**DEVELOPMENT OF WEAR-RESISTANT CERAMIC COATINGS
FOR DIESEL ENGINE COMPONENTS**

VOLUME 1: COATING DEVELOPMENT AND TRIBOLOGICAL TESTING

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ABSTRACT

The tribological properties of a variety of advanced coating materials have been evaluated under conditions which simulate the piston ring - cylinder liner environment near top ring reversal in a heavy duty diesel engine. Coated "ring" samples were tested against a conventional pearlitic grey cast iron liner material using a high temperature reciprocating wear test rig. Tests were run with a fresh CE/SF 15W40 lubricant at 200 and 350°C, with a high-soot, engine-tested oil at 200°C and with no lubrication at 200°C.

For lowest wear under boundary lubricated conditions, the most promising candidates to emerge from this study were high velocity oxy-fuel (HVOF) Cr_3C_2 - 20% NiCr and WC - 12% Co cermets, low temperature arc vapor deposited (LTAVD) CrN and plasma sprayed chromium oxides. Also, plasma sprayed Cr_2O_3 and Al_2O_3 - ZrO_2 materials were found to give excellent wear resistance in unlubricated tests and at extremely high temperatures (450°C) with a synthetic oil. All of these materials would offer substantial wear reductions compared to the conventional electroplated hard chromium ring facing and thermally sprayed metallic coatings, especially at high temperatures and with high-soot oils subjected to degradation in diesel environments. The LTAVD CrN coating provided the lowest lubricated wear rates of all the materials evaluated, but may be too thin (4 μm) for use as a top ring facing.

Most of the coatings evaluated showed higher wear rates with high-soot, engine-tested oil than with fresh oil, with increases of more than a factor of ten in some cases. Generally, metallic materials were found to be much more sensitive to soot/oil degradation than ceramic and cermet coatings. Thus, decreased "soot sensitivity" is a significant driving force for utilizing ceramic or cermet coatings in diesel engine wear applications.

1 INTRODUCTION

This report describes the results of a three year program to develop and evaluate wear-resistant coatings for in-cylinder components for future, advanced diesel engines. The following goals were set for piston ring and cylinder liner coatings and substrates:

1. low wear (as measured in laboratory rig tests at 200 and 350°C), with target wear coefficients (for 350°C tests) of 10^{-12} $\text{mm}^3/\text{mm}/\text{N}$ for piston ring coatings and 10^{-10} $\text{mm}^3/\text{mm}/\text{N}$ for cylinder liner materials.
2. low friction coefficients when tested under boundary lubricated conditions (target 0.1) and unlubricated conditions (target 0.2) at ambient temperature and 350°C.

3. good thermal shock resistance.
4. high adherence and compatibility with substrate materials up to 650°C.
5. high uniformity and reproducibility.

This volume of the report describes the coating development activities (section 2.0), experimental procedures (section 3.0), results of tribological testing (section 4.0) and conclusions (section 5.0). Volume 2 contains the appendices and documents the wear surfaces of each of the coatings tested. In the remainder of section 1, the background to the project is described, including the motivation for developing improved wear-resistant piston ring facings, and the selection criteria for coating processes and materials.

The requirement for improved wear performance of advanced diesel engine components, especially for the piston ring-cylinder liner interface, is driven by several needs:

1. improved fuel economy/emissions tradeoffs, requiring improvements to the combustion system which typically result in higher mechanical and thermal stresses on in-cylinder components.
2. improved control of oil consumption (for low particulate emissions), which requires that critical component dimensions and surface finishes be maintained for longer periods of time, with reductions in oil supply to in-cylinder components.
3. improved engine performance for the same displacement, resulting in higher in-cylinder temperatures.
4. overall increased engine durability, hence lower component wear rates.
5. increased maintenance (e.g. oil change) intervals, requiring greater tolerance to soot, abrasive contaminants and oil degradation products.

1.1 SELECTION CRITERIA FOR A PISTON RING COATING PROCESS

In the U.S., the industry-standard ring coating for heavy duty diesel engines is currently electroplated hard chromium. Moderately thick (150 - 250 μm) coatings are used because piston rings for on-highway trucks are typically required to last for upwards of 500,000 miles prior to being replaced at the first major overhaul. This durability/thickness requirement has a major impact on the selection of a coating process. For example, a 10 μm thick coating would require a wear coefficient 15 - 25 times lower than electroplated hard chromium for the material to be useful, which is a difficult goal for this environment. Many otherwise promising coating technologies are unsuitable for piston ring applications because sufficient thicknesses cannot be achieved.

Another important requirement of the coating process is that it should not subject the piston ring substrate to excessive temperatures. Thermally induced distortions of the ring would potentially change the radial pressure distribution with the cylinder liner, which is critical in controlling oil consumption and blowby in the engine [e.g. 1]. In fact, a common method of producing the optimum ring shape is to form the ring over a heated mandrel. Thus, the coating temperature should generally not exceed the heat forming temperature, which is typically 500 - 600°C for conventional materials, although selection of ring substrate materials with better high temperature properties may raise this limit. For piston rings shaped by cam turning processes rather than heat forming, the coating temperature limit is set by the stress relief temperature of the ring substrate material.

Additional process requirements include adequate adherence of the coating to the substrate, with low residual stresses. In particular, the process must not compromise the fatigue properties of the ring substrate material. Adequate process control must be available with the capability to produce highly reproducible coatings with uniform microstructures and properties. Finally, the combination of coating process, material and finishing operation should have maximum cost effectiveness.

The following sections give brief descriptions of the coating processes evaluated during this program. In particular, the relative advantages and disadvantages of each system for piston ring face coatings is discussed.

1.1.1 Thermal Spray Processes

Thermal spraying is a generic category of processes which involve applying a consumable in the form of a spray of finely divided molten or semimolten droplets to produce a coating. The consumable can be introduced into the heat source in the form of powder, rod or wire. For this program, all coatings were sprayed from powders. There are two basic methods of heating the consumable: gas combustion and electric arc. Within these two categories, there are a variety of basic processes, including flame spray, "wire gun", detonation gun and high velocity combustion jet spray (combustion processes) and wire/arc and arc plasma (electric arc processes). The different techniques are reviewed in more detail in reference [2], for example.

Thermal spray processes are generally suitable for applying any material which melts or becomes plastic in the heating cycle and does not degrade in heating. Thus, a wide variety of metals, ceramics, cermets and polymers are suitable for thermal spraying. The deposit does not fuse with the substrate, and so does not form a "metallurgical" bond. Although this can be a disadvantage from an adherence standpoint, issues of metallurgical compatibility (e.g. ability to form solid solutions with the substrate) are avoided. Further, substrate temperatures are typically low (100 - 200°C), so the choice of substrate materials is almost unlimited, giving thermal spray processes great versatility. Coating thickness limitations are generally specific to the process and material, but typical coating thicknesses are in the range 50 - 500 μm , which is ideal for piston ring applications. Piston ring fatigue tests at Cummins have shown lower fatigue debits for thermal spray coatings than for conventional electroplated hard chromium.

Recent advances in thermal spray technology, coupled with advances in powder processing, have resulted in the potential for producing extremely high quality coatings with low porosity and excellent adherence. An important objective of this program was to evaluate the potential of these new processes and powder materials for diesel engine applications. The two thermal spray processes used for development work in this program were plasma arc and high velocity oxy-fuel. These processes are described briefly below.

1.1.1.1 Plasma Arc Coating

Plasma arc spraying is the process of applying a material by melting and atomizing it in powder form in a plasma which is obtained by passing a gas through an electric arc between nonconsumable electrodes within the torch. A schematic of a plasma torch is shown in Figure 1. Powder is delivered by a powder feeder that usually consists of a hopper pressurized with an inert gas, a vibrator to keep the powder from clumping and a gear pump to meter the powder into the carrier gas. Powder sizes are normally in the range 30 - 100 μm . The gas used to form the plasma is a process variable, argon or helium being commonly used. The plasma temperature is typically in excess of 28,000°C, well above the temperatures attained in gas combustion processes. The velocity of the plasma/droplet stream that exits the nozzle is usually subsonic, although high-velocity plasma torches with constricted nozzle designs are available.

The final stage in the spray process is for the molten or semi-molten droplets to impinge on the target as "splats" of material. Splat cooling rates are extremely high, sometimes high enough to produce amorphous deposits. Coatings normally contain porosity (typically 5 - 15%) and oxide inclusions caused by exposure of the molten droplets to oxygen prior to hitting the target. With carbides, a certain amount of decarburization may also occur. A number of methods are available to minimize this effect:

1. use of inert or reducing carrier and arc gases.
2. shrouding the spray emerging from the nozzle with an inert or reducing gas envelope.
3. spraying inside a chamber evacuated to low pressure or containing an inert atmosphere. In this program, the low pressure plasma spray process is designated "LPPS", as distinct from "APS" for air plasma spray.

Figure 1. Schematic of the plasma arc spraying process.

A number of parameters must be controlled to obtain high-quality, consistent coatings. These include nozzle-to-work distance, powder size and type, point of powder introduction, arc current and voltage, type of plasma gas, particle carrier gas and powder fluence.

Since bonding of the coating to the substrate occurs largely by mechanical interlocking rather than by metallurgical bonding, surface preparation is important for thermal spray coatings. Surfaces to be coated are roughened, typically by grit blasting. Often, improved mechanical bonding can be achieved by using an intermediate or "bond" coat.

Although plasma spray processes produce high quality coatings and provide great versatility compared to many other thermal spray techniques, there are some disadvantages. The biggest drawback is probably the high cost of the equipment. Also, due to the large number of spray parameters, process control is more difficult than for gas combustion processes. As with all thermal spray processes, coating is line-of-sight, and thus unsuitable for components such as small internal diameters and complex shapes with re-entrant angles. Generally, coating adherence is not as high for thermal spray coatings as for coating systems such as CVD, electroplating and PVD, and coating "break-out" is recognized as an important issue for piston ring face coatings [3].

Plasma sprayed piston ring coatings have been available commercially for a number of years, although in limited production quantities in the U.S. In Europe, wire sprayed and plasma sprayed molybdenum-based coatings have gained increasing popularity due to improved scuffing/seizure resistance compared to electroplated chromium, although this is achieved at the expense of slightly higher wear rates under well-lubricated conditions [4].

During this project, advanced plasma spray coatings were obtained from APS Materials, Inc. (Dayton, OH), Northwestern University Basic Industrial Research Laboratory (Evanston, IL), Boyd Machine and Repair Company, Inc. (Kimmell, IN) and United Technologies Research Center (East Hartford, CT).

1.1.1.2 High Velocity Oxy-Fuel Coating

High velocity oxy-fuel (HVOF) processes are relatively new, having been introduced commercially in 1981. Several systems are now available, including "Jet-Kote" (a registered trademark of Stoodly/Deloro Stellite, Inc.), "Top Gun" (a registered trademark of Miller Thermal Technologies) and "Diamond Jet" (a registered trademark of Metco Division of Perkin Elmer).

The HVOF process is illustrated schematically in Figure 2. The heat source and carrier for the powder is a continuous gas combustion jet emanating from a combustion chamber within the torch. The fuel gas, typically hydrogen, propylene or acetylene, is mixed with oxygen and ignited. The consumable to be sprayed is introduced into the center of the jet stream from a powder feeder using a carrier gas that is compatible with the fuel gas mixture. The flame temperature at the point of powder introduction is typically about 2,800°C. Gas exhaust velocities approach 1370 ms⁻¹ (approximately four times the speed of sound in air). Powder particles melt or become plastic as in other thermal spray processes, and the bond strength and porosity levels are controlled by the particle velocity and temperature.

Advantages of HVOF processes compared to plasma spraying include:

1. greater bond strength, arising from the higher impingement velocity. Often, the need for a bond coat may be eliminated. However, bond strengths are still generally low compared to coating systems which give metallurgical bonding.
2. porosity levels are typically lower for HVOF than for plasma sprayed coatings.
3. HVOF processes are inherently simpler, resulting in improved process control and greater uniformity and reproducibility of coatings. In particular, coating quality is less sensitive to the nozzle-to-work distance.
4. equipment cost is often lower for HVOF processes. Offsetting this is higher operating costs due to increased usage of oxygen and combustion gases.

Figure 2. Schematic of the high velocity oxy-fuel spraying process (Metco Diamond Jet).

A disadvantage of HVOF processes is the requirement for powders with closely controlled size distributions. Since the process is fairly new, the availability of suitable powders is somewhat limited compared to plasma spray materials. A second disadvantage is the high level of sound emitted by the process, requiring sound-proof spray booths and remote operation. Also, flame temperatures are lower for HVOF processes than for plasma spraying, which makes these systems less suitable for spraying ceramic coatings (although considerable success was achieved with HVOF chromium oxide coatings in this program). Even though flame temperatures are lower than for plasma spraying, the combustion process results in a long flame front which can give rise to greater heat input into the substrate, which is an issue for ring coating. As for all thermal spray techniques, the HVOF process is line-of-sight.

During this project, HVOF coatings were obtained from APS Materials, Inc. (Dayton, OH), Northwestern University Basic Industrial Research Laboratory (Evanston, IL), Boyd Machine and Repair Company, Inc. (Kimmell, IN), Turbine Metal Technology, Inc. (Tujunga, CA) and United Technologies Research Center (East Hartford, CT).

1.1.2 Diffusion Alloying

Diffusion alloying is a process in which a part to be coated is heated in a closed, protective atmosphere and, at the appropriate temperature (typically in the range 800 - 1100°C), gaseous species of the elements desired are introduced. Examples of the reactant gases include BCl_3 for boride coatings, AlCl_3 for aluminides and $\text{TiCl}_4 + \text{CH}_4$ for TiC coatings. The gases decompose on contacting the heated part, and atoms of the desired element are available for diffusion into the substrate. In this respect, the process is similar to chemical vapor deposition (CVD), except that the deposition rates and the rate of diffusion into the substrate are balanced to limit the buildup of unreacted material on the surface. Both alloys and intermetallic compounds can be formed by this method. It is important to realize that the process is essentially a surface conversion rather than a true "coating", since the composition of the processed surface is derived from a combination of elements from the original metal part with elements derived from the reactant gas. Thus, the bonding of the surface layer to the substrate is metallurgical, and the process requires no special preparation techniques to enhance bonding, as do thermal spray (and other) processes.

Advantages of diffusion alloying processes for producing piston ring coatings would include:

1. Excellent bond strengths, far exceeding those for electroplated, thermal spray and PVD coatings.
2. Ceramic surface layers (e.g. borides and carbides) and intermetallic compounds (e.g. aluminides) can be formed with high hardness levels (> 1500 Knoop) and excellent tribological properties.
3. Surface layers are very uniform and contain low levels of porosity.
4. The process is not line-of-sight, which reduces the complexity of fixturing large numbers of parts within a reactor.

Disadvantages of the diffusion alloying process include:

1. The high process temperatures (typically in the range 800 - 1100°C) would cause distortion problems with most potential ring substrates. Substrate selection is limited to hot work tool steels, stainless steels and superalloys. With special precautions, hardenable materials can be heat treated after coating.
2. Coating thicknesses are typically limited to less than 10 - 50 μm .
3. Diffusion alloying processes normally require long cycle times (typically 10 - 20 hours).

During this project, a boride diffusion alloy was obtained from Turbine Metal Technology, Inc.

1.1.3 Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) processes involve the creation of a vapor (often in partially ionized form) from a source contained within a vacuum system and the subsequent deposition of atoms or ions from this vapor onto a substrate. There are three generic types of PVD process, according to the method of producing the vapor:

1. *thermal evaporation*: the source is heated to produce a non-ionized vapor, which subsequently condenses on any material exposed within the vacuum chamber. The kinetic energy of incident atoms is typically low (a few tenths of an electron volt (eV)) for this type of process.
2. *sputtering*: ions from a gas-generated plasma are used to dislodge ("sputter") atoms or molecules from a target made from the coating material. The plasma is established between the negatively biased target (cathode) and the substrate (anode) by the application of a DC potential or a radio frequency (RF) power source. An inert gas such as argon is introduced into the vacuum chamber to form a glow discharge between the electrodes. Positively charged argon ions are accelerated towards the target, where ionic bombardment results in a sputtered flux of target atoms/molecules, ions and electrons. As electrons are accelerated towards the anode, collisions occur with neutral argon atoms, causing dissociation, excitation and ionization, thus sustaining the glow discharge. A portion of the flux of target atoms/molecules and ions reaches the substrate and is deposited to form a coating. The kinetic energy of incident atoms/ions is typically 6 - 10 eV for sputtered PVD coatings.
3. *ion plating*: ion plating is a hybrid process in which a vapor of the material to be coated is directed into a DC or RF glow discharge around the negatively biased (cathodic) substrates. There are various methods of introducing the vapor, the simplest method being to evaporate the coating material such that vaporized atoms enter the plasma, where some are ionized and accelerated towards the substrate. At the substrate, a combination of deposition (from ions and thermally evaporated atoms) and sputtering processes takes place. The rate of evaporation from the source is controlled such that the deposition rate is higher than the rate of sputtering. Deposition of the coating in partially ionized form, coupled with sputter cleaning of the surfaces, is claimed to improve coating adhesion. Although the percentage of ionized target species is often very low (< 1%), conventional ion plating processes give incident ion energies of around 10 eV.

One important modification of the above coating techniques is "reactive deposition", in which reactive gases (e.g. N_2 , NH_3 , CH_4) are mixed with the plasma gas (usually argon), causing a reaction with the target species to form a compound coating. By this method, ceramic coatings such as TiN and TiC can be formed using metallic titanium targets and appropriate reactive gases.

The PVD process selected for piston ring coating development in this program was *cathodic arc PVD (CAPVD)*, which is essentially a variant of the ion plating process in which the vapor source is one or more electric arcs contained within the vacuum chamber. Arcing is initiated by applying a high-voltage pulse to an electrode placed near a cathode (composed of the source material) or by mechanical ignition. Evaporation occurs as a result of cathodic arc spots that move rapidly across the cathode surface, either in a random fashion or magnetically guided. Arc spots are typically 1 to 3 μm in diameter and carry current densities as high as 10^{13} Am^{-2} . This high current density causes flash evaporation of the source material in the form of electrons, ions, neutral vapor atoms and microdroplets. The high degree of ionization in the arc plasma (typically 30 - 90%), coupled with the high energies imparted to each ion (60 - 100 eV), result in high deposition rates and high energy efficiency compared with other PVD processes, including conventional ion plating. CAPVD coatings are often more adherent, less columnar and less porous than PVD coatings produced by other methods.

With all PVD processes, substrates are normally heated to moderate temperatures in order to improve coating adhesion and reduce residual stress levels within the coating. Process temperatures are typically in the range 150 - 550°C, depending on the substrate material, the level of coating adhesion required for the application, the coating thickness, etc. Due to the high kinetic energy of incident ions/atoms in the CAPVD process, adhesion is inherently greater than for other PVD processes, which can allow the use of lower process temperatures.

The success of all PVD coating systems depends strongly on substrate preparation, particularly in the cleaning processes used to remove oils and other residues. Typically, ultrasonic solvent cleaning and/or vapor degreasing procedures are used prior to inserting parts into the vacuum system. Often, a sputter cleaning cycle is used in the vacuum chamber prior to initiating the coating process.

Advantages of the PVD processes for producing piston ring coatings would include:

1. Reactive sputtering techniques can produce very hard (> 2000 Knoop) ceramic coatings with excellent tribological properties.
2. PVD coatings are very uniform and contain low levels of porosity.
3. Coating bond strengths are typically in the same range as for electroplated coatings (> 70 MPa). Although lower than for CVD processes, bond strengths are adequate for piston ring applications, and are generally higher than for thermal spray coatings.
4. PVD coating processes often maintain the surface finish of the substrate to a large degree, potentially eliminating the need for machining after coating.

Disadvantages of PVD processes include:

1. The rate of deposition for reactive sputtering processes is limited by the rate of reaction between the vaporized metal and the plasma gas, and is generally much less than for metallic deposition. This imposes a severe cost premium on thick ($> 5 \mu\text{m}$) ceramic coatings. In addition, other factors, such as the development of a columnar grain structure with undesirable mechanical properties or the build-up of residual stresses in the coating, limit the maximum thickness of a ceramic coating to less than $15 \mu\text{m}$ with current technology.
2. All PVD processes require vacuum chambers, typically requiring pressures as low as 10^{-6} torr (1.3×10^{-3} Pa). This results in high equipment and maintenance costs. The cleanliness of the parts to be coated is a very important feature, often requiring additional purpose-built equipment integrated with the coating units.
3. Although process temperatures are lower than for CVD processes, distortion problems may be a factor for conventional piston ring substrate materials.
4. Most PVD processes are largely line-of-sight, which restricts the component geometries that can be coated. While this is not a big factor for piston rings, care must be taken in fixturing large numbers of parts in the vacuum chamber to achieve uniform coating rates across the whole surface.
5. Ceramic coatings formed by PVD processes are often found to contain nodules or "macroparticles". In the case of TiN, these macroparticles are Ti-rich and occur due to the formation of microdroplets in the vaporization of the metal or to flaking of material from the chamber walls. Microdroplet problems can be particularly severe for CAPVD coatings, unless the process is optimized, for example by magnetically steering the arc across the target. Excessive concentrations of macroparticles can compromise the surface finish of the coating and, for tightly toleranced parts, may result in the need to finish machine the coating, since macroparticles can be as large as $10 \mu\text{m}$ (greater than the coating thickness). Also, if the macroparticles are deeply embedded, their removal may cause fracture and spallation of the coating.

During this project, PVD coatings were obtained from Vapor Technologies, Inc. (Boulder, CO).

1.1.4 The Kaman Science Slurry-Dipped Silica-Chromia-Alumina Process

This patented process starts with the formation of a silica - chromia - alumina (SCA) skeletal structure formed on the metal surface by dipping or spraying the part with a slurry of ceramic powders in chromic acid (CrO_3). The skeletal structure is densified by a series of CrO_3 solution impregnation - heat treatment cycles. The heat treatment results in conversion of CrO_3 to Cr_2O_3 .

The advantages of this technique are that relatively high bond strengths can be obtained by the formation of iron - chromium spinels at the interface with the substrate and high hardnesses can be obtained through multiple processing cycles.

Disadvantages include the toxicity of hexavalent chromium used in the process, and attendant waste disposal issues, and the requirement for multiple processing steps which add cost.

SCA coatings were prepared at Cummins Engine Company under license from Kaman Sciences, Inc. (Boulder, CO).

1.1.5 Diamond-Like Coatings

Considerable excitement has recently been generated by the discovery that crystalline diamond films can be produced using low-pressure gases rather than the high pressures and temperatures previously considered essential [e.g. 5, 6]. These developments offer such potential applications as wear resistant coatings, bearings and cutting tools, free standing windows, lens coatings for visible and infrared transmission and high-temperature, high-power semiconductor devices.

One of the diamond coating processes which has generated recent interest is a chemical vapor deposition (CVD) process based on the reaction

In addition to methane, a wide variety of carbon-containing reactant gases can be used. The typical process uses a reactant gas at less than atmospheric pressure and containing > 95% hydrogen, which is activated by passing it through a plasma or past a heated filament (at approximately 2000°C) before contacting a heated substrate (at 800 - 1000°C). The purpose of the hydrogen is to continually etch out any graphite formed in the deposit. Thus, kinetic factors allow the formation of diamond even though graphite is clearly the stable form of carbon at the temperature and pressure conditions used.

Several other processes have been developed for producing "diamond-like" carbon coatings, in which the diamond phase is created and stabilized by bombardment of the film by energetic species. The term "diamond-like carbon" (DLC) is used to describe a variety of noncrystalline carbon materials ranging from amorphous to microcrystalline, and typically containing anywhere from 0 to 50 atomic percent hydrogen. DLC coatings may be classified according to the method of preparation [7]. One group of methods uses solid carbon as a source of carbon-vapor atoms and molecules. High-energy particle bombardment (> 40 eV and up to several MeV) is used during growth of the film, either from energetic carbon primary ions or inert gas secondary ions. The second group of methods uses hydrocarbon gases as a source of carbon atoms, with some kind of electrical discharge to produce ionized and excited gas phase species. In these cases, the bombardment occurs due to floating potential differences between the substrate and the plasma.

The primary advantage of diamond or DLC films for wear resistant applications is obviously the extremely high hardness attainable. Also, very low susceptibility to adhesive wear (transfer of material) would be anticipated for diamond, due to the strong sp^3 covalent bonding between carbon atoms. In addition, the high thermal conductivity should provide excellent thermal shock resistance.

Processing temperatures for CVD diamond films would be much too high for piston rings, limiting the selection of processes to lower temperature ion-assisted methods, which tend to give higher contents of amorphous carbon and hydrogen. As with many ion-assisted processes, coating thicknesses are generally small (e.g. < 1 μm), which would require extreme wear resistance to be useful for piston ring applications. Due to the high elastic modulus of diamond, such coatings are anticipated to contain very high levels of residual stress, and adhesion to ferrous substrates would be an issue. For high temperature use, two factors may prove to be limiting: (1) graphitization and oxidation (the maximum use temperature for natural diamond in air is approximately 600°C, depending on impurity content) and (2) the high

solubility and diffusivity of all forms of carbon in ferrous materials (thus, the coating may dissolve in the substrate or the wear counterface). However, neither of these should be limiting factors for piston ring applications.

Since the processes for manufacturing diamond or DLC films are so new, it is unclear how the morphology of the films may be controlled to optimize tribological properties. For example, the presence of large, faceted crystallites of diamond may cause abrasion of the sliding counterface, which would be desirable for a cutting tool, but highly undesirable for a sliding machine element (such as a piston ring) where low counterface wear is also important.

One diamond-like coating, obtained from Implant Sciences Corporation (Danvers, MS), was evaluated during this program.

1.2 MATERIALS SELECTION

Requirements for a piston ring face coating material include:

1. extremely low wear rates under oil-starved boundary lubrication conditions (especially at top ring reversal, where temperatures and pressures are highest and sliding speeds are low).
2. compatibility with the in-cylinder tribo-chemical environment (high soot content, sulphur-contaminated, acidic, oxidized lubricant films, high relative humidity and oxidizing conditions).
3. good "scuff resistance" is desirable in case of temporary loss of oil film in the engine (under short duration conditions of extreme hot running or on start-up, for example). The term "scuff resistance" is not well-defined but, in the context of piston ring coatings, an important factor is the resistance to adhesive wear (transfer of material to the counterface). In the piston ring industry, the need for improved scuffing properties has been a driving force for selecting plasma sprayed and wire sprayed molybdenum-based coatings in place of electroplated hard chromium [4, 8].
4. the coating must not cause excessive wear of the cylinder liner material (typically pearlitic or hardened grey cast iron). Extensive engine testing of alternative coatings by one ring manufacturer established a general trend of increasing liner wear as the wear resistance of the ring was improved [4]. Thus, the selection of a tribological system involves a trade-off between ring and liner wear.
5. low friction coefficients in the mid-stroke of the piston (hydrodynamic lubrication), requiring excellent control of surface finish and low coating porosity. Engine friction studies by one ring manufacturer have shown that coatings with high porosity, such as wire-sprayed molybdenum, caused high friction compared to denser coatings [9].
6. high adherence and compatibility with piston ring substrate materials. Residual stresses arising from differential thermal expansion of the coating and substrate can result in "break-out" of the coating during operation [3].
7. acceptable fatigue properties. Propagation of fatigue cracks from the coating to the ring substrate would lead to ring breakage. Also, residual tensile stresses in the coating or substrate would be undesirable.
8. good thermal shock resistance.

Given the diversity of processes suitable for coating piston rings and cylinder liners, the range of materials which could be applied is virtually unlimited. The selection criteria place a premium on good tribological properties, however a major problem in materials selection for wear resistant applications is that there are no simple predictive tools. For example, the lack of correlation between coating microhardness values and wear coefficients is illustrated graphically in Figure 3 (using data generated during this program). For this reason, Cummins has taken an experimental approach, developing laboratory wear test procedures to screen candidate materials under conditions simulating the top ring reversal environment. Engine testing to validate the screening tests and, if necessary, refine the test procedures is in progress.

Figure 3. Microhardness values and lubricated sliding wear coefficients (fresh oil, 200°C) for a range of coatings tested in this program.

Selection of the initial candidate coatings for evaluation in this program was made largely on the basis of recommendations from suppliers based on successful applications (often not in diesel engines), and also on the basis of some limited engine testing of thermal sprayed coatings during TACOM-funded "Adiabatic Diesel Engine" programs at Cummins in the early 1980's. In view of the lack of objective selection criteria, it was decided to include as broad a range of materials and advanced coating processes as possible. During the program, further coatings were selected, and work on other systems was discontinued on the basis of the test results obtained.

Due to the large number of coatings evaluated and the multiplicity of test conditions, screening of ring coating materials was performed using one liner material as the counterface. The decision to test coated rings rather than coated liners was made primarily because current high speed diesel engines normally use a hard ring facing (typically electroplated hard chromium) sliding against a softer cylinder liner, although in some automotive, motorcycle and medium/low speed diesel engines, the reverse combination (coated liners and uncoated grey iron rings) is used. In order to maintain low oil consumption of the engine over a long service life (commonly greater than 500,000 miles to first major overhaul), it is essential to maintain certain critical dimensions of the ring profile. Liner wear depths are typically low enough with current materials that geometry and surface finishes (at least in the mid-stroke region) are not changed to the point of affecting oil consumption. For these reasons, the approach taken was to develop a highly wear resistant ring facing which would not cause increased liner wear compared to traditional ring materials. A conventional liner material (pearlitic grey cast iron) was selected as the sliding counterface for this program because it is likely that any new ring coating would have to be compatible with existing cylinder liner materials. Alternative liner materials and coatings were also evaluated for one ring coating; a HVOF Cr_3C_2 - 20% NiCr identified as providing the best combination of low ring and liner wear in the first round of testing with conventional liners.

2 COATING DEVELOPMENT ACTIVITIES

This section contains detailed descriptions of the coating development activities and characterization of coating microstructures. Wear-resistant coatings evaluated during this program are listed in Table 1 (metallic coatings), Table 2 (ceramic coatings) and Table 3 (cermet materials). Coatings were developed and supplied by various organizations, as summarized in Tables 1 - 3. The coating subcontractors were:

APS Materials, Inc., Dayton, Ohio

Basic Industrial Research Laboratory (BIRL), Northwestern University, Evanston, Illinois

Boyd Machine & Repair Company, Inc., Kimmell, Indiana

Implant Sciences Corporation, Danvers, Massachusetts

Turbine Metal Technology, Inc., Tujunga, California

United Technologies Research Center, East Hartford, Connecticut

Vapor Technologies, Inc., Boulder, Colorado

Coating development activities at each subcontractor are described in the following section. The coatings evaluated are listed in Tables 1 (metallic), 2 (ceramic) and 3 (cermet). Microhardness values were determined for each coating, where possible (Tables 1 - 3). For these tests, a Tukon microhardness tester equipped with a Knoop indenter was used. The applied load was normally 100 gf. Indentations were aligned such that the long diagonal was parallel to the substrate interface, i.e. with the indentations parallel to the splat boundaries for thermal sprayed coatings.

Table 1. *Metallic ring coating materials investigated.*

Coating	Substrate	Supplier	HK ₁₀₀
Electroplated Chromium	Ductile Iron	Cummins	880
APS ¹ Chromium	422 Stainless	APS Materials	250
HVOF ² NiCrBSi	422 Stainless	UTRC	900
APS Mo - 25% Ni	422 Stainless	BIRL	510
HVOF Mo - 25% Ni	422 Stainless	BIRL	540
APS Mo-MoO ₂	422 Stainless	BIRL	770
APS Tribolite	422 Stainless	APS Materials	630
APS Armacor M	HK40 Stainless	APS Materials	760
APS Armacor T	HK40 Stainless	APS Materials	810

1 APS = Air Plasma Spray

2 HVOF = High Velocity Oxy-Fuel

Table 2. Ceramic ring coating materials investigated.

Coating	Substrate	Supplier	HK ₁₀₀
APS Cr ₂ O ₃	HK40 Stainless	APS Materials	770
APS Cr ₂ O ₃	422 Stainless	BIRL	1440
HVOF Cr ₂ O ₃	422 Stainless	BIRL	1320
APS Metco 136 Cr ₂ O ₃ - 5% SiO ₂ - 3% TiO ₂	HK40 Stainless	APS Materials	960
APS Metco 136 + 3% SiO ₂ (mix)	HK40 Stainless	APS Materials	1020
APS Metco 136 + 15% Al ₂ O ₃ (mix)	HK40 Stainless	APS Materials	1260
APS Cr ₂ O ₃ - 50% Al ₂ O ₃	422 Stainless	BIRL	650
APS Cr ₂ O ₃ - 2% SiO ₂ - 2% other oxides	422 Stainless	UTRC	850
APS Boron Carbide	422 Stainless	APS Materials	.3
APS ZrO ₂ - 18% TiO ₂ - 10% Y ₂ O ₃	422 Stainless	UTRC	450
APS Al ₂ O ₃ - 26% ZrO ₂	422 Stainless	BIRL	1050
APS Al ₂ O ₃ - 41% ZrO ₂	422 Stainless	BIRL	840
Boride Diffusion Coating	422 Stainless	TMT	1490 ⁴
LTAVD ⁵ CrN	H13 tool steel	Vapor Tech	1520 ⁶
LTAVD Ta ₂ N	H13 tool steel	Vapor Tech	.7
Diamond-like	H13 tool steel	Implant Sci	.8

Table 3. Cermet ring coating materials investigated.

Coating	Substrate	Supplier	HK ₁₀₀
APS WC - 12% Co	HK40 Stainless	APS Materials	1240
LPPS ⁹ WC - 12% Co	HK40 Stainless	APS Materials	1130
HVOF WC - 12% Co	HK40 Stainless	APS Materials	880
HVOF WC - 12% Co	HK40 Stainless	Boyd Machine	1120
HVOF WC - 12% Co	422 Stainless	TMT	960
HVOF Cr ₃ C ₂ - 20% NiCr	422 Stainless	TMT	500 ¹⁰
HVOF Cr ₃ C ₂ - 20% NiCr	422 Stainless	UTRC	990
LPPS Ferrotic CM TIC + Tool Steel	422 Stainless	APS Materials	990
LPPS Ferrotic CS40 TIC + Mart. Stainless	422 Stainless	APS Materials	940
LPPS Ferrotic HT6A TIC + Nickel Alloy	422 Stainless	APS Materials	620
APS Metco 136 Cr ₂ O ₃ + 33% Stellite 6	HK40 Stainless	APS Materials	1250 ¹¹
			440 ¹²

3 Coating was too porous for microhardness test

4 25gf load

5 LTAVD = Low Temperature Arc Vapor Deposition

6 10gf load.

7 too thin to measure.

8 too thin to measure.

9 LPPS = Low Pressure Plasma Spray

10 50gf load

11 Matrix Cr₂O₃ phase (HK₁₀)

12 Stellite 6 phase (HK₁₀)

2.1 COATING DEVELOPMENT AT APS MATERIALS INCORPORATED

2.1.1 Chromium Oxide-Based Coatings

Chromium oxide was selected as a promising candidate for piston ring coatings on the basis of previous successful performance during uncooled engine tests at Cummins [10].

A study of the effect of plasma spray process variables on coating adhesion and microstructure was conducted for air plasma sprayed (APS) chromium oxide (Cr_2O_3). Two powders were used: a commercial Cr_2O_3 - 5% TiO_2 - 3% SiO_2 (Metco 136) and a pure Cr_2O_3 material (UCAR). In all cases, a Metco 447 bond coat was used. The test parameters are listed in Table 4, key variables being powder composition, powder feed gas (argon or oxygen), powder feed rate and spray velocity (arc gas flow rate). Two guns were used: an Avco gun for lower velocities, and a Plasmadyne SG-100 gun with various nozzles for higher velocities (tests 9, 10, 13 and 14 produced Mach 1 spray velocities). In addition, test 15 used an inert argon shroud around the plasma spray.

Table 4. Chromium oxide plasma spray parameters.
Test 15 used an inert argon shroud with nitrogen coolers.

Test	Amps	Volts	Arc Gas Feed	Mix Gas	Pwdr Gas Feed	Hopper Speed	Gun	Nozzle	Powder
1	600		40	12-He		40%	Avco	065	M-136
2	500		40	12-He		40%	Avco	065	M-136
3	500		60	3-Hyd	10	30%	Avco	315	M-136
4	500		60	3-Hyd	10	30%	Avco	315	UCAR
5	600		40	12-He	20-Oxy	1%	Avco	315	M-136
6	600		40	12-He	20-Oxy	1%	Avco	315	UCAR
7	900	35	50	60-He	12	1%	SG-100	165	M-136
8	900	35	50	60-He	12	1%	SG-100	165	UCAR
8-A	700	34	50	60-He	15	1%	SG-100	165	UCAR
8-B	700	34	50	60-He	15	1%	SG-100	165	M-136
9	700	52	270	45-Ar,N	18	3 rpm	SG-100	360	M-136
10	700	52	270	45-Ar,N	18	3 rpm	SG-100	360	UCAR
11	700	34	50	60-He	15	1%	SG-100	165	M-136
12	700	34	50	60-He	15	1%	SG-100	165	UCAR
13	1000	45	115	45-Ar,N	10	1.4 rpm	SG-100	360	M-136
14	1000	45	115	45-Ar,N	10	1.4 rpm	SG-100	360	UCAR
15	900	51	116	83-He	6	1.4 rpm	SG-100	165	M-136

Figure 4. Tensile bond strength data for APS chromium oxide coatings produced by various spray conditions (listed in Table 4).

The bond strengths of coatings sprayed onto steel test coupons were measured by tensile pull tests (using fixtures bonded to the coating with epoxy cement). Bond strength data are presented in Figure 4 and Table 5. Light microscopy was used to determine the relative porosity levels of the coatings on these sample coupons (Table 6).

The following conclusions were drawn from the above study:

1. The pure Cr_2O_3 had slightly greater adherence than the Metco 136 (disregarding failures in the epoxy), but there was no significant effect on density.
2. The oxygen powder feed gas produced higher densities but lower bond strengths than with argon. The lower bond strength may have resulted from oxidation of the bond coat.
3. Reducing the powder feed rate resulted in slightly higher bond strength, but had no effect on density.
4. Higher velocity coatings generally had lower bond strengths. There was no consistent effect of velocity on density for these conditions.
5. The argon shroud with inert cooling produced a coating with fairly low bond strength and average density.

Table 5. Tensile bond test data for APS chromium oxide coatings produced by various spray conditions (listed in Table 4).

Test	Force (kN)	Tensile Bond Strength (MPa)	Mean Bond Strength (MPa)	Std. Deviation (MPa)	Powder	Failure Mode
1	29.4 25.8 32.9	57.9 50.9 64.9	57.9	5.7	Metco 136	Bond/25% Cer Bond Ceramic
2	34.7 31.6 29.6	68.5 62.3 58.4	63.1	4.2	Metco 136	Bond/Epoxy Bond/Epoxy Epoxy
3	39.1 37.8 34.3	77.3 74.6 67.6	73.2	4.1	Metco 136	Epoxy Epoxy Epoxy
5	17.8 24.5 23.1	35.1 48.3 45.7	43.0	5.7	Metco 136	Bond/Cer Int Bond/Cer Int Bond/Cer Int
6	22.4 25.4 28.0	46.1 50.0 55.3	50.5	3.8	UCAR	Bond/Cer Int Bond/Cer Int Int/Cer
9	13.1 15.1 12.5	25.9 29.8 24.6	26.8	2.2	Metco 136	Bond/Cer Int Bond/Cer Int Int/Bond
10	16.2 14.7 14.5	32.0 29.0 28.5	29.8	1.6	UCAR	Bond/Cer Int Bond/Cer Int Int/Bnd
11	35.6 32.0 35.6 35.1 31.4 36.4	70.2 63.2 70.2 69.4 61.9 71.8	67.8	3.8	Metco 136	Epoxy Epoxy Epoxy Epoxy Epoxy Epoxy
12	32.9 34.3 31.7	65.0 67.6 62.6	65.0	2.1	UCAR	Epoxy Epoxy Epoxy
13	23.0 28.2 30.9	45.4 55.7 61.0	54.1	6.5	Metco 136	Ceramic Ceramic Ceramic
14	25.1 22.4 33.1	49.6 44.1 65.4	53.0	9.0	UCAR	Epoxy Epoxy Epoxy
15	14.9 13.3 16.2	29.4 26.3 32.0	29.3	2.3	Metco 136	Bond/Cer Int Bond/Cer Int Bond/Cer Int

Table 6. *Relative levels of porosity/microcracking of chromium oxide coatings assessed by light microscopy. 1 = LOWEST, 5 = HIGHEST.*

Test	1	2	3	4	5	6	7	8	8A	8B	9	10	11	12	13	14	15
Porosity	2	3	2	2	1		1		3	1	3	3	5	4	1		2

Wear test samples were prepared using the conditions of tests 3 and 4 (the optimum combination of bond strength and density), for all types of powder. The coatings were applied to an HK40 austenitic stainless steel substrate (100 mm diameter).

The microstructure of the coating sprayed from UCAR powder is shown in Figure 5 (SEM, backscattered electron mode). Bonding between the coating, the bond coat and the substrate was generally good. The coating contains lines of microcracks/voids running parallel to the interface, which are more prevalent near the surface. These features are evidence of incomplete adhesion between splats of molten material. Regions of large-scale porosity and pull-out were observed throughout this coating, especially in areas adjacent to the bond coat. These large pores were possibly caused by interconnected crack/void networks which gave rise to weak regions in the coating which were then removed during metallographic polishing.

The Metco 136 coating showed much lower porosity and inter-splat microcrack/void formation than the above coating (Figure 6). Pores were much smaller and were equiaxed rather than elongated parallel to the interface. Again, bonding between the coating, bond coat and substrate was good.

A 3% SiO₂ addition was made to the Metco 136 powder in order to try to increase coating density and splat adherence by forming increased amounts of glassy binder phase. The microstructure of this coating was intermediate between the UCAR and Metco 136 materials (Figure 7) in terms of porosity and microcracking. Differences in grey scales between splats are probably due to elemental contrast between SiO₂ (lower mean atomic number, hence darker imaging) and Cr₂O₃. This indicates that the mixed powder particles melt and solidify separately, with little mixing in the plasma. Bonding between the SiO₂ and Cr₂O₃ splats was good. Equiaxed regions containing porosity and a very fine-scale microstructure are evidence of unmelted particles being entrapped within this coating (Figure 7). The tensile bond strength was 54.1 MPa (mean of three tests).

In order to investigate the effects of coating composition on wear, a coating was sprayed from a Metco 136 powder mixed with 15% Al₂O₃ by weight. The microstructure shows darker imaging Al₂O₃ which is clearly differentiated from the lighter Cr₂O₃-rich matrix material (Figure 8). Both phases were melted in the plasma and solidified without mixing, and with no apparent cracking or debonding at the Cr₂O₃-Al₂O₃ interfaces. The content and morphology of pores and microcracks were approximately the same for this coating as for the Metco 136 coating.

Attempts were made to spray a Cr₂O₃ - 33% Stellite 6 cermet material by mixing Metco 136 and Stellite 6 powders. The microstructure showed discrete splats of Cr₂O₃ and Stellite 6, both phases having been melted in the plasma. Bonding between the two phases appeared to be good, with very little inter-splat cracking/voiding in this material (Figure 9). The levels of porosity and microcracking were very low for this coating. The tensile bond strength was 56.2 MPa (mean of three tests).

Figure 5. *Microstructure of APS UCAR chromium oxide coating (SEM, backscattered electron). High levels of inter-splat microcracking and porosity/pull-out are visible.*

Figure 6. *Microstructure of APS Metco 136 chromium oxide (SEM, backscattered electron). Low levels of porosity and inter-splat microcracking are visible.*

Figure 7. Microstructure of APS Metco 136 + 3% silica (SEM, backscattered electron). Darker phase is SiO_2 . Intermediate levels of porosity/microcracking are visible.

Figure 8. Microstructure of APS Metco 136 + 15% alumina (SEM, backscattered electron). Darker phase is Al_2O_3 . Porosity levels are low, with good interphase bonding.

Figure 9. *Microstructure of APS Metco 136 + 33% Stellite 6 (SEM, backscattered electron). Light phase is Stellite 6. Both phases were melted in the plasma. Interphase bonding is good, with low porosity and inter-splat microcracking.*

2.1.2 Tungsten Carbide - Cobalt Coatings

Tungsten carbide - cobalt coatings are widely used for wear-resistant applications, especially those involving abrasive or erosive wear conditions, and powders suitable for all forms of thermal spray process are readily available. On this basis, tungsten carbide materials were evaluated as potential ring coatings. The emphasis was to evaluate coatings produced by the most state-of-the-art thermal spray processes, including low pressure plasma spray (LPPS) and high velocity oxy-fuel (HVOF) in addition to more conventional air plasma spray (APS) methods.

Two important factors for thermally sprayed WC - Co coatings are (a) the degree of solutionizing of the carbides in the matrix phase and (b) the amount of decarburization in the plasma or combustion gas. Various phases can be formed by combinations of dissolution and decarburization, including (in addition to WC and Co): W_2C , Co_6W_6C , Co_2W_4C , $Co_3W_9C_4$, Co_3W_3C and non-stoichiometric phases generally described as WC_{1-x} . All WC - Co coatings tested in this program were sent to BIRL for detailed X-ray diffraction (XRD) analysis (Table 7). In addition, microstructures were characterized using backscattered electron SEM micrographs, using a quadrupole detector switched for 100% atomic number (elemental) contrast. In these images, contrast varies in proportion to the mean atomic number of the material (mean atomic numbers for several phases are listed in Table 8). Note that pure Co is always the darkest imaging of the possible phases. Qualitatively, the volume fraction of the darkest phase (remaining Co) gives a measure of the degree of solutionizing, and the volume fraction of phases brighter than WC (if this can be identified) gives a measure of the amount of combined decarburization and solutionizing.

APS Materials produced WC - 12% Co coatings by three different spray methods: air plasma spray, low pressure plasma spray and high velocity oxy-fuel using a "Jetkote II" system. The starting powder was the same (Miller Thermal 1172) for all coatings, in order to compare the effects of the different processes on microstructure and wear properties. It should be appreciated that optimizing the powder for each process would perhaps have given different results.

The XRD data in Table 7 clearly show that all the thermally sprayed WC - Co coatings exhibited some degree of solutionizing, although this is not easy to quantify, in view of the range of phases identified. The percentage values shown in brackets [] represent the peak intensity of the strongest peak from the minor phase divided by the strongest WC peak intensity. These numbers do not indicate that the minor phase exists in that abundance.

Table 7. Phase analysis of WC - Co coatings used in this program. X-ray diffraction analysis and phase identification was performed at BIRL.
Important: Percentage values in brackets [] represent the peak intensity of the strongest peak from the minor phase divided by the strongest WC peak intensity. These numbers do not indicate that the minor phase exists in that abundance.

Coating Process	Supplier	Analysis
Air Plasma	APS Materials	WC + $Co_3W_9C_4$ [12%] + Co_3W_3C [10%]
Low Pressure Plasma	APS Materials	WC + Co_2W_4C [16%] + $Co_3W_9C_4$ [14%]
HVOF (Jetkote II)	APS Materials	WC + Co_2W_4C [24%] + $Co_3W_9C_4$ [10%]
HVOF (Jetkote II)	Boyd Machine & Repair	WC + α - W_2C [13%]
HVOF (proprietary gun)	Turbine Metal Technology	WC + WC_{1-x} [7%] + Co_6W_6C [6%]

Backscattered electron SEM images of the APS material (Figure 10) revealed "blocky" carbide particles with a bimodal size distribution. At least five levels of grey scale are visible, indicating the presence of several phases. The pure Co phase is present only in small concentrations, and the "matrix" phase is actually a W-Co-C phase in most regions. XRD phase analysis (Table 7) showed the presence of $\text{Co}_3\text{W}_9\text{C}_4$ and $\text{Co}_3\text{W}_3\text{C}$ phases in addition to WC. The coating also contained porosity, ranging from small, equiaxed pores within the matrix phase to large-scale porosity and pull-out extending across one or more carbide grains.

The microstructure of the LPPS WC - 12% Co coating (Figure 11) appeared qualitatively similar to that of the APS material described above. XRD analysis revealed a different phase mixture, however, the LPPS material containing $\text{Co}_2\text{W}_4\text{C}$ and $\text{Co}_3\text{W}_9\text{C}_4$ phases. Porosity levels were similar to those for the APS material.

One difficulty encountered with the LPPS process was that thick coatings (greater than approximately 150 μm) tended to shatter on cooling after spraying, indicating high substrate temperatures and/or high residual stress in the coating. In this case, the substrate was a castable austenitic stainless steel (HK40), which would have a greater thermal expansion mismatch with the coating than 422 martensitic stainless steel. Adherence to the substrate was found to be excellent for the LPPS material, however, since tensile bond strengths in excess of 65 MPa were measured for coatings which survived the cool-down process.

The HVOF WC - 12% Co coating (Figure 12) showed various differences in microstructure from the APS and LPPS materials. For example, it is difficult to differentiate the original WC grains from the matrix phases in the HVOF material. The matrix phase showed evidence of a fine-scale microstructure developing in some areas (perhaps due to precipitation of solid phases), and some of the carbides or W-Co-C phases appeared to be fractured (perhaps due to high residual stresses). XRD analysis showed the presence of $\text{Co}_2\text{W}_4\text{C}$ and $\text{Co}_3\text{W}_9\text{C}_4$ phases, as for the LPPS material, but the $\text{Co}_2\text{W}_4\text{C}$ peak was stronger (24 vs 16% relative intensity) and the $\text{Co}_3\text{W}_9\text{C}_4$ peak slightly weaker (10 vs 14% relative intensity). Overall, the level of solutionizing appeared to be greater for the HVOF than for the APS and LPPS coatings. This is somewhat unexpected, since the flame temperature for HVOF processes is generally much lower than for air plasma spray.

Microhardness values for the APS, LPPS and HVOF coatings were, respectively, 1240, 1130 and 880 kgfmm^{-2} (KHN_{100}), although there was considerable scatter from one location to another for each coating. The differences are probably caused by different amounts of decarburization and carbide solutionizing, as discussed above.

Table 8. Mean atomic number for several phases which may occur in WC - Co coatings.

Phase	Mean Atomic Number
W ₂ C	51.3
Co ₂ W ₄ C	50.9
Co ₃ W ₉ C ₄	48.2
Co ₆ W ₆ C	47.1
Co ₃ W ₃ C	44.1
WC _{1-x}	$\frac{74 \cdot 6(1-x)}{(2-x)}$
WC	40.0
Co	27.0

Figure 10. Microstructure of APS WC - 12% Co coating (SEM, backscattered electron image). Coating shows blocky carbides, with evidence of several phases formed by solutionizing, re-precipitation and decarburization. The "matrix" phase is actually a W-Co-C phase in most regions.

Figure 11. *Microstructure of LPPS WC - 12% Co coating (SEM, backscattered electron image). The microstructure appears to be similar to that of the APS material (Figure 10).*

Figure 12. *Microstructure of HVOF (Jet-Kote) WC - 12% Co (SEM, backscattered electron). Microstructure as in Figures 10 and 11, but showing a higher degree of solutionizing.*

2.1.3 Ferro-Tic Coatings

Ferro-Tic¹³ materials (steel- or nickel alloy-bonded TiC) were investigated in order to broaden the range of cermet compositions studied, since WC-Co and Cr₃C₂-NiCr coatings had been found to give excellent wear properties. Product literature from Alloy Technology, Inc. claims that an important advantage of Ferro-Tic materials is that the carbide particles are rounded in shape and consequently the materials are very "lubricious". For this program, it was hoped that smooth, rounded carbides would be less abrasive to soft pearlitic iron cylinder liner counterfaces.

Three grades of Ferro-Tic powder were evaluated. Coatings were sprayed using a LPPS system, in order to minimize decarburization effects and retain the highest possible hardness levels. The materials investigated were:

1. Ferro-Tic CM 45% TiC in a high chrome tool steel matrix
2. Ferro-Tic CS-40 45% TiC in a martensitic stainless steel matrix
3. Ferro-Tic HT-6A 35% TiC in an age hardenable nickel base matrix.

The microstructure of the CM grade material comprised 5 μ m sized TiC particles in a metallic matrix, with some porosity/pull-out and inter-splat microcracking (Figure 13). The carbide morphology was found to be equiaxed, but is best described as "blocky" rather than rounded. A fine dispersion of sub-micron sized carbides is also evident in Figure 13. It is not known whether this was due to a bimodal carbide size distribution in the starting powder or to solutionizing and re-precipitation of carbides in the matrix phase during the spray process. The steel matrix phases are assumed to have contained carbides in addition to the TiC hard phase.

Figure 13. Microstructure of LPPS Ferro-Tic CM coating (SEM, backscattered electron image). Microstructure comprises blocky carbides (darker phase) in a steel matrix. Finer carbides may be evidence of solutionizing and re-precipitation.

¹³ "Ferro-Tic" is a registered trademark of Alloy Technology, Inc., Nyack, NY

Figure 14. *Microstructure of LPPS Ferro-TiC CS-40 coating (SEM, backscattered electron image). The microstructure appears to be similar to that for the CM grade (Figure 13).*

The microstructure of the CS-40 grade material (Figure 14) was essentially similar to that of the CM grade, the major difference being the chemical composition of the matrix phase.

The HT-6A material (Figure 15) contained fewer 5 μm sized TiC particles than the CM and CS-40 grades, consistent with the lower carbide content of the starting powder. The fine dispersion of carbides observed for the steel matrix grades was also observed for this material. The HT-6A coating was significantly softer (320 kgfmm^{-2} , HK_{100}) than the CM and CS-40 grades (990 and 940 kgfmm^{-2} , HK_{100} respectively).

It is important to note that, compared to the microstructures observed for the WC - Co coatings, all the Ferro-TiC materials showed less evidence of carbide solutionizing. From the microstructural evaluation, coating adherence was identified as a concern for the Ferro-TiC materials, since all three grades showed evidence of debonding at the substrate interface (Figures 13 - 15). However, tensile bond strengths measured for the three coatings were high: 70.9 MPa for the CM grade, 73.0 MPa for the CS-40 and 68.0 MPa for the HT-6A, all tests giving fracture in the epoxy.

Figure 15. *Microstructure of LPPS Ferro-Tic HT-6A coating (SEM, backscattered electron image). The carbide content of this coating is lower than for the CM and CS-40 grades.*

2.1.4 Metallic Coatings

Although the primary objective of this program was to develop ceramic and cermet coatings, a limited amount of effort was devoted to evaluating alternative metallic coatings which might show greater wear resistance than the baseline electroplated hard chromium.

Plasma sprayed chromium samples were obtained for comparison with electroplated hard chromium. The microstructure of the plasma sprayed material showed a dispersion of dark-imaging, lamellar features, presumed to be chromium oxide, with excellent inter-splat bonding and adherence to the substrate (Figure 16). The microhardness of this coating was low ($250 \text{ kgfmm}^{-2} \text{ HK}_{100}$) compared to electroplated hard chromium (880 kgfmm^{-2}).

Figure 16. Microstructure of APS chromium coating (SEM, backscattered electron image). Darker imaging lamellar features are thought to be oxides. The coating shows excellent inter-splat bonding and adhesion to the substrate.

Figure 17. *Microstructure of APS Tribolite coating (SEM, backscattered electron image). Etched with Marbles reagent. The coating comprises an extremely fine dispersion of boron carbide in an austenitic steel matrix. Porosity is very low, with excellent inter-splat bonding and adherence to the substrate.*

Coatings were sprayed with a "Tribolite" powder, which is a proprietary material of Wear Management Services, Inc. Wear Management Services product literature describes the material as a very fine boron carbide dispersion in an austenitic steel matrix. The microstructure of the coating sprayed from this powder by APS Materials was found to contain a mixture of light imaging and dark-imaging phases, with very low porosity levels and excellent inter-splat bonding and adherence to the substrate (Figure 17). Energy dispersive X-ray analysis in the SEM gave a bulk coating composition of 68% Fe, 28% Ni, 2% Si and 2% Cr. Boron and carbon would not have been detected by this analysis technique.

Figure 18. *Microstructure of APS Armacor M coating (SEM, backscattered electron image). The coating shows a fine dispersion of carbides/borides in a metallic matrix. Porosity levels are high, and inter-splat oxidation and microcracking is visible.*

Two proprietary powders, "Armacor M" and "Armacor T", were obtained from Amorphous Metals Technologies, Inc. (Irvine, CA). Armacor M is an iron-based material which is claimed to produce an amorphous surface layer during grinding and abrasion processes. Product literature shows dry sand abrasive wear properties which are comparable to WC - Co hard facings. Information about the "T" grade was not available.

The microstructure of the Armacor M coating sprayed by APS Materials, using conventional air plasma spray methods, is shown in Figure 18. Splat sizes were relatively large for this coating, indicating a fairly coarse starting powder. Porosity levels were relatively high, perhaps due to poor powder feeding due to the coarser particle size. Oxide films and microcracks were observed between splats, indicating poor inter-splat adhesion. Bonding between the coating, bond coat and substrate was, however, good. Within the splats, a fine dispersion of a slightly darker imaging phase is visible in some regions (Figure 18). EDS analysis of the Armacor M coating revealed high levels of Cr (47 wt%) and Fe (44 wt%) with some Ni (2 wt%) and Si (6 wt%). WDS light element analysis was not performed for this coating.

Figure 19. *Microstructure of APS Armacor T coating (SEM, backscattered electron image). Dark phase: as Armacor M. Light phase: tungsten. The tungsten phase shows evidence of incomplete melting. Inter-splat bonding was better than for the Armacor M material.*

The Armacor T coating (Figure 19) showed a mixture of two distinct powders, the darker imaging phase having a similar composition to Armacor M, the lighter imaging phase being essentially pure tungsten metal (by EDS analysis). The tungsten phase contained a high level of porosity and pull-out, suggesting incomplete melting. Inter-splat oxidation and microcracking was less than for the Armacor M coating. Bonding between the coating, bond coat and substrate was good.

Table 9. *Microhardness values for LPPS Metco 350 Fe - 15% Mo - 3% C coatings with various additions.*

Coating	HK ₁₀₀
Metco 350 with 25% titanium	588
Metco 350 with 25% boron	738
Metco 350 with 50% TiB ₂	623
Metco 350 with 25% B ₄ C	662

A series of test coupons were sprayed with a Metco 350 Fe - 15% Mo - 3% C powder blended with various metallic and ceramic additions, in an attempt to create microstructures comprising a relatively hard metallic matrix phase with a hard carbide or boride dispersion. Additions of (a) titanium and (b) boron were made to investigate whether the high processing temperatures inherent with the plasma spray process would cause significant reaction of the added element with carbon in the matrix phase. In addition, coatings were sprayed with (c) TiB₂ and (d) B₄C additions to form more conventional cermet microstructures. The powders were sprayed with a LPPS system in order to retain the highest carbon content possible in the matrix phase. The coating mixtures sprayed were:

(a)	Metco 350 with 25% titanium	Reactive system
(b)	Metco 350 with 25% boron	Reactive system
(c)	Metco 350 with 50% TiB ₂	Non-reactive system
(d)	Metco 350 with 25% B ₄ C	Non-reactive system

The first two materials essentially formed mixtures of the two components, with no apparent carbide formation (Figures 20 and 21). It is concluded that more intimately mixed powders would be required to achieve sufficient reaction of the carbon with the reactive metal phase. The boride/carbide additions resulted in typical cermet microstructures, but with low hard phase contents (Figures 22 and 23). Microhardness values were similar (in the range 590 - 740 kg/mm² HK₁₀₀) for all four coatings (Table 9). On the basis of the microstructural evaluation, it was decided not to undertake further development or testing of these systems.

Figure 20. Microstructure of APS Metco 350 + 25% Ti coating (light micrograph). Darker phase is titanium metal. There is no evidence of reaction to form TiC .

Figure 21. Microstructure of APS Metco 350 + 25% B coating (light micrograph). Darker phase is boron. There is no evidence of reaction to form B_4C .

50 μ m

Figure 22. *Microstructure of APS Metco 350 + 50% TiB₂ coating (light micrograph). The image shows a low concentration of blocky TiB₂ particles in a metallic matrix.*

50 μ m

Figure 23. *Microstructure of APS Metco 350 + 25% B₄C coating (light micrograph). A low concentration of large, angular B₄C particles (darker imaging) is visible.*

2.1.5 Boron Carbide Coating

Ceramic materials with extremely high hardness levels generally have low wear coefficients, but "ultra-hard" materials (microhardness values greater than 2000 kgfmm⁻²) are not generally available as thermally sprayed coatings. Ceramic materials commonly used include a wide range of oxides (e.g. aluminum oxide, zirconium oxide, chromium oxide and various mixed or alloyed compositions such as alumina-titania, alumina-zirconia, etc.) with microhardness values ranging to about 1500 kgfmm⁻², but relatively few carbides, borides or nitrides (except as cermet coatings). Various factors contribute to the difficulty in spraying ultra-hard ceramic materials, including:

1. extremely high melting points of most covalently bonded hard materials.
2. some compounds (e.g. silicon nitride) do not melt, but rather sublime or dissociate.
3. high residual stresses on cooling molten splat droplets from extremely high temperatures, especially for a material which has high elastic modulus. This results in low coating cohesion due to inter-splat cracking.

In this program, attempts were made to produce boron carbide coatings using thermal spray processes (low pressure plasma spray and inert gas shrouded air plasma spray). Boron carbide was selected on the basis of prior development efforts at APS Materials, Inc.

An initial series of spray trials was made using low pressure plasma spray methods, utilizing a wide variety of test conditions (Table 10), but no deposition occurred. A disadvantage of LPPS processes is that the rate of heat transfer to the powder particles is much lower than for air plasma spray processes, so melting of refractory materials is more difficult.

Following these attempts, a much finer Starck powder (selected by BIRL), was sprayed using nitrogen shrouded air plasma spray techniques developed at APS Materials. Although a coating could be formed from this powder, porosity levels were extremely high (Figure 24).

Further attempts to develop a process for spraying boron carbide were discontinued after reviewing the results of an Internal Cummins project to evaluate wear properties of monolithic ceramics. A series of Falex 1 block-on-ring wear tests were conducted with various ceramic materials sliding against 52100 steel. One conclusion of this study was that monolithic sintered boron carbide had relatively poor wear properties compared to other ceramic materials such as alumina, zirconia, silicon carbide and silicon nitride, especially when lubricated with a high-soot oil obtained from a diesel engine [11].

Table 10. Plasma spray parameters for the first series of boron carbide tests. For each test, 4 coupons were placed at distances of 10, 19, 28 and 34 inches. No deposition occurred at any setting. The 115 and 093 anodes are 20° rear injection; 114 is a straight injection anode.

Test	Pressure Torr	Arc CFH	Mix CFH	Powder CFH	Hopper RPM	Volts	Amps	Anode
1	20	140	80-He	25	6	48	1550	115
2	20	120	12-H ₂	25	2	51	1475	115
3	280	120	80-He	25	2	44	1600	115
4	10	120	60-He	25	2	44	1600	115
5	10	120	80-He	20	2	46	1625	114
6	20	120	15-H ₂	20	4.6	48	1500	114
7	50	120	15-H ₂	25	3	46	1525	093
8	20	120	80-He 15-H ₂	25	2	52	1525	093

Figure 24. *Microstructure of LPPS boron carbide coating (SEM, backscattered electron image). The coating is extremely porous, with little inter-splat bonding.*

2.1.6 Silicon Nitride Coating

From a variety of laboratory bench tests and engine component testing, Cummins has previously established that monolithic silicon nitride is a highly wear-resistant material. Pure silicon nitride coatings cannot be formed by conventional thermal spray methods, however, because the material does not melt, but rather sublimates in the temperature range 1700 - 1900°C. Despite this, silicon nitride powders are available in size distribution ranges that would be suitable for thermal spraying, intended for mixing or cladding with metallic components to form cermet coatings. As an experiment, attempts were made to spray a Starck silicon nitride powder (selected by BIRL) with no metallic binder phase using LPPS processes. The substrates were flat steel test plates.

The LPPS process was found to essentially sublime the silicon nitride powder, some of which condensed on the substrates as a thin deposit (essentially an evaporative physical vapor deposition process). The deposit adhered to the substrates as a 15 μm thick, dense, fine-grained coating containing large cracks parallel to the surface within the coating and at the interface with the substrate (Figure 25). Arrested cracks running perpendicular to the surface were also observed. The high crack content suggests high residual stress levels within the coating. X-ray diffraction verified that the coating was composed of predominantly $\alpha\text{-Si}_3\text{N}_4$ (Figure 26), as was the starting powder.

Although these preliminary efforts to produce a silicon nitride coating showed promise, it was thought that the low adherence and high residual stress levels would be unsuitable for piston ring applications, and further development was not undertaken. Wear tests were not conducted with this material.

Figure 25. *Microstructure of LPPS silicon nitride coating (SEM, backscattered electron image). Cracking parallel to and perpendicular to the surface indicate high residual stresses.*

Figure 26. *X-ray diffraction pattern from LPPS Si_3N_4 coating, showing $\alpha\text{-Si}_3\text{N}_4$ peaks.*

2.2 COATING DEVELOPMENT AT NORTHWESTERN UNIVERSITY BASIC INDUSTRIAL RESEARCH LABORATORY

2.2.1 Molybdenum-Based Coatings

Combustion wire sprayed and air plasma sprayed molybdenum-based piston ring coatings have been available commercially for a number of years, although in limited production quantities in the U.S. In Europe, such coatings have gained increasing popularity due to improved scuffing/seizure resistance compared to electroplated chromium, although this is achieved at the expense of slightly higher wear rates under well-lubricated conditions [4]. Recently, GTE Products Corporation have made significant advances in developing molybdenum-based powders for plasma sprayed piston ring applications [12]. Two of the more recently available powders were obtained from GTE for spray process development at BIRL. The first powder was a blend of 75% Mo with 25% Ni, designated SA-901. Specifications for this powder are listed in Table 11. The second powder was a molybdenum - molybdenum dioxide composite powder containing 10.07% oxygen and designated SA-110 (specifications in Table 12).

The Mo - 25% Ni powder was analyzed by scanning electron microscopy (Figure 27). The molybdenum powder particles were agglomerations of smaller particles with a "spongy" texture. The nickel phase was found to contain 14% Cr, 5% Si and 5% Fe by weight (balance Ni). This powder was sprayed by two methods: air plasma spray and high velocity oxy-fuel ("Top Gun"). Plasma spray parameters were established by a series of spray trials, detailed in Table 13, followed by microstructural characterization of the coatings and SEM analysis of the as-sprayed surfaces. The final spray parameters are listed in Table 14. HVOF spray parameters were determined in the same way, an example being shown in Table 15.

Table 11. Specifications for GTE SA-901 Mo - 25% Ni powder.

MOLYBDENUM:			
Lot No.	90A-026	<u>Screen Analysis:</u>	
Bulk Density	2.16 gcm ⁻³	+170	1.4%
Hall Flow	28 s/50g	-170 +200	21.6%
O ₂	620 ppm	-200 +270	35.3%
Mo	99.5% +	-270 +325	23.0%
		-325	18.7%
NICKEL:			
Lot No.	90A-022	<u>Screen Analysis:</u>	
Alloy	AP-575 Type "A"	+270	6.1%
		-270 +325	14.7%
		-325	79.2%
FINAL BLEND:			
Lot No.	90A-029		
Hall Flow	22 s/50g		
Bulk Density	2.57 gcm ⁻³		

Table 12. Specifications for GTE SA-110 Mo - MoO₂ powder.

Lot No.	K-188S	<u>Screen Analysis:</u>	
Hall Flow	32 s/50g	+270	1.5%
Bulk Density	2.32 gcm ⁻³	-270 +325	18.6%
O ₂	10.07%	-325	79.9%

Figure 27. SEM micrograph of GTE SA-901 Mo - 25% Ni powder, showing Mo line scan across the center of the image. The powder is a mixture of Mo particles ("spongy" agglomerations) with Ni particles containing Cr, Si and Fe.

The microstructure of the air plasma sprayed Mo-Ni coating is shown in Figure 28. The coating was clearly two phase (lighter phase: Mo), with little or no mixing of the two metallic components. The coating contained some coarse porosity/pull-out, but little unmelted material. Inter-splat and inter-phase bonding was excellent. X-ray diffraction of the coating showed only the cubic phases of Mo and Ni. The microhardness of the coating was 510 kgfmm^{-2} , which was low compared to many of the other coatings evaluated.

Figure 29 shows the same powder sprayed by HVOF (Top Gun). The "spongy" character of the Mo powder was retained to a much greater degree in this coating, indicating that the powder was not melted as completely as in the plasma spray process. However, porosity levels, inter-splat bonding and bonding to the substrate were approximately the same as for the plasma sprayed coating. X-ray diffraction again showed cubic Mo and Ni. The microhardness of the HVOF coating was 540 kgfmm^{-2} : similar to the plasma sprayed coating.

Early commercial processes for wire spraying molybdenum coatings with an oxy-fuel torch tended to produce oxidation, resulting in the incorporation of MoO_2 in the coating, giving increased wear resistance compared to pure molybdenum. Plasma spray processes, although allowing much greater flexibility in powder selection and improved coating density, tend not to produce as much oxidation. Thus, Mo - MoO_2 composite powders were developed to produce plasma sprayed coatings with wear properties similar to wire sprayed materials. For this program, a Mo - MoO_2 powder containing 10.07% oxygen (GTE SA-110) was obtained, and coatings were sprayed by air plasma spray (parameters listed in Table 14).

The SA-110 Mo - MoO_2 powder was found to comprise agglomerations of smaller particles (Figure 30). The air plasma sprayed coating (Figure 31) showed evidence of some unmelted material and large pores. Inter-splat adhesion was not as good as for the Mo - Ni materials, as evidenced by a pronounced degree of inter-splat microcracking and voiding. Faint differences in image grey scales within the coating are indicative of varying oxygen content: the more oxygen, the darker the image. X-ray diffraction of the coating showed a mixture of cubic Mo and monoclinic MoO_2 . The Mo - MoO_2 coating was considerably harder (770 kgfmm^{-2}) than the Mo - Ni coatings.

Table 13. Spray trial parameters for APS Mo-Ni and Mo-MoO₂ coatings.
 Miller Thermal SG 100 plasma gun
 Gun configuration 145/129/113
 Powder gas: 25 - 30
 Arc gas: 50
 Helium: 50

Test	Feed Rate	Amps	Spray Distance (in.)
1	1.5	500	2.5
2	2.0	500	2.5
3	2.5	500	2.5
4	1.5	550	2.5
5	2.0	550	2.5
6	2.5	550	2.5
7	1.5	600	2.5
8	2.0	600	2.5
9	2.5	600	2.5
10	1.5	500	3.0
11	2.0	500	3.0
12	2.5	500	3.0
13	1.5	550	3.0
14	2.0	550	3.0
15	2.5	550	3.0
16	1.5	600	3.0
17	2.0	600	3.0
18	2.5	600	3.0
19	1.5	500	3.5
20	2.0	500	3.5
21	2.5	500	3.5
22	1.5	550	3.5
23	2.0	550	3.5
24	2.5	550	3.5
25	1.5	600	3.5
26	2.0	600	3.5
27	2.5	600	3.5
28	1.5	500	4.0
29	2.0	500	4.0
30	2.5	500	4.0
31	1.5	550	4.0
32	2.0	550	4.0
33	2.5	550	4.0
34	1.5	600	4.0
35	2.0	600	4.0
36	2.5	600	4.0

Table 14. Optimized spray parameters for APS Mo-Ni and Mo-MoO₂ coatings.
 Miller Thermal SG 100 plasma gun
 Gun configuration 145/129/113
 Powder gas: 25 - 30
 Arc gas: 50
 Helium: 50

Arc Current	Arc Voltage	Plasma Gas	Hopper		Spray Distance (in.)
			RPM	Pressure (psi)	
650	37	Ar/He	2.0	30	3.0

Table 15. An example of Top Gun HVOF deposition parameters.

Material:	Molybdenum	Timer 3 oxygen to ramp fuel	1.00
Particle size:	-325 + 15	Timer 4 ramp fuel to main fuel	1.50
Spray distance:	6"	Timer 10 oxygen to ramp fuel	0.10
Traverse speed:	1200 ipm	Timer 5 main fuel to main carrier	0.30
Increment:	.100	Timer 6 water delay after shut-down in auto	20.0
Number of passes:	22	Timer 34 oxygen delay after shut-down in auto	2.00
Powder feed rate:	20 g/m 1.30 rpm		
Coating thickness:	.012	Deposit efficiency:	40%

	Oxygen	Propylene	Hydrogen	Acetylene	Carrier	Water	Temperature (°F)
Gun back pressure	96	0	0	10	27	150	IN 72
Flow	500 SCFH	0 SCFH	0 SCFH	95 SCFH	35 SCFH	7 GPM	OUT 86
Ignition flow:	30	N/A	110	N/A	30 SCFH 9 psi	N/A	N/A
Ramp flow	200	0	0	60	N/A	N/A	N/A
Supply pressure	150	0	150	15	100		68

Figure 28. *Microstructure of BIRL APS Mo - 25% Ni coating (SEM, backscattered electron). The coating is two-phase (lighter phase Mo), with some coarse porosity/pull-out.*

Figure 29. *Microstructure of BIRL HVOF (Top Gun) Mo - 25% Ni (SEM, backscattered electron). Microstructure similar to Figure 28, the Mo phase retaining more of the powder texture.*

Figure 30. SEM micrograph of agglomerated GTE SA-110 Mo - MoO₂ powder.

Figure 31. Microstructure of BIRL APS Mo-MoO₂ coating (SEM, backscattered electron image). Unmelted particles, large pores and inter-splat cracks are visible. The higher the oxygen content, the darker the image.

2.2.2 Chromium Oxide and Chromium Oxide-Aluminum Oxide Coatings

Chromium oxide coatings were sprayed by air plasma and HVOF (Top Gun), using a powder of high purity and closely-controlled, fine grain size. Plasma spray parameters are detailed in Tables 16 and 17.

The plasma sprayed chromium oxide is shown in Figure 32. The coating was found to be extremely dense compared to other chromium oxides evaluated. Porosity was rounded in character, rather than elongated parallel to the splats, and was evenly distributed. Inter-splat bonding was excellent in this coating. X-ray diffraction showed the dominant phase to be α -Cr₂O₃. The microhardness of this coating (1440 kgfmm⁻²) was high compared to other chromium oxides (Table 2), probably due to the high density.

The HVOF coating (Figure 33) was similar to the plasma sprayed coating, the porosity being a little finer and the microhardness a little lower (1320 kgfmm⁻²). In all other respects, the coatings were identical.

A pre-alloyed (fused and crushed) Cr₂O₃ - 50% Al₂O₃ powder was obtained to investigate the effects of solid solution alloying. Although the powder appeared uniform in composition (Figure 34), the plasma sprayed coating showed variations in grey scales suggesting that some segregation had occurred (Figure 35), either in the powder processing or in the plasma spray process. This powder proved to be very difficult to plasma spray, and impossible to spray by HVOF, possibly due to poor flow properties of the powder through the feeder. The plasma sprayed Cr₂O₃ - 50% Al₂O₃ showed a large amount of porosity and inter-splat voids/microcracks (Figure 35). The X-ray diffraction pattern from this coating was consistent with a solid solution based on α -Cr₂O₃ and α -Al₂O₃. The low microhardness (650 kgfmm⁻²) probably reflects the high porosity rather than inherent softness of the Cr₂O₃ - 50% Al₂O₃ material.

Table 16. Spray trial parameters for APS Cr₂O₃ and Cr₂O₃ - 50% Al₂O₃ coatings. Miller Thermal SG 100 plasma gun, gun configuration 165/129/113. Powder gas: 40, Arc gas: 50, Helium: 50

Test	Feed Rate	Amps	Spray Distance (in.)
1	1.5	800	2.5
2	2.0	800	2.5
3	2.5	800	2.5
4	1.5	800	3.0
5	2.0	800	3.0
6	2.5	800	3.0
7	1.5	800	3.5
8	2.0	800	3.5
9	2.5	800	3.5
10	1.5	800	4.0
11	2.0	800	4.0
12	2.5	800	4.0

Table 17. Optimized spray parameters for APS Cr₂O₃ and Cr₂O₃ - 50% Al₂O₃ coatings. Gun configuration 165/129/113. Powder gas: 40, Arc gas: 50, Helium: 50

Powder	Arc Current	Arc Voltage	Plasma Gas	Hopper		Spray Distance (in.)
				RPM	Pressure (psi)	
Cr ₂ O ₃	800	38	Ar/He	1.2	30	2.5
Cr ₂ O ₃ -Al ₂ O ₃	800	38	Ar/He	1.5	30	3.0

Figure 32. Microstructure of BIRL APS Cr₂O₃ coating (SEM, backscattered electron). The coating is extremely dense, with excellent inter-splat bonding.

Figure 33. Microstructure of BIRL HVOF (Top Gun) Cr₂O₃ (SEM, backscattered electron). Microstructure similar to that of the plasma sprayed coating (Figure 32).

Figure 34. SEM micrograph of Cr_2O_3 - 50% Al_2O_3 powder with X-ray line scans for Al (top) and Cr (bottom). The angular particles appear fairly uniform in composition.

Figure 35. Microstructure of BIRL APS Cr_2O_3 - 50% Al_2O_3 coating (SEM, backscattered electron). High levels of porosity and inter-splat de-bond are visible.

2.2.3 Alumina-Zirconia Coatings

Two alumina - zirconia compositions were evaluated: Al_2O_3 - 25.7% ZrO_2 and Al_2O_3 - 41.4% ZrO_2 (approximately the eutectic composition). The Al_2O_3 - ZrO_2 system exhibits a deep eutectic, the eutectic temperature being approximately 1710°C compared to melting points of 2040 and 2700°C, respectively, for Al_2O_3 and ZrO_2 [13]. The two compositions selected should be within the two phase region of the phase diagram (Al_2O_3 and ZrO_2 solid solutions). The solubility of ZrO_2 in Al_2O_3 is reported to be less than 1% and up to 7% Al_2O_3 is soluble in ZrO_2 [13].

Powders were obtained from Japan Abrasives, and were designated PC-AZ (Al_2O_3 - 25.7% ZrO_2) and PC-AZE (Al_2O_3 - 41.4% ZrO_2). A SEM image of the Al_2O_3 - 25.7% ZrO_2 powder is shown in Figure 36. Some of the particles appear to show a ZrO_2 -rich shell surrounding a core of Al_2O_3 -rich material. By comparison, the Al_2O_3 - 41.4% ZrO_2 powder was much more uniform (Figure 37), most particles showing a fine eutectic microstructure. Both powders contained small amounts of Ti, as revealed by EDS.

Both powders were plasma sprayed using the parameters listed in Table 18. Coatings were of exceptionally high quality in terms of low porosity, inter-splat adhesion and bonding to the substrate. Both coatings were optically translucent.

The Al_2O_3 - 25.7% ZrO_2 coating, shown in Figure 38, showed compositional variations consistent with those observed in the starting powder. In the backscattered electron image, ZrO_2 -rich material images lighter than Al_2O_3 -rich material. The Al_2O_3 - 41.4% ZrO_2 coating (Figure 39) showed a fine-scale eutectic microstructure in many locations, with some more uniformly imaging regions which may be single phase or too finely dispersed to resolve. In addition to a few larger inter-splat pores, this coating contained small, spherical ("pin hole") porosity within splats and at splat boundaries.

X-ray diffraction of the Al_2O_3 - ZrO_2 coatings revealed some interesting information. The powders both showed mixtures of α - Al_2O_3 with tetragonal and monoclinic ZrO_2 . The as-sprayed Al_2O_3 - 25.7% ZrO_2 coating showed weak γ - Al_2O_3 peaks, but appeared largely amorphous (Figure 40), showing no ZrO_2 peaks. The Al_2O_3 - 41.4% ZrO_2 coating, on the other hand, revealed a mixture of α - Al_2O_3 and cubic and/or tetragonal zirconia (Figure 41). Heat treating the Al_2O_3 - 25.7% ZrO_2 coating at 400°C for one hour resulted in larger γ - Al_2O_3 peaks and the appearance of some weak cubic/tetragonal ZrO_2 (Figure 42). Heat treating the Al_2O_3 - 41.4% ZrO_2 coating under the same conditions resulted in essentially no change in the XRD pattern (Figure 43). Comparing the Al_2O_3 - 25.7% ZrO_2 and Al_2O_3 - 41.4% ZrO_2 coatings, it is evident that the dominant alumina phase is gamma for the former and alpha for the latter (Figure 44). A further series of heat treatments at 600 and 800°C (for one hour) gave the same results as for the 400°C treatment. After heat treating at 1000°C, however, both coatings showed large tetragonal/cubic zirconia peaks, of much greater intensity than the alumina peaks (Figures 45 and 46). Again, the dominant alumina phases were gamma for the Al_2O_3 - 25.7% ZrO_2 coating and alpha for the Al_2O_3 - 41.4% ZrO_2 material.

Thus, it would appear that the Al_2O_3 - 25.7% ZrO_2 coating was largely amorphous as-sprayed. Gamma alumina crystallized fairly readily in this coating at or below 400°C, but the zirconia phase remained largely amorphous until 800 - 1000°C. The Al_2O_3 - 41.4% ZrO_2 coating contained more crystalline material as-sprayed: some crystalline zirconia was present, and the dominant alumina phase was alpha. Again, crystallization of the remaining amorphous zirconia phase did not occur until 800 - 1000°C. The microhardness values of the two as-sprayed coatings were 1050 kgfmm⁻² for the Al_2O_3 - 25.7% ZrO_2 coating and 840 kgfmm⁻² for the Al_2O_3 - 41.4% ZrO_2 .

It would have been interesting to conduct wear tests with the 1000°C heat treated samples in order to investigate the effects of crystallinity on wear. Unfortunately, the coatings debonded from the substrates during the heat treatment and could not be tested.

Table 18. Optimized spray parameters for APS Al_2O_3 - ZrO_2 coatings.
Miller Thermal SG 100 plasma gun

Arc Current	Arc Voltage	Plasma Gas	Hopper		Spray Distance (in.)
			RPM	Pressure (psi)	
600	36	Ar/He	1.5	30	3.5

Figure 36. SEM micrograph of PC-AZ Al_2O_3 - 25.7% ZrO_2 powder, with line scans for Zr (top), Al (middle) and Ti (bottom). Some particles appear "cored", with a ZrO_2 -rich shell.

Figure 37. SEM micrograph of PC-AZE Al_2O_3 - 41.4% ZrO_2 powder with line scans for Ti (top), Al (middle) and Zr (bottom). Many particles show a fine eutectic microstructure.

Figure 38. Microstructure of BIRL APS Al₂O₃ - 25.7% ZrO₂ coating (SEM, backscattered electron). Good inter-splat bonding. Segregation as for powder (lighter phase ZrO₂-rich).

Figure 39. Microstructure of BIRL APS Al₂O₃ - 41.4% ZrO₂ coating (SEM, backscattered electron). Good inter-splat bonding. Fine-scale eutectic microstructure visible in many locations.

Figure 40. X-ray diffraction pattern of APS Al_2O_3 - 25.7% ZrO_2 coating, as-sprayed. Pattern shows weak γ - Al_2O_3 peaks, but no crystalline ZrO_2 phases.

Figure 41. X-ray diffraction pattern of APS Al_2O_3 - 41.4% ZrO_2 coating, as-sprayed. Pattern shows α - Al_2O_3 peaks with cubic/tetragonal ZrO_2 .

Figure 42. X-ray diffraction patterns for APS Al_2O_3 - 25.7% ZrO_2 coating, as-sprayed (blue) and after 1 hour at 400°C (orange). The heat treatment resulted in larger γ - Al_2O_3 peaks, and the formation of some weak cubic/tetragonal ZrO_2 peaks.

Table 19. JCPDS files used for the analysis of APS Al_2O_3 - ZrO_2 coatings.

Al_2O_3		ZrO_2	
10-173	α - Al_2O_3	27-997	F- ZrO_2
10-425	γ - Al_2O_3	24-1164	T- ZrO_2
		36-420	M- ZrO_2

Figure 43. X-ray diffraction patterns for APS Al_2O_3 - 41.4% ZrO_2 coating, as-sprayed (orange) and after 1 hour at 400°C (blue). The heat treatment caused no phase changes.

Figure 44. X-ray diffraction patterns for Al_2O_3 - 25.7% ZrO_2 (blue) and Al_2O_3 - 41.4% ZrO_2 (orange) coatings, after 1 hour at 400°C. The dominant Al_2O_3 phases are γ and α , respectively.

Figure 45. X-ray diffraction patterns for APS Al_2O_3 - 25.7% ZrO_2 coating after 1 hour at 1000°C. The heat treatment resulted in the formation of large cubic/tetragonal ZrO_2 peaks.

Figure 46. X-ray diffraction patterns for APS Al_2O_3 - 41.4% ZrO_2 coating after 1 hour at 1000°C. The heat treatment resulted in the formation of large cubic/tetragonal ZrO_2 peaks.

2.2.4 Laser Processed Alumina-Zirconia Coatings

Lasers or electron beams appear to be suitable tools for densifying the surface of coatings without affecting the substrate. Their extremely high energy densities can be used to melt a very thin surface layer and, under certain conditions, cause rapid re-solidification.

Features of laser treatment processes include:

1. High energy densities are applied to the surface over very short contact times.
2. For materials with a deep eutectic the quench rate is sufficient for the liquid to supercool to the glass transition temperature and form an amorphous microstructure upon solidification.
3. Where crystallization does occur, an extremely fine-grained microstructure can be produced, with improved wear and corrosion properties in some cases.
4. Supersaturated solid solutions can be formed.
5. For ceramic coatings, laser glazing provides the opportunity to produce smoother, denser, more homogeneous surface layers with compressive surface stresses.
6. For metallic and cermet systems, laser processing is a method of increasing hardness or causing non-equilibrium reactions to occur which may create novel microstructures.

The alumina-zirconia system was selected as a good candidate for laser glazing, since the system has a deep eutectic, and possibilities exist for producing novel phase distributions. Since the as-sprayed coatings were found to contain amorphous phases, there was interest in whether these phases could be crystallized using laser treatment processes and, if so, what phases would be formed.

All samples were glazed using an ElectroX 1200 W laser operating with helium shielding gas at 10^{10} W cm⁻² power density and 2×10^{-10} s contact time.

X-ray diffraction patterns for the laser processed Al₂O₃ - 25.7% ZrO₂ and Al₂O₃ - 41.4% ZrO₂ coatings are shown in Figures 47 and 48. The laser treatment crystallized the surface layers of both coatings to produce mixtures of mostly tetragonal ZrO₂ and α -Al₂O₃. It is interesting that the laser treatment produced a different alumina phase than conventional heat treating for the Al₂O₃ - 25.7% ZrO₂ coating.

SEM images of the laser processed coating surfaces and cross sections through the coatings are shown in Figures 49 - 52. There was little evidence of surface melting, except perhaps for localized regions on the Al₂O₃ - 41.4% ZrO₂ coating (Figure 52). For both coatings, networks of 50 - 100 μ m deep radial cracks were formed at the surface due to the thermal shock associated with the laser treatment. The effect of these crack networks was to roughen the surface considerably, rather than produce a "glaze". In fact, the surface roughness was too high for meaningful wear tests to be conducted with these samples. Unfortunately, the surfaces could not be lapped without removing the laser-affected regions.

Figure 47. X-ray diffraction pattern of laser-processed APS Al_2O_3 - 25.7% ZrO_2 coating. The pattern shows a mixture of mostly tetragonal ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$.

Figure 48. X-ray diffraction pattern of laser-processed APS Al_2O_3 - 41.4% ZrO_2 coating. The pattern shows a mixture of mostly tetragonal ZrO_2 and $\alpha\text{-Al}_2\text{O}_3$.

Figure 49. Section through BIRL laser processed APS Al_2O_3 - 25.7% ZrO_2 coating (SEM, backscattered electron image), showing thermal shock cracks.

Figure 50. Surface of BIRL laser processed APS Al_2O_3 - 25.7% ZrO_2 coating (SEM, backscattered electron image), showing thermal shock cracks.

Figure 51. Section through BIRL laser processed APS Al_2O_3 - 41.4% ZrO_2 coating (SEM, backscattered electron image), showing thermal shock cracks.

Figure 52. Surface of BIRL laser processed APS Al_2O_3 - 41.4% ZrO_2 coating (SEM, backscattered electron image), showing thermal shock cracks.

2.3 COATING DEVELOPMENT AT BOYD MACHINE AND REPAIR COMPANY, INC.

2.3.1 Chromium Oxide Coating

The microstructure of the Boyd chromium oxide coating contained a substantial amount of unmelted particles, as evidenced by equiaxed regions containing porosity and a very fine-scale microstructure (Figure 53). Inter-splat microcracking was average for plasma sprayed chromium oxides, but the coating contained a relatively high concentration of large pores.

Figure 53. *Microstructure of Boyd plasma sprayed chromium oxide coating (SEM, backscattered electron image), showing a high proportion of unmelted particles (fine, equiaxed microstructure) and high porosity.*

2.3.2 Tungsten Carbide - Cobalt Coating

A WC - 12% Co coating was sprayed using a Jetkote II HVOF system. The resulting microstructure is shown in Figure 54. The coating showed almost continuous cracking at the substrate interface, indicating poor adherence (Figure 54). At 250 μm thickness, this coating was thicker than other WC - Co coatings evaluated, and it is speculated that the poor adherence was due to high residual stresses. The coating microstructure was comprised of 5 μm carbide particles in a Co and W-Co-C matrix with low levels of porosity (< 10%). SEM images (Figure 54) were similar to those for the APS Materials APS and LPPS WC - Co coatings described in section 3.1.2. X-ray diffraction revealed WC and $\alpha\text{-W}_2\text{C}$ phases (evidence of decarburization), with relatively little solutionizing of the carbides (Table 7, section 2.1.2). The hardness of the Boyd coating was 1120 kg/mm^2 (HK_{100}), which was comparable to many of the other WC - Co materials evaluated in this program.

Figure 54. Microstructure of Boyd HVOF WC - Co coating (SEM, backscattered electron image). This coating shows a similar microstructure to the APS Materials APS and LPPS materials (Figures 10 and 11), with blocky carbides and evidence of several phases formed by solutionizing, re-precipitation and decarburization. The "matrix" phase is actually a W-Co-C phase in most regions. Cracking at the coating - substrate interface is evidence of poor adherence.

2.4 COATING DEVELOPMENT AT CUMMINS ENGINE COMPANY, INC.

Coating activities at Cummins focussed on the Kaman process silica-chromia-alumina coating. The coating was developed primarily for cylinder liner applications, since it was felt that the maximum thickness (approximately 20 μm) and the coating adherence would be insufficient for a piston ring coating.

The microstructure of a slurry-sprayed silica-chromia-alumina (SCA) coating prepared at Cummins is shown in Figure 55. The coating was produced by 12 densification cycles (impregnation with chromic acid followed by heating) with no surface finishing operations. The coating comprised a mixture of SiO_2 and Al_2O_3 particles from the original sprayed slurry with Cr_2O_3 formed in the densification cycles. Porosity levels were low. The grain size was approximately 5 μm , much less than the coating thickness (20 μm). A thin layer of pure Cr_2O_3 was formed on the surface, and in places extended into the bulk of the coating to fill cracks in the original slurry coating. The composition of the coating was determined by EDS analysis to be 55% Cr_2O_3 - 41% SiO_2 - 4% Al_2O_3 by weight.

X-ray diffraction was performed to compare the phase content of the present coating with a sample obtained from Kaman Sciences Inc. (Boulder, Colorado) (1986 vintage). The Cummins material was found to contain more Cr_2O_3 and less Al_2O_3 than the Kaman coating (Figure 56).

Figure 55. Microstructure of Cummins slurry-sprayed silica-chromia-alumina coating after 12 densification cycles (SEM, backscattered electron image). The coating comprises 5 μm grains of SiO_2 and Al_2O_3 from the original slurry, with a reaction-formed Cr_2O_3 matrix. A thin layer of pure Cr_2O_3 has formed on the surface.

Figure 56. X-ray diffraction patterns from Cummins (red - a) and Kaman Science (black - b) SCA coatings. The Cummins material was found to contain slightly more Cr_2O_3 and less Al_2O_3 than the Kaman coating.

2.5 COATING DEVELOPMENT AT IMPLANT SCIENCES CORPORATION

Diamond-like coatings were prepared using a proprietary ion-assisted CVD process. Substrate materials were H13 tool steel (cylindrical "ring" and flat "liner" samples) and pearlitic grey cast iron (flat "liner" samples only). Substrate materials were lapped prior to coating, since the surface finish of a thin coating of this type is often controlled by the finish of the substrate. SEM micrographs of the coating are shown in Figures 57 - 59. The coating was approximately 1 μm thick and highly uniform. In some locations, large areas of the coating had spalled from the substrate (Figure 58), indicating high residual stress and/or low coating adhesion. High residual stress would be expected because of the extremely high elastic modulus of diamond compared to other materials. At high magnification, the surface texture of the coating was characteristic of a sputtered surface, with shallow craters and ridges. This coating contained a low concentration of sub-micron crystallites, which are presumed to be diamond crystals. Information from the supplier suggested that this coating probably contained a substantial amount of amorphous carbon. The film was too thin for microhardness measurements.

Figure 57. Microstructure of Implant Sciences diamond-like coating (SEM, backscattered electron image). The coating thickness is approximately 1 μm .

Figure 58. As-coated surface of Implant Sciences diamond-like coating, showing spallation of the coating (SEM, backscattered electron image).

Figure 59. As-coated surface of Implant Sciences diamond-like coating (SEM, backscattered electron). Occasional sub-micron crystallites (presumably diamond) are evident.

2.6 COATING DEVELOPMENT AT TURBINE METAL TECHNOLOGY INCORPORATED

2.6.1 Chromium Carbide - Nichrome Coating

A Cr_3C_2 - 20% NiCr powder was sprayed by a proprietary HVOF process at Turbine Metal Technology (TMT). The powder was a mixed Cr_3C_2 + (Ni - 20% Cr) material, as shown in Figure 60. The HVOF coating (Figure 61), although fairly dense, was very inhomogeneous, showing large unmixed regions of Cr_3C_2 and Ni-Cr reflecting the mixture present in the original powder blend. A better dispersion of the carbide in the matrix phase would have been obtained with a clad powder, where each carbide particle would be pre-coated with the metallic binder phase. Grey-imaging phases elongated parallel to the splats may be evidence of oxidation of the matrix phase or of carbide melting or solutionizing (Figure 61). The microhardness of the coating was 500 kgfmm^{-2} (HK_{100}), which was low compared to the UTRC Cr_3C_2 - 20% NiCr coating sprayed from a clad powder, and probably reflects the compositional inhomogeneity of the coating.

Figure 60. SEM micrograph of Turbine Metal Technology HVOF Cr_3C_2 - 20% NiCr powder, showing X-ray line scans for Cr (top) and Ni (bottom). The powder was a mixed Cr_3C_2 + 20% (Ni - 20% Cr) material.

Figure 61. Microstructure of Turbine Metal Technology HVOF Cr_3C_2 - 20% NiCr coating (SEM, backscattered electron image). The coating shows substantial inhomogeneity. Grey-imaging phases elongated parallel to the splats may be evidence of oxidation of the matrix phase or of carbide melting or solutionizing.

2.6.2 Tungsten Carbide - Cobalt Coating

A WC - 12% Co powder was sprayed by a proprietary HVOF process at Turbine Metal Technology. The powder appears to be a very uniform, fine grained sintered and crushed material (Figure 62). The fine grain size of the HVOF coating (Figure 63) reflects that within the powder. Porosity levels were extremely low and adherence to the substrate was good. X-ray diffraction revealed WC, WC_{1-x} and $\text{Co}_6\text{W}_6\text{C}$ phases, with comparatively little oxidation and/or solutionizing (Table 7, section 2.1.2). The microhardness of the TMT coating was 960 kgfmm^{-2} (HK_{100}), which was similar to many of the other WC - Co materials evaluated in this program.

Figure 62. SEM micrograph of TMT WC - 12% Co powder. The powder appears to be a very uniform, fine grained sintered and crushed material.

Figure 63. Microstructure of Turbine Metal Technology HVOF WC - 12% Co (SEM, backscattered electron), showing fine grain size, low porosity and good adherence to the substrate.

2.6.3 Boride Diffusion Coating

Attempts were made to boride diffusion alloy the HVOF WC - Co coating described above. The process resulted in an interesting microstructure (Figure 64), with a 10 μm thick darker imaging surface layer, and a 20 μm thick lighter-imaging second layer. The inter-phase regions were highly porous. WDS analysis of the coating showed no evidence of the original WC - Co coating, since no Co was present, and only W levels consistent with the 422 stainless steel substrate (0.23% C, 12% Cr, 1% Mo, 1% W, 0.8% Ni, 0.25% V, bal. Fe). It is speculated that the WC - Co coating may have de-bonded from the substrate during the diffusion treatment. The surface layers of the boride coating were found to contain iron, chromium and carbon (from the 422 stainless steel substrate) and boron. WDS line scans for these elements are shown in Figures 65 - 68. The darker-imaging top layer contained a higher concentration of boron than the lighter-imaging second layer and a slightly lower Iron content. Chromium appeared to be randomly distributed through the surface layers. Carbon appeared to be concentrated at the interface between the two layers. The hardness of the coating, measured with 25 gf Knoop indentations in the lighter-imaging second layer, was approximately 1490 kgfmm^{-2} .

Figure 64. Microstructure of Turbine Metal Technology boride diffusion coating (SEM, backscattered electron image), showing various surface layers of different compositions.

Figure 65. *Turbine Metal Technology boride diffusion coating: backscattered electron image with WDS line scan for Fe $K\alpha$.*

Figure 66. *Turbine Metal Technology boride diffusion coating: backscattered electron image with WDS line scan for Cr $K\alpha$.*

Figure 67. *Turbine Metal Technology boride diffusion coating: backscattered electron image with WDS line scan for C K α .*

Figure 68. *Turbine Metal Technology boride diffusion coating: backscattered electron image with WDS line scan for B K α .*

2.7 COATING DEVELOPMENT AT UNITED TECHNOLOGIES RESEARCH CENTER (UTRC)

2.7.1 Chromium Carbide - Nichrome Coating

A Metco Diamalloy 3007 Cr_3C_2 - 20% NiCr powder, in which each Cr_3C_2 particle was first clad with Ni and then with Cr metal, was sprayed with a Metco "Diamond Jet" HVOF system. The coating was found to comprise an even distribution of fine (approximately 8 μm diameter) chromium carbide particles in a NiCr matrix, with little carbide solutionizing and very low (approximately 1%) porosity levels (Figure 69). The microhardness of the coating was 990 kgfmm^{-2} , comparable to the hardness of the WC - 12% Co coatings, and higher than for the TMT HVOF Cr_3C_2 - 20% NiCr sprayed from a mixed powder.

Figure 69. Microstructure of UTRC HVOF Cr_3C_2 - 20% NiCr coating (SEM, backscattered electron image). The coating was homogeneous, with little carbide solutionizing and very low porosity levels

2.7.2 Zirconia-Titania-Yttria Coating

A Metco 143 ZrO_2 - 18% TiO_2 - 10% Y_2O_3 (ZTY) powder was plasma sprayed. The coating was less porous than many of the chromium oxide coatings evaluated, but showed very poor inter-splat bonding as evidenced by a "brick wall" type of inter-splat microcrack distribution (Figure 70). A small amount of unmelted powder was present in the coating, associated with large pores. The backscattered electron signal from this material showed substantial variations in atomic number contrast within the coating (Figure 70), suggesting inhomogeneity of the starting powder. Also, a series of 10gf Knoop microhardness indentations showed extreme variations in microhardness (from 390 to 1180 kgfmm^{-2}) across the microstructure (Figure 71). This variation is not thought to have been caused solely by interactions with cracks/pores, but may reflect a high degree of compositional inhomogeneity and/or the presence of amorphous material within the coating. X-ray diffraction showed the presence of a cubic ZrO_2 -based solid solution, but it is possible that amorphous phases may also have been present, as for the Al_2O_3 - ZrO_2 coatings. The mean hardness of the coating (450 kgfmm^{-2}) was surprisingly low compared to other ceramic coatings evaluated.

Approximately 10% of the ZTY test samples were found to have cracked or chipped to some degree during grinding of the coating, ranging from complete de-bond to small corner chips. Bonding of the ceramic materials to the substrate (422 stainless steel) was generally poor, as revealed by light microscopy of the interface, but may be improved by the use of a bond coat (none was used for these samples).

Figure 70. Microstructure of UTRC plasma sprayed ZrO_2 - 18% TiO_2 - 10% Y_2O_3 coating (SEM, backscattered electron image). The coating showed very poor inter-splat bonding with substantial inter-splat microcracking. A small amount of unmelted powder was present, associated with large pores. Compositional inhomogeneity was revealed by the atomic number contrast between different grains.

Figure 71. 10gf Knoop indentations in UTRC plasma sprayed ZrO_2 - 18% TiO_2 - 10% Y_2O_3 coating (light micrograph - Nomarski d.i.c.), showing substantial variations in microhardness (from 390 to 1180 kgfmm^{-2}) across the microstructure.

2.7.3. Chromium Oxide Coating

A coating was plasma sprayed from a Metco 106 FP Cr_2O_3 powder containing 2% SiO_2 and 2% other oxides. The coating showed high porosity levels (approximately 20%) with extensive networks of inter-splat cracks and voids, with apparently loose material trapped in the microstructure (Figure 72). Adherence to the substrate was poor, primarily because no bond coat was used for this coating. The microhardness of this coating was low ($850 \text{ kgfmm}^{-2} \text{ HK}_{100}$) compared to other chromium oxides evaluated, probably due to the high porosity rather than intrinsic softness of the material.

Figure 72. Microstructure of UTRC plasma sprayed Cr_2O_3 coating (SEM, backscattered electron image). The coating showed high porosity levels with extensive networks of inter-splat cracks and voids, with apparently loose material trapped in the microstructure.

2.7.4 Nickel-Chromium-Boron-Silicon Coating

A Diamalloy 2001 NiCrBSi powder was sprayed using a Metco "Diamond Jet" HVOF system. The coating showed some coarse porosity, primarily associated with a high volume fraction of unmelted powder particles (Figure 73). Porosity/pullout occurred within the unmelted particles and at the interface between unmelted and melted material. The microstructure showed an extremely fine dispersion of sub-micron sized low atomic number particles (presumably carbides or borides) in a metallic matrix (Figure 73). The coating microhardness was relatively high: 900 kgfmm⁻² HK₁₀₀.

Figure 73. *Microstructure of UTRC HVOF NiCrBSi coating (SEM, backscattered electron image), showing coarse porosity associated with a high volume fraction of unmelted powder particles. Porosity/pullout occurred within the unmelted particles and at the interface between unmelted and melted material. The microstructure showed an extremely fine dispersion of sub-micron sized low atomic number particles (presumably carbides or borides).*

2.7.5 Property Measurements

In any coatings development effort, it is important to have reliable materials property data to facilitate thermal and stress modelling. UTRC have used this "engineered coatings" approach successfully in many applications, including abradable seal coatings for gas turbine engines and thermal barrier coatings for diesel engines. Thermal and mechanical property measurements were made for HVOF $\text{Cr}_3\text{C}_2\text{-NiCr}$ and NiCrBSi coatings and plasma sprayed zirconia-titania-yttria (ZTY) coatings. Properties were measured on free-standing coating materials sprayed to 2.5 mm thickness and removed from the substrate. Attempts were also made to produce thick chromium oxide coatings for evaluation, with no success. The properties measured were: four point bend strength (Figure 74), four point strain to failure (Figure 75), four point bend modulus (Figure 76), thermal expansion coefficient (Figure 77), thermal conductivity (Figure 78) and specific heat capacity (Figure 79). Mechanical properties were determined at room temperature and 316°C, while thermal properties were determined from room temperature to 538°C.

The tensile stress-strain response during four-point bending was linear regardless of test temperature for the three coatings. The average four-point tensile bend strength for both NiCrBSi and ZTY remained relatively constant with temperature up to 316°C, at approximately 620 and 70 MPa, respectively (Figure 74). Not surprisingly, the ceramic ZTY coating had a significantly lower tensile loading capability than the metallic NiCrBSi coating. The mean tensile bend strength of $\text{Cr}_3\text{C}_2\text{-NiCr}$ at 316°C was slightly reduced relative to the room temperature value (534 vs 618 MPa) but was still comparable with the NiCrBSi material.

The mean strain-to-failure of the NiCrBSi system was approximately 50% higher than that of ZTY and more than 80% higher than for $\text{Cr}_3\text{C}_2\text{-NiCr}$ (Figure 75). The higher strain capacity of NiCrBSi may make the coating more accommodating to tensile loads. In absolute terms, the mean strain-to-failure values for ZTY and $\text{Cr}_3\text{C}_2\text{-NiCr}$ were comparable, but since the elastic modulus of $\text{Cr}_3\text{C}_2\text{-NiCr}$ was approximately five times higher than for ZTY, the $\text{Cr}_3\text{C}_2\text{-NiCr}$ tensile strength was significantly higher.

The mean elastic modulus of both the $\text{Cr}_3\text{C}_2\text{-NiCr}$ and ZTY coatings remained relatively constant up to 316°C (Figure 76), at approximately 162 and 33 GPa, respectively. The mean elastic modulus for NiCrBSi decreased slightly from 141 GPa at room temperature to 126 GPa at 316°C. The ceramic ZTY elastic modulus was substantially less than for the NiCrBSi and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings, probably due to the porosity and microcracking described above.

For all three coating systems, the coefficient of thermal expansion (CTE) was relatively constant from room temperature to 538°C (Figure 77). The mean CTE was greatest for NiCrBSi at $13.1 - 14.0 \times 10^{-6} \text{ K}^{-1}$, with $\text{Cr}_3\text{C}_2\text{-NiCr}$ next at $10.8 - 11.7 \times 10^{-6} \text{ K}^{-1}$ and ZTY the lowest at $9.4 - 9.9 \times 10^{-6} \text{ K}^{-1}$. These values are consistent based on general metallic and ceramic properties with the metallic NiCrBSi coating having a larger CTE than the ceramic ZTY.

As expected, the metallic and cermet coating materials had a significantly greater thermal conductivity than the ceramic ZTY material (Figure 78). The thermal conductivity of both NiCrBSi and $\text{Cr}_3\text{C}_2\text{-NiCr}$ increased substantially (by more than two times) from room temperature to 538°C. However, the thermal conductivity of ZTY remained essentially constant at $1 \text{ Wm}^{-1}\text{K}^{-1}$ over the evaluated temperature range.

Specific heat capacity increased with temperature for all three coating systems (Figure 79). $\text{Cr}_3\text{C}_2\text{-NiCr}$ had the greatest specific heat, followed by ZTY and NiCrBSi . The specific heat for $\text{Cr}_3\text{C}_2\text{-NiCr}$ was higher than expected, but the results were repeatable. In general, the specific heat capacity of a cermet material should lie between that for the ceramic and metallic phases. Possibly, the low porosity of this coating was a factor. However, this discrepancy did not affect the relative ranking of the thermal conductivity values which are calculated from a material's density, specific heat capacity and thermal diffusivity.

Figure 74. Variation of four point bend strength with temperature for UTRC coatings.

Figure 75. Variation of strain-to-failure with temperature for UTRC coatings.

Figure 76. Variation of four point bend modulus with temperature for UTRC coatings.

Figure 77. Variation of thermal expansion with temperature for UTRC coatings.

Figure 78. Variation of thermal conductivity with temperature for UTRC coatings.

Figure 79. Variation of specific heat capacity with temperature for UTRC coatings.

2.8 COATING DEVELOPMENT AT VAPOR TECHNOLOGIES INCORPORATED

Vapor Technologies deposited two ceramic coatings for evaluation using a proprietary cathodic arc physical vapor deposition process, which is designated "Low Temperature Arc Vapor Deposition" (LTAVD).

2.8.1 Chromium Nitride Coating

A LTAVD CrN coating was deposited to a thickness of approximately 4 μm (Figure 80) onto lapped H13 tool steel substrates. The substrate temperature used for processing these samples was approximately 350°C. A substantial amount of spallation of the coating was observed near the edges of some of the samples, indicating high residual stress or low adhesion (Figure 81). High magnification SEM images of the coating surface showed a typical "sputtered" surface, with shallow craters and ridges (Figure 82). In addition, several 5 μm sized Cr-rich macroparticles are observable on the coating surface (Figure 82). These macroparticles are a common feature for PVD coatings, and are caused by the formation of molten microdroplets in the vaporization of the metal from the target. Knoop microhardness values for a 10 gf load were approximately 1520 kgfmm^{-2} for the CrN coating, although it was questionable whether the coating was sufficiently thick for the measurements to be accurate.

Figure 80. Microstructure of Vapor Technologies LTAVD CrN coating (SEM, backscattered electron image). Coating thickness was approximately 4 μm .

Figure 81. *Low magnification image of as-coated surface of LTAVD CrN (SEM, backscattered). Some samples showed spallation, indicating high residual stress or low adhesion.*

Figure 82. *As-coated surface of Vapor Technologies LTAVD CrN (SEM, backscattered electron image), showing Cr macroparticles and "cratered" surface.*

2.8.2 Tantalum Nitride Coating

A LTAVD tantalum nitride coating was deposited to a thickness of approximately $3.2\text{ }\mu\text{m}$ (Figure 83) onto lapped H13 tool steel substrates. SEM images of the coating surface showed a high concentration of $5 - 15\text{ }\mu\text{m}$ sized Ta-rich macroparticles (Figure 84). Macroparticles were embedded in the coating more deeply than for the CrN coating. The tantalum nitride coating was too thin for microhardness measurements. The phase composition of the coating was investigated by X-ray diffraction (Figure 85). The closest match to the observed peaks was found to be hexagonal Ta_2N , with some metallic Ta also present, presumably due to the macroparticles. Some of the predicted Ta_2N peaks were absent, perhaps due to a preferred texture of the coating. Neither of the two TaN phases referenced in the JCPDS file (9-257 and 32-1283) gave good matches with the observed pattern.

Figure 83. Microstructure of Vapor Technologies LTAVD Ta_2N coating (SEM, backscattered electron image). Coating thickness was approximately $3\text{ }\mu\text{m}$.

Figure 84. As-coated surface of Vapor Technologies LTAVD Ta_2N coating (SEM, backscattered electron image), showing large Ta macroparticles and "cratered" surface.

Figure 85. X-ray diffraction pattern for Vapor Technologies LTAVD Ta_2N coating, showing peaks for hexagonal Ta_2N , with some metallic Ta.

3 EXPERIMENTAL PROCEDURES FOR WEAR EVALUATION

3.1 TRIBOLOGICAL TEST CONFIGURATION

Wear tests were performed using test conditions chosen to represent the ring-liner engine environment close to the top ring reversal position, and are detailed in Table 20. Tests were performed using a Cameron Plint TE77 reciprocating wear tester, shown schematically in Figure 86. The test geometry was a line contact cylinder against flat configuration, where the "piston ring" samples had a 50 mm cylindrical radius on the (coated) test face (Figure 87) and the "cylinder liner" samples were flat plates (Figure 88). This sample geometry was chosen for three reasons: (a) to simulate a barrel faced piston ring geometry, (b) for ease of sample fabrication and (c) to facilitate measurements on the "ring" samples after wear tests.

The test load of 225 N (30 Nmm^{-1}) was determined by estimating the maximum loading which would be experienced by the top compression ring at top dead center in a heavy duty diesel engine, making allowances for friction between the ring and piston groove. This level of loading is fairly high compared to that used by many laboratories for materials evaluation. In particular, the load used was approximately an order of magnitude higher than the "mild wear" to "severe wear" transition load found for unlubricated tests with many ceramic materials. For example, alumina is reported to show a transition to "ultra severe wear" (seizure) in the load range 10 - 100 N in dry air at a sliding speed of 0.3 ms^{-1} [14].

Table 20. Wear test conditions.

Test Schedule for Each Coating:
Fresh CE/SF 15W40 mineral oil lubricant, 200°C
Fresh CE/SF 15W40 mineral oil lubricant, 350°C
3.3% Soot Engine-tested CE/SF 15W40 oil, 200°C
Unlubricated, 200°C
Test Conditions:
225 N on a 7.5 mm wide sample (30 Nmm^{-1})
"Ring" samples crowned (50 mm radius of curvature)
"Liner" samples flat
5 mm stroke (2.5 mm amplitude)
20 Hz frequency
Speed at mid-stroke: 0.314 ms^{-1}
Lubricated tests: 6 hrs, 1 drop of oil every 10 seconds
Unlubricated tests: 5 minutes

Figure 86. Schematic of the reciprocating wear tests (Cameron Plint TE77 tester).

Figure 87. Simulated piston ring sample geometry.

Figure 88. Simulated cylinder liner sample geometry.

3.2 TRIBOLOGICAL TEST VARIABLES

After reviewing the literature on commercial piston ring coatings [e.g. 4], it became apparent that materials could score highly in some wear categories, but perform poorly in others. For example, a coating might be very "scuff resistant" but have only average wear resistance under well-lubricated conditions. Accordingly, it was decided to rank tribological properties under a multiplicity of test conditions, rather than comparing materials properties under one fixed test condition.

During the tribological testing program, emphasis was placed on the variables of greatest interest for diesel engine piston ring coatings: (1) lubricated wear rates as a function of temperature, (2) the effects of lubricant contamination and degradation on wear and (3) scuff resistance. For each coating, tests were conducted at 200 and 350°C with a fresh CE/SF 15W40 lubricant, at 200°C with a high-soot, engine-tested oil and at 200°C with no lubrication. The 200°C test temperature was selected to represent the top ring reversal temperature for a typical current commercial heavy duty diesel engine. The 350°C target temperature was selected to represent an advanced design low heat rejection engine with conventional liquid lubrication. 350°C was considered to be the highest temperature attainable with current lubricant technology. A liquid lubricated system is considered to be necessary for a high-durability (e.g. 1 million miles to first major overhaul) commercial engine. In addition to these tests, some of the most promising coatings were tested at 450°C with a synthetic (poly-alpha-olefin) lubricant, in order to demonstrate what might be possible with more advanced lubricant systems.

Lubricated tests were run with: (a) a fresh commercial CE/SF quality 15W40 mineral oil based lubricant and (b) a lubricant obtained from an experimental engine test, in order to assess the effects of oil contamination and degradation from a realistic diesel engine environment on wear of ring and liner materials. The starting lubricant used for this engine test was a CE/SF 15W40 mineral oil based lubricant with identical wear properties to fresh oil (a), but with a slightly different formulation. Characterization of the fresh and engine-tested oils is summarized in Table 21. The engine-tested oil was highly soot-loaded, with moderate levels of oxidation and little additive package depletion. Soot levels were higher than would normally be produced in a commercial engine.

In addition to the lubricated tests, materials were evaluated with no lubrication (at 200°C), in order to rank the sliding wear properties of different materials under "scuffing" conditions. A material with good scuff resistance is desirable in case of temporary loss of oil film in the engine (on start-up or under short duration conditions of extreme hot running, for example). Due to the high loads experienced at top ring reversal, it is generally accepted that dry wear coefficients are too high to permit extended engine operation without lubrication [15].

Although not treated explicitly as a test variable, a factor which is likely to have influenced wear rates of the coatings and especially of the comparatively soft liner material is the coating surface finish. This was found to be a function of the finish machining operations and also of the coating microstructure, porosity and microcrack content being critical. Initially, coatings were tested in the as-ground condition, with R_a values in the range 0.2 - 0.7 μm . As the program progressed, techniques for diamond lapping surfaces to better finishes (down to 0.02 μm in some cases) were developed. R_a values for each coating, measured parallel to and at 90° to the sliding direction, are listed in Tables 22 - 24. For as-ground surfaces, the sliding direction was always parallel to the grinding direction (the direction of minimum R_a).

Table 21. Properties of fresh and engine-tested lubricants used for wear tests.

Property	Fresh	Engine Tested
Viscosity, 40°C (cSt)	95.2	161.0
Viscosity, 100°C (cSt)	14.1	18.6
Viscosity Index	152	130
TBN (mg KOH/g)	6.8	4.2
TAN (mg KOH/g)	2.9	8.3
Zinc Content (ppm)	1800	1750
Phosphorus Content (ppm)	1480	1380
Calcium Content (ppm)	1500	960
Magnesium Content (ppm)	0	1280
Fe Wear Metal (ppm)	0	285
Cr Wear Metal (ppm)	0	10
TGA Soot (%)	0.5	3.3

Table 22. Surface roughness (R_a) of metallic ring coating materials evaluated

Coating	Supplier	Finish	R_a parallel to sliding direction (μm)	R_a 90° to sliding direction (μm)
Electroplated Chromium	Cummins	Ground	0.27 - 0.63	
APS Chromium	APS Materials	Lapped	0.694	1.047
HVOF NiCrBSi	UTRC	Ground	0.215	0.385
APS Mo-Ni	BIRL	Lapped	0.018	0.023
HVOF Mo-Ni	BIRL	Lapped	0.055	0.088
APS Mo-MoO ₂	BIRL	Lapped	0.194	0.232
APS Tribolite	APS Materials	Lapped	0.079	0.043
APS Armacor M	APS Materials	Ground	0.660	
APS Armacor T	APS Materials	Ground	0.881	

Table 23. Surface roughness (R_a) of ceramic ring coating materials evaluated

Coating	Supplier	Finish	R_a parallel to sliding direction (μm)	R_a 90° to sliding direction (μm)
APS Cr_2O_3	APS Materials	Ground Lapped	0.523 0.656	0.653
APS Cr_2O_3	BIRL	Lapped	0.022	0.019
HVOF Cr_2O_3	BIRL	Lapped	0.045	0.065
APS Metco 136 Cr_2O_3 - SiO_2 - TiO_2	APS Materials	Ground Lapped	0.448 0.344	0.350
APS Metco 136 + 3% SiO_2 (mix)	APS Materials	Lapped	0.574	0.554
APS Metco 136 + 15% Al_2O_3 (mix)	APS Materials	Ground Lapped	0.578 0.570	0.564
APS Cr_2O_3 - 50% Al_2O_3	BIRL	Lapped	0.201	0.195
APS Cr_2O_3 - 2% SiO_2 - 2% other ox.	UTRC	Ground	0.526	0.451
APS Boron Carbide	APS Materials	Lapped	0.894	0.986
APS ZrO_2 - 18% TiO_2 - 10% Y_2O_3	UTRC	Ground	0.495	0.561
APS Al_2O_3 - 26% ZrO_2	BIRL	Lapped	0.119	0.124
APS Al_2O_3 - 26% ZrO_2	BIRL	Laser Treated	0.368	0.333
APS Al_2O_3 - 41% ZrO_2	BIRL	Lapped	0.087	0.094
APS Al_2O_3 - 41% ZrO_2	BIRL	Laser Treated	2.194	1.892
Boride diffusion coating	BIRL - TMT	Lapped	0.664	0.563
LTAVD CrN	Vapor Tech	As coated	0.173	0.205
LTAVD Ta_2N	Vapor Tech	As coated	1.059	1.102
Diamond-like	Implant Sci	As coated	0.096	0.084

Table 24. Surface roughness (R_a) of cermet ring coating materials evaluated

Coating	Supplier	Finish	R_a parallel to sliding direction (μm)	R_a 90° to sliding direction (μm)
APS WC - 12% Co	APS Materials	Ground	0.315	0.710
LPPS WC - 12% Co	APS Materials	Ground	0.177	0.626
HVOF WC - 12% Co	APS Materials	Lapped	0.246	0.173
HVOF WC - 12% Co	Boyd Machine	Lapped	0.042	
HVOF WC - 12% Co	BIRL - TMT	Lapped	0.172	0.236
HVOF Cr_3C_2 - 20% NiCr	BIRL - TMT	Lapped	0.051	0.076
HVOF Cr_3C_2 - 20% NiCr	UTRC	Ground	0.182	0.416
LPPS Ferrotic CM TIC + Tool Steel	APS Materials	Lapped	0.159	0.146
LPPS Ferrotic CS40 TIC + MSS	APS Materials	Lapped	0.126	0.105
LPPS Ferrotic HT6A TIC + Ni Alloy	APS Materials	Lapped	0.130	0.092
APS Metco 136 + 33% Stellite 6 mix	APS Materials	Lapped	0.435	0.465

3.3 SELECTION OF THE COUNTERFACE MATERIAL FOR COATING WEAR TESTS

An important factor to be considered in evaluating the tribological properties of a piston ring coating material is the amount of wear it produces on the cylinder liner counterface. For optimum engine durability, low wear rates are required of both rings and liners, therefore a systems approach is necessary in materials selection, rather than simply minimizing the wear on one surface. Published engine test data for commercial piston ring coatings has shown that there is generally a trade-off between the wear rates of the ring coating and the cylinder liner material, the more wear resistant ring coatings generally giving higher liner wear [4].

Due to the large number of coatings evaluated and the multiplicity of test conditions, screening of ring coating materials was performed using one liner material as the counterface. The decision to test coated rings rather than coated liners was made primarily because current high speed diesel engines normally use a hard ring facing (typically electroplated hard chromium) sliding against a softer cylinder liner, although in some automotive, motorcycle and medium/low speed diesel engines, the reverse combination (coated liners and uncoated grey iron rings) is used. In order to maintain low oil consumption of the engine over a long service life (commonly greater than 500,000 miles to first major overhaul), it is essential to maintain certain critical dimensions of the ring profile. Liner wear depths are typically low enough with current materials that geometry and surface finishes (at least in the mid-stroke region) are not changed to the point of affecting oil consumption. For these reasons, the approach taken was to develop a highly wear resistant ring facing which would not cause increased liner wear compared to traditional materials. A conventional liner material (pearlitic grey cast iron) was selected as the sliding counterface for this program because it is likely that any new ring coating would have to be compatible with existing cylinder liner materials. Alternative liner materials and coatings were also evaluated for one ring coating: a HVOF Cr_3C_2 - 20% NiCr identified as providing the best combination of low ring and liner wear in the first round of testing with conventional liners.

The pearlitic grey cast iron material selected as the counterface for coating wear tests was chosen to be representative of materials used for heavy duty diesel engine cylinder liners. The chemical composition of the material is given in Table 25. The microstructure of this material consisted of predominantly type A graphite flakes in a matrix of fine pearlite with less than 5% ferrite. Carbides and steadite phases were less than 5% each. The hardness of this material was in the range 70 - 90 HRG. All grey cast iron test samples for this program were machined from cylinder liners in order to provide a realistic counterface for the wear tests. However, a common practice in diesel and automotive industries is to apply a thin manganese phosphate ("Lubrite") coating to the cylinder liners, to facilitate "break-in" of the engine. Except where otherwise stated, the wear tests performed during this program used uncoated (non-Lubrited) grey cast iron cylinder liners.

In addition to the coating evaluation tests, which all used the conventional cylinder liner material, a second series of tests was performed with various alternative cylinder liner counterface materials in order to optimize the system for lowest total wear (ring plus liner). Tests were conducted with only one ring coating, the UTRC HVOF Cr_3C_2 - 20% NiCr, which was selected because it gave one of the best combinations of low coating and liner wear in the initial screening tests. The coating was used in the as-ground condition, with a surface finish of $0.18 \mu\text{m}$ measured parallel to the sliding direction (the grinding direction) and $0.42 \mu\text{m}$ RA measured perpendicular to the sliding direction. The following liner materials were evaluated (see Table 25 for compositions):

1. pearlitic grey iron (70 - 90 HRG)
2. hardened grey cast iron (42 HRC)
3. high-phosphorus grey cast iron (79 - 83 HRG)
4. bainitic grey cast iron (88 - 90 HRG)
5. centrifugally cast H13 tool steel hardened to 50 HRC
6. a slurry-sprayed silica-chromia-alumina (SCA) coating (960 kg/mm^2 , HK_{100})
7. an ion-assisted CVD "diamond-like" coating supplied by Implant Sciences, Inc. The coating substrate was H13 tool steel.

Table 25. Chemical composition of cylinder liner materials evaluated.

Liner Material	C	Si	Mn	P	S	Mo	Ni	Cr	V
Pearlitic, Hardened Grey Irons	3.2 - 3.5	1.8 - 2.6	0.5 - 0.8	0.15 max	0.1 max	0 - 0.5	0 - 0.5	0.2 - 0.8	
High Phosphorus Grey Iron	3.2 - 3.5	1.8 - 2.3	0.5 - 0.8	0.6 - 0.9	0.1 max			0.15 - 0.4	
Bainitic Iron	2.6 - 2.8	1.1 - 1.6	0.8 max	0.08 max	0.08 max	1.0 - 1.5	1.0 - 1.5		
H13 Tool Steel	0.35	1.0	0.35			1.5		5.0	1.0

3.4 WEAR MEASUREMENT ERRORS AND TEST REPEATABILITY

For each test, wear volumes were determined from binocular microscope measurements of wear scar widths for the rings and by stylus profilometry (longitudinal and transverse directions) for the liners. Wear results were then expressed as wear coefficients, calculated by dividing the total volume of wear (mm^3) by the product of sliding distance (mm) and applied normal load (N).

Since wear coefficients were normally much lower for the ring coatings than for the pearlitic grey cast iron liners, measurement errors were greater for the coatings, particularly for the most wear resistant materials after the least severe tests (200°C with fresh oil). The equation relating wear volume to scar width for the crowned ring coating samples is:

$$V = l \left[R^2 \sin^{-1} \left(\frac{w}{2R} \right) - \frac{w}{2} \left(R^2 - \frac{w^2}{4} \right)^{1/2} \right]$$

where: V = wear volume (mm^3)
 l = breadth of sample (approximately 7.5 mm)
 R = crown radius (approximately 50 mm)
 w = scar width (mm).

Observing that this is a very non-linear function, estimates were made of the effect of scar width measurement error on volumetric wear (hence wear coefficient). For the lowest wear conditions, end-of-test scar widths were of the order of 0.5 mm with a measurement error of approximately ± 0.1 mm (representing the uncertainty in defining the edge of the wear scar, rather than the accuracy of reading the graticule in the microscope). This results in a potential measurement error of $\pm 60\%$ in the wear volume. For high wear conditions, scar widths of the order of 4 mm with the same measurement error would give a volumetric error of only $\pm 7.5\%$. Note that the maximum depth of wear would be only $0.16 \mu\text{m}$ for a 0.5 mm wide scar (less than many of the initial R_a values) and $10 \mu\text{m}$ for a 4 mm wide scar. One advantage of the sample geometry used, apart from simulating a barrel-faced piston ring, was that very small wear volumes could be measured relatively easily.

In addition to measurement errors, errors would also arise due to non-repeatability of tests (statistical scatter in the actual wear rates). This factor was not investigated at length, due to the already large test matrix, but an idea of the potential scatter (measurement error plus non-repeatability) is given by Table 26, which shows data for four repeat tests for electroplated chromium sliding against pearlitic grey cast iron with fresh oil at 350°C . The standard deviation for the wear coefficients was approximately 50% of the mean, indicating a high degree of scatter. In order to differentiate one material from another, a difference in wear coefficient of at least a factor of two would be required. Since the results often showed orders of magnitude differences between materials and test conditions, this does not invalidate the study, although subtle microstructural effects would probably not have been detected. Normally, only one test was completed for each coating and for each of the test conditions described above, although repeat tests were performed to establish consistency in many cases.

Table 26. Friction and wear coefficients for four repeat tests with electroplated chromium ring coatings sliding against pearlitic grey cast iron liners at 350°C with fresh oil.

	Ring Wear ($\text{mm}^3/\text{mm}/\text{N}$)	Liner Wear ($\text{mm}^3/\text{mm}/\text{N}$)	Friction Coefficient
	3.44×10^{-11}	7.09×10^{-9}	0.128
	9.96×10^{-11}	1.42×10^{-8}	0.148
	1.67×10^{-10}	7.73×10^{-9}	0.101
	1.47×10^{-10}	4.52×10^{-9}	0.103
Mean:	1.12×10^{-10}	8.39×10^{-9}	0.120
St. Deviation:	0.59×10^{-10}	4.12×10^{-9}	0.022
Standard Error:	0.29×10^{-10}	2.06×10^{-9}	0.011

4 WEAR TEST RESULTS

In this section, tribological data for the coatings evaluated are presented and discussed. Detailed discussion of wear mechanisms and microstructural effects is deferred to the Appendices, in which SEM micrographs of wear surfaces are presented.

4.1 RESULTS USING FRESH LUBRICANT

4.1.1 Piston Ring Coating Wear

A summary of wear results for all the coatings evaluated is shown in Figures 89 (200°C tests) and 90 (350°C tests). Ring and liner wear coefficients are shown for each material couple on a logarithmic scale. Under the test conditions imposed, all materials systems operated in the boundary lubrication regime at both test temperatures, with friction coefficients in the range 0.1 to 0.3. For the lubricant and oil supply rate used in these tests, the "scuffing" temperature (the temperature above which an oil film could not be maintained and friction coefficients in excess of 0.5 were measured) was approximately 360°C. Thus, the 350°C tests are very close to the scuffing limit of the mineral oil based lubricant.

Wear coefficients for the coatings investigated ranged over approximately three orders of magnitude (Figures 89 and 90). Broadly, the ranking of coatings was similar at both 200 and 350°C. In general, the lowest wear rates were obtained with ceramic and cermet materials and the highest wear rates with metallic thermal spray coatings, even though some of the metallic coatings showed comparatively high hardness levels (Table 1). There was virtually no correlation between microhardness and wear for these tests (Figure 3). Although many ceramic coatings performed well (e.g. CrN, Cr₂O₃), others were found to give much higher wear rates (e.g. zirconia - titania - yttria, boron carbide). No data are shown for the diamond-like material because the coating was removed from the substrate in all tests, presumably due to low bond strength.

The baseline for comparison of coating wear rates was electroplated hard chromium (EP Cr). Wear coefficients for EP Cr shown in Figures 89 and 90 were measured for sections machined from production piston rings sliding against pieces machined from grey cast iron cylinder liners, rather than the test geometry described in section 4.1. At 200°C, EP Cr was one of the more wear resistant materials compared to other coatings (Figure 89), but at 350°C many other materials gave better wear performance (Figure 90). The wear tests clearly showed that coating materials are available which would provide substantial improvements in wear resistance compared to the conventional materials, particularly at high temperatures. The LTAVD CrN, HVOF Cr₃C₂ - 20% NiCr and WC - 12% Co and APS Cr₂O₃ coatings all showed outstanding wear properties at both test temperatures.

Figure 89. Wear coefficients for various coatings sliding against pearlitic grey iron liners at 200°C. Tests were run with fresh CE/SF 15W40 mineral oil based lubricant.

Figure 90. Wear coefficients for various coatings sliding against pearlitic grey iron liners at 350°C. Tests were run with fresh CE/SF 15W40 mineral oil based lubricant.

4.1.1.1 Metallic Coatings

At 200°C, none of the thermally sprayed metallic coatings showed lower wear than electroplated hard chromium (Figure 89), although many showed only slightly higher wear. At 350°C, both Armacor coatings and the Mo - MoO₂ material showed superior wear properties to EP Cr (Figure 90). Note that the electroplated and plasma sprayed chromium showed virtually identical wear properties at the higher test temperature, despite the big difference in microhardness measured at room temperature (880 kgfmm⁻² for EP Cr versus 250 kgfmm⁻² for APS Cr). The plasma sprayed material was observed to contain substantial amounts of chromium oxide in a soft chromium matrix, which may have offset the difference in bulk hardness. Tribolite and Mo - Ni coatings showed comparatively high wear at 350°C, and would not be candidates for high temperature applications.

A surprising result was that wear coefficients for the HVOF NiCrBSi material were found to be high at both test temperatures, despite a relatively high Knoop microhardness of approximately 900 kgfmm⁻². The general lack of correlation between microhardness and wear suggests that some mechanism other than abrasion may be important for these test conditions. It is speculated that the wear mechanism may involve chemical interactions between the lubricant and the metal, for example. However, it would be instructive to repeat the correlation using high temperature hardness data.

4.1.1.2 Ceramic Coatings

Of the ceramic coatings studied, the LTAVD CrN gave the lowest wear coefficients at both test temperatures. Wear rates were approximately six times lower than for EP Cr at 200°C and forty times lower at 350°C. However, even these low wear rates would probably not compensate for the low thickness (4 µm) of this coating compared to typical thickness values of 150 µm for EP Cr.

Surprisingly, the LTAVD Ta₂N coating gave relatively high wear rates. In fact, for this coating, test durations had to be reduced to 30 minutes for 200°C fresh oil tests and 5 minutes for 350°C fresh oil and 200°C high-soot tests in order not to wear through the coating.

Chromium oxide coatings showed lower wear coefficients than for the baseline electroplated hard chromium material. Figures 89 and 90 show values for one of the best Cr₂O₃ materials, the BIRL air plasma sprayed coating. Microstructural effects on wear of chromium oxides are discussed in section 4.5.1. In addition to the Cr₂O₃-rich materials, a Cr₂O₃ - 50% Al₂O₃ coating, sprayed from pre-alloyed powder, was tested and found to give comparatively high wear coefficients, which is thought to be due to the high levels of porosity and microcracking in this coating.

Of the two Al₂O₃ - ZrO₂ coatings studied, the more crystalline eutectic composition (Al₂O₃ - 41.4% ZrO₂) gave wear coefficients two to three times lower than the largely amorphous Al₂O₃ - 26% ZrO₂ material, despite lower microhardness. The Al₂O₃ - 41.4% ZrO₂ coating gave lower wear rates than EP Cr at both test temperatures.

The zirconia - titania - yttria material gave consistently disappointing wear results, possibly due to the high degree of inter-splat cracking/voiding present in the coating (Figure 70, section 2.7.2), or to low hardness or chemical incompatibility with the lubricant. Wear surfaces showed an "etched" morphology, with evidence of fine-scale spallation and fracture, and no large contiguous load-bearing areas (see Appendix A3.4).

The boron carbide coating was found to be highly porous, giving extremely high wear coefficients due to the poor bonding of the powder particles. In many cases, the coating was completely removed by the end of the test. The wear properties of this coating were probably controlled by the microstructure, rather than intrinsic to boron carbide materials.

The boride diffusion coating was found to show very high wear in these tests, perhaps due to fracture of the highly porous surface layers.

4.1.1.3 Cermet Coatings

Several WC - 12% Co materials were evaluated, generally giving very low wear coefficients. Figures 89 and 90 show data for one of the best WC - Co coatings, the Turbine Metal Technology HVOF WC - 12% Co material. Microstructural effects are discussed in section 4.5.2.

The HVOF Cr_3C_2 - 20% NiCr coatings gave similar wear coefficients to the WC - 12% Co materials. Data for the UTRC material sprayed from clad powder is shown in Figures 89 and 90. Microstructural effects are discussed in section 4.5.3. Both WC - 12% Co and Cr_3C_2 - 20% NiCr coatings can be thermally sprayed to the same thickness as EP Cr, making these two coatings the top contenders for top compression ring facings.

LPPS Ferro-Tic materials showed excellent wear properties at 200°C, but comparatively high wear at 350°C (although still better than EP Cr). The CS40 grade (martensitic stainless steel matrix phase) gave the best wear characteristics of the Ferro-Tic materials investigated, and data for this material are shown in Figures 89 and 90. Microstructural effects are discussed in section 4.5.4.

4.1.2 Cylinder Liner Wear

An important factor to be considered in evaluating the tribological properties of a piston ring coating material is the amount of wear occurring on the cylinder liner counterface. For optimum engine durability, low wear rates are required of both rings and liners, therefore a systems approach is necessary in materials selection. Wear coefficients for pearlitic grey cast iron counterface materials are shown in Figures 91 (200°C) and 92 (350°C). Liner wear coefficients varied by two to three orders of magnitude for the range of ring coatings investigated, with less sensitivity to ring material at 350°C than at 200°C. Generally, there was a reasonable correlation between liner wear rankings at the two test temperatures, with some exceptions such as the relatively good performance of the ZTY coating at 350°C compared to 200°C.

For a hard vs soft wear couple, the wear of the softer material will generally be influenced by the surface finish of the harder. In this study, as-ground chromium oxide coatings were found to produce much higher liner wear than lapped coatings, especially at the lower test temperature. At 200°C, a lapped Cr_2O_3 (0.02 μm R_a) gave approximately twenty times less liner wear than the same coating abraded with 320# SiC paper to an R_a of 0.4 μm (Table 27). However, at 350°C, the difference was only a factor of 2.5. The temperature sensitivity may arise because the higher coating wear rate at 350°C would cause the original surface finish to be removed in a shorter time than at 200°C. Thus, the original coating surface finish should be less important at the higher test temperature. This factor may explain the reduced liner wear sensitivity to ring material at the higher test temperature.

Although the lapped coatings generally produced the lowest liner wear, an interesting finding was that the as-ground (0.4 μm R_a) HVOF Cr_3C_2 -NiCr coating (one of the best for ring wear) gave consistently low values for liner wear at both test temperatures. In fact, this as-ground coating gave lower liner wear than lapped WC - Co coatings. Thus, the microstructure of the coating may also play an important role in influencing liner wear, although the controlling factors are difficult to resolve. For example, the softer ring coatings (e.g. APS chromium, Mo-Ni) did not necessarily produce the lowest liner wear in these tests, so again hardness may not be an important factor. The Tribolite coating gave the lowest liner wear at both test temperatures. Many of the plasma sprayed ceramic coatings (especially Cr_2O_3 and Al_2O_3 - ZrO_2) also gave very low liner wear, especially at the higher test temperature.

Figure 91. Wear coefficients for pearlitic grey cast iron cylinder liners at 200°C. Tests were run with fresh CE/SF 15W40 mineral oil based lubricant.

Table 27. Wear coefficients of a pearlitic grey cast iron cylinder liner material as a function of the pre-test surface finish of the ring counterface for an APS chromium oxide ring coating, at 200 and 350°C.

R _a Parallel to Sliding Direction (μm)	R _a 90° to Sliding Direction (μm)	Cylinder Liner Wear Coeff. at 200°C (mm³/mm/N)	Cylinder Liner Wear Coeff. at 350°C (mm³/mm/N)
0.242	0.398	2.11x10 ⁻⁹	3.20x10 ⁻⁹
0.022	0.019	1.14x10 ⁻¹⁰	1.34x10 ⁻⁹

Figure 92. Wear coefficients for pearlitic grey cast iron cylinder liners at 350°C. Tests were run with fresh CE/SF 15W40 mineral oil based lubricant.

4.1.3 Friction Coefficients

Friction coefficients for the fresh oil tests are shown in Figures 93 (200°C) and 94 (350°C). At 200°C, friction coefficients were relatively insensitive to the sliding materials, with the exception of the highly porous boron carbide coating, which showed comparatively high friction. For most coatings, the friction coefficient was in the range 0.10 - 0.13. At 350°C, friction coefficients were more dependant on materials, ranging from approximately 0.08 to 0.18. For some materials, friction decreased compared to the 200°C values; for others it increased. The magnitude of the friction coefficients indicates that all tests ran under boundary lubricated conditions.

A surprising feature of the friction data was the lack of any clear correlations with other measured data, such as wear rates or microhardness values. Also, there was no correlation between the initial surface finish (R_a values) of the coatings and friction coefficient. In the boundary lubricated regime, friction is thought to occur primarily due to energy dissipation in lubricant films adsorbed onto the sliding surfaces, and may thus depend primarily on the chemistry and thickness of the adsorbed films. This, in turn may depend on the chemistry of the sliding surfaces rather than on mechanical properties such as hardness. Clearly, there is a need for further characterization of surface films in order to explain the friction data obtained. From a practical standpoint, it is unfortunate that the best wear materials do not necessarily give the lowest friction coefficients.

Figure 93. Friction coefficients for 200°C fresh oil tests.

Figure 94. Friction coefficients for 350°C fresh oil tests.

4.1.4 High Temperature Wear Tests With A Synthetic Lubricant

Tests were performed with various coatings sliding against hardened H13 tool steel at 450°C with a poly-alpha-olefin (PAO) base stock as the lubricant, in order to demonstrate the potential for extremely high temperature tribological systems using a synthetic lubricant. The viscosity of the PAO was relatively high: 39 cSt at 100°C, compared to 14 cSt at 100°C for the 15W40 lubricant used for other tests. The benefits of higher viscosity are greater oil film thickness and, usually, greater oxidation resistance and lower volatility. For engine use, the major disadvantages would be poor fluidity at low temperatures and excessive deposits at high temperatures.

Three coatings were tested at 450°C: HVOF Cr_3C_2 -NiCr, APS Cr_2O_3 and APS Al_2O_3 - 41% ZrO_2 . During several of these tests, the oil film periodically underwent spontaneous combustion due to the high test temperature. Despite this, low friction coefficients were maintained throughout the tests (Table 28). Wear coefficients were much higher than for 200 and 350°C tests, but low compared to unlubricated values. The ceramic coatings were slightly more wear resistant than the cermet material at this temperature, the Cr_2O_3 material showing the lowest wear coefficient (Figure 95). At lower temperatures, with a fully formulated mineral oil lubricant, the HVOF Cr_3C_2 -NiCr coating showed greater wear resistance than either ceramic material (Figures 89 and 90).

Table 28. Friction coefficients for various piston ring coatings sliding against hardened H13 tool steel at 450°C. Tests were run with unformulated poly-alpha-olefin lubricant.

Ring Coating	Liner Material	Friction Coefficient
HVOF Cr_3C_2 - 20% NiCr (UTRC)	H13 Tool Steel	0.17
APS Al_2O_3 - 41% ZrO_2	H13 Tool Steel	0.12
APS Cr_2O_3 (BIRL)	H13 Tool Steel	0.10

Figure 95. Wear coefficients for various coatings sliding against hardened H13 tool steel liners at 450°C. Tests were run with unformulated poly-alpha-olefin lubricant.

4.2 WEAR AS A FUNCTION OF TEMPERATURE (FRESH OIL)

4.2.1 Piston Ring Coating Wear

Figure 96 shows the variation of wear coefficients with temperature for electroplated hard chromium piston rings sliding against lubrited (manganese phosphate coated) pearlitic grey cast iron cylinder liners, lubricated with fresh CE/SF 15W40 oil.

A reasonably good fit to the observed variation of wear coefficient with temperature was obtained with an Arrhenius function of the form

$$W = W_0 \exp\left(-\frac{Q}{RT}\right)$$

where: W is the wear coefficient ($\text{mm}^3/\text{mm}/\text{N}$)
 W_0 is a constant with the same dimensions as the wear coefficient ($\text{mm}^3/\text{mm}/\text{N}$)
 Q is an "activation energy" (J mol^{-1})
 R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
 T is the absolute temperature (K).

"Activation energies" were determined to be 26.5 kJ mol^{-1} for the chromium plated rings and 15.6 kJ mol^{-1} for the lubrited pearlitic iron liners. The above analysis is empirical only, since wear coefficients are not true rate constants (dimensions s^{-1}) and wear processes are probably stress-activated as well as thermally activated (perhaps more analogous to "power-law creep", if the rate of material loss is controlled by plastic deformation, for example). More detailed analysis would require a greater understanding of wear mechanisms for the tribological systems investigated, and is beyond the scope of this study. In particular, we would like to be able to separate the effects of thermally induced changes in lubricant properties (e.g. viscosity; chemical reactivity with the surfaces) from materials properties (e.g. hardness, oxidation rate).

Figures 89 and 90 clearly show that wear coefficients increased markedly with increasing temperature for all of the coating materials tested with grey iron counterfaces. Typically, wear coefficients increased by almost an order of magnitude between 200 and 350°C. For the purpose of comparing the temperature sensitivities of wear coefficients, Arrhenius equations were fitted to wear data obtained for several metallic, ceramic and cermet coatings (Figures 97 - 99). This is an extrapolation through only two temperature points, so the analysis should be viewed with caution.

For the metallic coatings shown in Figure 97, the extrapolated fitting curves were relatively parallel, with "activation energies" falling in the range 25 - 45 kJ mol^{-1} . Thus, ranking materials in order of decreasing wear coefficients produced broadly similar results at 200 and 350°C (Figures 89 and 90).

The ceramic coatings showed a much greater range of wear coefficients (Figure 98), although the "activation energies" were mostly in the same range as for the metallic coatings. One exception was the boron carbide coating, which essentially showed no variation of wear coefficient with temperature. For this coating, it is speculated that the wear process was dominated by fracture of the highly porous material.

The cermet coatings showed two kinds of behavior (Figure 99). The HVOF WC - Co and $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings showed relatively small changes in wear coefficient with temperature (activation energies 18.4 and 24.3 kJ mol^{-1} , respectively), while the Ferro-Tic coatings all showed a greater temperature dependency (47 - 51 kJ mol^{-1}). It is speculated that wear of the Ferro-Tic materials was controlled by the wear of the ceramic phase at low temperatures, but by the softening/wear of the metallic binder phases at high temperatures. The Cr_2O_3 -Stellite curve was essentially parallel to the curve for Cr_2O_3 in Figure 98.

An interesting observation was that plasma sprayed Cr_2O_3 sliding against slurry-sprayed silica - chromia - alumina (fresh oil lubricated) showed no variation of wear coefficient with temperature for either material (Figure 100). This observation suggests that the form of the temperature dependence of wear for the ring coating is influenced by the liner material. For example, with pearlitic grey cast iron liner materials, wear of the ring coating may be controlled by the amount of corrosive wear debris (e.g. oxide) generated by the liner rather than (or, perhaps, in addition to) abrasion by the hard phases present in the cast iron (e.g. Fe_3C or other alloy carbides). With a Cr_2O_3 -based liner material, liner oxidation would obviously not be a factor. However, understanding of the materials interactions on the temperature sensitivity of wear must await more detailed understanding of wear mechanisms for these systems.

Figure 96. Variation of wear coefficients with temperature for the baseline system: electroplated hard chromium rings and lubrited (manganese phosphate coated) pearlitic grey cast iron liners. Tests were run with fresh oil.

Figure 97. Extrapolated variation of wear coefficients with temperature for metallic coatings sliding against uncoated pearlitic grey cast iron liners. Tests were run with fresh oil.

Figure 98. Extrapolated variation of wear coefficients with temperature for ceramic coatings sliding against uncoated pearlitic grey cast iron liners. Tests were run with fresh oil.

Figure 99. Extrapolated variation of wear coefficients with temperature for cermet coatings sliding against uncoated pearlitic grey cast iron liners. Tests were run with fresh oil.

Figure 100. Variation of wear coefficients with temperature for APS chromium oxide (APS Materials UCAR and Boyd materials) sliding against slurry-sprayed silica-chromia-alumina liner coatings. Tests were run with fresh oil.

4.2.2 Cylinder Liner Wear

The temperature sensitivity of lubricated wear coefficients for non-lubrited pearlitic grey iron cylinder liners is shown in Figures 101 (metallic and cermet ring coatings) and 102 (ceramic coatings). For metallic and cermet coatings, the liner wear showed a similar form of temperature dependence to the coating wear. Activation energies were typically in the range 40 - 70 kJ/mol⁻¹, averaging approximately 55 kJ/mol⁻¹, slightly higher than for the coatings. The APS Mo-Ni coating produced an anomalously high temperature sensitivity of liner wear (Figure 101).

The similarity of activation energies for both sliding surfaces indicates that the wear processes may be controlled by a common mechanism (e.g. both surfaces undergoing corrosive wear), or that the wear of one surface is controlled by the rate of wear of the other (e.g. abrasive wear of the coating controlled by the rate of oxidative wear of the liner).

Figure 101. Variation of wear coefficients with temperature for pearlitic grey cast iron cylinder liner material tested against various metallic and cermet coatings with fresh oil.

Figure 102. variation of wear coefficients with temperature for pearlitic grey cast iron cylinder liner material tested against various ceramic coatings with fresh oil.

The ceramic coatings showed much greater diversity in the temperature sensitivity of liner wear (Figure 102), activation energies ranging from -5 to 62 kJmol⁻¹. Data is included for a lapped plasma sprayed chromium oxide (activation energy for liner wear: 40.3 kJmol⁻¹) and the same coating abraded with 320# SiC paper to a coarser surface finish (activation energy for liner wear: 6.8 kJmol⁻¹). Increasing surface roughness thus appears to decrease the temperature sensitivity of liner wear, perhaps due to an increased contribution of mechanical abrasion processes. The ZTY and boron carbide coatings, which gave almost flat liner wear curves, tended to give fragmented wear surfaces which may have maintained a high degree of abrasive wear throughout the tests. The LTAVD coatings, which had somewhat high surface roughness due to the presence of macroparticles, both gave intermediate liner wear activation energies of 16.4 kJmol⁻¹. The lapped Al₂O₃ - ZrO₂ coatings gave values of 40 and 62 kJmol⁻¹.

4.3 RESULTS USING HIGH-SOOT, ENGINE-TESTED LUBRICANT

Bench wear tests conducted with engine-tested lubricants have established that wear rates may be significantly increased compared to tests with fresh oil. The reasons for this behaviour have not been fully determined, however an important factor for diesel engines is the accumulation of combustion-derived soot (typically 50 - 500 nm sized particles of microcrystalline carbon) in the lubricating oil [16]. Many hypotheses have been proposed to explain the "pro-wear" characteristics of soot, including removal of lubricant anti-wear films, chemical attack by species adsorbed on the soot particles and mechanical abrasion [e.g. 16 - 20]. Evidence for all these mechanisms is claimed in the literature, but there is currently no consensus of opinion as to which mechanisms are most important.

It is emphasized that the increases in wear rates observed with used diesel engine oils are not necessarily all attributable to soot. Other contributing factors might include, for example, build-up of corrosive species (e.g. sulphuric acid, organic acids) in the oil, increasing levels of abrasive contaminants not removed by the oil filter and depletion of anti-wear additives. The mechanisms by which wear rates are increased may perhaps also depend on the sliding materials. However, Falex 1 block on ring wear experiments at Cummins have established that, for 52100 steel self-mated sliding wear couples at least, soot is the most likely cause of increased wear rates for used diesel oils [21]. This was determined by extracting the soot from a used oil by means of high-speed centrifugation for many hours and verifying that wear rates of the centrifuged oil were the same as for the fresh oil. It was also verified that the centrifugation process removed soot without changing the additive metal content of the oil significantly. In view of the lengthy test matrix, and the difficulty of removing soot from large quantities of oil in a reasonable time, no attempts were made to repeat this experiment for coatings investigated in this program.

4.3.1 Piston Ring Coating Wear

Wear coefficients measured for 200°C tests with the high-soot, engine-tested CE/SF 15W40 lubricant described previously are shown in Figure 103. Comparing Figures 103 (3.3% soot) and 89 (fresh oil), it is apparent that most of the coatings evaluated showed higher wear rates with high-soot, engine-tested oil than with fresh oil, with increases of more than a factor of ten in some cases. Wide variations in the sensitivity to degraded, soot-loaded oil were observed, and so it is important to take these effects into account when evaluating materials for diesel engine applications.

Metallic coatings were generally found to show dramatically accelerated wear in high-soot oil, whereas ceramic and cermet coatings showed only modest increases. For example, wear rates for electroplated chromium were approximately sixteen times higher with used oil than with fresh, whereas chromium oxide coatings were subject to only a twofold increase on average. For used oil, the only coatings with wear coefficients less than $2 \times 10^{-11} \text{ mm}^3/\text{mm/N}$ were ceramic and cermet materials (Figure 103). Thus, decreased "soot sensitivity" is a significant driving force for utilizing ceramic and cermet coatings in diesel engine wear environments.

The best coatings for resistance to soot/oil degradation were plasma sprayed chromium oxide and LTAVD CrN, both ceramic coatings. Cermet coatings such as the Cr_3C_2 - 20% NiCr, WC - 12% Co and Ferro-Tic materials also performed extremely well in these tests.

Figure 103. Wear coefficients for various coatings sliding against pearlitic grey iron liners. Tests were run with 3.3% soot, engine-tested oil at 200°C.

4.3.2 Cylinder Liner Wear

Wear coefficients for pearlitic grey cast iron cylinder liners tested against various coatings with high-soot, engine-tested oil are shown in Figure 104. Comparing Figure 104 with Figure 91 (fresh oil, 200°C), it is apparent that liner wear rates generally increased with high-soot, degraded oil, as for the coatings. However, for some coatings, such as the WC - 12% Co materials, liner wear increased very little compared to fresh oil values; for other materials, such as the UTRC HVOF Cr₃C₂ - NiCr, wear rates increased substantially (by up to an order of magnitude). The BIRL plasma sprayed chromium oxide gave the lowest liner wear in these tests, but it should be pointed out that other chromium oxides, which were not lapped to the same excellent surface finish, tended to give much higher liner wear (section 5.5.1). In general, there was little correlation between liner wear with fresh and used oils.

Figure 104. Wear coefficients for pearlitic grey iron liners tested against various ring coatings. Tests were run with 3.3% soot, engine-tested oil at 200°C.

4.3.3 Friction Coefficients

Friction coefficients for the high-soot oil tests are shown in Figure 105. Compared with fresh oil data for the same test temperature (Figure 93), the high-soot oil friction values showed slightly more dependence on materials, friction coefficients ranging from approximately 0.08 to 0.15. Some materials showed lower friction with high-soot oil; others showed higher friction. Ranking the materials in order of decreasing friction produced a different order for the high-soot tests than for fresh oil tests (at either temperature). A general result for both fresh and high-soot oil tests was that no correlation between friction and wear could be found. Again, explanation of these results must await further clarification of the mechanisms of friction and wear for these systems. For these tests, it is interesting that the three lowest friction materials (Cr_2O_3 , WC - 12% Co and Al_2O_3 - 26% ZrO_2) also gave low wear.

Figure 105. Friction coefficients for 200°C high-soot oil tests.

4.4 UNLUBRICATED WEAR TEST RESULTS

4.4.1 Piston Ring Coating Wear

Wear data for unlubricated tests at 200°C are shown in Figure 106. All tests were conducted with a pearlitic grey iron "liner" counterface and were of five minute duration. Unlubricated wear coefficients were typically two to four orders of magnitude higher than for lubricated tests. None of the coatings evaluated would provide sufficiently low wear coefficients to provide acceptable engine durability without lubrication. Generally, there was little correlation between lubricated and unlubricated wear values.

These tests operated in a "severe wear" regime, with the cast iron liner material producing large amounts of oxide debris which transferred to the coating surface and would presumably have created three-body abrasive wear conditions for both ring and liner surfaces. Many of the ceramic coatings showed evidence of local fracture and spallation in these tests: evidence of high asperity contact stresses.

One of the objectives of the unlubricated tests was to evaluate "scuff resistance", which is here taken to mean the tendency of a material to show severe adhesive wear (material transfer) under conditions of temporary loss of oil film. Literature on commercial piston ring coatings suggests that scuff resistance is not necessarily related to wear resistance under well-lubricated conditions [4]. For example, engine test experience suggests that Mo-based ring coatings are more scuff resistant than electroplated chromium (EP Cr) under severe operating conditions, but EP Cr shows slightly better wear resistance under well lubricated conditions. The data obtained in this program (Figure 106) showed the unlubricated wear resistance of EP Cr to be intermediate between that of Mo - Ni and Mo - MoO₂ coatings. For fresh oil lubricated tests at 200°C, EP Cr showed lower wear than either of the Mo-based coatings. Thus, there is at least a partial correlation between the unlubricated test data and engine experience.

Figure 106 shows that the best materials for scuff resistance were ceramic coatings: chromium oxide and the two alumina - zirconia materials. However, not all the ceramic coatings showed low wear in these tests, since the ZTY and Cr₂O₃ - 50% Al₂O₃ coatings gave the highest wear. Wear surfaces of these latter two coatings showed evidence of spallation and fracture, which may have been caused by the high degree of inter-splat microcracking observed in both materials. The BIRL chromium oxide and alumina - zirconia coatings contained much less microcracking, and exhibited less fracture on the unlubricated wear surfaces (Appendix A3).

The performance of the BIRL chromium oxide in these tests was spectacular, since the wear rate was approximately an order of magnitude lower than for the next best material. Abrading the surface of this coating with 320# SiC paper prior to the test was found to cause a significantly higher wear coefficient of 1.32×10^{-9} mm³/mm/N (six times higher than for the lapped coating). This may indicate that a flaw-free surface provides the best wear resistance under fracture-controlled sliding conditions. However, even the abraded surface gave outstanding wear performance compared to other coatings.

The HVOF WC - Co and Cr₃C₂ - NiCr cermet materials showed low wear in these tests, but the Ferro-Tic coatings showed much higher wear rates, more typical of the metallic coatings. Thus, it appears that under severe test conditions (350°C lubricated and 200°C dry), scuffing and wear of the Ferro-Tic materials is dominated by the properties of the metallic binder phase. Only in the 200°C lubricated tests were low wear coefficients obtained with these materials.

The metallic coatings showed comparatively small differences in wear rates, the best coatings being the Mo - MoO₂, Amacor, EP Cr and Mo - Ni materials.

Figure 106. Wear coefficients for various coatings sliding against pearlitic grey iron liners. Tests run with no lubrication at 200°C.

4.4.2 Cylinder Liner Wear

Unlubricated wear coefficients for the pearlitic grey cast iron liner counterfaces showed comparatively little sensitivity to the coating material in these tests (Figure 107), the wear coefficients varying by approximately one order of magnitude from best to worst case. For fresh oil lubricated tests at 200°C, the variation was approximately three orders of magnitude (Figure 91). The lowest liner wear rates were obtained for the four most wear resistant ceramic coatings: APS Cr_2O_3 , Al_2O_3 - 26% ZrO_2 , LTAVD CrN and Al_2O_3 - 41% ZrO_2 . Thus, for unlubricated conditions, a variety of coatings are available which provide comparatively low ring and liner wear.

Figure 107. Wear coefficients for pearlitic grey iron liners tested against various ring coatings. Tests run with no lubrication at 200°C.

4.4.3 Friction Coefficients

Friction coefficients for the unlubricated tests varied from approximately 0.4 to 0.7 for the range of materials investigated (Figure 108). There was little correlation between lubricated and unlubricated friction values, or between dry friction and dry wear coefficients. Under the test conditions used, and with cast iron cylinder liners, it is thought unlikely that the program goal of 0.2 dry friction coefficient can be met, at least without the use of a solid lubricant. The test conditions used for this program were designed to simulate the top ring reversal environment in a heavy duty diesel engine, and the load selected (225 N) was sufficiently high to create "severe" wear conditions (transfer of material, severe oxidation of the liner, fracture of some coatings) in unlubricated tests. Possibly, "mild" wear conditions with lower friction coefficients may have prevailed at lower test loads, but this would be of no practical value for a diesel engine ring facing material.

Figure 108. Friction coefficients for 200°C unlubricated tests.

4.5 MICROSTRUCTURAL EFFECTS ON FRICTION AND WEAR

In this section, correlations between coating microstructures and measured friction and wear properties are examined for four types of coating: plasma sprayed chromium oxides, tungsten carbide - cobalt (various coating methods), HVOF chromium carbide - nichrome and LPPS Ferro-tic materials. For more detailed analysis of the effects of microstructure on wear mechanisms, see the Appendices.

4.5.1 Chromium Oxide Coatings

A breakdown of the wear coefficients for various chromium oxide materials is shown in Figure 109. With fresh oil, differences in wear rates were relatively small, the variation from best to worst material being a factor of approximately 4. With high-soot oil, the differences were somewhat greater (14x variation), and the unlubricated tests showed a factor of 1000 difference between best and worst materials. The ranking of materials was not consistent from one test condition to another, in part because the differences between materials for fresh oil tests were mostly within experimental error. However, the BIRL Cr_2O_3 - 50% Al_2O_3 (material 7 in Figures 109 - 11) and UTRC APS Metco 106FP (material 8) coatings were generally found to have the highest wear, especially in unlubricated tests. The best wear coatings were the BIRL APS Cr_2O_3 (material 2) and APS Materials Metco 136 (material 4).

An important microstructural feature of thermally sprayed chromium oxide materials is the degree of inter-splat microcracking and porosity. For the eight¹⁴ materials shown in Figure 109, the ranking from lowest microcrack levels to highest was:

BIRL APS Cr_2O_3	(material 2 in Figures 109 - 111)
BIRL HVOF Cr_2O_3	(material 3 in Figures 109 - 111)
APS Materials Metco 136 + 15% Al_2O_3	(material 6 in Figures 109 - 111)
APS Materials Metco 136	(material 4 in Figures 109 - 111)
APS Materials Metco 136 + 3% SiO_2	(material 5 in Figures 109 - 111)
APS Materials UCAR Cr_2O_3	(material 1 in Figures 109 - 111)
BIRL Cr_2O_3 - 50% Al_2O_3	(material 7 in Figures 109 - 111)
UTRC APS Metco 106FP	(material 8 in Figures 109 - 111)

The first four coatings on this list all showed generally excellent microstructures.

Thus, it appears that the wear data show an approximate correlation with the level of microcracking and porosity within the coating, especially for the most severe test conditions (which were most likely to cause fracture of the coating).

Attempts to determine the effect of Al_2O_3 additions on the tribological properties of chromium oxide were compromised by the poor microstructure of the Cr_2O_3 - 50% Al_2O_3 coating. The Metco 136 + 15% Al_2O_3 coating (material 6) showed low wear coefficients with fresh oil (200 and 350°C), but comparatively high wear with high-soot oil.

¹⁴ The Boyd material was not included in this series of tests due to insufficient test samples. This material was tested against the SCA liner coating (data included in Figure 100).

Figure 109. Wear coefficients for various chromium oxide based coatings sliding against pearlitic grey cast iron liners.

Figure 110. Liner wear coefficients for various chromium oxide based coatings sliding against pearlitic grey cast iron liners.

Liner wear coefficients are shown in Figure 110. Generally, it is difficult to resolve consistent trends from these data, suggesting that the wear values were mostly similar, within experimental error. However, the highly lapped BIRL Cr₂O₃ coating (material 2) gave the most consistently low liner wear values for the four test conditions. Materials 4, 5 and 6 (powders based on Metco 136) tended to show the highest liner wear in lubricated tests. Interestingly, the Cr₂O₃ - 50% Al₂O₃ (material 7) showed very low liner wear in lubricated tests, despite the high porosity and microcracking within this coating. However, the Metco 136 + 15% Al₂O₃ coating (material 6) gave consistently high liner wear in lubricated tests. In unlubricated tests, materials 7 and 8, the most porous, microcracked coatings, showed the highest liner wear.

Figure 111. Friction coefficients for various chromium oxide based coatings sliding against pearlitic grey cast iron liners.

Friction coefficients were similar for all coatings at 200°C with fresh oil (Figure 111). For fresh oil, 350°C and high-soot oil, 200°C tests, the BIRL Cr₂O₃ material gave the lowest friction coefficients. This material was lapped and had the lowest R_a value of all the coatings tested (Table 23). Otherwise, it is difficult to resolve consistent trends in friction. In unlubricated tests, the more pure Cr₂O₃ coatings (materials 1 and 2) showed lower friction than the Metco 136 based coatings (materials 4, 5 and 6).

4.5.2 WC - Co Coatings

Five WC - 12% Co coatings were evaluated during the program, including air plasma sprayed, low pressure plasma sprayed and HVOF materials. The coatings are listed in Table 29, together with X-ray diffraction data showing the phase contents of each coating. It is difficult to draw firm conclusions from the analysis, but it appears that the Boyd and Turbine Metal Technology HVOF coatings showed relatively low degrees of carbide solutionizing, and the APS Materials HVOF coating showed a relatively high amount.

Wear data for the five coatings are shown in Figure 112. In order of increasing wear, the ranking of the coatings was: Boyd HVOF, APS Materials APS, TMT HVOF, APS Materials LPPS and APS Materials HVOF. The ranking of the coatings was relatively consistent for all test conditions. Typically, wear coefficients varied from best to worst material by a factor of 9 with fresh oil, 20 with high-soot oil and 3 with no lubricant. Although the Boyd material generally showed the lowest wear, the coating was found to crack during several of the tests, particularly at high test temperatures. This coating was the thickest of the WC - Co materials evaluated (250 μm), and may have contained high levels of residual stress.

From the above ranking, it appears that there may be a correlation between the degree of carbide solutionizing and wear: the greater the amount of solutionizing, the higher the wear rate.

Wear data for cast iron cylinder liner counterfaces are shown in Figure 113. The as-ground coatings (APS Materials APS and LPPS coatings) showed higher liner wear than the lapped surfaces in lubricated tests. Figure 113 also shows that liner wear was a strong function of temperature, but was not affected appreciably by soot/oil degradation for WC - Co ring coatings.

Friction coefficients showed no consistent trends from one material to another (Figure 114).

Table 29. Phase analysis of WC - Co coatings used in this program. X-ray diffraction analysis and phase identification was performed at BIRL.
Important: Percentage values in brackets [] represent the peak intensity of the strongest peak from the minor phase divided by the strongest WC peak intensity. These numbers do not indicate that the minor phase exists in that abundance.

Coating Process	Supplier	Analysis
Air Plasma	APS Materials	WC + $\text{Co}_3\text{W}_9\text{C}_4$ [12%] + $\text{Co}_3\text{W}_3\text{C}$ [10%]
Low Pressure Plasma	APS Materials	WC + $\text{Co}_2\text{W}_4\text{C}$ [16%] + $\text{Co}_3\text{W}_9\text{C}_4$ [14%]
HVOF (Jetkote II)	APS Materials	WC + $\text{Co}_2\text{W}_4\text{C}$ [24%] + $\text{Co}_3\text{W}_9\text{C}_4$ [10%]
HVOF (Jetkote II)	Boyd Machine & Repair	WC + $\alpha\text{-W}_2\text{C}$ [13%]
HVOF (proprietary gun)	Turbine Metal Technology	WC + WC_{1-x} [7%] + $\text{Co}_6\text{W}_6\text{C}$ [6%]

Figure 112. Wear coefficients for various tungsten carbide - cobalt coatings sliding against pearlitic grey cast iron liners.

Figure 113. Liner wear coefficients for various tungsten carbide - cobalt coatings sliding against pearlitic grey cast iron liners.

Figure 114. Friction coefficients for various tungsten carbide - cobalt coatings sliding against pearlitic grey cast iron liners.

4.5.3 Chromium Carbide - Nichrome Coatings

Two HVOF Cr_3C_2 - 20% NiCr materials were evaluated during this program: a clad powder sprayed by UTRC and a mixed powder sprayed by Turbine Metal Technology (see section 3 for microstructural characterization). Wear data for the two materials are shown in Figures 115 (coating wear) and 116 (liner wear). The clad UTRC material was found to give lower wear under all test conditions, typically by a factor of two.

Liner wear was approximately the same for both materials, even though the surface finish of the lapped TMT material was much finer ($0.08 \mu\text{m RA}$) than for the ground UTRC material ($0.42 \mu\text{m RA}$). For both materials, liner wear was much higher with high-soot oil than with fresh oil. In this respect, the Cr_3C_2 - NiCr coatings differed from WC - Co materials, for which liner wear was relatively insensitive to soot/oil degradation. For the UTRC Cr_3C_2 - 20% NiCr, wear was higher at 200°C with high-soot oil than at 350°C with fresh oil.

Friction coefficients for the two coatings were broadly similar, although the UTRC material gave a much higher friction coefficient than the TMT coating in the high-soot oil test (Figure 117).

Figure 115. Wear coefficients for Cr_3C_2 - NiCr coatings sliding against pearlitic grey cast iron liners.

Figure 116. Liner wear coefficients for Cr_3C_2 -NiCr coatings sliding against pearlitic grey cast iron liners.

Figure 117. Friction coefficients for Cr_3C_2 -NiCr coatings sliding against pearlitic grey cast iron liners.

4.5.4 Ferro-Tic Coatings

Three Ferro-Tic materials were evaluated:

1. Ferro-Tic CM 45% TIC in a high chrome tool steel matrix
2. Ferro-Tic CS-40 45% TIC in a martensitic stainless steel matrix
3. Ferro-Tic HT-6A 35% TIC in an age hardenable nickel base matrix.

Microstructures for the three materials are described in section 3.1.3.

In lubricated tests, the three materials gave similar wear performance (Figure 118), the CS-40 grade giving marginally lower wear. All three materials showed a dramatic increase in wear rates with increasing temperature (for example, compare the WC - Co data in Figure 112 with Figure 118). In unlubricated tests, the HT-6A material, containing a lower percentage of TIC, showed substantially higher wear than the steel matrix grades.

Liner wear coefficients for the Ferro-Tic materials were generally a strong function of temperature and a weaker function of soot/oil degradation (Figure 119). In this respect, the Ferro-Tic materials behaved similarly to the WC - Co coatings. There were no consistent differences between the three Ferro-Tic materials as regards liner wear. It is perhaps surprising that the HT-6A grade, which contains a lower volume fraction of TIC, did not show lower liner wear than the other grades.

Friction coefficients were similar for all the Ferro-Tic coatings in lubricated tests (Figure 120). The HT-6A grade showed a relatively low friction coefficient in the unlubricated tests, despite a much higher wear coefficient.

Figure 118. Wear coefficients for Ferro-Tic coatings sliding against pearlitic grey cast iron liners.

Figure 119. Liner wear coefficients for Ferro-Tic coatings sliding against pearlitic grey cast iron liners.

Figure 120. Friction coefficients for Ferro-Tic coatings sliding against pearlitic grey cast iron liners.

4.6 CYLINDER LINER OPTIMIZATION

The results of the cylinder liner optimization tests, performed with the UTRC HVOF Cr_3C_2 - NiCr ring coating sliding against various alternative cylinder liner materials are described in this section. The cylinder liner materials evaluated were (see Table 25, section 3.3 for compositions):

1. pearlitic grey iron (70 - 90 HRG)
2. hardened grey cast iron (42 HRC)
3. high-phosphorus grey cast iron (79 - 83 HRG)
4. bainitic grey cast iron (88 - 90 HRG)
5. centrifugally cast H13 tool steel hardened to 50 HRC
6. a slurry-sprayed silica-chromia-alumina (SCA) coating (960 kg/mm^2 , HK₁₀₀)
7. an ion-assisted CVD "diamond-like" coating supplied by Implant Sciences, Inc. The coating substrate was H13 tool steel.

Coating and liner wear rates for lubricated tests are shown in Figure 121. Of the cast iron liners, the pearlitic iron and high-phosphorus materials gave approximately the same ring and liner wear coefficients, but the bainitic material showed significantly (up to ten times) lower liner wear rates in lubricated tests, with only slightly higher ring wear (Figure 121). The excellent wear properties of the bainitic iron may have been partly due to the alloy content, which results in a fine dispersion of molybdenum carbides through the microstructure, in addition to the effect of the slightly higher matrix hardness. Hardening the pearlitic grey iron material resulted in three times lower liner wear in the 200°C tests but very little effect at 350°C, even though the tempering effect during the wear test was small at 350°C (38 HRC at end of test compared to an initial value of 42 HRC). It is speculated that this result may be due to the increased importance of corrosive wear processes at the higher test temperature.

The diamond-like coating was found to be too thin to survive the six hour tests, and liner wear rates for the fresh oil tests were often higher than for uncoated H13 tool steel. In addition, wear rates of the Cr_3C_2 - NiCr ring coating were extremely high, suggesting that the diamond-like coating was very abrasive while still intact.

Of the cylinder liner materials tested, the SCA coating showed the lowest liner wear rates, especially with high-soot, engine-tested oil, but this was at the expense of significantly higher ring wear (Figure 121).

Overall, the best wear performance was obtained with the hardened H13 tool steel liner material, which gave consistently lower wear than all the cast irons evaluated, and even produced lower wear of the ring coating. Thus, by optimizing piston ring and cylinder liner materials, very low wear coefficients may be achieved, coming very close to meeting the aggressive wear goals described in the objectives. It should be noted that tests were conducted with an as-ground surface finish of $0.42 \text{ } \mu\text{m RA}$ for the HVOF Cr_3C_2 - NiCr. Lapping the coating would result in a significantly better surface finish and potentially lower liner wear.

Unlubricated tests showed relatively little difference between the cast iron materials (Figure 122). The best liner material for dry tests was the SCA coating. H13 tool steel also gave lower wear than cast irons in these tests. The diamond-like coating was completely removed during the unlubricated test, and the wear coefficient was the same as for the H13 tool steel substrate.

Figure 121. Wear coefficients for HVOF $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating sliding against various cylinder liner materials (lubricated tests).

Figure 122. Wear coefficients for HVOF $\text{Cr}_3\text{C}_2\text{-NiCr}$ coating sliding against various cylinder liner materials (unlubricated tests).

4.7 CORRELATIONS BETWEEN WEAR DATA FOR DIFFERENT TEST CONDITIONS

The testing philosophy adopted in this program was to evaluate coatings under multiple test conditions (fresh oil: 200 and 350°C, high-soot oil: 200°C, unlubricated: 200°C). This decision was made after reviewing the literature on commercial piston ring coatings [e.g. 4, 8], which showed that materials could score highly in some wear categories, but perform poorly in others. For example, a particular coating might be very scuff resistant but have only average wear resistance under well-lubricated conditions. The test conditions used were designed to provide the maximum information from the smallest number of tests. It is instructive to review the level of correlation between the four kinds of wear tests. Conceivably, if there were sufficient correlation, it would be unnecessary to perform each kind of test on every sample because it would be possible to extrapolate data from one type of test to predict the performance under every test condition. Conversely, if the correlation between tests were poor, our original test design would be justified. This is an extremely important point for future tribological evaluations of materials for diesel engine applications.

Least squares regression analysis was performed to try to correlate wear coefficients measured under one test condition with those measured under another. The correlation coefficients are shown in Tables 30 (ring coatings) and 31 (cylinder liners). In no case was the correlation coefficient significantly greater than 0.9 but, for the ring coating wear, there appeared to be a reasonable correlation between fresh oil (200°C) and fresh oil (350°C) data, and also between fresh oil (200°C) and high-soot oil (200°C) results. There was little correlation between lubricated and unlubricated wear data, although the best fit was with the fresh oil (350°C) vs unlubricated (200°C) tests. For cylinder liner wear, correlation coefficients were very low for all combinations of test conditions (Table 31).

An attempt was made to correlate ring wear with liner wear for the four different test conditions (Table 32). The best correlation was for fresh oil (200°C) tests, for which the correlation coefficient was 0.728. Ring wear was found to increase with increasing liner wear (or vice versa). Under all other test conditions, the liner wear was found to be independent of ring wear. This conclusion is drawn for a set of data using coating material as the variable, for fixed test conditions. However, for a particular ring coating - liner wear couple and varying the temperature, there was found to be a correlation between ring and liner wear, as discussed in section 4.2.

No correlation was found between coating wear coefficients and microhardness values for any test condition (Table 33). This is shown graphically for 200°C fresh oil wear data in Figure 3, section 1.2.

An example of one of the correlations identified, coating wear at 350°C vs coating wear at 200°C, is shown in Figure 123. Plotting the data on a logarithmic scale showed relatively low scatter. Coating wear data for the 200 and 350°C tests with fresh oil are shown on the same graph in Figure 124. The materials are listed in order of decreasing wear coefficient, using the 200°C values. If the 350°C results were to correlate with the 200°C results, the graph should show the same trend of decreasing wear on both sides. Figure 124 shows that there was a fairly good correlation between 200 and 350°C wear coefficients, although there were some exceptions. For example, the Ferro-Tic coatings showed very low wear at 200°C compared with other materials, but comparatively high wear at 350°C.

Comparison of results for fresh and high-soot, engine-tested lubricants at 200°C are shown in Figures 125 and 126, using the same format. In this case, although there was a broad correlation, there were many significant exceptions, giving rise to a greater amount of scatter. Ceramic and cermet coatings were found to perform well compared to metallic coatings in high-soot tests, which distorts the correlation.

A comparison between fresh oil lubricated and unlubricated test results (at 200°C) is shown in Figures 127 and 128. In this case, there was very little correlation. In particular, the alumina-zirconia and chromium oxide coatings performed much better in dry tests than would be expected from 200°C lubricated tests, and the Ferro-Tic coatings performed much worse.

In summary, it is evident that the performance of a particular coating and liner couple relative to other combinations depends on the test conditions used, at least within the range of variables evaluated here. Tribological testing of materials for diesel engine environments must include the key variables of temperature and lubricant soot loading/oil degradation and should evaluate lubricated and unlubricated performance. Without this information, attempts to predict the behavior in engine tests would be potentially very inaccurate.

Table 30. Correlation coefficients (r^2) for ring coating wear under the four different test conditions.

Coating Wear	Coating Wear			
	Fresh Oil 200°C	Fresh Oil 350°C	3.3% Soot 200°C	Dry 200°C
Fresh Oil 200°C	-	0.902	0.898	0.365
Fresh Oil 350°C	0.902	-	0.809	0.761
3.3% Soot 200°C	0.898	0.809	-	0.017
Dry 200°C	0.365	0.761	0.017	-

Table 31. Correlation coefficients (r^2) for cylinder liner wear under the four different test conditions.

Liner Wear	Liner Wear			
	Fresh Oil 200°C	Fresh Oil 350°C	3.3% Soot 200°C	Dry 200°C
Fresh Oil 200°C	-	0.013	0.239	0.023
Fresh Oil 350°C	0.013	-	0.007	0.138
3.3% Soot 200°C	0.239	0.007	-	0.035
Dry 200°C	0.023	0.138	0.035	-

Table 32. Liner wear vs ring coating wear regression: correlation coefficients (r^2).

Test Condition	Liner vs Coating Wear
Fresh Oil 200°C	0.728
Fresh Oil 350°C	0.011
3.3% Soot 200°C	0.092
Dry 200°C	0.160

Table 33. Ring wear vs coating microhardness regression: correlation coefficients (r^2).

Test Condition	Ring Wear vs Microhardness
Fresh Oil 200°C	0.032
Fresh Oil 350°C	0.052
3.3% Soot 200°C	0.012
Dry 200°C	0.075

Figure 123. Coating wear at 350°C plotted against coating wear at 200°C with fresh oil.

Figure 124. Coating wear coefficients measured at 200 and 350°C with fresh oil.

Figure 125. Coating wear with 3.3% soot oil plotted against coating wear with fresh oil at 200°C.

Figure 126. Coating wear coefficients measured for fresh and 3.3% soot engine-tested oil at 200°C.

Figure 127. Coating wear without lubricant plotted against coating wear with fresh oil at 200°C.

Figure 128. Coating wear coefficients measured for lubricated and unlubricated wear tests at 200°C.

5 CONCLUSIONS

The tribological properties of a variety of advanced coating materials have been evaluated under conditions which simulate the piston ring - cylinder liner environment near top ring reversal in a heavy duty diesel engine. Coated "ring" samples were tested against a conventional pearlitic grey cast iron liner material using a high temperature reciprocating wear test rig.

Emphasis was placed on the variables of greatest interest for diesel engine piston ring coatings: lubricated wear rates as a function of temperature, the effects of lubricant contamination and degradation in diesel environments and scuff resistance. For each coating, tests were conducted at 200 and 350°C with a fresh CE/SF 15W40 lubricant, and at 200°C with a high-soot, engine-tested oil. Materials were also evaluated with no lubrication (at 200°C), in order to rank the sliding wear properties of different materials under "scuffing" conditions. A material with good scuff resistance is desirable in case of temporary loss of oil film in the engine (on start-up or under short duration conditions of extreme hot running, for example).

In this program, advanced piston ring coating - cylinder liner tribological systems have been developed. The best materials combination identified (HVOF Cr_3C_2 - 20% NiCr sliding against H13 tool steel) showed lower boundary lubricated ring and liner wear coefficients at 350°C than the conventional electroplated hard chromium - pearlitic grey cast iron system gave at 200°C. In addition, many ceramic and cermet coatings displayed greater tolerance to lubricant soot loading and oil degradation than the conventional materials, and also provided improved anti-scuff (unlubricated) properties. Thus, a significant improvement in wear control technology for future, advanced diesel engines has been demonstrated.

For lowest coating wear under boundary lubricated conditions, the most promising candidates were high velocity oxy-fuel (HVOF) Cr_3C_2 - 20% NiCr and WC - 12% Co cermets, low temperature arc vapor deposited (LTAVD) CrN and plasma sprayed chromium oxides and Al_2O_3 - ZrO_2 materials. These materials generally showed lower wear than electroplated hard chromium or thermally sprayed metallic coatings. The latter two materials were also found to give excellent wear resistance in unlubricated tests and at extremely high temperatures (450°C) with a synthetic oil. The LTAVD CrN coating provided the lowest lubricated wear rates of all the materials evaluated, but may be too thin (4 μm) for use as a top ring facing.

The effects of microstructure on wear were investigated for several systems, including plasma sprayed chromium oxides and tungsten carbide - cobalt coatings. For chromium oxides, wear rates increased with increasing porosity and inter-splat microcracking, with a factor of approximately four difference between the best and worst materials in fresh oil lubricated tests. For WC - 12% Co materials, wear rates appeared to increase with increasing degree of carbide solutionizing, varying by a factor of nine from best to worst materials with fresh oil. Thus, it is important to optimize the powder and spray process in order to obtain the lowest possible coating wear.

For lubricated tests against pearlitic grey cast iron, ring coating and cylinder liner wear rates were a strong function of temperature, typically increasing by almost an order of magnitude between 200 and 350°C. The relative ranking of coating materials was broadly similar at both temperatures. In contrast to the behaviour with cast iron liners, a chromium oxide ring vs silica-chromia-alumina liner wear couple was found to display almost no temperature sensitivity. From examination of wear surfaces, it is speculated that cast iron cylinder liner materials may undergo corrosive wear (etching and pitting), giving rise to abrasive surface films and wear debris which in turn cause wear of the coating. In a series of liner optimization tests, the use of an H13 tool steel liner resulted in decreased wear of a HVOF Cr_3C_2 - 20% NiCr ring counterface compared to wear with cast iron liners.

Most of the coatings evaluated showed higher wear rates with high-soot, engine-tested oil than with fresh oil, with increases of more than a factor of ten in some cases. Wide variations in the sensitivity to soot loading, oil degradation and contamination were observed, and so it is important to take these effects into account when evaluating materials. Generally, metallic materials were found to be much more sensitive to soot/oil degradation than ceramic and cermet coatings. Thus, decreased "soot sensitivity" is a significant driving force for utilizing ceramic or cermet coatings in diesel engine wear applications.

A HVOF Cr_3C_2 - 20% NiCr coating showed the best combination of low ring and liner wear. WC - Co materials, although very wear resistant, tended to produce high liner wear. Several alternative cylinder liner materials were evaluated as counterfaces for the HVOF Cr_3C_2 - 20% NiCr ring coating, in order to optimize the tribological system. Overall, the best wear performance was obtained with a hardened H13 tool steel liner, which gave lower wear than several cast irons, and even produced lower wear of the ring coating. A silica-chromia-alumina liner coating gave very low wear, but at the expense of higher ring wear.

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