High Temperature Corrosion Protection of Exhaust Valves with Laser Welded Layers

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Abstract

Low-speed two-stroke diesel engines in the power range between 7'000 and 80'000 kW are employed as main engines for ship propulsion and as stationary engines for electrical generation plants. These large engines burn heavy fuel oil and the engine parts forming the combustion chamber can be subjected to corrosion problems at elevated temperatures. Topic of the presented paper is an attempt to protect the exhaust valve spindle disc that may face high-temperature corrosion. Cladding tests and experimental investigations are carried out in close co-operation between Wärtsilä Switzerland and BIAS Bremen. Valve spindles of Sulzer engines are made of Nimonic 80A, an alloy with sufficient resistance to high temperature corrosion in a distinct temperature range. However, when exceeding this temperature range, even spindle discs made from this nickel based alloy fail by loss of material under the influence of above mentioned corrosion. For protection the discs of the valves are, for the tests, deposited with functional coatings by laser welding to improve the corrosion behaviour and extend the life cycle of these components. The coatings consisted of different nickel-based alloys. In the preliminary stages of the study, the process window of various corrosion-resistant materials are determined and the most promising ones are applied on valve discs. The laser-clad valves are installed for test runs in a modern container ship. Depending on the process parameters and the corrosion resistant materials used, the functionally laser generated coatings were inspected after every 1000 service hours and afterwards evaluated comparatively. The investigations have been carried out over a period of three years. The results of this study are presented.

Introduction

Seagoing merchant ships are mainly equipped with low speed two-stroke diesel engines as propulsion in the power range up to 80'000 kW. Economy reasons force them to use residual oils as fuels. Such heavy fuel oils contain agents which can become highly corrosive. Burning of heavy fuel oil in low-speed, two-stroke diesel engines can lead to loss of material on combustion chamber parts at elevated temperatures. Topic of our presented work is the valve disc of the exhaust valve spindle, which may face high-temperature corrosion when exceeding distinct temperatures.
Valve spindles of Sulzer engines are made of Nimonic 80A, an alloy with sufficient resistance to high temperature corrosion up to usual present service temperatures.

Table 1: Nominal composition of Nimonic 80A

	C	Fe	Cr	Ti	Al	Ni
Nimonic 80A	0.1	3	20	2.4	1.4	bal

However, when exceeding this temperature range, even spindle discs made from Nimonic 80A may suffer loss of material under the influence of high temperature corrosion.

To increase the resistance of exhaust valve spindles against such loss of material is one aim of modern engine development. One promising solution is to clad the affected component area with a resistant layer. In case of the valve disc this can be done with different welding processes like electrode welding, MIG, TIG or by using the laser beam process. The latter process allows exact and highly localised heat input and therefore a precise clad deposition with a low dilution and low thermal stress of the components. A fine microstructure of the welding can be achieved and the process allows a wide variety in the alloy composition when using metal powders. Although one is facing high costs with this advantageous technology today, the laser beam cladding process is of economic interest for repair and reconditioning of valuable components and for the application of protective layers.

Cladding tests and experimental investigations

In the laser beam cladding process, a consumable powder is fed continuously into the melt pool on the surface of the substrate. In doing so, the added powder melts in the interaction zone of the laser beam and forms a clad track after solidification. The surface of the base material is melted marginally and a good layer-substrate composite with a low dilution is obtained. An outstanding characteristic of this welding method is the local and limited heat input because the high-intensity heat source results in low thermal stress of the component.

By depositing tracks successively side by side, single layers are formed and by depositing multiple layers on top of each other, multilayer structures are generated. In this study a 5 kW CO_2 laser was used depositing layers of one to somewhat more than two millimetres in thickness. These relatively thin layers are characterised by a high purity and offer in comparison to thick weldings further advantages concerning stress and strain properties.

For this work, various alloys with promising corrosion resistance were deposited on valve discs and tested in the main engine of a modern container ship. The vessel sailed between Europe and Far East, which granted a wide variety in real service conditions.

Burning heavy fuel oil in diesel engines results in the formation of residual ash. The ash contains compounds such as calcium sulphate and several sodium-vanadium compounds. Collecting ash from combustion surfaces of large diesel engines, sodium vanadyl vanadate type 1 ($Na_2O.V_2O_4.5V_2O_5$) and type 2 ($5Na_2O.V_2O_4.11V_2O_5$) are often identified in X-ray microstructure investigations. Also V_2O_5 could sometimes be detected in traces but its presence is judged to be of minor importance owing to the low content. It is known that the vanadium containing compounds can cause severe corrosion. During service, the ash is localised on more or less all surfaces in the engine's combustion chamber. Heavy fuel oils have a high content of sulphur, at present up to 5 % is possible. Therefore, sulphur oxides are generated during the combustion process, which have a great potential for corrosion. Depending on the temperature, the corrosive agents from ash and gas start to attack the different metals and form corrosion layers which adhere more or less to the base material. Focused on the exhaust valve disc made of Nimonic 80A, a complex structure is formed which contains, beside the above-mentioned ingredients from the fuel side, also nickel oxides, chromium oxides and nickel-chromium oxides, as well as nickel sulphide. Owing to erosive effects occurring in the combustion chamber, through gas velocity and fuel injection, weakly adherent corrosion layers are removed and thus the base material is exposed again for further corrosion attack. This alternating process may result in the loss of material whereby the loss rate differs according to experience among different affected areas [1].

One possibility for keeping the material loss within acceptable limits could be a protection with corrosion-resistant laser generated claddings. Resistance to corrosion and oxidation is generally obtained through the formation of a continuous and stable film of surface oxides. In the considered temperature range below 900 °C, chromium oxide films proved to be among the most protective, and therefore corrosion and oxidation resistant alloys are generally those of high chromium type. Studies of the corrosion morphologies observed on the valve materials have shown that corrosion rates are reduced as the chromium content of the alloy is increased, with high chromium containing scales forming a more protective barrier to vanadic ash attack [2].

Thus several nickel base alloys with high Cr-content were deposited and tested on the valves. Three valve discs were clad partially with different cladding materials and parameters, i. e. different beam forming and consequently different heat (or residual stress) input. In the beginning, preliminary experiments on Nimonic 80A samples were carried out to determine the process parameters for depositing nearly pore- and crack-free claddings. At first, two different NiCrAlY alloys and one NiCrW alloy were used as cladding material. The high-temperature corrosion resistance of numerous alloys is, in practice, provided by scales consisting of chrome, alumina and silica, or more complex oxides based on these. It has been known that small alloy additions of oxygen-active elements (“reactive elements”) may improve the oxidation resistance and particularly the scale adherence on high temperature alloys [3]. Indeed, there are still considerable gaps in our understanding of the properties and growth mechanism of these scales [4]. For this reason, two different NiCrAlY alloys with different addition of yttrium were used. Beyond it, chromium-rich materials (NiCr, NiCrLa) were tested. The addition of rare earths enhances the adherence of the protective oxide layers on the metal and consequently the oxidation stability [5].

The valve discs were sectioned and plated with different cladding materials, so that a comparable evaluation between the single cladding materials among themselves and between cladding material and base material was possible. These clad exhaust valves were installed in an engine and were checked periodically.

Results and discussion

The corrosion attack of the laser-generated claddings depends strongly on the service conditions, i. e. mainly on the resulting valve temperature, and the zone of the valve disc. On average, every 1000 service hours a visual inspection was carried out.

The corrosion behaviour of different materials at elevated temperature is in the foreground of our study so that most protection layers were applied as single layers. However, in two cases double layer claddings consisting of NiCrW and NiCr were also tested. As an example fig. 1 shows a realised clad thickness of NiCrAlY 1 which is in this case below 1 mm. The microstructure is free of cracks and pores, and possesses a dendritic structure.

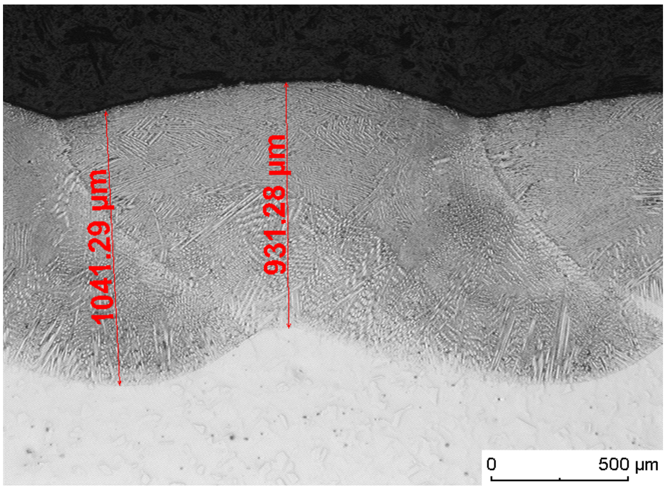

Fig. 1: Microstructure of NiCrAlY 1 after cladding using a 5 kW CO_2 laser and parabolic optics

Visual Inspection

At first, test valve claddings of the same material were deposited in the disc centre as well as near the disc edge to learn about the behaviour and the progress under high-temperature corrosion attack. In general, all claddings applied in the area near the disc edge show slight corrosion attack after 2000 to 3000 h in service independent of the alloy composition. Their surface structure of parallel welding runs changes to a morphology showing slight paving stone structure, a clear indication for corrosion attack. Loss of material on such layers is negligible within the first 1000 h. However, the surrounding Nimonic 80A in this area also shows only slight corrosion attack. These findings confirm experience and expectation because the corrosion attack in this area was always found to be very small.

The more affected disc centre showed other results. Beside severe corrosion attack, already slight spalling could be observed after about 1500 to 2000 service hours independent of the materials used. After about 3000 to 4000 h, the layers were badly damaged. Spalling and corrosion partly removed the cladding and base material was attacked. After 5000 to 6000 h, more or less all claddings were at least partially consumed independent of their composition. Different double layer claddings consisting of the mentioned alloys that were tested also showed a similar long-term behaviour and also disappeared after more than 6000 h.

Using different laser beam profiles showed no clear influence on the corrosion behaviour. Also the different microstructure, which was generated by using different laser optics, did not significantly influence the corrosion resistance.

In comparison to the platings the valve base material Nimonic 80A was extensively corroded as expected. Already after 1500 hours, extensive spalling of the corrosion products occurred. Under about 3000 h, a two-layer composite consisting of NiCrW and NiCr also showed an attack but, contrary to the other laser-generated claddings, the best result. During the service period below 3000 h, it may be interpreted that the NiCr types show the best corrosion resistance followed by double layer claddings with NiCr type as the top layer. A significant influence of La was not observed. However, it has to be kept in mind that the different claddings were tested during different sea voyages within 3 years. But it can clearly be stated that all tested layers show a better corrosion resistance than the valve original material Nimonic 80A. Representative for all laser generated claddings fig. 2 illustrates the appearance of NiCrLa and NiCr corroded surfaces beside Nimonic 80A in the more affected disc centre after about 2100 service hours.

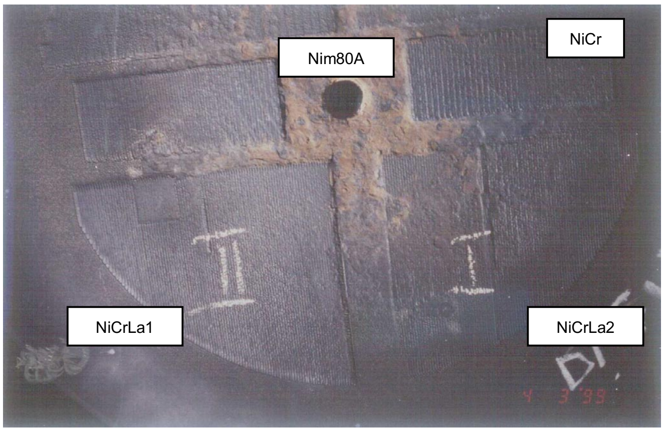

Fig. 2: Morphology of laser generated claddings in comparison to Nimonic 80A after about 2100 hours in service

Conclusion

The results of a number of investigations for providing exhaust valves with corrosion resistant cladding are presented. Using the laser beam cladding process various nickel base alloys were deposited on valve discs and tested in real service conditions in the main engine of a world-wide sailing merchant vessel. The most extensive corrosion attack of the exhaust valve appeared near disc centre. There, the various materials tested were heavily corroded, whereas in the outer zone of the valve disk near to its edge corrosion attack was less and the single stages of the corrosion attack could be observed in detail. No influence on the long-term corrosion behaviour was observed by using different focussing optics to generate the platings. However, it is important to control the state of residual stresses of the substrate-layer composite and to minimise the heat input. With increasing chromium content the corrosion resistance of the alloys tested increases. Alloying with rare earths element had in these tests no significant influence on the long-term corrosion behaviour. However, an aspired sufficient protection against high-temperature corrosion could not be achieved with the thin test layers applied. The material loss with the chosen nickel base alloys is less than that of the valve material Nimonic 80A, but ultimately the corrosion attack could not be prevented and the protection cladding will be consumed with time. Owing to its cost a sufficiently thick multilayer deposition is at present not reasonable.

Outlook

Corrosive agents will be formed when burning heavy fuel oil in diesel engines and consequently the combustion chamber materials may face the risk of corrosion attack. Developments in the petrochemical industry will tendentiously intensify these problems because more and more high-value distillation products are required and modern techniques allow a greater proportion to be extracted from crude oil. In the remaining residual oils, which are the basis for heavy fuel oils, the content of possibly harmful elements may therefore increase in the future. Thereby also the risk of corrosion increases. In addition, these problems strengthening development is the present diesel engine development. Modern seagoing ships require smaller and more powerful engines with low fuel consumption. This tendentiously imposes higher stresses, strains and temperatures in the materials used for engine construction. For these reasons, the mentioned corrosion problems will increase in general.

One practicable possibility to fight these problems is the protection of combustion chamber parts with corrosion-resistant layers. A mechanism for self-healing repair in the case of rupture and failure of the cladding is required. To achieve such a coating a reservoir of the component forming the protective scale is necessary. In practice this means that the protective coating must consist of a layer of a highly corrosion-resistant alloy where the protective oxide scales consist of thermally formed oxide scales of chrome, alumina or silica.

Using a laser beam for application of protective layers is proven. However, also a 1 to 2 mm thick layer has the function to work as barrier between base material and corrosive agents independent of whether they are solid, liquid or gaseous. Ideally, such a layer should completely resist corrosion attack. If material consumption appears due to corrosion, a layer thickness has to be within a range that a distinct service time can be reached before the parts could be reconditioned again.

This presentation shows results of thin layers made of different materials and applied by laser welding due to numerous advantages of this process. Compared to the base material that should be protected by the cladding the alloys used showed improved corrosion resistance. However, they are not fully resistant and therefore, the layers are consumed in an unacceptable time and the base material will become attacked again. At present an applicable alloy, which will resist this loss of material process, is not available. One possible step further in this problem area should be to develop thicker layers. A raising question for the near future is, how such layers can be produced economically by laser welding with all its advantages.

References

[1] D. Schlager: Ph.D. Thesis TU Karlsruhe, 1992

[2] J.R. Nicholls, D.J. Stephenson: Metals and materials 156

[3] P. Kofstad: High Temperature Corrosion (Eds. P. Kofstad), Elsevier Applied Science Publishers Ltd, London and New York 1988

[4] I. Rommerskirchen: Ph.D. Thesis Max Planck-Institut für Eisenforschung GmbH, Düsseldorf, 1996

[5] U. Heubner: Nickelwerkstoffe und hochlegierte Sonderedelstähle (Eds. U. Heubner und 8 Mitautoren), expert verlag, Ehningen 1993, pp. 1-37