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Summary

The present state of development of thick thermal barrier coatings for truck diesel engines is assessed and areas where improved fundamental understanding is needed to properly pursue development are identified. Emphasis is given to the coating systems and design approaches that are being developed for the next generation of truck diesel engines under DOE/NASA support. It is noted that, while considerable progress has been made, the current level of understanding of coating system behavior is inadequate and this lack of fundamental understanding may impede current and future development. Several areas where improved understanding would be especially valuable are identified and recommendations for research into those areas are offered.

Introduction

The first objective of this study is to assess the present state of development of thick thermal barrier coatings (TTBCs) for truck diesel engines. Thick shall be defined here as a total coating system thickness of at least 0.060 inch (0.15 cm). This is in contrast to thin (less than about 0.015 inch or 0.04 cm) thermal barrier coatings which were initially developed for high temperature service in aircraft gas turbine engines (ref. 1). However, a brief overview of relevant materials aspects of thin thermal barrier coatings will be given in Part IV of this paper. The second objective is to identify those areas where fundamental understanding is needed to properly pursue further development. This paper is based on discussions with representatives of diesel and gas turbine engine manufacturers, research institutions, plasma spray equipment manufacturers, spray powder manufacturers, and coating vendors. Input was taken from site visits, phone interviews, and the publicly available literature. Site visits where made to Caterpillar Inc., Peoria, Illinois; Cummins Engine Company, Columbus, Indiana; Southwest Research Institute, San Antonio, Texas; United Technologies Research Center, East

Hartford, Connecticut; Purdue Thermophysical Laboratory, West Lafayette, Indiana; and Union Carbide Coatings, Indianapolis, Indiana. Phone and mail discussions were held with Alloy Metals, Inc., Troy, Michigan; Allison Gas Turbines, Indianapolis Indiana; Detroit Diesel Corporation, Detroit, Michigan; Pratt & Whitney Aircraft, East Hartford, Connecticut; Solar Turbines, San Diego, California; and State University of New York, Stony Brook, New York.

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Part I. Needs for Future Truck Diesel Engine

Truck diesel engines by approximately the year 2000 will be characterized by: higher fuel economy; improved reliability and durability; higher power density; lower NO_x and hydrocarbon emissions, much lower particulate emissions; and lower noise (ref. 2).

In order to meet these goals the Low Heat Rejection (LHR) Diesel Engine Concept has evolved (ref. 3). This engine will have insulated pistons, cylinder heads, and/or exhaust ports. The insulation may be TTBCs, monolithic ceramics, or air gaps -- most likely, combinations of the three approaches will be used. The water cooling system will be eliminated. Advanced lubricants capable of higher temperature operation will be used, and wear coatings will be applied to the piston rings and the cylinder liners. Waste energy in the exhaust will be recovered through turbocharging and turbocompounding (ref. 4). A Rankine bottoming cycle may also be included but only if fuel prices rise enough for it to be cost effective (ref. 5). A schematic of a LHR engine is shown in figure 1. A TTBC coated piston cap and cylinder head from a Caterpillar single cycle research engine are shown in figures 2a and 2b.

Anticipated benefits associated with the LHR engine include: improved fuel economy (especially when combined with exhaust gas recovery); increased power density for greater horsepower from smaller displacement; and decreased maintenance costs along with increased reliability from elimination of the water cooling system (refs. 2, 6, and 7).

Several questions, however, still remain. For example, the thermodynamic benefits must still be quantified (ref. 3). Many other of the remaining questions are related to materials technology. That is, questions about the durability, reliability, and cost effectiveness of materials in the LHR engine must be demonstrated.

Part II. Current Status of TTBCs for Diesel Engines

II A. The Heavy Duty Transport Technology Program (HDTT)

II.A.1 Background to the HDTT program

Most of the discussion in this part will focus on the DOE/NASA Heavy Duty Transport Technology Program (HDTT). This is because most of the ongoing, publicly available research and development in TTBCs is being conducted under this program. HDTT is also the most "scientific" of current ongoing programs. The source of funding for the HDTT program is the DOE Office of Transportation Systems in Washington D.C. The program manager is John Fairbanks. The program is managed by the NASA-Lewis Research Center, Terrestrial Propulsion Office. James Wood is the NASA HDTT program manager and M. Murray Bailey is the TTBC project engineer.

The overall objective of the HDTT program is to develop a technology base that can be applied to Low Heat Rejection diesel engines. The technology of thick thermal barrier coatings is one of the options being explored under HDTT (ref. 8). This is because TTBCs are believed to be very promising, especially for insulating the piston. The goals of the TTBC program are to develop the analytical tools needed to allow the TTBCs and the components to be designed as a system, to improve control or processing to the point where near-net shapes coatings can be applied, to improve NDE inspection for analysis of the component after processing, and to verify the reliability and durability of coated components in an engine environment (Private communication, M. M. Bailey, NASA-Lewis Research Center, 1989). Additional goals are evolving in this program as reference engine designs for meeting overall fuel economy goals evolve.

TTBC research under the HDTT program is component and performance oriented and has been conducted primarily via research at diesel engine companies. An initial research and development contract was awarded to Allison Gas Turbines (ref. 9). This initial contract demonstrated 24 hour durability, which is over one million firing cycles, in an uncooled research engine having 0.100 inch (0.25 cm) coating system on the head and a 0.060 inch (0.15 cm) coating system on the piston and valves . The TTBC system on the head included a sintered metal fiber strain isolator pad, a thin metallic bond coat layer and two layers of zirconia-yttria with the outer layer being more porous than the inner layer. This is shown schematically in figure 3a, and the coated components are shown in figure 3b. Allison is no longer involved in diesel engine research (that portion of the business is now a separate company named Detroit Diesel Corporation), however, they are continuing to pursue the strain isolator approach for certain gas turbine applications.

II.A.2 Ongoing HDTT contracts

There are two ongoing TTBC contracts supported by the HDTT program. One is with Caterpillar Inc. under program manager H. J. Larson, and the other is with Cummins Engine Company under program manager T. M. Yonushonis. Coatings under these contracts are being designed and evaluated for application to pistons and cylinder heads. Performance benefits and durability are being confirmed in a single cylinder engine test modified to LHR conditions. The specific coating system conductance goal for these contracts is 0.5 BTU/hr-°F (408 W/M^2-K), and the durability goal is 100 hours under accelerated conditions. Selection of TTBC systems drew heavily from prior aircraft engine experience on plasma sprayed abradable seals. Cummins selected a system based on the aircraft ceramic seals experience of subcontractor UTRC (United Technologies Research Center). Caterpillar developed a similar coating system. On both contracts, coating system selection was based on analytical design, mechanical properties determination, and a limited amount of rig testing. Since the programs were component and performance oriented and not materials oriented, there was no attempt to test a wide variety of coating system concepts.

In each case four layer coating system designs were developed. These designs consisted of a metallic bond coat, two layers of mixed ceramic and metal, and a layer of a zirconia-yttria ceramic. A schematic of each companies design is given in figure 4. Some of the key properties measured for each coating system are given in table 1.

The extensive analysis conducted under the HDTT program at Caterpillar and Cummins has quantified our knowledge of the cyclic stresses and strains encountered by thick coatings on diesel engine components. This analysis began with a recognition of low cycle and high cycles stress and temperature excursions encountered in the diesel engine. As shown schematically in figure 5, the low cycle excursions involve stop/start transients and no load/full load transients (e.g., down hill/up hill) and the high cycle transients are due to combustion in the cylinder. These combustion transients are, of course, superimposed on the lower cycle transients. The cyclic environment in the diesel engine differs greatly from the typical commercial aircraft engine cycle which involves take off, climb, and steady state cruise. The transfer of the aircraft ceramic seals technology to the diesel engine began with the assumption that the designs which perform well in commercial aircraft engine cycle could be adapted to perform well in the very different diesel engine cycle. While that assumption was a good starting point, the task of developing thick thermal barrier coatings for diesel engines is proving to be more challenging than a simple adaptation of gas turbine seals technology.

Figure 6 is an example of the temperature and stress excursions predicted to occur in a TTBC system on a piston based on a 1D infinite plate finite element analysis (refs. 7 and 10). These calculations predict a very low gradient across the coating system thickness for no-load operation. At full load a gradient of about 500 °C is predicted for the conditions of this calculation. The figure 6a also shows that, as the load is decreased the surface of the coating cools significantly faster than the interior. Also note that the metal temperatures remain below 300 °C which is well below the 800 °C required to oxidize the MCrAlY in the graded layers. As shown in figure 6b, the coating surface is in a high state of compression during full-load conditions. At no load the residual stress state dominates. This residual stress state still involves compression at the surface and tension in the graded layer just above the bond coat. Both UTRC and Caterpillar have chosen to preheat the components before spraying which reduces the tensile residual stresses at the interface region while placing the surface further into compression. This differs from the practice with thin aircraft thermal barrier coatings where substrates are kept comparatively cool to minimize compressive residual stress. The cyclic stress state described above may be designated as a low cycle thermal fatigue (a LCF thermal fatigue). Figure 7 from a Caterpillar study (Private communication, H. J. Larson, Caterpillar, Inc, 1989) illustrates how temperatures vary across the complicated geometry of the diesel piston with the highest temperatures occurring at the edge of the bowl region.

The HDTT program has also revealed that severe temperature fluctuations occur on the surface of the coating. This is due to the combustion of the mixture of diesel fuel and air every two revolutions of the crank shaft in a four cycle engine. This means that the piston is subjected to, for example, 22 explosions per second when the engine is operating at 2600 RPM. Gas temperatures, cylinder pressures, and heat flux rise to very high instantaneous values with every explosion. In fact, peak cylinder pressures over 3000 psi, gas temperatures up to 1400 °C (2600 °F), and heat fluxes up to 5 MW/M^2 are predicted for some advanced designs. These peak, instantaneous conditions are more severe than those encountered in a gas turbine engine. On the other hand, the mean conditions are much less severe than those encountered in the gas turbine. Figure 8a illustrates schematically how the gas temperature, cylinder pressure, and heat flux of an engine operating at full load rise to very high instantaneous values once every 2 revolutions (720°) of the crank shaft. The temperature gradient in the coating system is illustrated in figure 8b. This is similar to the upper curve in figure 6a except that figure 8b shows that the outer 0.5 mil (0.13mm) of the coating experiences severe temperature gradients. Temperature swings at the surface have been calculated to be on the order of 225 °C for a LHR engine operating at 2600 RPM (refs. 7 and 10). This effect has also been demonstrated experimentally in an HDTT sponsored program (ref. 11) where thin film thermocouples were used to experimentally measure this temperature swing. Temperature swings of 140 °C were measured for an engine operating at 1300 RPM at 75% of full load. These temperature swings lead to high cycle cyclic thermal stress at the surface superimposed on the compressive mean stress as shown in figure 8c. The instantaneous nature of the temperature maximum leads to asymmetry of the cyclic stress about the mean stress with a greater amplitude of the compressive component. In reference 7 the maximum compressive stress was calculated to be approximately equal to the compressive strength of the coating. The preheat applied during processing increases the magnitude of the compressive mean stress at the surface and therefore may increase the possibility of fatigue damage. Additionally, a high cycle mechanical stress is superimposed on this thermal stress as the high peak pressures cause the piston to bend about the pin. The magnitude of this bending stress is sensitive to piston design and is therefore and important factor to consider when designing for TTBCs. This cyclic stress state may be designated as a high cycle fatigue (HCF).

Surface spalling of specimens prepared by Caterpillar was induced in a purely mechanical four point bend fatigue test conducted at the Southwest Research Institute under HDTT funding (refs. 12 and 13). Tensile and compressive S-N curves taken from that study are presented in figures 9a and b. The tensile fatigue specimens used for these tests were free standing ceramic coatings while the compressive fatigue specimens remained attached to a substrate. It should be noted that although these curves are drawn with upward curvature suggesting the presence of an endurance limit, it is still not know whether an endurance limit actually exists. This is an important question because if an endurance limit exists a coating which survived to that limit in a test should not suffer fatigue failure in a much longer test.

In the diesel engine, the LCF type of delamination spalling and the HCF type of surface spalling are two conditions that could lead to coating failure. The relative importance of these two potential failure modes and the conditions which would favor one mode over the other are still unknown. When spalling has occurred, as evident in the publicly referenceable engine tests at Cummins (refs. 14 and 15), it appears from post test inspection that a delamination type of failure has occurred. An example is shown in figure 10. Although, in certain cases it may be possible for repeated surface (HCF) spalling to mimic the appearance of delamination (LCF) spalling. Caterpillar, in their publications under the HDTT program, indicates a concern with at least the possibility of the HCF failure mode.

The laboratory test rigs which have been used at UTRC for Cummins and at Solar Turbines for Caterpillar have been successful in duplicating the LCF type of stress state that is found in the engine but much less able to reproduce a severe HCF type of stress state. A schematic of the test rig used at Caterpillar/ Solar Turbines is shown in figure 11. A similar rig was used to a limited extent by Cummins/UTRC. These rigs subject flat specimens to front side heating and back side cooling to duplicate the temperature gradients encountered in the engine. Stop/start and no load/full load transients are achieved by moving the specimen in and out of the flame. The rotating carousel produces a HCF cycle which in these rigs is much milder than the HCF cycles encountered in the engine. Coating failure in the laboratory rigs is generally associated with edge initiated delamination or surface initiated vertical cracking. Edge initiated failure is a concern for coatings tested in an engine -- especially for coatings on the cylinder head.

In summary, the HDTT TTBC program is component, design, and performance oriented and not strongly materials oriented. The program has been successful in taking the ceramic abradable seals developed by the aircraft industry and adapting them to create the first generation diesel engine TTBCs. Finite element modeling has been conducted under the program, first generation coating system designs have been established, coating system properties have been measured, and engine testing which will be published in the open literature is being conducted. A risk of the HDTT TTBC program is that experience on TTBCs is being gained on very few coating concepts. Thus, the success or failure of coatings based on these few concepts will influence decisions as to the viability of TTBCs that may effect their use in diesel engines well into the next century.

II.A.3 Future HDTT efforts

The next phase of the HDTT TTBC program will continue to develop the technology for applying coatings to diesel engines. Efforts will focus on establishing an NDE technology for inspecting coatings on components, on improving processing so that near-net-shape coatings can be sprayed, on expanding characterization of materials properties, and possibly on developing seal coatings. Coatings in the next phase will have a 10000 hour design life, and will be verified in a 1000 hour engine test run at accelerated conditions. Failure mechanisms and life prediction will also be emphasized.

The HDTT program has also supported the in-house NASA-Lewis thermal barrier coatings program. Initially this support consisted of upgrading the plasma spray process automation, monitoring, and control equipment to bring capabilities up to the state-of-the-art. A study, supported by NASA aeronautical base research and technology funding, was than conducted to learn how to use the equipment to produce a wide variety of coating microstructures from a variety of starting powders each of which had nominally the same chemistry . Each of the coatings sprayed under this effort has been characterized with respect to porosity, microstructure, deposition efficiency, and in the near future thermal conductivity. Current plans are to extend characterization to mechanical properties and to construct a room temperature flash diffusivity apparatus and to study the effects of high temperature exposure on properties. Also a test rig is being constructed to determine whether a plasma torch impinging on a rotating, coated disc can produce high temperature swings on the surface of the coating.

II.B. Other Research into Thick Thermal Barrier Coatings for Truck Diesel Engines

II.B.1 Army research into TTBCs

The U.S. Army - TACOM supported the first research into low heat rejection engines and has continued to support work in this area. Army requirements for their on-road trucks are rather similar to needs of the commercial industry. One important difference is that they wish to have the capability to burn lower quality fuels. Army supported research has concentrated on evaluating commercially available coatings in diesel engines. Most of the reports published under Army contracts have limited distribution (e.g., references 16 and 17) and therefore will not be discussed here. A discussion of the Army's efforts as of 1987 may be found in reference 6.

II.B.2 LHR diesel engine research in Europe and Japan

One of the most prolific researchers into TTBCs for diesel engines are I. Kvernes and his associates in Oslo, Norway. This research into diesel engine coatings has been going on for many years, and in fact some of it received U.S. DOE support (ref. 18). Recently, Kvernes reported test results for TTBCs on a single cylinder version of a marine diesel engine. The tests showed that a 1 mm thick coating on the cylinder head and a 2 mm coating on the piston reduced heat losses into the water coolant by 9% while increasing the heat losses into the oil by 3% for an overall 6% reduction.

Other European research into TTBCs for diesel engines and in LHR engines are
reported to be at a standstill (ref. 6). This is based on the discouraging experimental results on insulated European engines (ref. 3) and their interpretation by Waschni et al. (ref. 19). The "Waschni analysis" concluded that, at least for engines of European design, heat transfer would actually increase with increasing component temperature causing a net loss in efficiency. This analysis has been disputed in another study (ref. 20).

Japanese researchers are developing LHR engines but are focussing on monolithic ceramics (ref. 6).

Part III. Areas Where Fundamental Materials Understanding is Incomplete

The purpose of Part III is to identify and discuss briefly the many areas where understanding of the fundamentals aspects of thick thermal barrier coatings for diesel engines is incomplete. This discussion draws heavily from discussions with representatives of the companies and research institutions noted in the introduction. Ultimately, the opinions are those of the author. Prior to the interviews a list of those areas where fundamental knowledge is lacking was drawn up and mailed to potential interviewees. This list, which is reproduced in a revised form in the appendix, served as a starting point for discussion. Interviewees were encouraged to comment as to the relevance of each topic and to offer additional topics. Six general areas selected for discussion were A) Fundamental Knowledge Needed to Optimize Zirconia TTBCs, B) Effect of Environment and Stress State on Properties and Performance, C) Thermophysical and Thermomecanical Properties Measurement, D) Lower Cost TTBCs, E) Alternate Approaches, and F) Development of Meaningful Bench Tests

Before discussing the above areas, it is necessary to adopt a working definition of "fundamental research" and of "materials research." Thus for the purposes of this discussion "fundamental research" shall be research enabling but not including the design and testing of thick thermal barrier coatings on diesel engine components or the commercialization of those designs. That is, the actual design, engine testing, and commercialization will be considered to be beyond the scope of this study, but all of the background knowledge that goes into those efforts shall be considered to be fundamental. "Materials research" is research related to processing and evaluation of current and future TTBCs and does not include thermodynamic effects such as performance improvements and fuel savings. However, the diesel engine companies stress that all fundamental materials work must be calibrated to engine experience, and that a considerable amount of fundamental engine-related thermodynamic and mechanical engineering research is also needed.

III.A. Fundamental knowledge needed to optimize zirconia TTBCs

In this section the factors affecting optimization and reproducibility of thick thermal barrier coatings are considered. The factors considered include those associated with the starting powder, with the processing, with selection of optimum materials, and with scaling up from the laboratory to the component.

III.A.1. Effect of powder preparation method, chemistry, manufacturer, and lot on properties and performance

A set of spray parameters developed for one lot of zirconia powder will not necessarily yield the same coating when another lot of zirconia is sprayed. Sources of variability include manufacturer, preparation method, and even lot-to-lot variations. There is no universal standard for plasma spray powders, and our understanding of which factors are most important is incomplete. Furthermore, these factors will vary depending on the application. In the aircraft industry each turbine engine company has developed specifications for spray powders. Powder vendors must then meet the specification in order to compete for orders, with competition being encouraged for cost reasons. Current specifications are tighter than they were a few years ago out of necessity for maintaining high quality. This is one area where a fundamental study designed to determine the nature of this variability would help to provide the background needed for future TTBC specifications.

III.A.2 Effect of processing, microstructure, and phase distributions on properties and performance

The variations in coating properties and performance arising from processing variability may be as significant as the powder lot variabilities unless great care is taken to monitor the quality control during processing. This fact is being accepted more and more by the plasma spraying industry. However, there is no generally accepted approach for dealing with processing variability. In addition to problems of variability, there are optimization related problems. In fact it may be argued that no coating can be fully optimized without resorting to an infinite amount of testing and evaluation. Thus optimization becomes a trade off between the need to develop a reliable coating system and the need to minimize development costs. Furthermore, variability problems compound optimization problems. This is because excessive variability makes it difficult to optimize a given coating system or to evaluate a new system against an old one. As described in Part II, the HDTT program was component oriented and not materials oriented. Therefore only a few coating systems could be considered and the amount of time that could be devoted to optimization was limited. Therefore fundamental research designed to identify and solve variability problems, improve quality control, and find viable back-up coating systems would be very useful.

III.A.3 Optimum zirconia composition for TTBCs

Even if spray powder preparation and the plasma spray process were "optimized" it would still be necessary to ensure that the ceramic material selected for the TTBC was theoretically the best available material for use in the diesel engine. Zirconia based materials, especially zirconia-yttria, has received the most serious consideration based on the successful use of these materials in the gas turbine industry and the lack of any strong contenders. One major difference between the two coating systems developed under HDTT is that Cummins/UTRC employs ZrO_2-20%Y_2O_3 and Caterpillar employs ZrO_2-8%Y_2O_3. These two compositions are very different from each other with the 20% yttria composition forming an equilibrium cubic phase when sprayed and with the 8% yttria composition forming a non-equilibrium tetragonal phase plus lesser amounts of the monoclinic and cubic phases (refs. 21 and 22). Additionally, the starting powders for these two coatings come from two different manufacturers and are prepared by two very different techniques. Thus, a fundamental question is how do these two materials compare with respect to properties and performance when compared head to head? A second question is how would the properties and performance of other zirconias compare?

III.A.4 Effect of scaling up from test coupons to components on properties and performance

This is a very important factor -- especially when the processing is transferred from spraying flat coupons in a research shop to spraying components in a production shop as was the case with the UTRC coatings (refs. 23 and 24). While this topic may be more applied than fundamental, a fundamental study of such factors as the effect of spray angle on coating properties and the effect of substrate mass could help to identify potential problem areas.

III.B The effect of environment and cyclic stress on properties and performance

In this section the environmental and stress related factors which contribute to coating degradation will be considered. A variety of cyclic, time at temperature, chemical and mechanical conditions that may be encountered in the engine will be considered

III.B.1 Effects of cycling

The cyclic conditions in the diesel engine are much more severe than was generally realized before the HDTT program. Under HDTT the magnitude of the start/stop transients, no load/full load transients, and combustion transients have been characterized. However, the thermal and mechanical LCF and HCF response of TTBCs is still not well characterized. A concern over the detrimental effect of edges and corners has been raised, as well as the possibility that the hot spots which result from the fuel injector pattern may contribute to the fatigue of the coatings. Mudflat cracking has been observed on the surface in some tests but it is not even known whether this is a beneficial or detrimental effect. Subcritical crack growth and microcrack link up mechanisms have been proposed for thin TBCs, and similar effects may occur in diesel TTBCs. Thus, numerous opportunities exist for important, fundamental research into the fatigue response of TTBCs.

III.B.2 Deposit related effects

The effects of the deposits which plate out on the coating are not well understood. These deposits form from the additives in the oil and the sulfur contaminant in the fuel. Calcium sulfate is a commonly observed deposit. It is interesting to note that although there are many papers in the literature which discuss the destabilization of zirconia from reactions between a deposit and yttria, the calcium ion should instead further stabilize the zirconia if a reaction occurred. It is not known whether the presence of a deposit on the surface effects the HCF response of the coating. Also, Cummins has noted that a deposit can build up at the edge of the piston to the point where it may slide against the liner. This sliding could then damage the edge of the TTBC. If diesel engines were run on lower grade fuel containing higher levels of sulfur plus other contaminants then the deposit could be much more detrimental. Fortunately, the trend is towards even cleaner fuels for environmental reasons. However, dirty fuel could be used in certain situations by Army trucks. The effect of deposits originating from the oil could be one factor used in the selection of the particular additive package for the oil. A fundamental experimental and thermodynamic analysis of the interaction between the observed deposits and the coating material would help to clarify whether chemical reactions may be expected at the temperatures encountered in the diesel engine.

A conceivable beneficial effect of the deposits would be to block the radiation of infrared energy through the partially translucent TTBC. It has been suggested that translucence would reduce the effective thermal conductivity of ceramic materials (ref. 25). This would be especially important if the coatings were not going to be sealed. Emisivity measurements on deposit-plated TTBCs could be informative.

III.B.3 Time at temperature related effects

Time at temperature factors such as oxidation, phase transformations, sintering, and creep are very important for ceramic coatings and seals operating in gas turbine engines. In the diesel engine, materials temperatures are comparatively low so that very long times would be required for these factors to become important. While extremely long time testing is generally impractical, in many cases the effect of time may be "accelerated" by conducting tests at elevated temperatures. That is the behavior of a material at very long times often can be estimated by shorter time testing at higher temperatures. Furthermore, the interest of the DOE in gas turbines for transportation and power generation also warrants investigation at higher temperatures.

III.B.4 Erosion and foreign object damage

Erosion and to a lesser extent foreign object damage is another topic that is important under certain conditions for gas turbine engines but is not believed to be very important for diesel engines. This is primarily because diesel engines employ filtered air. The possibility of damage of other engine components from spalled pieces of the coating is not considered to be a problem.

III.C Thermophysical and thermomechanical properties measurement

Characterization of thermomechanical and thermophysical properties of TTBCs will be considered in this section. Mechanical properties such as various strengths and moduli, physical properties such as thermal conductivity and permeability, and NDE techniques will be addressed. This topic has assumed increasing importance as thermal barrier coatings begin to be designed into engines. This is having a positive effect on thermal barrier coating development which in the past had tended to be rather "Edisonian". Properties of thin bill-of-material aircraft TBCs have only recently been well characterized under the NASA HOST program (ref. 26). UTRC has historically done the best job in characterizing the properties of TTBCs, and UTRC and Caterpillar are now both characterizing the properties of the TTBC systems being developed under HDTT.

III.C.1 Thermomechanical properties

The coatings and the components for the next generation of diesel engines are being designed together as a system. Thus, measuring the properties has become effectively the first step in design, and close cooperation between designers and the experimentalist is now essential. Among the properties to be considered are ultimate strength, yield strength, strain to failure, and modulus measured in tension and compression over a range of temperatures through the use of uniaxial or bend tests. The high and low cycle fatigue behavior of the coating system should also be considered as well as tensile adhesion tests for bond strengths and fracture toughness tests. Anisotropy in properties and nonlinear effects should also be addressed. For each of the above tests care should be taken to ensure the use of proper specimen geometries. The properties in this section are fundamentally important and necessary for any coating systems under consideration.

III.C.2 Thermal conductivity measurement

Thermal conductivity is a property with obvious relevance to thermal barrier coatings. Despite the great relevance, this is another property which in the past has historically been given secondary importance by coating developers who have been more concerned with durability than the conductivity. Included among the approaches which may be used to measure thermal conductivity are flash diffusivity, thermal wave (modulated), cut bar, and radial techniques (ref. 27).

The flash diffusivity approach appears to have gained the most favor for measuring the conductivity of thermal barrier coatings. That is because, with proper care, this approach is able to quickly yield accurate results on simple specimens. However other techniques cannot yet be ruled out, and with any technique erroneous results may be obtained by the naive. Thermal conductivity measurements should included as part of any fundamental study of TTBCs.

III.C.3 NDE and metrology

There is currently a strong need for NDE techniques which would be sensitive to coating properties, porosity, and thickness. No techniques have yet been found which will yield an accurate measure of properties and porosity (with porosity the accuracy needed is probably about +2%). An optical technique has recently been developed for measuring coating thickness on-line during processing (ref. 28 and 29), and this and other techniques will be considered for diesel engines under HDTT. There are many other opportunities for fundamental research into NDE/property relationships which could have a place in a fundamental program.

III.C.4 Residual stress measurement

The residual stress in a TTBC system (defined as the "macrostress" imposed on the ceramic layer by the constraints of the substrate) may be manipulated during processing by substrate heating or cooling, ceramic-side cooling, varying the thickness per pass, and varying the traverse speed. UTRC has measured residual stress by applying strain gages to thin coated substrates and grinding off successive layers of the coating. Caterpillar has experimented with using x-ray technique to measure residual stresses at the surface. The Brookhaven National Laboratory synchrotron radiation facility has been used to measure residual stress at the ceramic-metal interface in thin plasma sprayed alumina coatings (ref. 30). Others have deduced residual stress from the deflection observed when coatings are placed on thin substrates (Private communication, R.C. Novak, United Technologies Research Center, 1989). Since residual stress is intimately connected to coating durability, fundamental research in this area would useful.

Another type of residual stress present in plasma sprayed ceramics is the "microstress" which develops as the plasma sprayed ceramic splats rapidly solidify. This type of stress may be deduced from the broadening of x-ray diffraction peaks (ref. 31).

III.C.5 Permeability

As discussed in Part III pressure in the cylinder will rapidly vary from atmospheric pressure to possibly over 3000 psi many times per second. The response of the porous TTBC to these fluctuations has not been well characterized and therefore represents another opportunity for fundamental research. The intrinsic oxygen conductivity that zirconia displays at high temperatures is not considered to be a issue for concern for the temperatures encountered in diesel engines. Oxygen conductivity may become important for zirconia in higher temperature gas turbine engines.

III.D. Lower cost TTBCs

Cost is obviously an important factor since the overall costs of the LHR engine must not exceed the value of the fuel economy, power density, and durability gains. The cost of the ceramic powders alone is so significant that high deposition efficiency spraying techniques must be developed and the possibility of overspray reclamation must be considered. There appears to be low interest at the present time in searching for lower cost ceramics since much work in the past has yielded few alternatives. The high costs of metallic bond coats, especially the large amount used in the graded regions of layered coatings, is a concern. Low cost alternatives to NiCrAlY and CoCrAlY should be considered.

III.E Alternative approaches

In this section alternatives to the current four layer approach (figure 4) and alternatives to plasma spray processing are considered. In general, there appears to be satisfaction with the four-layer approach ,and there is relatively low interest in investigating how bonding might be improved to the point where the intermediate layers would not be necessary. Approaches discussed included efforts to improve bond strength, to tailor surface roughness, and to manage residual stress. Strain isolator pads appear to be ruled out for automotive applications although they still may have a place in certain aircraft gas turbine designs. Garrett (ref. 32) has developed a thick ceramic seal whose design avoids the need for graded layers by inducing vertical segmentation cracking through most of the thickness of the ceramic. This is accomplished by plasma spraying the ceramic at a low angle onto a substrate with finely spaced ridges machined onto its surface.

The possibility of using molecular orbital theory to provide insights into the detailed mechanisms of bonding came up in discussions at Southwest Research (Private communication, J. F. Maguire, Southwest Research Institute, 1989) Similar calculations, performed under a NASA grant, have investigated the bonding of alumina to nickel aluminum alloys (refs. 33 and 34). The insights provided by a quantum mechanical study could potentially influence the design of the next generation of thermal barrier coatings.

There was low interest in investigating alternatives to plasma spray processing, especially for the ceramic layer. One area that could be looked into would be to see if any of the new flame and plasma spray approaches that were developed for wear coatings have the potential to spray TTBCs. Shrouded plasma spraying (which is a low cost alternative to low pressure plasma spraying) is a technique to limit the amount of bond coat oxidation that occurs upon spraying. Possible benefits of reduced oxide content of diesel TTBC bond coats are not immediately apparent, however.

III.F. Development of Meaningful Screening Tests

There appears to be a need to evaluate many more coatings in an engine environment or an engine simulative environment. These tests are needed both to thoroughly evaluate current systems, to study failure mechanisms, and to investigate new concepts. Caterpillar through subcontractor Solar Turbines and Cummins through subcontractor UTRC have used bench rig tests to a limited extent but otherwise have relied on past aircraft experience and design to optimize coatings. As described in Part II these rigs were able to simulate the no load/full load type of LCF cycle but were not designed to reproduce a severe HCF cycle. If a simple bench test that reproduced the thermal gradients encountered in a diesel engine could be developed, then it could be used to evaluate a much greater number of coating systems than can be handled with current test engines.

Part IV. Materials Aspects of Current Thin Thermal Barrier Coatings (TBCs) for the Turbine Section of Aircraft Gas Turbine Engines

In this section, thin TBCs for the turbine section of aircraft gas turbine engines will be examined with emphasis on the history of their development and on certain aspects of their performance with emphasis on the materials science view point. Factors which have led to the selection of the current state-of-the-art zirconia-yttria/MCrAlY TBCs will be emphasized as will observations fundamentally related to the their behavior. Oxidation related TBC failure mechanisms and life prediction approaches for aircraft gas turbine engines will not be discussed since those topics are not directly relevant to diesel engines and they have been covered in detail elsewhere (e.g. references 1 and 35). The plasma spray process will not be discussed in detail either. Again several reviews are available on this topic (e.g., references 36, 37, and 38).

IV.A. The current state-of-the-art thin TBC

Current TBCs for the turbine section of gas turbine engines consist of a layer of ZrO_2-(6-8%)Y_2O_3 (by weight) ceramic over a layer of MCrAlY bond coat. Typical thicknesses for the ceramic and bond coat layers are 0.010 and 0.005 inch (0.025 and 0.012 cm.), respectively. The ceramic layer is applied by air plasma spraying which produces a porous and microcracked structure with a density of about 90% of the theoretical value and a phase composition that is predominantly a non-equilibrium, high-yttria tetragonal phase (T'). The 10% "porosity" in the ceramic lowers the thermal conductivity and the elastic modulus by factors that are much greater than predicted by a simple rule of mixtures. As a result the plasma sprayed ceramic layer is both strain tolerant and highly insulating. The effect that the non-equilibrium phase distribution has on coating system behavior is not well understood.

The MCrAlY bond coat is typically applied by low pressure plasma spraying which produces a dense structure that is free of internal oxidation. Coating systems that have low pressure plasma sprayed bond coats generally have greater cyclic lives at higher temperatures than systems with air plasma sprayed bond coats. Also, low pressure plasma sprayed bond coats are inherently more protective of the underlying substrate. There is no generally agreed upon composition of the MCrAlY bond coat. Typically chromium is in the range of 16 to 36% (by weight), aluminum is in the range of 5 to 12%, and yttrium is less than 1%. The balance "M" usually consists of nickel or nickel plus cobalt.

The evolution from early TBCs to the current standard thin TBC and fundamental observations regarding the performance of thin TBCs will be examined in the remainder of this part of the paper.

IV.B. Early ceramic coatings for aerospace applications

The first ceramic coatings for aerospace applications were frit enamels. The first of these frit coatings were developed by NACA and the NBS (refs. 39 and 40. Frit enamels found considerable use in aircraft engines throughout the 1950's (ref. 41). Later, flame sprayed ceramic coatings were developed (refs. 42-47). Of the various early ceramic materials that were evaluated for thermal barrier applications, alumina and zirconia-calcia evolved as the leading materials. The bond coat material for these early applications, if one was used at all, was typically nichrome or molybdenum for non-oxidizing environments. Early applications included the protection of sheet metal in jet engines and in rocket engine thrust chambers. The most visible coatings during this period were the flame sprayed zirconia-calcia coatings on the regeneratively cooled XLR99 thrust chambers for the X-15 experimental rocket planes (refs. 45 and 46). With the subsequent development of plasma spray processing -- which evolved from research into low thrust plasma arc engines for space craft and from plasma arc test facilities developed for reentry simulation (ref. 48) -- the utility of using the very high temperature plasmas for spraying ceramics was soon recognized (refs. 44, 47, 49, and 50). By 1964, plasma sprayed thermal barrier coatings were in use on the combustors in commercial gas turbine engines (ref. 51).

Alumina and zirconia-calcia did not prove to be a viable material for the more advanced thermal barrier applications. In the case of alumina this is primarily because its thermal conductivity is relatively high (ref. 52). Also, alumina forms non-equilibrium phases which are variously described as gamma, eta, or delta and these non-equilibrium phases shrink when they convert to the equilibrium alpha phase upon high temperature exposure. This shrinkage is expected to have a detrimental effect on coating life. The phase transformation to alpha alumina appears to become a factor above about 1100 °C (refs. 36, 42, 50, 53, 54, and 55). The problem with zirconia-calcia is related to "destabilization" from the cubic fluorite (F-ZrO_2) phase that is observed in the as-sprayed material to the monoclinic (M-ZrO_2) phase. Zirconia-based ceramics containing excessive amounts of this monoclinic phase are not usable as structural materials -- due to the shrinkage observed upon a rapid martensitic transformation from the low temperature monoclinic phase to the higher temperature tetragonal phase. Although the calcia is added to zirconia with the intent of extending the high temperature cubic phase field down to room temperature, it is now known that the cubic phase in zirconia-calcia is actually not stable below about 1140 °C (ref. 56). Therefore, even though the cubic phase is observed in the plasma sprayed material, diffusional rearrangement below 1140 °C can destabilize the material.

Magnesia stabilized zirconia (often called magnesium zirconate) has been widely used as a substitute for calcia stabilized zirconia. However, magnesia, like calcia, does not stabilize the F-ZrO_2 phase at low temperatures. According to the equilibrium phase diagram, this stabilization only occurs above about 1400 °C (ref. 56), and therefore diffusional rearrangement at temperatures below 1400 °C destabilize this material. The upper use temperature for zirconia-calcia or zirconia-magnesia will be related to the temperature above which cation diffusion becomes important in these materials. An apparently small but detectable decomposition to the monocolinic phase was observed after ZrO_2-MgO was heated for 40 days at 800 °C (ref. 57). Toriz et al. (ref. 58) gave 950 °C as the practical upper use temperature for zirconia magnesia in gas turbine applications, and a similar upper use temperature may apply for zirconia-calcia.

There are two other potential difficulties with zirconia-calcia and zirconia-magnesia. One problem with zirconia-magnesia and, certainly also with zirconia-calcia, is a sulfation reaction that occurs between the alkaline earth oxide and sulfur dioxide (refs. 59 and 60). This reaction -- which is analogous to the industrial use of limestone or dolemite scrubbers for the removal of sulfur dioxide from power plant exhausts -- converts the magnesia portion of the solid solution to magnesium sulfate. The effect of this sulfation reaction on coating behavior is uncertain. Another difficulty is the volatility of the alkali earth oxides -- especially magnesia -- at very high temperatures. This volativity could cause loss of the stabilizer upon plasma spraying (ref. 61) and could affect the performance of coatings subjected to surface temperatures of perhaps 1600 °C (ref. 62).

In summary, application processes for aerospace ceramic coatings evolved from frit enamels to flame spray and finally to plasma spray. During this time alumina and initially zirconia-calcia but later zirconia-magnesia were the ceramic materials most often used. However, alumina proved to be inadequate because of high thermal conductivity and questions about high temperature phase stability. Zirconia-calcia and zirconia-magnesia were found to have upper use temperatures of about 950 °C and were susceptible to sulfation reactions.

IV.C. Current zirconia-yttria/MCrAlY TBCs

IV.C.1 Zirconia-yttria thermal barrier coatings

The current era in thermal barrier coatings began in the mid 1970's with the development at NASA-Lewis of a two layer TBC consisting of a plasma sprayed zirconia-yttria ceramic over a plasma sprayed NiCrAlY bond coat (refs. 63, 64, 65) and the successful testing of this coating on the turbine blades in a research gas turbine engine (ref. 66).

There were three keys to the success of this new coating system. First, yttria was used to stabilize the zirconia. Second, the bond coat was an oxidation resistant NiCrAlY alloy of the type that was being developed for metallic overlay coatings. Finally, their approach employed only two layers -- the ceramic and the bond coat. The approach being taken at that time by Pratt & Whitney also involved zirconia-yttria and an MCrAlY. However their approach favored an intermediate region of mixed metal and ceramic to mitigate thermal expansion mismatch stresses (ref. 67). It was soon discovered that this graded expansion approach was inappropriate for temperatures high enough for oxidation to occur in the graded region (ref. 35). Later work places an upper limit of about 800 °C for the maximum temperature to which the graded region may be exposed (refs. 59 and 60). Union Carbide was another early developer of zirconia-yttria/MCrAlY TBCs (ref. 68).

The initial zirconia-yttria TBCs contained from 12 to 20% of yttria which was added to fully stabilize the cubic phase. Later, Stecura showed that better performance could be achieved by using only 6-8% yttria (ref. 69). The TBC literature, in general, now supports the view that zirconia-(6-8%)yttria is superior to zirconia-(12-20%)yttria for advanced gas turbine applications and that zirconia-yttria TBCs are in turn superior to zirconia-magnesia and zirconia-calcia (refs. 58-60, 70-72).

IV.C.2 Phase distributions in plasma sprayed zirconia-yttria

The predominant phase observed in plasma sprayed partially stabilized zirconia-yttria is a high yttria, non-equilibrium tetragonal phase (refs. 21, 22, 73-75). This phase was first observed by Scott (ref. 76) who showed that this non-equilibrium phase forms when partially stabilized zirconia-yttria is quenched from high temperature. This phase may be called "nontransformable" tetragonal, $T'-ZrO_2$. This distinguishes it from the low yttria tetragonal phase, $T-ZrO_2$, which is an equilibrium phase in partially stabilized zirconia between about 600 and 2000 °C. The term nontransformable refers to the fact that, in contrast to the low yttria $T-ZrO_2$ tetragonal phase, the $T'-ZrO_2$ phase does not undergo a martensitic transformation to the $M-ZrO_2$ monoclinic phase upon cooling. A version of the zirconia-yttria phase diagram from reference 76 -- taken from reference 21 -- is presented in figure 12. The bars near the bottom of this figure represent the phases having the lowest free energy for a diffusionless transformation, i.e. these are the phases encountered upon quenching. The arrows in the figure represent, schematically, the processes of plasma spraying and subsequent high temperature ageing. The "X" in the figure represents ZrO_2-8%Y_2O_3 (in weight percent) or ZrO_2-8.6%$YO_{1.5}$ (in mole per cent) that has been melted by the plasma. Quenching this composition, as indicated by the virtical line extending to room temperature, yields the nontransformable T' phase. It is believed that this phase forms because the process of quenching does not allow sufficient time for diffusional rearrangement to the lower free energy (i.e. equilibrium) combination of phases. These equilibrium phases are the $M-ZrO_2$ monoclinic and $F-ZrO_2$ cubic fluorite phases that are predicted by the phase diagram.

The $T'-ZrO_2$ phase that is predominant in the state-of-the-art zirconia-yttria thermal barrier coatings is, of course, inherently unstable. However, the high temperature transformations to the equilibrium phases are found to be sluggish. For example, for the particular batch of plasma sprayed ZrO_2-8%Y_2O_3 reported in reference 21, 10 hours at 1200 °C was an insufficient amount of time to produce a detectable decrease in the $T'-ZrO_2$ phase. However 100 hours at 1200 °C and only 1 hour at 1400 °C did produce a detectable change. (Tie lines drawn on figure 12 indicate the path of the 1400 °C decomposition.) In current aircraft gas turbine engines the temperatures at the interface, where stresses are maximum, remain well below 1200 °C even in hot streaks during the takeoff portion of the cycle. Also, the total accumulated time that a component spends at the maximum temperature is relatively short. Therefore, decomposition of the T'-ZrO_2 phase to the equilibrium M-ZrO_2 and F-ZrO_2 phases is not expected to be important near the interface region of current TBCs in current engines. Transformations near the higher temperature surface of these coatings does appear to be possible. However, at the present time there are no known adverse effects of transformations near the surface.

Powder preparation method and plasma spray processing parameters are two factors which strongly affect the microstructures, phase distributions, thermophysical properties, and thermomechanical properties of thermal barrier coatings. As a result the performance of two nominally identical coatings may vary widely. In theory this variability could be beneficial if coating engineers fully understood how to vary starting powders and processing parameters to produce coatings tailored for a specific need. Unfortunately, the technology is still in a rather chaotic state where no two coatings from any two sources can be counted on to give comparable performance.

It is interesting to compare the nontransformable T'-ZrO_2 phase that forms in plasma sprayed, partially stabilized zirconia-yttria to the metastable T-ZrO_2 phase that forms in yttria-stabilized tetragonal polycrystals -- Y-TZP (ref. 77). Y-TZP is a fine grained material containing greater than about 2% and less than 4 or 5% yttria that has been processed to form a metastable T-ZrO_2 phase. This metastable phase can undergo a stress-induced martensitic transformation to the M-ZrO_2 phase which imparts a high fracture toughness on Y-TZP via the transformation toughening mechanism. The fracture toughness is generally observed to fall off rapidly with increasing yttria as the T'-ZrO_2 phase begins to replace the T-ZrO_2 phase (refs. 78 and 79). An exception is the zirconia-yttria material described by Lange (ref. 80) which retained low yttria, metastable T-ZrO_2 precipitates in a cubic matrix throughout the entire partially stabilized range. The gradual fall off of the measured fracture toughness values with increasing yttria content can be taken as evidence that metastable T-ZrO_2 precipitates had formed rather than the higher yttria, nontransformable T'-ZrO_2. In Lange's material, the metastable tetragonal zirconia phase was retained at higher yttria compositions by processing so as to produce fine grain size and high density.

The transformation toughening mechanism does not appear to play a role plasma sprayed ZrO_2-(6-8%)Y_2O_3 -- i.e., the predominant T'-ZrO2 phase cannot transform martensitically at temperature too low for diffusional rearrangement and there is no evidence that metastable T-ZrO_2 is present. The fracture toughness values for this material are low (refs. 81 and 82) and the force of grinding does not cause an increase in the amount of the M-ZrO_2 phase (ref. 21). Also, plasma sprayed materials do not have the high density needed to retain the metastable T-ZrO_2 phase in the partially stabilized range -- even though the grain size is fine (ref. 83). However, there is evidence that the metastable T-ZrO_2 is present in plasma sprayed ZrO_2-4%Y_2O_3. This is because the amount of M-ZrO_2 increases by a factor of two when that material is ground. A similar increase in the amount of the monoclinic phase also occurs upon ageing this material for two years at room temperature (ref. 22). (Decomposition of metastable T-ZrO_2 to M-ZrO_2 is now know to occur when the Y-TZP material is aged at temperatures as low as 100 °C in the presence of water or water vapor (ref. 84)). When ZrO_2-4%Y_2O_3 is sprayed as a thermal barrier coating and subject to thermal cycling it performs rather well but is apparently mechanically unstable since it gradually crumbles to powder (ref. 69). It is not clear what role possible compositional inhomogenaities may have played in this mechanical instability.

IV.C.3 Effects of impurities in plasma sprayed zirconia-yttria

Most impurities in typical lots of zirconia-yttria plasma spray powder are low level with few apparent effects -- the most obvious of which is a yellowing of the color of the ceramic. On the other hand, hafnia and silica may be present in zirconia-yttria plasma spray powders in amounts up to about 2% (by weight). The effects of a few percent of hafnia are generally considered minor because hafnia and zirconia are chemically very similar (although in certain nuclear applications it is desirable to remove the hafnia component due to its higher neutron cross section; also, pure hafnia has a higher M_s temperature than pure zirconia). The silica impurity, on the other hand, may strongly affect coating behavior. The typical level of silica in the zirconia-yttria compositions reported by Stecura, e.g., in reference 69, was below 0.2%. When a sample of zirconia-yttria powder that had been prepared to Stecura's specifications was analyzed using x-ray photoelectron spectroscopy (XPS), a considerable amount of silicon was detected on the surface. In fact, the estimated percentage of silicon atoms in at least the outer 20 A of the powder particles was about two-thirds as large as the sum of the percentages of zirconia plus yttria (Informal report from M.V. Zeller of NASA-Lewis Research Center to R.A. Miller, 1988). This implies that a low melting silica-rich compound such as zircon may be present on the surface of these plasma spray powders. In another study, XPS was used to show that a sodium-yttria-silicon oxide was present on the surface of a zirconia-yttria powder (ref. 85).

When that powder was fabricated and evaluated as an electrical ceramic, anomalous electrical and grain growth behavior was observed. The silica rich phase was offered as an explanation for this anomalous behavior. Hoel and Kvernes (ref. 83) have used TEM with EDX-spectroscopy to study thin foils of plasma sprayed zirconia-yttria. They observed, by employing techniques involving "careful tilting and diffuse dark-field imaging," a silica-rich glassy phase concentrated at the grain boundaries. TEM observations of silica-rich intergranular phases have also been observed in certain monolithic zirconia-yttria ceramics (e.g., references 86 and 87). It is believed that these silica-rich layers may affect high temperature creep properties, sintering rates, grain growth, and possibly the T'to M plus F transformation. Additionally, United Technologies (Private Communication, R.C. Novak, United Technologies Research Center, 1989) has observed a direct relationship between sintering rate and silica level in plasma sprayed zirconia-yttria.

IV.C.4 Bond coat development

The composition of bond coats for aircraft TBC applications has generally followed the development of oxidation resistant overlay coatings. The early compositions were materials such as NiCr and NiAl. Stecura (ref. 63) was the first to report the use of a MCrAlY coating. Examples of bond coat compositions in use today for higher temperature applications include Ni-22%Co-18%Cr-12%Al-0.4%Y which is the bill-of-material bond coat at Pratt & Whitney (ref. 88) and Ni-22%Cr-10%Al-0.3%Y which is bill-of-material at General Electric (ref. 89). Stecura (ref. 90) achieved the best TBC performance in furnace tests using Ni-36%Cr-6%Al-1%Y.

The bond coats initially reported by Stecura and others were prepared by air plasma spraying. However, low pressure plasma spraying is now considered the state-of-the-art for the more advanced applications (ref. 35) where bond coat temperatures may exceed about 1000 °C. Other approaches which have not yet been fully evaluated include shrouded spraying (ref. 81) and various types of flame spraying including the new high velocity torches.

There are also many materials besides NiCrAlY and NiCoCrAlY that are available for use as bond coats. For example Stecura (ref. 91) has reported that FeCrAlY bond coats are the best performers on iron-based superalloys. For relatively low temperature operation (even in oxidizing conditions such as encountered in diesel engine operation) a wide number of bond coats may be considered. These may include for example stainless steel or any of various mechanically alloyed bond coat materials such as NiAl which is so adherent even to a relatively smooth substrates that it is called "self-bonding".

IV.D. Other zirconia-based TBCs

Other zirconia-based thermal barrier coatings that have been reported in the recent literature are zirconia-ceria (refs. 82, 92-94), zirconia-yttria-ceria (ref. 95), and zirconia-ytterbia (ref. 96). The ceria-based ceramics are believed to be more resistant to hot corrosion than zirconia-yttria (refs. 92 and 93). The levels of ceria in those ceramics tends to be greater than 15% (by weight), i.e., 20 mol% -- which is the amount of ceria needed to place the material in the tetragonal plus cubic region of the equilibrium zirconia-ceria phase diagram (ref. 97).

For somewhat lower levels of yttria there is a discrepancy between the phase diagram and recent experimental observations. That is, according to the phase diagram only the tetragonal phase should be stable between about 10 and 14% (by weight), i.e. 14 to 18 mol%. However, plasma sprayed ZrO_2.10%CeO_2 contains 8% of the M-ZrO_2 phase while ZrO_2-15%CeO_2 contains 23% M-ZrO_2 Furthermore both of these compositions exhibit transformation toughening (ref. 82). Those observations and other fracture toughness measurements on monolithic zirconia-ceria (ref. 98) indicate that M-ZrO_2 is the room temperature equilibrium phase even in the 14 to 18% ceria range. Also, it should be noted that the behavior of plasma sprayed ZrO_2-(10-15%)CeO_2 appears to be similar to the behavior discussed earlier for plasma sprayed ZrO_2-4%Y_2O_3 -- a material which is in or near the Y-TZP range.

Zirconia-ytterbia thermal barrier coatings have performed well in furnace tests. The optimum composition of those tested was 12% (by weight), i.e. 4 mol% (ref. 96). This composition appears to be in the same position relative to the equilibrium phase diagram (ref. 56) as zirconia-yttria in the 6 to 8% range.

IV.F. Bonding of zirconia to MCrAlY or alumina

Plasma sprayed zirconia adheres to the underlying bond coat with a strength that is comparable to the tensile strength of the plasma sprayed zirconia. This value has been variously measured to be in the 6-36 MPa (1000-5000 psi) range (refs. 70, 99-101). The detailed mechanism of this adherence and the detailed effect of MCrAlY oxidation on adherence are not well understood. Inspection by transmission electron microscopy of the interface between intragranular alumina and zirconia particles in zirconia toughened alumina has revealed certain aspects of the zirconia to alumina bond (refs. 102 and 103) That is, the interface appeared to be sharp with no discernible interaction zone, although in some locations faceted particles were noted at the interface indicating a low energy interface. In most locations the particles were spherical with ledge-like or misfit dislocation-like structures. Molecular orbital calculations such as those reported for alumina-metal interfaces (refs. 33 and 34) have not yet been reported for zirconia-alumina or zirconia-MCrAlY interfaces.

IV.G. Brief overview of the mechanical behavior of zirconia-yttria

Plasma sprayed zirconia-yttria is a material with very interesting mechanical properties (refs. 81, 88, and 89). The stress-strain curve as measured in uniaxial tension is nonlinear with the modulus decreasing with increasing load. The compressive strength is more than an order of magnitude greater than the tensile strength. Strain to failure in compression as large as -4% have been measured at 1200 °C. Creep like behavior is observed at temperatures below half of the melting point (refs. 88 and 104). It is possible that the very high strain tolerance and and creep observed at higher temperature are a function of splat sliding which may in turn be controlled by low melting phases at the splat boundaries. This low temperature phase may involve the silica impurity in zirconia (ref. 83). As noted earlier, silica impurities may also strongly affect sintering rates.

Part V. Prioritized List of Fundamental Materials Research Needs

The list of areas where our understanding of the fundamentals of the behavior of TTBCs in diesel engines is formidable. (For gas turbine engines the list is even greater since temperatures are higher.) Due to competitive, time, and financial pressures the immediate interests of diesel engine companies tends towards the more applied problems. Similar pressures are encountered at gas turbine companies, coating companies, as well as research institutions. As a result, most fundamental needs remain unmet. While the HDTT and Army funded programs help to meet the more pressing applied needs of the diesel engine companies, there are numerous areas where fundamental research would compliment and potentially greatly benefit the more applied research programs.

It is instructive to review the immediate technical barriers identified by the HDTT program. These include:

1) improving design tools,
2) improving understanding of failure mechanisms,
3) improving materials characterization approaches,

4) investigating variations in properties across the piston head,
5) developing the capability for near-net-shape plasma spraying,
6) developing seal coatings, and
7) developing one-sided NDE techniques for inspection of coated components.

Most of these items will be addressed in future HDTT programs. Several of the items in the above list have fundamental aspects -- especially those items involving failure mechanisms and properties characterization. Thus, the remainder of Part IV will be devoted to identifying those areas where fundamental research would complement the ongoing applied research and which would provide the insights needed to help properly pursue future developments in this area. Recommendations will be divided into two broad classes. Those with near-term relevance to diesel engine TTBC development will be referred to as "Fundamental/Problem-Solving Recommendations." Those with perhaps more far-reaching but less near-term relevance will be referred to as "Fundamental/Basic Recommendations."

V.A Fundamental/Problem-Solving Recommendations

Recommendation A1. Development of Bench Screening Tests which Duplicate the Thermal Gradients and Cyclic Stresses Encountered in the Engine

Only a few types of coating systems have been evaluated in the diesel engine under the current design-oriented programs. There is a need to develop the capability to inexpensively evaluate a wider range of options, to develop statistically significant life data, and to conduct critical experiments designed to elucidate failure mechanisms (to be discussed in Recommendation II). The aircraft industry relies heavily on relatively simple laboratory burner rigs for screening, life data collection, and mechanistic studies. These rigs duplicate the high temperature exposure and the cyclic thermal expansion mismatch stresses experienced in the engine. They do not fully duplicate the severity of the heating transients but they are believed to be secondary in importance. As a result these rigs are known to rank coating performance in the same order as in the engine. In the author's opinion. the diesel industry needs a comparable rig to allow low cost simulation of the diesel engine cyclic environment. Current Caterpillar/ Solar and UTRC rigs have been used to a limited extent to screen coatings. These rigs are useful for low cycle thermal fatigue testing and they would probably work very well for screening out the worst of any new coating concepts. However, they do not duplicate the high cycle fatigue component of the diesel engine cycle. If the high cycle fatigue component proves to be important these existing rigs may not be adequate to accomplish the goals outlined above.

Therefore the first recommendation is that an effort be initiated to design and construct a laboratory test rig capable of reproducing the cyclic temperature swings and thermal stresses encountered in the diesel engine (as depicted in figures 5 to 7). This rig may involve rotating carousel (or rotating disk) similar to the rigs mentioned above but with a higher heat flux input combined with front side cooling to create the HCF type of cycle. Alternatively, the rig could involve intermittent combustion such as occurs in a D-gun (ref. 105) or a pulsejet combustor (ref. 106), or it could involve a mechanical HCF load superimposed on thermal LCF loads. Once completed, this rig could be used to evaluate a wide variety of coatings. Items to investigate include variations in processing parameters and properties, variations in starting powders, low cost bond coats, the effect of yttria level, lot-to-lot variability, and the effect of sealing. Specimens which perform well in this rig could then be engine tested under the more applied programs. The rig could also be used for basic mechanism studies, as will be discussed in the next recommendation.

It should be mentioned that rig tests are being recommended primarily so that coating designers would have the opportunity to evaluate many more coating systems then can be accommodated by engine testing. However, rig testing would only supplement and not replace engine testing. The performance of coatings in the engine still must be the final arbitrator for evaluating new materials and new designs. Also, the current trend of attempting to minimize the need for the trial and error "Edisonian" approach by relying more heavily on analytical design should continue. Still, the experience of the gas turbine industry has demonstrated the value of screening a wide variety of coating systems. This experience has shown that stress analysis cannot be used reliably to predict the behavior of new coating systems and that rigs may be used to elucidate failure mechanisms and to collect life data that can be fed into life prediction models.

Recommendation A2. Investigations of the Conditions Leading to LCF and HCF Coating System Failures

There is no general agreement as to the relative importance of failure modes due to low cycle fatigue (LCF) and high cycle fatigue (HCF). With the LCF mode, the relative importance of frequent no load/full load transients versus fewer but more severe stop/start transients needs to be quantified. With the HCF mode, the relative importance of thermal stress (due to surface temperature swings) versus bending stress (due to deflections of the pistons) needs to be quantified. An understanding of the conditions favoring failure by one mode versus failure by the other is needed to guide future design and to enable the development of a life prediction methodology.

Therefore the second recommendation is that an effort be initiated to determine which factors can shift failure from the LCF mode to the HCF mode. This study would require a rig -- such as the one suggested in Recommendation A1 -- that could produce severe LCF and HCF transients, and the use of this rig to independently vary the relative amplitude of the LCF and HCF cycles. The study should also include mechanical fatigue tests capable of producing HCF and possibly LCF by purely mechanical means. The mechanical HCF tests would help to determine the relative importance of the thermal and mechanical components to HCF failure. Mechanical tests would also be available for generating S-N plots, Goodman diagrams, and to search for the existence of an endurance limit. Materials factors to vary include coating layer thicknesses, substrate temperature, coating chemistry (especially 8% vs. 20% yttria), coating strength, coating pre-stress, specimen geometry (flat vs. concave vs. convex), sealing of the surface, and surface contamination.

Recommendation A3. Properties Tailoring, Characterization, and Degradation

The plasma spray process can be manipulated to produce a wide variety of microstructures. It should be possible to use this processing flexibility to tailor microstructures and properties to meet the needs of engine designers. While a detailed study to learn how to tailor coatings would be extremely useful, support for this type of work is not generally available.

Therefore, the third recommendation is that a thorough study be conducted to learn how to manipulate properties by means of plasma spray processing variations. This study would include an investigation of the best ways to measure each property, a statistically significant number of measurements including several lots of powder to yield lot-to-lot variability, finite element sensitivity analysis to determine which properties are most important, and a correlation between NDE measurements and properties. The effect of the engine environment, cyclic stress, contaminants and surface treatments on properties should also be investigated. The value of such a study to the general thermal barrier coatings community would be enhanced if properties were also collected at temperatures above those expected in the diesel engine. Such information would then be of value to the gas turbine community.

Properties to consider would include deposition efficiency, porosity, phase distributions, thermal conductivity, and failure strains, strengths, and moduli. The study should also consider non-linear stress strain response and property anisotropy.

V.B Fundamental/Basic Recommendations

Recommendation B1. Mapping the effects of time and temperature on phase transformations, microstructure, sintering, and selected thermomechanical and thermophysical properties

Thermal barrier coatings in diesel and other heat engines are subject to high temperatures and high cyclic strains in oxidizing or corrosive environments. These conditions may combine to degrade the microstructure, phase distributions, and properties of zirconia-yttria thermal barrier coatings. A basic understanding of the kinetics (and in certain instances the thermodynamics) of these time/temperature/cycle dependent processes is needed to help guide the design of future coating systems. While certain aspects of this topic have been reported previously, no studies to date have thoroughly characterized all of the important degradative processes that can occur. Unfortunately, this is a very difficult task. One major difficulty is that there is no standard thermal barrier coating. That is, both intentional and happenstance variability in starting powders, process parameters, etc. causes coatings which may be nominally identical to vary widely in properties and performance. Therefore the results of even the most thorough study on any one coating system cannot be assumed to apply to any other coating system. Since, the cost in time and money of a thorough study on a large number of coatings would be prohibitive, it would be necessary to compromise and limit the scope of such a study.

Therefore, the recommendation is to select a limited number of plasma sprayed ceramic coating materials and a limited number of spray parameter sets (perhaps three widely differing starting powders and two sets of parameters for each) and to conduct a detailed investigation of the effect of time and temperature on a wide variety of properties. These properties may include qualitative features of the microstructure, phase distributions (especially the percentage of the monoclinic phase), porosity (sintering rate), thermal conductivity, strength, strain tolerance, modulus (actually secant modulus if nonlinear effects are to be ignored. Temperatures should be extended to above those involved in diesel engine operation under the assumption that mathematical relationships could be developed to allow an exchange between time and temperature (e.g., a Larsen-Miller approach). Since it would be desirable to multiply replicate all measurements, the amount of effort required would be great for even a modest study. Also, while this recommendation overlaps those made in Recommendation A3, that recommendation was aimed at providing information for the design engineer while Recommendation B1 is aimed at providing basic materials science knowledge.

Recommendation B2. Investigation of the role of silica impurities on microstructure, high temperature strain tolerance, creep rate, sintering, and phase transformations

As discussed in Part IV, silica impurities may play an important role in the microstructural development of plasma sprayed zirconia-yttria which in turn may affect the T'-ZrO_2 to M-ZrO_2 plus F-ZrO_2 phase transformation. Also, the presence of silica at grain or splat boundaries could strongly affect high temperature properties such as sintering rates, creep rates, and strain tolerances (where values up to 4% have been measured at 1200 °C in uniaxial compression). Silica on the surface of plasma spray particles could also affect plasma spray deposition rates.

Thus, it is recommended that a detailed study be conducted on the effect of silica impurities on the properties mentioned above and that emphasis be given to the measurement of thermomechanical properties at high temperatures, sintering rates, and any effect on phase transformations. Such a study should involve plasma sprayed ceramic materials having at least three levels of silica -- from very low to high -- in otherwise identical zirconia-yttria spray powder, and at least two different sets of plasma spray parameters. Also, analytical techniques such as TEM or XPS should be incorporated in such a study and used to determine the "micro-distribution" of the silica-rich phases in the starting powder and in the plasma sprayed ceramic material.

Recommendation B3. Residual stress measurement

Residual stress plays a very important role in the TBC behavior and techniques are needed for measurement of these stresses both in the as-sprayed coating systems and in coatings that have been subject to high temperature cyclic exposure.

It is recommended that a variety of approaches be evaluated for measuring the residual stresses present in the ceramic at room temperature due to the constraints imposed by the substrate and that the results from the various techniques compared against each other. The study should also include a detailed investigation on the effect of processing conditions and high temperature exposure on residual stress state, and it should include finite element modeling of residual stress. Processing properties to vary could include substrate temperature, ceramic temperature, thickness per pass, and traverse speed. Measurement of the microstressses present in the ceramic splats as a result of the plasma spraying should also be considered.

Recommendation B4. Basic molecular orbital theory analysis of zirconia to NiCrAlY and alumina bonding

Very little is known about the detailed mechanism of bonding of plasma sprayed zirconia to the underlying metallic bond coat and of the bonding of zirconia to the layer of alumina or other oxides which may form on the surface of the NiCrAlY. Such knowledge would have low short term value and has therefore never received support even though the cost of such a study should be modest. However, there are potential long term benefits since understanding in this area would help to influence future coating system concepts.

Therefore the fourth recommendation is that molecular orbital theory be employed to investigate the detailed mechanisms of the bonding of zirconia to both the oxidized and unoxidized bond coat be supported.

Concluding Remarks

Fundamental research into thermal barrier coatings has historically received only modest support. Now that thermal barrier coatings are becoming accepted by designers, the gaps in our knowledge are threatening to impede further development.

Many opportunities for fundamental research in thick thermal barrier coatings for diesel engines have been identified and cataloged in Part III of this paper. Most of these areas have direct and near term relevance to the ongoing TTBC development programs which are discussed in Part II. A brief discussion of the factors which have lead to current state-of-the-art thin thermal barrier coatings for aircraft applications and certain aspects of the materials science of these coatings are discussed in Part IV. Recommendations for future fundamental research are given in Part V. The three recommendations in Part V.A were selected for their relatively near term relevance to problems encountered while developing coatings for diesel engine applications. The recommendations in Part V.B are more basic and are believed to have significant long term value. Both sections include topics that have in general been neglected in the past. Additional materials based research into these topics, into other topics from Part III, and into still others that the reader may wish to include will begin to fill many of the gaps in our knowledge. This research will also ensure that future decisions regarding the viability of thick thermal barrier coatings for diesel engines are made from an adequate experience base.

APPENDIX I. AREAS WHERE THE TECHNOLOGY OF THICK TBCs FOR DIESEL ENGINES MAY BENEFIT FROM FUNDAMENTAL RESEARCH

A. FUNDAMENTAL KNOWLEDGE NEEDED TO OPTIMIZED ZIRCONIA TTBCs

1. EFFECT OF POWDER PREPARATION METHOD, CHEMISTRY, MANUFACTURER, AND LOT ON PROPERTIES AND ON PERFORMANCE
   a. TYPES OF POWDERS INCLUDE FUSED AND CRUSHED, SINTERED, SOL GEL, SPRAY DRIED, AND HOSP

2. EFFECT OF PLASMA SPRAY PROCESSING, MICROSTRUCTURE, AND PHASE DISTRIBUTION ON THERMOPHYSICAL AND THERMOMECHANICAL PROPERTIES AND ON PERFORMANCE

3. OPTIMUM ZIRCONIA COMPOSITION FOR THICK TBCs
   a. CANDIDATES INCLUDE ZrO_2 - 8%Y_2O_3, ZrO_2 - 20%Y_2O_3, ZrO_2-CeO-Y_2O_3 AND, ZrO_2-MgO
   b. OTHERS?

4. EFFECT OF SCALING UP FROM COUPONS TO COMPONENTS ON PROPERTIES AND PERFORMANCE

B. EFFECT OF ENVIRONMENT AND STRESS STATE ON PROPERTIES AND PERFORMANCE

1. EFFECTS OF CYCLING
   a. TRANSIENTS ENCOUNTERED IN THE ENGINE
      i. STOP/START TRANSIENTS
      ii. NO LOAD/FULL LOAD TRANSIENTS
      iii. IGNITION TRANSIENTS
   b. FATIGUE
      i. LOW CYCLE VS. HIGH CYCLE
      ii. THERMAL VS. MECHANICAL
      iii. POSSIBLE ENDURANCE LIMIT
   c. FACTORS WHICH MAY EFFECT THE RESPONSE TO TRANSIENTS
      i. EDGES AND CORNERS
      ii. HOT STREAKS
   d. CRACK GROWTH
      i. MUDFLAT CRACKING
      ii. MICROCRACK LINK UP

2. DEPOSIT RELATED EFFECTS
   a. POSSIBLE STABILIZATION OR DESTABILIZATION FROM DEPOSITS
   b. MECHANICAL DAMAGE FROM DEPOSITS AT LOAD POINTS
   c. EFFECT ON HCF
   d. EFFECT OF EMISIVITY CHANGES ON HEAT TRANSFER

3. TIME AT TEMPERATURE RELATED EFFECTS
   a. OXIDATION
   b. PHASE TRANSFORMATIONS
   c. SINTERING
   d. CERAMIC CREEP

4. EROSION AND FOREIGN OBJECT DAMAGE
    a. DAMAGE TO THE CERAMIC
    b. DAMAGE CAUSED BY THE CERAMIC

C. THERMOPHYSICAL AND THERMOMECHANICAL PROPERTIES MEASUREMENT

1. THERMOMECHANICAL PROPERTIES
    a. DEFINITION OF APPROPRIATE PROPERTIES
        i. COMPRESSIVE UTS, YIELD STRENGTH, CREEP, MODULUS
        ii. TENSILE
        iii. FATIGUE
        iv. FOUR POINT BEND STRENGTHS AND FATIGUE VS. UNIAXIAL
        v. BOND STRENGTH
        vi. FRACTURE TOUGHNESS
        vii. PROPERTY ANISOTROPY
        viii. OTHERS?

    b. BEST SPECIMEN CONFIGURATION FOR EACH MEASUREMENT

2. THERMAL CONDUCTIVITY MEASUREMENT
    a. BEST APPROACH
        i. FLASH DIFFUSIVITY, THERMAL WAVE, CUT BAR, RADIAL
        ii. OTHERS?

3. NDE AND METROLOGY
    a. DENSITY, PROPERTIES AND/OR FLAW SENSITIVE TECHNIQUES
        i. ULTRASOUND, X-RAY, GAMMA RAY
        ii. OTHERS?

    b. THICKNESS MEASUREMENT
        i. SUITABLE FOR POST TEST INSPECTION
        ii. SUITABLE FOR ON-LINE NON-CONTACT

4. RESIDUAL STRESS MEASUREMENT
    a. X-RAY
    b. STRAIN GAGE

5. PERMEABILITY
    a. SEALING
    b. OXYGEN CONDUCTION

D. LOWER COST TTBCs

1. HIGH DEPOSITION EFFICIENCY SPRAYING

2. LOWER COST ALTERNATE CERAMICS
    a. eg $CaTiO_3$, $CaSiO_4$, $ZrSiO_4$
    b. PERFORMANCE/PROPERTIES CHARACTERIZATION WOULD BE NEEDED

3. LOWER COST AND LOWER CTE ALTERNATIVE BOND COATS
    a. STAINLESS STEEL?

E. ALTERNATIVE APPROACHES

1. ENHANCED BONDING/INTERFACIAL STRAIN ACCOMMODATION
   a. ALTERNATIVES TO MIXED CERAMIC/METAL INTERMEDIATE LAYERS
      i. IMPROVED CHEMICAL BONDING
      ii. INCREASED ROUGHNESS
      iii. RESIDUAL STRESS MANAGEMENT

   b. STRAIN ISOLATOR PADS

2. ALTERNATIVE PROCESSING
   a. ROCKIDE OR OTHER FLAME SPRAYING, PVD, SPUTTERING, SLURRY, SOL GEL
   b. FIBER TOUGHENING
   c. LPPS BOND COATS, SHROUDED BOND COATS

F. DEVELOPMENT OF MEANINGFUL BENCH TESTS

1. SIMPLIFICATION OF SINGLE CYLINDER ENGINE TESTS
2. DEVELOPMENT OF RIGS ABLE TO SIMULATE COMPONENT THERMAL STRESS

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TABLE 1. - SELECTED PROPERTIES FOR CATERPILLAR AND CUMMINS/UTRC TTBCs

	K(W/M-°C)	α(μm/M-°C)	E(GPa)	Tensile bend strength, MPa[a]	Compressive strength, MPa[a]	Tensile failure strain[a]	Compressive failure strain,[a] %
Caterpillar:							
NiCrAlY	----	12.0	61	380	----	0.75	----
50% ZrO_2-Y_2O_3/ 50% NiCrAlY	3.25	9.3	49	150	----	.45	----
75% ZrO_2-Y_2O_3/ 25% NiCrAlY	1.95	8.8	43	80	----	.35	----
ZrO_2-8%Y_2O_3	.94	7.7	44	50	600	.15	-1.3
Cummins/UTRC:							
NiCraAl	3.7	13.8	105	252	1048	----	----
40% ZrO_2-Y_2O_3/ 60% CoCrAlY	2.0	12.6	66	140	748	----	----
85% ZrO_2-Y_2O_3/ 15% CoCrAlY	1.0	10.3	51	47	437	----	----
ZrO_2-20%Y_2O_3	.5	9.0	37	40	390	----	----

[a]Measured in bending at 400 °C.

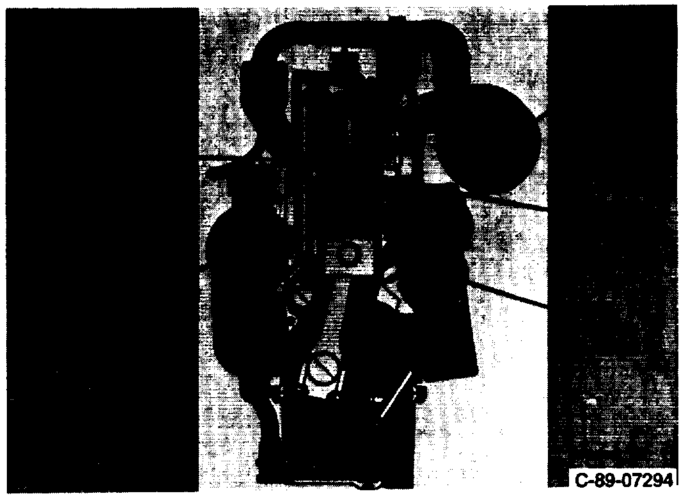
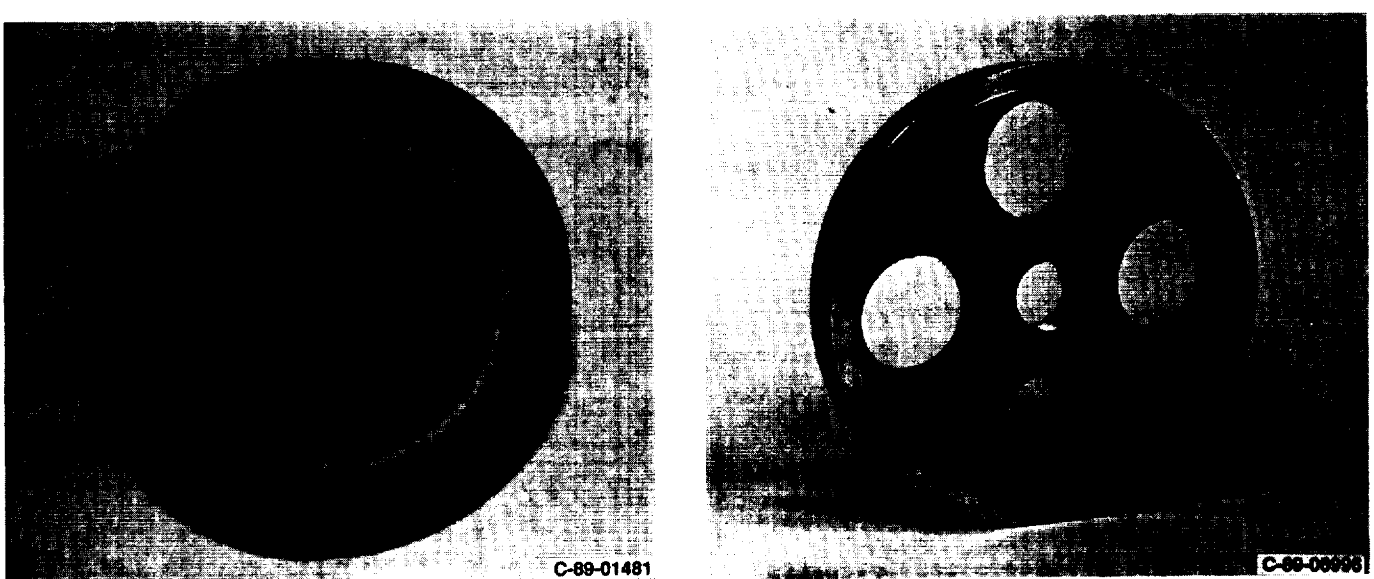


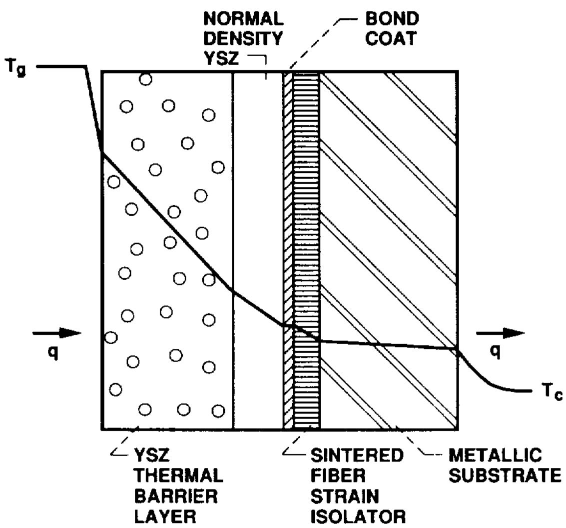
Figure 1. - Schematic of the low heat rejection diesel engine showing key problem areas (ref. 8).



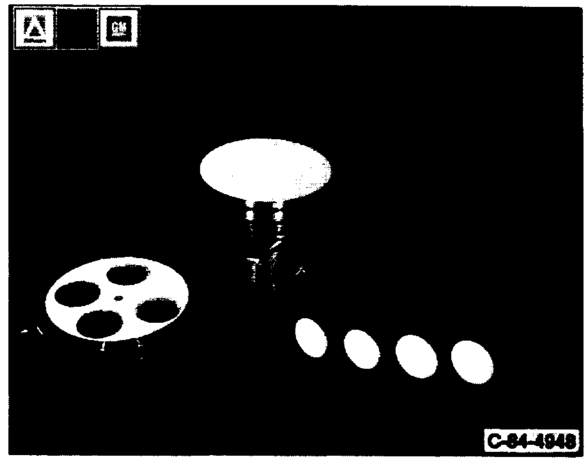
(a) Piston cap.

(b) Cylinder head (before final grinding of valve seats).

Figure 2. - TTBC coated Caterpillar Inc. research engine.



(a) Schematic of the coating system.



(b) Coated piston, cylinder head, and valves before engine testing.

Figure 3. - Strain isolator based TTBC developed by Allison under HDTT.

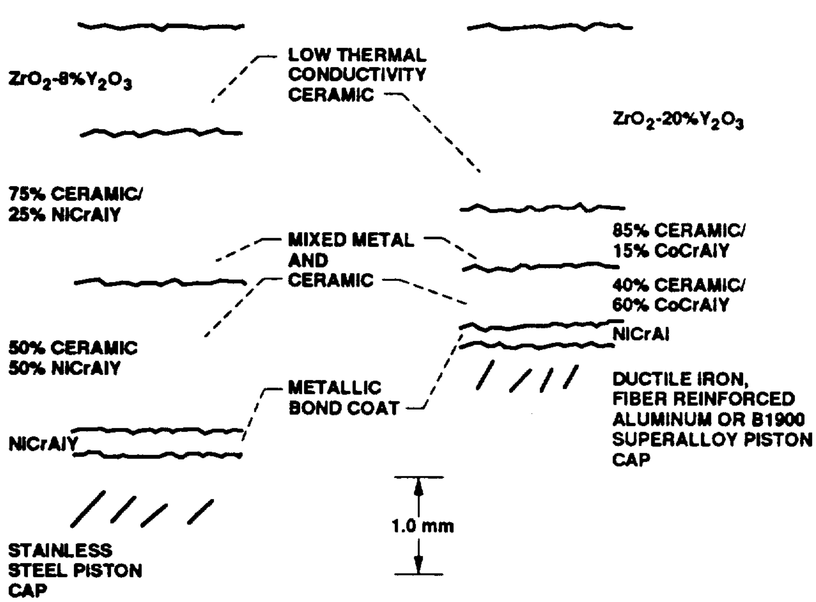


Figure 4. - Schematic of Caterpillar and Cummins/UTRC TTBC designs developed under HDTT.

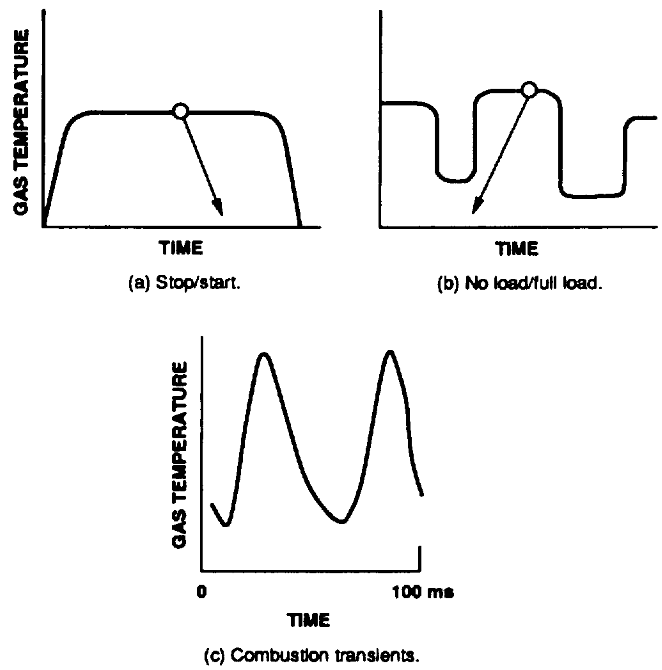


Figure 5. - Schematic of cyclic environment in truck diesel engines.

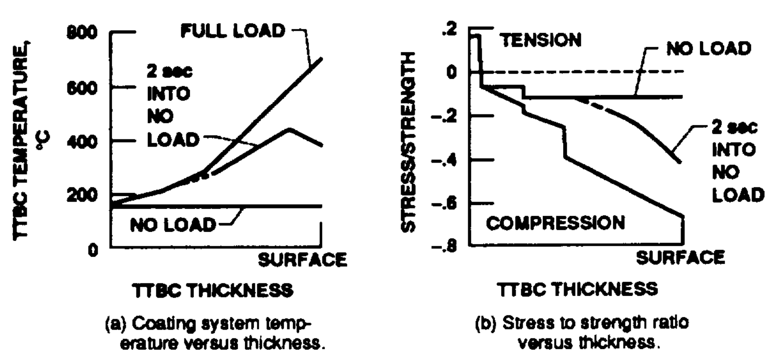


Figure 6. - Schematic of temperatures and stress states across the coating system for full load, two seconds into no load, and no load conditions (refs. 7 and 10).

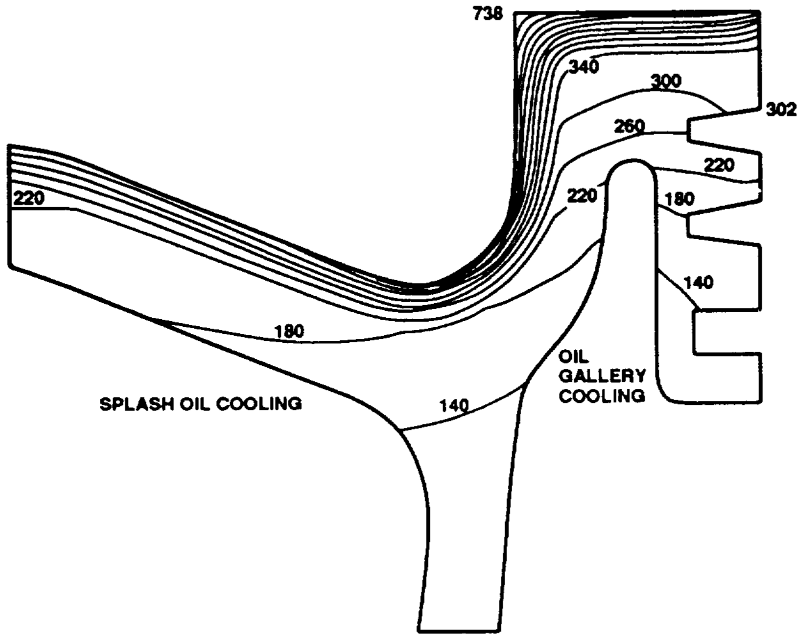
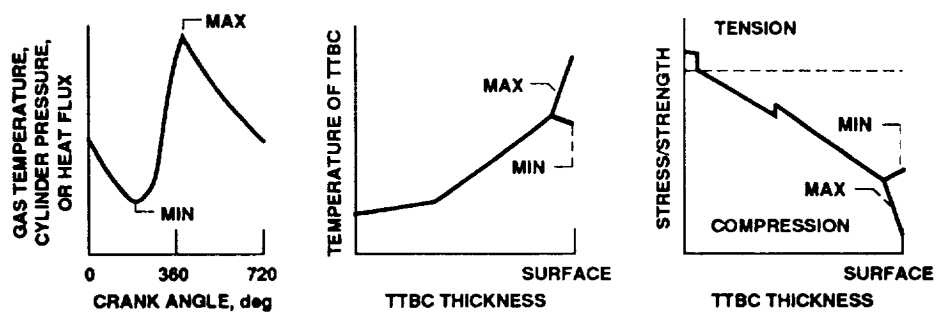


Figure 7. - Mean temperature contours calculated for a LHR piston assuming gas temperature of 756 °C and heat flux of 2080 watts.



(a) Gas temperature, cylinder pressure, or heat flux.

(b) Coating system temperature versus thickness.

(c) Stress versus thickness.

Figure 8. - Schematic of the effect of combustion transients.

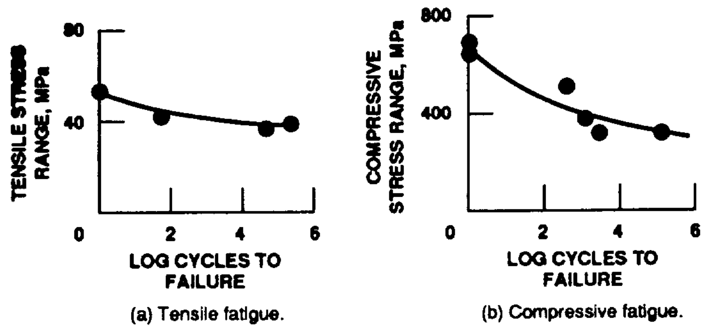


Figure 9. - Example of high cycle fatigue results for the Caterpillar ceramic (refs. 12 and 13).

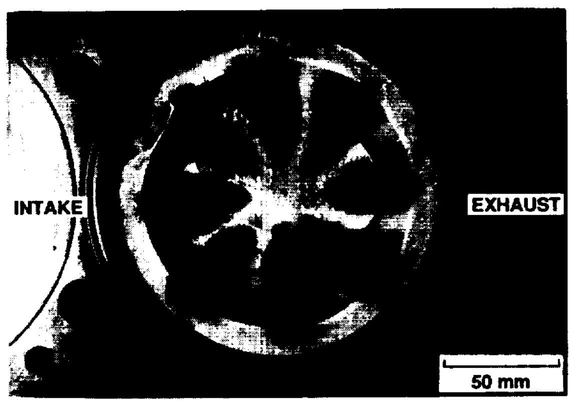


Figure 10. - Example of a coating system failure in an engine test (refs. 14 and 15).

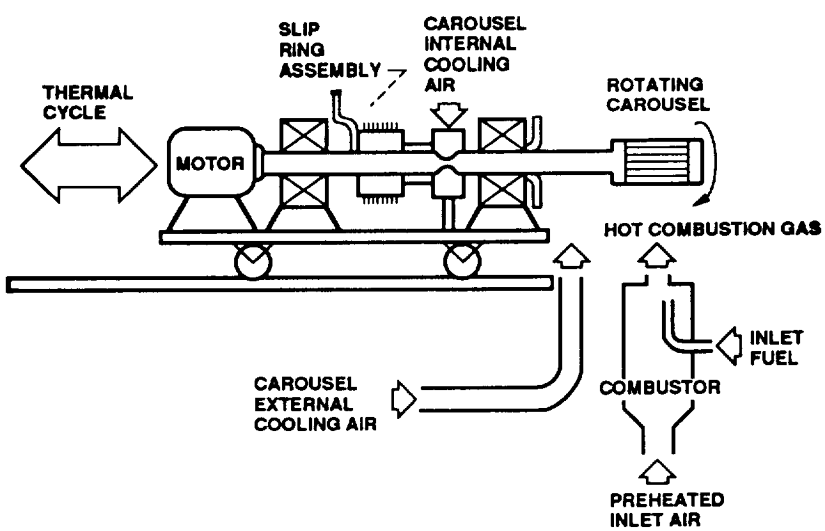


Figure 11. - Bench rig used by Caterpillar/Solar to simulate thermal shock exposure (refs. 12 and 13).

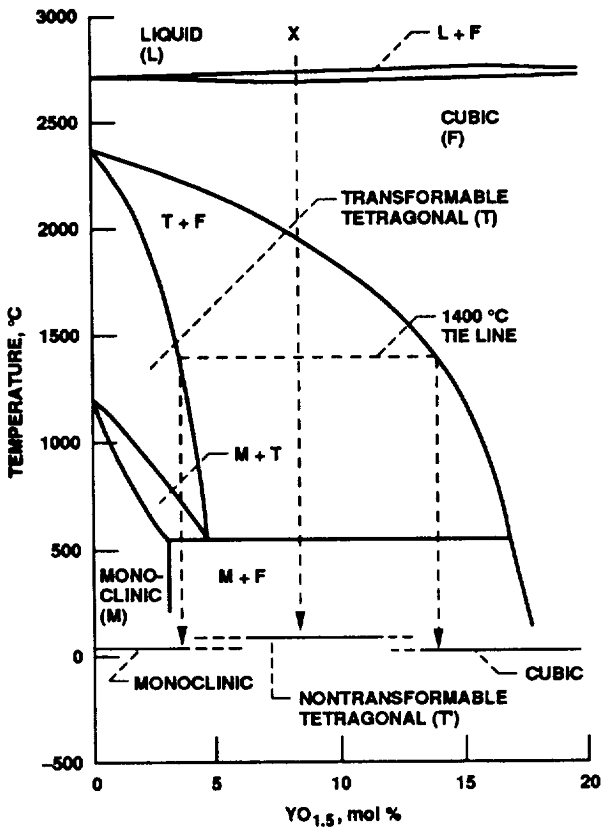


Figure 12. - Zirconia-yttria phase diagram showing phases encountered on quenching and upon high temperature ageing (ref. 21).

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16. Abstract

The present state of development of thick thermal barrier coatings for truck diesel engines is assessed and areas where improved fundamental understanding is needed to properly pursue development are identified. Emphasis is given to the coating systems and design approaches that are being developed for the next generation of truck diesel engines under DOE/NASA support. It is noted that, while considerable progress has been made, the current level of understanding of coating system behavior is inadequate and this lack of fundamental understanding may impede current and future development. Several areas where improved understanding would be especially valuable are identified and recommendations for research into those areas are offered.

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