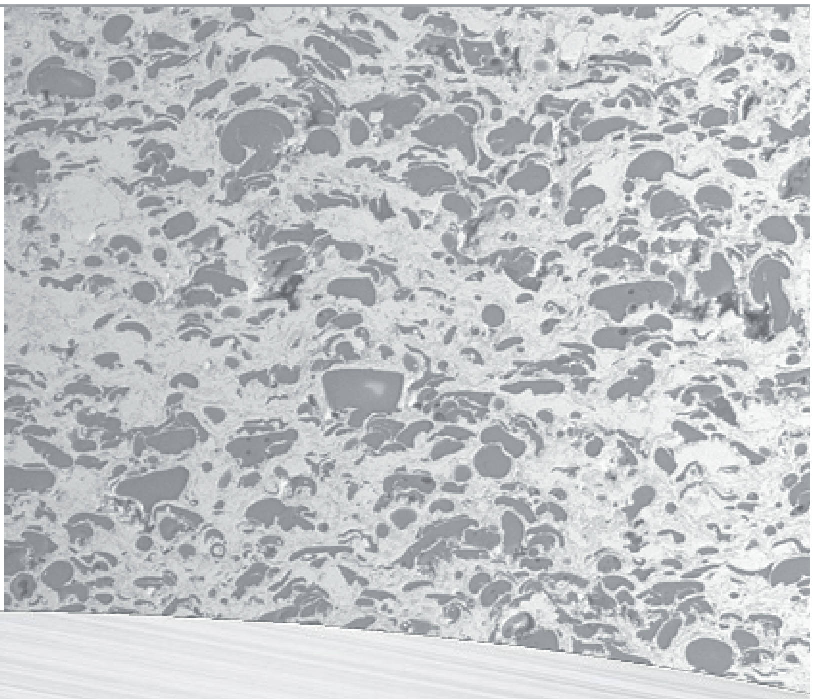
MW-C²

An Impermeable Mineral-Metal Multiphase Coating



MÄRKISCHES WERK

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INTRODUCTION

Power density and service life of high performance and large-bore engines are frequently limited by thermal loading of the exhaust valves. For engines that operate on Heavy Fuel Oil (HFO) the limitation is caused primarily by the corrosive environment within the combustion chamber and exhaust system. Exposure to HFO combustion products can lead to severe chemical attack on combustion chamber components and the exhaust valves for HFO fueled engines must typically be manufactured from expensive, Nickel-based super-alloys. However, even such valves suffer from hot-gas corrosion in highly-loaded engines and must be replaced frequently. Since materials with even higher resistance to hot-gas corrosion are not available, or are not economically viable, MWH has pioneered the development of coatings to protect engine valves and other engine components against hot-gas corrosion.

Multi-Phase, Thermally-Sprayed, Mineral-Metal Coatings

MWH initiated the development of hot-gas corrosion protection coatings in 2004. The first multi-phase corrosion protection coating suitable for use on engine components was demonstrated in 2006 and this so called Glass-Metal coating was presented at the CIMAC Congress 2007 in Vienna [1]. The first generation coating was composed of only 2 phases (one glass, one metal) and was applied using flame spraying. A microscopic view of the first generation MWH Glass-Metal coating is shown in Figure 1.

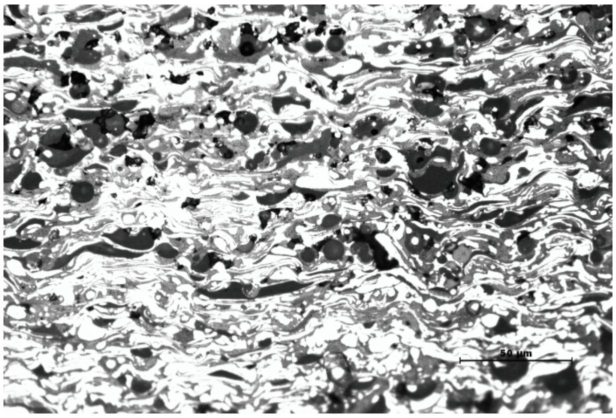

Figure 1 – Microscopic view of the first generation, MWH Glass-Metal coating structure (2 phases, applied through flame spraying).

The first generation MWH Glass-Metal coating proved that multi-phase, thermally-sprayed coatings can withstand the harsh environment of a combustion chamber. Moreover, the first field tests demonstrated that these types of coatings can protect exhaust valves from corrosive attack in an HFO-fueled engine. The MWH Glass-Metal coating showed improved corrosion protection on engines burning HFO with a Vanadium:Sodium (V:Na) ratio of about 8:1. The MWH Glass-Metal coating corroded at a slower rate than Nimonic 80A and prevented the formation of the “cobblestone” pattern, characteristic of accelerated corrosive attack at the metal’s grain boundaries.

Further laboratory and engine tests with the MWH Glass-Metal coating showed, however, that when the V:Na ratio of the fuel approached 2:1, the corrosion rate of our Glass-Metal coating was higher than that of Nimonic 80A. This behavior was traced to the formation of Na_2SO_4 formation in environments with low V:Na ratios and the relatively low melting temperature of the glass phase employed in that coating.

Hot-Gas Corrosion on Combustion Chamber Components

A further recognition from the trials with the first generation MWH Glass-Metal coating was that the corrosive loading on components within the combustion chamber of HFO-fueled engines can be even more severe than was previously believed. Specifically, the instantaneous localized surface temperature of combustion chamber components can exceed their average bulk temperature by 100 °C, or more. Hence, while the maximum operating temperature of exhaust valves is generally accepted to be below 700 °C, the chemical processes responsible for the hot-gas corrosion at the surface are driven by much higher temperatures. This effect is confirmed by the fact that many Nimonic 80A exhaust valves experience corrosion wear rates on the valve face of 200-500 μm/1000hrs. In some instances, wear rates of 1000 μm/1000hrs have been documented on 2-stroke Nimonic 80A valve spindles.

In order to effectively protect combustion chamber components against hot-gas corrosion under real-world conditions, it was necessary to develop coatings with chemical resistance to more corrosive combustion byproducts, and with higher application temperatures. The development, testing, and application of such coatings are discussed in the following sections.

MW-C^2

Following our experience with the first MWH Glass-Metal coating [1], a new generation of multi-phase mineral-metal coatings was developed for use on engine components. These coatings carry the name MW-C^2 and are composed of 3 or more phases.

MW-C^2 employs mineral (glass and ceramic) components which are resistant to Na_2SO_4 and $Na_2O \cdot 6V_2O_5$, as well as mixtures thereof. This is achieved by employing mineral components with high melting points (>1300 °C), and application through plasma spraying. Other general characteristics of MW-C^2 include:

- High bonding strength between coating and substrate (interface).
- Thermal expansion coefficient matched to the substrate.
- Elastic and highly resistant to thermal shock.
- Low porosity (< 2%).
- Impermeable and thermodynamically stable up to high temperatures (resistant to hot-gas corrosion).

In order to more precisely characterize the hot-gas corrosion resistance of MW-C^2, a laboratory test procedure for accelerated corrosion tests was developed at MWH. This test procedure, as well as the hot-gas corrosion resistance of the resulting MW-C^2 formulations, is discussed in the next section.

MW-C^2 Development and Laboratory Testing

Modern engine components have an expected lifetime of several thousand hours in the field. As a result, engine tests can take a very long time and the performance of a corrosion-protection layer can only be evaluated after many months or even years. In order to aid the development of MW-C^2, an accelerated corrosion test was developed at MWH.

This test consists of:

1) Coating the outer perimeter of cylindrical test samples to the desired thickness.
2) Placing the test samples in Al_2O_3 crucibles, and covering them with a mixture of $Na_2O \cdot 6V_2O_5$ and Na_2SO_4. (9:1 ratio).
3) Placing the test samples in a laboratory furnace (tests conducted at 700 and 900 °C). The crucibles must be refilled with the $Na_2O \cdot 6V_2O_5$ & Na_2SO_4 mixture every 20 hrs.

4) At the conclusion of the test, the samples are cleaned by light sandblasting, and the remaining coating thickness is measured.

Figure 2 shows a typical coated test sample for the accelerated corrosion test and a microscopic view of the corroded cross-section at the conclusion of the test.

Guided by the MWH accelerated corrosion test, a formulation for MW-C^2 was developed and the plasma spraying parameters were optimized. The resulting 3-phase (2 mineral phases and one metallic phase) coating structure is shown in Figure 3. A comparison with the first generation Glass-Metal coating (Figure 1) reveals a better dispersion of the mineral phases (darker color), which results in improved corrosion resistance. The ratio of the mineral phases within MW-C^2 can be varied to adjust the thermal expansion coefficient within the range of 11 to $19 \times 10^{-6} K^{-1}$ (at 20 °C). This thermal expansion coefficient adjustment is necessary so that different substrate materials can be coated. The base MW-C^2 formulation is suitable for all Iron and Nickel-based materials. MW-C^2 also features a low thermal conductivity (1.5 – 2 W/mK) so that the coating can also form an effective thermal barrier in applications where this is desired. Laboratory and field testing have shown that the base MW-C^2 formulation is highly effective as a corrosion protection layer to HFO combustion byproducts up to about 700 °C. These field tests, however, have also shown that localized instantaneous surface temperatures in excess of 700 °C occur on combustion chamber components, and that a coating with corrosion resistance at higher temperatures is required to protect the most highly loaded exhaust valves (4-stroke and 2-stroke).

Figure 2 – Typical test sample for the laboratory corrosion test (left) and microscopic view of corroded cross-section (right).

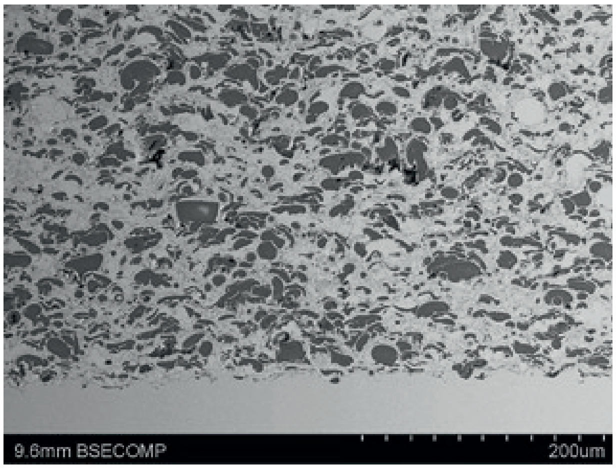

Figure 3 – Microscopic view of the MWH MW-C^2 coating structure (3 phases, applied through plasma spraying).

A high-temperature formulation of MW-C^2 (called MW-C^2 HT) was developed for application at even higher temperatures. MW-C^2 HT employs 5 phases (4 mineral phases and one metallic phase) and its structure is shown in Figure 4.

In particular, the mineral phases of MW-C^2 HT consist of “inactive” oxides with extremely high melting points. Just like for MW-C^2, the relative ratio of the mineral phases can be varied to adjust the thermal expansion coefficient, and MW-C^2 HT is also suitable for all Iron and Nickel based materials. The main characteristics of MW-C^2 and MW-C^2 are summarized in Table 1.

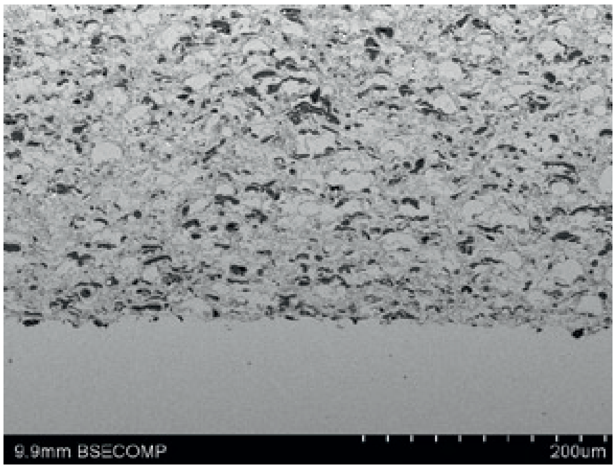

Figure 4 – Microscopic view of the MW-C^2 HT coating structure (5 phases, applied through plasma spraying).

	MW-C^2	**MW-C^2 HT**
Number of phases (mineral/metal)	3 (2/1)	5 (4/1)
Application Temp. in HFO combustion	Up to 700 °C	Up to 900 °C
Max. Temp. in air	1000 °C	1000 °C
Thermal conductivity at 20 °C	1.5 – 2 W/mK	3 – 4 W/mK
Range of thermal expansion coefficients at 20 °C	11-19x10^{-6}K^{-1}	10 -19x10^{-6}K^{-1}

Table 1 – Main properties and application ranges of MW-C^2 and MW-C^2 HT.

The measured corrosion rates of MW-C^2 and MW-C^2 HT, as well as Nimonic 80A, are shown in Figure 5. Although these corrosion rates were measured using the laboratory procedure described previously, these results provide a good indicator of the improved resistance to hot-gas corrosion achievable with MW-C^2 and MW-C^2 HT.

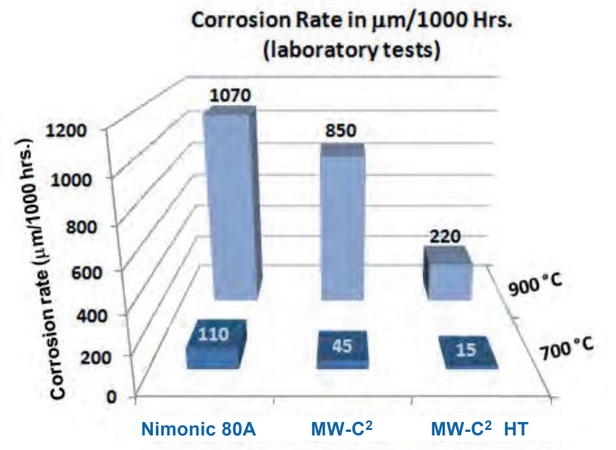

Figure 5 -- Measured corrosion rates of Nimonic 80A, MW-C^2, and MW-C^2 HT in laboratory testing. Hot-gas corrosion tests were performed at 700 and 900°C.

Field Validation on 4-Stroke Engines:

Several new Nimonic 80A exhaust valve spindles were installed on a 320mm bore power generation engine, operated on HFO. These valves were coated with MW-C^2 on the valve face, outer diameter, and underhead radius, as illustrated in Figure 6. The engine was operated as normal, and no incidents were reported during the duration of the trial. Periodic inspections of the valves were conducted by MWH personnel and two coated valves were removed for destructive evaluation in our laboratory after 4630 and 7323 running hours, respectively. The valve spindles were cleaned of deposits, measured, and sectioned. Cross-sectional and microscopic views of these valves are shown in Figures 7 and 8, respectively.

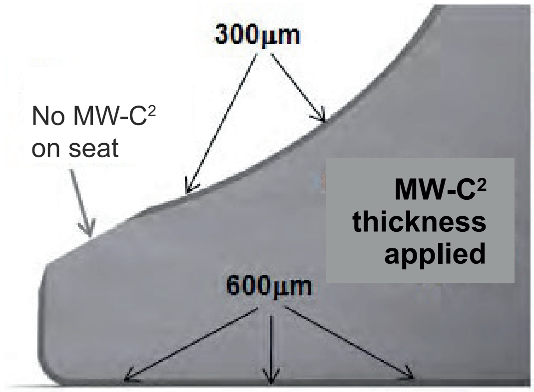

Figure 6 – Illustration of the MW-C^2 4-stroke exhaust valve spindles. The The MW-C^2 thicknesses applied are indicted on the figure. Valve material was Nimonic 80A.

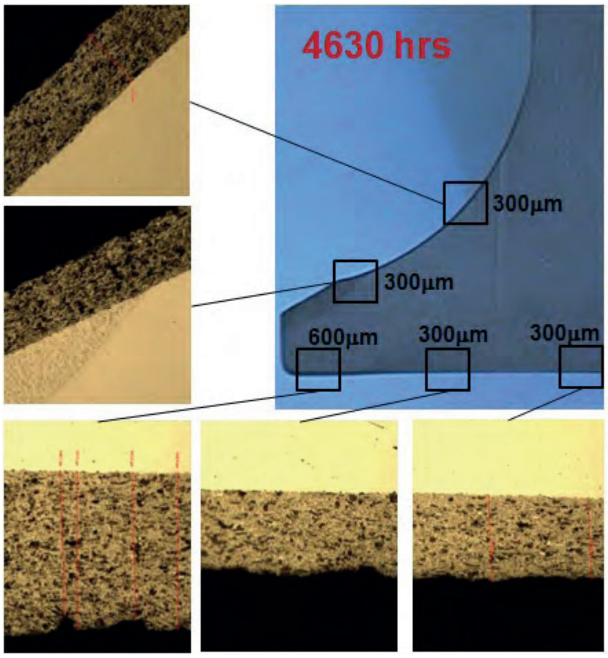

Figure 7 – Cross-section and microscopic views of 4-stroke MW-C^2 exhaust valve after 4630 hrs of operation. Remaining MW-C^2 thicknesses at the various locations are indicated on the figure.

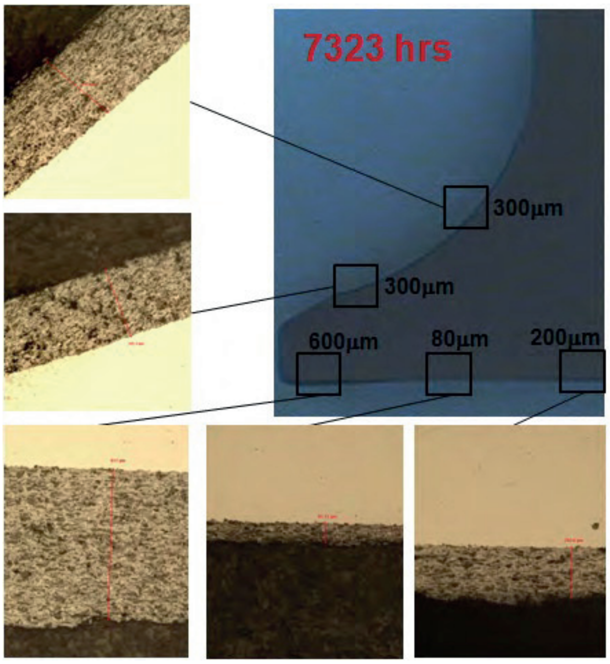

Figure 8 – Cross-section and microscopic views of 4-stroke MW-C^2 exhaust valve after 7323 hrs of operation. Remaining MW-C^2 thicknesses at the various locations are indicated on the figure.

The MW-C2 exhaust valves were in very good condition overall. Figures 7 and 8 show that the MW-C2 coating was still present on every surface where it was applied, even after more than 7000hrs of operation. Note specifically that no debonding or spalling is observed, and that the base valve material is completely protected by the coating. That is, no intergranular “cobblestone” corrosion is found underneath the coating. The MW-C2 thickness is unchanged on the lower temperature regions of the valves (underhead radius, and outer diameter of the valve face). This is of great value because hot-gas corrosion on the underhead radius can ultimately lead to catastrophic valve failure, as illustrated in Figure 9. The MW-C2 thickness does decrease gradually at the highest temperature regions (about ½ radius location on the valve face). The maximum measured corrosion rate of MW-C2 at this location is about 70 µm/1000hrs, as shown in Figure 10. This maximum measured corrosion rates on the valve face would correspond to an instantaneous localized surface temperature above 700 °C (see results on Figure 5). Based on the field trials on this engine, it is expected that the underhead radius of the valve would be protected indefinitely with a 300µm coating and that the entire valve face would be protected for about 14,000hrs with a 1mm (1000µm) thick coating. This performance is quite acceptable and represents a quantum improvement from conventional uncoated valves. Note that even after the MW-C2 layer wears off the valve face, the valve can continue to operate without risk of failure until the normal valve wear limits are reached. Hence, the operating limit due to hot-gas corrosion is extended by at least 14,000 hrs. As discussed below, application of MW-C2 HT can provide an even more durable barrier against hot-gas corrosion and may eliminate the requirement for using Nickel-based super-alloys altogether.

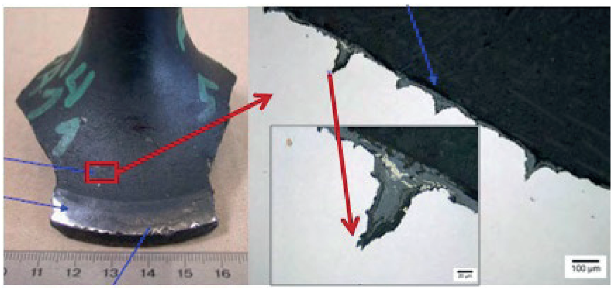

Figure 9 – Example of catastrophic failure caused by a crack originated at the underhead radius of an uncoated Nimonic 80A valve. The crack most likely started at the sharp notches formed by the intergranular hot-gas corrosion.

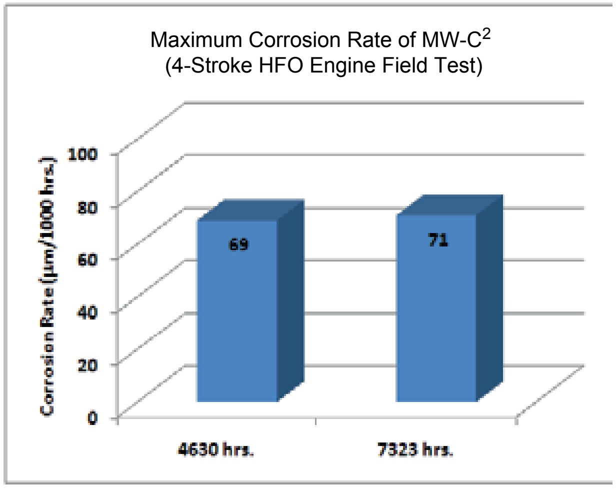

Figure 10 -- Maximum measured corrosion rate on the 4-stoke HFO exhaust valve spindles during field trials. (Note: Maximum corrosion rate occurs at roughly the ½ radius position on the valve face).

<u>Field Validation on 2-Stroke Engines:</u>

Field validation of MW-C2 for 2-Stroke engine applications was conducted on an MC50 valve spindle. Two new Nimonic 80A spindles, one with the valve face coated with MW-C2, and one uncoated, were installed on two cylinders of a 6 L 50 MC marine propulsion engine. The coated valve is shown on Figure 11, prior to its initial installation in the engine.

The two valve spindles were inspected periodically by MWH personnel and the "burnt depth" (corrosion depth) on the valve face was measured and documented. Both spindles were in good overall operating condition, but some important differences were visually apparent. Specifically, the appearance of "cobblestone" marks, indicative of the typical intergranular corrosion pattern, was clearly visible on the valve face and outer diameter of the Nimonic 80A valve spindle. The MW-C^2 spindle, on the other hand, showed no visible "cobblestone" marks. As previously shown (see Figures 7 and 8), MW-C^2 wears (corrodes) uniformly. The visual appearance of the Nimonic 80A and MW-C^2 spindles after approximately 4000 hrs of operation is shown on Figure 12. The intergranular "cobblestone" pattern on the surface of the Nimonic 80A valve indicates that the corrosion damage has penetrated into the valve material. The microscopic structure of these intergranular corrosion "cobblestones" is illustrated in Figure 13, on a typical Nimonic 80A valve face. The corrosion notches in between the "cobblestones" can frequently penetrate more than 1mm from the valve face surface.

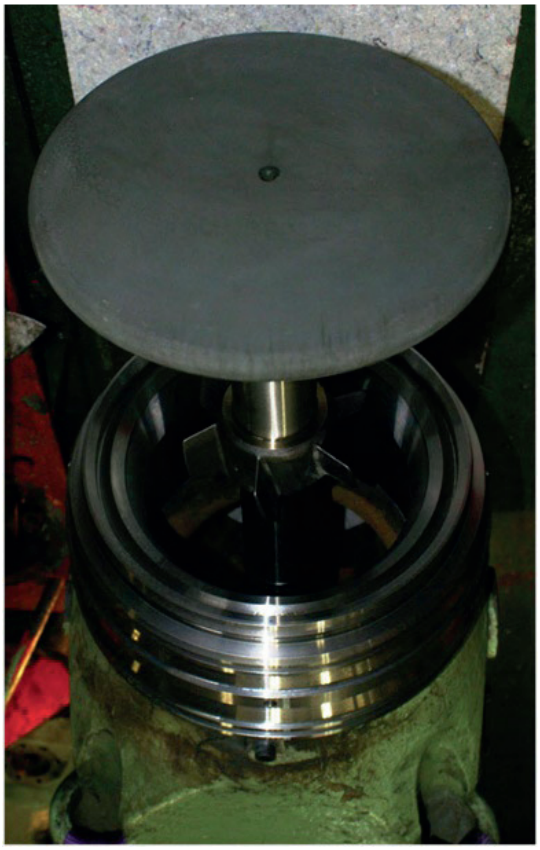

Figure 11 – Picture of the MC50 Nimonic 80A valve spindle with 600µm thick MW-C^2 coating on the valve face and outer diameter, prior to initial engine installation.

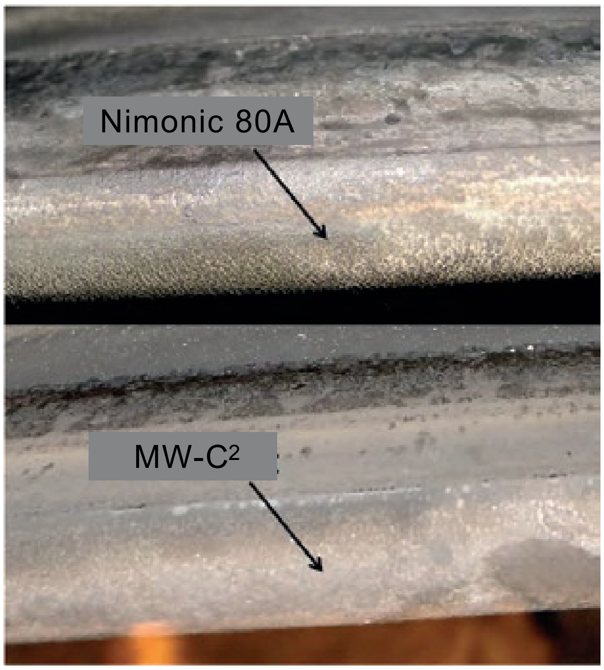

Figure 12 – Close-up photographs of the 50MC valve spindles, illustrating the

formation of intergranular "cobblestone" corrosion marks on the Nimonic 80A valve face and outer diameter, but not on the MW-C^2 valve.

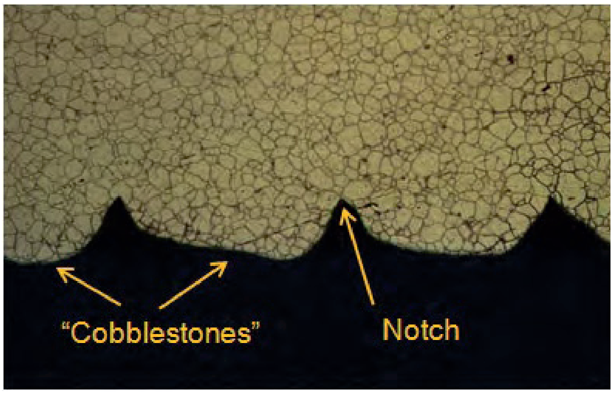

Figure 13 – Microscopic view of the typical "cobblestone" corrosion on a Nimonic 80A valve face, illustrating the depth of the notches in between the "cobblestones".

The "burnt depth" measurement procedure on the face of the 50MC valves was performed on the field employing a vernier caliper and an iron ruler, as shown in Figure 14. This is the standard procedure recommended by the engine manufacturer. Since the coated and uncoated valve spindles had not accumulated identical running times (due to varying service intervals on different cylinders of the engine), the "burnt depth" measurements were converted to corrosion rates (corrosion depth / operating time), and are presented in Figure 15. The upper range of the corrosion rate for the Nimonic 80A valve face on Figure 15 assumes that the average notch depth in between the "cobblestones" is 500µm.

These field validation results demonstrate that MW-C^2 can be used to protect the face of a 2-stroke valve spindle. Furthermore, MW-C^2 shows a moderately lower corrosion rate than Nimonic 80A (MW-C^2 corrosion rate is about ½ that of Nimonic 80A) under these conditions. These results are generally in good agreement with the laboratory measurements presented in Figure 5, and suggest that the instantaneous localized temperature on the face of the valve spindles could reach around 800 °C. However, the lower corrosion rate of MW-C^2 is most likely not sufficient to provide hot-gas corrosion protection on a 2-stroke valve spindle over the long term. Based on these measurements, a 1mm (1000µm) thick MW-C^2 coating could only be expected to protect the face of a 2-stoke valve spindle for approximately 5000hrs on this engine. Hence, the higher-temperature MW-C^2 HT coating is recommended for application on 2-stroke valve spindles.

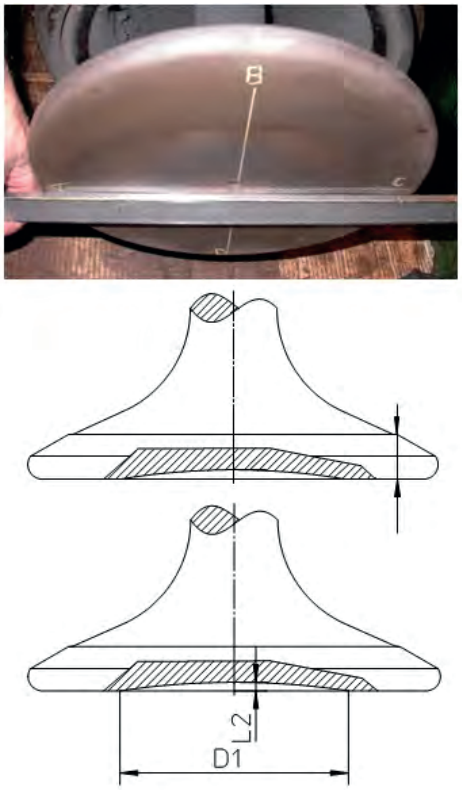

Figure 14 – Illustration of the valve face "burnt depth" (corrosion depth) measurement procedure on 2-stroke valve spindles.

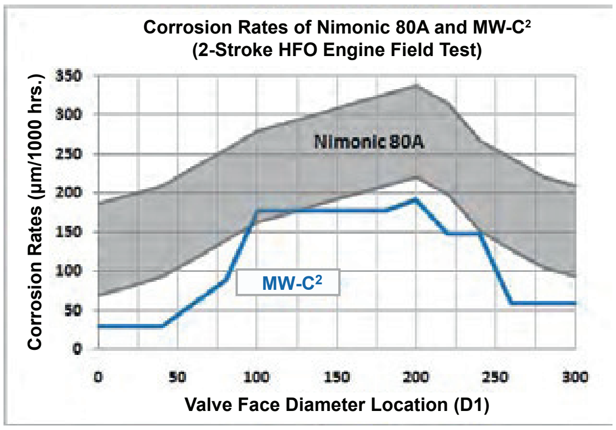

Figure 15 – Comparison of measured corrosion rates in µm/1000hrs, along the face of the Nimonic 80A and MW-C^2 50MC valve spindles.

Recently, several 2-stroke valve spindles (Nimonic and SNCRW) have been coated with MW-C^2 HT and installed in marine propulsion engines. However, results from those field trials are not yet available.

Other Applications for MW-C^2:

As mentioned previously, MW-C^2 and MW-C^2 HT are suitable for application on all Iron and Nickel based alloys. As such, these coatings may be used to protect almost any component against hot-gas corrosion and thermal loading. Initial field tests on HFO engine piston crowns and injection nozzles are under way at this time. Other interesting applications on engines may include highly-loaded turbocharger turbines and cylinder heads.

TECHNOLOGY OUTLOOK

MW-C^2 and MW-C^2 HT are fully developed coatings and their manufacturing and spraying processes have been industrialized by MWH. Initial series of MW-C^2 valves have been produced and are currently running on various 2 and 4-stroke engines. The initial market demand for MW-C^2 valves has concentrated on applications with very high rates of hot-gas corrosion. Hence, MW-C^2 has been used to improve the lifetime of valves manufactured from Nickel-based alloys (Nimonic, Inconel, etc.). However, a more interesting use of this coating technology will be to reduce the cost of "mainstream" valves. This will be achieved by replacing Nickel-based superalloys with cheaper Iron-based alloys and MW-C^2. In this fashion, it will be possible to produce valves with comparable, or even superior, hot-gas corrosion performance, and at a reduced cost.

CONCLUSIONS

MWH has developed a family of mineral-metal, multi-phase coatings to improve the hot-gas corrosion resistance of engine components in a cost-effective manner. These innovative coatings have demonstrated high resistance to corrosive attack from HFO byproducts. Engine trials on 2 and 4-stroke engines have demonstrated that these coatings can withstand the harsh environment of a combustion chamber and protect exhaust valves from hot-gas corrosion. The standard MW-C² formulation has been shown to provide adequate hot-gas corrosion protection on 4-stroke HFO applications. However, this coating could not provide long-term protection on 2-stroke engine applications. A new coating formulation, with improved resistance to hot-gas corrosion at very high-temperatures, (MW-C² HT) has been developed and is currently undergoing field trials on 2 and 4-stroke valve spindles.

REFERENCES

[1] STANGLMAIER, R. H., T. GROSS, G. MOORMANN, V. VERLOTSKI, and R. CONRAD, "An Innovative Glass-Metal Coating to Provide Corrosion Resistance and a Thermal Barrier for Highly Loaded Engine Components," Proceedings of the CIMAC Congress 2007, Vienna. Paper # 184.

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