text{V}_2\text{O}_5$ and $\text{Na}_2\text{SO}_4$ with a ratio of 4:6 can be found, placing it within the operating temperatures of the exhaust valve spindle.

\[\text{Figure 3.2. The } V_2O_5 - Na_2SO_4 \text{ phase diagram}^{1}.\]
Protective metal oxides are readily dissolved by such a melt. The solubility of metal oxides in a V$_2$O$_5$-Na$_2$SO$_4$ melt depends on the Na:V ratio, and is up to 60 and 50 molar % for NiO and Cr$_2$O$_3$, respectively.

The resulting corrosion situation where the metal surface is covered in molten salt is termed hot corrosion, and differs significantly from that outlined for pure oxidation.

**Hot corrosion: Metal oxide fluxing by liquid salts**

Corrosion due presence of a liquid salt at high temperature is termed hot corrosion, and is traditionally divided into an incubation period with low corrosion rate, and a propagation stage with catastrophic corrosion rates. The length of the incubation period is believed to be associated with the time-dependent interdiffusion of salt deposit and metal oxide. When an eutectic composition is reached and a salt melt is formed, the propagation stage begins. The incubation period may be very short or completely absent, if the metal temperature is above the melting point of the combustion deposits. When covered by a molten salt, the metal oxide is continually dissolved as shown in Fig. 3.3, where the gradients of metal ion solubility and pO$_2$ promote a constant removal rate of the metal oxide. After dissolution, the oxide reforms as discrete particles further into the melt, where the pO$_2$ is higher. This leads to a porous oxide. Generally, the resulting metal loss rate is much higher than that observed without a liquid deposit.
Molten salt chemistry

In the case of a Na$_2$SO$_4$ based melt, the metal oxide dissolution reaction has been shown to depend on the type of metal oxide and the SO$_3$ content of the melt. At constant temperature, a relation exists between the SO$_3$ and Na$_2$O content, shown in Eq (3.3) for a temperature of 1200K.

\[
\log(a_{Na_2O}) + \log(a_{SO_3}) = -16.7
\]  

(3.3)

Each oxide has a solubility minimum for a given SO$_3$ salt content and temperature. If this minimum is positioned in a SO$_3$ rich melt, the metal oxide is termed acidic, as is the case for Cr$_2$O$_3$ and Al$_2$O$_3$ in Fig. 3.4. Conversely, a metal oxide with a solubility minimum positioned in a SO$_3$ lean Na$_2$SO$_4$ melt is termed basic, such as NiO and Co$_3$O$_4$. 

Figure 3.3. Hot corrosion caused by salt deposits.$^3$. 
For each metal oxide, the solubility curve is composed of two dissolution reactions, one on the basic side of the solubility minimum, and one on the acidic side of the solubility minimum. The basic dissolution reaction causes the metal oxide to enter the salt melt as an anionic species, while the acidic dissolution causes the metal oxide to enter the melt as a cationic species. An acidic metal oxide is therefore likely to enter the melt as an anionic species by a basic dissolution reaction. For $\text{Cr}_2\text{O}_3$, the acidic and basic dissolution reactions are shown in Fig. 3.5.
The basic dissolution mechanism of Cr$_2$O$_3$ releases $CrO_4^{2-}$ ions into the melt. These ions have been theorized to reduce to Cr$_2$O$_3$ at cracks in the oxide layer, where the pO$_2$ is low, as shown in Fig. 3.6. By that mechanism, Cr$_2$O$_3$ may be self-healing in a basic salt melt.$^5$

Another metal oxide which has been found to be resistant towards hot corrosion is SiO$_2$. This is attributed to a very low solubility of SiO$_2$ in the salt melt, which is also apparent in Fig. 3.4.$^7,8$
Formation of sulphides below the oxide scale

Besides the constant dissolution of the protective metal oxide barrier by the liquid salt deposit, S diffuses into some alloys to form a zone of internal dispersed sulphide particles below the metal oxide. Fig. 3.7 shows the stability diagram for Ni-S-O at 700°C, where it is apparent that NiS₂ is stable at the low pO₂ conditions under the oxide scale. Similar stability diagrams exist for Cr, which forms CrS⁹.

![Phase stability diagram for the Ni-O-S system at 700°C in terms of the activities of O₂ and SO₃³.](image)

At higher pO₂, the sulphides oxidize. In the case of CrS particles which transform to Cr₂O₃, this oxide is not protective when formed as dispersed particles within the bulk metal. Thereby the sulphide formation can indirectly disrupt the continued formation of a protective metal oxide⁹. Among common alloy additions, Cr is found to be most effective at reducing the harmful effect of an S bearing environment⁹,¹⁰.

Practical experience with heavy fuel related corrosion

To define recommendations for spindle alloy development, a review of the available experience is required. Historically, heavy fuel equivalents were used in boilers for steam engines. These boilers suffered from “ash deposit corrosion”, and the importance of removing these deposits was stressed in “The Marine Corrosion Handbook”, published 1960¹¹. The magnitude of this corrosion was limited due to low metal temperatures, and indeed a bigger corrosion issue was condensation of H₂SO₄ at inconvenient places in the heater tube.
arrangements. Higher metal temperatures and more dramatic corrosion was found in the early 1950’s in gas turbines as well as steam generation power plants burning heavy fuel\(^{12-14}\). A comparative experimental study found that the corrosion rate was drastically accelerated in the 650-750°C range, as shown in Fig. 3.8. Knowing that a liquid salt causes high material loss, it seems that the maximum material loss must have been found at the melting point of the combustion product deposits. Below that temperature the products did not melt, and above it, the metal temperature was higher than the dew point, keeping the metal relatively deposit-free.

![Figure 3.8. Results from a comparative alloy study in a heavy fuel fired boiler. (Left) The temperature band of the rods as a function of distance to the cooled wall. At any position, the minimum and maximum temperatures are defined by part load and full load service. (Right) The rods after 9,590 h. The material loss at 650-750°C was dramatically increased. The best corrosion resistance was obtained with high Cr and high Si alloys.](image)

The relative performance of alloy groups in fuel ash has also been investigated, and is shown in Fig. 3.9. Fe-based alloys were rapidly consumed in fuel ash, while Ni-based alloys performed comparably better than Co-based ones. The superiority of NiCr alloys, specifically Ni50Cr, over FeCr alloys is supported by the results from a field test from a crude oil heater.
A burner rig study specifically designed to test the corrosion performance of exhaust valve spindle materials showed that the corrosion resistance depends heavily on the Cr content. However, as shown in Fig. 3.10, other alloying elements play an important role, as there is a marked difference between the corrosion resistance of Nimonic 80A and Alloy 718 despite their identical Cr content. The Al and Ti content of Nimonic 80A (2.5 and 1.5 wt% respectively) and Alloy 718 (1 and 0.6 wt%, respectively) may explain the very high resistance of Nimonic 80A. Indeed sources have described Ti doping of Cr₂O₃ as a significant means of improving the protective effect of the oxide in specifically a S bearing environment. The 5.2 wt% Nb in Alloy 718 has not been ascribed to have any effect on the hot corrosion resistance. The Fe content of Alloy 718 (18 wt%) compared to that of Nimonic 80A (3 wt%) is a significant difference between the alloy chemistries. A high Fe content stabilizes Fe oxides such as FeCr₂O₄, which is also known as Spinel, which is highly non-stoichiometric and does not form a protective scale.
Conclusion

The aim of the present project is to develop a new alloy or a series of alloys which can effectively resist the exhaust valve spindle environment, an environment which is characterized by the presence of a molten salt deposit. Literature on the fundamental principles of hot corrosion as well as practical experience on related conditions as well as actual engine environments, all agree that Ni based alloys with high amounts of Cr and moderate amounts of Si are effective in resisting hot corrosion\textsuperscript{16,18–20}.

References


\textbf{Figure 3.10. A burner rig study of exhaust valve alloys\textsuperscript{18}.}
Exhaust valve spindle alloy design considerations

The objective of the present project is to increase the temperature capability, i.e. the corrosion resistance, of the exhaust valve spindle. Additionally, a number of demands are made for the mechanical properties of the spindle seat; it should be work hardenable by rolling after production, precipitation hardenable to the same hardness level as Alloy 718 and non-embrittlening during service. Finally, an optional requirement exist for both the spindle bottom alloy as well as the spindle seat alloy, being that an alternative to the costly hot isostatic pressing production method is desirable. For a high hot corrosion resistance, literature recommends a Ni-based alloy with a high Cr content alloyed with moderate amounts of Si.

The NiCr system

The phase diagram of Ni-Cr is shown in Fig. 4.1. It is a relatively simple system with two primary phases, γ-Ni (f.c.c.) and α-Cr (b.c.c.). γ-Ni has a high solubility of Cr, while α-Cr has a low solubility of Ni, at least below 1100°C. Most commercial Ni-based alloys contain 20 wt% Cr or less, meaning that the α-Cr phase is completely absent from the alloy microstructure.
Figure 4.1. The Ni-Cr phase diagram. The primary phases of Ni (f.c.c.) and Cr (b.c.c.) are known as respectively γ-Ni and α-Cr, or simply γ and α. In Fig. 4.1, γ' refers to the Ni2Cr ordered structure, which is shown in Fig. 4.2. This ordering takes place during long term heat treatment, and causes a slight density increase in the order of 0.48%.

Figure 4.2. The arrangement of Ni and Cr atoms on the f.c.c. lattice, forming the Ni2Cr ordered phase. The broken lines refer to the original f.c.c. lattice.
Ni-based alloys alloyed with Cr and Si

Due to low ductility and low high temperature strength, Ni-based alloys with high Cr contents have been largely avoided by the superalloy development industry, which has rather focused on turbine foils. A very simple cast 50Cr-50Ni alloy found use in boilers burning low-grade oil during the 1960’s, but experience showed that it lost all ductility after long term exposure. This was attributed to the formation of a brittle α-Cr lamellar microstructure, as shown in Fig. 4.3.6

1 wt% Si has been added to Alloy 718 where it was found to decrease the alloy ductility from 16 to 2%. This was attributed to formation of Laves phases. In contrast, for Cr, empirical alloy development has led to the relatively ductile Alloy 657 (48% Cr, 1.5% Nb, rest Ni), the microstructure of which contains α-Cr with a globular morphology, as opposed to the lamellar type found without Nb addition. Compared with 50Cr-50Ni, Alloy 657 has higher ductility during long term high temperature exposure, as shown in Fig. 4.4.8

Figure 4.3. Microstructure of cast Ni50Cr, with brittle lamellar precipitates of α-Cr. Optical micrograph by Parry, Bridges and Taylor.
The higher ductility of Alloy 657 is attributed to the low N content (<0.16 wt%), as a higher N content caused brittle lamellar α-Cr precipitates during the alloy development. The Nb content of Alloy 657 is believed to further decrease the matrix content of N, by preferential NbN formation during solidification. During development of Alloy 657, Ta was noted to have the same effect as Nb, and further work revealed that addition of Zr, Ce, Hf or Y had a similar effect on the ductility of high Cr Ni-based alloys. The detrimental effect of the N content on the ductility of α-Cr is also known for Cr-based alloys, and the ductile to brittle transition temperature of such alloys is most sensitive towards this. The reason for this has been proposed to be due to precipitation of Cr₂N, however this theory is being debated by literature, and the exact physical explanation seems yet to be found. Generally cast alloys may experience a high degree of segregation during production. For a Ni-based high Cr alloy, this may create large interdendritic α-Cr formations, and if they solidify as the last phase, the impurity content will be high. Powder metallurgy (PM) eliminates this issue, due to the extreme cooling rate during powder atomization. This effect, and the absence of pores in hot isostatic pressed material will increase the ductility of most HIP’d alloys compared with cast counterparts. Considering Alloy 657 which contains 49 wt% Cr and retains some ductility even during high temperature exposure, it seems that the maximum value of Cr content that can be allowed...
before the alloy becomes brittle is very high indeed. For the exhaust valve bottom, for which only limited
demands for the mechanical properties exist, using Alloy 657 may indeed lower the material loss rate
considerably. For the exhaust valve seat however, a ductility drop as that observed in Fig. 4.4 cannot be
tolerated. Furthermore, the seat alloy should be precipitation hardenable in order to match the hardness of
the Alloy 718 spindle seat.

Precipitation hardening of Ni-based alloys

Precipitation hardening of Ni-based superalloys depends on the formation of a dispersed matrix coherent
phase. Alloying with Al and Ti stabilizes the f.c.c. Ni$_3$(Al,Ti) phase, which is normally known as γ'. Alloying
with Nb or Ta causes formation of metastable b.c.t. Ni$_3$(Nb,Ta) phase, which is known as γ''$^d$. The crystal
structures are illustrated by Fig. 4.5. The range of ordering required to form γ'' is longer than that of γ', but
besides from that the structures are closely related.

![Figure 4.5. The lattice arrangement of γ' (a), and γ'' (b). Empty circles are Ni atoms, while filled circles are Al or Ti and Nb, respectively.](image-url)
The actual microstructure appearance of both phases is shown in Fig. 4.6, which shows codependent precipitation of γ' and γ'' in Alloy 718. γ' has a cuboidal morphology, while γ'' forms as elongated elliptical discs, oriented perpendicularly to each other.

Figure 4.6. The appearance of γ' (blurred rectangular blobs) and γ'' (bright elongated ellipses oriented vertically or horizontally). SAD TEM image adapted from Cozar and Pineau\textsuperscript{11}.

In practice, γ' is the most used precipitation hardening phase as it is stable at higher temperatures than γ'', which transforms to the chemically identical matrix incoherent δ phase when exposed for prolonged periods above 650°C\textsuperscript{4}. Therefore, Alloy 718 is unique in the sense that it is primarily precipitation hardened by γ''\textsuperscript{11–15}. Compared with γ', the lattice misfit between γ-Ni and γ'' is higher. Because of this, the precipitation process and thereby the strength increase proceeds at a lower rate than that observed for γ' hardening. In Fig. 4.7 it is shown how a complete formation of γ'' at a heat treatment temperature of 700°C takes up to 100 hours\textsuperscript{11}.
Slow or sluggish age hardening is a main feature of Alloy 718, as it allows welding and hot forging with little or no crack susceptibility. The alloy simply does not age harden during cooling. Alloy 625, which is applied as a weld coating on the bottom of DuraSpindles, also experiences precipitation hardening by γ'' precipitation, however it happens so slowly (1000+ hrs) that it is without practical application. Historically, Nb raw material contained at least 10 wt% Ta, which made Ta unavoidable as an extra constituent in empirical alloy development. To date the Nb content of Alloy 718 is defined as Nb + Ta. Ta has, in spite of having a molar mass almost exactly twice that of Nb, the same strengthening effect as Nb, when added in the same atomic concentration. It is however not used as such due to higher cost.

**Prediction of phase compositions**

It is tempting to seek to modify Alloy 718 in an attempt to increase the hot corrosion resistance without impairing the attractive properties of the alloy: High ductility as produced combined with the option of precipitation hardening by γ'' formation. Such an alloy should have a γ'' content similar to that of Alloy 718, and in order to identify meaningful alloy compositions, a tool is needed which can link the chemical composition of a multi-component alloy such as Alloy 718, with the resulting microstructure. Phase diagrams as that shown in Fig. 4.1 have been established experimentally, and give the equilibrium phase.
composition and thereby the equilibrium microstructure of binary NiCr alloys. While ternary diagrams exist, the equilibrium phase composition of a multicomponent alloy requires thermodynamic modeling. ThermoCalc\textsuperscript{23} readily produces the equilibrium phase composition of multi-component alloy such as Nimonic 80A (Fig. 4.8), where $\gamma'$ refers to the Ni$_3$(Al,Ti) phase. From the $\gamma'$ stability range it follows that Nimonic 80A is precipitation hardenable by $\gamma'$ formation if solution treated above 1000°C and aged below 800°C.

![Figure 4.8. The equilibrium phase composition of Nimonic 80A as a function of temperature. Calculated with Thermo-Calc, using the TCNIS Ni-based Superalloys Database, version 5.1\textsuperscript{23}.](image)

To produce these diagrams, Thermo-Calc employs the CALPHAD method.

**The CALPHAD method**

The CALPHAD (CALculation of PHAse Diagrams) method provides a general path to the prediction of the thermodynamic equilibrium of a definable system\textsuperscript{24}. For alloys, numerical thermodynamics is concerned with predicting the Gibbs energy of each possible phase in an alloy. The calculations are based on incomplete experimental data on related phase compositions. To do this, each phase is modeled using the general expression in Eq (4.1),

$$G = G_{srf} + G_{phys} - T \cdot S_{cnf} + G_E \quad (4.1)$$

where
$G$ is the Gibbs energy of the phase measured in J mol$^{-1}$, 

$G_{\text{sr}}$ is the Gibbs energy of the unreacted constituents in the phase, 

$G_{\text{phys}}$ is the contribution to the Gibbs energy from physical phenomena such as magnetic transitions, 

$T$ is the absolute temperature, 

$S_{\text{con}}$ is the configurational entropy of the phase which is calculated from the number of possible arrangements of the phase constituents and 

$G_{E}$ is the excess Gibbs energy.

Each term in Eq. (4.1) is modeled independently using phase-specific models, specified in databases which contain Gibbs energy functions. For pure elements and their phases, expressions for Gibbs energy can be found in databases such as The Scientific Group Database Europe (SGTE), and can be of the form

$$G(T) - H^{\text{SER}} = a + bT + cT\ln(T) + \sum dT^n$$  \hspace{1cm} (4.2)

where $H^{\text{SER}}$ is the tabulated enthalpy for the given phase at 298.15K, a, b, c and d are coefficients and n is a set of integers which can have values of 2, 3 and -1$^{25}$. For solution phases which can contain variable amounts of constituents, CALPHAD provides a framework which allows the calculation of Gibbs energy for compositions of solution phases which have not been experimentally determined$^{26,27}$.

**CALPHAD as implemented by Thermo-Calc**

Given a chemical composition, a system size, a temperature and a database which provides functions for the Gibbs energy of relevant phases, Thermo-Calc identifies the phase composition with the lowest Gibbs energy. This is done numerically for each solution phase by calculating the Gibbs energy at all possible contents of the specified constituents. In this way, a map with often more than $10^6$ points of the Gibbs energy of all phases in the system is formed. Thermo-Calc identifies the hyperplane in this point cloud, and
finds the Gibbs energy minima. In this way, the equilibrium phase composition is found. The results hinge on the databases used. In this project, two databases on Ni-based alloys have been used (Table 4.1).

<table>
<thead>
<tr>
<th>Database name</th>
<th>Version</th>
<th>Provider</th>
<th>Included elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNI (TCN15)</td>
<td>5.1</td>
<td>Thermo-Calc Software AB</td>
<td>Al, Ar, B, C, Co, Cr, Fe, H, Hf, Mo, N, Nb, Ni, Pd, Pt, Re, Si, Ta, Ti, V, W, Zr</td>
</tr>
<tr>
<td>Ni-data (NI4)</td>
<td>4</td>
<td>Thermotech Ltd</td>
<td>Al, B, C, Co, Cr, Fe, Hf, Mo, N, Nb, Ni, Re, Ta, Ti, W, Zr</td>
</tr>
</tbody>
</table>

When calculating the phase composition of alloys with metastable phases such as $\gamma''$, it makes sense not to include the equilibrium phase $\delta$, as it is not likely to appear within production related heat treatments. With the calculated phase compositions of Alloy 718 as an example (Fig. 4.9), the modest impact of database choice on the results is apparent. The phases, contents and stability ranges vary slightly, and it seems that TCNI5 predicts a lower $\gamma''$ content. Alloy contains 3 wt% Mo, which stabilizes the Sigma phase, and also the $\mu$-phase.

In contrast to the NI4 database, TCNI5 is capable of presenting results in terms of volume fraction, which in the case of a isotropic microstructure should equate directly to the area fraction which can be measured quite simply using microscopy. To do this, TCNI5 employs functions for the molar density of phases. In

*Figure 4.9. The equilibrium phase composition of Alloy 718 calculated with the NI4 database and the TCN15 database.*
practice the difference between the weight fraction and the volume fraction is little, and therefore the
weight fraction is a good indication of the area fraction in a given 2D metallurgical cross section.

**Conclusion**

To do alloy development, a sound knowledge of prior art is required. With that in hand, numerical
thermodynamic predictions can be used to reach the next level. For the exhaust valve spindle, the
emphasis is on hot corrosion resistance coupled with, for the exhaust valve seat, the possibility of work and
precipitation hardening. The creep rate is not important for those applications, and therefore high Cr
contents are allowed. The ductility requirement makes alloying with more than 0.5 wt% Si a poor option. It
seems appropriate to investigate the consequence of an increased Cr content of Alloy 718 by
thermodynamic calculations and, if those are promising, to validate the results experimentally.

**References**


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Experimental alloy development

With Thermo-Calc and an appropriate database, alloy development can be accelerated greatly from being an empirical step-wise process with many impasses, to instead being a number of informed leaps. The iterative approach used in the present project is described by Fig. 5.1.

![Diagram](image)

*Figure 5.1. The iterative alloy development sequence utilized in this project.*

In the preceding chapters, the exhaust valve spindle application was examined, and relevant literature concerning the hot corrosion and alloy development was reviewed. With this knowledge in hand, it makes sense to recap the requirements for the exhaust valve spindle materials:

**The spindle bottom**

1. A maximum corrosion rate of 0.1 mm / 1000 hrs with a service temperature of 750°C.
2. The alloy should not become brittle during service.

Considering the literature review, it seems that the spindle bottom alloy should be Ni-based, and contain as much Cr as possible. Alloy 657 (49 wt% Cr, 1.5 wt% Nb) appears a likely candidate.
The spindle seat

1. High ductility in the as-produced condition, to be suitable for the deformation hardening by rolling operation during production.
2. The as produced ductility of the seat alloy should allow work hardening by rolling.
3. Alloy should not become brittle during service.
4. Be resistant towards blow-by at a service temperature of 550°C.
5. Nice to have: An alternative to the HIP production method is desirable, but not crucial.

It should be possible to honour this demanding list of requirements, if it is possible to increase the hot corrosion resistance of Alloy 718, without compromising the possibility of precipitation hardening.

Calculated spindle seat alloys derived from Alloy 718

Alloy 718 has the proper mechanical and processing properties for a spindle seat alloy. However from a hot corrosion resistance standpoint, the Fe content is too high, and the Cr content is too low. Fig. 5.2 shows Thermo-Calc calculations, which indicate that an increased Cr content does not affect the content of the precipitation hardening $\gamma''$ phase. With higher Cr content comes a much increased content of $\alpha$-Cr. As described in the previous chapter, this may not lower the ductility, if only the N content is kept below 0.16 wt%, and Nb or other N-getter alloying elements are present.

![Figure 5.2. The phase composition of Alloy 718 when Fe and Mo contents are substituted with Cr, and Nb content is held constant. Results from Thermo-Calc\textsuperscript{18}, using the TCNi5 Ni-based Superalloys Database, version 5.1\textsuperscript{19}.](image-url)
Empirical alloy screening was initiated to determine the feasibility of such high-Cr low-Fe Alloy 718 derivatives, for application as exhaust valve spindle seat alloys.

**Alloy sample production by laser cladding mixed powders**

To screen Ni-based alloys containing high amounts of Cr and modest amounts of Nb, Ta and Ti, the experimental design shown in Fig. 5.3 was defined. As there might be a negative influence of Nb on the hot corrosion resistance of the alloy, Ta was included to verify whether it could indeed interchange for Nb. It was expected that Ti would stabilize γ', and was therefore included to study the influence on the kinetic of precipitation hardening.

![Figure 5.3. In this diagram, each sphere represents an alloy composition. The experimental design is a replicated 2^3 factorial design, fully exploring the space defined by 2-5 wt% Nb, 0.5-3 wt% Ta and 0.5-2 wt% Ti. All alloys contain 40 wt% Cr.](image)

As most alloy producers require orders of 25 kg alloy or more when producing custom alloys, a faster route was attempted, in which available stock welding powders where mixed in appropriate weight ratios and laser cladded. In this manner, 8 different powder mixes were laser cladded onto a stainless steel substrate, as shown in Fig. 5.4. Attempts to section most samples to obtain tensile test specimens were rendered impossible due to severe post weld cracking and low ductility. At the time this was worrying, but as the laser cladding procedure was highly experimental, it was attributed to suboptimal process parameters.
Figure 5.4. (Left) A laser cladded experimental alloy sample. (Right) Cut of alloy sample # 9, (36.5 wt% Cr, 2.1 wt% Nb, 0.4 wt% Ta, 0.8 wt% Ti). Arrows indicate the location of a crack.

The composition of all alloy samples was measured using calibrated EDS (Fig. 5.5), which was calibrated in-chamber with two suitable Ni superalloys. Even though the exact intended compositions were not produced by the cladding process, the alloys were reasonably well distributed within the intended composition space. The Cr contents were 38-40 wt%. The C and Si content was measured to be <0.01 wt% by glow dispersive optical emission spectroscopy on alloys #13, #15 and #20.

Figure 5.5. The measured compositions of the laser cladded alloys. The intended compositions are marked by red circles, each representing two alloys with 0.5 and 2 wt% Ti, respectively.
In order to investigate the rate of hardening, the samples were solution treated at 1100°C for 1 h and quenched in water. Subsequent heat treatments were performed at 800°C and 700°C. The hardness of the samples was measured after water quenching. The results are shown in Fig’s 5.6 and 5.7. Most of the alloys experience a rapid initial hardness increase at 800°C, while 700°C produces a more gradual hardness increase.

As sluggish precipitation hardening was desired, the alloys 11, 12, 13, 14, 21 and 22 marked with arrows in Fig. 5.7 were of special interest due to slow hardening response culminating in high hardness after 81 hrs heat treatment at 700°C.
Micrographs of the laser cladded alloys is shown in Fig’s. 5.8 and 5.9. The dendrite arm distance, which in Fig. 5.8 is measurable as the distance between horizontal formations of $\alpha$-Cr and Nb, was approximately 10 $\mu$m. $\alpha$-Cr was found both as globular particles and, for most samples, elliptical precipitates.
In the shown case of sample #11 (38.4 wt% Cr, 2.1 wt% Nb, 1.8 wt% Ta and 0.6 wt% Ti), heat treatment at 700°C caused the appearance of very small elliptical precipitates, which are visible as a knitting pattern between the original α-Cr particles (Fig. 5.9).

Figure 5.9. BSE image of sample # 11 (38.4 wt% Cr, 2.1 wt% Nb, 1.8 wt% Ta and 0.6 wt% Ti) microstructure, after 1 hour at 1100°C and 81 hrs at 700°C. Dark areas are α-Cr, and white areas are Nb. Fine precipitates form a knitting pattern between the larger α-Cr particles.

The results of the laser cladded alloys confirmed the predicted existence of precipitation hardenable high Cr Ni-based alloys and showed that laser cladding produces a small dendrite arm distance, which limits the degree of segregation. Furthermore, microscopy investigations suggested the appearance of an ordered matrix-coherent precipitate. However, cracking of several alloy samples when sectioned raised concerns about low ductility. For the second alloy development iteration, it was decided to order high purity alloys in powder form for HIP production, in order to obtain production value data on the mechanical properties.

Definition of five alloys for hot isostatic pressing

Compositions of the selected alloy samples which exhibited slow hardness increase (indicated by arrows in Fig. 5.7) are collected in Table 5.1. Considering their very similar hardness increase when heat treated at
700°C, it seems that Nb, Ta and Ti can substitute for each other to a large degree in the role of precipitation hardener.

Table 5.1. Alloys with desirable precipitation hardening rate.

<table>
<thead>
<tr>
<th>Alloy #</th>
<th>C</th>
<th>Si</th>
<th>Nb</th>
<th>Ta</th>
<th>Ti</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>1.8</td>
<td>0.6</td>
<td>0.1</td>
<td>38.4</td>
<td>Bal.</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>2.8</td>
<td>0.5</td>
<td>0.4</td>
<td>38.6</td>
<td>Bal.</td>
</tr>
<tr>
<td>13</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>1.8</td>
<td>0.4</td>
<td>1.7</td>
<td>0.1</td>
<td>39.0</td>
<td>Bal.</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
<td>0.4</td>
<td>1.6</td>
<td>1.1</td>
<td>38.7</td>
<td>Bal.</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>-</td>
<td>3.5</td>
<td>0.6</td>
<td>0.5</td>
<td>0.3</td>
<td>38.9</td>
<td>Bal.</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>37.4</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

At this stage of the alloy development, the only tangible data originated from highly experimental laser cladded alloy samples. Therefore, for prudence, it was decided to focus on Nb as the primary hardening agent, but to maintain a limited Ti content. Ti on its own appeared capable of creating a heat treatment response similar to Nb and Ta, when those two were low (as seen in sample alloy #13 and #14), but there was no time to investigate whether this was due to formation of γ’ or γ’’. The behaviour might differ if the alloy was produced in a less experimental manner. To explore the interaction between Cr and Nb content, the five alloys with compositions given in Fig. 5.10 were ordered in powder form.

Figure 5.10. Compositions and designations of the first five Ni-based P/M alloys ordered. All alloys contained 0.5 wt% Ti.
Sample production and preparation as well as microscopy, mechanical testing and hardness testing of these powder metallurgical alloys is shown in Papers IV and V included in this thesis. TEM established that the alloys were indeed hardened by γ” precipitation. All alloys were precipitation hardenable.

**Definition of the sixth alloy**

The low ductility of some of the first five powder metallurgical alloys caused concern as high ductility is required for the rolling operation, which is part of the exhaust valve spindle production. As welded, Alloy 718 exhibits an elongation of approximately 30% (Source: Special Metals Cooperation). At this stage in the project, it was decided that a minimum of 40% elongation in the solution treated state (1100°C for 1 hour, water quench) should be the target for the sixth alloy, in order to have a wide margin of error. The solution treated state was chosen as reference for the powder metallurgical alloys as the HIP production process, which involves heating to +1000°C, can be perceived as a solution treatment. This microstructural state is also suitable for comparison with calculated equilibrium values, as it is likely to come close to the equilibrium microstructure due to the high diffusion rate at 1100°C. It was desirable to make the alloys calculable. A firm link had to be established between that which could be calculated, being the equilibrium phase composition, and the performance parameters, one such being the elongation in the solution treated state. If Thermo-Calc could predict the alloy microstructures, and if these results could be related to the mechanical properties, Thermo-Calc predictions would be generally applicable for design of the sixth alloy. The numerically calculated weight fractions of α-Cr compared with the solution treated elongations are shown in Fig. 5.11. At the time, the Ni4 database was the only one available.
Figure 5.11. Equilibrium calculation of the weight fraction of α-Cr at 1100°C compared with the solution treated elongation of selected alloys. Thermo-Calc calculations using the Ni4 database.

As only three datapoints were available, the tentative fit was linear. Using the fit from Fig. 5.11 and defining a desired solution treated elongation as 40%, the α-Cr content $x$ at the solution treatment temperature is then

$$40 = 53.375 - 299.61x \quad \Leftrightarrow \quad x = 0.045$$

(5.1)

With Thermo-Calc, a predicted relation was found between the Nb content of the alloy, and the equilibrium content of α-Cr at the solution treatment temperature (Fig. 5.12). With the allowable weight fraction of α-Cr being 0.045 from Eq. (5.1), the weight fraction of Nb was 0.035, or 3.5 wt%.
A Nb content of 3.5 wt% is the same as that of Alloy 625, which does experience precipitation hardening, albeit much delayed. None of the related laser cladded alloys had a delayed response, so accordingly, a 6th Ni-based powder metallurgical alloy was ordered, alloyed with 40 wt% Cr, 3.5 wt% Nb and 0.5 wt% Ti. This alloy was HIP’d, heat treated and characterized in the same manner as the first five alloys, and was found to experience precipitation hardening, although with a relatively low final hardness (Fig. 5.13).
The tensile properties were measured, and are for the sake of comparison shown with the first five powder metallurgical alloys in Table 5.2. It should be noted that in the design phase, the desired elongation in the solution treated state of Ni40Cr3.5Nb was 40%. After alloy production it was measured to be 40.4%.

### Table 5.2. Mechanical properties of the PM alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution treated (1100°C x 1h)</th>
<th>Aged (700°C x 9h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>436</td>
<td>840</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>443</td>
<td>874</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>533</td>
<td>939</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>646</td>
<td>1059</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As the current state of the art uses alloy 718 as exhaust valve seat coating, it is natural to compare that with the mechanical properties of Ni40Cr3.5Nb (Table 5.3). The mechanical strength and ductility of Ni40Cr3.5Nb is consistently higher than that of Alloy 718, regardless of heat treatment state.

### Table 5.3. Comparison of mechanical properties of Ni40Cr3.5Nb and Alloy 718. Source of alloy 718 properties is the Special Metals Corporation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ni40Cr3.5Nb (HIPd)</th>
<th>Alloy 718 (welded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield strength (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As produced</td>
<td>563</td>
<td>570</td>
</tr>
<tr>
<td>Solution treated</td>
<td>533</td>
<td>-</td>
</tr>
<tr>
<td>Precipitation hardened</td>
<td>990</td>
<td>970</td>
</tr>
<tr>
<td>As produced</td>
<td>972</td>
<td>850</td>
</tr>
<tr>
<td>Solution treated</td>
<td>939</td>
<td>-</td>
</tr>
<tr>
<td>Precipitation hardened</td>
<td>1227</td>
<td>1200</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As produced</td>
<td>39.3</td>
<td>30</td>
</tr>
<tr>
<td>Solution treated</td>
<td>40.4</td>
<td>-</td>
</tr>
<tr>
<td>Precipitation hardened</td>
<td>20.5</td>
<td>18</td>
</tr>
</tbody>
</table>

It appears that the mechanical properties of Ni40Cr3.5Nb are able to compete with Alloy 718, at least in the HIP’d version. To answer the question whether this was indeed the case in reality, full scale prototypes were needed.
Production and service testing of HIP spindles with Ni40Cr3.5Nb alloy seats

Laser cladding and plasma tungsten arc welding were tested as application methods for a Ni40Cr3.5Nb spindle seat. The results from heat treatment of laser cladded Ni40Cr3.5Nb seats showed that Alloy 718 level hardnesses were obtainable with a modified heat treatment. This work, which also established the appropriate heat treatment for spindles with Ni40Cr3.5Nb seats, is shown in MAN Diesel & Turbo reports N9177 and N9278 which are attached as appendix. Using these results, four HIP compound spindles were produced according to the DuraSpindle production process with the material selections shown in Fig. 5.14. Three of these prototype spindles were put into service testing by May 2013.

Figure 5.14. The HIP compound spindle with the Ni40Cr3.5Nb seat.
Papers

Six papers were produced during the course of this project. They generally divide into two categories; hot corrosion, and alloy development. Within each category, the papers are given in the order of production.

Hot corrosion papers (I-III)

In order to gain industry applicable data on the corrosion performance of combustion chamber alloys, an in-situ corrosion test of relevant alloys exhaust valve spindle alloys, both commercial and experimental, was initiated. Papers I and II describe this setup and the results.

**Paper I** provides a basic description of the corrosion morphology and documents the extent of the sulphidized zone within each alloy. Alloy 657 (Ni49Cr1.5Nb) is documented as most corrosion resistant compared to the other tested alloys. The superior corrosion performance of Nimonic 80A compared to Alloy 718, as well as to several other alloys with higher Cr contents, is also established.

**Paper II** applies Thermo-Calc calculations to calculate the equilibrium oxide scale composition of each alloy in the in-situ test. A positive correlation is found between the predicted stability range of (Cr,Al)₂O₃ as defined by pO₂, and the material loss. Specifically, the poor hot corrosion performance of Alloy 718 is attributed to the high Fe content, which stabilizes a nonprotective (Ni,Fe)Cr₂O₄ type oxide. On the spindle bottom, a band of combustion products were found covering a concentric area midways between the center and the rim. In that area, the material loss was significantly higher than at other positions. With an increasing temperature gradient going from the rim to the center, this suggests that a critical temperature interval exists in which combustion products deposit and melt, causing hot corrosion. Following this theory, combustion products do not condense on the spindle center as the metal temperature is above the dew point. Consequently, the corrosion rate is low for the rim of the spindle bottom (T < melting temperature of
products), high for a concentric band midways (T > melting temperature of salt), and low for the center of the spindle bottom (T > dew point of combustion products).

**Paper III** contains thermobalance exposures of the six powder alloys designed in this project, and of Nimonic 80A for reference. In-situ testing is costly and time consuming, and therefore it made sense to recreate at least some of the environment the alloys experience during service testing. All alloys were exposed at 650 and 700°C, with and without V₂O₅ deposit. For the HIP alloys, a higher Cr content meant a lower weight gain when exposed with V₂O₅ deposit, and for the alloys with 35 wt% Cr as well as for Ni40Cr3.5Nb, breakaway corrosion occurred. In all comparable cases Nimonic 80A had a stable, but higher weight gain. As Nimonic 80A is currently the most high temperature resistant exhaust valve spindle alloy, a lower weight gain as that found for Ni40Cr3.5Nb indicates that it will be more corrosion resistant in service than Nimonic 80A, and thereby also Alloy 718. The actual implication of the breakaway corrosion observed in the laboratory study is uncertain, as it may also be related to the experimental conditions. Also exposed at 700°C was Nimonic 80A with a mixed deposit of V₂O₅ and MgO, which caused an extraordinarily low weight gain. This is attributed to the formation of a diffusion limiting Mg vanadate.

**Alloy development papers (IV-VI)**

For the initial five powder alloys the question was two-fold; were the mechanical properties comparable to Alloy 718, and were the phase compositions and thereby the microstructures as predicted by Thermo-Calc. If these two conditions were met, Thermo-Calc predictions were suitable for the design of the sixth alloy. Quantification of phase composition was primarily performed on BSEM images, and it became apparent when producing the results for Paper V, that the sample preparation used in Paper IV had been insufficient to obtain high-quality data. Table 6.1 collects the experimental conditions followed in the papers.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Final polish step</th>
<th>Imaging</th>
<th>Investigated area (mm²)</th>
<th>Quantification software</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper IV</td>
<td>1 µm diamonds</td>
<td>SEM</td>
<td>0.083</td>
<td>ImagePro Plus</td>
</tr>
<tr>
<td>Paper V</td>
<td>Colloidal silica</td>
<td>FEG-SEM</td>
<td>0.180</td>
<td>Matlab</td>
</tr>
</tbody>
</table>
Table 6.2 compares the measured α-Cr fractions. The difference is most pronounced in the heat treated condition, where the fractions measured in Paper IV are generally higher than those obtained for Paper V. The overestimation of α-Cr is likely the result of γ-Ni precipitates within α-Cr which were not detected.

Table 6.2. Experimental α-Cr fractions measured by microscopy methods.

<table>
<thead>
<tr>
<th>Alloy \ Paper</th>
<th>α-Cr volume fraction after 1100°C x 1 h (vol %)</th>
<th>α-Cr volume fraction after 1100°C x 1 h + 700 x 9 h (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Paper IV</td>
<td>Paper V</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>20</td>
<td>23</td>
</tr>
</tbody>
</table>

Paper IV documents the microstructure and mechanical properties of the five first powder alloys designed in this project. The presence of γ'' is confirmed by TEM, and is shown to cause precipitation hardening. The kinetic of precipitation hardening is faster than that observed for Alloy 718.

Paper V documents the volume fractions, number densities and mean radii of α-Cr and δ particles for all six alloys designed in this project. This is documented for a number of heat treatments at both 650 and 700°C for up to 1656 hrs. Also shown is the quantification of γ'' precipitates. The α-Cr and δ volume fractions of the long term heat treated alloy are below the predicted equilibrium values. The platelike morphology of α-Cr is shown to be a sandwich structure of γ'' surrounded with α-Cr.

Paper VI outlines the total extent of the work done to validate the design and material selection of the new exhaust valve spindle, and as such contains selected data from Papers I-V. Novel to this project is the documentation of the expansion coefficient, microstructure and some high temperature properties of Ni49Cr1.5Nb. Ni2Cr ordering is found to take place during heat treatment at 700°C, causing the alloy to contract. The bonding zone between the stainless steel forming the bulk of the exhaust valve spindle and the high Cr Ni-based alloys (Ni49Cr1.5Nb and Ni40Cr3.5Nb) is protected from carbide precipitation by an AISI 316L buffer layer, and the required production considerations are shown. Finally some FEM simulations are shown on the residual stress within the spindle during operation.
Conclusion

The objective of the present project was to increase the high temperature capability of a well known two-stroke engine component, the exhaust valve spindle, by materials development. Specifically, the current allowable service temperatures of the spindle bottom and the spindle seat should be raised a substantial 50°C.

The environment which the spindle is exposed to contains S and V, which at high temperature causes an aggressive form of high temperature corrosion known as hot corrosion. This type of corrosion has been investigated by prior researchers, and NiCr alloys have been found to be the optimal choice for corrosion resistance. The half and half alloy, Ni50Cr, has been shown to be superior to other alloys. The relevance of these findings is supported by an in-situ corrosion test which has tested Ni50Cr and other NiCr alloys. The in-situ test was performed using an experimental exhaust valve spindle prototype, which was mounted in an actual engine. Laboratory hot corrosion trials in this project on relevant alloys confirmed that Cr was beneficial for the corrosion resistance.

NiCr alloys with Cr contents above 25 wt% suffer from reduced ductility due to a high ductile to brittle transition temperature of the Cr rich phase, α-Cr. A commercially available modified Ni50Cr alloy, named Alloy 657, which contains 1.5 wt% Nb, has been shown to avoid brittleness, and as such seems suitable for application on the exhaust valve spindle bottom. The results from the in-situ corrosion test indicate that Alloy 657 will fulfill the target of an 50°C increased allowable spindle bottom temperature.

For the spindle seat, a number of demands were made for the alloy. It should be ductile as applied, in order to facilitate a deformation hardening process, and it should be precipitation hardenable, to reach hardnesses high enough to withstand the wear situation of the seat. Numerical thermodynamic
calculations indicated that such an alloy could be produced by modifying the composition of the current spindle seat alloy, Alloy 718. An initial screening of the relevant composition space resulted in 16 alloys produced by experimental laser cladding. Heat treatment of these alloys led to a new iteration with five alloys, which finally led to a sixth alloy, Ni40Cr3.5Nb. An extensive investigation of the microstructure and heat treatment response of these alloys was performed in this project. Compared with Alloy 718, Ni40Cr3.5Nb contains twice the amount of Cr, which is expected to increase the corrosion resistance significantly. The high Cr content gives Ni40Cr3.5Nb a microstructure with α-Cr particles, which are shown not to embrittles the alloy. This is most likely due to a strict limit on the N content, which is supported by alloying with Nb, which acts as an N-getter. Ni40Cr3.5Nb is ductile as produced, while it can be precipitation hardened to a hardness which is suitable for the spindle seat application. By May 2013, three prototype spindles with Ni40Cr3.5Nb spindle seats and Alloy 657 spindle bottoms entered service, and results from these tests will serve to verify whether Ni40Cr3.5Nb is suitable for service at 550°C, as the corrosion tests indicated.

Outlook

During the course of this project, a fitted relation was found for the solution treated elongation of powder metallurgical NiCr alloys with 35-45 wt% Cr, and 4-6 wt% Nb. This relation depends on predictions on the microstructure of the alloy, which are obtained from computational thermodynamics. The validation of this fitted relation was impressive, with a predicted 40% elongation, and a measured elongation of 40.4% for a novel alloy. It would be natural to explore such simple relations further, and to seek to establish a firm link between the calculable equilibrium microstructure and the applicable mechanical properties.

The in-situ corrosion test performed using an experimental alloy has been duplicated with the three prototype spindles with Ni40Cr3.5Nb seats. Two of these spindles contain alloy samples, the corrosion performance of which can be ranked after the spindles have been removed from service. 14 alloys are included in the test. The results from this test will likely shed further light on the effect of alloy composition
on corrosion resistance, and it would be natural to investigate if the ranking of the alloys matches that which has been produced in the laboratory with hot corrosion testing during this project.

Currently this spindle of the future is produced by hot isostatic pressing, which is a costly method. However during this project, laser and plasma cladding has been attempted, which would lower the cost of applying Ni40Cr3.5Nb significantly.
In-situ hot corrosion testing of candidate materials for exhaust valve spindles


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**Danish Technical University, Lyngby, Denmark

Abstract
The two stroke diesel engine has been continually optimized since its invention more than a century ago. One of the ways to increase fuel efficiency further is to increase the compression ratio, and thereby the temperature in the combustion chamber. Because of this, and the composition of the fuel used, exhaust valve spindles in marine diesel engines are subjected to high temperatures and stresses as well as molten salt induced corrosion. To investigate candidate materials for future designs which will involve the HIP process, a spindle with Ni superalloy material samples inserted in a HIPd Ni49Cr1Nb matrix has been produced, and put into service for 2,200 hours allowing a unique in-situ corrosion test. 10 high Cr alloys have been tested this way. The corrosion appearance is found to be a factor of not only the chemical composition but also the production method. HIPd material with high Cr content and low content of Fe and Mo is found to be the best choice for hot corrosion resistance.

Keywords
Corrosion test, HIP, exhaust valve spindle, hot corrosion

Background
Because of its fuel flexibility and the low operating RPM, the direct coupled two stroke diesel engine is the propulsion method of choice for most large marine vessels. The fuel used is mostly of the heavy fuel type, which has a high content of none-hydrocarbon compounds and elements. Upon combustion, these compounds and elements condense onto the walls of the combustion chamber and form molten salts if the surface temperature exceeds 600°C. Generally, the corrosion rate is controlled by actively cooling most of the combustion chamber surfaces, keeping them well below this limit. However, active cooling is currently not an economically feasible method to protect the exhaust valve spindle. This component has traditionally been considered a consumable, and is usually replaced or reconditioned every 3-4 years even when constructed from a costly high-Cr Ni-base superalloy. Compared to an expected engine lifespan of 30-40 years this is a high rate.

A result of fuel efficiency improvement through process optimization is a hotter combustion chamber. This is reaching a point where spindle life is unacceptably reduced and too sensitive to normal operating fluctuations. Accordingly an urgent need has arisen for a more appropriate material and production method, to manufacture a spindle with improved high temperature capability. In order to decrease the impact of the fluctuating Ni price on the production costs, there is also a desire to reduce the amount of Ni in the spindle design.

Materials for exhaust valve spindles
Heavy fuel oil, as used in large bore two-stroke engines, consists not only of hydrocarbons, but contains also other elements and compounds as a residue from crude oil and refinery processes. Some of these elements condense onto the exhaust valve spindle during engine operation. By chemical analysis of solid deposits on the spindle surface, Umland and Ritzkopf found the following elements, arranged roughly in descending order of quantity present: V, S, Ca, Na, Zn, Fe, Cr, Ni, Co, P, Pb, Ba, K, Si and Cu. Kvernes et al identified the deposits as
mainly consisting of sodium sulphates and sodium vanadates. Kerby and Wilson\(^3\) found eutectic melting points for the compounds present in some cases to be below 600°C. This means that molten salts can occur at spindle operating temperatures, which locally can exceed 600°C. Molten salts containing V are very aggressive towards metals, and in order to protect against this type of corrosion, Nicholls and Stephenson\(^4\) conducted a comprehensive experimental study of candidate spindle materials. For Ni based alloys with low contents of Co, Mo and W a strong positive correlation was found between the corrosion resistance and the Cr content. The hot corrosion dependency on Cr is explained by Rapp\(^5\) as being a consequence of the solubility of Cr\(_2\)O\(_3\) in the salt melt. This means that the higher the Cr content, the better is the corrosion resistance. However the manufacturing of an exhaust valve spindle with a content of more than 20 wt\% Cr is not straightforward, as these alloys produced by welding or casting are generally brittle and essentially unforgeable. The brittleness stems from the interconnection of large segregated BCC Cr particles.

A possible solution is being offered by the Hot Isostatic Pressing (HIP) process, because it allows the production of very homogeneous materials with practically no segregation. It also allows the joining of materials which are normally unweldable. To explore the possibilities for the exhaust valve spindle, a number of materials have been in situ hot corrosion tested by taking full advantage of the design flexibility HIP’ing offers.

**Methods and materials**

A HIP’d compound exhaust valve spindle for a two-stroke engine with a cylinder diameter of 900 mm was produced. It was HIP’d at 1050°C for 3 hours. The corresponding spindle disk diameter is 490 mm. The design of the spindle is shown in **Figure 1**. In the bottom of the spindle 54 Ø11 samples of 9 different Ni based alloys were embedded in a P/M matrix consisting of Ni\(_{49}\)Cr\(_{1}\)Nb, thereby making an in-situ corrosion test of, simultaneously, 10 materials possible. Each material was arranged in a straight line radiating out from the spindle center, so as to evaluate the performance over the entire diameter. The fuel injector material NiCr\(_{22}\)WAl was included for comparative purposes. The remaining samples were placed at either 6 or 7 positions.

![Figure 1](image_url). The design of the compound exhaust valve spindle with corrosion sample inserts.
The material inserts are all Ni based superalloys with high contents of Cr, with compositions shown in Table 1. The production method is specified with suffixes W and F for welding and forging, respectively. No suffix means the material was HIP’d. The materials Mix25:75 and Mix50:50 were created as a HIP’d mixture of metal powders.

The spindle was put into service on a seagoing vessel with special fuel injection valves fitted, which caused an increased temperature of the spindle bottom, raising the maximum temperature from 600 to 670°C. Figure 2 shows an FEM mapping of the spindle temperature.

Table 1. Composition of material samples in wt% as specified by material certificates. The composition of the mixed metal powder samples Mix25:75 and Mix50:50 is calculated as a weighted average of the two powders.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>W</th>
<th>Ni</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni49Cr1Nb</td>
<td>0.01</td>
<td>0.05</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
<td>bal</td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>IN625F</td>
<td>0.03</td>
<td>0.21</td>
<td>22</td>
<td>4.08</td>
<td>8.7</td>
<td>0.29</td>
<td>3.61</td>
<td>0.22</td>
<td>bal</td>
<td></td>
<td>Forged</td>
</tr>
<tr>
<td>IN625W</td>
<td>0.01</td>
<td>-</td>
<td>22</td>
<td>0.48</td>
<td>11.4</td>
<td>0.05</td>
<td>3.22</td>
<td>0.09</td>
<td>bal</td>
<td></td>
<td>Welded</td>
</tr>
<tr>
<td>IN686F</td>
<td>0.01</td>
<td>0.1</td>
<td>17</td>
<td>0.15</td>
<td>16.7</td>
<td>0.11</td>
<td>0.03</td>
<td>0.29</td>
<td></td>
<td>4</td>
<td>bal</td>
</tr>
<tr>
<td>IN686W</td>
<td>0.01</td>
<td>0.3</td>
<td>19</td>
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<td>18.3</td>
<td>0.05</td>
<td>0.14</td>
<td>0.09</td>
<td></td>
<td>bal</td>
<td>Welded</td>
</tr>
<tr>
<td>IN718F</td>
<td>0.03</td>
<td>0.14</td>
<td>19</td>
<td>17.3</td>
<td>3.0</td>
<td>0.94</td>
<td>5.21</td>
<td>0.49</td>
<td></td>
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<td>Forged</td>
</tr>
<tr>
<td>Mix25:75</td>
<td>0.02</td>
<td>0.31</td>
<td>29</td>
<td>3.23</td>
<td>6.8</td>
<td>0.00</td>
<td>2.83</td>
<td>0.00</td>
<td></td>
<td>bal</td>
<td>25% Ni49Cr1Nb 75% IN625</td>
</tr>
<tr>
<td>Mix50:50</td>
<td>0.02</td>
<td>0.23</td>
<td>35</td>
<td>2.15</td>
<td>4.5</td>
<td>0.00</td>
<td>2.23</td>
<td>0.00</td>
<td></td>
<td>bal</td>
<td>50% Ni49Cr1Nb 50% IN625</td>
</tr>
<tr>
<td>NiCr22WAl</td>
<td>0.42</td>
<td>0.1</td>
<td>20</td>
<td>0.21</td>
<td>0.1</td>
<td>0.06</td>
<td>6.07</td>
<td>6</td>
<td>bal</td>
<td></td>
<td>Designed custom alloy</td>
</tr>
<tr>
<td>Nim80AF</td>
<td>0.06</td>
<td>0.08</td>
<td>19</td>
<td>0.22</td>
<td></td>
<td>2.41</td>
<td>1.7</td>
<td></td>
<td>bal</td>
<td></td>
<td>Forged</td>
</tr>
</tbody>
</table>

Figure 2. (Left) The hottest surfaces of the combustion chamber are marked with red. In this work the spindle bottom is treated. (Right) An FEM contour map of temperatures in °C. Because the cylinder is fitted with off-spec fuel injection valves, the spindle bottom temperature is increased to reflect a worst-case scenario.
Results and discussion

After 2223 hours of service the spindle was extracted and investigated. Visual inspection showed that all material inserts were heavily corroded and recessed below the surface of the matrix. A circular band of porous combustion products adhered to the surface, covering positions Ø220 and Ø280. As the band was evenly distributed regardless of substrate material, it is thought to consist primarily of condensed exhaust species, and not corrosion products. The center of the spindle was not corroded, as the marks from the final machining were still visible. Using this as guidance, the material loss of Ni49Cr1Nb across the spindle bottom could be established. By adding this to the measured hole depths, the true corrosion depth was found for each material at each position. The corrosion data are shown in **Figure 3**. The middle positions at Ø220 and Ø280 are most corroded, which suggests that not only the bulk spindle temperature shown in **Figure 2** decides the corrosion rate. Alloys IN718F and Ni49Cr1Nb represent maximum and minimum corrosion, respectively.

**Figure 3.** Corrosion depth compensated for the loss of Ni49Cr1Nb at same radial position.

The center of the spindle was not corroded, as the marks from the final machining were still visible. Using this as guidance, the material loss of Ni49Cr1Nb across the spindle bottom could be established. By adding this to the measured hole depths, the true corrosion depth was found for each material at each position. The corrosion data are shown in **Figure 3**. The middle positions at Ø220 and Ø280 are most corroded, which suggests that not only the bulk spindle temperature shown in **Figure 2** decides the corrosion rate. Alloys IN718F and Ni49Cr1Nb represent maximum and minimum corrosion, respectively.

**Figure 4.** Cross section of IN625F material insert after 2223 hours of service. (Left) Overview. The surface has a wavy macro structure with peaks and valleys. This is found for all material inserts. (Right) Magnification of a peak. A sulphidized layer is found to be thickest at the peaks, but present throughout the surface, which is covered by an oxide layer of varying thickness.
The metallurgical cross sections shown in Figure 4 have a common appearance with a wavy macro structure of peaks and sharp valleys. An outer oxide layer consisting of V- and Cr-oxide was found on all specimens. The presence of V indicates the interaction with solid deposits on the spindle surface. Below the outer oxide a a transition layer, which is thickest at the peaks of the macro structure is found. This layer is depleted of Cr that has diffused out to the oxide layer and also contains a large number of primarily Cr sulphides. The appearance of the sulphidised layer is consistent with the sulphidation phenomenon described in literature as a possible mechanism of corrosion. Only IN686F differed from this mechanism, here the high combined content of W and Mo promoted the formation of an intermetallic phase below the outer oxide, as shown in Figure 5. Very limited internal sulphidation was observed below this layer indicating a low permeability of S.

Corrosion rates, calculated from the measured corrosion depths, are compared with the maximum sulphidised layer thickness in Figure 6. All HIP’d materials have a low corrosion rate and similar low sulphidised layer thicknesses. In this group as well as overall, Ni49Cr1Nb has the lowest corrosion rate. A thin outer oxide was observed on this alloy combined with very limited Cr depletion and sulphidation of the underlying layer. It is believed that the good corrosion properties are a result of the high Cr content. IN718F has the highest corrosion rate measured. This suggests that a given high content of Cr is less effective as corrosion protection if Fe is present in greater amounts. Likewise all materials containing 7 wt% or more Mo have comparably high corrosion rates.

![Figure 5. Cross sections of IN686W and IN686F material inserts at position Ø280. Investigations of all other materials but IN686F show results with similar morphology as for IN686W with an outer V,Cr-oxide followed by a Cr-depleted (as shown by EDS map) transition layer of varying thickness containing sulphides. The cross section appearance of IN686F is unique, as it has only a very thin transition layer. The high resolution image (right) shows the presence of an intermetallic Mo-,W- rich layer forming beneath the oxide (EDS: 27 wt% Mo, 6 wt%W, bal. Ni at arrow). The lack of internal sulphidation indicates that this intermetallic layer has a low permeability of S.](image-url)
In-situ hot corrosion testing of candidate materials for exhaust valve spindles

The results from Nim80AF and IN686F suggest that the sulfidized layer thickness is not related to the corrosion rate. For all HIP’d materials, the thickness is moderate. The high combined content of Mo and W in IN686F results in very little internal sulphidation because of the formation of a Mo, W-rich barrier layer but the alloy has an excessive corrosion rate compared to HIP materials.

Figure 6. The corrosion rate measured over 2223 h of service time. The sulphidised layer for all HIP’d materials is moderate, while it for all others except IN686F is thicker. There does not seem to be any relation between the sulphidised layer thickness and the corrosion rate.

Conclusion

Parts of the combustion chamber environment in the two-stroke heavy fuel diesel engine is highly corrosive because of molten salts. In the present work, a number of conventional and experimental Ni based materials have been evaluated in a unique in-situ corrosion test, made possible by the HIP production process. The best corrosion properties were obtained for the high Cr Ni49CrNb HIP material. This alloy has the lowest corrosion rate combined with very limited internal sulphidation. Excellent sulphidation resistance was observed for the IN686F alloy with a high combined content of Mo and W, however the corrosion rate of this alloy is too high to compete with the high Cr HIP materials. Chemical composition of the material samples is established as important, with the results confirming prior knowledge of the importance of high Cr content to the hot corrosion resistance. Fe and Mo are both established as having a detrimental effect when substituting Ni.

References


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In-service Hot Corrosion Testing of Ni-based Superalloys in a Two Stroke Heavy Fuel Diesel Engine

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Abstract. Most large marine vessels are powered by a two stroke heavy fuel diesel engine. Inside the combustion chamber of the engine, the compounds V\textsubscript{2}O\textsubscript{5} and Na\textsubscript{2}SO\textsubscript{4} are formed and deposited onto available surfaces as a consequence of the high S and V content of the fuel. On high temperature parts, such as the exhaust valve spindle these deposited salts melt and cause hot corrosion. In this study, the bottom of an exhaust valve spindle was used as in-situ corrosion test by embedding various alloy samples in P/M Ni\textsubscript{49}Cr\textsubscript{1}Nb. In this way, 10 Ni based superalloys were exposed for 2223 hours in service. Comparison of the corrosion performance of the alloys with thermodynamic calculations of the composition of the forming oxide layer on the alloys show a clear qualitative relation between the calculated amount of Cr\textsubscript{2}O\textsubscript{3} and the corrosion performance.

Keywords: Hot corrosion, oxides, thermodynamic calculation

INTRODUCTION

Because of its high reliability and its great tolerance towards fuel quality, the direct coupled two stroke diesel engine is the propulsion method of choice for most large marine vessels. The fuel used is known as heavy fuel, which contains up to 4.5\% S and 0.0450 \% V, along with a number of other contaminants\textsuperscript{1}. During combustion, some of these contaminants form solid compounds, which are deposited onto the combustion chamber surfaces. This is also the case for the exhaust valve spindle, the bottom of which forms the roof of the combustion chamber. Holmes et al\textsuperscript{2} examined the layer formed on the exhaust valve spindle and found the composition shown in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>V\textsubscript{2}O\textsubscript{5}</th>
<th>Na\textsubscript{2}O</th>
<th>CaO</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>NiO</th>
<th>SO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>38-75</td>
<td>4-11</td>
<td>4-9</td>
<td>1-10</td>
<td>5-11</td>
<td>11-22</td>
</tr>
</tbody>
</table>

Kvernes et al\textsuperscript{3} found solidified droplets of Na\textsubscript{2}SO\textsubscript{4} on the spindle after service. Molten salt on a metal surface causes hot corrosion, a phenomenon originally discovered on gas turbine blades, which were exposed to molten Na\textsubscript{2}SO\textsubscript{4}. Stringer\textsuperscript{4} describes Type I hot corrosion as a broad front corrosion occurring at temperatures of 800-950°C where a layer of internal sulphides (sulphidation) is present. Type II is characterized by pitting attack with little or no sulphidation for the temperature range 650-775°C\textsuperscript{1}. The Cr content of the alloy influences the resistance against hot corrosion of both type I and type II.

Sulphidation is a corrosion mechanism proposed by Bornstein and Decrescente\textsuperscript{5,6} and further elaborated by Goebel and Pettit\textsuperscript{7} as well as Stringer\textsuperscript{4}. By this mechanism, formation of metal sulphides formed by S diffusing into

\textsuperscript{1} In practice the temperature range where hot corrosion of type II occurs has been shown to be much broader.
the metal lower the S activity in the salt melt and thereby increase the O activity to a level where it oxidizes the metal oxide film (basic dissolution) to an anionic species (e.g. $\text{Cr}_2\text{O}_3 + \text{O}^{2-} = \text{Cr}_2\text{O}_4^{2-}$), which is then transported towards the gas-melt interface where the lower O activity reduces this species to metal oxide. The result is a porous metal oxide film.

The deposited layer does not cause corrosion problems for the majority of the combustion chamber surfaces, as they are actively cooled. However the exhaust valve spindle is not cooled and the bottom of it experiences a metal temperature exceeding 600°C. Hot corrosion is also a problem for heat exchangers in the power industry. Jahn exposed various Ni based alloys in an oil fired boiler and found that a critical temperature interval exists (650-750°C) in which the corrosion rate of all tested alloys is accelerated. He concluded that the accelerated corrosion was a direct consequence of $\text{V}_2\text{O}_5$ deposition, and that the diminished corrosion at higher temperatures was due to the volatility of $\text{V}_2\text{O}_5$. He also found that Si alloying increases the corrosion resistance. Swaminathan et al deposited $\text{V}_2\text{O}_5$ on Ni base superalloys and also found heavy corrosion at 700°C whereas no influence from $\text{V}_2\text{O}_5$ deposition could be found at 650°C. The phase diagram for $\text{V}_2\text{O}_5$-$\text{Cr}_2\text{O}_3$ presented by Kerby and Wilson shown in Figure 1 indicates that a liquid phase forms at temperatures higher than 655°C. As the salt contains other components than $\text{V}_2\text{O}_5$, the lowest melting temperature could be lower than in Figure 1. To control the corrosion rate, the most thermally stressed spindles are forged from the Ni based superalloy Nimonic 80A, which contains 19 wt% Cr. Inconel 718 which also contains 19 wt% Cr has been used as hardfacing layer on the spindle seat. Current engine development is leading to an increased combustion chamber temperature, which challenges the hot corrosion resistance of these alloys. Nicholls executed a laboratory corrosion test study on a wide range of exhaust valve materials and coatings. He found that the Cr content of the alloys is important, but also that some effects are not accounted for, such as the wide performance spread between Nimonic 80A and Inconel 718 shown in Figure 1. The high importance of Cr content is thought to be due to the formation of $\text{Cr}_2\text{O}_3$. An explanation for the superior hot corrosion resistance of $\text{Cr}_2\text{O}_3$ forming alloys was proposed by Rapp, who found that the dominant basic oxide dissolution reaction produces $\text{CrO}_4^{2-}$, which reduces to $\text{Cr}_2\text{O}_3$ at low oxygen potentials like those found at flaws and cracks in the oxide film closest to the substrate, thus producing a “self-healing” effect. It appears likely that the corrosion taking place on the spindle during service is a combination of sulphidation, which depletes Cr from the Ni matrix, and oxide fluxing caused by molten salts on the surface.

FIGURE 1. (a) The phase diagram for $\text{V}_2\text{O}_5$-$\text{Cr}_2\text{O}_3$ presented by Kerby and Wilson. A liquid phase forms at temperatures higher than 655°C. (b) Laboratory study performed by Nicholls. For the Cr content of 19-20 wt%, Nimonic 80A suffers half the material loss of Inconel 718.
Oxide scale composition

The oxide scale forms as a reaction product between the metal and the atmosphere and preferably acts as a barrier for further oxidation or corrosion attack. The alloy composition, the exposure atmosphere, in particular the partial pressure of oxygen (pO\textsubscript{2}) and the temperature affect the oxide layer composition. For binary Ni20Cr alloys, three phases are expected to form, Cr\textsubscript{2}O\textsubscript{3} (Corundum), NiO (Halite) and NiCr\textsubscript{2}O\textsubscript{4}, (Spinel), as found by Giggins and Pettit\textsuperscript{13}. The most stable oxide, Cr\textsubscript{2}O\textsubscript{3}, is located closest to the metal, as it forms at the lowest (equivalent) partial pressure of oxygen. Elevated temperature oxidation tests with Nimonic 80A and Inconel 718 have shown that the oxide scale composition is influenced by the alloy composition. Ingo et al\textsuperscript{14} exposed Nimonic 80A to atmospheric air at 850°C and found an oxide consisting primarily of Cr\textsubscript{2}O\textsubscript{3} with some TiO\textsubscript{2}. Similar treatment of Inconel 718 performed by Delaunay et al\textsuperscript{15} caused formation of a Spinel phase along with Cr\textsubscript{2}O\textsubscript{3}. It appears likely that the hot corrosion resistance of these alloys is related to the oxide scale composition and their effectiveness as a barrier for continued oxidation.

EXPERIMENTAL PROCEDURES

An exhaust valve spindle for a marine two-stroke engine with a cylinder diameter of 900 mm was produced according to the layout shown in Figure 3.

![Figure 3](image)

**FIGURE 3.** The test setup with the alloy samples embedded in the bottom of the test spindle. Not shown are the guide vanes fitted on the spindle shaft which cause a spindle rotation of 2-3° for every combustion cycle. This ensures leveling out wear of the spindle.

In the bottom of the spindle 54 samples of 9 different Ni based alloys of dimension Ø11 were embedded in a P/M matrix consisting of Ni49Cr1Nb. The composition of the tested alloys is shown in Table 2. Common for the alloys was that they contained 17 wt% Cr or more. Some alloys were present in both a welded (“W”) and a forged (“F”) state. Samples were positioned at radial positions Ø40 (center), Ø100, Ø160, Ø220, Ø280, Ø340 and Ø400 mm. Some samples were not placed at position Ø40, and due to practical reasons during spindle production NiCr22WAl was not placed on positions Ø280, Ø340 and Ø400. After hot isostatic pressing, the spindle was put into active service in the engine of an ocean sailing vessel for a total of 2223 h. In order to establish a worst case the cylinder was fitted with non-optimal fuel atomizers, which are known to increase the temperature experienced by the spindle bottom.
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After the test period the spindle was extracted and inspected. Material loss was quantified by measuring the hole depth and compensating for the loss of the surrounding Ni49Cr1Nb. This correction was possible, because Ni49Cr1Nb was not corroded to any measurable degree in the center and perimeter of the spindle bottom. On those positions, turning marks were still visible, showing the original level of the machined surface. Using this reference the material loss of Ni49Cr1Nb could be measured at the intermediate positions. Microstructural cross sections were made of IN718F and Nim80AF, by standard metallographical techniques and investigated with scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

RESULTS

Solidified particles covered positions Ø220 and Ø280 on the spindle bottom surface after test, indicating that hot corrosion has occurred at these locations. These are shown in Figure 4, which also shows the material loss of IN718F, which is measurable in the mm scale.

![FIGURE 4. The spindle bottom after test. IN718F was severely corroded, especially at positions Ø220 and Ø280 which were covered with solidified particles.](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>W</th>
<th>Ni</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni49Cr1Nb</td>
<td>0.01</td>
<td>0.05</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>bal</td>
<td>P/M alloy</td>
</tr>
<tr>
<td>IN625F</td>
<td>0.03</td>
<td>0.21</td>
<td>22</td>
<td>4.1</td>
<td>8.7</td>
<td>0.3</td>
<td>3.6</td>
<td>0.2</td>
<td>-</td>
<td>bal</td>
<td>Forged</td>
</tr>
<tr>
<td>IN625W</td>
<td>0.01</td>
<td>-</td>
<td>22</td>
<td>0.5</td>
<td>11.4</td>
<td>0.1</td>
<td>3.2</td>
<td>0.1</td>
<td>-</td>
<td>bal</td>
<td>Welded</td>
</tr>
<tr>
<td>IN686F</td>
<td>0.01</td>
<td>0.1</td>
<td>17</td>
<td>0.2</td>
<td>16.7</td>
<td>0.1</td>
<td>0.0</td>
<td>0.3</td>
<td>4</td>
<td>bal</td>
<td>Forged</td>
</tr>
<tr>
<td>IN686W</td>
<td>0.01</td>
<td>0.3</td>
<td>19</td>
<td>2.1</td>
<td>18.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>bal</td>
<td>Welded</td>
</tr>
<tr>
<td>IN718F</td>
<td>0.03</td>
<td>0.14</td>
<td>19</td>
<td>17.3</td>
<td>3.0</td>
<td>0.9</td>
<td>5.2</td>
<td>0.5</td>
<td>-</td>
<td>bal</td>
<td>Forged</td>
</tr>
<tr>
<td>Mix25:75</td>
<td>0.02</td>
<td>0.31</td>
<td>29</td>
<td>3.2</td>
<td>6.8</td>
<td>0.0</td>
<td>2.8</td>
<td>0.0</td>
<td>bal</td>
<td>bal</td>
<td>25% Ni49Cr1Nb, 75% IN625</td>
</tr>
<tr>
<td>Mix50:50</td>
<td>0.02</td>
<td>0.23</td>
<td>35</td>
<td>2.2</td>
<td>4.5</td>
<td>0.0</td>
<td>2.2</td>
<td>0.0</td>
<td>bal</td>
<td>bal</td>
<td>50% Ni49Cr1Nb, 50% IN625</td>
</tr>
<tr>
<td>NiCr22WAl</td>
<td>0.42</td>
<td>0.1</td>
<td>20</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>6.1</td>
<td>6</td>
<td>bal</td>
<td>P/M alloy</td>
</tr>
<tr>
<td>Nim80AF</td>
<td>0.06</td>
<td>0.08</td>
<td>19</td>
<td>0.2</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td>bal</td>
<td>Forged</td>
</tr>
</tbody>
</table>

Compositions of the tested alloys (wt%). Mix25:75 and Mix50:50 were produced in the HIP process by physically mixing metal powders of Ni49Cr1Nb and IN625. The chemical composition is taken as a weighted average of the two powders.

Material loss shown in Figure 5 was most severe at intermediate positions, with a clear maximum loss at Ø220. Samples at Ø400 are generally less corroded than those closer to the center at Ø100. Samples of NiCr22WAl, which were only included on positions Ø400-Ø280, show the same trend as the other samples with increasing material loss towards Ø220. For each position, the alloys performed similarly, with some fluctuations at lower material loss levels. The most resistant alloy at all positions was Ni49Cr1Nb, which shows no corrosion at positions Ø340 and Ø400. IN718F was more severely attacked than all other samples for all positions except for Ø340, where IN686F
suffered a slightly more severe material loss. Most of the alloys contained approximately 20 wt% Cr, and they perform comparably with the exception of Nim80AF the corrosion resistance of which is comparable to that of Mix50:50, which contains 35 wt% Cr on average.

Cross sections of samples Nim80AF and IN718F were investigated with back-scatter electron imaging, shown in Figure 6. An approximately 60 µm thick oxide layer containing V, Ni and Cr was detected by EDX on the surface. Close to the metal-oxide interface the dark layer has a fine structure, which turns coarse and more porous approximately 20 µm from the surface. EDX measurements detected a Cr peak in the immediate transition from metal to the V containing oxide layer. This indicates that a Cr₂O₃ layer is formed in the interface. Both alloys have an intermediate layer inside the metal containing CrS particles. This intermediate layer is Cr depleted, and deeper for IN718F than for Nim80AF.

FIGURE 5. The material loss after 2223 h of service. Material loss peaks at Ø220. The sequence of diameters given in the legend corresponds to the sequence for each of the alloys. For Ni22CrWA1 only Ø280-Ø400 is given; for Ni49Cr1Nb no material loss occurs at Ø340-Ø400.

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For IN718F, the V₂O₅ layer also contains bright regions, which suggest the presence of oxides containing heavier atoms than V and Cr. These could be Nb rich particles, however due to their limited size this could not be verified with EDX.

**DISCUSSION**

Upon the 2223 hours of exposure, all alloys exhibited measurable corrosion, with the exception of Ni49Cr1Nb at positions Ø340 and Ø400 (Figure 5). It is assumed that the temperature along the bottom of the spindle increases towards the center of the spindle, because the primary cooling of the spindle occurs through the spindle seat during the compressive and combustive stages of the combustion cycle. Some cooling also takes place during the air flushing stage, however this cooling is anticipated to be most effective at the spindle perimeter. The maximum in material loss at position Ø220 and the presence of particles on the spindle surface suggests the existence of molten salts. Assuming that the peak is caused by molten salt which rapidly dissolves the protective Cr₂O₃, it seems that the higher temperature closer to the spindle center either causes these deposits to boil off or to prevent deposition. In Figure 7, the material loss at each position is plotted as a function of the Cr content of the alloy. Clearly, no straightforward relation exists between the material loss and the Cr content. This is primarily related to the difference in performance of IN718F and Nim80AF alloys. For Cr contents over 25 wt% a linear relation appears to apply; for Cr contents lower than 25 wt% the corrosion resistance behaves differently. Using the Cr content of the bulk alloy as a indicator for the resistance against hot corrosion was proposed by Nicholls. In this respect it is noted that Nicholls used a logarithmic scale to present his results (Figure 1). This may have obscured the different behaviours of alloys containing >25 wt% Cr and those containing <25 wt% Cr, as observed here. The alloys used in the present study contain Mo, Fe, Nb, Ti and Al, elements which have been mentioned to affect the hot corrosion resistance by Nicholls, Johnson et al, Kofstad and others.

**FIGURE 7**

The material loss at positions Ø220 and Ø280 as a function of Cr content. Positions Ø100, Ø160, Ø340 and Ø400 produced similar plots. Nim80AF and IN718F have the same Cr content but different corrosion resistance, causing vertical spread in the plots.

**Oxide scale calculations on Nim80AF and IN718F with Therm-Calc**

The effect of alloying elements on the oxide scale composition was investigated with thermodynamic calculations. Thermodynamically, a gradient of the O activity, or more commonly used, pO₂, occurs over the thickness of the oxide scale. Assuming that the alloy composition does not change in the immediate vicinity of the oxide-metal interface, the oxide scale composition was calculated with Thermo-Calc, a CALPHAD based commercial software package. In the present work, a combination of the Thermo-Calc databases TCFE6 and SSUB3 as well as the Thermotech database NI4 was applied. The first two for information on oxide phases, and NI4 for data on FCC and intermetallic phases, such as γ’, σ and δ. Varying ln(pO₂) from -100 to 1 (corresponding to a pO₂ range of approximately 10⁻⁴⁴ to 0.3 atm), the equilibrium quantities of the phases were calculated for each alloy. The temperature was taken as 670°C and the ambient pressure at 1 atm. The calculations do not address the influence of S and V which are present in the combustion chamber atmosphere. It is important to note that the results only show the equilibrium phase distribution for each individual oxygen activity. Considering the depth distribution over the oxide scale from gas/oxide interface to oxide/metal interface as a sequence of local equilibrium, the calculated results reflect the depth distributions of equilibrium phases for the different alloys. In this respect it should be realized that as a consequence of growth of growth of the oxide scale, the equilibrium distributions
requiring long range diffusion of atoms and nucleation of new phases may be prevented. Generally, the oxide scale compositions found for the alloys used in this test can be exemplified by those given for IN718F and Nim80AF in Figure 8. Moving outwardly from the metal/oxide interface to the oxide/gas interface Corundum containing first primarily Al and then Cr is stable closest to the metal. For Nim80AF, this zone continues up to a ln($pO_2$) of -42, although a small tail continues to be stable; for IN718F the stability of Corundum ends completely already at a ln($pO_2$) of -55. In both cases it is followed by a Spinel phase, which has some solubility for Cr. The earlier stability of the Spinel for IN718F is a consequence of the 17 wt% Fe contained in the alloy. For both alloys the oxide scale consists primarily of Spinel and Halite for a ln($PO_2$) beyond -38. This sequence of oxides is similar across the alloys, however it should be noted that IN686F, IN686W, IN625F and IN625W additionally form MoO$_2$, as a consequence of the presence of Mo in the alloy. At higher O activities, also TiO$_2$, Nb$_2$O$_3$ and WO$_2$ were formed for the alloys containing those elements.

**FIGURE 8.** Computed oxide layer compositions at 670°C and 1 atm of pressure. γ-Ni, δ and γ' are metal phases.

Even though Nim80AF and IN718F contain the same amount of Cr, their equilibrium response to oxidation is remarkably different. This difference is a result of the alloy composition. The relatively early stabilization of Spinel for IN718F is a consequence of the high Fe content. On the other hand the early Corundum appearance for Nim80AF is a result of the higher Al content. The height and width of the Corundum peak in this logarithmic representation correlates with the hot corrosion resistance: The higher and broader the Corundum region in Figure 8 the better is the protection against hot corrosion. In order to verify this, the material loss due to hot corrosion is given as a function of the integrated area under the Corundum distribution in Figure 9.

**FIGURE 9.** A linear relation is found between the area under the Corundum equilibrium distribution as found on Figure 8. Alloy NiCr22WAl, which was not placed on position Ø220, is a clear outlier. Similar plots are produced for the remaining positions tested.

Surprisingly, a linear relation is found between the material loss and area integrated area under the equilibrium Corundum distribution. Only clear exception is NiCr22WAl, which is a clear outlier. Also noted is that IN686W and IN686F which fall below the trend at position Ø220 are the alloys containing the most Mo. The reason for the linear relation will be the topic of future research. A parameter as proposed here, could pave the way to alloy development for superior hot corrosion resistance.
CONCLUSION

Hot corrosion in two stroke diesel engines has so far been solved pragmatically by utilization of materials originally developed for aircraft jet engine applications. Literature suggests that the Cr content of the alloys is directly related to hot corrosion resistance. Investigation of 10 Ni based superalloys tested in service on an exhaust valve spindle bottom showed that Nimonic 80A experienced approximately half the material loss compared to Inconel 718, despite their identical Cr contents. Thermodynamic equilibrium calculations showed that the equilibrium phase distribution for a range of oxygen activities are remarkably different for the alloys: For Nimonic 80A the Corundum phase \((\text{Al,Cr})_2\text{O}_3\) is both more abundant and stable over a broader oxygen activity interval than for Inconel 718. A surprising linear relation was observed between the material loss and the area under the calculated distribution of equilibrium Corundum content vs. \(\ln(pO_2)\). This parameter may pave the way to design the composition of hot corrosion resistant alloys.

REFERENCES

1. ISO 8217 Fuel Standard.
**Abstract**

Hot corrosion caused by molten salt containing V$_2$O$_5$ is a known serious metal degradation mechanism found when using low-grade fuels. In the present work, the hot corrosion of six Powder Metallurgical (PM) Ni-based alloys containing 35-45 wt% Cr and 3.5-6 wt% Nb under exposure to V$_2$O$_5$ in synthetic air was investigated using gravimetry and electron microscopy. The results are compared with those of the commercial alloy Nimonic 80A. Exposure temperatures were chosen above and below the melting point of V$_2$O$_5$ (670°C), at 650 and 700°C. Hot corrosion from the V$_2$O$_5$ deposit was found both above and below 670°C. All tested PM alloys had lower weight gains than Nimonic 80A. Among the PM alloys, a high Cr content was found to reduce the weight gain during exposure. Also, Nimonic 80A was exposed to a mixed deposit of V$_2$O$_5$ and MgO at 700°C, which led to the formation of Mg$_3$(VO$_4$)$_2$. The resulting weight gain was lower than that of an uncovered Nimonic 80A sample at the same temperature, suggesting that Mg$_3$(VO$_4$)$_2$ formation prevented further oxidation of the substrate.

**Introduction**

Hot corrosion caused by mixed molten salts continues to be an important materials degradation mechanism for both the energy and the marine propulsion industry, and has been so since the discovery of accelerated corrosion of furnace wall tubes some sixty years ago\textsuperscript{1-6}. A compound often found in such a mixed salt is V$_2$O$_5$, which is formed during the combustion of low-grade oil. When mixed with other combustion products such as Na$_2$SO$_4$, V$_2$O$_5$ forms eutectic melts with melting points down to 500°C\textsuperscript{7}. These mixed salt melts dissolve most metal oxides, leaving the substrate metal unprotected against further...
attack. The end result is catastrophic corrosion rates\textsuperscript{3,8}. Two strategies have been employed to control this type of corrosion; changing the environment by fuel additives or changing the chemistry of the exposed metal, being a bulk alloy or a coating, so that it forms a protective metal oxide. Fuel additives should increase the melting temperature of the condensed combustion products beyond the service temperature. In practice this has been accomplished with some success by adding MgO to fuel oil such that a MgO:V weight ratio of 3:1 is obtained\textsuperscript{1,9–14}.

It is economically appealing to solve the corrosion problem by modifying the chemistry of the exposed metal, as oil additives or a change of oil quality carries a continued expense, while a protective surface is likely an investment that lasts. Some hot corrosion resistance has been found for Cr-based alloys and for Ni-based alloys with high Cr contents and moderate Si contents\textsuperscript{15–21}. Hot corrosion by a mixed salt melt is described by literature as a fluxing mechanism, which is driven by a high solubility of metal ions in the salt melt, and a low pO\textsubscript{2} at the metal-melt interface. As a result, the metal oxide is dissolved, and metal ions which are released in the salt melt reacts with oxygen to form dispersed oxides closer to the melt-air interface, where the pO\textsubscript{2} is higher\textsuperscript{8,22}. In the present study, the hot corrosion response under oxidizing conditions of Ni-based Powder Metallurgical (PM) model alloys containing 35-45 wt% Cr and 3.5-6 wt% Nb with V\textsubscript{2}O\textsubscript{5} deposit was investigated by differential thermal gravimetry at 650°C and 700°C; Nimonic 80A was used as a reference. The effect of a mixed V\textsubscript{2}O\textsubscript{5} and MgO deposit on Nimonic 80A was also investigated.

**Experimental**

Test bars of six Ni-based Ar atomized PM alloys were produced by compacting powder filled Ø20x500 mm stainless steel pipes by hot isostatic pressing, which was performed at 1050°C and 800 bar for 3 hours. The Nimonic 80A reference alloy was cast and forged. The compositions of all investigated alloys are listed in Table 1.
Table 1. Chemical composition in wt% of PM alloys as specified by supplier certificates. Nimonic 80A composition was assessed by Glow Discharge Optical Emission Spectroscopy with a Spectruna 650. For all alloys Ni is balance.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni35Cr4Nb</td>
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<td>3.8</td>
<td>0.5</td>
<td></td>
<td>≤0.02</td>
<td>0.11</td>
<td>0.027</td>
<td>0.002</td>
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<tr>
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<td>6.0</td>
<td>0.5</td>
<td>0.01</td>
<td>0.005</td>
<td>0.019</td>
<td>0.001</td>
<td>0.01</td>
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<td>0.009</td>
<td>0.013</td>
<td>-</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
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<td>0.5</td>
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<td>0.014</td>
<td>0.032</td>
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<td>0.5</td>
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<td>0.013</td>
<td>0.032</td>
<td>0.001</td>
<td>0.03</td>
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<td>Ni45Cr6Nb</td>
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<td>6.0</td>
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<td></td>
<td>≤0.02</td>
<td>0.013</td>
<td>0.025</td>
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<td>-</td>
<td>2.4</td>
<td>1.7</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>0.22</td>
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</tbody>
</table>

For exposure experiments the alloy samples were machined to the shape of discs with dimensions Ø11x1 mm; for Nimonic 80A the dimensions were Ø12x1 mm. For each sample one side was polished to a 3 µm diamond finish. On that side, an aqueous 0.03M NH₄VO₃ solution was deposited as drops and left to dry at room temperature. This was repeated until the accumulated weight gain after repeated depositions reached 0.8-1.7 mg/cm². On heating above 200°C, NH₄VO₃ decomposes, leaving V₂O₅ on the sample surface according to Eq. (1)\(^{16,23}\).

\[
2NH₄VO₃ ⇔ 2NH₃ + V₂O₅ + H₂O
\]  

With the chosen method of salt deposition, an even distribution could not be formed on both sides of the sample. Consequently, the other side of the sample was ground with 1000 grit SiC paper and sputter coated with Pt in a Cressington sputter coater for 6x10 seconds, to keep it inert during sample exposure. One Nimonic 80A sample was polished to 3 µm diamond finish on both sides and covered with a solution of NH₄VO₃ and 30 nm particle size MgO so that the MgO:V molar ratio would correspond to 3:1 during exposure testing.

Exposure temperatures were 650 or 700°C with a heating rate of 20°C / min and a holding time of 12 hours under synthetic air in a Netzsch thermobalance, with a gas flow rate of 50 ml / min. Samples of Nimonic 80A, Ni35Cr6Nb, Ni40Cr3.5Nb and Ni45Cr6Nb with V₂O₅ deposit were vacuum embedded on edge in epoxy after the exposure, and prepared for cross sectional investigation by water-free grinding and polishing.
Scanning electron micrographs and Energy Dispersive X-ray spectroscopy investigations were performed on an FEI Quanta 200 ESEM. For phase identification, X-ray diffraction (XRD) was performed on the surface of the Nimonic 80A sample exposed with V$_2$O$_5$ + MgO deposit using a Bruker D8 Discovery diffractometer applying a symmetric Bragg-Brentano geometry and Cu K-α radiation.

**Results and interpretation**

**Weight loss during heating**

Fig. 1 shows the weight change behaviour of Nimonic 80A with and without deposited NH$_4$VO$_3$ during heating to 700°C. The large weight loss with salt is caused by water and ammonia evaporation, according to the reaction in Eq. (1).

![Figure 1. The weight loss of Nimonic 80A with and without deposited NH$_4$VO$_3$.](image)

Upon reaching 650°C, no further weight loss takes place. The weight gain curves in this manuscript are presented with reference to the time where 650°C was reached on heating, (i.e. 30 minutes).

**Weight gain curves**

The weight gain curves of all alloys exposed at 650°C are shown in Fig. 2. Without salt, Nimonic 80A has a final weight gain of up to 8 times the weight of the PM alloys. Relative to Nimonic 80A, the PM alloys had a
much lower initial weight gain, and after that a lower, stable weight gain rate. Without salt, the weight gains of alloys Ni45Cr6Nb, Ni45Cr4Nb and Ni40Cr5Nb were as a whole slightly higher than the weight gains of Ni40Cr3.5Nb, Ni35Cr6Nb and Ni35Cr4Nb. The sequence of the PM alloy weight gain curves suggest that higher Cr or Nb content results in a higher initial weight gain. With V₂O₅ deposits, all tested alloys gained more weight compared with the results without salt. The PM alloys experienced both higher initial weight gain compared to the results without salt, and higher final weight gain rates. The weight gains of Ni40Cr3.5Nb and Ni35Cr6Nb accelerated after approximately 6 hrs exposure, which indicates the occurrence of breakaway corrosion. Except for Ni40Cr3.5Nb, the final weight gains of the PM alloys with V₂O₅ suggest that a higher Cr content results in a lower weight gain, and in a lower risk of breakaway corrosion.

Figure 2. Weight gain during oxidation at 650°C with and without V₂O₅ deposit.

The weight gain curves of all alloys exposed at 700°C are shown in Fig. 3. The level of weight gain found after 12 hours at 650°C was reached after only 2 hours at 700°C. For samples without V₂O₅ deposit, Nimonic 80A had a final weight gain up to 5 times that of the PM alloys. In contrast to the results obtained without salt at 650°C, the weight gain rate of Nimonic 80A found a constant value within the time frame of the exposure at 700°C. Except for Ni40Cr3.5Nb, the ranking of final weight gains of PM alloys without V₂O₅ deposit indicates that the aggregated content of Cr and Nb is positively correlated with the weight gain. For
samples with a V$_2$O$_5$ deposit all weight gains were higher than those without. Ni35Cr4Nb and Ni35Cr6Nb seem to experience breakaway corrosion after approximately 8 hours, resulting in an increased weight gain rate. Ranking the final weight gain of the PM alloys exposed with V$_2$O$_5$ deposit at 700°C suggests that a higher Cr content results in a lower weight gain, and that a certain risk of breakaway corrosion exists, for all alloys with relatively low Cr content. In spite of a much lower Cr content, Nimonic 80A appears not to experience breakaway corrosion at 650 or 700°C with V$_2$O$_5$ deposit, and had lower final weight gain rates than those of the alloys which suffered from breakaway corrosion.

**Figure 3. Weight gain during oxidation at 700°C with and without V$_2$O$_5$ deposit.**

The weight gains of Nimonic 80A are collected in Fig. 4, including the weight gain with mixed V$_2$O$_5$ and MgO deposit. Comparing the results at 650°C, the initial weight gains are comparable regardless of the presence of a V$_2$O$_5$ deposit. Under V$_2$O$_5$ deposit, a slight acceleration of the weight gain rate occurs at about 6 h; perhaps this is associated with the onset of breakaway oxidation. At 700°C, the initial weight gain without V$_2$O$_5$ was higher than that observed at 650°C, while at 700°C, the subsequent weight gain rate was lower. The higher weight gain rates at 650°C may simply indicate that the metal ion saturation of the V$_2$O$_5$ deposit and buildup of a protective oxide scale on the metal substrate, a process which may happen within the first two hours of exposure at 700°C, is a slower process at 650°C. Exposure of Nimonic 80A with MgO and V$_2$O$_5$ at 700°C resulted in a weight gain three times lower than that obtained without salt. In
appearance and magnitude the weight gain was similar or even lower than that obtained with the 40-45% Cr PM alloys with V₂O₅ deposit shown in Fig. 3.

Figure 4. Weight gains of Nimonic 80A under several experimental conditions.

The Nimonic 80A sample with mixed MgO and V₂O₅ deposit was examined with XRD after exposure (Fig. 5). Some remaining MgO was detected, while the only V containing compound found was Mg₃(VO₄)₂, which has a melting point of 1150°C. This indicates that all V₂O₅ was consumed during the exposure by reaction with MgO.

Figure 5. Nimonic 80A exposed at 700°C with mixed V₂O₅ and MgO deposit.
Microstructure investigation

NH$_4$VO$_3$ was added only to the Pt free side of the samples. However, upon microscopy investigations of the cross sections, it became apparent that V$_2$O$_5$ had covered both sides of the samples during exposure, both at 650 and 700°C. The Pt coating was also found to be of insufficient thickness to prevent attack, and in some cases, even the worst attack was actually found on the Pt side. Fig. 6 shows the cross section of Nimonic 80A after exposure at 650°C with V$_2$O$_5$ deposit. The surface has corroded unevenly, giving it a wavy macro appearance with peaks and shallow valleys. Between peaks, internal oxidation has occurred, producing a mixed oxide containing Cr, Al, and Ti. The oxide layer found immediately on top of the metal has a dark color in Fig. 6. EDS measurements of this layer found primarily Cr and V, while the oxide further away from the metal contains Cr and Ni.

Figure 6. Cross section of Nimonic 80A after exposure at 650°C with V$_2$O$_5$ deposit. BSE images.

Exposed at 700°C with V$_2$O$_5$ (Fig. 7), the cross section appearance of Nimonic 80A is similar to that produced at 650°C, but with a more pronounced wavy appearance. The peaks of the wavy macro pattern have formed where grain boundaries meet the surface. This indicates that the fast diffusion of Cr along grain boundaries has served to reduce the material loss locally.
The cross section appearances of Ni35Cr4Nb, Ni35Cr6Nb and Ni45Cr6Nb after exposure at 700°C are shown in figures 8, 9 and 10 respectively. The locations shown represent worst-case locations. Breakaway corrosion is visible for Ni35Cr4Nb and Ni35Cr6Nb while much less attack is visible for the high Cr Ni45Cr6Nb. Within the alloys Ni35Cr6Nb and Ni45Cr6Nb Ni3Nb and α-Cr areas are found in the bulk material structure and the Ni3Nb particle shapes can be re-found as Nb-rich areas in the oxide layers. For Ni35Cr4Nb Ni3Nb and α-Cr areas are only found along grain boundaries.

For Ni35Cr6Nb the worst-case location was found on the Pt coated side, and small bright Pt-rich areas can be observed in Fig. 9. The oxide layer on this side is thicker than that of the Pt free side, and within the oxide bright streaks indicate the Nb rich areas.

The cross section of Ni45Cr6Nb (Fig. 10) shows the high content of α-Cr in the microstructure, as well as the high content of Ni3Nb. The surface is marked by the same microscopic pits which were found on the cross section of Ni35Cr4Nb and Ni35Cr6Nb (Fig’s 8 and 9), but the oxide layer on the surface is less continuous and no deep grooves in the surface are observed.
Figure 8. Cross section of Ni35Cr4Nb after exposure at 700°C with V$_2$O$_5$ deposit. BSE images.

Figure 9. Cross section of Ni35Cr6Nb after exposure at 700°C with V$_2$O$_5$ deposit. BSE images.

Figure 10. Cross section of Ni45Cr6Nb after exposure at 700°C with V$_2$O$_5$ deposit. BSE images.
At 650°C with V$_2$O$_5$ deposit samples of Ni35Cr4Nb, Ni35Cr6Nb and Ni40Cr3.5Nb had morphologies corresponding to breakaway. On the remaining alloys only very thin oxide layers have formed. Figure 11 shows the cross section of Ni40Cr3.5Nb with V$_2$O$_5$ deposit exposed at 650°C. Blocky crystals are found on the surface metal surface, below which breakaway corrosion has occurred as local material loss. EDS measurements of the crystals show that they are primarily composed of V$_2$O$_5$, with trace amounts of Ni and Cr.

![Figure 11. Cross section of Ni40Cr3.5Nb with V$_2$O$_5$ after exposure at 650°C.](image)

Discussion

As expected, the investigated PM alloys had better corrosion resistance than Nimonic 80A, both with and without V$_2$O$_5$ deposit. For PM samples without a V$_2$O$_5$ deposit it is hardly possible to rank the corrosion resistance. It appears that a higher Cr content caused higher final weight gain, and for alloys with identical Cr contents, a higher Nb content caused a higher weight gain. For samples with V$_2$O$_5$ deposit, a ranking is more difficult. Nimonic 80A had in all cases the poorest corrosion resistance, but, within the exposure time, it did not suffer from breakaway corrosion, as was the case for Ni35Cr4Nb and Ni40Cr3.5Nb at 650°C and for Ni35Cr4Nb and Ni35Cr6Nb at 700°C with V$_2$O$_5$ deposit. It appears that an increased Cr content gives a better corrosion resistance. This may however be an artefact of the exposure duration. Breakaway corrosion is a stochastic process, and could have manifested itself at a later stage for some alloys, had they
been exposed for longer than 12 hours. The occurrence of breakaway corrosion may also be affected by the salt deposit method, which did not create perfectly even salt coatings. Cross section of the PM samples showed many pits in the micrometer scale, and samples which had experienced breakaway corrosion had an overall irregular metal surface. The surface of Nimonic 80A exposed with V₂O₅ had a wavy macro appearance, with crests where grain boundaries met the surface. This indicates that the diffusion of Cr, which is enhanced along ground boundaries, retards the corrosion mechanism. The discovery of partly dissolved V₂O₅ on the surface of the Ni40Cr3.5Nb exposed at 650°C indicate that diffusion with the substrate acted to form a molten salt below the melting temperature of pure V₂O₅.

The Nimonic 80A sample with V₂O₅ and MgO exposed at 700°C had the lowest weight gain measured with Nimonic 80A. The XRD measurements confirmed the dominating presence of a Mg₃(VO₄)₂, which melts at 1150°C, and as such must therefore be considered inert during the exposure. The sequence of events during heating may have been the initial melting of V₂O₅, which rapidly reacted with MgO according to the reaction shown in Eq. (2).

\[ 3\text{MgO} + V_2O_5 \Leftrightarrow Mg_3(VO_4)_2 \] (2)

The final weight gain rate of the Nimonic 80A sample with mixed V₂O₅ and MgO deposit matched that of the deposit free sample. This suggests that the formation of Mg₃(VO₄)₂ not only neutralized the V₂O₅ present, but that it furthermore functioned as a protective deposit, limiting O₂ diffusion to the metal substrate.

**Conclusion**

The present work has explored the response of model Ni-based alloys containing high amounts of Cr and moderate amounts of Nb to a V₂O₅ deposit environment. As a reference, the commercial alloy Nimonic 80A has been used. The following conclusions can be drawn:

- All tested alloys were attacked by V₂O₅, both at 650 and 700°C.
The PM alloys were more resistant to $V_2O_5$ induced hot corrosion than Nimonic 80A. However, Nimonic 80A did not at any point experience breakaway corrosion, which was found for several of the PM alloys containing up to 40 wt% Cr.

For the PM alloys, a higher Cr content improves the resistance against $V_2O_5$ induced hot corrosion.

For the Nimonic 80A sample exposed with a salt mix of $V_2O_5$ and MgO at 700°C, $Mg_3(VO_4)_2$ was formed which not only hindered further hot corrosion but which seemed to act as a protective deposit, limiting $O_2$ diffusion to the substrate. This resulted in the lowest weight gains measured for Nimonic 80A.

Acknowledgments

The authors wish to acknowledge Sandvik Powder Solutions A/B for producing the metal powder for the Ni40Cr3.5Nb PM sample and for compacting all samples.

References

V₂O₅ induced hot corrosion of Ni-base alloys containing 35-45 % Cr and 3.5-6% Nb


DESIGN AND CHARACTERIZATION OF NOVEL PRECIPITATION HARDENABLE HIGH CR NI-BASED SUPERALLOYS

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Kristian V. Dahl*
Marcel A. J. Somers*

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ABSTRACT

Among the Ni-based superalloys, Alloy 718 stands apart with the ability to be precipitation hardened after welding, by the slow formation of nano-scale $\gamma''$ ($\text{Ni}_3\text{Nb}$) particles. This slow formation gives it a very low crack susceptibility, which has made it widely applied since its introduction in the aircraft industry in the 1960’s. Five powder metallurgical Ni-based superalloys containing 35-45 wt % Cr and 4-6 wt % Nb were designed with the aim of maintaining the hardening mechanism found in Alloy 718, while drastically increasing the hot corrosion resistance. The alloys were manufactured and the actual precipitation of $\gamma''$ was verified with TEM. The mechanical properties of the hardened P/M alloys are comparable to those of Alloy 718.

1. INTRODUCTION

The resistance against vanadium- and sulphur-induced hot corrosion of Ni-based superalloys can in principle be improved by enhancing the Cr content (Singh, Puri, Prakash, 2007). However, for Cr contents higher than ~22 wt % the mechanical properties are negatively influenced; welding, machining and cold forming processes are difficult or impossible due to the formation of brittle $\alpha$-Cr (b.c.c.) as a separate phase in the f.c.c. matrix. An example of a compromise between corrosion resistance and processing parameters is Alloy 718. This alloy contains 19 wt % Cr, and is precipitation hardenable after welding. Similar properties, combined with a higher Cr content, would be valuable for hot corrosion applications. A relatively ductile Ni-based alloy containing over 30 wt % Cr is obtained by addition of ~1 wt % of a suitable N-getter, such as
Design and characterization of novel precipitation hardenable high Cr Ni-based superalloys

Nb, and by careful selection of heat treatment parameters (Ennis and Bridges, 1972; Dong, Bi, Xie, Wang, Wang, 2008). The mechanical properties as well as the corrosion resistance can be further enhanced by P/M manufacturing such as Hot Isostatic Pressing (HIP). Such alloys are however not precipitation hardenable, and hence lack an important feature of Alloy 718. Precipitation hardening of most Ni-superalloys is caused by the development of ordered f.c.c. γ′ Ni₃(Al,Ti), which is coherent with the matrix, and precipitates readily (<1 h) during heat treatment. By contrast, in Alloy 718 precipitation hardening is based on the development of ordered b.c.t. γ″ Ni₃Nb, which is coherent with the matrix but grows slowly due to the rate of diffusion of Nb in the f.c.c matrix (Devaux, Naze, Molins, Pineau, Organista, Guédou, Uginet, Héritier, 2008). The size is in the nano-scale range (He, Fukuyama, Yokogawa, 1994). Slow precipitation hardening is a main feature of Alloy 718, as it allows welding and hot forging with little or no crack susceptibility. As the HIP treatment involves both a holding step at a temperature above 1000°C and a relatively slow cooling it can be perceived as a precipitation hardening treatment. If machining or cold working of the material after the HIP process is required, a slow precipitation hardening as that found for Alloy 718 is valuable as it can eliminate a solution heat treatment step. γ″ is a metastable phase, and upon prolonged aging at temperatures higher than 650°C it transforms into the stable orthorhombic δ (Ni₃Nb) phase, which is incoherent with the matrix, and associated with a loss of yield strength (Sims and Hagel, 1972).

So far, much effort was devoted to improving the high temperature stability of Alloy 718 (Cozar and Pineau, 1973; Collier, Wong, Tien, Phillips, 1988), while increasing the Cr content to improve the hot corrosion resistance has received less attention. Modern alloy development takes advantage of numerical methods for screening alloys. The CALPHAD (Saunders and Miodownik, 1998) approach is employed in the commercially available software package Thermo-Calc (Andersson, Helander, Höglund, Shi, Sundman, 2002) and can, when combined with an appropriate thermodynamic database, provide fast predictions of the equilibrium phase contents in multiphase alloys. Fig. 1 shows the volume fractions of γ″ and α-Cr obtained by such calculations for five alloys with different combinations of Ni, Cr and Nb contents. Clearly for Ni-based alloys with 35-45 wt % Cr and 4-6 wt % Nb it should be possible to achieve precipitation hardening as for Alloy 718. However, these calculations do not comprise the rate of precipitation hardening nor the possible loss of ductility as an influence of the α-Cr fraction, which is much lower in Alloy 718. The alloys collected in Fig.1 were investigated experimentally to verify whether it is indeed possible to manufacture an alloy with twice the Cr content of Alloy 718, while retaining the precipitation hardening ability.

![Fig. 1. Equilibrium volume fractions calculated with Thermo-Calc using the TCNI5 database.](image)

In order to calculate the amounts of the metastable γ″ phase, the development of stable δ phase was suppressed.
2. EXPERIMENTAL

Five experimental P/M alloys were produced, with compositions shown in Table 1. Rods with the dimensions Ø20x400 mm were HIPd in steel 316 capsules. Specimens of Ø20x10 mm were cut from the rods and solution treated for 1 h in air at 1100°C, followed by water quenching.

Table 1. Chemical composition of powder metallurgical alloys as specified by the supplier certificate. Ni bal.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mo</th>
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<td>Ni45Cr4Nb</td>
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<tr>
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</table>

Aging was performed in air at 700°C for up to 9 h followed by water quenching. The Vickers hardness was measured with a load of 10 kgf on samples prepared by wet grinding with grit 220 and 800 SiC paper. Tensile testing was performed on all alloys in the fully aged (9 h) state, and on Ni35Cr4Nb, Ni35Cr6Nb and Ni40Cr5Nb in the solution treated state. The microstructure was investigated with backscatter SEM and quantification of the area content of α-Cr was performed using ImagePro Plus on a total surface area of 0.083 mm² for each sample. A FIB-section of aged Ni35Cr6Nb was investigated using TEM. Thermo-Calc calculations were performed with the TCNI5 database using the TC-Matlab programming interface.

3. RESULTS

The results from hardness measurements are shown in Fig 2. All alloys exhibited an increase of about 100 HV10 after 1 h. Hereafter, Ni45Cr6Nb showed the lowest rate of hardening; even a tendency for overaging was observed after aging for 3 h. The hardness of the remaining 4 alloys continued to increase up to 9 h.

![Fig. 2. Hardness of alloys when exposed to 700°C after a 1 h solution treatment at 1100°C followed by water quenching. Solution treated state shown as 0 h.](image)

The yield strength (YS) and ultimate tensile strength (UTS) of the alloys are collected in Table 2. The data shows that aging more than doubles the yield strength and enhances the tensile strength, while the elongation is reduced appreciably. After aging only Ni35Cr4Nb shows an acceptable elongation.
Table 2. Mechanical properties of the alloys.

<table>
<thead>
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<th>Solution treated</th>
<th>Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>436</td>
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</tr>
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<td>Ni35Cr6Nb</td>
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<td>Ni45Cr6Nb</td>
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</tbody>
</table>

Backscatter electron micrographs before and after aging are shown in Fig. 3.

Fig. 3. BSE micrographs after solution treatment and after aging at 700°C for 9 h. α-Cr and δ phases appear as dark and bright particles, respectively.
For both Ni35Cr alloys, only limited development of $\alpha$-Cr along grain boundaries takes place. For the alloys with more than 4 wt % Nb, aging causes the appearance of a fine $\alpha$-$\gamma$ lamellar structure growing from the Cr regions. In the case of Ni35Cr6Nb, the lamellae grow from the grain boundaries. For alloys containing more than 35 wt % Cr grain boundaries are not visible. Nevertheless the bimodal size distribution of $\alpha$-Cr regions suggests that the larger particles developed at grain boundaries, while the smaller particles developed in the grain interiors. Aging has only a limited effect on the amount and the distribution of the $\delta$ phase as follows from comparing the solution treated and aged Ni45Cr6Nb micrographs. In contrast the $\alpha$-Cr regions coarsen and for Ni45Cr6Nb $\gamma$ phase precipitates within the $\alpha$ particles. The measured area fractions of $\alpha$-Cr are given in Fig. 4. For the alloys containing more than 35 wt % Cr, there is an initial increase in the content of $\alpha$-Cr after aging for 1 h. After this initial increase, a slight increase of the $\alpha$-Cr fraction is observed for all samples.

![Fig. 4. Area fraction of $\alpha$-Cr as a function of the aging duration.](image)

The results of preliminary TEM investigations on Ni35Cr6Nb provide evidence for the development of nano-scale $\gamma''$ precipitates (Fig. 5). Dark field imaging in the same figure indicates that the $\gamma''$ particles are smaller than 10 nm.

![Fig. 5. TEM of Ni35Cr6Nb after aging for 9 h. (Left) diffraction pattern indexed relative to the ordered b.c.t. $\gamma''$ crystal system. (Right) Dark field image of the 10(-1)diffraction spot.](image)

4. DISCUSSION

It is apparent that the alloys are precipitation hardenable. In solution treated state the two 35 % Cr alloys exhibit elongations in the order of 50 %, which makes them very suitable for forging. The precipitation hardening mechanism is similar to that for Alloy 718, i.e. caused by the
precipitation of γ” within the γ matrix (Fig. 5). The small difference between as HIPd and solution treated hardness shown in Fig. 2 indicates that premature aging, which could have been a consequence of the relatively slow cooling taking place in the HIP cycle, is limited. The hardening response is however not slow, with an, for all alloys, almost identical high hardness increase found within the first hour of aging. After this, a slower rate of increase is seen. This is a different behaviour than that of Alloy 718, which maintains a linear hardness increase for up to 4 h at 750°C (Cozar and Pineau, 1973). The overall as HIPd hardness of each alloy seems to be primarily a product of the amount of α-Cr present, as the hardness of Ni35Cr6Nb almost falls to the level of Ni35Cr4Nb after solution treatment, at which Cr is in solid solution for both alloys. The considerable difference in hardness and strength before and after heat treatment seems not to be an effect of the microstructural changes observed in the micrographs in Fig. 3, which are mostly related to α-Cr development, but instead should be attributed to development of γ”.

In Table 3, the fractions of experimentally determined α-Cr are compared with the Thermo-Calc calculations. Generally good correspondence is found. For the aged samples (700°C), the calculated equilibrium values for all but the 45 wt % Cr alloys are much higher than the experimental values. For the two 35 wt % alloys no Cr precipitates are present after solution treatment and nucleation of α-Cr should occur during aging. For the alloys with at least 40 wt % Cr, α-Cr is present after solution treatment. These observations suggest that nucleation rather than growth and coarsening is the rate determining step in reaching an equilibrium α-Cr fraction.

The strongest evidence for hardness and strength increase by the precipitation of γ” particles in an early stage of aging is the hardness increase in Ni35Cr6Nb of more than 100 HV within the first hour of aging, while in this time interval no α-Cr is observed in the micrographs in Fig. 3 (see Fig. 4). For the same alloy the ductility deteriorates from 49 to 6.1 %. The strength of the alloys is comparable to that of aged Alloy 718, which has an UTS of ~1400 MPa. The elongation in the present alloys is however not as good as that for Alloy 718, which is about 20%(ASM International. Handbook Committee, 1990).

### Table 3. α-Cr fractions. Measured area fractions compared to equilibrium volume fractions calculated with Thermo-Calc using the TCNI5 database.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution treated</th>
<th>Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>TCNI5</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>0.20</td>
<td>0.21</td>
</tr>
</tbody>
</table>

5. CONCLUSIONS

Casting of high Cr superalloys leads to brittle and essentially not workable materials. The application of P/M fabrication, such as HIP, result in a fine microstructure. This opens the possibility for manufacturing new types of high performance alloys with desirable hot corrosion resistance properties. The CALPHAD calculations done prior to this study indicated the existence of a γ” precipitation hardenable Ni based superalloy family with 35-45 wt % Cr. The experimental work validates these calculations, and establishes that these P/M alloys have mechanical and precipitation hardening properties comparable to those of Alloy 718.
REFERENCES


Microstructure of precipitation hardenable powder metallurgical Ni alloys containing 35-45% Cr and 3.5-6% Nb

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Abstract

Ni-based alloys with high Cr contents are known for their excellent high temperature and hot corrosion resistance, but are also known for poor mechanical properties and difficult workability. Powder metallurgical (P/M) manufacturing of alloys may overcome several of the shortcomings encountered in materials manufacturing involving solidification. In the present work, six P/M Ni-based alloys containing 35-45 wt% Cr and 3.5-6 wt% Nb were produced and compacted via hot isostatic pressing. Samples were heat treated for up to 1656 hrs at either 650 or 700°C, and the microstructures and mechanical properties were quantified and compared to thermodynamic calculations. For almost all alloys, the high Cr content caused a primary population of globular $\alpha$-Cr and, for some alloys, also one of $\delta$ ($\text{Ni}_3\text{Nb}$). TEM of selected alloys confirmed the additional presence of metastable $\gamma''$ ($\text{Ni}_3\text{Nb}$). A co-dependent growth morphology was found where the preferred growth direction of $\gamma''$, the $\{001\}$ planes of $\gamma$-Ni, caused precipitates of both $\alpha$-Cr and $\delta$ to appear in the form of perpendicularly oriented disks or plates. Solution heat treatment at 1100°C followed by aging at 700°C produced a significant strength increase for all alloys, and an aged yield strength of 990 MPa combined with an elongation of 21% is documented for Ni 40 wt% Cr 3.5 wt% Nb.

Introduction

The resistance against high temperature corrosion and specifically hot corrosion of Ni-based superalloys can in principle be improved by increasing the Cr content\textsuperscript{1-4}. However, for Cr contents higher than approximately 22 wt % the mechanical properties are negatively influenced. Furthermore, welding, machining and cold forming processes are difficult or impossible due to the formation of brittle $\alpha$-Cr (b.c.c.) as a separate phase in the f.c.c. matrix\textsuperscript{5}. The morphologies and mechanical properties of $\alpha$-Cr have been studied, and it has been shown that a relatively ductile cast Ni-based alloy containing over 30 wt% Cr can be produced by addition of about 1 wt % of a suitable N-getter, such as Nb, Zr or even Hf, and by careful optimisation of heat treatment parameters\textsuperscript{6-10}. The mechanical properties of most alloys can be further enhanced by Powder Metallurgical (P/M) manufacturing processes such as Hot Isostatic Pressing (HIP)\textsuperscript{11}. Another desirable alloy property, which allows metal forming and prevents post weld heat cracking, is sluggish precipitation hardening, similar to that exhibited by Alloy 718, which develops slowly growing ordered metastable nano-scale b.c.t. $\gamma''$ ($\text{Ni}_3\text{Nb}$) particles during aging\textsuperscript{12,13}. Overaging transforms the metastable $\gamma''$ phase into the matrix-incoherent orthorhombic $\delta$ phase, which leads to a loss in strength\textsuperscript{14}. It appears that a combination of the above properties in the form of a P/M Ni based high Cr alloy stabilized
by Nb has the potential to yield a hot corrosion resistant alloy which is ductile in the produced state, and heat treatable should high hardness or strength be required. The CALPHAD\textsuperscript{15} approach as employed in the commercially available software package Thermo-Calc\textsuperscript{16} can, when combined with an appropriate thermodynamic database, provide fast predictions of the equilibrium phase contents in multiphase alloys. The results of such calculations are shown in Fig. 1, where the phase composition of Alloy 718 (19 wt% Cr, 19 wt% Fe, 5.3 wt% Nb, 3 wt% Mo, 0.5 wt% Ti, 0.5 wt% Al) is shown for a number of cases where Fe and Mo is substituted with increasing levels of Cr, while Ni, Nb, Ti and Al contents are held constant. To produce the results shown in Fig. 1 the formation of the $\delta$ phase has been suppressed.

Since the equilibrium content of $\gamma''$ is only slightly influenced by the Cr content, the calculations suggest a possibility for obtaining a precipitation hardenable high Cr containing Ni-based alloy. The possible interaction between the microstructural manifestation of $\alpha$-Cr and $\gamma''$ is however not obtainable via these equilibrium calculations. The microstructure of Alloy 718 aged for 25,000 hours at 538 °C (1000 °F) has been shown to be stable, however at higher temperatures a broad range of microstructures develop, and co-formation of $\alpha$-Cr, $\gamma''$ and $\delta$ has been found in the form of disk shaped precipitates\textsuperscript{18-20}. The microstructure and thereby the mechanical properties of high Cr Ni-based alloys containing Nb can therefore be expected to be a complex interplay between $\alpha$-Cr, $\gamma''$ and $\delta$. In the present work, the microstructure and mechanical properties of six Ni based alloys containing between 35 and 45 wt% Cr and between 3.5 and 6 wt% Nb were quantified in order to shed light on the practical feasibility of these alloys in mechanically demanding high temperature applications.

**Experimental**

Six Ni-based Ar atomized P/M alloys with compositions given in Table 1 were produced by external suppliers. Test bars were produced by compacting powder filled Ø20x500 mm stainless steel pipes by Hot Isostatic Pressing (HIP), which was performed at 800 bar and 1050°C for 3 hours. Subsequently the bars were cooled with air at a rate of >100°C per minute while still in the HIP chamber. Alloy samples for microstructural analysis were cut to Ø20x10 mm, while mechanical tensile testing was performed on ISO 6892 cylindrical specimens of Ø16x100 mm with a parallel reduced diameter section of Ø10x55 mm.
Table 1. Chemical composition in wt% of powder metallurgical alloys as specified by supplier certificates. Ni ball.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Al</th>
<th>Fe</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni35Cr4Nb</td>
<td>34.4</td>
<td>3.8</td>
<td>0.5</td>
<td>0.011</td>
<td>0.027</td>
<td>0.002</td>
<td>&lt;0.02</td>
<td>0.03</td>
<td>&lt;0.005</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>35.2</td>
<td>6.0</td>
<td>0.5</td>
<td>0.005</td>
<td>0.019</td>
<td>0.001</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>41</td>
<td>3.4</td>
<td>0.5</td>
<td>0.007</td>
<td>0.009</td>
<td>0.013</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>39.3</td>
<td>5.0</td>
<td>0.5</td>
<td>0.014</td>
<td>0.032</td>
<td>0.001</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>44.8</td>
<td>4.1</td>
<td>0.5</td>
<td>0.013</td>
<td>0.032</td>
<td>0.001</td>
<td>0.01</td>
<td>0.03</td>
<td>&lt;0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>44.5</td>
<td>6.0</td>
<td>0.5</td>
<td>0.013</td>
<td>0.025</td>
<td>0.001</td>
<td>0.02</td>
<td>0.04</td>
<td>&lt;0.005</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Cross sections were prepared by standard metallographic grinding and polishing ending with a 15 minute colloidal silica step. Prior to SEM imaging the samples were carbon coated. Five randomly placed BSE images at a magnification of x1000 were produced using an FEI Quanta 200 ESEM, covering a total area of 0.18 mm² per sample. For TEM, FIB lamellae were produced with an FEI Quanta 200 3D SEM-FIB and FEG-TEM was performed using a JEOL 3000F at 300 kV. Table 2 shows an overview of the utilized heat treatments and characterization methods.

Table 2. Heat treatments and characterization methods. All heat treatments were performed in atmospheric air.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>As HIPd (1050°C x 3 h, rapid air cool)</td>
<td>BSE</td>
</tr>
<tr>
<td>Solution treated (ST): 1100°C x 1 h, water quench</td>
<td>BSE, Tensile testing (Ni35Cr4Nb, Ni35Cr6Nb, Ni40Cr5Nb)</td>
</tr>
<tr>
<td>ST + 700°C x 1 h (water quench)</td>
<td>BSE, TEM (Ni40Cr3.5Nb)</td>
</tr>
<tr>
<td>ST + 700°C x 9 h (water quench)</td>
<td>BSE, TEM (Ni40Cr3.5Nb, Ni35Cr6Nb), Tensile testing (all)</td>
</tr>
<tr>
<td>650°C x 528 h, (air cool)</td>
<td>BSE</td>
</tr>
<tr>
<td>700°C x 528 h (air cool)</td>
<td>BSE</td>
</tr>
<tr>
<td>650°C x 1656 h (air cool)</td>
<td>BSE</td>
</tr>
<tr>
<td>700°C x 1656 h (air cool)</td>
<td>BSE, TEM (Ni40Cr3.5Nb)</td>
</tr>
</tbody>
</table>

Thermodynamic calculations were performed using Thermo-Calc version S16. Databases used for calculations were Thermo-Calc TCNI5 version 5.117 and ThermoTech Ni-Data version 421. In order to obtain volumetric data from the NI-DATA database, which only offers weight fractions, density predictions from the TCNI5 database were used.

Results and interpretations

Scanning and transmission electron microscopy

All alloys have a Ni-based f.c.c. matrix, containing evenly dispersed α-Cr areas. δ particles are present in the alloys that contain more than 4 wt% Nb. Fig. 2 shows the appearance of the phases in a backscatter electron image (BSE), where α-Cr appears dark and δ appears bright, while the γ-Ni matrix is grey. α-Cr particles and δ, if present, both exist as a globular population located in clusters at grain boundaries and at prior powder particle boundaries, and as a population with smaller sizes dispersed in the bulk of the prior powder particles. At 35 wt% Cr content, the solution treatment dissolved both types of precipitates.
Aging for longer than one hour caused the appearance of plate- or disk-shaped α-Cr precipitates, oriented along three mutually perpendicular planes in the γ-Ni matrix (see insert in Fig. 3).

A TEM image of the α-Cr plates in the γ-Ni matrix in the insert in Fig. 3 is given in Fig. 4 and reveals that the α-Cr disc or plate is sandwiched in-between γ” plates. Due to their intermediate size, the size and phase fraction of these γ” particles could not be quantified, neither with TEM nor with SEM.
The length of these disc or plate-shaped precipitates for alloys with 4-5 wt% Nb was in the order of 1 µm or less. For the alloys with 6 wt% Nb a co-dependent morphology is evident, where \( \alpha \)-Cr and \( \delta \) have clearly precipitated interdependently (Fig. 5).

In addition to the precipitation of \( \delta \) within \( \gamma \)-Ni grain sections during heat treatment, \( \delta \) also appeared adjacent to globular \( \alpha \)-Cr, as shown in Fig. 6 (indicated by arrows). Moreover, a dense population of oriented \( \gamma \)-Ni discs or plates formed within the \( \alpha \)-Cr areas upon aging. This precipitation of \( \gamma \)-Ni took place inside globular \( \alpha \)-Cr areas to varying degrees and could not be quantified reliably using microscopy methods.
In alloys containing more than 35 wt% Cr, α-Cr was not dissolved during solution treatment. Consequently, the equilibrium solubilities of Ni in α-Cr and Cr in γ-Ni were approached. From 1100°C to 700°C the solubility of Ni in α-Cr is reduced (Fig. 7), which explains the rapid formation of γ-Ni precipitates in α-Cr regions. Similar γ-Ni precipitation in α-Cr was also observed for alloys which were not solution treated prior to aging treatment.

Aging for as short as one hour led to evenly dispersed γ” particles within the γ-Ni grains. The γ”-particles appear in pairs, giving them a “coffee bean” similarity, as shown for an Ni40Cr3.5Nb alloy after 9 hours aging treatment at 700°C in Fig. 8.
The mechanical properties of selected heat treatment states are collected in Table 3. Comparison of the yield strength (YS) and ultimate tensile strength (UTS) in solution treated and aged states shows that aging contributes with significant strengthening of all alloys. The most dramatic strengthening effect is obtained in the alloys with the highest Nb content, indicating that the precipitation of γ'' indeed is responsible for the strengthening effect. The strengthening is accompanied by a reduction in the ductility of the alloy. This is manifested by a significant decrease of the elongation (El) and a smaller plastic range, i.e. smaller difference between YS and UTS. Particularly the alloys with high Nb content suffer from loss of ductility.

Table 3. Mechanical properties at room temperature. Values are averages of two measurements.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>ST (1100°C x 1 h)</th>
<th>ST + 700°C x 9 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>436</td>
<td>840</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>443</td>
<td>874</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>533</td>
<td>939</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>646</td>
<td>1059</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Quantitative microstructure analysis from TEM: γ'' precipitates

The volume fraction, number density and average radius of γ'' particles was quantified by image analysis of dark field TEM images. Following the method of Sonderegger, the average true radius $r_{10}$ of particles observed as 2D projections in TEM images were calculated with:
where \( d_{\text{true},i} \) is the true diameter of particle with index \( i \) given by

\[
d_{\text{true},i} = \frac{2}{\pi} (d_{\text{obs},i} - t_i) + \sqrt{\frac{2}{\pi} (d_{\text{obs},i} - t_i)^2 + \frac{4d_{\text{obs},i}t_i}{\pi}}
\]

with \( d_{\text{obs},i} \) the projected diameter of the particle with index \( i \) and \( t \) is the thickness of the observed TEM specimen. In order to determine \( t \) for the image location energy filtered TEM was applied\(^{23}\). The phase fraction \( f_V \) is then given by:

\[
f_V = \frac{1}{A_{\text{sample}}} \sum_i A_i \left( \frac{2d_{\text{obs},i}/t_i}{2d_{\text{obs},i}/t_i + 3} \right)
\]

where \( A_{\text{sample}} \) is the area of the image. The volumetric number density \( N_V \) is given by\(^{22}\):

\[
N_V = \frac{1}{A_{\text{sample}}} \sum_i \frac{1}{t_i + d_{\text{obs},i}}
\]

Quantification on the dark field TEM images covering a total volume of \( 1.46 \times 10^{-18} \text{m}^3 \) is shown in Table 4. The \( \gamma'' \) precipitates grow measurably between 1 h and 9 h aging treatment, however the standard deviations of the measurements are very large.

Table 4. Quantitative analysis of \( \gamma'' \) precipitates measured on five TEM images. Values in parenthesis are standard deviations.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat treatment</th>
<th>Vol [%]</th>
<th>( N_V (10^{22}/\text{m}^3) )</th>
<th>( r_{3D} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni35Cr6Nb</td>
<td>ST + 700°C x 9 h (water quench)</td>
<td>0.26 (0.11)</td>
<td>1.36 (0.59)</td>
<td>3.34 (0.26)</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>ST + 700°C x 1 h (water quench)</td>
<td>0.15 (0.03)</td>
<td>2.59 (0.44)</td>
<td>2.23 (0.13)</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>ST + 700°C x 9 h (water quench)</td>
<td>0.32 (0.22)</td>
<td>1.72 (0.40)</td>
<td>3.24 (0.78)</td>
</tr>
</tbody>
</table>

Quantitative microstructure analysis from SEM: \( \alpha \)-Cr phase

For the SEM images an even spatial distribution of precipitates was assumed, making the area phase fraction equal to the volumetric phase fraction. The observed radius, \( r_{2D} \) was obtained by assuming spherical precipitates, and calculating an equivalent radius from the observed area of the particles. A straightforward correction valid for evenly dispersed spherical objects was then applied, where the true radius \( r_{3D} \) is:\(^{24}\)

\[
r_{3D} = \frac{4r_{2D}}{\pi}
\]

and the volumetric number density is given by\(^{22}\)

\[
N_V = \frac{N_A}{t + 2r_{3D}}
\]
where $t$ is the mean depth from which the observed backscattered electrons originate. This value was calculated to be approximately 200 nm using the CASINO software package\textsuperscript{25}. The data for the $\alpha$-Cr volume fraction and size distributions are collected in Table 5\textsuperscript{*}. For several alloy cross sections, one image out of five showed a large deviation from the mean. This was usually due to a microscope related artifact such as uneven image brightness. In these cases, denoted with an asterix in Table 5, data from the deviating image was not taken into account for the calculation of the mean. The standard deviations are generally one tenth or less of the average values reported, meaning that the results are consistent across the analysed images. In Fig. 9\textsuperscript{*}, the measured $\alpha$-Cr phase fractions are compared. There appears to exist a trend that the fraction of $\alpha$-Cr increases with the sum of Cr and Nb content. This is particularly apparent for the solution treated and short term aged alloys. The two 35 wt% Cr alloys had little or no actual $\alpha$-Cr present in the HIPd state, and the solution treatment was able to completely suppress the measurable volume percentage for Ni35Cr4Nb. It is not possible to discern a difference in volume fraction between 650 and 700°C. On the other hand, longer aging time without solution treatment appears to reduce the $\alpha$-Cr fraction. This is ascribed to coarsening of the $\gamma$-Ni precipitates within the $\alpha$-Cr, as shown in Fig. 5. When these $\gamma$-Ni precipitates reach a certain size, they can be distinguished from $\alpha$-Cr at the used magnification (x1000), leading to a lower, more accurate $\alpha$-Cr volume fraction. Fig. 10\textsuperscript{*} shows the $\alpha$-Cr number density. As compared to the HIPd level, aging at 650°C and 700°C caused an initial increase after 528 hrs, which for most alloys turned into a decrease after 1656 hrs. For some alloys the number density of $\alpha$-Cr after 1656 hrs aging drops below the HIPd level. The solution treatment reduced the number density of $\alpha$-Cr for all alloys, however 9 hrs at 700°C lead to at least the number density observed in the HIPd state for all alloys but Ni45Cr4Nb. Fig. 11\textsuperscript{*} shows the average 3d radii of the $\alpha$-Cr areas. For all alloys containing more than 35 wt% Cr, the solution treatment caused a growth of primary $\alpha$-Cr as compared to long term aged samples. The average radius quickly drops however as secondary $\alpha$-Cr particles appear during aging at 700°C.

Quantitative microstructure analysis from SEM: $\delta$ phase

The data on the volume fraction and size distribution of $\delta$ phase are collected in Table 6\textsuperscript{*}. As compared to the standard deviations obtained for the $\alpha$-Cr quantification, those obtained for $\delta$ phase are somewhat higher, except for Ni45Cr6Nb. Volume fractions of $\delta$ are shown in Fig. 12\textsuperscript{*}. For all alloys except Ni35Cr6Nb and Ni45Cr6Nb, the solution treatment almost completely suppressed the subsequent formation of $\delta$. No systematic difference was found between 650°C and 700°C heat treatment temperature. In contrast to the results of $\alpha$-Cr, no relation between the sum of Cr and Nb content and the volume content of $\delta$ is found. Fig. 13\textsuperscript{*} shows the $\delta$ number density. The long term aging treatment at both 650°C and 700°C with only one exception (Ni45Cr4Nb) produces a lower number density the higher the sum of Nb and Cr content is. This suggests that even though an increased sum of Cr and Nb does not influence the volume percentage of $\delta$, it does lower the number of $\delta$ areas. Fig. 14\textsuperscript{*} shows the true average radii of $\delta$. Compared with Fig. 12 and 13, it is apparent that the solution treatment dissolves the bulk of $\delta$ particles, only leaving a small number of large particles behind. Long term heat treatment causes a decrease of the average radius for Ni35Cr6Nb and Ni40Cr5Nb.

Discussion

\* Table 5, Table 6 and Figure 9-14 shown in Appendix.
Microstructure evolution in high Cr, Nb stabilized Ni-based alloys

The microstructures of the alloys are diverse and directly influenced by the chemical composition and the heat treatment length and temperature. Manufacturing by the P/M route, leads to a very fine microstructure due to the rapid solidification of the metal powder. In the HIPd state all alloys have relatively simple microstructures with only globular representations of the stable phases, α-Cr and δ in a matrix of γ-Ni. The fraction of the various phases is governed by the chemical composition of the alloy: More than 4 wt% Nb promotes δ phase as a separate phase, and all alloys but Ni35Cr4Nb contain globular α-Cr. For a given Cr content, an increased Nb content causes a higher α-Cr phase fraction, while an increase in δ fraction is not seen when increasing the Cr content and keeping the Nb content constant. The original metal powder particles which were HIPd together can be traced, as the bulks of prior particles are relatively precipitate free in solution treated condition. Heat treatment from the HIPd state at 650 or 700°C causes growth of existing particle areas as well as precipitation of new particles of both α-Cr and δ. The new particles appear to be plate- or disk-shaped, as they are represented only as needles in the microstructure cross sections. Globular, interdendritic α-Cr has earlier been observed in vacuum cast Ni 50 wt% Cr alloy containing 1.5 wt% Nb and a maximum of 0.16 wt% N. For that alloy “ellipsoidal” α-Cr precipitates are observed during heat treatment at 700°C.6 The present work shows that higher levels of Nb and lower levels of Cr produces a similar α-Cr morphology. For most alloys, the ellipsoidal particles consist of α-Cr, but for Ni35Cr6Nb α-Cr and δ appear simultaneously. When the precipitates reach a length of about 1 µm, they are oriented according to an edge-on configuration, as shown in Fig. 15. A similar morphology has been found in Alloy 718.18–20. It has been hypothesized that the morphology is governed by the growth of γ”/δ, both of which have a very low solubility for Cr and therefore cause an increase in the Cr content of the adjacent matrix. The plate or disc-like morphology then originates from the preferred orientation relation of the γ” discs with the matrix: {001}γ”/⟨001⟩γ and ⟨100⟩γ”/⟨100⟩γ.26

Figure 15. Ni40Cr3.5Nb aged for 528 hours at 700°C. Insert shows the mutually perpendicular orientation of plate or disc-shaped α-Cr precipitates. BSE image.

The γ-Ni precipitates found within globular α-Cr, as shown in Fig. 6, also have a preferred orientation relationsship. This is similar to earlier work which documents the presence of these particles and
establishes the preferred orientation relationship between γ-Ni and α-Cr to be (111)γ//(110)α. As shown in Fig. 9 the observed volume fraction of α-Cr decreases between 528 and 1656 hours. This drop may be caused by the coarsening or disappearance of γ-Ni precipitates from within the α-Cr areas. This makes the γ-Ni particles distinguishable from the α-Cr particles and thereby causes an apparent drop in α-Cr volume fraction. Solution treatment at 1100°C dissolves most smaller precipitates, leaving only larger globular areas, and for Ni35Cr4Nb and Ni35Cr6Nb even those are removed. Subsequent heat treatment at 700°C causes growth of existing globular areas and the appearance of plate- or disk-like precipitates of α-Cr and δ. For Ni45Cr6Nb, no plates or disks are observed, as all precipitates remain as a globular morphology regardless of heat treatment.

_Tensile strength and ductility_

Among the aged alloys, the highest strength level is found for Ni45Cr6Nb, and the lowest for Ni35Cr4Nb, so the aggregated amount of Nb and Cr clearly influences the mechanical properties. For the solution treated alloys, Ni35Cr4Nb and Ni35Cr6Nb have similar tensile strength and ductility. Slightly lower strengths and elongations are reported for the commercial alloy Inconel 690 which is Ni based and contains 30 wt% Cr and 9 wt% Fe. Comparing solution treated Ni40Cr3.5Nb and Ni40Cr5Nb shows a marked difference, with Ni40Cr5Nb having a slightly higher strength and a much reduced elongation (from 40 to 24%). Bearing in mind that in the solution treated condition neither Ni35Cr4Nb nor Ni35Cr6Nb contains α-Cr, this could indicate that the primary strength increase, observed to have a positive correlation with the aggregated amount of Nb and Cr content, is caused by the increased phase fraction of b.c.c. α-Cr. An example of this effect is Ni40Cr3.5Nb and Ni40Cr5Nb. Regarding the aging treatment a significant strength increase is observed for all alloys accompanied with a variable loss of ductility. Comparing the aged strength and ductility of Ni35Cr4Nb and Ni35Cr6Nb reveals that the increased content of Nb significantly increases the aged strength. This supports the claim that the alloys are strengthened by γ”. However also a significant difference is observed between the yield and tensile strength of Ni35Cr4Nb and Ni45Cr4Nb indicating that not only γ” content causes a hardening, but that α-Cr also plays a part. This may be due to the, compared to γ”, relatively large finely dispersed perpendicular α-Cr discs or plates which form in higher quantities in the alloys with high Cr contents. Earlier work on cast Nb stabilized Ni 50 wt% Cr alloys reported a ductility in the 20-30% range, however the tensile strength was not reported⁶. In another study where Zr was used as N-getter, a Ni based alloy with 60 wt% Cr was presented with a solution treated elongation of 0 %. In that study the alloy softens and acquires an elongation of 22% after 72 hours aging at 700°C, an effect which is to some extent attributed to the acquisition of thermodynamical equilibrium⁷.

_Comparison of quantitative microstructure data with thermodynamic calculations_

By excluding the δ phase from the thermodynamic calculations, the equilibrium amount of meta-stable γ” can be predicted. However in reality both δ and γ” are present during short time aging, as shown in Table 4. The amounts of δ and γ” are interdependent, as the chemical compositions of the phases are identical. Table 7 shows that the experimentally measured δ and γ” content is far from the predicted equilibrium values. A heat treatment of 9 hour duration is relatively short, so it is not surprising that thermodynamic equilibrium has not been achieved. Also, the exact phase fractions of γ” and δ are expected to be underestimated as the appearance of both particles, nano-scale for one and needle-shaped for the other, make an exact quantification of their volume difficult with microscopy methods.
Table 7. Comparison of experimental and predicted volume fractions of γ”.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat treatment</th>
<th>Experimental γ” (vol %)</th>
<th>Experimental δ (vol %)</th>
<th>Predicted δ content TCNI5/NI-DATA (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni35Cr6Nb</td>
<td>ST + 700°C x 9 h (water quench)</td>
<td>0.26 (0.11)</td>
<td>1.0 (0.0)</td>
<td>17.5/16.5</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>ST + 700°C x 1 h (water quench)</td>
<td>0.15 (0.03)</td>
<td>0.0</td>
<td>10.7/9.3</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>ST + 700°C x 9 h (water quench)</td>
<td>0.32 (0.22)</td>
<td>&lt;0.1</td>
<td>10.7/9.3</td>
</tr>
</tbody>
</table>

In Fig. 16 the experimentally measured α-Cr volume fractions are compared with equilibrium predictions. The databases largely agree on the content of α-Cr, though values obtained with NI-DATA are consistently higher than those produced by TCNI5. The experimental volume fractions are systematically lower than the calculated values. This is partly caused by a lack of thermodynamic equilibrium, as there is no indication that the alloys have reached thermodynamic equilibrium during the 1656 hours aging treatment. However a contribution also comes from the disc- or plate-shaped morphology of α-Cr particles formed during this prolonged heat treatment. These are difficult to image at the used magnification (x1000), and consequently some will remain unnoticed or will not be quantified to the full extent of their actual area.

In Fig. 17 the measured δ volume fractions are compared to equilibrium predictions. The values obtained with NI-DATA are consistently lower than those from TCNI5. As found for α-Cr, generally experimental volume fractions are lower than predicted values. For the higher Nb contents (Ni35Cr6Nb and Ni45Cr6Nb) a satisfactory correspondence between experimental and predicted vol % δ is obtained.
Traditional, Cr contents higher than 25 wt% in Ni alloys lead to a brittle alloy. The present work demonstrates that it is possible to combine high ductility as produced with precipitation hardenable for a P/M Ni based alloy containing up to 40 wt% Cr. The microstructure of such alloys is a mix of globular and disk- or plate shaped α-Cr and δ as well as finely dispersed nano-scale γ”. Since γ” forms quickly on {001} planes of the γ-Ni matrix, it seems possible that the observed macroscopic disc shaped morphologies of both α-Cr and δ originate from this. As a whole, a compromise between the possibility of precipitation hardenable and high ductility as produced appears obtainable, and seems reached for Ni40Cr3.5Nb. This alloy could prove valuable for mechanically demanding applications exposed to hot corrosion.

Acknowledgement

The authors gratefully acknowledge Flemming Bjerg Grumsen at the Technical University of Denmark, for production of TEM lamellae and TEM operation. Funding for this project was provided by MAN Diesel & Turbo SE and the Danish Ministry of Science, Innovation and Higher Education.
Microstructure of precipitation hardenable powder metallurgical Ni alloys containing 35-45% Cr and 3.5-6% Nb

References


Table 5. Volume fractions, number densities and mean radii of α-Cr. Standard deviation shown in parenthesis. One outlier has been removed from values marked with asterix.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Quantity</th>
<th>Ni35Cr4Nb</th>
<th>Ni35Cr6Nb</th>
<th>Ni40Cr3.5Nb</th>
<th>Ni40Cr5Nb</th>
<th>Ni45Cr4Nb</th>
<th>Ni45Cr6Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST + 700°C x 9 h (water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>3.0 (0.0)</td>
<td>4.6 (0.5)</td>
<td>10.8 (0.4)</td>
<td>21.2 (0.4)</td>
<td>23.6 (1.1)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>-</td>
<td>11 (1)</td>
<td>10 (1)</td>
<td>34 (4)</td>
<td>48 (3)</td>
<td>11 (1)</td>
</tr>
<tr>
<td></td>
<td>Vol [%]</td>
<td>0</td>
<td>&lt;0.1*</td>
<td>4.0 (0.1)</td>
<td>7.8 (0.4)</td>
<td>18.3 (1.3)*</td>
<td>22.8 (0.8)</td>
</tr>
<tr>
<td>ST (1100°C x 1 h, water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>0.2 (0.1)*</td>
<td>8.0 (0)</td>
<td>2 (4)</td>
<td>26 (2)*</td>
<td>7 (0)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>-</td>
<td>274 (30)*</td>
<td>559 (11)</td>
<td>507 (29)</td>
<td>624 (29)*</td>
<td>1083 (5)</td>
</tr>
<tr>
<td>ST + 700°C x 1 h (water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>0.2 (0.4)</td>
<td>4.0 (0.0)</td>
<td>7.6 (0.9)</td>
<td>17.2 (1.1)</td>
<td>23.0 (1.0)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>-</td>
<td>3 (2)</td>
<td>9 (0)</td>
<td>19 (2)</td>
<td>26 (3)</td>
<td>7 (0)</td>
</tr>
<tr>
<td>ST + 700°C x 9 h (water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>1.4 (0.5)</td>
<td>5.0 (0.7)</td>
<td>11.4 (1.1)</td>
<td>19.2 (1.1)</td>
<td>25.0 (1.4)*</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>-</td>
<td>17 (4)</td>
<td>12 (2)</td>
<td>41 (7)</td>
<td>34 (2)</td>
<td>12 (2)*</td>
</tr>
<tr>
<td>650°C x 528 h, (air cool)</td>
<td>Vol [%]</td>
<td>7 (1.4)*</td>
<td>15.0 (1.6)</td>
<td>13.2 (0.8)</td>
<td>23.2 (1.3)</td>
<td>26.4 (2.7)</td>
<td>29.5 (1.9)*</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>318 (10)*</td>
<td>373 (8)</td>
<td>424 (9)</td>
<td>492 (9)</td>
<td>547 (33)</td>
<td>901 (5)*</td>
</tr>
<tr>
<td>700°C x 528 h (air cool)</td>
<td>Vol [%]</td>
<td>10.2 (1.5)</td>
<td>16.0 (0.8)*</td>
<td>13.8 (1.9)</td>
<td>19.6 (1.8)</td>
<td>29.0 (1.9)</td>
<td>30.0 (1.2)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>79 (5)</td>
<td>71 (5)*</td>
<td>57 (4)</td>
<td>57 (4)</td>
<td>50 (5)</td>
<td>12 (1)</td>
</tr>
<tr>
<td>650°C x 1656 h (air cool)</td>
<td>Vol [%]</td>
<td>9.0 (1.6)</td>
<td>12.6 (1.5)</td>
<td>13.0 (1.4)</td>
<td>18.2 (2.7)</td>
<td>25.6 (1.8)</td>
<td>28.4 (1.1)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>71 (5)</td>
<td>62 (6)</td>
<td>51 (5)</td>
<td>44 (4)</td>
<td>45 (7)</td>
<td>14 (2)</td>
</tr>
<tr>
<td>700°C x 1656 h (air cool)</td>
<td>Vol [%]</td>
<td>8.2 (1.1)</td>
<td>13.0 (1.2)</td>
<td>13.0 (1.2)</td>
<td>18.2 (2.2)</td>
<td>25.4 (1.5)</td>
<td>28.4 (0.5)</td>
</tr>
<tr>
<td></td>
<td>rₐ₀ [nm]</td>
<td>58 (7)</td>
<td>43 (7)</td>
<td>50 (3)</td>
<td>43 (4)</td>
<td>45 (0)</td>
<td>11 (1)</td>
</tr>
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</table>
Figure 9. Measured volume percentage of α-Cr.

Figure 10. Number density of α-Cr particles.
Figure 11. True average radius of α-Cr particles.
Table 6. Volume fractions, particle densities and true average radii of δ precipitates. Standard deviation shown in parenthesis. As with the results for the α-Cr quantification, one outlier has been removed from values marked with asterisk.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Quantity</th>
<th>Alloy</th>
<th>Ni35Cr4Nb</th>
<th>Ni35Cr6Nb</th>
<th>Ni40Cr3.5Nb</th>
<th>Ni40Cr5Nb</th>
<th>Ni45Cr4Nb</th>
<th>Ni45Cr6Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>As HIPd (1050°C x 3 h, rapid air cool)</td>
<td>Vol [%]</td>
<td>0</td>
<td>7 (0.7)</td>
<td>0</td>
<td>4 (0.7)</td>
<td>0.4 (0.9)</td>
<td>8.6 (0.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>0</td>
<td>18 (3)</td>
<td>-</td>
<td>13 (4)</td>
<td>5 (8)</td>
<td>22 (1)</td>
<td></td>
</tr>
<tr>
<td>ST (1100°C x 1 h, water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>0.8 (0.4)</td>
<td>0</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>4.8 (0.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>0</td>
<td>503 (16)</td>
<td>-</td>
<td>469 (49)</td>
<td>331 (28)</td>
<td>506 (13)</td>
<td></td>
</tr>
<tr>
<td>ST + 700°C x 1 h (water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>4.8 (0.5)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>0</td>
<td>449 (55)</td>
<td>-</td>
<td>443 (31)</td>
<td>395 (64)</td>
<td>554 (9)</td>
<td></td>
</tr>
<tr>
<td>ST + 700°C x 9 h (water quench)</td>
<td>Vol [%]</td>
<td>0</td>
<td>1.0 (0.0)</td>
<td>&lt;0.1</td>
<td>0.8 (0.4)</td>
<td>&lt;0.1</td>
<td>4.8 (0.5)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>0</td>
<td>453 (46)</td>
<td>-</td>
<td>412 (63)</td>
<td>282 (63)</td>
<td>517 (11)</td>
<td></td>
</tr>
<tr>
<td>650°C x 528 h (air cool)</td>
<td>Vol [%]</td>
<td>4.8 (2.4)*</td>
<td>12.6 (2.3)</td>
<td>2.0 (0.0)</td>
<td>9.8 (1.5)</td>
<td>3.6 (0.9)</td>
<td>10.8 (0.5)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>297 (18)*</td>
<td>412 (11)</td>
<td>257 (5)</td>
<td>356 (3)</td>
<td>292 (2)</td>
<td>509 (6)*</td>
<td></td>
</tr>
<tr>
<td>700°C x 528 h (air cool)</td>
<td>Vol [%]</td>
<td>7.6 (1.1)</td>
<td>14.4 (0.9)</td>
<td>2.8 (0.8)</td>
<td>8.6 (1.8)</td>
<td>4.6 (0.5)</td>
<td>14.4 (0.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>324 (10)</td>
<td>435 (16)</td>
<td>263 (7)</td>
<td>376 (7)</td>
<td>324 (5)</td>
<td>538 (5)</td>
<td></td>
</tr>
<tr>
<td>650°C x 1666 h (air cool)</td>
<td>Vol [%]</td>
<td>10.3 (1.3)*</td>
<td>15.4 (1.1)</td>
<td>4.1 (1.1)</td>
<td>10.6 (1.7)</td>
<td>5.4 (0.5)</td>
<td>15.0 (1.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>354 (7)*</td>
<td>441 (5)</td>
<td>288 (9)</td>
<td>417 (13)</td>
<td>335 (4)</td>
<td>540 (6)</td>
<td></td>
</tr>
<tr>
<td>700°C x 1666 h (air cool)</td>
<td>Vol [%]</td>
<td>7.6 (1.1)</td>
<td>17.5 (2.6)*</td>
<td>3.8 (0.8)</td>
<td>9.2 (0.8)</td>
<td>7.8 (0.8)</td>
<td>15.0 (0.1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rδ [nm]</td>
<td>58 (4)</td>
<td>55 (7)*</td>
<td>44 (5)</td>
<td>45 (4)</td>
<td>57 (10)</td>
<td>29 (1)</td>
<td></td>
</tr>
</tbody>
</table>

Microstructure of precipitation hardenable powder metallurgical Ni alloys containing 35-45% Cr and 3.5-6% Nb
Figure 12. Measured volume percentage of $\delta$.

Figure 13. Number density of $\delta$ particles.
Microstructure of precipitation hardenable powder metallurgical Ni alloys containing 35-45% Cr and 3.5-6% Nb

Figure 14. True average radius of δ particles.
Future HFO/GI exhaust valve spindle
Uffe D. Bihlet, MAN Diesel and Turbo, Denmark
Harro A. Hoeg, MAN Diesel and Turbo, Denmark

ABSTRACT
State of the art for exhaust valve spindles for large two stroke heavy fuel diesel engines is currently either a fully forged Nimonic 80A version or a cost effective version based on an austenitic valve steel weld coated by a specially hardened Inconel 718 seat hardfacing and Inconel 625 disc coating. These three alloys, originally developed more than 50 years ago for the gas turbine and process industry, show comparable corrosion resistance at usual heat load. The general trend in engine design is steadily pushing combustion chamber component temperatures towards higher levels and the hot corrosion resistance of these alloys is currently being tested to the limit. Furthermore operation on LNG will introduce new challenges. Indeed, it would appear that there is much room for improvement as no focused alloy development has been performed aimed at the special conditions found on the thermally and mechanically stressed parts of the exhaust valve spindle. In the present work new coating alloys, meeting the requirements for the future valve spindle, have been developed by combining literature study, service experience, experimental data and numerical thermodynamic calculations. This paper describes the considerations and results of this alloy development as well as the details of a required new production technique for manufacturing a compound product by the Hot Isostatic Pressing (HIP) technology which has been developed applying advanced Finite Element Method (FEM) modelling.

INTRODUCTION
In the modern large bore two-stroke diesel engine, the exhaust valve spindle remains a thermally stressed component. The increase in thermal load is not only related to the ever increasing load density but is also seen in connection with engine service at low loads, which offer the benefit of a low fuel consumption, but which may also involve performance conditions with increased valve temperatures. Elevated temperatures adversely affect the service life and reliability of spindles because of “hot corrosion”, a term which covers accelerated material loss caused by molten combustion products, such as Na₂SO₄ and V₂O₅, which rapidly dissolve the protective Cr₂O₃ oxide surface coating, Ref. [1]. This primarily takes place in a temperature interval of 650-750°C. In practice this phenomenon is normally seen on parts of the spindle bottom which, depending on the temperature level, usually experience corrosion rates between 0.1 and 0.4 mm/1,000 hrs. and, in extreme cases, up to 1 mm/1,000 hrs. However, it can also be seen attacking the spindle seat, as a result of local temperature increases in connection with a local gas leakage.

Furthermore, additional challenges can be expected for the spindle seat operating in future two-stroke engines running on LNG and other clean fuels. The amount of combustion products will decrease, and so will the amount of seat deposits. The consequence is expected to be a reduced lubricating effect between the valve seat and the bottom piece seat, which is likely to introduce a new wear mechanism on the spindle seat.

This paper presents a novel design of an exhaust valve spindle which is intended to meet the above requirements and perform equally well on heavy fuel oil as on LNG and other clean fuels. The novel design is based on both a novel production technology and on novel materials.

A part of the research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2077-2011) under grant agreement no. 265861 (Helios), Ref. [2], while another contribution originates from an industrial PhD project at MAN Diesel & Turbo (MDT) and the Technical University of Denmark.

STATE-OF-THE-ART
Present design specifications of MAN B&W two-stroke diesel engines include the DuraSpindle and Nimonic spindle as standard components. The DuraSpindle is a welded design based on an austenitic valve steel with welded Inconel coatings, including a special hardened-seat coating. The Nimonic spindle is fully forged with usually the entire spindle being produced of Nimonic 80A. In the large-bore version, the service performance of the two versions is quite comparable. However, the DuraSpindle offers superior strength and wear resistance, while the Nimonic seat offers superior corrosion resistance.

At usual heat loads, both types of spindles perform reliably with service intervals of usually 30,000 hrs. The deciding factor for the service interval is normally the corrosion rate on the spindle disc bottom, which typically is found in the interval between 0.1 and 0.4 mm/1,000 hrs. This interval relates to service conditions when running at a relatively high load. Low load conditions however may involve drastically increased corrosion rates on
the disc bottom, and figures up to 1 mm/1,000 hrs have been reported.

In addition, a recent engine design has implied a general increase of the temperature level of both the disc bottom and the seat area. As illustrated in Fig. 1, local burn marks on the spindle seat have been seen in a few cases.

Hence, the overall object of the new design concept is to combine the two above-mentioned coatings in a compound disc in which the coatings are fully dense, have a metallurgic bond to the substrate and have bonding zones with satisfactory mechanical properties.

NEW DESIGN CONCEPT

Materials with low wear rates under severe high temperature corrosive conditions have been known for more than 50 years, the most prominent being high Cr bearing Ni-base alloys and high Ni bearing Cr-base alloys. These alloys are also known for becoming brittle at temperatures in the range of 700°C when fabricated by conventional production processes, Ref. [3]. However, during the mid 1990s, MDT demonstrated that powder metallurgical (P/M) Ni48Cr compacted via hot isostatic pressing (HIP) retained excellent mechanical properties even after more than 4,000 hrs. exposure at 700°C, Ref. [4].

With respect to the seat hardfacing, a review of commercially available hardfacing alloys led to the conclusion that in order to meet the requirements for a high corrosion resistance and wear resistance, it would be necessary to develop a custom-made material.

As to the wear resistance of the seat coating, it is important to acknowledge that, so far, the nature of a possible wear mechanism of the seat during service on e.g. LNG has not yet been identified. Therefore, it is anticipated that a possible subsequent modification of the seat material is necessary to meet the wear requirements. The necessary flexibility for such a modification is evaluated to be best met within the P/M technology, specifically hot isostatic pressing (HIP).

The HIP process

The HIP production technology can produce fairly large components based on a welded capsule design applying thin sheet material of either low C steel or austenitic stainless steel.

DEVELOPMENT OF P/M MATERIALS

In order to rank the corrosion resistance of current exhaust valve materials, a modified DuraSpindle for a marine two-stroke engine with a cylinder diameter of 900 mm was produced according to the layout shown in Fig. 3. At the bottom of the spindle, 54 samples of 9 different Ni-based Ø11 alloys were embedded in a P/M matrix consisting of Ni49Cr1Nb. The composition of the tested alloys is shown in Table 1. Common for the alloys was that they contained 17 wt% Cr or more. Some alloys were present in both a welded (“W”) and a forged (“F”) state. Samples were positioned at radial positions Ø40 (centre), Ø100, Ø160, Ø220, Ø280, Ø340 and Ø400 mm. Some samples were not placed at position Ø40, and due to practical
reasons during spindle production, NiCr22WAl was not placed at positions Ø280, Ø340 and Ø400. After hot isostatic pressing, the spindle was put into active service on the engine of an ocean-going vessel for a total of 2,223 hrs. In order to establish a worst-case, the cylinder was fitted with non-optimal fuel atomisers, which are known to increase the temperature experienced by the spindle bottom.

![Figure 3 – The design of the modified DuraSpindle with HIP compound embedded samples configured for corrosion testing. Position of corrosion samples was named by their position on the diameter, spanning from Ø40 to Ø400](image)

After the test period, the spindle was extracted and inspected. The material loss was quantified by measuring the hole depth and compensating for the loss of the surrounding Ni49Cr1Nb. This correction was possible, because Ni49Cr1Nb was not corroded to any measurable degree in the center and perimeter of the spindle bottom. On those positions, turning marks were still visible, showing the original level of the machined surface. Using this reference, the material loss of Ni49Cr1Nb could be measured at the intermediate positions.

![Figure 4 – Material loss of each alloy specimen at the positions on the spindle diameter](image)

The material loss shown in Fig. 4 was most severe at the intermediate positions, with a clear maximum loss at Ø220. Samples at Ø400 were generally less corroded than those closer to the centre at Ø100. Samples of NiCr22WAl, which were only included at positions Ø400-Ø280, show the same trend as the other samples with increasing material loss towards Ø220. For each position, the alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni49Cr1Nb</td>
<td>0.01</td>
<td>0.05</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>1.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IN625F</td>
<td>0.03</td>
<td>0.21</td>
<td>22</td>
<td>4.08</td>
<td>8.7</td>
<td>0.29</td>
<td>3.61</td>
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<td>-</td>
<td>22</td>
<td>0.48</td>
<td>11.4</td>
<td>0.05</td>
<td>3.22</td>
<td>0.09</td>
</tr>
<tr>
<td>IN686F</td>
<td>0.01</td>
<td>0.1</td>
<td>17</td>
<td>0.15</td>
<td>16.7</td>
<td>0.11</td>
<td>0.03</td>
<td>0.29</td>
</tr>
<tr>
<td>IN686W</td>
<td>0.01</td>
<td>0.3</td>
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<td>2.09</td>
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<td>0.05</td>
<td>0.14</td>
<td>0.09</td>
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<tr>
<td>IN718F</td>
<td>0.03</td>
<td>0.14</td>
<td>19</td>
<td>17.3</td>
<td>3</td>
<td>0.94</td>
<td>5.21</td>
<td>0.49</td>
</tr>
<tr>
<td>Mix25:75</td>
<td>0.02</td>
<td>0.31</td>
<td>29</td>
<td>3.23</td>
<td>6.8</td>
<td>0</td>
<td>2.83</td>
<td>0</td>
</tr>
<tr>
<td>Mix50:50</td>
<td>0.02</td>
<td>0.23</td>
<td>35</td>
<td>2.15</td>
<td>4.5</td>
<td>0</td>
<td>2.23</td>
<td>0</td>
</tr>
<tr>
<td>NiCr22WAl</td>
<td>0.42</td>
<td>0.1</td>
<td>20</td>
<td>0.21</td>
<td>0.1</td>
<td>0.06</td>
<td>-</td>
<td>6.07</td>
</tr>
<tr>
<td>Nim80AF</td>
<td>0.06</td>
<td>0.08</td>
<td>19</td>
<td>0.22</td>
<td>-</td>
<td>2.41</td>
<td>-</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 1 – Composition of material samples in wt% as specified by material certificates. The composition of the mixed metal powder samples Mix25:75 and Mix50:50 are calculated as a weighted average of the two powders. IN686F and NiCr22WAl contains 4 and 6% W, respectively.
Future HFO/GI exhaust valve spindle

performed similarly, with some fluctuations at lower material loss levels. The most resistant alloy at all positions was Ni49Cr1Nb, which shows no corrosion at positions Ø40, Ø340 and Ø400. IN718F was more severely attacked than all other alloys for all positions except for Ø340, where IN686F suffered a slightly higher material loss. Most of the alloys contained approximately 20 wt% Cr, and they perform comparably with the exception of Nim80AF, the corrosion resistance of which is comparable to that of Mix50:50, which contains 35 wt% Cr on average.

Ni-base disc bottom coating

The above corrosion test clearly illustrates the superior corrosion resistance of the Ni49Cr1Nb material and, as illustrated in Fig. 5, earlier investigations have proven the suitability as an engineering material under prolonged service conditions at 700°C. Contrary to material produced by conventional production methods, the P/M HIP compacted material retains a high ductility level. Therefore, this material has been selected as the coating material for the firing side of the spindle disc.

![Figure 5 - The influence of heat treatment of Ni49Cr1Nb at 700°C on mechanical properties](image)

For the Ni49Cr1Nb charge applied in the actual project, the mechanical properties and the relevant physical properties have been established. These properties form the basis of the material data applied as boundary conditions in the FEM simulations.

The mechanical data shown in Fig. 6 is regarded as satisfactory, whereas the physical properties, density and thermal expansion coefficient shown in Figs. 7 and 8 revealed a feature that required special consideration during the subsequent FEM simulation.

![Figure 6 - Yield strength (YS) and tensile strength (UTS) dependency on test temperature for P/M HIP Ni49Cr1Nb. Elongation values remain constant at 23% for the tested temperatures](image)

![Figure 7 - Density of Ni49Cr1Nb exposed at 700°C](image)

The time-dependent density change is most likely related to Ni2Cr ordering, which has been shown to take place in high Cr Ni based alloys over time at elevated temperatures, Ref. [5].

![Figure 8 - Thermal expansion coefficient measured from 30-700°C for Ni49Cr after exposure at 700°C](image)

Also, the initial phase distribution of the two phases (α-Cr and γ-Ni) present in the alloys is different from...
the phase distribution established during the process temperature, shown in Figs. 9 and 10.

Figure 9 – Phase distribution of Ni49Cr1Nb calculated with Thermo-Calc using the TCNI5 database. γ-Ni phase is balance

The phase composition is calculated with Thermo-Calc using the TCNI5 database, which contains empirical free energy functions, built in the manner described by Saunders and Midownik, Ref. [6].

Diffusion causes successive phase redistribution towards the equilibrium condition at service temperature.

New Ni-base seat hardfacing

The very low crack susceptibility and high ductility of welded Inconel 718 (nominal composition 19%Cr, 18%Fe, 5.2%Nb, 0.5%Ti and 0.5%Al, bal Ni) are decisive material properties when performing the combined work hardening and precipitation hardening of the DuraSpindle seat hardfacing. It is possible because the alloy has a sluggish precipitation response, which requires several hours of heat treatment to complete. During such a heat treatment, which typically takes place at 650-750°C, finely distributed nano-scale particles of Ni3Nb (γ'') are formed. The structure of these particles is semi-coherent with the atomic matrix of the alloy. This impedes crystal deformations, contributing greatly to the strength and hardness of the alloy. It is possible to calculate the stable phase composition of Inconel 718 with the commercial software Thermo-Calc. The phase composition has been calculated for Inconel 718 and for a number of derived alloys in which the Fe and Mo content is replaced with Cr, see Fig. 11.

The results of the corrosion test and literature (Ref. [7]) confirm that a decrease of Fe and increase of Cr should vastly increase the hot corrosion resistance of Inconel 718. It is clearly illustrated in Fig. 11 that the γ'' content by and large is not affected by a higher Cr content, while the volume fraction of the α-Cr phase is greatly increased. However, the question of whether this is a problem remains. The α-Cr is traditionally regarded as brittle and weak compared to the bulk Ni matrix. However, recent work by Dong et al, Ref. [8], indicates that the morphology of the α-Cr heavily influences the mechanical properties, and indeed experiments shown later in this paper, with P/M specimens of Ni49Cr1Nb with a high amount of globular α-Cr particles, show that an elongation of up to 20 % is not uncommon.

Figure 10 – The influence of heat treatment at 700°C on the α-Cr content of Ni49Cr1Nb

Figure 11 – The phase composition of Inconel 718 when Fe and Mo are substituted with Cr, and Nb content is held constant. Results from Thermo-Calc, using the TCNI5 database

An iterative process was carried out to investigate whether it is indeed possible to create a precipitation hardenable Inconel 718 derivative with twice the Cr content without disastrous loss of elongation and, thereby, processability. The iterative process included a factorial experiment with 5 P/M alloys. The results were used to elucidate a 6th composition named Ni40Cr3.5Nb. For comparative purposes, both iterations are shown together in the following. Table 2 shows the chemical composition of the tested alloys.

New Ni-base seat hardfacing

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The results of the corrosion test and literature (Ref. [7]) confirm that a decrease of Fe and increase of Cr should vastly increase the hot corrosion resistance of Inconel 718. It is clearly illustrated in Fig. 11 that the γ'' content by and large is not affected by a higher Cr content, while the volume fraction of the α-Cr phase is greatly increased. However, the question of whether this is a problem remains. The α-Cr is traditionally regarded as brittle and weak compared to the bulk Ni matrix. However, recent work by Dong et al, Ref. [8], indicates that the morphology of the α-Cr heavily influences the mechanical properties, and indeed experiments shown later in this paper, with P/M specimens of Ni49Cr1Nb with a high amount of globular α-Cr particles, show that an elongation of up to 20 % is not uncommon.

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Table 2 – Chemical composition in wt% of powder metallurgical alloys as specified by the supplier certificate. Ni bal

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni35Cr4Nb</td>
<td>34.4</td>
<td>3.8</td>
<td>0.5</td>
<td>0.011</td>
<td>0.027</td>
<td>0.002</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>35.2</td>
<td>6.0</td>
<td>0.5</td>
<td>0.005</td>
<td>0.019</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>41</td>
<td>3.4</td>
<td>0.5</td>
<td>0.007</td>
<td>0.009</td>
<td>0.013</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>39.3</td>
<td>5.0</td>
<td>0.5</td>
<td>0.014</td>
<td>0.032</td>
<td>0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>44.8</td>
<td>4.1</td>
<td>0.5</td>
<td>0.013</td>
<td>0.032</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>44.5</td>
<td>6.0</td>
<td>0.5</td>
<td>0.013</td>
<td>0.025</td>
<td>0.001</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The alloys were HIP’ed to form Ø20 rods. These rods were solution treated by heating to 1,100°C followed by water quenching. Aging was performed at 700°C for up to 9 hours. The test methods were conventional tensile testing and 10 kgf Vickers hardness (HV) measurements. The hardness measurements performed during the heat treatment are shown in Fig. 12. All alloys responded rapidly to the aging treatment with a hardness increase of at least 100 HV within the first 2 hours. The high Cr high Nb alloys rapidly reached a high plateau from which only marginal improvement occurred.

The results from mechanical testing are shown in Table 3, with literature values for similarly treated P/M Inconel 718. It appears that there is a cross-influence between the Cr and Nb content. Also, Ni35Cr6Nb appears to have almost the same properties as Inconel 718, Ref. [9].

Table 3 – Mechanical properties of the alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution treated</th>
<th>Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>Ni35Cr4Nb</td>
<td>436</td>
<td>840</td>
</tr>
<tr>
<td>Ni35Cr6Nb</td>
<td>443</td>
<td>874</td>
</tr>
<tr>
<td>Ni40Cr3.5Nb</td>
<td>533</td>
<td>939</td>
</tr>
<tr>
<td>Ni40Cr5Nb</td>
<td>646</td>
<td>1059</td>
</tr>
<tr>
<td>Ni45Cr4Nb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni45Cr6Nb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>480</td>
<td>975</td>
</tr>
</tbody>
</table>

Considering the results from mechanical testing and hardness measurements, it seems that the mechanical properties of Ni35Cr6Nb, by and large, correspond to the performance of Inconel 718, while nearly doubling the Cr content. However, Ni40Cr3.5Nb will, because of the higher Cr content, have a superior hot corrosion resistance and, due to the high ductility in the aged condition, there appears to be a potential for a combined work and precipitation hardening which will further increase the strength level. As these samples are produced by P/M processes, it is possible to mix foreign particles into the powder before consolidation, leading to a bulk alloy with embedded functional particles which could improve the abrasive wear resistance.

**Bonding layer**

During the compaction in the HIP chamber, diffusion processes are responsible for the metallurgical bonding between substrate and coating. Elements diffuse across the bonding zone driven by activity gradients. Depending on the atomic number, diffusion distances of up to 1 mm have been observed in HIP’ed components. As the C content of the valve steel substrate is far higher than that of the coatings (0.25 vs 0.01 wt%), a direct coupling would lead to C-diffusion from the valve steel into the Ni-base coating and extensive chromium carbide precipitation in the bonding zone. The consequence would be a brittle bonding zone with inferior mechanical properties. Consequently, an intermediate zone with a bonding material must be established between the valve steel substrate and the coatings in order to hinder the detrimental effect of C-diffusion. For this purpose, an austenitic stainless steel (AISI 316L) with a C content of 0.025 wt% has proved to be very effective. As shown in Fig. 13, no appreciable C-diffusion has taken place across the bonding zone with the Ni-base coating during the HIP process. The C-diffusion into the AISI 316L at the bonding zone towards the valve steel causes a moderate carbide precipitation which is evenly distributed in the microstructure. This
results in a strengthening of the AISI 316L that is comparable with the strengthening of C in the valve steel.

![XRD mapping of the bonding zone between the valve steel substrate (top) and Ni49Cr1NB (bottom) illustrating the magnitude of C-diffusion into the AISI 316L (centre)](image)

**Figure 13** – XRD mapping of the bonding zone between the valve steel substrate (top) and Ni49Cr1NB (bottom) illustrating the magnitude of C-diffusion into the AISI 316L (centre)

Tensile tests of bonding zones have verified a sound and ductile bonding with the majority of the elongation taking place in the bonding material and the fracture position within the bonding material away from the bonding zones.

Direct bonding of the Ni49Cr1Nb and Ni40Cr3.5Nb coatings has been performed without any bonding layer showing satisfactory mechanical properties.

**PRODUCTION TECHNOLOGY**

The present capsule design involves both forged and powder materials made of four different materials, and when deciding the HIP process parameters, both economical and metallurgical considerations need to be made. Full compaction and bonding can usually be assured during a relatively short process time of 3 hours operating at 1,000 bar and a temperature above 1,000°C.

Furthermore, the process includes ramping up and down for at least another 3 hours. Fixing the process time and pressure at 3 hours and 1,000 bar respectively, the process temperature was set to variable due to its prominent influence on the metallurgic processes. With the criterion of a temperature as low as possible, below 1,150°C on grounds of the microstructure of the forged substrate, and the criterion for optimum mechanical properties of the bonding zone and the coating materials, the possible process temperature range came out as 1,050-1,150°C.

**HIP compound capsule design**

In case of the compound spindle disc, it was decided to apply a forged disc substrate which accounts for the majority of the disc capsule volume. The advantage of this solution, compared to a solution applying only powder, is that the total capsule shrinkage during HIP is relatively low, allowing for a near-net-shape production.

Furthermore, small tolerances for the coating geometries can easily be obtained. A solution based solely on powder would involve a more complicated capsule design. While preparing the prototype capsule design, the major concern is to assure that no unintended mixing of dissimilar metal powders takes place and that this can be done in the most economical way. Once these principles have been established, the next concern is the stress and strain condition of the finished valve during service. This information is obtained by FEM simulation and may lead to changes in the capsule design. On the basis of input from e.g. production and FEM modelling, the capsule design is going through an iterative process until service tests have confirmed a sound design. The present prototype capsule design is presented in Fig. 14, and this design will be applied on the first prototype spindle intended for service tests.

![The capsule design. The grey capsule parts are produced as deep drawn steel sheet being assembled by gas tungsten arc welding (GTAW). The forged disc substrate is green while the coating materials are red and orange, respectively. The bonding zone material is blue](image)

**Figure 14** – The capsule design. The grey capsule parts are produced as deep drawn steel sheet being assembled by gas tungsten arc welding (GTAW). The forged disc substrate is green while the coating materials are red and orange, respectively. The bonding zone material is blue
EVALUATION OF COMPOUND DISC DESIGN BY FEM

The prototype valve is designed in four separate parts, see Fig. 15. The valve steel is separated from the disc coating and seat material by a buffer layer. All parts have an outer skin simulating the capsule design. The outermost skin is removed in a final machining operation to give the valve spindle its final geometry.

The entire valve is modelled using three-noded axisymmetric triangles CAX3, Ref. [10]. The model characteristics are listed in Table 4. Two different meshes are used to analyse different aspects of the valve service. The stress-strain analysis is made using the fine mesh to get a good resolution of stress and strain gradients. The coarse model is used for a creep analysis, i.e. to analyse the deformation of the spindle during its service life.

<table>
<thead>
<tr>
<th>Part</th>
<th>Fine model</th>
<th>Coarse model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nodes</td>
<td>Elements</td>
</tr>
<tr>
<td>Valve</td>
<td>49,455</td>
<td>97,686</td>
</tr>
<tr>
<td>Valve skin</td>
<td>1,280</td>
<td>2,254</td>
</tr>
<tr>
<td>Buffer</td>
<td>26,242</td>
<td>50,634</td>
</tr>
<tr>
<td>Buffer skin</td>
<td>144</td>
<td>232</td>
</tr>
<tr>
<td>Seat</td>
<td>5,205</td>
<td>9,998</td>
</tr>
<tr>
<td>Seat skin</td>
<td>948</td>
<td>1,715</td>
</tr>
<tr>
<td>Corrosion layer</td>
<td>24,214</td>
<td>47,055</td>
</tr>
<tr>
<td>Corrosion layer skin</td>
<td>1,816</td>
<td>2,924</td>
</tr>
</tbody>
</table>

The HIP process is simulated by applying the HIP temperature and pressure. Afterwards the temperature is stepped down to room temperature. During the last stages of the simulation of the manufacturing, the outer skin elements are removed and the seat material is replaced. The latter simulates the phase change resulting from hardening the seat material.

The residual stress field after finish-machining is illustrated in Fig. 16. The results show that the area where three different materials meet is heavily loaded.

Therefore, an updated geometric design of the seat area is under development. However, it should be noted that the exact magnitudes of the peak stresses at the corner, and in the material interfaces, come with an added degree of uncertainty. Some local mixing of the powder materials is to be expected at the interface. The mixing results in a gradient transition, which is not included in this model.

The simulation then continues by applying a number of "operating" cycles. Each cycle consists of:

- heating up the engine to operating temperature (Fig. 17)
- applying combustion pressure
- cooling the engine down to room temperature.
Fig. 17 shows von Mises stress for the first operating cycle. The loading consists of operating temperature and combustion pressure. According to the simulation, the highest stresses and strains are located at the seat contact. Although, high stresses are expected in this region, the numerical maximum values shown are unrealistic and a consequence of the numerical model. In reality, the seat will deform plastically and distribute the applied load over a larger area. The figure also displays high levels of stress at the point where the residual stresses after finish-machining are high. Again, it is expected that local mixing of powders will influence the level of the maximum stress and strain towards lower values than calculated by the model. However, the simulation clearly indicates the necessity for a detailed analysis of this position.

To conclude, the initial simulations of the new valve design show that this concept generally is performing satisfactorily. One highly stressed region, where three materials meet, has been identified, and a remedy is about to be implemented. Furthermore, the first creep simulations are under evaluation, and a model taking care of time dependency of material properties is under preparation.

OUTLOOK

The latest design of the novel HIP compound valve spindle represents an important milestone as presently four prototype spindles of this design are under production. One spindle will be applied for verification of the capsule design and material properties. In addition, this spindle will be used for developing the procedure for the combined work- and precipitation hardening of the new seat alloy.

The remaining spindles are intended for service tests to evaluate their performance. Two of these spindles will also include corrosion tests on the disc bottom similar to the aforementioned corrosion test, however with a number of new materials including several versions of the new seat material.

At a later stage, preparations will be made to produce spindles for a first service test on a dual fuel (LNG) engine in order to document the service performance of the seat and to identify the wear mechanism, should it be different than the present one. If required, these data will represent the basis for the continued development of the seat material to a wear-optimised version.

Under the condition that the design is confirmed, the new spindle, when entering regular service, is expected to represent an increase of the design temperature of up to 50°C for both the disc face and seat hardfacing.

In conclusion, it is important to note that the present application of an advanced production technology has the implication that reconditioning of this type of spindle, using presently available technology, cannot regenerate the original properties.

ACKNOWLEDGEMENT

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REFERENCES


[2] HELIOS is a cooperation research project within the EU’s 7th Framework programme for Research and Technical Development/Transportation.


**N9177 Rolling and heat treatment of laser welded Ni35Cr4Nb and Ni40Cr3.5Nb on S46MC-C spindles**

**Background**

In order to reduce the risk of hot corrosion of the spindle seat which has been known to happen in some cases for the present standard consisting of Nimonic 80A or Inconel 718, the seats of five 46 bore spindles have been laser cladded with two unique seat alloys. The seat has been rolled as is standard procedure for DuraSpindles, and this report describes the development work performed in order to establish a suitable heat treatment in order to ensure an optimal precipitation hardening.

**Data :**

Component : Exhaust valve spindle  
Plant :  
Engine type :  
Engine builder :  
IMO no. :  
Service hours :  
Material : Ni35Cr4Nb, Ni40Cr3.5Nb  
Marking :  
Drawing :  

**Content**

1. Discussion and conclusion  
2. Experimental  
3. Rolling and aging treatment  
4. Weld quality  
5. Micro hardness measurements
1. Discussion and conclusion

The application of high Cr alloys by welding is traditionally difficult if at all possible. The alloys have a tendency to become brittle both during deposition and while in service.

In the present work the alloys Ni40Cr3.5Nb and Ni35Cr4Nb were laser cladded on the seats of 5 46MC-C DuraSpindle substrates, two of which had been prepared for service test with Inconel 625 welded onto the bottom. The aim was to produce spindles for service testing in order to investigate the corrosion and wear performance of the seat alloys.

Also, the results from the required aging treatment trials will be valid for upcoming HIP compound spindles which will incorporate Ni40Cr3.5Nb seats.

After cladding, one "Ni40Cr3.5Nb" spindle and one "Ni35Cr4Nb" spindle were rolled and cross sections were investigated and heat treated. Microscopy revealed the existence of some minor solidification cracks running perpendicularly to the substrate surface in both welds.

Heat treatment trials showed that heat treatment simulating that experienced by a spindle exposed to 4 hours at 700°C in an industrial scale furnace produces a hardness very much comparable to that of the present DuraSpindle seat alloys, Inconel 718, at least for Ni40Cr3.5Nb. Ni35Cr4Nb however remains too soft for practical application and further work needs to be done to establish a suitable heat treatment for this alloy, if any exists.

The 700°Cx4h heat treatment was applied to two rolled "Ni40Cr3.5Nb" spindles, which were machined to DuraSpindle dimensions. Penetration testing revealed that porosities existed along the entire surface of the substrate-weld interface, for both spindles, one more severe than the other. Because of this the spindles are not fit for service tests.

At present time one "Ni35Cr4Nb" spindle is waiting for the determination of a correct heat treatment.

2. Experimental

The alloys Ni35Cr4Nb and Ni40Cr3.5Nb was laser cladded onto the seat of 46MC-C spindles according to the following table:

<table>
<thead>
<tr>
<th>Spindle</th>
<th>Material</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni35Cr4Nb</td>
<td>Sectioned and heat treated</td>
</tr>
<tr>
<td>2</td>
<td>Ni40Cr3.5Nb</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ni40Cr3.5Nb</td>
<td>Sectioned and heat treated</td>
</tr>
<tr>
<td>4 (Inconel coated bottom)</td>
<td>Ni35Cr4Nb</td>
<td></td>
</tr>
<tr>
<td>5 (Inconel coated bottom)</td>
<td>Ni40Cr3.5Nb</td>
<td></td>
</tr>
</tbody>
</table>
3. Rolling and aging treatment

Rolling was performed as with DuraSpindle, that is 3 grooves and a pressure of up to 8 ton. A rolling depth of 2.2 mm was used.

Heat treatment was performed at 700°C for up to 5 hours on ~5 mm thick cross sections of the seat area from spindle 1 and 3. The aim was to achieve identical hardness distribution as that found for Inconel 718 Duraspindle seats.

In order to simulate an actual aging treatment as it would occur for a full sized spindle, a slower heat treatment was designed in which the 700°C was obtained with a ramping temperature of 4°C/min, requiring 3 hours to obtain the actual aging temperature. Holding time was 4 hours. Cooling was slowed down similarly.

After heat treatment, a map of the hardness was created by HV0.5kg measurements.

As preliminary results were promising, spindles 2 and 5 were rolled, heat treated in the industrial furnace at 700°C for 4 hours, and machined to DuraSpindle dimensions.

4. Weld quality

Cross sections of spindles 1 and 3

Cladding of both alloys contains fine dendrites. Cracks perpendicular to the substrate surface were found in both welds. These are indicated in Figure 1, which shows both placement and appearance of the cracks, which seem to be associated with a high dilution of the base material (SNCrW) and the contraction during solidification.

![Figure 1. As rolled Ni35Cr4Nb (Top), Ni40Cr3.5Nb (Bottom). Arrows indicates crack positions. Areas at arrows magnified in right column.](image-url)
**Penetration tests of spindles 2 and 5**

After machining, penetration testing was performed on spindles 2 and 5 (Figure 2).

![Figure 2. Penetration testing of spindles 2 and 5 after machining.](image)

Porosities were found on both spindles, however where spindle 2 had porosities on both inner and outer weld-substrate interface, spindle 5 had only porosities on the inner.

**5. Micro hardness measurements**

For the sake of comparison, micro hardness was measured on a cross section of a conventional DuraSpindle seat after 30k hours of service.

**Inconel 718**

![Figure 3. Hardness of Inconel 718 seat cross section after 30k hours service. Axis units in µm.](image)

The cross section hardness of the Inconel 718 seat is between 450 and 550 HV0.5.
**Ni40Cr3.5Nb**

<table>
<thead>
<tr>
<th>HV0.5</th>
<th>11 Mar 2013</th>
<th>Laser welded Ni40Cr3.5Nb as rolled</th>
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<td><img src="#" alt="Hardness Map" /></td>
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</table>
Figure 4. Hardness maps of Ni40Cr3.5Nb.

The hardness of the Ni40Cr3.5Nb seat reaches up to 650 HV0.5 after long term treatment at elevated service temperature.
Ni35Cr4Nb

HV0.5 | 11 Mar 2013 | Laser welded Ni35Cr4Nb as rolled

HV0.5 | 08 Mar 2013 | Laser welded Ni35Cr4Nb rolled and 700x1h

HV0.5 | 08 Mar 2013 | Laser welded Ni35Cr4Nb rolled and 700x3h

HV0.5 | 08 Mar 2013 | Laser welded Ni35Cr4Nb rolled and 700x5h
Figure 5. Hardness maps of Ni35Cr4Nb.

Hardness obtained for Ni35Cr4Nb is somewhat lower than that of Inconel 718.
N9278 Comparison of PTAW, HIPd and laser cladded Ni40Cr3.5Nb exhaust valve spindle seats

Background

Ni40Cr3.5Nb is a promising exhaust valve seat alloy, but would be more promising if it could be applied with other methods than hot isostatic pressing.

Related report:
N9177 Rolling and heat treatment of laser welded Ni35Cr4Nb and Ni40Cr3.5Nb on S46MC-C spindles.

Data :

Component : Exhaust valve spindle
Material : Ni40Cr3.5Nb

Content
1. Discussion and conclusion
2. Experimental
3. Results
1. Discussion and conclusion

The Ni40Cr3.5Nb alloy is suitable as seat material for the Hot Isostatic Pressing (HIP) compound exhaust valve spindle. However, if the alloy could be applied without using the costly HIP method, it would be a more desirable solution.

This report compares microhardness measurements from HIPd Ni40Cr3.5Nb with experimental laser and plasma cladding of HIP specification powder.

The hardness of rolled and heat treated laser and plasma cladded seats was found to be higher than that of the HIP'd seats. The higher hardness is probably due to microsegregation taking place during solidification, creating high local chemical concentrations of Nb and Cr. Upon heat treatment, this caused accelerated precipitation of the $\alpha$-Cr and $\gamma''$ phases, both of which increase the hardness.

The current heat treatment used for Ni40Cr3.5Nb was defined by experiments with laser cladded seats (shown in N9177), and as such may not be aggressive enough for the HIP'd seat, which appears to precipitation harden at a lower rate. Regardless, three HIP spindles with Ni40Cr3.5Nb are currently in service, results from which will reveal the impact, if any, of the slightly lower seat hardness.
2. Experimental

Ni40Cr3.5Nb was applied to spindle seats according to the table below.

<table>
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<th>Application method</th>
<th>Engine bore size (cm)</th>
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<td>Laser cladding</td>
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<tr>
<td>Plasma cladding</td>
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<td>HIP</td>
<td>60</td>
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After cladding, the spindles were rolled as DuraSpindles, and cross sections with a thickness of approximately 5 mm were cut from the seat areas for heat treatment.

The heat treatment used was defined in MDT report N9277, and is shown in Fig. 1. The slow heating and cooling rates were intended to simulate the actual metal temperature of a whole spindle being heat treated.

![Heat treatment of spindle cross sections](image)

Figure 1. Heating sequence used for heat treatment of spindle cross sections.
Microhardness measurements were performed with HV0.5g for the laser cladded samples, and with HV0.2g for the remaining samples on cross sections of the seat as shown in Fig. 2.

Figure 2. A cross section of a rolled spindle seat after microhardness indentation.

2. Results

The results are shown in Fig. 3. It seems that the HIPd Ni40Cr3.5Nb seat experiences a more sluggish precipitation hardening than that of the laser or plasma cladded counterparts. There appears to be no difference between the hardness of laser cladded and HIPd Ni40Cr3.5Nb in the rolled condition before heat treatment. However, after heat treatment the laser cladded seat was generally harder than the HIP’d version, indicating a faster precipitation hardening response. Judging by the hardness after heat treatment, the plasma cladded seat seems to have experienced the same fast hardening.
Figure 3. Microhardness measurements of rolled seats. The microhardness of the plasma cladded seat in the as-rolled condition was not measured.