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Thermal spray coatings for corrosion and wear protection of naval Diesel engines components

L. Baiamonte, G. Pulci, E. Hlede, F. Marra, C. Bartuli

Intake and exhaust valves of naval Diesel engines suffer from several problems due to the combined and synergistic effects of mechanical stresses and a chemically aggressive environment.
Hard chrome plating has been widely used as the standard solution for valves stem, but its limited wear-corrosion resistance and the high toxicity of its galvanic baths suggest to look for suitable alternatives, such as thermal sprayed ceramic-metallic (cermet) and self-fluxing alloys.
The present study aims to compare different solutions in terms of corrosion resistance under a selected acid environment and of wear resistance both for as-sprayed and post-corrosion samples.
Coatings have been deposited by HVOF both on martensitic steel and Ni-based superalloy. A Design of Experiment procedure has been used for spray parameters optimization, based on porosity and deposition efficiency of the coatings. Corrosion tests have shown the effect of porosity of the coatings, while wear tests confirmed the fundamental role of the dispersed hard phases.
All the solutions here proposed have shown a significant improvement in terms of corrosion and wear resistance compared to hard chrome plating.

Keywords: Corrosion - Wear - Valve - Cermet - HVOF - Thermal Spray - Self-Fluxing Alloys - Diesel Engine

INTRODUCTION

Intake and exhaust valves of naval diesel engines are subject to severe wear and corrosion because of the combined and synergistic action of mechanical stresses and aggressive environment produced by high impurity contents within the fuel.
Under particular engine running conditions, valves can be damaged by a “cold corrosion” mechanism: sulfides contained in fuel may condensate on the cooler parts of the valve stem, forming sulfuric acid that may attack and corrode the material. This phenomenon can combine with wear given by the valve movement within the guide, leading to premature failure of the component.
The state-of-art protection coating for valve stems consists of hard chrome plating, that provides a very efficient protection against wear but a poorer protection from corrosion in the aggressive environment created by sulfuric acid. Moreover, hard chrome plating processes are subjected to severe restrictions and even ban by European laws because of the toxicity of galvanic baths and wastewaters, due to the high content of hexavalent chromium [1, 2, 3].
In recent studies, alternative coatings such as metal-ceramic composites (called cermets, in which hard ceramic phases are dispersed in a metal matrix) [4] and self-fluxing alloys [5] (resulting in very dense and hard coatings) have been proposed.
The present study aims to compare different cermet coatings deposited by High Velocity Oxygen-Fuel (HVOF) [6], by testing their resistance to corrosion and wear in the specific environment.

Lidia Baiamonte, Giovanni Pulci, Francesco Marra, Cecilia Bartuli
Department of Chemical Engineering Materials Environment, University of Rome “La Sapienza”, INSTM Reference Laboratory for Engineering of Surface Treatments, Roma, 00184, RM, Italy

Edoardo Hlede
Wärtsilä Italia S.p.A. Bagnoli della Rosandra 334, San Dorligo della Valle, 34018 Trieste, Italy

MATERIALS AND METHODS

Metal-ceramic coatings feature a hard ceramic phase dispersed in a metallic matrix. This means that the ceramic hardness adds up to the metal high toughness, making the final material suitable for wear and corrosion applications.
For the present study, three different cermet compositions were chosen and compared: i) Cr_3C_2 reinforced Ni-Cr alloy (indicated as CRC); ii) WC-Co-based alloy (WCN); iii) WC reinforced self-fluxing alloy (WSF). Four WSF coated sam-

ples were heat treated at 1100°C for 30 to 60 seconds, in order to optimize the coating porosity and adhesion to the substrate and to investigate whether or not heat treatment affected wear and corrosion response [7].
Wear and corrosion tests were also performed on hard chrome plated samples (HC), for direct comparison of the proposed coatings with state-of-art solutions.
Cermet coatings were sprayed on two different substrates: a self-hardening martensitic steel (STL) and a Ni-based superalloy (called NSA), employed for inlet and exhaust valves respectively.
Coatings were obtained from Sultzer Metco powders and sprayed with a JP-5000 HP/HVOF gun operated with oxygen and kerosene.
Spray parameters were optimized with a multivarying approach through Design of Experiment (DoE) procedures. Specifically, Response Surface Modeling (RSM) was adopted: each surface was developed on the basis of the coatings' properties, and RSM was used to optimize deposition parameters as a function of the expected properties. Thermal spray process was studied and modeled by a factor analysis with two parameters (oxygen flow rate and spray distance) and three levels (low/medium/high) producing a 3x3 experimental matrix in which every element represents a given combination of parameters. Response surfaces were built in terms of porosity, deposition efficiency and Vickers microhardness as functions of deposition parameters. Coated samples were tested for corrosion and wear resistance.
Corrosion tests were carried out by dipping disc-shaped samples (Ø 33 mm) in a boiling water solution with 5% sulfuric acid (T=105°C). Samples were degreased and cleaned with ultrasonic bath in acetone, dried in furnace at 105°C and weighted with a precision balance. Every sample was inserted in a purposely designed Teflon case, so that only a known area of the coating was exposed and any contact between the acid solution and the substrate was avoided. Corrosion test duration was 60 minutes. Samples were ultrasonically cleaned and weighted after each test. Corroded samples were then cut, embedded in epoxy resin and polished. Optical and electronic (SEM) microscopic analysis was performed on mounted and polished samples.
Comparative wear tests were performed at room temperature on as-sprayed and corroded coatings (after immersion in the described boiling solution for 10 minutes). A PLINT TE53 Multi Purpose Friction and Wear Tester tribometer was used in block-on-ring inverted configuration (ASTM G77) [8, 9, 10, 11]. Tribological tests were not intended for numerical prevision of mass loss of the components in real operating conditions.
Cubic-shaped samples (12.7 mm) were ultrasonically cleaned in acetone and dried in furnace at 105°C, then were weighted. Samples were tested for 2000 seconds against a steel ring rotating at 318 rpm (~1 m/s), applying a 91 N normal force on the sample. After wear tests, every specimen was cleaned and weighted, then wear marks on the coating surfaces were measured by profilometric analysis using a Taylor Hobson Talyscan 150 profilometer with contact probe.

RESULTS AND DISCUSSION

Results from tests performed on the three selected coatings were analyzed following three main requirements: i) corrosion resistance; ii) wear resistance; iii) limited damage of the steel counterpart during the valve's movement within its guide.
DoE-based statistical analysis gave the following results:
Cr_3C_2-based cermet shows an increase in porosity, hardness and deposition efficiency with increasing oxygen flow rate;
WC-based coating reaches its optimum with high oxygen flow rates and medium spray distance;
WC-self-fluxing alloy needs an intermediate oxygen flow rate and a low spray distance to reach optimum microstructures and performance.
Each coating was deposited with a spray angle of 90°, spray distance varying from 300 to 450 mm. Kerosene flow rate was varied between 5 and 6 slph, while oxygen flow rate ranged between 1400 and 1700 scfh.
The ranges of porosity and hardness for the selected coatings are reported in Table 1:

Coating	Porosity (%)		Hardness (HV, 50gf)	
	Min	Max	Min	Max
CRC	4	6	1300	1400
WCN	3	6	1500	1700
WSF	1	4	1000	1100

Table 1 - porosity and Vickers hardness for thermal sprayed coatings.

Tab. 1 - porosità e durezza Vickers per i rivestimenti thermal spray

Corrosion resistance was evaluated in terms of weight loss and microstructural modifications.
While CRC and WSF coatings showed a weight loss of about 7 mg/cm^2, corresponding values for WCN coatings are two orders of magnitude smaller (0.065 mg/cm^2). Hard chrome coatings suffered catastrophic weight loss (191,02 mg/cm^2), with consequent exposure of the substrate to the acid solution and partial detachment of the coating.
Optical and electronic microscopy investigations results offer an overview of the microstructure of degraded coatings (Fig. 1).
The overall results of corrosion tests can be summarized as follows:
- SEM micrographs of CRC sample (Fig. 1a) show selective corrosion of the metal matrix. It is reasonable to ascribe the measured weight loss almost entirely to metal phase dissolution, since no evident carbides pull out was detected. This coating exhibits the same behavior both on steel and on Ni-superalloy substrates;
- WCN cermet (Fig. 1b) offer a very efficient barrier against corrosion (as-sprayed and corroded surfaces are hardly distinguished). No specific influence of the substrate was evidenced;

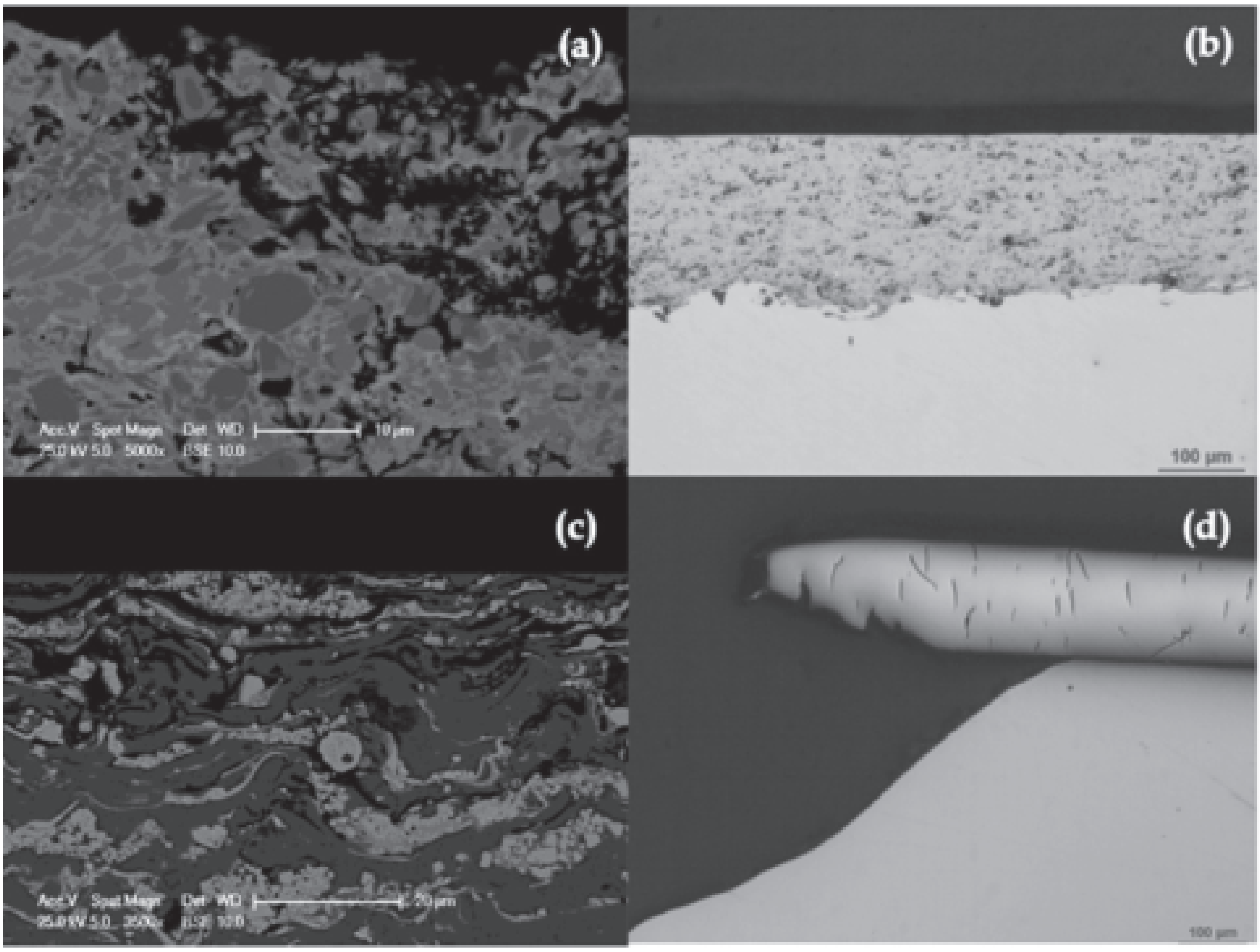

Fig. 1 - SEM (a, c) and optical (b, d) micrographs of the coatings exposed to corrosion test: (a) Cr_3C_2-Ni-based alloy cermet; (b) WC-Co-based alloy cermet; (c) WC-self-fluxing alloy cermet; (d) hard chrome plating on martensitic steel substrate.

Fig. 1 - Micrografie SEM (a, c) e ottiche (b, d) delle zone sottoposte ad attacco corrosivo dei rivestimenti: (a) rivestimento cermet Cr_3C_2-lega base Ni; (b) rivestimento cermet WC-lega base Co; (c) rivestimento cermet WC-lega self-fluxing; (d) rivestimento in cromo duro su substrato di acciaio martensitico.

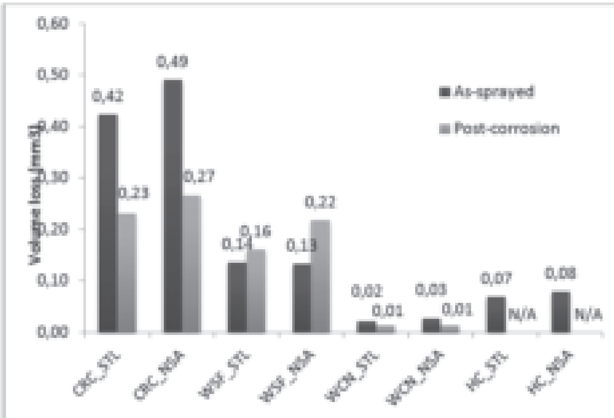

Fig. 2 - volume losses due to wear test for as-sprayed and post-corrosion samples

Fig. 2 - Perdite in volume dei campioni sottoposti a test tribologici, sia tal quali che post-corrosione

- SEM micrographs for un-treated WSF coating (Fig.1c) show that there is an increase in porosity in the area exposed to the acid solution. An inter-lamellar corrosion is visible, resulting in a lack of adhesion at the interface between phases. This result suggests the occurrence of galvanic effect due to coupling between different phases [12];
- Heat-treated WSF cermet corrosion mechanisms are very similar to those of the un-treated specimens. The overall porosity is lower though, suggesting a negligible correlation between total porosity and corrosion behavior, and therefore confirming that porosity is mainly non-interconnected. As a consequence, both for heat-treated and un-treated coating substrates do not give significant contribution;
- The exposure of HC platings to the acid solution results in a catastrophic loss of material, showing that these coatings are not protective in such a corrosive environment. In this case the nature of the substrate can indeed make a relevant difference: while Ni-superalloy is not corroded, martensitic steel is severely damaged by the acid attack (Fig. 1d).

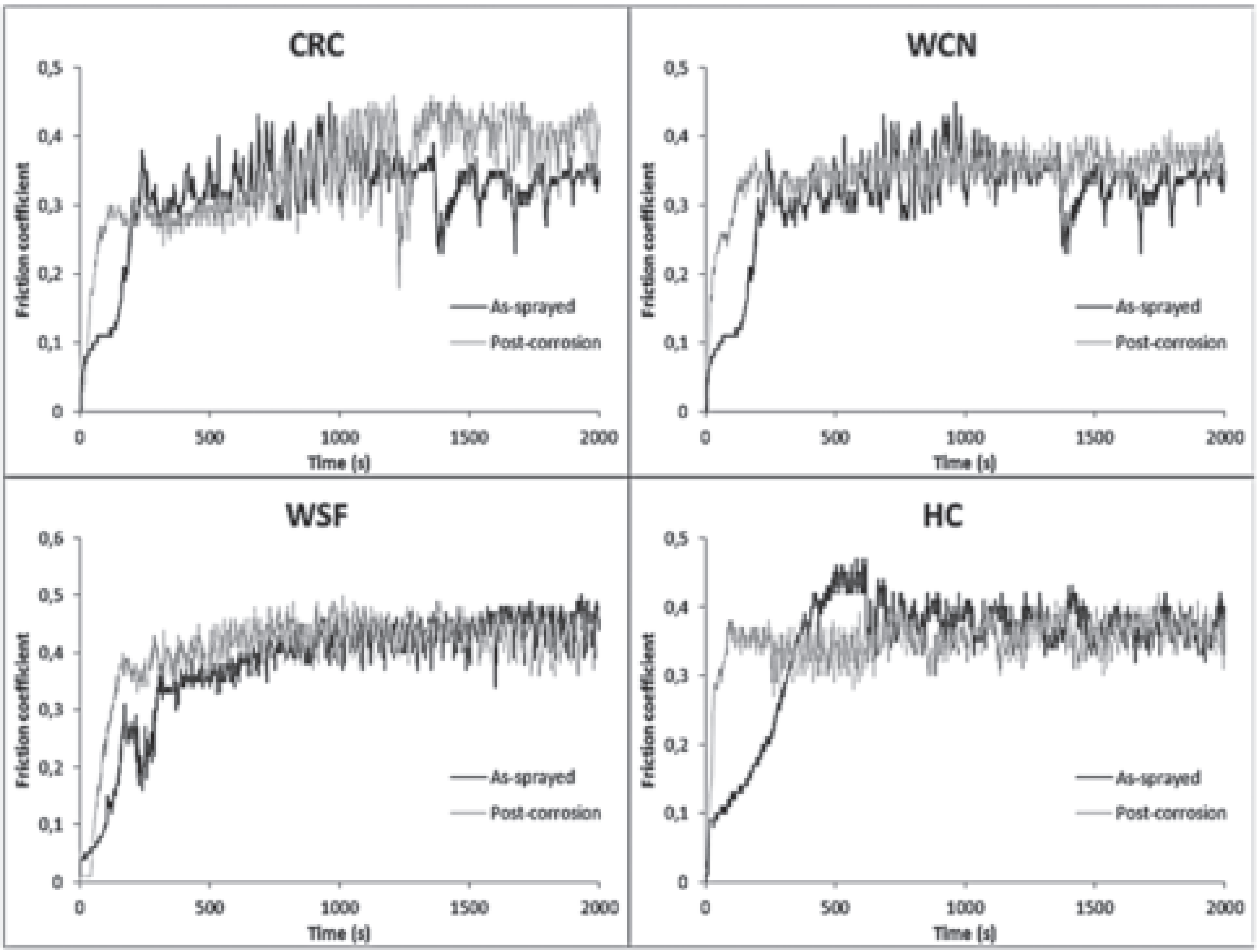

Fig. 3 - friction coefficient vs. time for each coating, evaluated both on as-sprayed and on post-corrosion samples

Fig. 3 - andamento dei coefficienti di attrito in funzione del tempo per ciascun rivestimento, sia su campioni tal quali che su campioni post-corrosione

Results from wear resistance tests were elaborated in terms of weight and volume loss, the latter being the most representative parameter (Fig. 2).

Experimental data gathered from tribological tests gave the following results:

- Wear performance of as-sprayed CRC coatings is poor as compared to other cermet coatings. Post-corrosion CRC behaves similarly, regardless of the substrates;
- WCN coated samples, both as-received and post-corrosion, show a very good wear behavior: both weight and volume losses are in the order of a few tens of milligrams on both substrates;
- WSF alloy response to wear test results in a lower volume loss than the one of CRC coatings. WC and self-fluxing cermet, in fact, are significantly denser than the Cr_2C_3-based. Post-corrosion and as-sprayed wear test results are very similar, with no specific effect of the substrate;
- As-received hard chrome coated samples show a very good wear resistance. A different behavior was exhibited by post-corrosion samples: the damage of the galvanic coating is so severe that volume loss evaluation is practically impracticable and, in some cases, the exposed area is actually that of the substrate.

Every coating suffers from adhesive wear mechanism, and it is more marked in the post-corrosion samples.

A comparison among friction coefficients for each kind of coating has been made, and its evolution with time is shown in Fig. 3.

Friction coefficient values after the transient state are stabilized between 0.3 and 0.5, for both as-received and corroded samples.

- For as-sprayed and post-corrosion samples CRC has an unstable evolution for the whole test time;
- After a rapid transient state, as-sprayed and post-corrosion WCN curves keep a low and stable value of friction coefficient (~0.3);
- WSF coatings reach the highest value of friction coefficient (nearly 0.5) both in as-sprayed and in post-corrosion test conditions;
- Friction coefficient curve of the as-received hard chrome coating slowly reaches a stable trend. The post-corrosion friction coefficient curve is not representative of the HC's friction behavior, since the acidic solution severely damaged the coating.

CONCLUSIONS

HVOF-sprayed cermet coatings for wear and corrosion protection of valves for naval diesel engines have been proposed as potential replacement of hard chrome plating on stems.
Spray parameters were optimized with a multivarying approach through Design of Experiment (DoE) procedures.
Corrosion and wear tests led to the following conclusions:

1. Cr_2C_3-based cermet is the worst performing coating when compared to the other cermets here proposed, due to the relatively high weight and volume losses;
2. WC-self-fluxing alloy provides overall satisfactory results in terms of weight and volume losses, but its interlamellar corrosion and high friction coefficient make this alloy not eligible as a protective coating for the specific application. It is important to point out that heat treatment does not seem to affect alloy's behavior;
3. WC-based cermet is the most promising solution because of its excellent corrosion and wear resistance and its relatively low friction coefficient. These results can be attributed to the tungsten carbide high hardness and to the good response to corrosion provided by the selected metallic matrix.
4. It is important to highlight that every cermet composition here proposed exhibited overall corrosion/wear behavior that is far more satisfactory than that of hard chrome plating: hard chrome coated samples, while providing suitable wear resistance, were found inadequate to offer the necessary corrosion protection in the specific environment.

The nature of the substrate has no apparent influence on the coating performance in the investigated conditions. HVOF-sprayed WC-based cermet exhibits the best performance for the specific chemical and mechanical environment. Installation of WCN-coated valves on test-bench will allow to verify the behavior of the selected cermet in real conditions under the synergistic action of wear and corrosion.

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Rivestimenti thermal spray per la protezione da corrosione ed usura di componenti di motori diesel marini

Parole Chiave: Acciaio inox - Nichel e leghe - Corrosione - Rivestimenti - Metallografia - Microscopia elettronica - Tribologia - Valutazione materiali - Selezione materiali

Le valvole di aspirazione e scarico dei motori diesel marini soffrono di diversi problemi causati dagli effetti combinati e sinergici di sollecitazioni meccaniche cicliche e di un ambiente aggressivo.
Rivestimenti galvanici in cromo duro sono stati largamente impiegati quali protezione standard per gli steli valvola, ma la loro limitata resistenza a corrosione-usura e l'elevata tossicità dei bagni galvanici utilizzati per applicare la cromatura hanno suggerito di ricercare soluzioni più efficaci, quali ad esempio possibili rivestimenti cermet e le leghe self-fluxing deposti per thermal spray.
Nello studio presente diverse soluzioni sono state confrontate analizzandone la resistenza alla corrosione nello specifico ambiente acido e la resistenza all'usura, prima e dopo l'attacco corrosivo.
I rivestimenti sono stati depositati mediante spruzzatura HVOF su substrati in acciaio martensitico o in superlega a base nichel. L'ottimizzazione dei parametri di spruzzatura è stata condotta attraverso procedure di sperimentazione fattoriale (Design of Experiment), sulla base di porosità e durezza dei rivestimenti e dell'efficienza della loro deposizione. I test di corrosione hanno evidenziato l'effetto importante del substrato selezionato e della porosità del rivestimento. I test di usura-strisciamento hanno confermato il ruolo fondamentale delle caratteristiche delle fasi dure disperse. Tutte le soluzioni analizzate hanno mostrato una combinazione di proprietà tribologiche e resistenza alla corrosione fortemente migliorata rispetto alla convenzionale cromatura.