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# In-situ hot corrosion testing of candidate materials for exhaust valve spindles

**Uffe Bihlet*, Harro A. Hoeg*, Kristian V. Dahl**, Marcel A.J. Somers****

***MAN Diesel & Turbo, Copenhagen, Denmark**

****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[1] 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[2] 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 $Cr_2O_3$ 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 straight forward, 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 Ni49Cr1Nb, 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 NiCr22WAl was included for comparative purposes. The remaining samples were placed at either 6 or 7 positions.

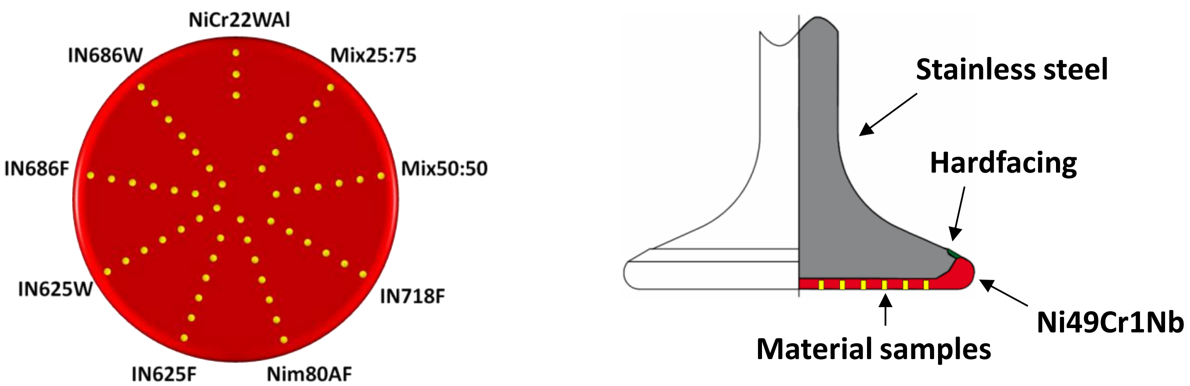


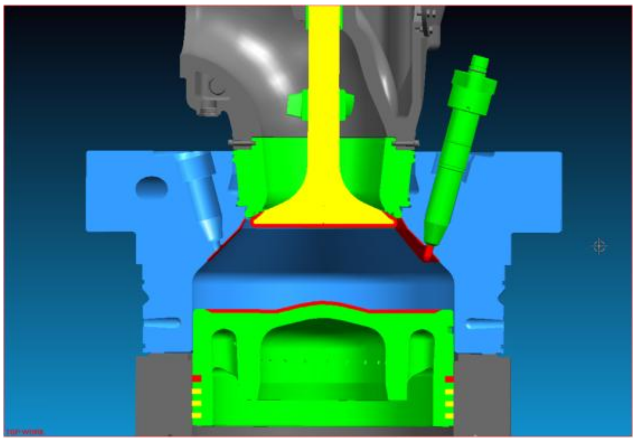

**Figure 1.** The design of the compound exhaust valve spindle with corrosion sample inserts.

**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.

| Material | C | Si | Cr | Fe | Mo | Ti | Nb | Al | W | Ni | Comment |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni49Cr1Nb | 0.01 | 0.05 | 48 | - | - | - | 1.04 | - | - | bal | Experimental |
| IN625F | 0.03 | 0.21 | 22 | 4.08 | 8.7 | 0.29 | 3.61 | 0.22 | - | bal | Forged |
| IN625W | 0.01 | - | 22 | 0.48 | 11.4 | 0.05 | 3.22 | 0.09 | - | bal | Welded |
| IN686F | 0.01 | 0.1 | 17 | 0.15 | 16.7 | 0.11 | 0.03 | 0.29 | 4 | bal | Forged |
| IN686W | 0.01 | 0.3 | 19 | 2.09 | 18.3 | 0.05 | 0.14 | 0.09 | - | bal | Welded |
| IN718F | 0.03 | 0.14 | 19 | 17.3 | 3.0 | 0.94 | 5.21 | 0.49 | - | bal | Forged |
| Mix25:75 | 0.02 | 0.31 | 29 | 3.23 | 6.8 | 0.00 | 2.83 | 0.00 | - | bal | 25% Ni49Cr1Nb 75% IN625 |
| Mix50:50 | 0.02 | 0.23 | 35 | 2.15 | 4.5 | 0.00 | 2.23 | 0.00 | - | bal | 50% Ni49Cr1Nb 50% IN625 |
| NiCr22WAl | 0.42 | 0.1 | 20 | 0.21 | 0.1 | 0.06 | - | 6.07 | 6 | bal | Designed custom alloy |
| Nim80AF | 0.06 | 0.08 | 19 | 0.22 | - | 2.41 | - | 1.7 | - | bal | Forged |

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.



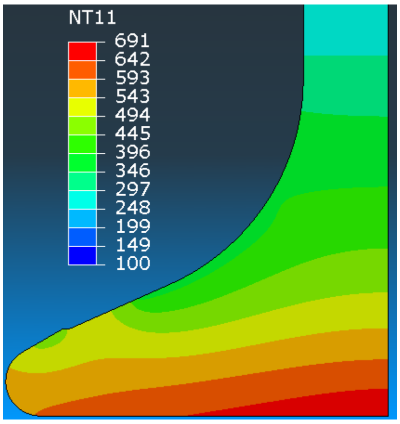



**Figure 2.** (Left) The hottest surfaces of the combustion chamber are marked with red. In this work the spindle bottom is treated. (Right) An FEM contour map of temperatures in °C. Because the cylinder is fitted with off-spec fuel injection valves, the spindle bottom temperature is increased to reflect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

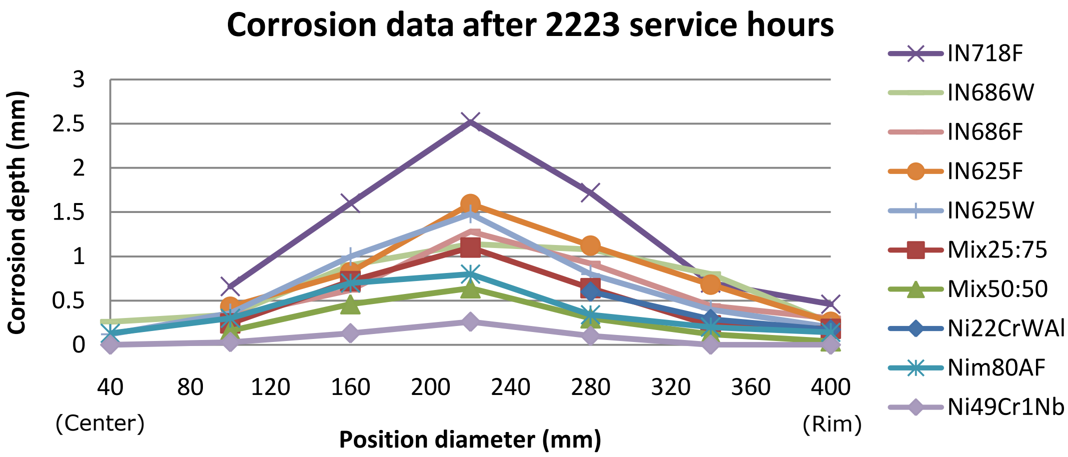



**Figure 3.** Corrosion depth compensated for the loss of Ni49Cr1Nb at same radial position.

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.

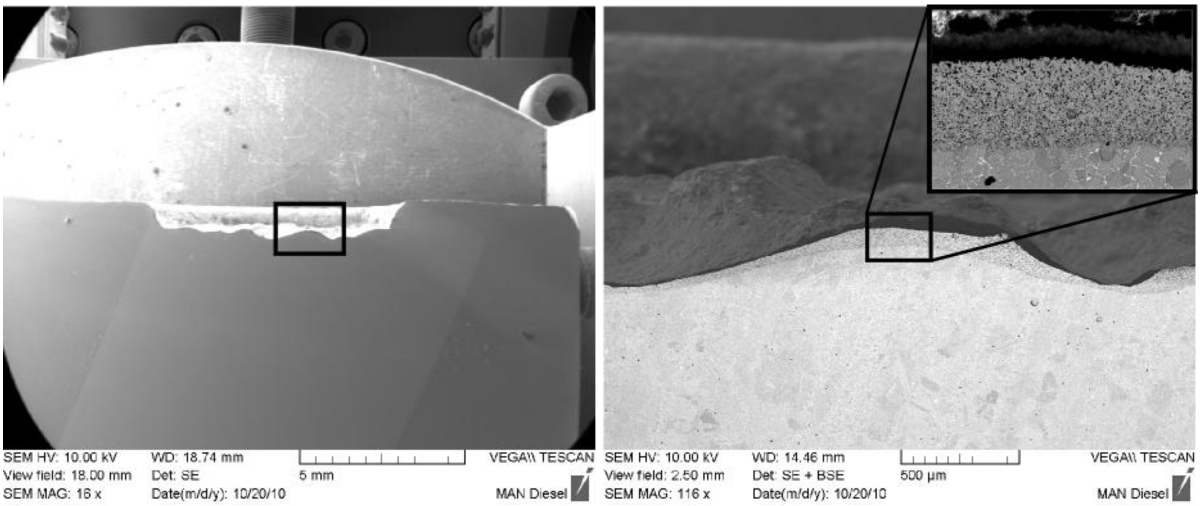



**Figure 4.** Cross section of IN625F material insert after 2223 hours of service. (Left) Overview. The surface has a wavy macro structure with peaks and valleys. This is found for all material inserts. (Right) Magnification of a peak. A sulphidized layer is found to be thickest at the peaks, but present 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[6]. 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 similiar 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.

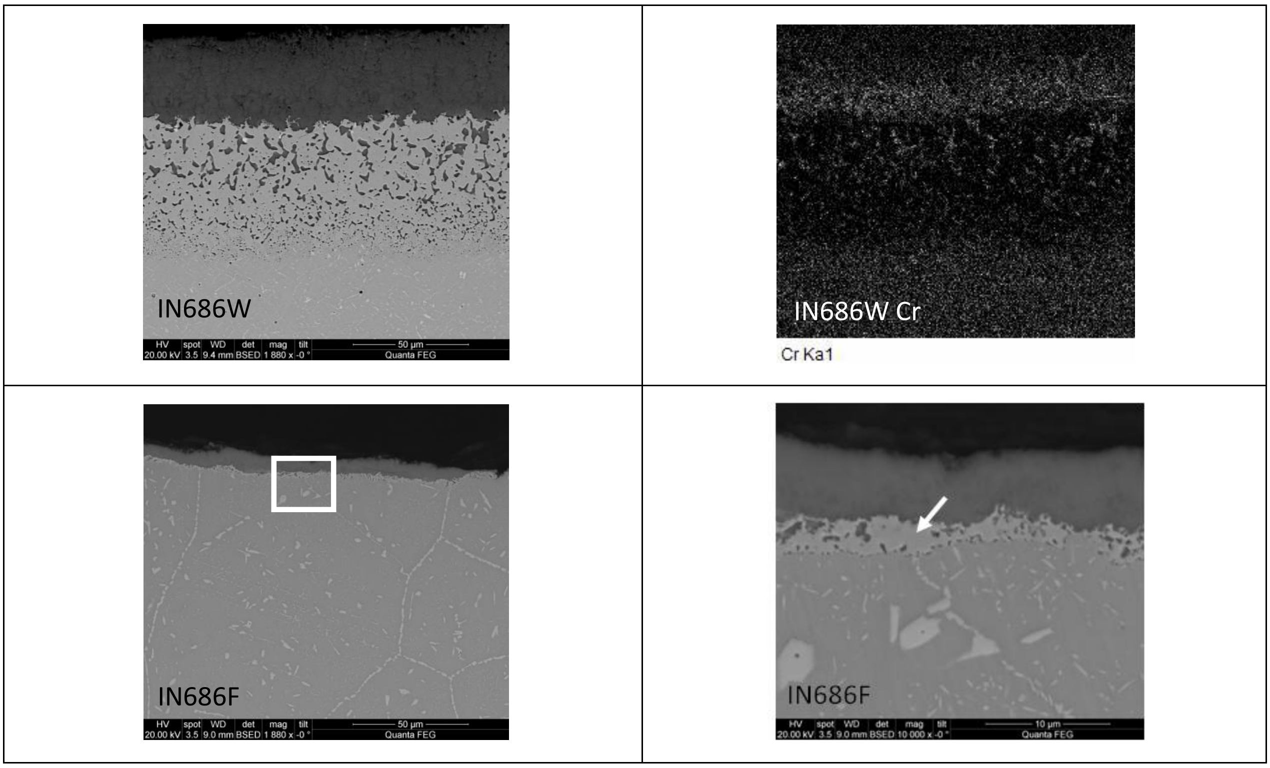



**Figure 5.** Cross sections of IN686W and IN686F material inserts at position Ø280. Investigations of all other materials but IN686F show results with similar morphology as for IN686W with an outer V,Cr-oxide followed by a Cr-depleted (as shown by EDS map) transition layer of varying thickness containing 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.

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.

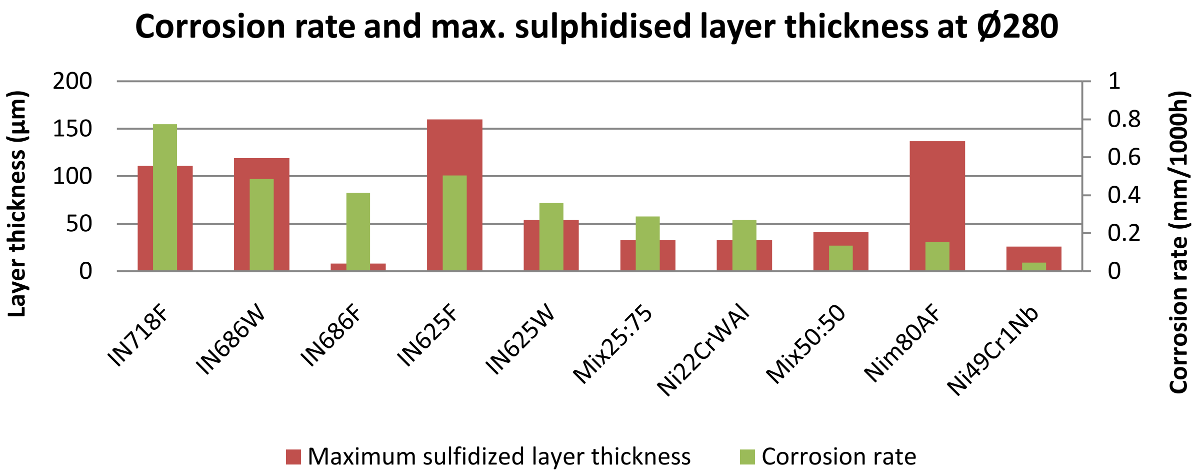



**Figure 6.** The corrosion rate measured over 2223 h of service time. The sulphidised layer for all HIP'd materials is moderate, while it for all others except IN686F is thicker. There does not seem to be any relation between the sulphidised layer thickness and the corrosion rate.

## 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.

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## Contact details

**Uffe Bihlet**
MAN Diesel & Turbo
Teglholmsgade 41
DK-2450 KBH SV
Denmark

E-mail: Uffe.Bihlet@man.eu