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CERAMIC COATINGS ON DIESEL ENGINE COMPONENTS

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1. INTRODUCTION

Future diesel engines must meet the requirements created by the diminishing of the oil resources in the world. Light and medium distillates make up an increasing percentage of refined fuels with residual becoming even more concentrated. This means increased viscosity, higher vanadium and sodium content, higher amounts of asphaltenes and slower burning elements, more CCR, etc. Only engines with improved thermal efficiency and fuel economy or flexibility to burn low cost fuels will be on the market in the future.

One approach to these objectives is to minimize heat loss to the coolant. This can pay dividends in improved thermal efficiency and increased turbocharger output. Use of an insulating barriere on the surface in the combustion space will in addition to reduced heat flux also decrease metal temperature and thereby reduce the corrosion and thermal stresses.

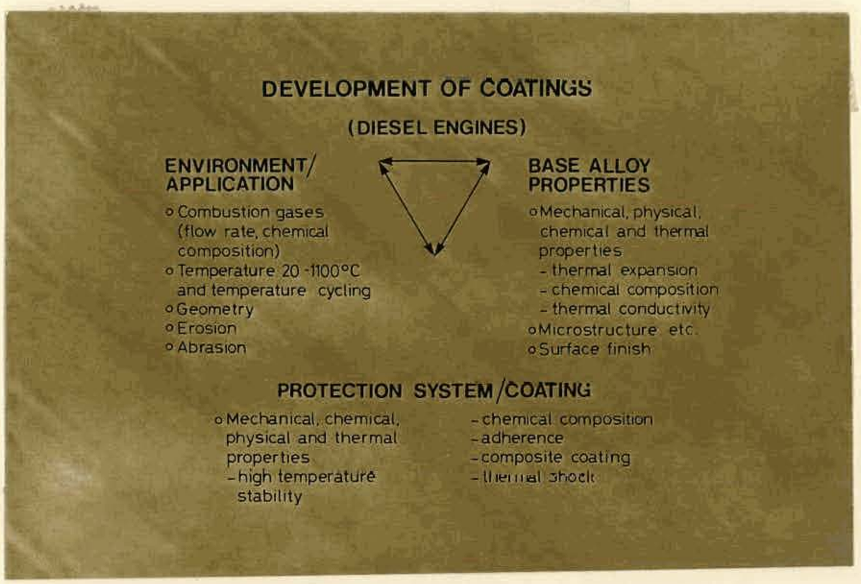
2. COATING

Ceramic coatings on heat loaded components in diesel engines may improve component life through increased corrosion and wear/erosion resistance and by serving as a thermal barrier. Such a barrier allows higher operational temperatures or reduced metal temperatures.

In the selection of protection systems for diesel engines three major factors require consideration: The environments, the base alloys and the coating systems. This is illustrated in Figure 2/1, which also includes a number of parameters which have to be considered for each parameter.

The prime basis of selecting a protection system is its inherent environmental resistance. However, since the protection system forms a three-dimensional composite with the alloy, its properties can influence those of the substrate. There are today two types of ceramic coatings which seem promising for use in diesel engines. These are:

I Thermal barrier coating materials
II Wear resistant coating materials



DEVELOPMENT OF COATINGS

(DIESEL ENGINES)

ENVIRONMENT/ APPLICATION

- Combustion gases (flow rate, chemical composition)
- Temperature 20 -1100°C and temperature cycling
- Geometry
- Erosion
- Abrasion

BASE ALLOY PROPERTIES

- Mechanical, physical, chemical and thermal properties
  - thermal expansion
  - chemical composition
  - thermal conductivity
- Microstructure etc.
- Surface finish

PROTECTION SYSTEM/COATING

- Mechanical, chemical, physical and thermal properties
  - high temperature stability
  - chemical composition
  - adherence
  - composite coating
  - thermal shock

Fig. 2/1. The development of coatings (diesel engines).

2.1 Thermal barrier coating materials

ZrO_2 has a relatively low thermal conductivity and a thermal expansion coefficient closer to metals than for most other oxides. Table 2/1 shows a comparison of the thermal conductivity and the thermal expansion coefficient for some actual oxides. A coating of ZrO_2 is therefore a candidate as a thermal insulator. ZrO_2 can exist in three modifications, with cubic, tetragonal and monoclinic structures respectively, depending on temperature, composition and impurity concentration. The cubic structure can be stabilized by additions of di- and trivalent metal oxides like CaO, MgO, Y_2O_3, etc.

At this place it should be important to notify that the quality of the powder is critical. Some powder manufacturers produce stabilized powders which are partly mechanical mixtures, e.g. ZrO_2 and Y_2O_3. Figure 2/2 shows an example of the inhomogenity of such powders (1). The unstabilized ZrO_2 particles will initiate cracks and thereby destroy the coating.

It is extremely important to obtain a homogeneous chemically stabilized powder by using ceramic coating at higher temperatures. Published results in the open literature on using thermal barrier coating on diesel engine components are scarcely available. This review is therefore mainly based on examination carried out at Central Institute for Industrial Research.

Backscattered electron image   Cathode luminescence image

Fig. 2/2. Only "pure" ZrO_2 lights up when it is hit by the electron beam. Unstabilized ZrO_2 particles are therefore white in the CLI picture. Cracks and porosity are black in the BEI picture. The number of cracks are especially large around the unstabilized ZrO_2 particles.

Powder	Thermal conductivity cal.(s cm^{o}C)$^{-1}$	Thermal expansion x 10^{-6} K^{-1}
Al_2O_3	ca. 0.06	8.0
Cr_2O_3	" 0.08	9.6
ZrO_2	" 0.01	8
MgO	" 0.07	-
SiO_2 cryst.	" 0.02	3.0 (300-1100 ^{o}C)
SiO_2 amorft	" 0.004	0.5
TiO_2	" 0.02	8.0
Cao	-	13.7

Table 2/1. Comparison of thermal conductivity and thermal expansion.

2.1.1 Application of thermal barriers

During combustion in a diesel engine, components like pistons, valves, liners, cylinder covers, etc. have high surface temperature. The erosive burning of piston crowns in the fuel jet region seems to be a wide spread symptom in large crosshead engines. The heat exchange occurs by convection, radiation from or by direct contact with the flame. The absorbed heat must be transported away in order to retain the mechanical, thermal and corrosive properties of the material.

A great deal ($\sim$ 25%) of the energy which is produced during combustion process, is for that reason removed with cooling water/air. In order to save energy it is of advantage to protect the hot parts by a thermally insulating layer. This will reduce the heat transfer through the engine walls, and a greater part of the produced energy can be utilized, involving an increased output effect per unit of fuel.

2.1.2 Calculation of possible benefit by using a thermal barrier in diesel engines

In a diesel engine, it is of advantage to use isolating coatings on valves, pistons, cylinder covers, etc. Generally, a surface coating of this kind reduces the heat transfer. An insulating layer on the hot metal side facing the combustion involves an increased surface temperature towards the combustion gas, while the surface temperature of the piston is lowered. For purpose of demonstration or first order approximation, the graphical method shown as illustrated by Sarsten (2) in Figure 2/3 is useful. Here the various barriers between the mean effective gas temperature and the coolant temperature are represented by equivalent thicknesses of the component metal. The gradient through this equivalent total metal thickness at the boundaries is infinite, so that these attain the temperature of the adjacent fluid.

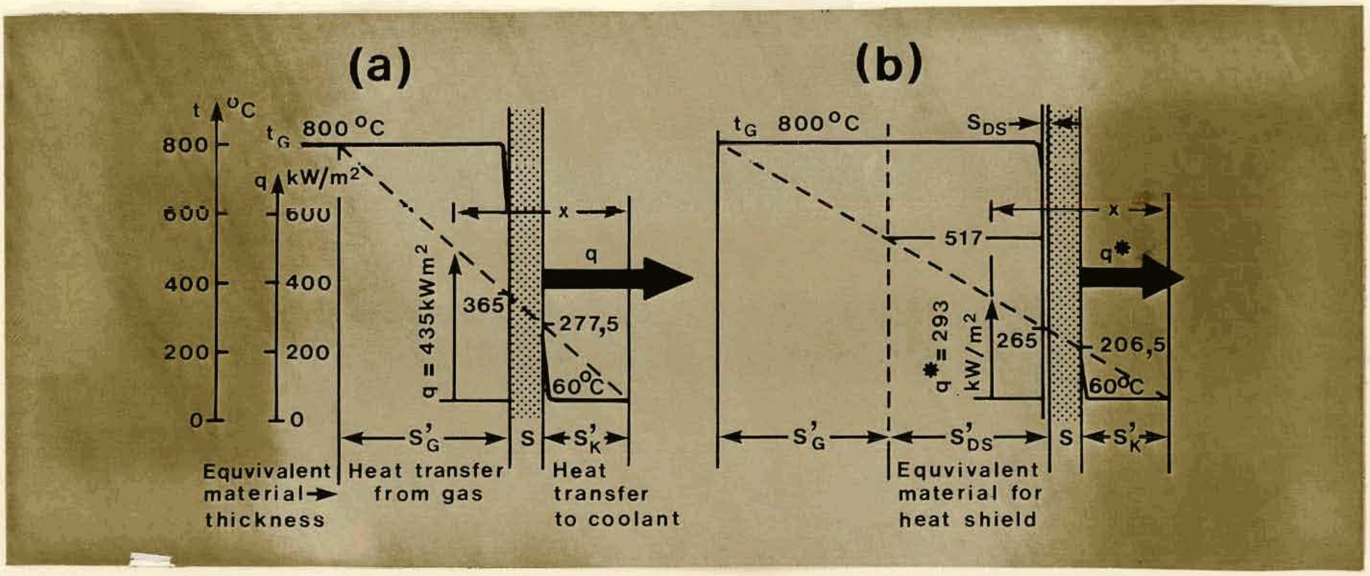


Fig. 2/3. Demonstration of the isolating ability of a ceramic coating.

The symbols used in the figure and in the text are:

α - heat transfer coeff. W/m^{2}K
λ - thermal conductivity W/mK
S - thickness mm
q - heat flux W/mm^2

The heat transfer coefficient of the upper part of the piston crown depends strongly on its surface roughness. The spraying of an isolating coating on a smooth, metallic surface increases the roughness of the surface due to the powder and porosity of the coating. According to the literature, the heat transfer coefficient for a plasma-sprayed surface is a factor 1.3 - 1.9 higher than for a smooth, metallic surface. The reason for this is two-fold: first, the roughness of the coating increases the efficiency of the surface for heat absorption, secondly turbulations are formed in the gas layer adjacent the surface.

For a diesel engine it is difficult to estimate how surface depositions of combustion products (coke) and ingredients of the lubrication oil influence the heat transfer coefficient. If these deposits completely cover the surface, the heat transfer coefficient will be the same for a coated surface as for a metallic one.

The heat transfer depends on the emission from and on the thermal diffusivity of the material.

Thermal diffusivity = $a = \frac{\lambda}{\zeta\ c}$

λ = thermal conductivity
ζ = density
c = heat capacity

A theoretical calculation has been carried out to estimate the influence from a ceramic layer on the heat flux through a known piston crown construction. The finite element method for heat flux was employed on a known piston crown design. The calculations have been carried out using $\lambda = 1.0$ W/mK, which is too low, but for which is corrected later. 2-3 W/mK is a more correct value for λ.

The heat flux was calculated to be 435 kW/m^2 for an unprotected piston and 293 kW/m^2 for a piston covered with a shield material. This corresponds to 4 g bhp h of the fuel consumption. Using a more realistic value for λ (i.e. 2.0), the figure will be reduced to 2 g bhp h.

Another aspect is that, according to calculations carried out, the stresses in the piston crown were reduced by about 10%. This is of course an overall advantage, but especially advantageous for constructions just under the limit where cast steel is being used, and where a reduction in stress could imply the use of cheaper cast irons.

2.1.3 Measurements in laboratory engine

In order to confirm the calculated values experimentally, a two-test run was carried out. Tests have been carried out in a 225 kW diesel engine (diesel fuel), where the piston tops and cylinder covers were coated with the CIIR-duplex layered coating. The layer was 0.2-0.3 mm thick. The waste heat through cylinder cover, cylinder liner and piston crown was measured.

The increased thickness of the cylinder cover and piston head was compensated for, so that the compression pressure was the same in both cases.

Even though the above figures will be re-checked and perhaps corrected by further tests, it is interesting to notice the observed tendencies. The heat flux through the cylinder cover is considerably reduced by the ceramic, but at the same time the heat flux through the uncovered cylinder liner is increased so that the total heat flux figure is the same. However, the heat flux through the piston head is not included. It is also interesting to notice that the exhaust gas temperature has increased, which is a consequence of less waste heat through the cooling surfaces. The engine load was the same during the tests. Correcting for the scavening air temperature, the exhaust gas temperature has increased by about 3%. This low value is due to the relatively small coating thickness.

The decrease in heat loss to the coolant goes partly to decrease the fuel consumption, partly to increase the exhaust gas temperature. The increase in exhaust gas energy may, however, be partly regained via increased airflow from the turbocharger, and via the waste heat boiler, if a such one is installed. One other, but more complicated way to make use of the increased heat is to make engines with longer stroke.

2.1.4 Test on ship in service, piston for medium speed engine

Parallel to the above tests, one piston protected by heat shield material had been installed in a ferryboat engine exposed to heavy changes in load (3). Diesel fuel was used and no problem regarding vanadium corrosion was observed. The condition of the material was examined after 3000 running hours, and no defects were found. The thickness of the heat shield material was in this case 0.2-0.6 mm. A metallographic cross-section is shown in Figure 2/4.

Valves for medium speed engines. Results reported (3) so far from tests on ceramic coated valves in medium speed engines are not very promising. These tests have, however, used heavy fuel with a vanadium content of 130 ppm and the engine was run on overload. The overload was estimated to be approximately 100 °C above normal load. It is also to notify that the spray powder used was only partly stabilized which of course results in crack formations.

The valves were coated with a $NiCrAlY/Cr/ZrO_2+Y_2O_3$ coating system. It is reported that during operation a low melting liquid salt phase containing Na_2SO_4, and $Na_2O \cdot V_2O_4 \cdot V_2O_5$ was deposited on the valve. This salt flows to the seat area and solidifies due to water cooling of the valve in closed position.

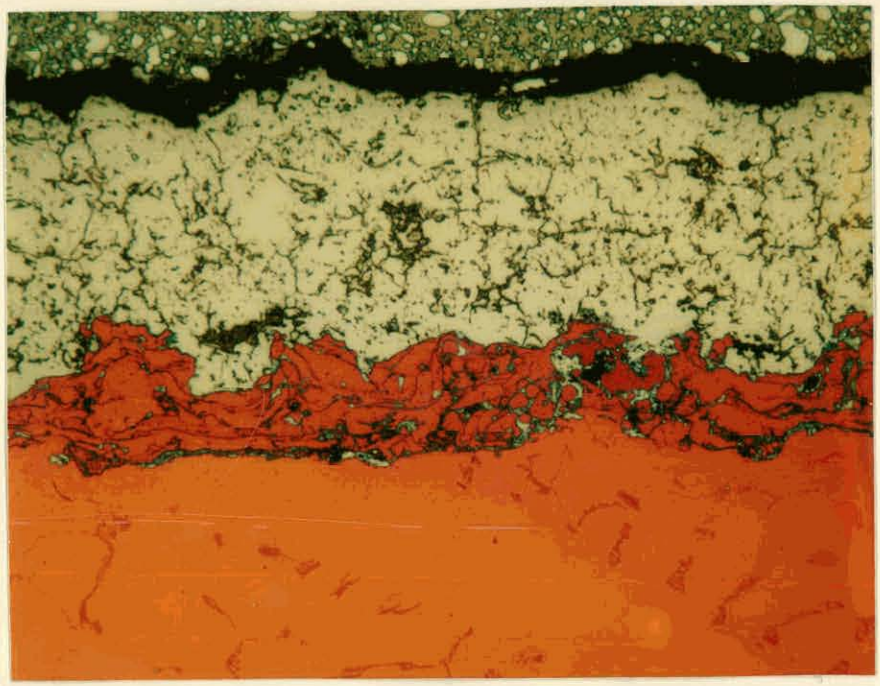


Fig. 2/4. Metallographic cross-section through the coating on the ferryboat piston.

The destruction of the layer was caused by the following mechanisms.

i) Corrosion

  a) Formation of cracks and partly spallation of the "solid salts" layer result in a "blow through" and increased corrosion.

  b) A part of the "solid salt" layer on the valve seat adjacent to the metal melts due to reduced cooling rate. The result of this process is increased corrosion.

ii) Thermal stresses

iii) Mechanical stresses

Comments to the above described destruction mechanisms:

i) The rig tests previously discussed have shown that yttrium oxide in the coating reacts easily with vanadium containing compounds from the combustion gases. Phases analyzed on the surface and in cracks contain both yttrium and vanadium. These observations indicate that a reaction has taken place.

ii) $ZrO_2 \cdot Y_2O_3$ coatings are in laboratory tests shown to resist temperature loads fairly well. On the other hand, however, a thick coating and partly unstabilized ZrO_2 particles may result in thermal stresses during temperature cycling.

iii) Only the coating on the valve seat is exposed to mechanical load. If the mechanical load should be the main reason for the destruction of the coating, it should be intact on the other coated areas. This is not the case, and this leads to the assumption that the life time of a coating is only slightly effected by mechanical loading.

Large bore engines. Thermal barrier coating of the $ZrO_2 \cdot Y_2O_3$ type on large bore valves in operation is reported to behave very well after ∿ 6000 hrs. The engine runs on heavy fuels. It is, however, to be noted that the temperature level is lower compared to medium speed engine. None of the valves is up to now analysed.

In connection with large bore engine it is also interesting to see how the coating behaves in the combustion space. A temperature sensor coated with the same type of thermal barrier as for the valves was placed in the combustion space between the jets from the nozzle. The sensor behaved well the first 3000 hrs. in low vanadium fuel at 850 °C, but broke down after another 300 hrs. The temperature was then raised to 1050 °C and the vanadium to 400 ppm. Figure 2/5a shows a schematic drawing of the sensor, and Figure 2/5b shows the cross-section of the sensor one cm behind the tip. The coating was at this place in good shape, but it was evident that corrosion had taken place. Figure 2/5c illustrates the element distribution on the surface of the corroded sensor. Figure 2/5d shows the composition of the inner layer of the deposit. The vanadium content in this area is much higher than in the surface. The outer part of the coating contains a mixture of zirconium and vanadium.

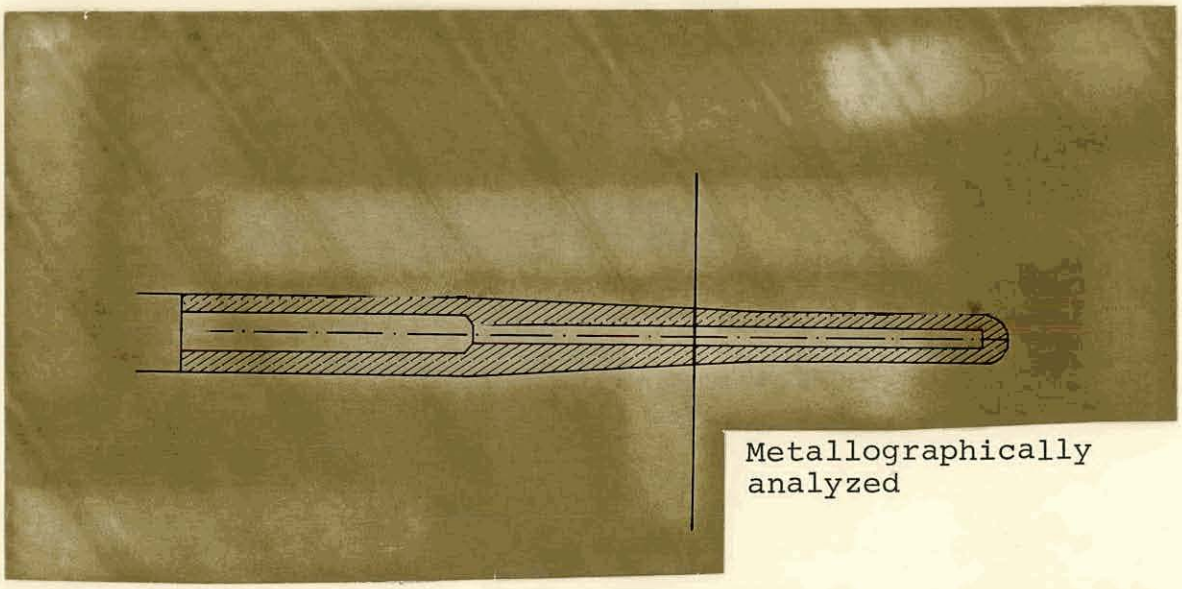


Fig. 2/5a. Schematic drawing of the sensor.

Fig. 2/5b. Cross-section of the plasma-sprayed coating on the sensor, 3 cm from the tip. 320 x

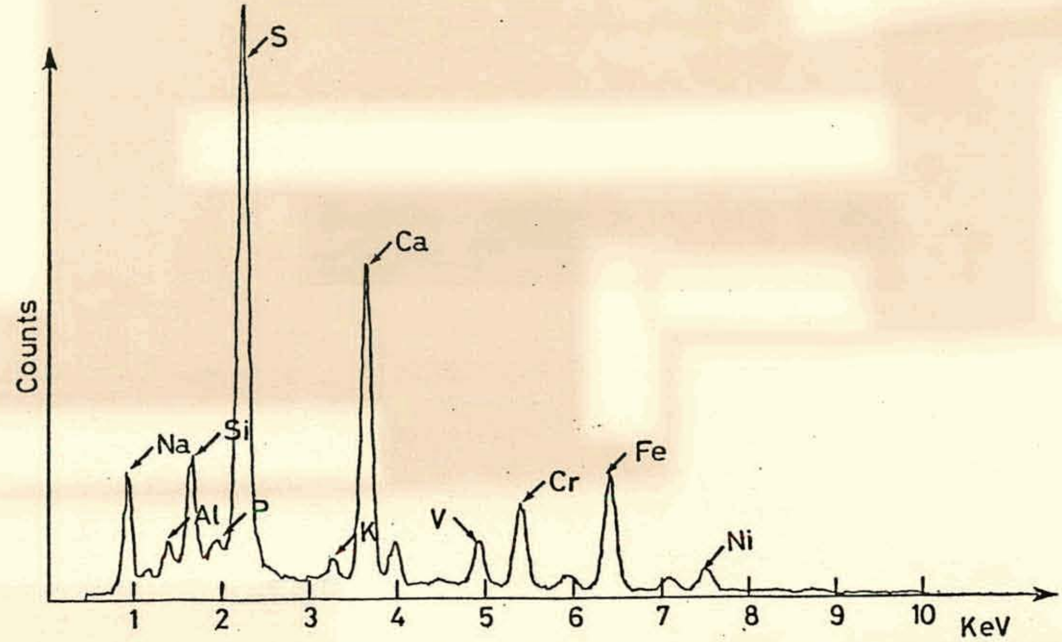


Fig. 2/5c. EDS X-ray spectrum from the surface layer on the corroded sensor.

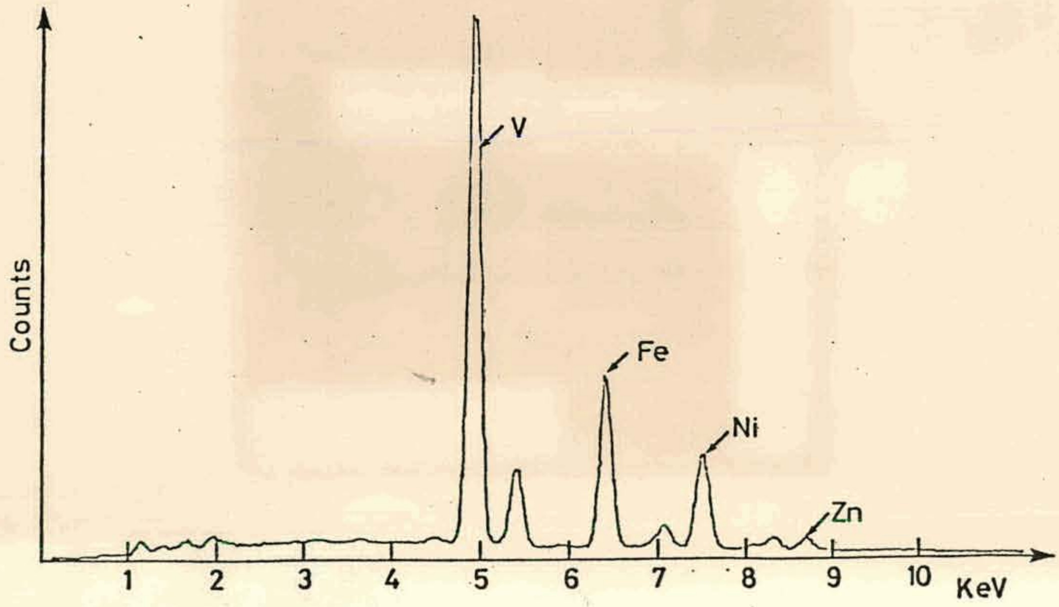


Fig. 2/5d. EDS X-ray spectrum from the inner layer of the deposit.

2.2 Wear resistant coating on piston rings

Hard chromium layers on top compression rings in internal combustion engines have given excellent service. In the future, however, the conditions for the rings in high performance engines will be so severe that hard chromium layer can not meet them. Under such conditions the occurrence of scuffing and scoring may course the engine to fail completely.

The authors are aware of one publication (3) concerning ceramic coating on piston rings which briefly will be summarized.

2.2.1 Materials

Possible piston ring coating materials are shown in Figure 2/6 as presented by reference (3). The various material combinations can be obtained from the diagram by pairing together the horizontally and vertically listed materials. Presently metallic coatings based on Cr and Mo are used.

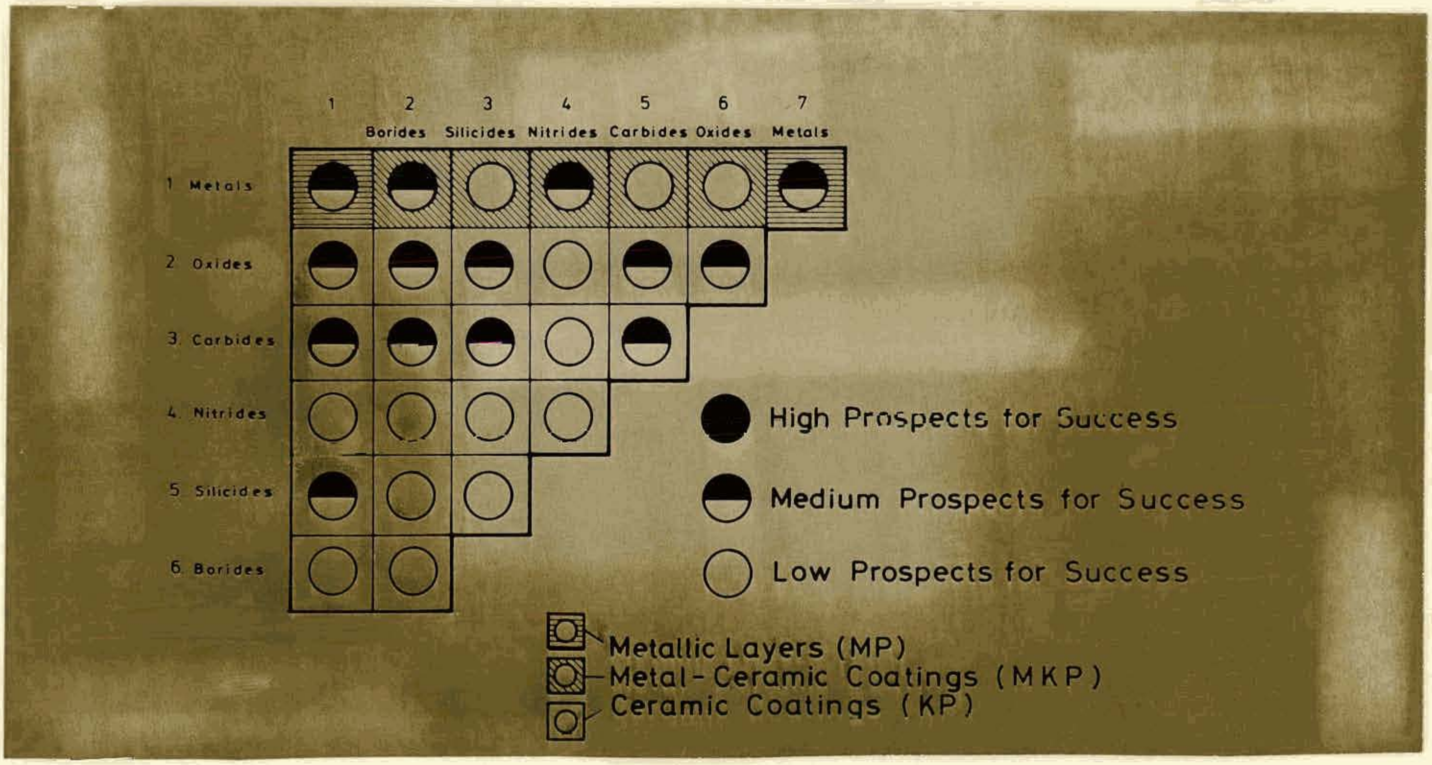


Fig. 2/6. Selection of Materials for Plasma-Sprayed Coatings.

The following requirements must therefore be met if a piston ring coating is to attain an extra working life:

1.	Wear of coating	$<$ Cr
2.	Wear of cylinder	$\leq$ Cr
3.	Resistance to scuffing	$\geq$ Mo
4.	Resistance to break out	$\geq$ Cr

2.2.2 Test results

The engine testing of ceramic coating has shown that the successful function of the sliding piston ring/cylinder bore system is not dependent only on the surface condition of the piston ring, but also on the material of the cylinder. The most promising ceramic coatings for piston rings consist mainly of molybdenum carbide or chromium carbide.

The chromium carbide coating possesses a coarser structure and porosity compared to the molybdenum carbide coating. The hardness of chromium carbide coating is relatively low and consequently this coating has, for a metal ceramic, a very high ductility.

Plasma-sprayed coatings would never achieve the high resistance to break-out as hard chrome. This of course raises the question as to whether such high resistance is at all necessary. Flame-sprayed molybdenum coatings for example provide no greater safety than plasma-sprayed coatings and are nevertheless successfully used on a large scale.

It is important to keep in mind that the development work discussed above is not yet completed, and optimization of the process has to be carried out.

3. DEGRADATION OF CERAMIC COATINGS

3.1 Corrosion

The results of laboratory and trial tests (4) have shown that the impurities in the fuel oil react with the stabilizing compounds in zirconia, e.g. yttria (Y_2O_3) and calcia (CaO) forming stable compounds. Magnesia (MgO) stabilized ZrO_2, however, shows a better resistance to the combustion gases.

Stable yttrium vanadates are formed on a Y_2O_3-stabilized ZrO_2 coating when this is covered with a vanadium rich deposit. The surface of CaO-stabilized ZrO_2 coating is usually enriched with $CaSO_4$ which is formed by a reaction between SO_2/SO_3 in the combustion gas and CaO from the coating. This corresponds very well to the results reported in the literature on gas turbines (5). By these reactions the stabilizing elements are removed from the ZrO_2 layer which therefore forms cracks and spalls off due to the transformation in structure.

Figure 3/1 gives a comparison of thermograms obtained from reactions between ZrO_2 stabilized with Y_2O_3, CaO or MgO on one side and a mixture of V_2O_5+Na_2SO_4 on the other. The black area is proportional to the energy involved in the reaction. It may be concluded that the salt mixture has a smaller affinity to react with ZrO_2·MgO than the two other ones.

3.2 Build-up of residual stresses in the coatings

The extent of coating degradation or failure can be significantly enhanced by residual stresses in the materials. These depend on a variety of mismatch strains and on the extent to which the mismatch strains result in mismatch stresses. It is well known that thermal gradients and the transition from molten to solid state may generate stresses in plasma-sprayed ceramic coatings. The liquid-solid volume shrinkage, which is often large in ceramic (e.g. for ZrO_2 not less than 10 vol%) results in large strains in all melt coating processes. These are also an important source of porosity and hence stress concentrations, but under normal cooling, they should not be a source of residual stress. However, whether the very rapid and inhomogeneous nature of cooling in such spraying-processes results in some stresses from such strains, is unknown.

The most general source of mismatch strains is the difference in thermal expansion between the substrate and the coating. For ZrO_2 coatings the steel thermal expansion coefficients are about a factor of 1.5 greater than that of dense ZrO_2. Continuous and multilayer composition-graded coatings are often used to limit and distribute this thermal-expansion-induced mismatch. The extent to which these strains result in stresses is determined by how much they are relieved (e.g. by plastic deformation or by microcracking), and by how they interact.

The transformation strains, which are inversely dependent on the degree of stabilization in ZrO_2, may or may not counteract some of the thermal expansion strain depending on the degree and nature of texturing. Further, microcracking associated with either the phase transition or the porosity (in the plasma-sprayed coating) is a potential mechanism of relieving mismatch strains. Microcracking is initiated above a critical grain size, which in turn is a function of fracture energy divided by elastic modules times the square of the local mismatch strain.

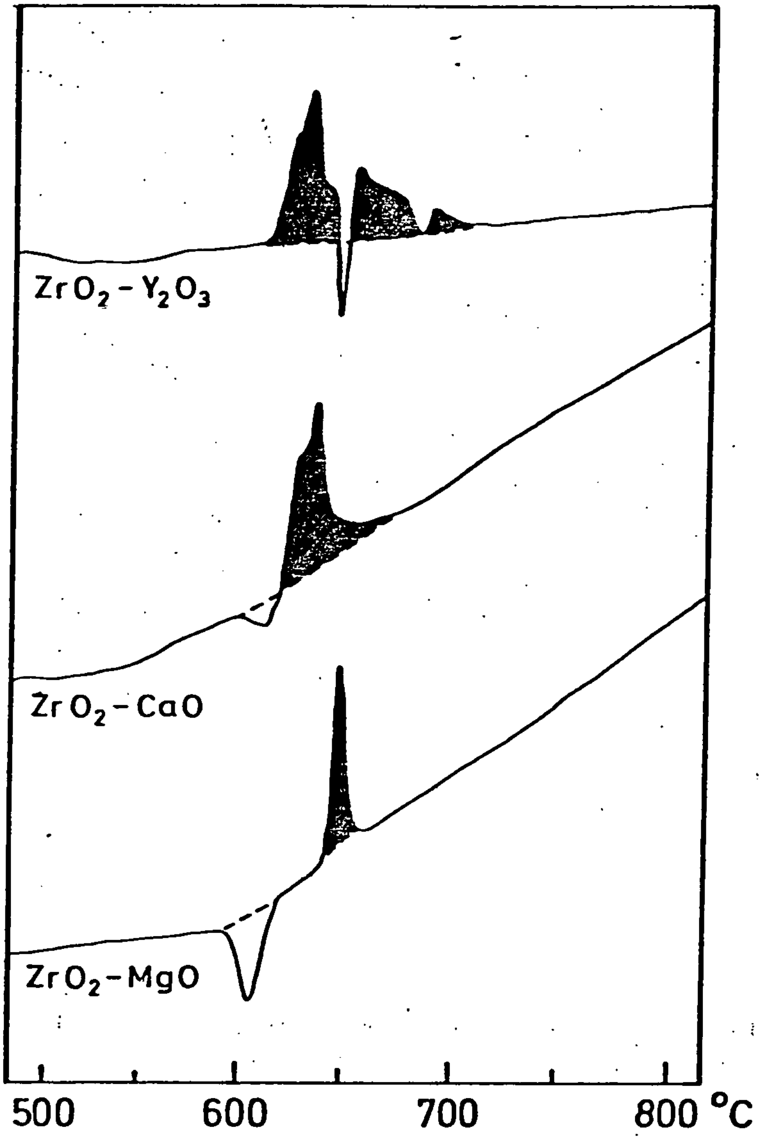


Fig. 3/1. A comparison between thermograms from the reactions between V_2O_5+Na_2SO_4 and ZrO_2 stabilized with Y_2O_3, CaO and MgO. Pure V_2O_5+Na_2SO_4 mixture is used as reference substance. The black area is proportional to the energy evolved in the reaction. The endothermal reactions at 620 °C are probably due to the fusion of the salt mixture.

3.3 Fracture of the coating materials

The adherence of a thick coating to a steel matrix is of the order of 10-20 N/mm^2. The adherence of thick coatings can be improved by increasing the fracture resistance of the ceramic layers present (6). This fracture resistance is measured by the critical stress intensity factor K_{IC} or the critical fracture energy γ_{IC}, both of which control the stress necessary to propagate existing flaws. Thus an increase in the K_{IC} of ZrO_2 should increase its adherence when coating failure (or spalling) occurs within the ZrO_2 coating. This is generally observed. The toughness of cubic ZrO_2 can be increased by the use of controlled precipitation of fine monocline ZrO_2 needles.

4. CONCLUSION

Plasma-spray technology has made it possible to coat diesel engine components with ceramic materials. The test results discussed on stabilized ZrO_2 and Mo- and Cr-carbide have been obtained with diesel engines in service. Diesel and residual fuel oils have been used. Note, however, that the spraying processes used are not optimized, and the results may be improved. Although the project is not yet completed, some preliminary conclusions can be drawn.

Valves and piston crowns:

- Stabilized ZrO_2 coating under certain conditions increases the working life of various components.
- Higher combustion temperature may improve the thermal efficiency by increased turbocharger air delivery.
- Reduction in the component temperatures decreases the thermal stresses.
- The $ZrO_2 \cdot MgO$ shows improved corrosion resistance in combustion gases compared to $ZrO_2 \cdot Y_2O_3$ and $ZrO_2 \cdot CaO$.
- The limitations of the coatings have to be defined in more detail.
- The adherence of thicker coatings has to be improved. Optimization of the spraying process with respect to particle fusion is necessary.

Piston ring:

- Molybdenum and chromium carbide coatings increase the service life of piston rings.

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