Thermomechanical fatigue characterization of zirconia ($8\%Y_2O_3$–ZrO_2) and mullite thermal barrier coatings on diesel engine components: effect of coatings on engine performance

P Ramaswamy[1], **S Seetharamu**[1], **K B R Varma**[2], **N Raman**[3] and **K J Rao**[2]*
[1]Materials Technology Division, Central Power Research Institute, Bangalore, India
[2]Materials Research Centre, Indian Institute of Science, Bangalore, India
[3]Department of Mechanical Engineering, Indian Institute of Science, Bangalore, India

Abstract: $8\%Y_2O_3$-stabilized zirconia (8YPSZ) and mullite ($3Al_2O_3 \cdot 2SiO_2$) powders, which were made plasma sprayable by using an organic binder (polyvinyl alcohol), have been plasma spray coated on to the piston head, valves and cylinder head of a 3.8 kW single-cylinder diesel engine, previously coated with Ni–Cr–Al–Y bond coat. The engine with components coated with 250 µm thick 8YPSZ and 1 mm thick mullite thermal barrier coatings has been evaluated for fuel efficiency and for endurance during 500 h long rigorous tests. Improved fuel efficiency was shown by the engine with coated components and the results are discussed. The coatings and the coated components have also been examined for phases, microstructure and chemical composition by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). Mullite coatings were found to exhibit increased resistance to microcracking compared with 8YPSZ during the 500 h endurance test.

Keywords: thermal barrier coating, partially stabilized zirconia, mullite, diesel engine, thermomechanical fatigue, fuel efficiency

NOTATION

b.s.f.c.	brake specific fuel consumption
BHP	brake horse power
EBPVD	electron beam physical vapour deposition
ECC	engine with coated components
EDAX	energy dispersive X-ray analysis
EMULC	engine components coated with mullite
EUC	engine with uncoated components
E8YZC	engine components coated with 8YPSZ
FHP	frictional horse power
s.f.c.	specific fuel consumption
SEM	scanning electron microscope
TBCs	thermal barrier coatings
XRD	X-ray diffractometry
8YPSZ	$8\%Y_2O_3$-stabilized zirconia

The MS was received on 19 December 1998 and was accepted after revision for publication on 7 July 1999.
* *Corresponding author: Materials Research Centre, Indian Institute of Science, Bangalore-560 012, India.*

1 BACKGROUND

Thermal barrier coatings (TBCs) have been a topic of much scientific interest worldwide for several decades [**1–4**]. They have been increasingly used as thermal insulation for engine components in turbine and aircraft engines in order to achieve improved engine performance and fuel efficiency [**5–7**] by increasing the actual temperature of engine operation. Generally, TBCs are thermally insulating materials, and a film of TBC of about 250 µm applied to metals produces a temperature drop of about 150–200 °C between ceramic and metal sides of the coating at temperatures of about 1000 °C. The coating also increases the life of the metal component by protecting it against high temperature degradation and eliminates the need for complex cooling systems. In the 1980s, efforts were focused upon extending the advantages of using TBCs in diesel engines, with the aim of:

(a) reducing specific fuel consumption, emissions and noise,

(b) improving the engine life and cold start reliability and
(c) imparting multifuel capability [8–11].

The containment of heat within the cylinder of the engine was expected to cause a better overall 'burn' of diesel, thereby improving fuel efficiency as well as reducing harmful engine emissions. A further advantage was expected to be achieved by utilizing the increased energy of exhaust gas for turbocompounding. However, there is a significant difference in the application of TBCs for diesel engines and their application for aircraft engines, because the latter is mainly intended for enhancing component life [5]. Although diesel engine TBCs operate at lower temperatures than aircraft engine TBCs, they are subjected to much greater compressive loads and more frequent thermal shock than their aircraft counterparts. The criteria for choosing a particular material (generally ceramics) as TBCs are low thermal conductivity, high coefficient of thermal expansion (a value high enough to match the expansion coefficient of the metal) and resistance to thermomechanical shock and fatigue in a diesel gas environment. Coating failures commonly known to occur in diesel engines are due to:

(a) loss of cohesion in the ceramic layers and
(b) loss of adhesion between the ceramic or the bond coat and the substrate.

Loss of adhesion takes place above a temperature of 1000 °C owing to oxidation of the bond coat. Hence, debonding between the coatings and the substrate does not occur in a diesel engine component because the maximum temperature experienced within a cycle by a water-cooled engine may not exceed 800–1000 °C. Thus, failure in cohesion of the ceramic caused by thermomechanical fatigue may be more relevant when assessing the coating durability.

Published research reports regarding the exact nature of TBC applications in diesel engines are unfortunately both sparse and uninformative. Indeed, they often provide conflicting information. Thus, it is not clearly known whether TBC applications are aimed at improving engine life and/or improving engine performance. Yonushonis [12] has reported that an understanding of delamination mechanisms in TBCs has resulted in the formulation of improved coatings that survive severe fatigue tests in high-output diesel engines. However, the improvement in fuel consumption in state-of-the-art diesel engines is only marginal (or even negative) owing to its dependence on both engine parameters and coating characteristics. Nevertheless, a huge expansion of the application of TBCs in diesel engines is anticipated by the year 2005. In the automobile market 50 per cent is expected to be captured by 'ceramized' diesel engines [7].

The general scheme for obtaining TBCs is to plasma spray ceramic powders over metal substrates already covered by a suitable bond coat. However, considerable efforts are also directed towards processes such as electron beam physical vapour deposition (EBPVD), laser glazing, etc. [13, 14] to improve the coating qualities. Among the several ceramic materials evaluated for TBC applications, 6–8% Y_2O_3-stabilized ZrO_2 has been found to be most suited for the purpose because of its very favourable thermal conductivity, thermal shock resistance, thermal expansion coefficient and phase stability characteristics [8]. Mullite ($3Al_2O_3 \cdot 2SiO_2$) also has considerable potential as a TBC for engine applications [12, 15].

The results of work on thermomechanical properties, phase stability and microstructure of plasma-sprayed stabilized zirconia and mullite coatings [16, 17] have been reported earlier from this laboratory. Plasma-sprayable powders of stabilized zirconia compositions for these coatings have been prepared by using organic binders (polyvinyl alcohol). The coatings made by using these powders have been found to possess excellent characteristics suitable for TBC applications, as revealed by simulated burner rig conditions. Encouraged by these results, the work has now been extended to evaluation on an actual single-cylinder 3.8 kW diesel engine. Both the performance evaluation of 8% Y_2O_3–ZrO_2 and mullite coatings as TBCs on engine components such as the piston, cylinder head and valves and the overall performance evaluation (e.g. fuel consumption) of the engine as a system are presented in this paper. The diesel engine itself has been used as both a high-frequency and a low-frequency thermal cycling device. The variation in mechanical and thermal loads within a cycle of the engine is considered as constituting the high-frequency component of the experiment, whereas the start and stop conditions every 16 h in the 500 h test are taken as constituting the low-frequency thermal cycling. Hourly load variations during the test also form part of the low-frequency thermal cycling schedule. The coatings have also been evaluated for phases, microstructure and chemical composition at the end of a rigorous 500 h life endurance test under severe thermomechanical stresses of cyclic and maximum loads in the engine.

2 EXPERIMENTAL PROCEDURE

2.1 Powder preparation and coating

8% Y_2O_3-stabilized zirconia (8YPSZ) and mullite compositions were made into plasma-sprayable powders by the binder method. The details of the powder preparative methods have been described elsewhere [18].

The diesel engine chosen for carrying out the present investigation was an open combustion chamber, water-cooled Kirloskar AV1 engine (Kirloskar Engines Pvt.

Limited, India) with an 80 mm bore and a 110 mm stroke. The engine was rated at 3.8 kW at 1500 r/min with a compression ratio of 16:1.

The piston (Al–Si alloy), cylinder head (cast iron) and valves (steel) were coated with TBC as described below. Thus, the integrity of the coatings could be evaluated on three different metal substrates. In addition, valuable information about the coating behaviour on valves could be gained since the valves undergo impact loading in addition to cyclic thermal stresses. The two coating configurations employed in the present work are as follows.

2.1.1 *8YPSZ coating*

An as-received (commercial) piston crown was machined to a close tolerance so that 350 μm of the piston material was removed uniformly from the top surface, including the combustion chamber cup. The cylinder head and valves were employed as-received for the present investigations. The purpose of removing the material from the piston crown was to keep the compression ratio unchanged after ceramic coating. Any increase in compression ratio owing to coating on the cylinder head is offset by using proper gaskets. About 100 μm of oxidation-resistant bond coat Ni–22Cr–10Al–1.0Y (AMDRY 962) was spray coated on the freshly grit-blasted and degreased surface of the engine components. This was followed by the application of ~260 μm thickness of 8YPSZ by using 80 kW PLASMATECHNIK plasma spray equipment. The coating was carried out without interruption of the spray process between the passes. Based on trial experiments carried out on flat substrates, the deposition efficiency was found to be ~30 μm/pass, and hence the number of passes employed in the present process was nine. The details of the plasma spray parameters used for this work have been reported elsewhere **[18]**. The surfaces were mildly buffed in order to make the ceramic surface smooth.

2.1.2 *Mullite coating*

Mullite was spray coated on the piston, cylinder head and valves in a similar manner to that in Section 2.1.1 employing appropriate spray parameters **[17]**. However, a major difference from 8YPSZ was that the bond coat thickness was ~450 μm and the ceramic overlayer thickness was 1.0 mm in the case of mullite. This was prompted by the reported longer life of mullite coatings compared with that of zirconia. Also, the superiority of thick mullite coatings over thin zirconia coatings in resisting the formation of surface cracks is fairly well established **[19]**. This has been attributed to the decreased stress relaxation behaviour of mullite at high temperatures. The piston head was machined accordingly to accommodate the 1.45 mm thick coating without altering the original shape of the piston. The cylinder head and valves were used as such, and the coating thickness was kept the same (~250 μm) as in the case of 8YPSZ. Modifications to the cylinder head (cast iron) were not carried out because of problems associated with machining.

2.1.3 *Plasma spraying*

The plasma spray facility used in the present work (PLASMATECHNIK, 80 kW, 1982) was capable of spraying both the bond coat and ceramic overlayer sequentially without interruption. The facility was supported with a six-axis articulating robot and a nine-axis turntable to facilitate uniform coating to the contours of the cup area in the piston which was otherwise difficult to coat. Efforts were focused on obtaining a uniformly thick coating, especially on the piston crown owing to its complex geometry. In order to confirm whether the thickness of the coatings was to the desired value, sections were cut from as-sprayed coated pistons and polished for metallographic examination.

2.2 Evaluation of engine with uncoated and coated components

The engine underwent the 500 h endurance test accordingly to IS 1600–1960 **[20]**. Engine performance was evaluated by fuel efficiency. The fuel efficiency of an engine is considered as improved if the fuel consumed for a particular power output is found to be lower than its normal consumption. Thus, in the present work, the performance evaluation was restricted to the study of the following basic parameters:

(a) power,
(b) specific fuel consumption (s.f.c.) and
(c) exhaust temperature.

The basic measurements undertaken to evaluate the above were as follows:

(a) speed,
(b) time to consume 50 ml of diesel fuel,
(c) brake power,
(d) exhaust gas temperature.

The cooling water supplied to the engine was maintained constant at 1.0 l/min.

The test consisted of measuring the fuel consumption when the engine was running under no load, then at part loads and finally at full load. The engine was run at each load for 30 min to achieve stability before the measurements were made. Similar measurements were carried out while decreasing the loads to confirm the repeatability of performance. Several trials (> 50) were carried out during the running of the engine for endurance testing at cyclic load conditions between zero and 500 h. The error/scatter (from the mean values) observed in the present data is less than or equal to the size of the symbols (□, △, ◇) used in the figures (graphs). The engine is derated for the high-altitude condition of Bangalore according to IS 1601–1960 [**21**]. The loading of the engine is carried out with the help of a swinging field electrical dynamometer mounted on a test bed.

2.3 Evaluation of the coatings

Qualitative and quantitative phase analyses were carried out using X-ray diffractometry (XRD) with Cu K_α radiation. The phase fractions of m-ZrO_2 and c/t-ZrO_2 were determined by the polymorph technique [**22**], in which $X_{c/t}$, the phase fraction of the cubic/tetragonal phase, is given by

$$X_{c/t} = I_{c/t(111)}\{1/[I_{c/t(111)} + I_{m(111)} + I_{m(11\bar{1})}]\}$$

where I_m and $I_{c/t}$ are the intensities of the reflections (measured from the area under the respective peaks) corresponding to the monoclinic and cubic/tetragonal phases respectively. A slow scan rate (1°/min) and scan speed (0.5°/cm) were used to obtain XRD patterns with good resolution, especially to determine the phase fractions. Although phase fraction data are generally obtained by this procedure, it is likely to be inexact in the case of films. However, comparisons made and conclusions drawn concerning the effect of engine tests remain unaffected by any inherent errors of phase fraction determination. Scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDAX) was employed to study the microstructural details and to determine quantitative elemental composition.

3 RESULTS AND DISCUSSION

The results of the present investigations concerning engine performance and coating characteristics are presented in the following two sections.

3.1 Engine performance

Extensive data were collected during performance measurements of an engine with uncoated components (EUC) and compared with those of the same engine with coated components (ECC). The components coated with 8YPSZ and mullite will be referred to as E8YZC and EMULC respectively. The performance evaluation for ECC and EUC was carried out under similar conditions and with all engine parameters held at constant values. Both the E8YZC and EMULC exhibited fuel economy compared with the EUC. The reduction in brake specific fuel consumption (b.s.f.c.) in the 8YPSZ-coated engine is particularly significant (6–7 per cent) compared with that of EMULC, which is marginal (2–3 per cent) at the maximum brake power (BHP) of 3.4 kW (derated) (Fig. 1). The deviation observed in the present data was found to be less than 2 per cent from the mean value. The differences in b.s.f.c. of the EUC and the two ECC were found to be almost uniform throughout under part load conditions, except at 0.805 kW load where mullite showed a higher b.s.f.c. The ECC exhibited poor engine fuel efficiency from zero to about 50 h of running, which may be attributed to the time taken for running-in of the engine. It is interesting to note that, once the ECC was stabilized, the performance did not deteriorate even after running the engine for 500 h. This is most probably due to the improved combustion characteristics of the fuel in the chamber of the ECC, which is further reflected in the exhaust temperatures. The exhaust

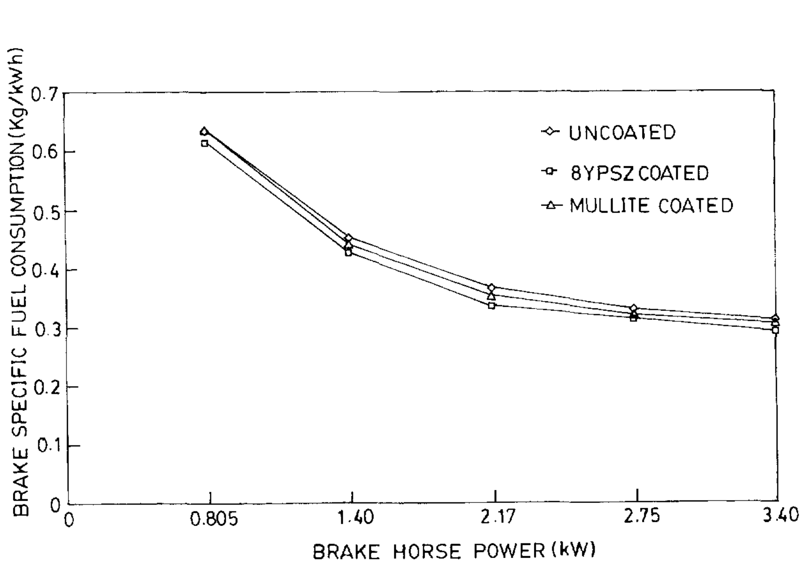

Fig. 1 Graphs of b.s.f.c. versus BHP for engines with uncoated and coated components

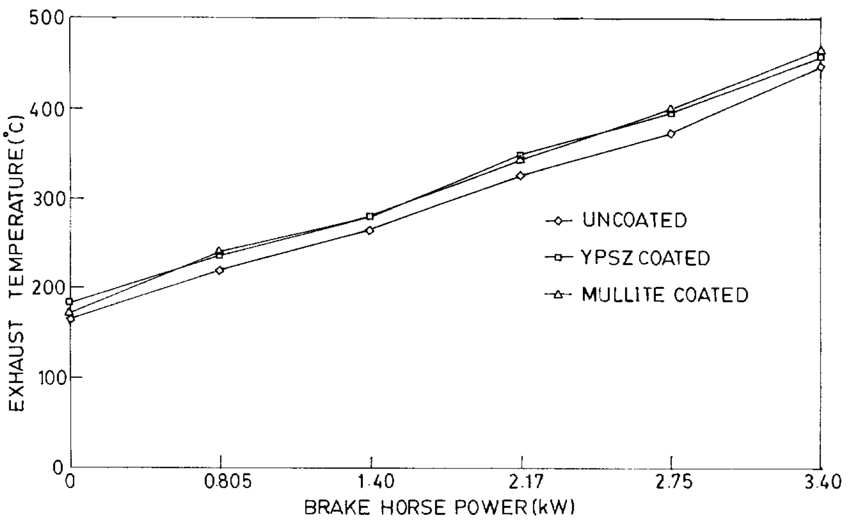

Fig. 2 Exhaust temperature versus BHP graphs for engines with uncoated and coated components

temperature as a function of brake power generated is shown in Fig. 2, which indicates an increase of about 5–6 per cent in the case of the ECC. This increased exhaust temperature is a result of the higher heat value in the chamber, which in turn is probably due to better combustion. Thus, the better burning of the fuel, and hence the higher availability of energy, improves the engine efficiency and leads to a cleaner engine. A visual examination of the skirt of both the coated pistons revealed that they were clean with very little deposit of carbon. Figure 3 shows a photograph of a mullite-coated piston

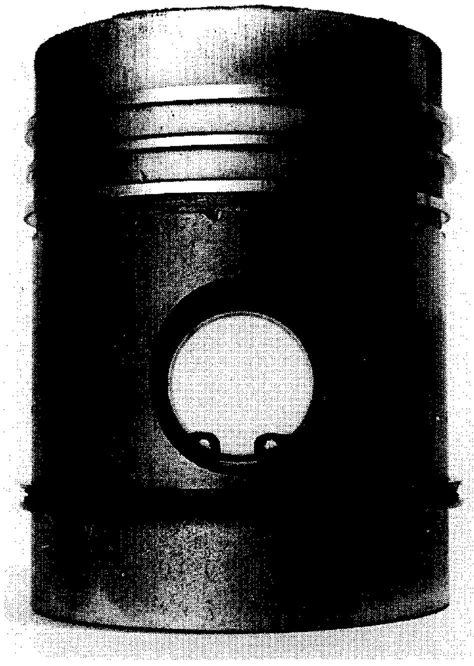

Fig. 3 Skirt of the piston coated with mullite after 500 h of endurance test

(skirt region) after a 500 h endurance test. The EUC, however, started to exhibit relatively poor engine economy after running for about 350 h. Figure 4 shows the b.s.f.c. values of two systems (EUC and 8YPSZ-coated ECC) studied at regular intervals of evaluation. The poor engine economy of the ECC during the first 50 h may be contrasted with the better engine economy of the same engine after 350 h compared with that of the EUC.

Frictional horse power (FHP) data, obtained from motoring the engine, showed marginal improvement in coated engines compared with uncoated engines investigated here. The EUC, EMULC and E8YZC systems gave FHP values of 1.7, 1.62 and 1.6 kW respectively. It is evident that TBC leads to a reduction in frictional torque in the engines. The marginal reduction in the FHP of the ECC may be attributed to a decrease in the viscosity of the lubricating oil surrounding the piston owing to a higher cylinder temperature. Also, an increase in temperature causes an increase in the viscosity of the combustion gases and of the air in the combustion chamber, which increases the pumping effort and hence the FHP. The observed reduction in FHP is actually a measure of the excess reduction in FHP against the pumping effort and the rubbing friction of components. However, if the viscosity reduction of the oil exceeds a particular limit, formation of the oil film will be impaired owing to the hydrodynamics of the lubricant between the rubbing surfaces, which will lead to a steep increase in rubbing friction. The present TBCs appear to allow an increase in the chamber temperature only to such an extent that the decrease in viscosity remains beneficial. In this regard they have an edge over other thermal barrier and non-thermal barrier coatings. Frictional horse powers determined by the 'Willan line' method were also found to agree with data collected by

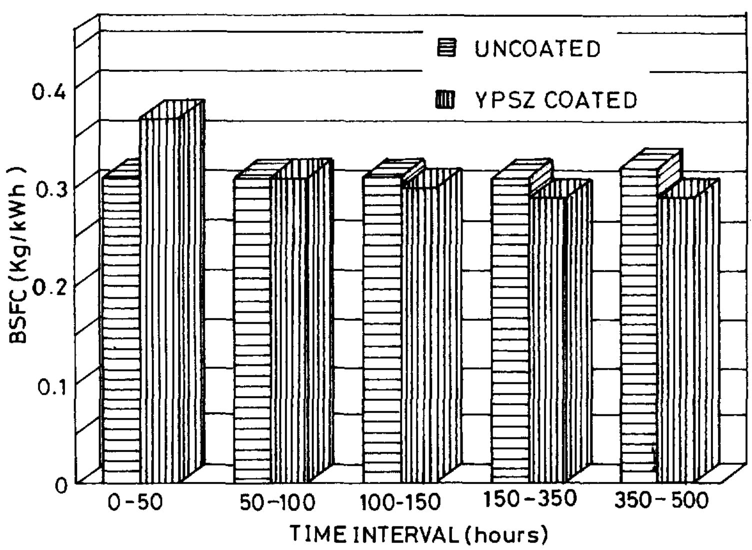

Fig. 4 The b.s.f.c. with time interval for engines with uncoated and YPSZ-coated components

the 'motoring method'. In the Willan line method, a graph is plotted between total fuel consumption (kg/h) and BHP. The straight line portion of the curve is extrapolated to meet the x axis (BHP). The intercept on the negative x axis gives the FHP.

3.2 Coating characteristics

The effect of plasma spraying and endurance testing on the structure of 8YPSZ is shown in Fig. 5. The X-ray diffractograms are for:

(a) plasma-sprayable powder
(b) a plasma spray coating on the piston head and
(c) the coating on the piston head after a 500 h endurance test.

The XRD of sprayable powder of 8YPSZ (Fig. 5a) reveals that stabilized tetragonal zirconia (t-ZrO_2) constitutes the major phase (73 per cent) and that unstabilized monoclinic zirconia (m-ZrO_2) is the minor phase (27 per cent) in the powder. However, the diffraction peaks marked by an asterix in Fig. 5a could be indexed to Y_2O_3, also suggesting the presence of a small amount of unreacted Y_2O_3 in the powder. The XRD of the as-sprayed coating (Fig. 5b) confirms that t-ZrO_2 is again the major phase and that m-ZrO_2 is the minor phase. However, the peaks that could be attributed to Y_2O_3 have disappeared, indicating that more m-ZrO_2 has been stabilized by the dissolution of Y_2O_3, resulting in the formation of t-ZrO_2 during the process of plasma spraying. This is also confirmed by the increase in the percentage of t-ZrO_2 ($\sim$80 per cent) in the as-sprayed coating. During the endurance test (500 h in the present investigation), the temperature of gases surrounding the coated surfaces of the cylinder head, piston and valves is expected to be high, with the surfaces themselves experiencing a temperature of about 870 °C [12]. The insulating characteristics of the TBCs, which restrict the flow of heat away from the combustion chamber, help raise the surface temperature. The XRD pattern of the endurance-tested surface (observed after cooling to room temperature) (Fig. 5c) shows increased conversion of m-ZrO_2 to t-ZrO_2, with only 6.5% m-ZrO_2 remaining. The coatings on the exhaust valve also indicated a similar increase in t-ZrO_2 ($\sim$90 per cent) at the end of a 500 h endurance test. This clearly establishes the phase stability of the 8YPSZ coating in the combustion chamber environment of an engine. More importantly, it confirms the suitability of the plasma powders prepared by the binder method for engine applications.

Similar structural studies were performed for the case of plasma-sprayable mullite powders, an as-sprayed mullite coating on a valve and a coating of mullite on a valve after a 500 h endurance test in the engine (figures not given). The plasma-sprayable mullite powder showed predominant diffraction peaks of mullite and the presence of α-Al_2O_3 in small quantity. The XRD of the as-sprayed mullite coating is very similar to that of the sprayable powder, with only minor changes in the α-Al_2O_3 peak intensity, indicating no further formation of mullite during the process of spray coating. The coating on the valve surface after the engine test also exhibited no significant change in the nature of the phases present as compared with the XRD patterns of the mullite powder and coatings. It was reported that, in the XRD of mullite coatings heat treated at 1150 °C for 2 h, the α-Al_2O_3 peak disappeared and the mullite peaks were strengthened [17]. Such behaviour was not seen in the coating on the valve after exposure to high temperatures, even for a longer duration. This implies that only slow heating and cooling schedules combined with

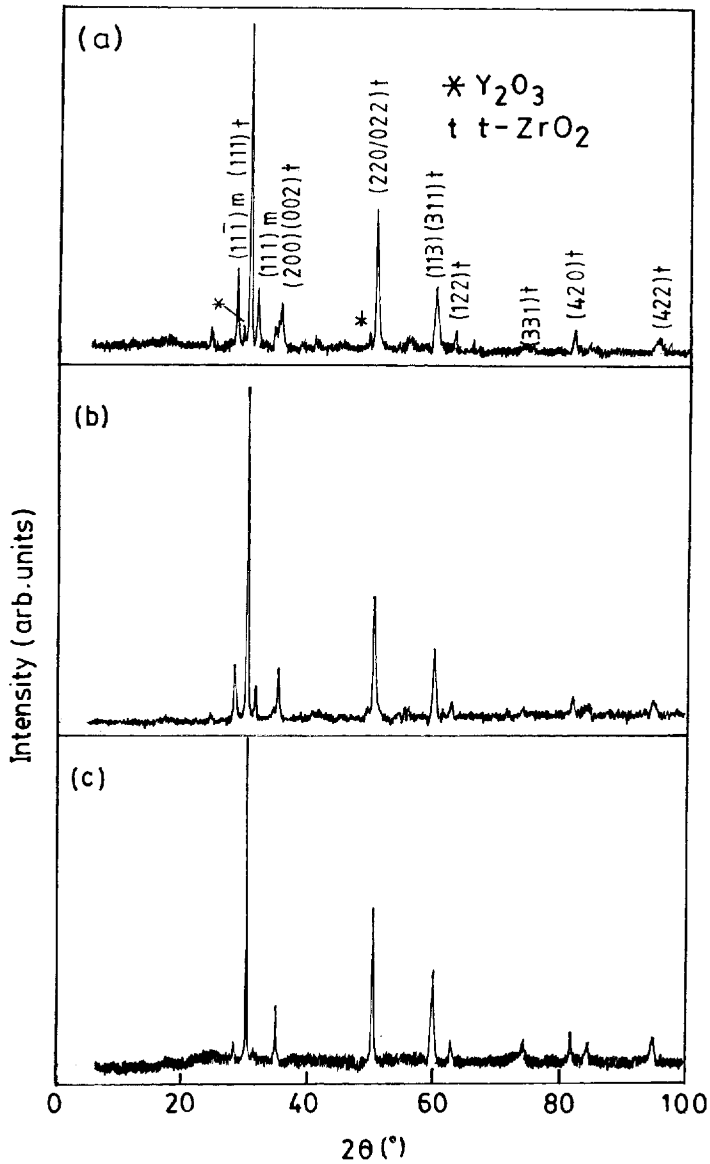

Fig. 5 X-ray diffraction patterns of (a) an 8YPSZ plasma sprayable powder, (b) an 8YPSZ as-sprayed piston and (c) the top surface of an 8YPSZ-coated piston after 500 h of endurance test

a temperature higher than that of the combustion chamber are required to bring about complete stabilization of the mullite phase.

3.3 Microstructure

Figure 6 shows the scanning electron micrographs of:

(a) the as-sprayed surface,
(b) the surface after a 500 h endurance test,
(c) the cross-section after endurance testing of the piston coated with 8YPSZ.

The micrograph of the as-sprayed surface of the piston (Fig. 6a) shows a fine-grained microstructure of the ceramic, with grain sizes ranging from 1 to 5 μm. Note that the plasma-sprayable powder consisted of agglomerates of fine particles (1–2 μm) which are released during the process of plasma spraying to form the fine-grained smooth coating. The roughness average, R_a, of the as-coated surface measured 4–5 μm. However, the surface of the coating after the endurance test (Fig. 6b) shows considerable grain growth, with grain sizes ranging from 10 to 20 μm. The distribution of microcracks observed on the surface was a consequence of the severe thermomechanical stresses imparted during the working of the engine. It is interesting to note that the interface between the ceramic, bond coat and substrate (piston cup region) is fairly smooth (Fig. 6c), and there are no signs of detachment of the layers.

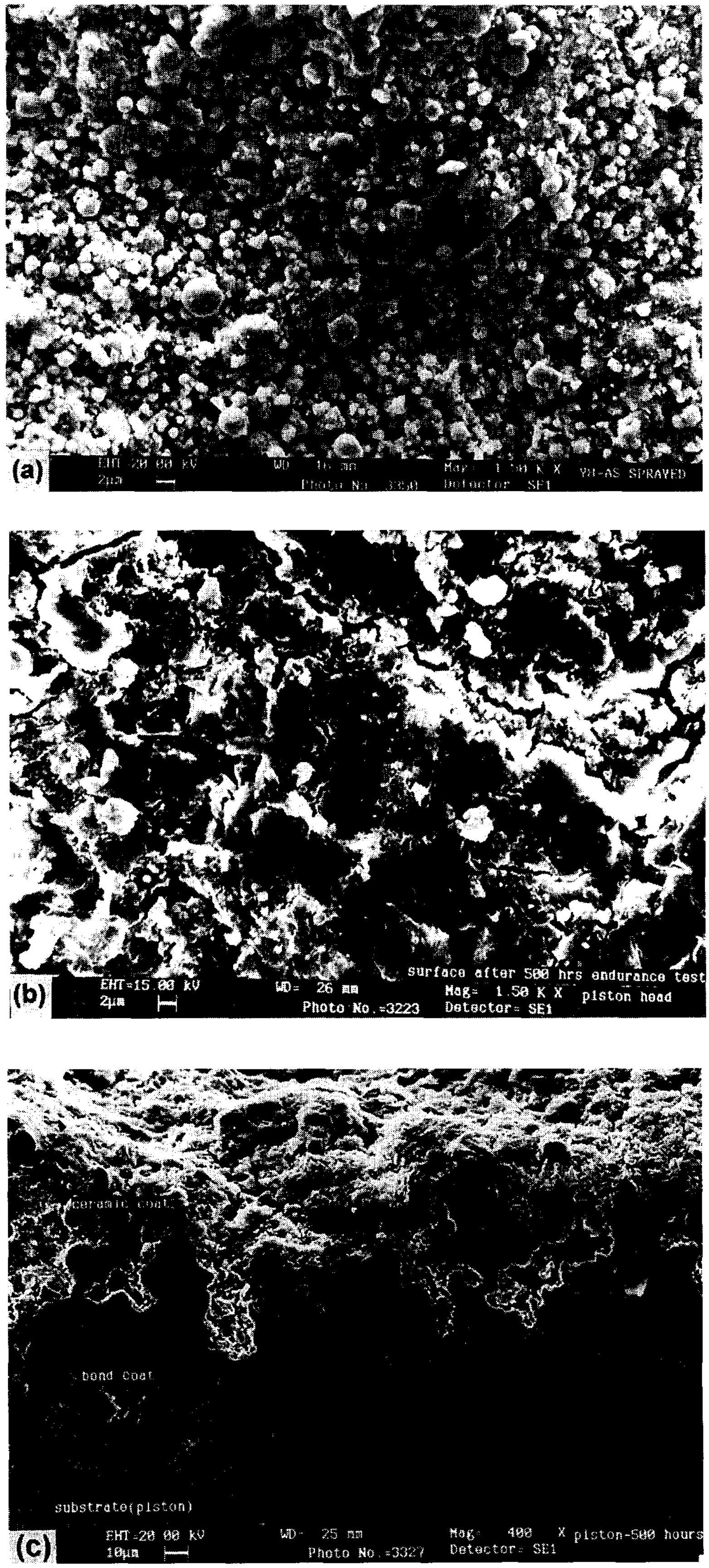

Fig. 6 Scanning electron micrographs of a piston coated with 8YPSZ: (a) as-sprayed surface, (b) surface after 500 h of endurance test and (c) cross-section after 500 h of endurance test

Scanning electron micrographs of the surface and the cross-section of the 8YPSZ coating on the exhaust valve at the end of the endurance test are shown in Figs 7a and b respectively. The microstructure of the surface is similar to that of the piston surface (Fig. 6b), except for the absence of microcracks. The smooth interface of the coating seen in the cross-section of the valve (Fig. 7b) confirms the integrity of the coating during the severe engine test. The micrographs of the surface of the piston (cup region) with as-sprayed mullite and after the 500 h endurance test are shown in Figs 8a and b. Compared with the as-sprayed surface (Fig. 8a), the surface after the endurance test shows the formation of coalesced grains with no significant changes in microstructure. The glassy nature of the surface that was observed in the as-sprayed coating has disappeared and given way to a microstructure with a well-defined grain structure. The surface is devoid of microcracks, unlike the 8YPSZ-coated surface. As pointed out earlier, improved resistance of mullite to microcrack formation in a diesel engine is already known **[12, 15]**. This feature of the absence of microcracks in mullite coatings and their presence in 8YPSZ coatings is attributed to the lower stress relaxation properties of mullite compared with zirconia.

The cross-sectional view of EMULC (piston crown region) after the endurance test is shown in Fig. 8c. Note that the thickness of the ceramic coating (1 mm) is

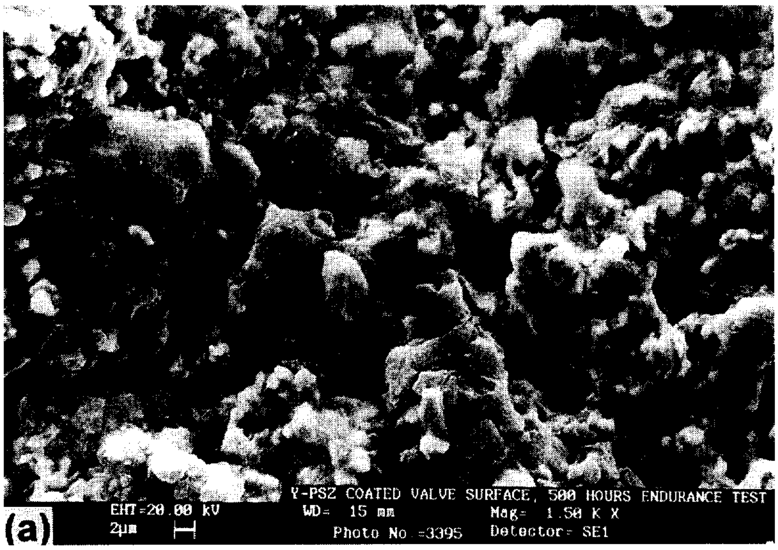

Fig. 7 Scanning electron micrographs of a valve coated with 8YPSZ after 500 h of endurance test: (a) surface and (b) cross-section

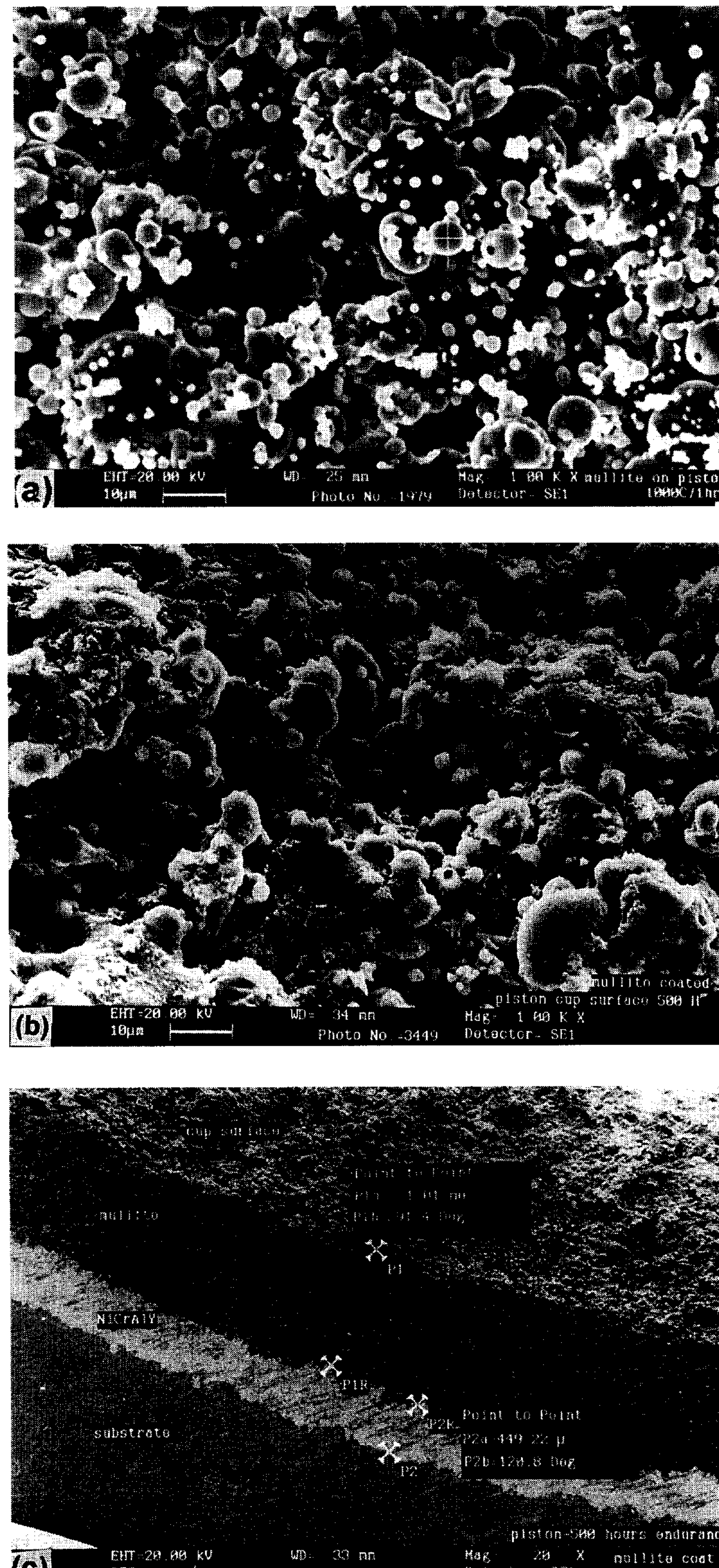

Fig. 8 Scanning electron micrographs of a mullite-coated piston: (a) as-sprayed surface, (b) surface after 500 h of endurance test and (c) cross-section after 500 h of endurance test

unaffected even after the severe endurance test. This confirms the suitability of the mullite coating from the point of view of thermomechanical stability, despite the higher thickness of the coating. The bond coat–substrate interface also appears to be smooth without any indications of detachment or oxidation.

3.4 Chemical composition

In a four-stroke engine, the piston:

(a) interacts with hot gases on its top surface where temperatures vary from 50 to 2000 °C
(b) interacts with cooling oil at a temperature of ~70 °C on its underside and
(c) is in contact through the piston rings with the water-cooled cylinder whose surface temperature varies between 100 and 300 °C [**23**].

It is evident that the high gas temperatures do not affect the piston surfaces because there are no signs of melting of aluminium (the melting point of Al is ~660 °C). In a normal engine, the Al alloy piston head does not attain a temperature above 450 °C [**23**]. However, the temperature experienced by the piston head in an engine with ceramic coatings is high (900 °C) because much heat is retained in the engine combustion chamber. That the coated surface has indeed experienced such high temperature is evident from the microstructure of the coating after the 500 h endurance test (Fig. 6b). However, this temperature (900 °C) is relatively low to be able to affect the phase stability of the ceramic coating. Hence, oxidation (caused by high temperature) is not considered to be a major limitation in determining the durability of TBCs in diesel engines (900 °C by the surface and ~600 °C by the bond coat). However, in EUC engines the temperatures in the combustion chambers are high enough to cause degradation of the surface of the uncoated components. Thus, TBCs act as a protection for the bare piston surface against damage (resulting from high temperature) and increase the engine life, at the same time raising the ambient temperature of the combustion chamber. The extent of oxidation of the surface of the components and the chemical composition of the surface and cross-section of the coated piston have been analysed by energy dispersive X-ray analysis (EDAX) and compared with the results of a similar analysis for an uncoated piston (both engine parts having undergone the 500 h endurance test under similar test conditions). The quantitative chemical analysis data are given as an inset to each spectrum.

The EDAX spectra of the surface of the uncoated piston before and after endurance tests are shown in Figs 9a and b respectively. The surface composition of the as-received commercial uncoated piston is predominantly tin (~97.92% Sn), with a small percentage of Al–Si alloy and a negligible oxygen content (~0.19 per cent), although the piston is supposed to be made of an Al–Si alloy. The origin or the reason for the presence of a thin layer of tin on the topmost surface of the piston is not clear. The present investigation (Figs 9a and 9b) confirms that there is an increase in oxygen on the surface after the engine tests, suggesting significant oxidation, but the dominant peak due to Sn on the surface remains unaffected. Irrespective of the role of the elements present on the surface, it is clear that severe oxidation (34.26 per cent oxygen on the surface after the endurance test) occurs during engine tests. The presence of carbon (~19.80 per cent) and sulphur (1.37 per cent) is only expected because of the environment of burnt diesel in the engine. This may be compared with the rather low oxidation of the bond coat of the 8YPSZ-coated piston after the endurance test, the EDAX spectrum of which is shown in Fig. 10a. The low oxygen percentage (~6.28 per cent), which is similar to that of the as-sprayed piston surface (EDAX spectrum not shown), indicates that the piston surface has not been degraded by the high temperature of the engine chamber. The substrate of the coated configuration (i.e. piston) after the endurance test shows a still lower percentage of oxygen (~3.6 per cent). There is a marginal decrease in the percentage of carbon (~15.33 per cent) on the coated surface (EDAX spectrum not shown). The presence of carbon when the surface temperature is around 900 °C is a puzzle. This may be attributed to the presence of unignited residual fuel on the surface of the piston when the engine was stopped.

The EDAX spectrum of the bond coat region of the mullite-coated piston after the endurance test is shown in Fig. 10b. The presence of only a low percentage of oxygen (~6.50 per cent) in the bond coat surface further confirms the suitability of mullite as TBC material, especially to prevent the engine components from oxidation during operation.

CONCLUSIONS

8YPSZ and mullite, which are potentially important TBC materials, have been examined using rigorous engine tests. After 500 h tests it can be concluded that:

1. Engine operating temperatures rise up to 900 °C.
2. There is a clear improvement in b.s.f.c.
3. There is a decrease in the frictional power loss.
4. There is clear protection afforded by the TBC for the engine parts (the piston, including the cup) against temperature-assisted oxidation and degradation.

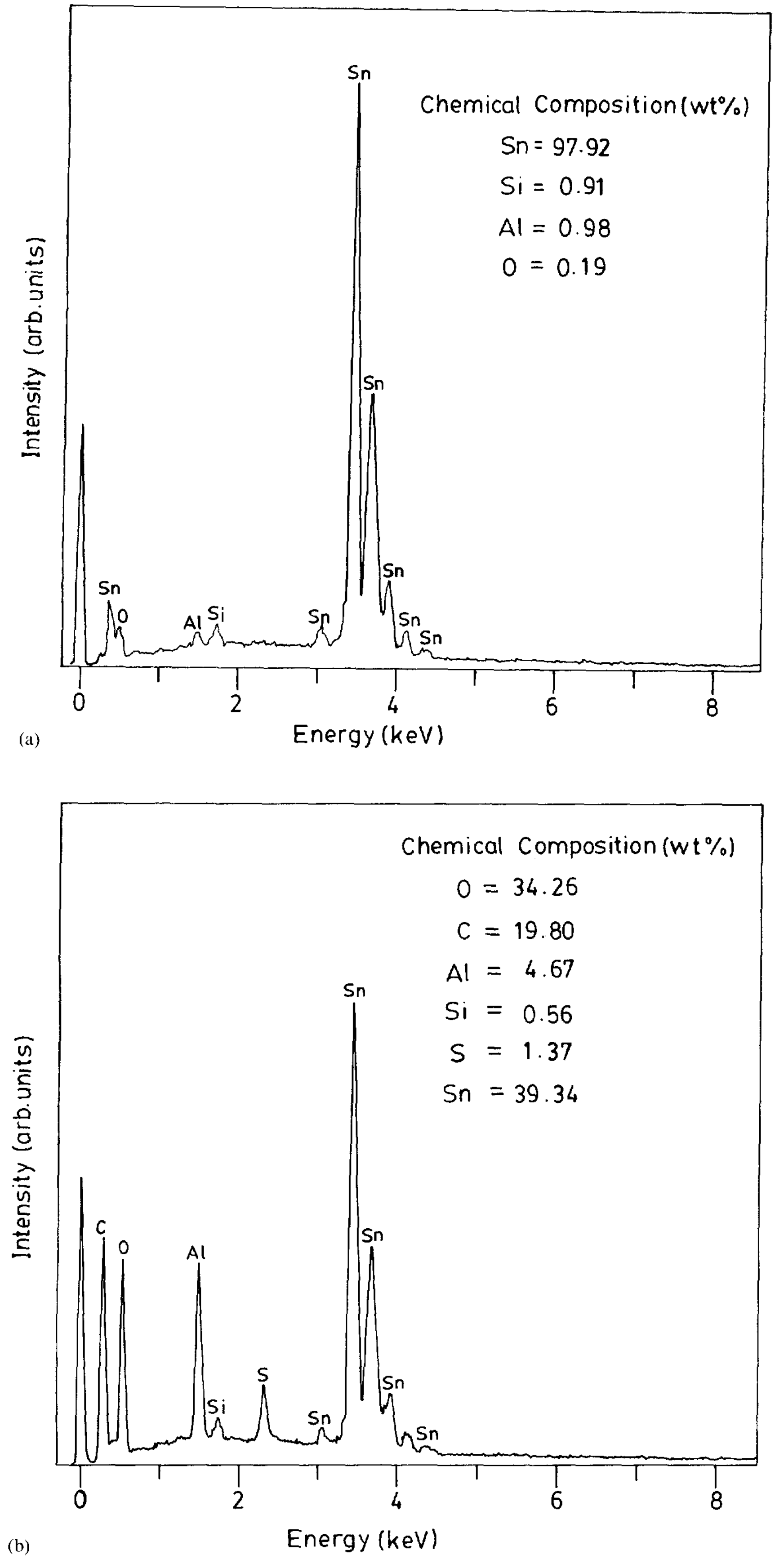

Fig. 9 EDAX spectrums of the surface of the cup of an uncoated piston: (a) as-received and (b) after 500 h of endurance test. The chemical compositions are given on the right

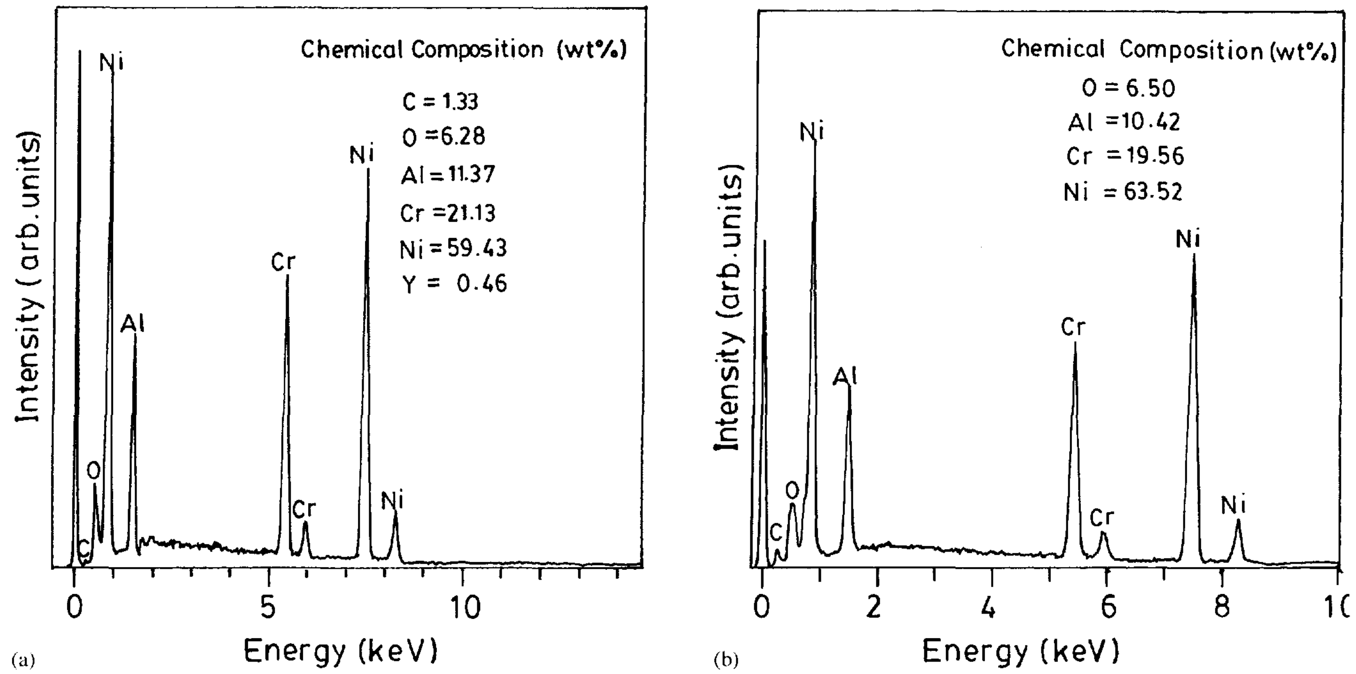

Fig. 10 EDAX spectrums of the bond coat region of coated pistons after 500 h of endurance test: (a) 8YPSZ and (b) mullite. The chemical compositions are given on the right

REFERENCES

1 **Carlson, N.** Thermal barrier coating on high temperature industrial gas turbine engines. NASA CR-135147, National Aeronautics and Space Administration and Energy Research and Development Administration, Ohio, USA, 1977.

2 **Miller, R. A.** Oxidation based model for thermal barrier coating life. *J. Am. Ceram. Soc.*, 1984, **67**(8), 517–521.

3 **Bennett, A.** Properties of thermal barrier coatings. *Mater. Sci. Technol.*, 1986, **2**, 257–261.

4 **Jones, R. L.** Some aspects of the hot corrosion of thermal barrier coatings. *J. Therm. Spray Technol.*, 1997, **6**(1), 77–84.

5 **Parks, W. P., Hoffman, E. E., Lee, W. Y.** and **Wright, I. G.** Thermal barrier coatings issues in advanced land based gas turbines. *J. Therm. Spray Technol.*, 1997, **6**(2), 187–192.

6 **Rigney, D. V., Viguie, R., Wortman, D. J.** and **Skelly, D. W.** PVD thermal barrier coating applications and process development for aircraft engines. *J. Therm. Spray Technol.*, 1997, **6**(2), 167–175.

7 **Troczynski, T., Cockcroft, S.** and **Wong, H.** Thermal barrier coatings for heat engines. In *Key Engineering Materials*, 1996, Vols 122–124, pp. 451–462.

8 **Vincenzini, P.** Zirconia thermal barrier coatings for engine applications. *Ind. Ceram.*, 1990, **10**(3), 113–126.

9 **Parker, D. W.** Improving thermal efficiency with ceramic thermal barrier coatings. In Proceedings of International Symposium on *Developments and Applications of Ceramics and New Metal Alloys*, Montreal, Canada, 1993, pp. 603–613 (Canadian Institute of Mining. Metallurgy and Petroleum).

10 **Winkler, M. F.** and **Parker, D. W.** Greener meaner diesels sport thermal barrier coatings. *Advd Mater. Processes*, 1992, **5**, 17–22.

11 **Beardsley, M. B.** Thick thermal barrier coatings for diesel engines. *J. Therm. Spray Technol.*, 1997, **6**(2), 181–186.

12 **Yonushonis, T. M.** Overview of thermal barrier coatings in diesel engines. *J. Therm. Spray Technol.*, 1997, **6**(1), 50–56.

13 **Fritscher, K.** and **Schulz, U.** Burner rig performance of density graded EB-PVD processed thermal barrier coatings. In Proceedings of ASME Winter Annual Meeting, New York, 1993, pp. 1–8 (Ceramic Coatings, ASME, Materials Division).

14 **Tsai, H. L., Tsai, P. C.** and **Tu, D. C.** Characterization of laser glazed plasma sprayed yttria stabilized zirconia coatings. *Mater. Sci. Engng A: Struct. Mater., Properties, Microstruct. and Processing*, 1993, **A161**(1), 145–155.

15 **Pierz, P. M.** Thermal barrier coating development for diesel engine aluminum pistons. *Surf. Coating Technol.*, 1993, **61**, 60–66.

16 **Ramaswamy, P., Seetharamu, S., Varma, K. B. R.** and **Rao, K. J.** Evaluation of CaO–CeO_2-partially stabilized thermal barrier coatings. *Ceram. Int.*, 1999, **25**, 317–324.

17 **Ramaswamy, P., Seetharamu, S., Varma, K. B. R.** and **Rao, K. J.** Thermal shock characteristics of plasma sprayed mullite coatings. *J. Therm. Spray Technol*, 1998, **7**(4), 497–504.

18 **Ramaswamy, P., Seetharamu, S., Varma, K. B. R.** and **Rao, K. J.** A simple method for the preparation of plasma-sprayable powders based on ZrO_2. *J. Mater. Sci.*, 1996, **31**, 6325–6332.

19 **Kokini, K., Choules, B. D.** and **Takeuchi, Y. R.** Thermal fracture mechanisms in ceramic thermal barrier coatings. *J. Therm. Spray Technol.*, 1997, **6**(1), 43–49.

20 IS 1600-1960: Indian standard code for testing of constant speed IC engines for general purposes.

21 IS 1601–1960: Indian standard specification for performance of constant speed internal combustion engines for general purposes.

22 **Garvie, R. C.** and **Nicholson, P. S.** *J. Am. Ceram. Soc.*, 1972, **55**, 303.

23 Thermal loading of diesel engines. Proceedings of Symposium arranged by Internal Combustion Engines Group, 21–22 October 1964. *Proc. Instn Mech. Engrs*, 1964–5, **179**(3c).