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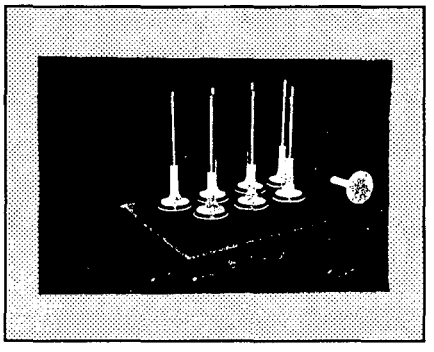
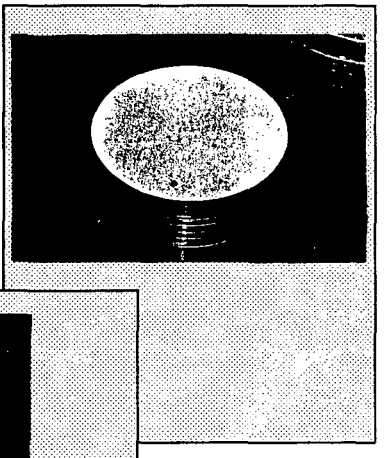
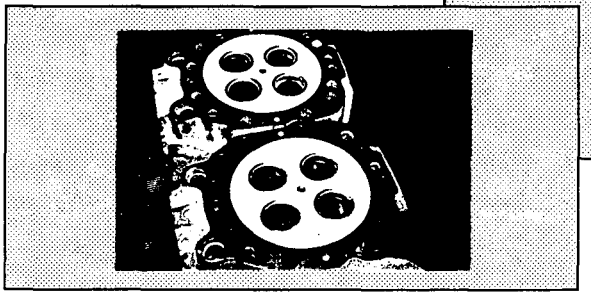
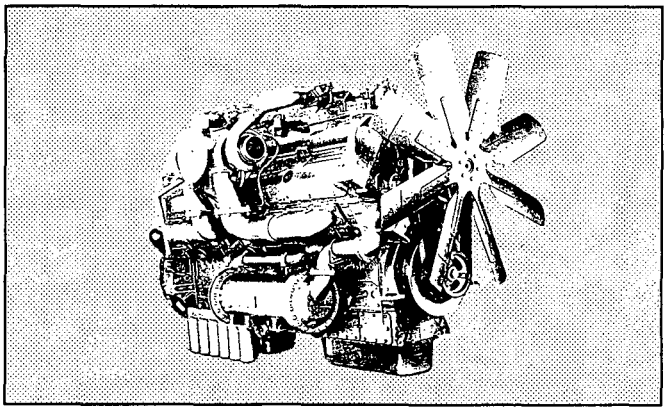
Application of Ceramic Coatings to High Speed Diesel Engine Combustion Zone Components of Off-Highway Transport Vehicles









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The use of thin, zirconia ceramic coatings on the combustion zone surfaces, i.e. piston crowns, cylinder heads, and exhaust valve faces and stems, of large and small bore high speed diesel engines were evaluated in test stand and in-service engine operation. Several different coating compositions were plasma sprayed on engines that propelled a towboat on the U.S. inland waterways and off-the-road ore carrying trucks with great success. The pre-alloyed, yttria stablized zirconia coating, 0.008-0.015 in. (0.2 - 0.4mm) thick operated for 14,000 hours in the towboat engine and for thousands of hours in the truck engines without failure. The durability and certain performance characteristics of the engines were improved by the presence of the coatings. The technical considerations in the selection and application of thin ceramic coatings to diesel engines are presented.

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Application of Ceramic Coatings to High Speed Diesel Engine Combustion Zone Components of Off-Highway Transport Vehicles

September 30, 1990

Executive Summary

Reducing fuel and maintenance and repair costs of internal combustion engines are of paramount importance to vehicle operators. For engine designers and manufacturers, this translates into goals of reducing specific fuel consumption and increasing engine component reliability and durability. The project described herein primarily addressed the latter of these goals. However, as the project proceeded, it was soon realized that this latter goal could be achieved while at the same time achieving favorable results in terms of reducing fuel consumption and repair costs.

While there are many areas where improvements in engine reliability and durability can be pursued; those components that are exposed to the combustion process are of foremost consideration. Of specific interest are the following combustion zone surfaces: piston crowns, cylinder heads, liners and rings, intake and exhaust valves, exhaust manifolds and the turbocharger turbine and casing. The surfaces of these components operate at elevated temperatures and may experience localized overheating that can change the metallurgical structure of the component materials, and are subject to the corrosive and erosive effects of the chemical constituents in the products of combustion.

The means selected to achieve the project's goals was to adapt the technology of thin ceramic coatings, currently being applied to the combustion components of aircraft derivative gas turbines to the combustion components of high speed diesel engines used in off-highway transportation vehicles. The project had three major objectives:

- Demonstrate the reliability and durability of thin ceramic coatings as well as any engine performance improvements achieved in actual service in engines propelling different types of vehicles, i.e. towboats and off-road ore carrier trucks.

- Provide technical guidance to prospective users of ceramic coatings in efforts associated with the in-service test and evaluation of these coatings.

- Provide a basis for a broad range of engine types and applications to identify the technical considerations which play a significant role in ensuring the in-service durability and performance of ceramic coatings applied to diesel engine combustion components.

A most important consideration in adapting the technology was to stay within the bounds of gas turbine engine experience. Therefore, the composition of the ceramic coatings used, their thickness and physical characteristics, and the application method used to apply them to gas turbine engine combustion cans over a period of more than 10 years were rigidly

adhered to in their application to diesel engines. This project utilized partially stabilized zirconia ceramic coatings 0.008 in. - 0.015 in. (0.2 - 0.4 mm) thick that were plasma sprayed over thin, 0.004 in. - 0.006 in.(0.1 - 0.15 mm) thick metallic bond coats. The total thickness of the metallic bond and ceramic coatings was not to exceed 0.020 in..

The promise of the coatings to improve the durability/reliability of diesel engines was assessed by coating the combustion zone surfaces of two types of high speed diesel engines. The coatings, applied to the combustion components of each type of engine, were first tested under controlled environmental conditions in a test cell or on a test stand. This provided a means for measuring possible improvements in engine performance and an initial assessment of coating durability. Following this testing, the coatings were applied to the combustion zone components of the type of engine installed in selected off-highway transportation vehicles and subjected to extensive in-service test and evaluation.

One of the selected vehicles was an inland waterway towboat equipped with large bore 2-stroke high speed diesel engines. These types of engines are also commonly found in railroad locomotives. The second type of vehicle was an open-pit mine truck equipped with a small bore 2-stroke high speed diesel engine. These types of engines are also commonly used to propel small towboats, harbor tugs, fishing vessels and many other types of off-highway vehicles. Operational, in-service durability in excess of 14,000 hours was achieved.

Another project to use ceramics in diesel engines was initiated at the Cummins Engine Co. over 10 years ago to develop an "adiabatic" or low heat rejection engine[1,2] whose performance was to be improved by insulating the combustion zone components using thick, >0.1 in. (2.5 mm) monolithic or plasma spray coated ceramics on the combustion surfaces. This thick thermal barrier liner approach to the coating of diesel engine components has been pursued since that time in DOE/NASA jointly sponsored programs at the Cummins Engine Co. and Caterpillar, Inc.[3,4,5] Both projects finally settled on coating the piston crown, valves and cylinder head fire deck with 0.1 in. (2.5 mm) thick, partially stabilized zirconia ceramic coatings which were to have a thermal conductance of 0.5 BTU/hr in^2 °F (408 Watts/hr m^2 °K). The coated components were to demonstrate their durability and insulation characteristics in a 100 hr duration test in a single cylinder, laboratory engine that simulated an advanced on-highway truck diesel engine. After 4.5 years of development with considerable use of finite element analysis to establish thermal stress levels in the ceramic layer, much effort to refine the basic material, and other means to overcome the inherent brittleness of thick ceramics, one company is reported to have achieved the 100 hr. operation goal.

The use of thick (0.1 in.) coatings in diesel engines is a difficult technical challenge that is far removed from using thin, 0.01 in (0.25 mm) coatings that do not have thermal stress and other mechanical durability problems, as has been done in the project reported on herein. The thin, plasma sprayed

zirconia ceramic coatings documented in this report have many years of demonstrated reliability in production gas turbine engines and should not be confused with the thick, ceramic thermal barrier coatings for diesel engines being developed in the DOE/NASA program. Properly applied thin coatings using the quality assurance procedures described in Appendix A have been demonstrated to be reliable for thousands of hours of operation.

This report is organized to first describe the ceramic coatings technology and summarize their initial application in gas turbine engines, then to briefly describe the initial efforts to apply them in thick (> 0.1 in.) form in "adiabatic" diesel engines and, finally, to present the results of the thin coatings used in this project that were successfully used in several high speed diesel engines operating at different duty cycles. In Appendix A, the recommended quality assurance considerations for thin coatings are presented in a form that can be used to establish quality control procedures for application of the coating to internal combustion engine components in production. In Appendix B, the output of a computer literature search compiles the major quantity of papers that have been written since 1978 on the use of ceramic coatings in internal combustion engines.

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Nomenclature, Symbols, and Glossary of Terms

BTU	British Thermal Units
CTBC	Ceramic thermal barrier coatings
DOE	Department of Energy
EDS	Energy dispersive x-ray spectrometry
EPRI	Electric Power Research Institute
ERDA	Energy Reserch and Development Administration
ETCE	Energy Technology Conference and Exhibition
LBL	Lawrence Berkeley Laboratory
MARAD	Maritime Administration
MCrAlY	M, metals--iron, nickel or cobalt; Cr, chromium; Al, aluminum; Y, ytrrium
NASA	National Aeronautics and Space Administration
NDT	Non-destructive test
ORNL	Oak Ridge National Laboratory
PSZ	Partially stabilized zirconia
SAE	Society of Automotive Engineers
SAMPE	Society of Materials and Process Engineers
SEM	Scanning electron microscopy
XRD	X-ray diffraction

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APPLICATION OF CERAMIC COATINGS TO HIGH SPEED DIESEL ENGINE COMBUSTION ZONE COMPONENTS OF OFF-HIGHWAY TRANSPORT VEHICLES

Final Report

I. OVERVIEW

Reducing fuel and maintenance and repair costs of internal combustion engines are of paramount importance to vehicle operators. For engine designers and manufacturers, this translates into goals of reducing specific fuel consumption and increasing engine component reliability and durability. The project described herein primarily addressed the latter of these goals. However, as the project proceeded, it was soon realized that this latter goal could be achieved while at the same time achieving favorable results in terms of reducing fuel consumption and repair costs.

While there are many areas where improvements in engine reliability and durability can be pursued; those components that are exposed to the combustion process are of foremost consideration. Of specific interest are the following combustion zone surfaces: piston crowns, cylinder heads, liners and rings, intake and exhaust valves, exhaust manifolds and the turbocharger turbine and casing. The surfaces of these components operate at elevated temperatures and may experience localized overheating that can change the

metallurgical structure of the component materials, and are subject to the corrosive and erosive effects of the chemical constituents in the products of combustion.

The means selected to achieve the project's goals was to adapt the technology of thin ceramic coatings, currently being applied to the combustion components of aircraft derivative gas turbines to the combustion components of high speed diesel engines used in off-highway transportation vehicles. The project had three major objectives:

- Demonstrate the reliability and durability of thin ceramic coatings as well as any engine performance improvements achieved in actual service in engines propelling different types of vehicles, i.e. towboats and off-road ore carrier trucks.

- Provide technical guidance to prospective users of ceramic coatings in efforts associated with the in-service test and evaluation of these coatings.

- Provide a basis for a broad range of engine types and applications to identify the technical considerations which play a significant role in ensuring the in-service durability and performance of ceramic coatings applied to diesel engine combustion components.

A most important consideration in adapting the technology was to stay within the bounds of gas turbine engine experience. Therefore, the composition of the ceramic coatings used, their thickness and physical characteristics, and the application method used to apply them to gas turbine engine combustion cans over a period of more than 10 years were rigidly adhered to in their application to diesel engines. This project utilized partially stabilized zirconia ceramic coatings 0.008 in. - 0.015 in. (0.2 - 0.4 mm) thick that were plasma sprayed over thin, 0.004 in. - 0.006 in.(0.1 - 0.15 mm) thick metallic bond coats. The total thickness of the metallic bond and ceramic coatings was not to exceed 0.020 in..

The promise of the coatings to improve the durability/reliability of diesel engines was assessed by coating the combustion zone surfaces of two types of high speed diesel engines. The coatings, applied to the combustion components of each type of engine, were first tested under controlled environmental conditions in a test cell or on a test stand. This provided a means for measuring possible improvements in engine performance and an initial assessment of coating durability. Following this testing, the coatings were applied to the combustion zone components of each type of engine installed in selected off-highway transportation vehicles and subjected to extensive in-service test and evaluation.

One of the selected vehicles was an inland waterway towboat equipped with large bore 2-stroke high speed diesel engines. These types of engines are also commonly found in railroad locomotives. The second type of vehicle was an open-pit mine truck equipped with a small bore 2-stroke high speed diesel engine. These types of engines are also commonly used to propel small towboats, harbor tugs, fishing vessels and many other types of off-highway vehicles. Operational, in-service durability in excess of 14,000 hours was achieved.

Another project to use ceramics in diesel engines was initiated at the Cummins Engine Co. over 10 years ago to develop an "adiabatic" or low heat rejection engine[1,2] whose performance was to be improved by insulating the combustion zone components using thick, >0.1 in. (2.5 mm) monolithic or plasma spray coated ceramics on the combustion surfaces. This thick thermal barrier liner approach to the coating of diesel engine components has been pursued since that time in DOE/NASA jointly sponsored programs at the Cummins Engine Co. and Caterpillar, Inc.[3,4,5] Both projects finally settled on coating the piston crown, valves and cylinder head fire deck with 0.1 in. (2.5 mm) thick, partially stabilized zirconia ceramic coatings which were to have a thermal conductance of 0.5 BTU/hr in^2 °F (408 Watts/hr m^2 °K). The coated components were to demonstrate their durability and insulation characteristics in a 100 hr duration test in a single cylinder, laboratory engine that simulated an advanced on-highway truck diesel engine. After 4.5 years of development with considerable use of finite element analysis to establish thermal stress levels in the ceramic layer, much effort to refine the basic material, and other means to overcome the inherent brittleness of thick ceramics, one company is reported to have achieved the 100 hr. operation goal.

The use of thick coatings in diesel engines is a difficult technical challenge that is far removed from using thin, 0.01 in (0.25 mm) coatings that do not have thermal stress and other mechanical durability problems, as has been done in the project reported on herein. The thin, plasma sprayed zirconia ceramic coatings documented in this report have many years of demonstrated reliability in production gas turbine engines and should not be confused with the thick, ceramic thermal barrier coatings for diesel engines being developed in the DOE/NASA program. Properly applied thin coatings using the quality assurance procedures described in Appendix A have been demonstrated to be reliable for thousands of hours of operation.

This report is organized to first describe the ceramic coatings technology and summarize their initial application in gas turbine engines, then to briefly describe the initial efforts to apply them in thick (> 0.1 in.) form in "adiabatic" diesel engines and, finally, to present the results of the thin coatings used in this project that were successfully used in several high speed diesel engines operating at different duty cycles. In Appendix A, the recommended quality assurance considerations for thin coatings are presented in a form that can be used to establish quality control procedures for application of the coating to internal combustion engine components in production. In Appendix B, the

output of a computer literature search compiles the major quantity of papers that have been written since 1978 on the use of ceramic coatings in internal combustion engines.

II. CERAMIC COATINGS TECHNOLOGY

In gas turbines, thin ceramic coatings are used to provide a thermal barrier between the combustion gas and the metal substrate structures, such as burner cans to which they are applied. At the heat fluxes which occur in aircraft gas turbines, there is a considerable temperature reduction in the metal of the coated structure, of the order of 200°F. Hence the coatings have come to be known as *ceramic thermal barrier coatings* (CTBC) and will be referred to in this manner in this report. However, the degree of temperature reduction achieved in the use of the thin coatings on diesel engine components is considerably less and is generally of lesser importance. In the diesel engine, durability improvements, i.e., extension of the time between overhauls, and the degradation of engine performance with service time were the primary considerations.

A. Bond Coats

The types of coatings that are being evaluated for use in diesel engines are the culmination of several decades of coating development and application, primarily on the combustor cans of gas turbine engines. They had their genesis in the early 1950's when glass frits were applied on sheet metal combustor hardware from liquid slurries to add high temperature corrosion protection to the alloys of the period. Coatings of various compositions were applied that enhanced the oxidation resistance of the combustor cans, permitting higher combustion temperatures to be used.

Metallic protective coatings which contained greater amounts of chromium, and subsequently aluminum, were next developed, again primarily to provide enhanced oxidation resistance. As the understanding grew of the oxidation requirements of superalloys as traded off against their elevated temperature mechanical properties, primarily creep strength, the metallic coating compositions and microstructures were refined. Eventually a family of metallic corrosion resistant coatings were developed that are in use today. They contain a combination of iron, nickel, and/or cobalt, chromium, aluminum and an active element such as yttrium. The specific compositions are tailored to provide adherent, protective layers for different structural alloys and operating environments.

The metallic coatings are designated as MCrAlY's with the **M** standing for the metals iron, nickel or cobalt, the **Cr** for chromium, the **Al** for aluminum and the **Y** for yttrium. They are used on turbine engine components to protect structural metallic components that are low in such protective oxide forming

elements as chromium and aluminum because of strength considerations. The coatings are applied in thicknesses ranging from 0.003 in. (75μm) to 0.007 in. (175μm) by several techniques, primary among them being physical vapor deposition and plasma spraying. They are used to protect underlying superalloy substrates against high temperature oxidation and hot corrosion.

The MCrAlY coatings are also used extensively in CTBC's as a bond coat, located between the metal substrate and the porous ceramic thermal barrier outer coating. In this role they provide corrosion protection to the base metal, protecting it from combustion gas constituents that can readily move through a porous ceramic layer. The bond coats also provide a thermal expansion transition layer between the higher thermal expansion coefficient substrate metal and the lower thermal expansion coefficient ceramic thermal barrier layer. The rough surface of the as-applied bond coat also makes a good base on which the ceramic can deposit in a tightly adherent configuration.

The MCrAlY bond coats are applied primarily by the plasma spray process, resulting in a coating structure that is quite dense with randomly distributed, mostly noncontinuous, small pores. There is an inherent degree of oxidation within the bond coat located at particle splat boundaries. As a base for the outer ceramic layer, the MCrAlY bond coat is usually deposited between 4 and 8 mils (100 - 200 μm) thick. To decrease its porosity and internal oxidation in order to obtain increased corrosion protection for the substrate, it is sometimes sprayed in a low pressure chamber or within an inert gas shroud.

Thus, a coating material system that was initially developed to be used by itself as a corrosion protection barrier has been found to be an important constituent of the CTBC. The properties of MCrAlY coating systems, derived through many years of development and service experience, enhance the durability of the CTBC's.

B. Ceramic Coatings

Ceramic materials such as alumina (Al_2O_3) and zirconia (ZrO_2) have a number of properties that make them attractive for use as protective layers on engine components whose surfaces are subjected to elevated temperatures. Compared to metals, they have higher temperature performance capabilities as they are more resistant to oxidation, corrosion from sulfur or vanadium compounds and their salts, erosion and other forms of wear. They are also much better thermal insulators than metals, a key factor in their use in CTBC's. Their developmental and production use in gas turbine engines and more recently, their experimental evaluation in diesel engines is well documented in the technical literature.[6-12].

The components of a diesel engine which can most benefit from the use of ceramic coatings are those which have surfaces that form the combustion zone of a cylinder.[13] Thus, valve faces, piston crowns, cylinder heads and exhaust manifolds are prime candidates for the use of ceramic insulators. The thickness of the ceramic insulating layers on these surfaces can range from a few thousandths to several tenths of an inch. Many factors dictate the

thickness of the ceramic that will provide sufficient thermal insulation without sacrificing other factors such as durability or fabrication cost. Generally, ceramic thicknesses less than 0.060 in. (1.5 mm) are applied by some type of coating process. Thicknesses greater than this are typically fabricated in monolithic shapes and subsequently joined to the metal substrate. It should be stated at this point that thinner ceramic coatings deposited on substrates appear, at this time, to be more appropriate for use in diesel engines than thicker, monolithic ceramic bodies. The reasons for this will be discussed.

C. Ceramic Coating Selection Criteria

Many factors must be considered in the design of a ceramic material into a dynamic device such as a diesel engine. Several of the more important considerations are discussed below:

1. Mechanical Behavior

A ceramic layer is a brittle material. As such it has a relatively small tolerance for withstanding multi-axial loads, especially those which have a significant tension component. As the ceramic layer is made thicker it can develop greater stresses from a combination of mechanical and differential thermal forces. Its ability to withstand these stresses is limited because of its lack of ductility and the presence of defects that are potential crack starters. At the current stage in the development of structurally sound, load carrying ceramic materials, monolithic bodies, i.e., greater than about 0.060 in. (1.5 mm) thick have not shown to operate reliably in a diesel engine for any period of time.

However, the use of thin ceramics, i.e. less than 0.060 in. (1.5 mm) thick, with built in void and micro-crack structures to prevent the buildup of large stresses that result in catastrophic cracks have been demonstrated to perform reliably on gas turbine combustor components. Ceramics of this thickness are fabricated by a number of coating processes. It is this demonstrated approach to the use of ceramics in engines that should be pursued to provide the mechanical reliability that is required by diesel engines.

2. Physical Properties

The physical properties of the ceramics used in ceramic coatings play an important role in both their performance and durability. Table 1 lists the properties of the ceramic materials that are considered when thermal insulation is required.[14] Of all of the ceramics whose properties are suitable for coatings, zirconia has been, thus far, the most used ceramic in the gas turbine industry and is the most promising material for use in diesel engines. The other materials are listed to provide comparisons to the forms of ZrO_2 that are listed. Data sources are listed in Reference 14.

The most important physical properties that must be considered when a ceramic material is utilized in an engine component are its thermal

conductivity and thermal expansion. Thermal conductivity determines its insulation ability and thermal conductivity and thermal expansion are major factors in its durability. Other important properties that affect durability are Young's modulus, Poissons ratio, and fracture strength. All of these properties are affected by the microstructure of the ceramic which, in turn, is dependent upon the method of fabrication. Most of the properties listed in Table 1 were obtained from high density monolithic forms of the ceramic.

The exception in Table 1 is the plasma sprayed ZrO_2, which is the form that is the prime candidate for use in diesel engines. It can be seen that all of the key properties of plasma spray ZrO_2 compare very favorably with those of other ceramics. Its thermal conductivity is lowest, its thermal shock resistance parameter is lowest, its thermal expansion coefficient is on the high side, which helps in its adherence to higher expansion rate metals and its other properties are all in a desirable range.

3. Chemical Stability

The environment in which ceramic coatings on engine combustion zone surfaces will operate is primarily an oxidizing one. However, the combustion gases may contain aggressive sulfur or vanadium compounds that can cause corrosive attack.[12] The use of oxide ceramics generally precludes oxidation. Zirconia is resistant to gaseous sulfur attack, but can be affected by vanadium compounds, as will be discussed later. The deposition of compounds such as sodium or calcium sulfate, which occurs in diesel engines, on the coating's surface or in its pores can result in transport of sulfur into the coating which can combine with stabilizers in the zirconia such as MgO, with a deleterious effect. Also, the ceramic can undergo phase transformations at certain service temperatures which can adversely affect its performance by causing spalling of the coating to occur. Therefore, the chemical stability of the ceramic in the particular thermal and chemical environments in which it must serve is a significant consideration in the application of ceramic coatings.

4. Fabrication

The process by which the ceramic coating is applied to a metal substrate is a most important aspect of the use of ceramic coatings in diesel engines. The basic type of process and the processing parameters used affects the important mechanical and physical properties of the deposited coating as well as its composition and microstructure. These variables, in turn, affect the insulating ability of the coating and its corrosion resistance, adherence and durability.

The use of the plasma spray process has been determined to be the most advantageous method for applying ceramic coatings on turbine engine components. However, other processes can be considered. These include electron beam physical vapor deposition, chemical vapor deposition, pack diffusion, slurry deposition and sputtering. Coating surface refinements such as laser glazing, impregnation, and ion implantation are also used to modify the surface to resist particular operating conditions.

The economics of the coating application process also vary rather broadly. The cost of powders of various levels of purity and powder size distribution, the acquisition and operating costs of the spraying equipment, the versatility of the process with respect to part geometry, the amount and type of substrate metal preparation that is required and the post-application finishing cost all enter into the determination of the cost of depositing a ceramic coating on a valve face, piston crown or cylinder head. Since the plasma spraying process is one of the lowest in cost of the deposition methods and can be readily automated, its selection as the primary method to apply ceramic coatings on the surfaces of diesel engine components is a logical one.

D. Plasma Spray Process

Except for pack aluminizing, plasma spraying is the most commonly used deposition method for application of coatings to heat engine components.[14] Plasma spraying has been reviewed by Moss and Young[15] and by Tucker.[16] The preference for the plasma spraying process is based on simple equipment, fast deposition, ease of coating complex shapes, ability to vary coating composition, and economics. A typical plasma spray gun is shown schematically in Figure 2. Plasmadyne or Metco commercially available equipment is frequently used. Until recently, guns were either hand-held or attached to a lathelike table. Now sophisticated computer-controlled robotic equipment is being used.

A wire, rod, or more typically in the case of ceramics, a powder of the material to be deposited is fed through a plasma, typically 5 to 10% H_2 in argon. The material is partially or completely melted by the plasma and sprayed at high velocity onto the substrate. The plasma may be generated by arc discharge or by radio frequency induction. The spraying process can be conducted in air or at reduced pressure in low vacuum chambers. The somewhat similar flame-spraying process, where the material to be deposited is melted and propelled by an oxygen-acetylene flame, has been supplanted by plasma spraying for higher technology materials. Some important process variables are voltage, current, carrier gas composition, powder characteristics, powder feed rate, gun-to-substrate distance, substrate temperature, and post-coating heat treatment.[12,17,18].

Plasma sprayed coatings are typically low-density, porous, stressed, permeable structures. Attainment of densities above 90 or 95% of theoretical is difficult. For thermal barrier coatings the presence of porosity, microcracks, and possibly residual stress are beneficial in that they increase the resistance to heat transport and spalling. Depending on the application, certain types of porosity and microcracks are desirable in that they reduce the elastic modulus and thus improve toughness and thermal shock resistance. Excessive microporosity and larger cracks are, of course deleterious to strength, toughness, corrosion, wear, and erosion.

Kvernes and coworkers have described the criteria for powder selection and the qualities of some commercial powders as well as process variables.[19]

Important powder characteristics are precise composition, chemical homogeneity, particle size distribution and shape, flowability, moisture, content and impurities. To obtain the desired structure in stabilized-zirconia coatings, the powder should be pre-reacted with the stabilizer, which is usually an active element oxide such as Y_2O_3, MgO, or CaO, until the stabilizer cations are incorporated into the lattice structure of the zirconia. The need for stabilization will be discussed later. This should be done prior to the introduction of the powder into the plasma spray gun. This is not always the case with commercial powders. The worst case is a mechanical mixture of zirconia plus stabilizer which can segregate on spraying.

Fine powders and high gun power produce high-density coatings with a fine microstructure. The lower limit in powder particle size is about 5μm; the poor flowability of finer particles creates powder feeding problems. The maximum particle size is about 100μm; larger particles produce a coarse, very porous coating. Particle shape is important in that spherical particles flow better and cause less erosion of equipment. Many commercial powders are, however, not spherical because of the use of crushing and grinding to achieve the desired powder size.

E. Zirconia

Of the several oxide based ceramics that are appropriate for use as a thermal barrier coating on diesel engine components, partially stabilized zirconia (PSZ) has, by far, been the most investigated and used in production applications. It has primarily been applied by the plasma spray process to essentially static components in gas turbine engines, rocket thrust chambers, glass and metal-melting electrodes and molds. The surfaces in the combustion zone of diesel engines, i.e., valve faces and tulips, piston crowns and cylinder heads have the operating environments that are appropriate for the use of zirconia based ceramic coatings. The application of coatings to cylinder walls where sliding wear is an additional factor is not as certain.

In order to use zirconia based ceramic coatings on engine component surfaces with confidence, it is important to have an understanding of the nature of the material.[14] Pure zirconia has several crystal structures, with the equilibrium structure dependent on temperature. A phase diagram is shown in Figure 3.[20] The stable phase at room temperature is monoclinic. On heating, it converts to the tetragonal phase at 1170°C (2150°F), which in turn converts to a cubic structure at 2370°C (4300°F).[21] The tetragonal-to-monoclinic transformation for pure ZrO_2 upon cooling is rapid and is accompanied by a 4 to 6% volume expansion[22] which causes catastrophic cracking with resultant spalling and prevents the use of pure ZrO_2 ceramics. The need to modify this behavior is essential to the use of ZrO_2 in engines. The modified forms of ZrO_2 that are appropriate for use in diesel engines are designated partially stabilized zirconia.

Full stabilization of zirconia with yttria (Y_2O_3) and magnesia (MgO) has been known for over 30 years.[23,24] Additions of Y_2O_3, CaO, MgO, or rare earth oxides to ZrO_2 cause stabilization of the higher temperature phases[25,26] (i. e., the transformation temperatures are lowered). The additions of these elements is generally called "doping." If enough stabilizer is added, a nontransformable tetragonal phase occurs (see Figure 3) and/or the high-temperature cubic phase can be retained at room temperature. This allows the material to be cooled from the fabrication or service temperature without undergoing the disruptive tetragonal-to-monoclinic phase change. The cubic phase is not at equilibrium at room temperature but is retained metastably in a so-called fully stabilized material. Such material has been used industrially for many years.

King and Yavorsky first recognized 15 years ago the improved mechanical properties of partially stabilized, as opposed to fully stabilized, zirconia.[27] Since then the strength and toughness of partially stabilized material has received much attention.[12,14] In partially stabilized material, less dopant (8 - 10 mol % Y_2O_3) is used. The resulting microstructure of monolithic material prepared by sintering followed by heat treatment (aging) consists of cubic ZrO_2-Y_2O_3 solid solution as the major phase with minor amounts of monoclinic and tetragonal solid solutions. When plasma spraying is used to deposit the zirconia, the nontransformable tetragonal phase is retained in the deposited coating at room temperature.

The small tetragonal particles may contribute to transformation toughness in service as they can transform to the monoclinic state in the presence of a stress field. The tetragonal inclusions interact with stress fields by a variety of mechanisms to resist crack propagation and improve toughness. Even dispersed particles having the monoclinic structure can interfere with crack propagation and impart improved toughness. Since the poor toughness of nearly all ceramics frequently limits their use in structural application, any improvement in toughness is important. The doubling of the toughness of zirconia by partial stabilization is very significant.

Doping of zirconia not only influences temperature-phase stability but, fortunately, also decreases the thermal expansion coefficient of the material and reduces the volume change associated with the tetragonal-to-monoclinic transformation.[28] Partially stabilized material has a smaller expansion coefficient than does fully stabilized material; thus, the partially stabilized material has better thermal shock resistance. However, the smaller expansion coefficient of partially stabilized material causes more of an expansion mismatch in material deposited on higher-expansion metals.

Although the foregoing discussion is mostly appropriate for sintered zirconia, it is also applicable for understanding plasma sprayed zirconia base coatings. However, the different fabrication methods lead to important differences in the crystal structure, microstructure, and properties of sintered and plasma sprayed zirconia. These are discussed in the next section.

In the high-temperature applications of zirconia for thermal barrier coatings in turbine or diesel heat engine components, magnesia partially stabilized zirconia has been observed to become destabilized from attack by sulfur compounds and yttria partially stabilized zirconia from attack by vanadium compounds, with an associated lowering of mechanical properties such as toughness and thermal shock resistance and an increased propensity for cracking and spalling.

F. Plasma Sprayed Zirconia

Perhaps 90% or more of the development of thermal barrier coatings has been on plasma sprayed ZrO_2-base materials.[14] Typical materials are ZrO_2 stabilized with up to 24 wt % of either Y_2O_3, MgO, or CaO. Early successful work with plasma sprayed Y_2O_3-ZrO_2 was the application of a two-layer coating to gas turbine combustor cans. Reviews of this and more recent developments are available, and were the source of much of the following information. Development of zirconia thermal barrier coatings for gas turbines has been much more extensive than for diesels. Kvernes and Fartum in Norway[19] and Kamo and coworkers[10] have pioneered the use of ceramics in diesel engines.

1. Composition and Structure

The early success in applying thermal barrier coatings to gas turbine components in the early 1970's was with a 12 wt % Y_2O_3-ZrO_2 ceramic layer deposited over a Ni-16% Al-0.6% Y bond coat, which was previously deposited onto the metal substrate. Current coatings are most frequently stabilized with 6 to 12 wt % Y_2O_3, with 8 wt % being most common or with MgO with 22% being common.[12] Typically, the ceramic layer is about 0.020 in. (500 μm) thick; the thickness of the bond coat is about 0.004 in. (100 μm). A typical microstructure is shown in Figure 1. Recent development has focused on modification of the amount and type of stabilizer (such as CeO) added to the ZrO_2 and modification of the composition of the bond coat, particularly increasing the aluminum and chromium contents and adjusting the yttrium content. Additions of cobalt or replacement of nickel with cobalt in the bond coat has also been investigated.[29]

The bond coat discussed earlier, which is usually also deposited by plasma spraying, protects the substrate from oxidation and corrosion, which otherwise would lead to loss of adherence of the ceramic layer. Adherence of the ceramic layer to the bond coat is an important consideration as the ceramic-bond coat interface can be the location of thermal cycle-induced coating failures. An intermediate layer of chromium or nickel-chromium between the bond coat and the ZrO_2 layer has also been tried in diesel engine applications to prevent this type of failure.

Graded coatings have been investigated with the objective of improving coating adherence. The graded coating layer, which is between the NiCrAlY bond coat and the ceramic layer, consists of a mixture of zirconia and a metal

such as NiCrAlY. The concentration of zirconia increases as the distance from the substrate increases. The graded layer has a thermal expansion coefficient intermediate to those of the higher expansion bond coat and the lower-expansion ceramic layer. A problem with graded coatings is oxidation of isolated metal particles within the graded layer. The volume expansion associated with oxidation can cause coating failure. Graded coatings are currently being developed for thick ceramic thermal barrier coatings.

The as-deposited ZrO_2 has been determined by x-ray diffraction to consist primarily of a nontransformable tetragonal phase of about the same composition as the starting powder.[30-31] Nontransformable refers to the fact that the as-deposited material, because it contains about twice the Y_2O_3 content of the equilibrium transformable tetragonal phase, does not transform to the monoclinic phase on cooling, see Figure 3. The as-deposited material consisted of 80% of this nontransformable tetragonal phase, up to 8% of the transformable tetragonal phase (occurs as monoclinic at room temperature), and 12% cubic zirconia.

The plasma spraying process also influences the phases that are present. For example, phases present in the starting powder can be retained if some of the powder particles, particularly large particles or those near the periphery of the plasma spray, are not completely melted. There is no evidence that transformation toughening is operative in plasma sprayed partially stabilized zirconia coatings.[32]

2. Failure Mechanisms

Several mechanisms that can lead to failure of plasma sprayed zirconia and other ceramic thermal barrier coatings in heat engine applications have been identified. The discussion of these mechanisms should be considered in the context that the coatings have operated successfully in turbine engines for many years and that, generally diesel engine operating environments are not as severe as those of turbine engines. The critical failure mechanism varies with coating properties, severity of thermal cycling, and most importantly, with the quantity of contaminants such as vanadium, sodium, and sulfur, in the fuel. Coating failure, regardless of the mechanism, usually consists of loss of adherence by cracking and separation (spalling) of the coating from the substrate. This separation usually occurs at or near the oxide-bond coat interface, because this is the weakest region and is also a region of high stress. A common location for the failure is near the interface but within the ceramic layer.

Several factors contribute to stressing the coating.[32] An important factor is mismatch in the thermal expansion coefficients of the metal substrate, the MCrAlY bond coat, and the ceramic layer. The ceramic has a small expansion coefficient, near 10×10^{-6}°/C for plasma sprayed zirconia, compared with 15 to 16×10^{-6}°/C for the bond coat and typical substrates. Also, the steep temperature gradient across the ceramic insulating layer induces stress. These

stresses are present even at steady state and can be increased during transients such as a rapid startup or shutdown.

Another important source of stress is residual stresses in the as-deposited ceramic coating at room temperature. These stresses arise from the nature of the coating process, that is, rapid cooling of molten or partially molten drops which impact the cooler substrate surface. This creates a stressed coating. Residual stress in the coating also occurs because during the deposition process, the coating and substrate are at different temperatures. Consequently, on cooling, the coating and substrate have different thermal contractions. Clearly, control of substrate temperature can markedly influence the magnitude of such stresses and actually cause them to be either compressive or tensile.

Properties of the ceramic coating and the bond coat are not constant with time and temperature because of densification and phase changes within the ceramic and corrosion and oxidation of the bond coat. These stress-generating mechanisms usually cause propagation of cracks initiated at flaws during repeated thermal cycling, the most damaging cracks being in the plane of the coating. Flaw propagation and linkup lead to spalling, which can appear as gradual loss of the outermost region of the ceramic layer or, more typically, separation at or near the ceramic-bond coat interface. Because of the large number of stress origins and the complex manner in which they vary with temperature, temperature gradients, and relaxation (stress relief via annealing of residual stresses or creep of the ceramic and/or substrate), one cannot rigorously calculate the resultant stress state.[32] It is postulated that the stresses in the ceramic coatings which occur in diesel engine applications are not as severe as those which occur in gas turbine applications.

Perhaps the simplest failure results from thermal expansion mismatch between the ceramic layer and the NiCrAlY bond coat, causing spalling to occur. Another common failure mode is thermal fatigue. For less severe applications, these problems have essentially been solved by deposition of a ceramic layer that is compliant (low modulus and yielding) as a result of numerous cracks oriented both perpendicular to the substrate and randomly and high porosity induced in the coating by selected levels of the deposition process variables. This approach, however, is not completely satisfactory because the same microstructural features that yield a low-modulus material also reduce its tensile strength and increase its permeability to corrodents and susceptibility to wear and erosion. The lower strength makes the coating more susceptible to failure from stresses generated by other mechanisms, for example, thermal gradient and thermal shock. These are not as likely to occur in diesel engines as they are in gas turbine engines.

Spalling of the ceramic coating can also be caused by oxidation of the underlying metal. Partially stabilized zirconia has a defect crystal structure through which oxygen can rapidly diffuse, and the porosity in the zirconia layer also aids oxygen transport. The volume change associated with oxidation of the bond coat can cause the ceramic layer to spall.[33] Particulate

erosion, while not a usual consideration in diesel engines, can also progressively remove the porous ceramic coating.

3. Degraded Fuels

Ceramic coatings consisting of a 0.008 in. - 0.015 in. (0.2 - 0.4 mm) partially stabilized zirconia deposited over a 0.004 in. - 0.006 in. (0.1 - 0.15 mm) NiCrAlY bond coat, have been adequately developed for turbine combustor components when clean, high quality fuels are used. Such coatings have been used on aircraft burners and afterburners for over 12 years. However, it has been observed on numerous occasions that further improvements, particularly reduced hot corrosion, are needed before such coatings are routinely applicable for use in engines burning lower quality fuels. Such fuels can contain sufficient impurities such as vanadium, sodium, and sulfur to cause excessive hot corrosion and subsequent spalling or flaking of the ceramic thermal barrier.[32]

Evidence exists that liquid (Na_2SO_4, $MgSO_2$, $Mg_3V_2O_8$, $Na_2V_2O_6$, V_2O_5) formed from the fuel impurities condense onto and infiltrate the porous or micro-cracked ceramic coating until the temperature equals the melting point. On cooling, the molten material solidifies and produces disruptive stresses.[32,34] Alternatively the presence of the material in pores and cracks could make the coating less compliant and therefore less capable of accommodating thermal-cycle-induced stresses.

Corrodents can also chemically remove the stabilizing element Mg, Ca, or Y from the zirconia, allowing it to undergo disruptive phase changes on thermal cycling.[32,33] The susceptibility of fully or partially stabilized zirconia to undergo destabilizatlon depends, among other things, on the type of dopant, microstructure, service temperature schedule, and exposure to contaminants. Formation of the following phases that deplete the zirconia of dopant have been identified: YVO_4, $Mg_3V_2O_8$ and $MgSO_4$. Yttria depletion of the surface region of Y_2O_3-ZrO_2 has been observed in the presence of Na_2SO_4 and SO_3 gas and, although not fully understood, is correlated with the severity of the corrosive conditions.[35] In addition to the detrimental effect of destabilization, formation of the above compounds can also be deleterious because of the volume change (particularly expansion) associated with their formation.

The detrimental effects of corrodents is a major problem that remains to be solved for thermal barrier coatings in gas turbine engines that are exposed to combustion gases that contain aggressive compounds. Most diesel engine service environments are either free from these compounds or operate at temperatures where the activity of the compounds is low. However, the use of certain degraded fuels could introduce them into the diesel engine environment.

4. Properties

Thermal expansion of plasma sprayed zirconia coatings has been reviewed by Berndt and Herman.[36] The thermal expansion of plasma sprayed zirconia is aniostropic; that is, it differs for the longitudinal (parallel to the substrate surface) and transverse (perpendicular to the substrate surface) directions. The transverse expansion also varies with the thermal history of the coating, including the number of thermal cycles. Changes continue to occur even after a dozen or more heating and cooling cycles. For 8 wt % Y_2O_3-ZrO_2 the longitudinal thermal expansion coefficient was approximately constant at 10 x 10^{-6}/°C. Typical average values for zirconia containing 8 to 30 wt % yttria are 6 to 13 x 10^{-6}/°C, respectively.[37]

The thermal emittance radiation of heat from the hot surface of a heat engine component is important because it influences how much energy is radiated to other portions of the engine and may have an effect on the character of the combustion flame. Hemispherical total emittance measurements have been made for plasma sprayed 12 wt % Y_2O_3-ZrO_2 coatings on a NiCrAlY substrate.[38] Emittance decreased with increases in temperature and coating thickness. For coating thicknesses in the range 0.006 in. to 0.029 in. (155 - 725 μm), the emittance was 0.61 to 0.68 at 800°F. These low emittance values assist in reducing heat transfer to cooler portions of the engine.

III. COATING SELECTION

Based on the extensive amount of experience using partially stabilized zirconia with an MCrAlY bond coat between it and the metal substrate in the gas turbine industry the selection of the basic coating composition was made. However, several different detailed compositions have been used in various applications for specific reasons in the available body of experience. Therefore several different compositions of bond coat and ceramic were incorporated into the project. The reasons for their selection are discussed below.

One of the principal variables in the selection of the detailed ceramic coating compositions was the choice of the active stabilizer element in the partially stabilized zirconia (PSZ). There are several aspects of its behavior as a ceramic stabilizer that had to be considered:

- **High temperature stability** - Y_2O_3 provides stability of the desired phase to a higher temperature than MgO which, in turn, provides more stability than CaO.

- **Strength/erosion resistance** - Y_2O_3 results in the ZrO_2 having greater creep strength and erosion resistance than MgO or CaO stabilizers.

- **Resistance to sulfidation attack** - MgO has been reported to be attacked by SO_2/SO_3 in combustion gases, forming $MgSO_4$ which is readily removed by mechanical abrasion and destabilizing the ZrO_2, leading to spalling. In this regard it is more vulnerable to a high sulfur content combustion environment than is Y_2O_3.

- **Resistance to hot corrosion/fluxing attack** - Y_2O_3 has been reported to be attacked and removed by Na_2SO_4-V_2O_5 fluxes. Since the presence of Y_2O_3 is required for the stability of ZrO_2, this destabilization reaction can result in the premature loss of the coating strength. MgO has been reported to be less sensitive to this type of attack.

- **Cost** - MgO stabilized ZrO_2 is somewhat lower in cost than Y_2O_3- ZrO_2. The bond coat composition involved another series of variables that resulted in the selection of several different compositions.

The coatings were applied on the components of large bore, high speed and small bore, high speed diesel engines. The components were the valves, piston crowns and cylinder heads on both the large and small bore engines. The exhaust manifolds of the small bore engine were also coated on the inside and the outside surfaces. The specific compositions that were applied to each part are listed in Table 2 along with the suppliers. This selection of the coatings was based on the following:

- The 22 wt % MgO-ZrO_2 was selected because of its promising performance in the Norwegian ship program and its resistance to vanadium compounds.

- The 8 wt % Y_2O_3 ZrO_2 was selected because it has been the most successful material used to insulate combustor cans in the gas turbine industry and it is resistant to sulfur compounds. It was also the primary product of most all of the suppliers in the program.

- The NiCrAlY bond coat was selected because of the experience gained using it in foreign marine diesel engines.

- The NiCoCrAlY bond coat was selected because of its general use by several suppliers in coatings for the gas turbine industry. It is particularly compatible with the nickel and cobalt base alloys used in gas turbines.

The porosity of the zirconia coating was also varied to determine what level of tradeoff between thermal fatigue resistance and corrosion barrier behavior could be tolerated. This was accomplished by the selection of the supplier. Other variables that were incorporated into the test program were:

variations in the thickness of the ceramic and bond coats both on a single part and between components, surface variations in roughness and edge smoothness.

The procurement specifications for the coatings were made comparatively simple. Each supplier was asked to supply the composition of coating or coatings that had performed successfully in either gas turbine or diesel engine operation and that had a good chance to last for up to 6000 hours of operation in the large bore, high speed engine which was to propel a towboat on the inland river system. The bond coat thickness was specified to be 0.005 in. (0.125 mm) thick and the ceramic coating was specified to be 0.010 in. (0.25 mm) thick. Coating locations on each type of part were also specified. Application variables, starting powder purities, final surface color and texture, porosity and microstructure were all left to the discretion of the supplier.

Two coating suppliers were selected to provide a spectrum of coating compositions and microstructures that would permit the establishment of as wide an acceptance band for the coating systems as possible. Each supplier had an extensive performance record in supplying coatings to the gas turbine industry.

Other suppliers of ceramic coatings are available in this country and abroad. The coating suppliers for this project were selected on the basis of first hand knowledge of their successful experience and capabilities.

IV. PRE-SERVICE CHARACTERIZATION OF COATINGS

The coatings for the locomotive and the towboat large bore, high speed engine evaluations were processed at the same time by the same thermal spray vendors. The determination of their quality level was made using the same evaluation procedures at the same time. The coatings on the small bore, high speed engine components for the off-road vehicle evaluation were processed by one of the same vendors that coated the towboat's engine components, but at a later time. The same evaluation procedures were used as for the towboat's engine components. The quality checks consisted of destructive metallographic examination of components produced at the same time as the end-use components and a visual analysis of all coated components.

A. Large Bore, High Speed Engine Components

The examination at LBL consisted of sectioning each test part at various locations and studying the microstructures at 100 and 500X magnifications. The following elements of the microstructures were documented:

- thickness of the bond coat and ceramic coat
- nature of the bond between the bond coat and the base metal

- nature of the bond between the bond coat and the ceramic coating
- porosity of the ceramic coatings
- variation in the coatings' thickness and interfaces
- oxidation of the bond coat
- any obvious defects

The composition of the various layers was not determined at LBL. The certification of the coatings' compositions by the suppliers per the requirements of the purchase orders was accepted.

The visual examination of the components received at LBL consisted of determining the consistency of the color and surface texture continuity of the ceramic coatings, establishing whether the location of the coatings conformed to the specified locations on the part drawings that were sent to the suppliers, and observing with a 10X power magnifying glass whether there were any visible defects, especially cracks and foreign objects, in the coating surfaces.

The visual inspection of the components scheduled to be installed in towboat engines was carried out at the Ingram Barge Company warehouse and looked for the following:

- assurance that each serial number part had the assigned coating system on it and in the specified location
- ceramic coating color consistency and evenness of application
- undersprayed and oversprayed locations
- cracks, chips, other discontinuities, using a 10X power magnifying glass
- adherence by coin tap method

The large bore components for the locomotive engine were not individually inspected.

1. Visual Inspection

The components received at LBL for inspection and the components sent by each supplier to the Ingram Barge Company warehouse had essentially the same appearance. Photographs of components with representative appearances were taken of the components sent to LBL. A visual examination of each part sent to the Ingram Barge Company warehouse was carried out and a verbal description of the coated part was entered in a log book as it was inspected at the warehouse.

The photographs contained in this report are representative of the surfaces of each type of part that was plasma spray coated. They are identified by supplier, not by serial number. They do not include each type of part by each supplier. Several components inspected at the Ingram Barge company warehouse had discrepancies that separated them from the large majority of components which appeared to be entirely satisfactory. Notes on these discrepancies are contained in the log book. None of the differences from the norm were considered serious enough to prevent the components from being

installed in the engines. They were documented to provide a "before" base to compare with their "after" service appearance.

a. Valves

Supplier A - In Figure 4 are views of the valve with a face-only and a face and stem coated with 8 wt % Y_2O_3-ZrO_2-NiCoCrAlY coating. The surfaces were evenly colored and had a constant surface texture. There were no areas of overspray or underspray. They had an excellent appearance. Figure 5 is a valve face showing the evenness of the coating application. The dark spot is on the surface, not in the coating. Figure 6 is the valve stem showing the evenness of the coating application. The valve coated by Supplier B had the same uniform appearance as Supplier A valves.

Supplier B - The valve face in Figure 7 shows the coating of 22 wt % MgO-ZrO_2-NiCrAlY. The coating was even in color and surface finish. Figure 8 shows a valve stem that had an improper application of coating on the valve seat and side of the face. Coatings on the valve seats of components received at Ingram Barge Company were readily removed by surface grinding at the warehouse during the inspection procedure. Otherwise, the coating appeared to be satisfactory.

All of the valves sprayed by all suppliers with only MCrAlY had an even, gray appearance; none were photographed.

b. Piston Crowns

Supplier A - The surface shown in Figure 9 had an even appearing 8 wt %$Y_2O_3ZrO_2$-NiCoCrAlY coating with no areas of overspray at the edge or in the handling hole. The smudges are dirt from handling.

Supplier B - The surface shown in Figure 10 had an uneven color of the 22 wt % MgO-ZrO_2-NiCrAlY coating with segments of darker appearing rings. There was overspray at the edge and in the handling hole.

The appearance of all three coating suppliers products was typical of the piston crowns inspected at the Ingram Barge Company warehouse.

c. Cylinder Heads

Supplier A - An even, high quality application of 8 wt % Y_2O_3-ZrO_2-NiCoCrAlY with no areas of over or underspray is shown in Figure 11.

Supplier B - An even application of 22 wt % MgO-ZrO_2-NiCrAlY is seen in Figure 12. A significant undersprayed area is seen at the 10 o'clock position. Overspray also occurred in the injector hole.

2. Metallographic Analysis of Components

It is known that the polishing techniques used to prepare the ceramic coatings for microscopic analysis can directly affect their observed degree of porosity. Also, care must be taken in sectioning the components to preserve the ceramic coating on the cut edge. The techniques used were carefully repeated for all of the components that were inspected. Therefore, the

variation in degree of porosity between coatings is comparable. The cutting and polishing technique that was used was:

The specimens were cut on a water-cooled metallographic cut-off wheel. They were mounted in protective plastic mounts and polished as follows.

- Hand sanded successively on 180, 240, 320, 480, 600 grit silicon carbide sandpapers using water lubricant.
- Polished on a rotating polishing wheel using 6μm, then 1μm diamond paste.
- Polished in a Syntron machine using 0.05μm alumina for approximately 10 minutes.

The mounting of the specimens was also determined to be a critical element of specimen preparation. Microscopic observation of their adherence can be significantly affected by the method used to mount the specimen in plastic holders prior to specimen polishing. The hot mount used a phenolic type plastic that required heat and pressure to cure it. The ceramic to bond coat bond was destroyed by this mounting procedure. The cold mounting process used an epoxy plastic material that cures at ambient conditions. This method of mounting did not affect the integrity of the ceramic to bond coat bond. It was used for all specimen mounts.

a. Valves

The various locations from which specimens were taken are indicated in the sketch in Figure 14.

Supplier A S/N 109 - The coating thickness of the bond coat on the flat rim of the face shown in Figure 14 was of the specified thickness whereas the ceramic layer thickness was 40% greater than that specified. The interfaces between the PSZ and bond coat and bond coat and base metal are acceptable. The as-polished porosity of the PSZ coating was greater than that of the other suppliers' coatings, but is considered acceptable. The curved part of the face on valve S/N 109 seen in Figure 15 has a thinner, more porous coating than the rim part. The porosity of the ceramic coating, particularly in the area where it interfaces with the bond coat, is great enough to give some cause for concern. The coating is considerably more porous than those from the other suppliers. There is no basis for not trying the components in the engines.

In coatings used in aircraft gas turbines, the level of porosity shown in Figure 15 provides necessary thermal fatigue resistance. The interface bond between the layers shown in the right hand photos are acceptable. The same conditions exist at the center of the valve face shown in Figure 16 as existed in the curved part. The porosity near the ceramic coating-bond coat interface is questionable, but at this time is not cause for rejection.

Supplier B S/N 34 - Two cross sections are shown in Figure 17 of the three layer coating system that was typical of the microstructures of all of Supplier B's coated valves having both two and three layer systems. All aspects of the coating system are acceptable. The layer thickness shown in

Figure 18 on the flat part of the rim is near that specified. The porosity of the ceramic layer is acceptable. The interfaces between the three layers and the base metal are acceptable.

The coating system on the curved part of the face has the same thicknesses as that on the rim of the same valve, as can be seen in Figure 19. All aspects of the microstructure are acceptable. The coating system on the center of the face in Figure 19 has the same thickness of each layer as was deposited farther out on the face. The bond coat in this cross section appears to be somewhat more porous than that seen in Figures 17 and 18 but it is acceptable. All other aspects of the coating system are approximately the same as seen on the other locations across the face and are acceptable.

b. Piston Crowns

The configuration of a piston crown presents a somewhat difficult target to the plasma spray gun. The angles between direct overhead position of the gun and the surface range from near 0° to 90°. Furthermore, the circular shaped crater with a raised area at the center causes plasma flow patterns that can swirl around particles of coating being deposited either to or away from certain areas of the surface. This results in varying thicknesses and microstructures. These two factors must be added to the tooling considerations in setting up for plasma spraying this component. As the components sprayed for the large bore engines were basically the first piston crowns sprayed by the suppliers, considerable variation, especially in coating thickness, occurred.

Figure 20 is a plot of the total ceramic coating thickness variation across two piston crowns coated by Supplier B, top curve, and the thickness variation of the PSZ coating, middle curve, and the bond coat, lower curve. The top sketch is a full scale cross section of the piston crown. The three curves are linear representations of the coating surfaces, hence the difference in length of the sketch and the curves. It can be seen that while there is some variation at a given position on the crown surface from part to part, generally the thicknesses between components was quite uniform.

The thickness within a single part varies considerably as is seen in Figure 20. Generally, the greater the angle between the direct overhead position and the surface being coated, the greater is the coating thickness. At the shallow impingement angles on the side of the crown crater the coatings are markedly thinner. The significantly greater thickness on the flat, outer rim of the crown than on the balance of its surface is not desirable. The few places where the bond coat was less than 0.003 in. is also not desirable. Similar thickness variations occurred in the piston crowns coated by Supplier A. These thickness plots will provide guidance to the suppliers for coating future components. The variations show that considerable processing technique refinement is needed before uniform coatings can be applied on piston crowns.

Supplier A S/N 84B - 1465 - The greater porosity PSZ coatings applied by Supplier A are shown in Figure 21. With the exception of Section A where

the outer part of the coating was more dense than the inner part, the uniformity of the PSZ microstructure across the crown was good. The microstructure was very similar to that of the PSZ on the valves coated by Supplier A, indicating that they have a good control of their spraying parameters. The bond coat varied in thickness, but had a reasonably uniform microstructure. As can be seen, both the PSZ and the bond coats varied in thickness as was discussed earlier (see Figure 20). The bond between the coating layers, shown in Figure 21, was acceptable.

Supplier B **S/N 84B-1357** - Both the microstructure and the thickness of the PSZ vary across the piston crown shown in Figure 22. While the microstructure of the bond coat is quite consistent, its thickness varies considerably. The thickness at Section B is considered too thin to serve its purpose adequately. However, the post-service analysis will either verify or disprove this hypothesis.

The higher magnification bond area micrographs of the ceramic coating on the same piston crown are shown in Figure 23. Both bonds were acceptable at all locations.

c. Cylinder Heads

The cylinder head surfaces to be coated were flat which made the plasma spraying process relatively simple with regards to positioning the plasma spray gun except for the valve part area. However, each piece weighed over 150 lbs which required handling and positioning equipment that the coating suppliers were not prepared for. The tops of each cylinder head were sawed off the balance of the part and the more handleable slabs were then cut into sections using standard metallographic cutting equipment.

Supplier A **S/N 84L-2775** - Cross sections of the ceramic coating are shown in Figure 24. The microstructure was quite uniform, but the thickness of the PSZ coating was thicker in the center than it was further out. The bond areas shown were acceptable.

Supplier B **S/N 84D-0265** - The bond coat on the head that was sectioned, see Figure 25, was nearly non-existent, being only 0.0015 in. thick at its thickest point. If adherence in service is a problem, this coating may not survive. Special attention will be given heads coated by Supplier B during and after service to determine how important it is to have a bond coat on the head surface. The interfaces between the layers, were acceptable. The ceramic coating, with its low thermal expansion coefficient, was actually contacting the higher thermal expansion cast iron in places. However, as shown in Table 1, the expansion coefficients of plasma sprayed ZrO_2 and the cast iron are not too different.

B. Small Bore, High Speed Engine Components

The components for the small bore, high speed diesel engine were thermal sprayed by Supplier A. Exhaust manifolds, exhaust valve faces, piston crowns and cylinder head fire decks were coated for a 150 hour test

stand evaluation. Subsequently exhaust manifolds and piston crowns for three off-road vehicle engines were coated by Supplier A and sent for installation in large ore hauling trucks in an open pit copper mine. The components installed in the engines were visually examined using the criteria listed above for the large bore, high speed engine.

V. IN-SERVICE PERFORMANCE OF COATINGS

A. Performance of Coatings in Large Bore High Speed Locomotive Engine

Components coated at the same time as those coated for the large bore, high speed towboat engine by coating Suppliers A and B were used in a test stand engine at Southwest Research Institute operating over a representative railroad locomotive duty cycle for 500 hours before the components were removed from the engine for non-destructive and destructive analysis. Since this engine was the first to be tested, the performance of its coating will be discussed first.

1. Valves

After the 500 hour test, the 8 wt % Y_2O_3-ZrO_2 coating on the valve face from Supplier A had essentially the same appearance as before the test with some carbon deposit on it, Figure 26. The cross section of the coating shown in Figure 27 from the 500 hour test did have some evidence of localized, shallow spalling at the top of the ceramic as the thickness varies from 0.005 in. to 0.012 in. (0.12 to 0.3 mm). Comparing micrograph C which shows evidence of thinning with micrographs A and B which do not, it can be seen that the ceramic layer in C is more dense than those in A and B. The higher thermal stresses that can occur in the more dense areas could have been responsible for the localized spalling.

The shallow, localized spalling of the coating was a quite infrequent occurrence on the valve surface and seemed to occur only where the coating was more dense compared to adjacent areas and where cracks could be observed. It indicates that care must be taken in application of the coating to assure that the density variation is small. Other coatings that were denser but more consistent did not spall; so it was not the density level, per se, that caused the spalling.

No evidence of stabilizer depletion was found. The x-ray diffraction peaks in Figure 28 indicate that the Y_2O_3 was present and stabilizing the zirconia. Therefore, the observed spalling was not due to the phase transformation from tetragonal to monoclinic with its accompanying volume increase. The x-ray diffraction patterns for the before and after conditions (on two different valves) shows essentially the same amount of tetragonal + cubic, 95%, and monoclinic, 5%.

A valve that was coated with 22 wt % $MgO-ZrO_2$ by Supplier B had its coating almost completely removed during the engine test with only a thin layer of approximately one-tenth the original thickness remaining. The identified reason for the loss of the ceramic coating from the valve face was the uneven distribution of MgO stabilizer throughout the ZrO_2 coating. Quantitative energy dispersive x-ray spectrometry (EDS) of several locations on the surface of the coating and through its cross section revealed regions with MgO concentration as low as 0 to 5 wt % and some areas as high as 40 wt %.

Figure 29 shows the x-ray diffraction peaks for the before and after test conditions of the supposed 22 wt % $MgO-ZrO_2$ coating for two different valves. In the as-applied condition, the tetragonal phase was 90% and the monoclinic phase was 5%, as would occur when the partially stabilized zirconia is cooled rapidly on the steel substrate. The peaks from the test valve surface show that a major phase transformation from tetragonal to monoclinic had occurred in service. The volume increase accompanying this phase change could cause the coating to spall off almost down to the bond coat, as was observed. This transformation occurred because the ZrO_2 did not contain sufficient MgO throughout to prevent it from transforming to the monoclinic phase.

The observed uneven Mg distribution in the tested coating may have been present to some degree in the as-applied coating. However, more probably, it primarily occurred during service as the result of a reaction between the MgO and sulfur in either the combustion gases or in the extensive $CaSO_4$ deposits that occurred on the coating surfaces and in their pores. A possible gas reaction is $MgO + SO_3 = MgSO_4$.

No as-applied coatings were found to have such a wide variation in magnesium content as was measured after testing. No $MgSO_4$ was found in the thin layer of ceramic remaining after the test, but this could have been the result of the coating spalling off in those areas where the zirconia was unstable because of the formation of $MgSO_4$. The longer time test in the towboat engine helped in gaining a better understanding of what happened to the valve face coatings during service. The fact that the larger surface coated components i.e., the piston crowns and cylinder heads, tested in the engine from the same supplier did not spall off in service indicates that the valve faces were exposed to a more severe environment.

2. Piston Crowns

The piston crowns were 9 inches in diameter and had the cross section shape shown in Figure 30 (one-half of crown shown). Their surface contour represented a somewhat difficult problem for the manual plasma spraying operation. The change in the direction of the surface at the lip of the bowl portion from horizontal to vertical required that the angle between the spray gun and the part and its traversing speed across the part be significantly changed in order to keep the coating thickness near constant. While the

thicknesses varied considerably, their variation did not adversely affect the performance of the coatings. In production, the automation of the plasma spray operation should eliminate this variation.

The appearance of the 22 wt % $MgO-ZrO_2$ coating from Supplier B on the piston crown surface after the 500 hour test at all six locations in Figure 30 is shown in Figure 31. This coating is the same one as the middle coating in the untested condition shown in Figure 8. It can be seen that the coating was unchanged after the engine exposure, indicating that a ceramic coating can perform acceptably on a piston crown in the engine's operation environment, even with markedly different thicknesses. EDS analysis indicated the presence of the expected as-applied 22 wt % MgO concentration and x-ray diffraction confirmed that no transformation to the monoclinic structure had occurred. The difference in the behavior of the same MgO stabilized coating on the valve faces and on the piston crown indicates that the conditions on the valve face were favorable for the reaction between MgO and sulfur while they were not on the piston crown's surface. The piston crown's surface operates at a lower temperature than does the valve face. The piston crown is water cooled while the valve face is not. Also the valve face is made of a lower thermal conductivity alloy than is the piston crown. The 8 wt % $Y_2O_3ZrO_2$ coating on the piston crowns also performed in an acceptable manner. This performance is in stark contrast to the spalling of this material which occurred on a valve sprayed by the same supplier.

B. Performance of Coatings in Large Bore, High Speed Towboat Engine

The large bore, high speed coated engine that propelled the towboat on the inland waterways, along with a companion uncoated engine, was opened once during the 14,000 hours of operational time over the two year installation period when components were removed for destructive analysis as well as all components being visually inspected. This occurred at 8,990 hours. At the end of the 14,000 hour service duration, components also became available for detailed analysis. At each time, 8,900 hours and 14,000 hours, different aspects of the behavior of the coatings were observed and documented. The analyses of the performance of the coatings in the towboat engine will be presented in this report in two parts, one for each of the two time periods.

The effect of the coatings on the performance of the engine were measured and documented by Seaworthy Systems, Inc. and are contained in their final report.[39] A summary of the principal changes that were reported are listed in Table 3. The changes were determined by measuring the behavior of the same engine in service in uncoated and coated conditions using carefully calibrated instrumentation and the observations of the boats' captain.

1. 8990 Hour Performance of Coatings

Following 8990 hours of typical river service the engine cylinders containing the ceramic coated components were disassembled for visual

inspection of the coated components. The coatings on the exhaust valves, piston crowns and cylinder heads generally appeared to be in good condition. Five valves and a piston were removed from the engine for a destructive analysis of the coatings.

a. Engine Deposits

After solvent cleaning to remove oil and loose carbon deposits, all tested components were found to have whitish, powdery deposits of varying thicknesses on their surfaces. In some regions of the valve stems, these deposits were about 0.08 in. (2030μm) thick, while on the valve faces they were generally very thin and not visible to the naked eye. The X-ray diffraction (XRD) pattern for a coated valve face where no deposit was visible is shown in Figure 32. This trace clearly indicates that there exists a significant deposit of calcium sulfate ($CaSO_4$) over the valve coating. Because of the presence of the overlying $CaSO_4$ deposit, the XRD pattern of zirconia is overshadowed. The deposit had to be removed before any diffraction information for the zirconia was obtained.

Figure 33 shows the diffraction pattern for a tested valve surface after the specimen was ultrasonically cleaned. The cleaning removed much of the $CaSO_4$ and revealed the underlying zirconia. Note that the second major $CaSO_4$ peak is coincident with the second major monoclinic ZrO_2 peak. Also note that the tetragonal and cubic ZrO_2 peaks are indistinguishable. Fortunately the relative amounts of tetragonal and cubic ZrO_2 are of little concern. What is important to the survival of the coatings is the amount of monoclinic ZrO_2 present. The fact that some $CaSO_4$ remained after thorough cleaning and other metallographic evidence indicates that it penetrated into the coating.

Several deposits on the various coated components were similarly analyzed and all were found to consist entirely of $CaSO_4$. Its occurrence is understandable given the presence of calcium in the lubricating oil and sulfur (in the fuel in impurity concentrations). The combustion environment may produce SO_3 gas which can react with Ca to form the very stable $CaSO_4$.

b. Supplier A Coatings

Valves - Representative cross section micrographs of a Supplier A, flame stabilized powder coating applied to the face of Valve No. 90 are seen in Figure 34. A near complete loss of ceramic had occurred with only a thin layer of approximately .001 in. (0.02 mm) remaining. The remaining ceramic coating seen here was all that remained on the valve surface. So little ZrO_2 remained that there was no suggestion as to its former structure. Unfortunately, little information regarding its failure mechanism can be gained from what is left of the coating.

The pre-alloyed powder coating applied to the face of Valve No. 99, in contrast to all other valve coatings analyzed, survived the 8990 hours of engine service and remained in excellent condition. Seen in Figure 35 is the coating on the valve face after service exposure. It remained completely intact

and unaltered. The ceramic layer is about .010 in. (0.25 mm) thick, precisely that which was specified. The coating is considerably more dense than that of the Supplier B coating. This lower level of porosity may explain the observed absence of $CaSO_4$ penetration into the coating.

The strikingly different performance of the two Supplier A 8 wt % Y_2O_3-ZrO_2 coatings on the valves is attributed to a basic difference in the starting ZrO_2 powders. The ceramic coating on Valve No. 90 had the same overall composition as the powder used for the coating on Valve No. 99. The difference was in the distribution of the Y_2O_3 and the ZrO_2 in the powders and in the subsequent coating. The coating applied to Valve No. 90 was sprayed using a flame stabilized composite powder. This powder consists of a mixture of discreet ZrO_2 and Y_2O_3 particles in intimate contact. Alloying of the Y_2O_3 and ZrO_2 to form the partially stabilized zirconia is supposed to occur during the plasma spraying process. Because these powders are spray dried during their manufacture, they have the advantage of forming spherical, free flowing powders which can be more uniformly melted in the plasma gun. However, the alloying of separate particles in the flame is never complete and their chemical homogeneity and phase stability is less than that of a pre-alloyed powder.

Conventional pre-alloyed powders are sintered or fused and subsequently crushed to the desired particle size. These powders are chemically homogeneous and stabilized prior to entering the plasma flame. Their crushing results in angular and irregular shapes which have somewhat poorer flowability in the plasma gun and are, therefore, less uniform in melting than spherical powders. However, for most plasma spray coating applications the crushed powders are acceptable.

The successful coating applied to Valve No. 99 is a recent powder metallurgy development which combines the best qualities of the pre- alloyed crushed powders and the spray dried spherical composite powders. This powder is both pre-alloyed and spherical. Additionally, the powder particles are hollow. These qualities result in a powder which has excellent flowability, phase stability, and chemical homogeneity. Because the particles are spherical and hollow, they also melt much more consistently and produce coatings which are uniform in structure and composition and have less residual stress.

The x-ray diffraction pattern for the pre-alloyed coating applied to Valve No. 99 is shown in Figure 36. It is seen that the coating consisted entirely of tetragonal and cubic ZrO_2 with no detectable monoclinic content. In contrast the post-service pattern for the flame stabilized coating applied to Valve No. 90, shown in Figure 37, indicates a monoclinic concentration of approximately 13% by volume. This is somewhat higher than the concentration in the as-applied coating. It is believed that this coating has experienced a limited transformation to monoclinic ZrO_2 during engine exposure. This amount of monoclinic ZrO_2 is considered undesirable though it is uncertain whether it was substantial enough to be the primary cause of

failure. Evidence of other potentially contributing factors has disappeared with the bulk of the failed coating.

Piston Crown - Shown in Figure 38 is a representative cross section micrograph of the Supplier A piston crown coating. The coating has survived engine exposure with no apparent degradation. The ZrO_2 powder used was the composite, spray dried, flame stabilized material identical to that used in the Supplier A Valve No. 90 coating system. Shown in Figure 39 is the diffraction pattern for the piston crown ZrO_2 coating. There appears to be a monoclinic concentration of about 7% by volume. This is within the expected range of the as-applied monoclinic concentration in a partially stabilized zirconia coating and, hence, no transformation is believed to have occurred.

It is believed that the survival of this coating on the piston crown is due to the less severe thermal environment experienced by this surface. The piston is a large, cooled component that is able to dissipate heat rapidly. The valve on the other hand is small and uncooled; furthermore, it's Inconel 751 nickel-chromium composition has a relatively poor thermal conductivity and, therefore, dissipates heat slowly. It may well be that the composite spray dried, flame stabilized powder is adequate for all component surfaces with the exception of the valve face.

c. Supplier B Coatings

Valves - The faces of all three valves coated by Supplier B suffered major failures during the 9000 hours of engine exposure. This loss is apparent in Figure 40. Micrograph (a) is representative of the Supplier B, as-applied valve face coatings. Micrograph (b) is a typical cross section from the three engine tested coatings. It is seen that the ZrO_2 has experienced a near complete failure with only a very thin layer remaining attached to the bond coat. This thin, adherent layer is seen in the higher magnification micrograph, (c). It has a thickness of about .001 in. (25μm) or one-tenth of the specified original thickness. The failure seen here is representative of the behavior of the Supplier B coatings on 100% of the faces of two of the valves and 90% on the third. There was a region on the rim face of the third valve where the ZrO_2 had a remaining thickness of about .004 in. (100μm). This remaining coating was examined metallographically to determine what had caused the loss of the zirconia.

Figure 41 presents the diffraction pattern for one of the engine tested Supplier B valve face coatings (the $CaSO_4$ deposit having been removed). It is evident that a major transformation to monoclinic ZrO_2 has occurred during engine service. This coating consisted of greater than 45% monoclinic ZrO_2. The volume expansion associated with this transformation was probably the cause of the observed failure.

SEM/EDS analysis of several cross sections of the small amount of remaining coating on one engine tested Supplier B valve face consistently revealed a near complete absence of Mg (MgO) in the ZrO_2. Analysis of pre-test Supplier B coatings indicated the expected MgO concentration (converted from Mg concentration) of about 22 wt % in ZrO_2. Thus, the loss of MgO

occurred during engine exposure. The difference in MgO content before and after engine service is indicated in Figure 42. Micrograph (a) is an SEM image of a cross section from an untested coating. The corresponding x-ray map for Mg (MgO) is shown in micrograph (b). The engine tested valve coating where a partial thickness of ZrO_2 remained is shown along with its Mg map in (c) and (d). Note the much higher and relatively evenly distributed concentration of Mg in the pre-service coating. The remaining coating after engine service has an overall low MgO concentration but with some concentration near the ceramic-bond coat interface. The regions of very high Mg concentration seen in both (b) and (d) are particles of pure MgO which are normally present in the stabilized ZrO_2 along with MgO in solid solution; they are predicted by the MgO-ZrO_2 phase diagram.

The distribution of MgO shown in the post-service coating, i.e. a concentration gradient from the coating surface to the ceramic-bond coat interface (Fig. 42, d), indicates that the MgO is being sequentially removed from the coating surface. At the coating surface the Mg or MgO can react with SO_3 in the combustion gas to form $MgSO_4$, thereby depleting the ZrO_2 of Mg and creating a concentration gradient. The Mg or MgO is sufficiently mobile at the elevated service temperature to diffuse through the coating to the ceramic-combustion gas interface in response to the Mg gradient and to react there with sulfur in the combustion gas. The ZrO_2 porosity would aid in hastening the process as the Mg could rapidly migrate through the coating, along cracks and along pore walls toward the ceramic-combustion gas interface.

The combustion gases could also enter the coating through open pores and there react with Mg. No evidence of $MgSO_4$ deposits was found on the remaining coating's surface or within its pores. This is probably because the Mg-S reaction occurred in the outer layer of the coating and the product was removed with the spalled coating and carried away in the exhaust.

The region of the valve face where some coating remained was bordered by a shallow tapering off of coating thickness. This area indicates that coating loss occurred by the sequential spalling of thin ZrO_2 layers that became destabilized as a result of the MgO depletion reaction. The transformation of the surface layer of destabilized ZrO_2 to the monoclinic structure would occur during each cooling cycle and cause the spallation of a thin layer because of the 4% volume expansion that occurs when the zirconia transforms from the tetragonal to the monoclinic phase. The spalling would create a new ZrO_2 surface and the process would be repeated. It is not known which of the two removal mechanisms is dominant. What is certain however, is that a depletion of Mg has occurred which resulted in the destabilization of the ZrO_2.

2. 14,000 Hour Performance of Coatings

a. Supplier A Coatings

Piston Crowns - Both the flame stabilized and the prealloyed coatings on the piston crowns performed reliably with no detectable loss of coating. Shown on the left side of Figure 43 is one quarter of the Supplier A flame stabilized piston coating after a calcium sulfate engine deposit layer had been removed. Apart from some discoloration, the coating appears unaltered. This coating can be seen in cross section in Figure 44.

Valves - The flame stabilized coating was applied to the faces of valves analyzed but not to the stems. The valve face flame stabilized coating suffered a major failure on all four valves. This loss of coating can be clearly seen in Figure 45. The valve on the left is from cylinder No. 2; the one on the right is from cylinder No. 3. Both cylinder No. 2 flame stabilized valve coatings experienced loss over much of their surface. The only region where an acceptable thickness of ZrO_2 was retained was at the center in the cup region (see left side of Figure 45). This region is seen in Figure 46A in cross section.

A representative micrograph from the remainder of the valve face where the coating has failed is shown in Figure 46B. The failure seen here is typical of ZrO_2 system spallations; failure occurs within the ceramic just above the ceramic/bond coat interface. A thin ZrO_2 layer remains attached to the bond coat. This form of failure occurred over 70 to 80% of the flame stabilized valve face coating surface from cylinder No. 2. Both flame stabilized valve face coatings from cylinder No. 3 failed in this manner over 100% of their surfaces. The different performance of the same coating in cylinder No. 2 and No. 3 may be indicative of a more severe thermal environment in cylinder No. 3.

The flame stabilized 8 wt % Y_2O_3-ZrO_2 must be considered inadequate for valve face applications. Whereas this coating's performance on piston crowns was excellent, its survivability on valve faces was poor. A similar performance analysis carried out on selected coated components after 8990 hours service first revealed this survival pattern. The piston, being a large cooled component can dissipate heat more effectively than the small uncooled valve. Consequently, the valve surface temperatures can be as much as 200°C higher. The coatings were unable to withstand the higher thermomechanical stress at this location.

The pre-alloyed coating was applied to both the faces and stems of the valves analyzed. The valve face pre-alloyed coatings were mostly retained on all four valves from cylinder No.'s 2 and 3. The left valve in Figure 47 is from cylinder No. 2, the right valve from cylinder No. 3. Limited coating loss has occurred on these valves in regions of maximum curvature due to the concentration of stress within the coating at these locations. The cylinder No. 2 valve's coating remained adherent except in a thin band very near the outer edge of the rim where spalling occurred (see left side of Figure 47). The cylinder No. 3 valve coatings suffered some loss at both the outer edge and at the shoulder where the valve face starts curving towards the center. Greater

than 93% of the coating remained on the No. 3. cylinder No. 2 valves, while only around 80% remained on the cylinder No. 3 valves. Again the valves of cylinder No. 3 suffered a greater loss of coating than those of cylinder No. 2. This further supports the possibility of significantly different thermal environments within each cylinder. If it is possible to adjust the cylinder thermal environments to more closely reflect that of cylinder No. 2, then valve coating lifetimes could, ostensibly, be extended. In any case, the durability of the pre-alloyed 8 wt % Y_2O_3-ZrO_2 coating after 14,000 hours of service with only limited losses was well established.

The poorer performance of the flame stabilized coating on valves compared to the pre-alloyed coating of the same composition is attributed to the basic difference in the starting powders. This performance pattern was seen in the the 8990 hour study. Essentially, the pre-alloyed powder produces a more homogeneous coating with uniform mechanical and thermal properties and is therefore able to withstand the more severe thermal conditions.

A close inspection of the pre-alloyed valve coating surface indicates that even though it remained mostly adherent, it had experienced some alterations in structure. Shown in Figure 48 is a magnified region of the cylinder No. 2 valve face, pre-alloyed coating near the edge where some loss had occurred. It is evident that the ZrO_2 is segmented by cracks into regions of roughly 0.5 to 1.0 mm in diameter. Loss of coatings, where it has occurred, was due to spallation of individual segments. In some areas seen in Figure 48 an individual segment has been lost while the surrounding coating survived.

This process of segmentation and spallation of individual segments is likely to be beneficial to coating performance. A long running, near interfacial crack of the type often seen to cause coating failure can not develop because of the segmentation of the coating. Each segment is somewhat isolated from its neighbors so a horizontal crack may only propagate along a small number of segments before it meets with a vertical segment boundary. Were this segmentation not present a crack could propagate over several centimeters eventually surfacing and resulting in a large scale spallation.

Representative cross-section micrographs of the pre-alloyed coating on the valve face from cylinder No. 3 are seen in Figure 49. Micrograph A is from the bulk coating in the cup region. Micrograph B shows the near absence of coating on the rim area. A coating segment is seen in micrograph C at the transition region between the cup and rim. Clearly, the surface curvature has played a large role in causing this limited coating failure. It seems to have originated right at the point of maximum curvature and propagated a short distance along the flat rim. A thinner coating in regions of maximum curvature and a tapering of coating near edges would reduce the local stress, and thereby possibly eliminate this failure.

The pre-alloyed valve stem coatings all survived with no apparent degradation. One such valve stem is shown in Figure 50. The upper stem is still covered with a dark, very adherent layer of calcium sulfate. The lower region has been cleaned of calcium sulfate to reveal the ceramic layer. No

coating crack segmentation of the type seen on the valve faces was seen on the stem surfaces. A representative cross section of the prealloyed stem coating is seen in Figure 51. The lack of segmentation of the valve stem and piston crown pre-alloyed coatings as well as the durability of the flame stabilized coating on the piston crown is indicative of the less severe thermal environment in the piston crown and exhaust regions than on the uncooled valve faces. It is apparent that the flame stabilized coating is adequate for these less demanding applications whereas the valve faces must be coated with the pre-alloyed material if acceptable coating lifetimes are to be achieved.

b. Supplier B Coatings

Piston Crown - Both piston crown coatings composed of 22 wt % MgO-ZrO_2 applied by Supplier B survived the 14,000 hours of engine exposure without any noticeable degradation. Shown on the right side of Figure 43 is one quarter of one of these piston crowns. A representative cross sectional micrograph of this coating is seen in Figure 52. From these figures, it is clear that the Supplier B 22 wt % MgO-ZrO_2 coating along with both the flame stabilized and pre-alloyed Supplier A coating systems has the durability on piston crowns for extended periods of engine service to and probably beyond a typical overhaul period of 18 - 20,000 hours.

Valves - In contrast to its performance on the piston crowns, the Supplier B coating applied to all valve faces suffered a near total loss of the ceramic layer. One of these valve faces is shown in Figure 53. Representative micrographs of cross sections from these coatings are shown in Figure 54. The characteristic near-interfacial spalling is seen in micrograph B. The remaining ceramic has a thickness which varies from 0 to 0.5 mils (12μm). At its thickest point, it is still only one-twentieth its original thickness. This loss is characteristic of 100% of all Supplier B valve face coatings. Very similar results were seen in the previous 8990 hour study as well as in the limited 500 hour test. These results indicate that the Supplier B coating is inadequate for valve face service.

The underlying cause of all of the Supplier B valve face coating failures is the inherent instability of the 22 wt % MgO-ZrO_2 and its tendency to transform from the cubic ZrO_2 structure to the monoclinic ZrO_2 structure. The transformation to the monoclinic structure involves a volume expansion which will stress the coating, causing it to crack and spall. If the stabilizing compound is not in a solid solution with the ZrO_2 or if it is subsequently leached out of the coating during service because of a favorable reaction with a constituent of the combustion gas, i.e., sulfur, then the monoclinic transformation can occur.

Studies have indicated that the Supplier B valve face coatings have indeed experienced a significant transformation to the monoclinic phase. There are indications that this transformation is attributable to two causes. First, in the examination of the valves tested after 8990 hours exposure, in isolated regions of the valve face where some ceramic was still present, it was determined that the ceramic had a considerably lower MgO concentration

than pre-service coatings. The loss of MgO was believed due to a depletion reaction with SO_3 combustion gas which produced $MgSO_4$ though no residual $MgSO_4$ was found. The second cause of the monoclinic transformation is the poor initial distribution of MgO in the as-applied coatings. The coating is not a homogeneous solid solution of 22 wt % MgO-ZrO_2 but appears to be a mixture of two phases, one rich in MgO, the other having a very low MgO concentration. Indications of this mixture were found in past work, but were somewhat elusive. With the aid of an improved metallographic preparation technique, this MgO concentration variation could be easily distinguished.

Figure 55A is an optical image of the Supplier A pre-alloyed, 8 wt % Y_2O_3-ZrO_2 layer. Note the consistency of shading present suggesting a homogeneous solid solution. Figure 55B shows an optical image of the as applied Supplier B coating. Note the presence of light and dark regions. The light regions have been determined to contain between 5 and 10 wt % MgO. The dark regions (not including the pure MgO particles) have around 40 wt % MgO The overall average MgO concentration is near the designated 22%, but its distribution is highly irregular. Hence some regions are less stabilized than others, and therefore are prone to transform under stress and elevated temperatures.

The Supplier B coating applied to the valve stems experienced a limited success. Shown in Figure 56 is one such valve stem (after removal of $CaSO_4$ deposit). It can be seen that the ZrO_2 in the central stem region has spalled while that at the top and at the base has survived. This behavior is identical to that seen during the 9000 hour study. A transformation to monoclinic ZrO_2 was detected in the valve stem coating though to a lesser degree than on the valve face. Furthermore, the monoclinic concentration decreased higher up the stem as would be expected with the reduction in temperature.

It is speculated that three factors contributed to the failure of the bulk of the stem coating which helps to explain the survival of the coating nearest to the valve seat and furthest up the stem. First the tendency to form monoclinic ZrO_2 decreased moving up the shaft, away from the combustion chamber, as the amount of MgO retained in the coating increased. Second, the drop in temperature along the shaft resulted in a decreased thermal expansion difference between coating and substrate and hence, a decrease in thermal stresses higher up on the shaft. Third, the shaft curvature plays an important role in the concentrating stress within the coating. The coating in the tulip area, nearest to the valve seat has a less severe curvature than the stem proper, resulting in a lower stress concentration. In this region, the thermal and transformation stresses were insufficient to cause failure. Where the shaft becomes cylindrical, the coating has failed because of the additional stress concentration introduced by the shaft curvature. Farther up the cylindrical shaft, the curvature is the same but the lower temperature results in thermal stresses that are inadequate to cause failure.

C. Performance of Coatings in Small Bore, High Speed Off-The-Road Vehicle Engine

A plasma sprayed, pre-alloyed 8 wt % Y_2O_3-ZrO_2, 0.010 in. thick coating on a 0.004 in. thick MCoCrAlY bond coat was applied to the piston crown, exhaust valve faces, fire deck and exhaust manifolds of a test small bore, high speed engine which was operated on a test stand over a range of operating conditions for 150 hours. One piston crown and four exhaust valves were examined after the test, macroscopically and microscopically, to determine the state of the coatings.

1. Visual Appearance of Tested Components

The coating on the piston crown had no evidence of loss or structural deterioration of the coating, see Figure 57. The coatings on the valves lost a small amount of coating from their faces near their outer edges. The coating there is both spalled and delaminated inward from the outer edge of the valve, see Figure 58.

2. Microscopic Analysis

The piston dome coating performed in an excellent manner. There was no spalling, delamination or noticeable deterioration in the coating of any kind. Figure 57 shows the piston dome after the deposits were cleaned off. Note that the injection pattern has deeply stained the coating. The difficulty in removing this stain suggests a rather deep and thorough penetration into the coating. This penetration, however, did not appear to adversely affect the coating's performance. Figure 59A shows a typical cross section from the piston coating. The coating has maintained its original thickness and appears the same as the pre-test coating.

The valve face coatings survived well, for the most part. Shown in Figure 59 is a typical pre-alloyed 8 wt % Y_2O_2-ZrO_2 valve face coating cross section from a tested part. The ceramic is more dense than that on the piston crown, but it appears to be acceptable. All of the valves suffered some coating losses near their outer edges. Valve No. 1, shown in Figure 58 on the left, had the most extensive damage. The coating was spalled for a distance inward from one edge and was delaminated but not spalled over an additional 0.25 in. inward from the edge of the spalled area. This delaminated region is shown in cross section in Figure 60a.

Shown in Figure 60b is the valve edge of the No. 2 valve where the coating loss was restricted to very near the edge. The curvature at the edge of the valve appeared to have introduced stresses into the full cross section of the coating during thermal cycling because of the differential thermal expansion between the metallic valve and the ceramic coating. These stresses caused spalling cracks to develop starting from the outer edge of the coating and propagating inward. The edge crack in valve No. 2 propagated upward to the surface of the coating after traveling only a short distance into the coating.

The crack in Valve No. 1 coating propagated for a longer distance parallel to the metal-coating interface. It seems to have attempted to reach the surface several times, but each time, a new crack developed beneath it which then connected up with the original. This inability of the crack to surface is the primary reason why so much coating was lost. A tapered coating to the edge of the valve face would avoid the stress concentration which caused the crack development. A taper like the one formed naturally by the crack in Figure 60b would probably be sufficient. If an edge crack is avoided, then the coating would have a much longer life.

3. In-Service Performance

Piston crowns and exhaust manifolds for three small bore engines were coated with 0.01 - 0.15 in. thick, pre-alloyed, 8 wt % Y_2O_3-ZrO_2 by Supplier A and shipped out for installation in three off-the-road ore hauling trucks at an open pit copper mine. After 5,000+ hours of operation, the coated pistons were removed because of a ring wear problem not related to the ceramic coatings. The coated exhaust manifolds were left in place.

The components were solvent washed, but not glass bead blast cleaned, and visually observed. There was no apparent damage of the coatings. A darkening of the ceramic by a carbon deposit on the crowns was all that could be observed.

VI. CONCLUSIONS

- Properly applied partially stabilized zirconia thermal barrier coatings can withstand the service environment of a medium speed diesel engine combustion zone for at least 14,000 hours.

- The three coating systems (flame stabilized 22 wt % MgO-ZrO_2, flame stabilized 8 wt % Y_2O_3-ZrO_2, pre-alloyed 8 wt % Y_2O_3-ZrO_2) applied to piston crowns and cylinder heads were entirely retained and unaltered after the 14,000 hours of engine service.

- The 22 wt % MgO-ZrO_2 coatings applied to valves became depleted of MgO and underwent a major transformation to the monoclinic phase during service which resulted in failure by spalling.

- The flame stabilized 8 wt % Y_2O_3-ZrO_2 failed over most of the valve face surface and is therefore not adequate for long term service at this location. The coating failed due to thermomechanical stress.

- The pre-alloyed 8 wt % Y_2-ZrO_2 was retained on the valve faces with only minor loss at edges and regions of maximum curvature. Tapering the edge of the coating on the valve face should prevent the edge

spalling from occurring. This is the only coating that was evaluated that can reliably serve long periods on valve faces and is recommended for use in engines.

- The milder operating conditions of piston crown and cylinder head surfaces compared with valve faces resulted in the successful performance of coatings on piston crowns that failed on valve faces.

- All coated component surfaces had $CaSO_4$ deposits, the thickest being on the valve stem and the thinnest on the valve face.

- Coatings on components from a given cylinder perform, as a group, somewhat better or worse than coatings from another cylinder in the same engine. This indicates differing thermal environments and suggests the possibility of adjusting specific cylinder environments to maximize coating life.

- The contours of the diesel engine components coated will require automated, robotic plasma spraying equipment in production to control deposit thicknesses and morphology.

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TABLE 1

PROPERTIES OF CERAMIC MATERIALS[a]

Material	Thermal Conductivity [W/(m.k)]	Thermal Expansion (10^{-6} k^{-1})	Transverse Rupture Strentgth (MPa)	Young's Modulus (GPa)	Poisson's Ratio	Thermal[b] Shock Resistance Parameter,R
TiO_2	8.8 at 400 K [22] 3.3 at 1400K	9.4	69-103[20]	283[20]	0.28[20]	0.2
Al_2O_3	27.2 at 400K [18,22] 5.8 at 1400K	7.2-8.6[22,25,28]	276-1034 [24,25]	380 [24]	0.26 [24]	6.5
Cr_2O_3	10-33 at 350K [32,33]	7.5 [22]	>262 [30]	>103 [30]		2.7
Mullite	5.2 at 400K [18] 3.3 at 1400K	4.7 [18]	185 [36]	145 [24]	0.25	0.9
Partially Stabilized ZrO_2	1.8-2 [40]	8.9-10.6 [39]	600-700 [39]	205 [40]	0.23 [40]	0.5
Fully Stabilized ZrO_2	1.7 at 400K [20] 1.9 at 1600K	13.5 [22]	245 [38]	97-207 [20]	0.23-0.32 [20]	0.8
Plasma-Sprayed ZrO_2	0.69-2.4 [41,45,47]	y.6-10.5	6.80 [41-44]	48 [34,42] 21 at 1372K	0.25 [47]	0.2
CeO_2	9.6 at 400K [22] 1.2 at 1400K	13 [22]		172 [20]	0.27-0.31 [20]	

a. References from which data were taken are in reference 9.

b. $R = \frac{K\sigma(-\mu)}{E\alpha}$ where:

K = thermal conductivity

σ = fracture strentth

μ = Poisson's ration

E = modulus of elasticity

α = thermal expansion coefficient

Material	Theoretical Density (Mg/m^3)	Knoop or Vickers Hardness (GPa)	Fracture Toughness (k_{IC}) ($MPa \cdot m^{1/2}$)	Specific Heat [J (kg °K)]	Emittance[b]	Crystal Structure
TiO_2	4.25 (20) 3.84 4.17	7-11 (20,21)	2.5 (21)	799 at 400K (20) 920 at 1700K	0.83 at 450K (T) (18) 0.89 at 1300K(t)	Rutile tetragonal (20) Anatase tetragonal Brookite orthorhombic
Al_2O_3	3.97 (23)	18-23 (17,24)	2.7-4.2 (17,26,27)	1088 (25)	0.75 at 100K (N) (18) 0.53 at 1000K(N) 0.41 at 1600K (N)	Hexagonal (20)
Cr_2O_3	5.21 (29)	29 (20)	3.9 (31)	670 at 300K (22) 837 at 1000K 879 at 1600K	0.69 (N) (22) 0.91 (N)	Hexagonal (23)
Mullite	2.8 (35)		2.2 (37)	1046 (25)	0.5 at 1200K (N) (22) 0.65 at 1550K (N)	Orthorhombic (34)
Partially Stabilized ZrO_2	5.70-5.75 (39)	10-11 (40)	8-9 at 293K (40) 6-6.5 at 723K 5 at 1073K	400 (39)		Cubic, Monoclinic Tetragonal (38)
Fully Stabilized ZrO_2	5.56-6.1 (34)	10-15 (20)	2.8 (38)	502 at 400K (20) 669 at 2400K	0.82 at 0K (N) (22) 0.4 at 1200K (N) 0.5 at 2000K (N)	Cubic (34)
Plasma-Sprayed ZrO_2	5.6-5.7 (29,39)		1.3-3.2 (45,46)		0.61-0.68 at 700K (T) (49) 0.25-0.4 at 2800K (T)	Cubic, Monoclinic Tetragonal (38)
CeO_2	7.28 (20)			370 at 300K (22) 520 at 1200K	0.65 at 1300K (T) (22) 0.45 at 1550K (T)	Cubic (34)

Table 2

Candidate Coating Systems

Component	Coating System	Supplier
Valve Face and Stem	8%Y_2O_3-ZrO_2/NiCoCrAlY	A
	22%MgO-ZrO_2/NiCrAlY	B
Piston Crown	8%Y_2O_3-ZrO_2/NiCoCrAlY	A
	22%MgO-ZrO_2/NiCrAlY	B
Cylinder Head	8%Y_2O_3-ZrO_2/NiCoCrAlY	A
	22%MgO-ZrO_2/NiCrAlY	B

Table 3

Summary of Coated Engine Performance Characteristics

1. At average power level of 54%, net reduction in annual average fuel consumption of at least 9% was achieved.

2. A 20% increase in maximum power was measured by a torquemeter on the propeller shaft that correlated with throttle notch position.

3. The electronic combustion analysis implied that a reduction in ignition delay was the primary effect of the coating on the combustion process.

4. The coated engine picked up load more quickly than the uncoated engine and its speed did not drop (sag) as far when additional load was applied.

5. The engine operated more quietly with less diesel knock, smoother combustion, reduced combustion related vibration.

6. Lub oil and engine cleanliness at time of disassembly was better than normal.

7. The fuel injectors did not foul, plug, or build up tip deposits.

8. No cylinder head to liner gasket seal leakage was found, as typically occurs in uncoated engines.

9. Lubricating oil consumption was reduced by 16%.

Appendix A

Technical Considerations in the Selection and Application of Ceramic Coatings on the Combustion Zone Components of Diesel Engines

PURPOSE

The technical considerations presented here are intended to provide guidance to both the user and supplier in the selection and application of thin ceramic thermal barrier coatings on internal engine combustion zone components.

INTRODUCTION

The ability of thin, 0.010 - 0.015 in. (0.25 - 0.4 mm), plasma sprayed zirconia ceramic coatings to endure on the surfaces of valves, piston crowns and fire decks of diesel engines has been demonstrated. As of this date, well over 250,000 hours have been accrued on ceramic coated diesel engine components installed on various types (low, medium and high speed - two stroke and four stroke) diesel engines, installed in various types of off-highway transportation vehicles and commercial power generation stations using a variety of fuels ranging from natural gas to heavy blended liquid fuels.This author has either been directly or indirectly involved in a number of these applications and the technical considerations presented herein result from this involvement.

The relationships between the coatings' performance and their composition, microstructure, and processing has been established. This information, along with the knowledge gained by the gas turbine industry in over a decade of using the same type of ceramic coatings on burner cans and other components, has been utilized to prepare these technical considerations. It is intended that the coating technical considerations discussed herein provide guidance for the selection of the surfaces on which to use the coatings and the preparation of procurement documents to obtain coatings from thermal spray coating suppliers. Each aspect of the behavior of the ceramic coating will be discussed prior to presenting the specific technical considerations so that there will be an understanding of the need for each requirement.

BACKGROUND

Plasma sprayed ceramic thermal barrier coatings were developed by the aircraft gas turbine industry to extend the performance temperatures of super alloys used at high temperatures by insulating the metal surfaces and effectively lowering their operating temperatures. Development of durable

coatings has occurred for the past 20 years and the coatings have been in service on thousands of components for the past decade or more. During this period much has been learned about the roles of ceramic composition, microstructure, processing techniques and grit blasting and thermal spray equipment settings, compatibility of the ceramic coating with the substrate metal, the stress states of the coatings, the use of bond coats of sprayed metal, and many other factors that contributed to the reliable performance of the coating systems in the relatively severe operating environments of gas turbine combustion zones.

The available foundation of knowledge necessary for the effective and reliable use of ceramic coatings in high temperature combustion zones was used in the selection and application of the coating systems used on the large and small bore, high speed diesel engines.

TECHNICAL CONSIDERATIONS

A. Ceramic Coating Composition.

The single type of ceramic that has evolved from the research and development of the last 20 years for use as a thermal barrier coating on gas turbine components is zirconium oxide (zirconia, ZrO_2), stabilized to some extent.

Pure zirconia will undergo undesirable phase transformations which cause the material to spall during thermal cycling. To prevent this, the addition of small amounts of other oxides, such as calcium oxide, magnesium oxide, yttrium oxide, or cerium oxide are made. Thus, the resulting material is designated either fully stabilized or partially stabilized zirconia and contains usually one other oxide such as 8, 13 or 20 wt % yttria (Y_2O_3), 22 wt % magnesia (MgO), or 27 wt % ceria (Ce_2O_3 or CeO_2), or 5 - 10 wt % CaO.

Certain constituents in the combustion gases of diesel engines can be detrimental to the ceramic coating. Compounds containing such elements as sulfur, vanadium or sodium can react with the stabilizers in the zirconia, effectively destabilizing the ceramic and causing it to transform and spall. Standard No. 2 diesel oil, for example, may contain a sufficient quantity of sulfur to cause the MgO stabilizer to react with it to form $MgSO_4$. Removing the Mg0 from the zirconia in this manner during combustion causes it to transform to another phase upon cooling that has an attendant volume increase which causes the coating to spall off. Degraded fuels that contain even relatively low amounts of vanadium can potentially cause a similar leaching type reaction to occur with the Y_2O_3 stabilizer. It is not yet known whether the vanadium content in typical degraded diesel fuels is at a sufficiently high level to cause such a problem.

Therefore, discretion should be used in the selection of diesel fuels to be used with ceramic coated components. To date, ceria stabilized zirconia does not appear to be attacked as much by sulfur or vanadium. However, ceria stabilized zirconia is only now becoming commercially available and

demonstration of its acceptable performance must still be made. Thus, the selection of the specific zirconia ceramic coating composition must take into account the possible occurrence of such detrimental reactions with the combustion gases of specific fuels.

The ceramic coatings on the uncooled, higher surface temperature exhaust valves in the medium speed diesel engines installed in two types of off-highway transportation vehicles, whose composition was 22 wt % $MgO-ZrO_2$, spalled off during service as the result of a leaching type attack by the sulfur in the combustion gas from No. 2 fuel. The magnesia stabilized zirconia on the cooled, lower surface temperature piston crown and fire deck surfaces did not spall. The 8 wt % $Y_2O_3-ZrO_2$ was not attacked on either the hotter exhaust valve or the cooler piston crown and fire deck surfaces and, thus, remained intact during the service duration.

GUIDANCE SUMMARY

- Use only 8 wt % $Y_2O_3-ZrO_2$ ceramic coating on engine components where No. 2 diesel oil is the fuel.

- Do not use fuels that contain vanadium in engines containing ceramic coated combustion zone components at this time.

B. Ceramic Coating Thickness and Microstructure.

Plasma sprayed ceramic coatings have very little ductility. Therefore, they are prone to brittle failure upon the application of stresses from either mechanical or thermal origin. The thinner the coating is the lower are the stresses that can build up in it and the lesser is the chance of coating failure by cracking and spalling. The coatings that performed successfully over many cycles of operation in the large and small bore, high speed diesel engines were 0.010 - 0.015 in (0.25 - 0.4 mm) thick. This thickness range is the same as is used on gas turbine components. It is known from limited diesel engine tests of thicker coatings that coating failure will start to occur at thicknesses greater than about 0.060 in. (1.5 mm). Thus, it is important at this stage of coating development to use relatively thin coatings to have the required durability.

Another factor concerning coating thickness relates to the possibility of pieces of coating that do detach scoring critical surfaces such as the valve seat or the cylinder wall liner. It was observed in one coated diesel engine that in those cases where coating detachment did occur on the exhaust valve faces, the pieces of spalled ceramic were so small that they passed through the system and out the exhaust without causing any damage. Thus, coating failure caused no downstream damage to critically dimensioned or smooth surfaced parts.

The nature of the plasma spray process during deposition of the coatings causes a certain degree of porosity to occur in the coating. A few unmelted

ceramic particles may also be present. It has been determined that for aircraft gas turbine applications a level of porosity is desirable because it increases the thermal fatigue life of the coating. The presence of some unmelted particles has not been determined to be detrimental. Porosity levels commonly used in gas turbine coatings were also used in the coatings tested in the medium speed diesel engines. It was determined that a porosity range of approximately 10 to 20% performed satisfactorily in the engine. However, such a wide range could indicate that certain of the spray process parameters were nearing their limits. A somewhat tighter range of porosity would be indicative of an overall desirable control of the process parameters.

The observation of the degree of porosity of a ceramic coating can best be determined by a metallographic examination of the cross section. A porous ceramic material is difficult to cross section and polish because the nature of the ceramic can cause small pieces to be pulled out by the polishing abrasives. This gives the appearance of greater porosity than is actually present which adversely affects the reproducibility of the porosity determination from specimen to specimen. Precise metallographic techniques that are meticulously adhered to are an absolute requirement for effective quality control operations.

GUIDANCE SUMMARY

- Ceramic coating thickness should be controlled in the range 0.010 - 0.015 in. (0.25 - 0.4 mm).
- Porosity in the ceramic coating should be evenly distributed and in the range 10 - 15%.
- Precise metallographic polishing techniques should be used in quality control procedures. A recommended procedure is contained in Section I.

C. Metallic Bond Coat.

A metallic bond coat plasma sprayed directly onto the structural metal substrate is an absolute necessity for a successful ceramic thermal barrier coating. Its thickness is 0.003 - 0.007 in. (0.08 - 0.18 mm). Several different compositions containing various percentages of the elements nickel, cobalt, iron, chromium, aluminum and yttrium have been used. A typical composition that was used for some of the coatings tested in the diesel engines is Co-32Ni-21Cr-8Al-0.5Y. The coatings are generally designated MCrAlY's where the M usually stands for the cobalt and/or nickel but, sometimes, for iron.

The bond coat has several functions. Included are:

- developing a compatible metal to metal bond with the structural alloy surface.

- enhancing the coarse texture of the grit blasted substrate to aid the bonding of the ceramic.

- providing a transition between the different physical properties of the metal substrate and the ceramic coating, i.e., thermal expansion, thermal conductivity, elastic modulus.

- providing a corrosion barrier between the metal substrate and the porous ceramic coating to prevent combustion gases from attacking the structural alloy's surface.

Bond coat technology stems from the use of these metallic, elevated temperature, corrosion protection coatings in gas turbine stationary and moving components for many years. It is a refined technology that has been used to coat millions of components. The particular compositions that have been selected for use as the bond coat with ceramic thermal barrier coatings are adapted from the gas turbine industry. There is no single composition that is best suited for use with zirconia.

The importance of the bond coat as a corrosion barrier when used with an outer, porous ceramic coating in a diesel engine was demonstrated in the 500 hour initial endurance tests. The apparent changes in the composition of the combustion gas from uncoated engines and/or the possible immediate surface area heating of the coating caused corrosion of the substrate cast iron to occur at the exhaust port lip of the fire deck only at those areas where the bond coat was inadvertently missing. The corrosion products locally blistered and spalled off the ceramic coating, allowing more direct access of the combustion gases to the cast iron where measurable corrosion loss started to occur in the relatively short test exposure. In all areas that had some bond coat, as little as 0.001 in. (0.025 mm), no corrosion occurred, even after the 9000 hour exposure in the medium speed diesel engine.

The bond coat should have a relatively low porosity and a minimum of included oxide to be effective as a corrosion barrier and have the necessary structural integrity to be a thermal expansion transition material. In some aircraft gas turbine applications, the bond coat is densified by plasma spraying in a protective atmosphere or vacuum environment. For the less severe environment that is present in diesel engines an air plasma spray bond coat is acceptable.

All of the elements in a typical bond coat have a role in its performance and are required in its composition. It should be noted, however, that cobalt can be replaced by nickel. The compositions used in the diesel engine demonstrations contained either nickel and cobalt or just nickel in addition to the chromium, aluminum and yttrium.

- A bond coat of composition NiCoCrAlY or NiCrAlY that is 0.003 - 0.007 in. (0.08 - 0.18 mm) thick should be used between the structural alloy and the ceramic coating.

D. Ceramic Powder Characteristics

Control of the powders used in the plasma spray gun is very important to the end quality and resulting performance of the ceramic coatings. The composition of the powder, its state of alloying homogeneity, the particles' shape and size distribution, and its moisture content are factors which have a major effect on the nature of the deposited coating.

The use of pre-alloyed powders wherein each particle contains the stabilizing oxide (Y_2O_3) in the proper weight percentage with the zirconia is a requirement that was established during the performance analysis of the medium speed diesel engine coatings. Coatings that were deposited from a mixture of separate Y_2O_3 and ZrO_2 particles that combined in the plasma flame to produce the desired stabilized coating composition did not perform on the uncooled valve faces. Of the three types of pre-alloyed particles that are available, two types; sintered and crushed or a proprietary spray dry and plasma sintered process are desirable at this time. The method of powder manufacture should be specified.

The detailed composition of the pre-alloyed powders should be specified in all procurement activities. Powders should be procured that have a consistent color and condition from a given powder supplier. The compounds in the powder that should be controlled to a specified maximum amount include the oxides of yttrium, silicon, titanium, iron, aluminum, calcium, magnesium and zirconium with a small amount of hafnium oxide as a part of it. Small quantities of unidentified trace elements that change the visual appearance of the coating from different coating suppliers, primarily its color, surface texture and amount of speckling, do not appear to have a significant effect on the coating's performance.

The powder size distribution is an important variable that affects coating characteristics. It should be controlled to a precise set of percentages (min-max) over a closely divided range of sizes to assure that proper feed and melting of the particles will occur in the plasma gun gas stream. Each type of plasma gun can require a different powder size distribution. The basic characteristics of the deposited coating are strongly influenced by the powder size distribution. Tests to establish the flow rate of the powder should be used.

Coating deposition efficiency (DE) is an important variable of the process that is influenced by both the feedstock powder characteristics and the spray parameters. It is important in determining the cost of the coating on a given part geometry.

It is important to protect the powder during shipment and storage. The use of sealed containers that prevent foreign materials and moisture from entering the powder is a general requirement of the thermal spray industry. The amount of powder in each container is generally related to its use rate. Destructive metallographic analysis of specimens or components sprayed at the beginning of the use of each lot of powder is suggested as a quality assurance procedure.

GUIDANCE SUMMARY

- Use only pre-alloyed powders prepared by either 1) sintering and crushing or 2) spray drying and plasma sintering processes.

- Use ceramic coatings prepared from powders whose composition, particle size distribution, appearance, and handling and packaging have been specified and certified.

- The bond coat powders are best pre-alloyed, spherical i.e., gas atomized powders, that should have the same quality control procedures as the ceramic coating powders.

E. Base Metal Grit Blasting and Cleaning

In order to enhance the bond between the structural alloy substrate and the bond coat and, ultimately the ceramic coating, the metal surface is initially grit blasted to roughen it. The molten or semi-molten bond coat metal droplets mold themselves into the textured surface. The roughened texture is extended to the top of the bond coat and is enhanced by the solidified droplet nature of the plasma spray. The roughened surface of the bond coat is an ideal surface for the zirconia to bond to.

A suction grit blast using 20 - 60 mesh alumina grit at 60 to 80 PSI pressure is typically used to prepare ferrous metal surfaces for the application of the bond coat. The specific grit blasting equipment, conditions and schedule should be closely controlled by specification.

It is recommended, but not required, that the same robotic positioning or manipulator system used in the spraying of the components be used in their grit blasting. The variables in the grit blasting schedule that should be specified include grit composition and size, blasting air pressure, nozzle type and orifice size, grit feed rate and traverse rate and blasting duration. The grit blast nozzles tend to enlarge during use, reducing the quality of the blast. The maximum enlargement should be determined and the orifice size controlled by specification. Brushing the grit blasted surface with a stiff brush using a solvent is an acceptable way to remove most of the embedded alumina grit particles. Some embedded particles were found beneath the bond coat on the coated diesel engine components. They had disrupted the bond coat by

having it arch over the protruding part of the grit particle. The structural metal surface should be sprayed within a reasonably short time after grit blasting, such as one hour. One to two pre-heating passes of the plasma torch over the surface without feeding powder are used to dry the surface and dislodge any remaining embedded particles. Care must be taken to not oxidize the metal.

GUIDANCE SUMMARY

- Use a detailed grit blasting and cleaning schedule for preparing the substrate surface for coating deposition. Have it certified by the coating suppliers in the form of "frozen process" Process Operation Sheets, as part of their Quality control plan.

F. Plasma Spraying

There are three primary suppliers/manufacturers of plasma spraying equipment. Each company produces the several elements that constitute an operable system, ie., plasma spray gun, controls and powder feeder. The elements from different companies can be intermixed in a system although this practice is not recommended by the manufacturers. Both internal feed and external feed guns are acceptable. The settings of the equipment that must be controlled, ie. gas flow rates, power settings, traversing speeds and angles, gun to work separation distance, powder flow rates and the other factors which combine to determine the characteristics of the deposited coatings are best monitored by an automated, control system. Control of the diameter of the powder feed port is important and should be periodically monitored for wear. Masking the components prior to spraying to assure that no coating is deposited on surfaces where it is not desired is an important element of the process. It must be carefully considered and adequate tooling utilized.

An experienced, skilled, spray equipment operator using machine console settings and a programmed robot to maintain the physical relationships between the spray gun and the work can deposit reproducible quality, acceptable coatings. The effort to adequately qualify and periodically certify the operator can be difficult. Using a completely programmed and controlled automated system that integrates the powder feeder, the plasma gun, and the positioning of the gun with respect to the part is the safest way to go.

Machine settings for each part geometry need to be developed during a qualification period. The criteria for final settings should be based upon acceptable metallographic analysis of deposited coatings. The detailed settings should be documented as a part of the coating procurement requirements. Metal substrate temperatures should be controlled to <200°C when spraying. The ceramic coating should be kept between 200° and 300°C or less when spraying. Air blasts are used to cool the substrate. The post spray cooling rate is not critical.

GUIDANCE SUMMARY

- Use an automated control system that integrates the plasma spray gun, the powder feeder and the gun to part positioning.
- Mask surfaces in the spray path that should not be coated.
- Establish system settings for each part geometry during a qualification period that are established as the result of destructive metallographic analysis of the deposited coating.
- Document all details of the system settings in "frozen process" Process Operation Sheets and require coating suppliers to certify to their continued use as part of their quality control plan.

G. Robotics

Among the most critical variables in a plasma spraying operation are the relative positions of the plasma gun nozzle and the work piece during the spraying operation,ie., the separation distance and angle, and the traversing speed at which the gun travels across the surface being sprayed. These variables control the thickness and porosity of the deposited material more so than do other variables. The traversing speed determines the thickness of the layer deposited during each pass. There is no consensus among coating suppliers or users as to what is a desired deposition rate. Typical deposition rates that were used for some of the tested diesel engine components were 0.0005 in. (0.012 mm) per pass for the metallic bond coat and 0.001 in. (0.025 mm) per pass for the ceramic coating.

There was a large variation in the thickness and porosity of the coatings tested, which were manually sprayed by an operator holding the gun. Except for those areas where no bond coat was deposited, which occurred only on the exhaust port lip of the cylinder head fire deck, the bond coat varied from 0.001 to 0.0013 in. (0.025 - 0.3 mm) and the ceramic coating from 0.003 to 0.020 in. (0.08 - 0.58 mm). The porosity of the ceramic coating also varied over a large range, from less than 1% to more than 20%. These wide variations appeared to be tolerated by the engine as no coating loss could be directly related to the thickness or porosity variations.

The reason for the variations in the bond and ceramic coatings, which many times occurred on the same part, were related to the changes in the surface contours of the components. The spray gun operator did not account for these changes adequately during his manual traversing across the surfaces to be coated, primarily because of his unfamiliarity with diesel engine components. For example, the relatively sharp lip which occurred at the entrance to the bowl of the piston crown required gun traversing speed and

angle changes to account for the change from a horizontal to a vertical position relation between the gun and the surface being sprayed.Another, similar instance occurred at the lip of the exhaust port in the cylinder head's fire deck.

The changing surface contours of diesel engine combustion zone components require that a programmable robotic arm be used to position the plasma gun in order to control coating thickness and porosity to acceptable levels. Even though the components appeared to tolerate the wide ranges which occurred, quality coatings should be under tighter limits. The bond coats should be 0.003 - 0.007 in. (0.08 - 0.18 mm) and the ceramic coatings 0.010 - 0.015 in. (0.25 - 0.38 mm) thick. The porosity should range between 10 and 15% as determined by metallographic examination of coating cross sections.

The use of a robot to position the plasma gun with respect to the work piece surface will assure that the separation distance can be maintained in the optimum 3 - 5 in. (7.5 - 12 cm) range (depending on the spray system used), that the spraying angle will always be near to 90° and that the traversing speed will maintain a constant rate of material deposit.It is recommended that a narrow beam of spray be used with robotic control. A robot may also be used to position the grit blast nozzle for the pre-spray grit blasting operation.The robot settings should have the same degree of automated control as the plasma gun settings.

GUIDANCE SUMMARY

- Use a programmed robot to position the plasma gun and, wherever possible, the grit blast nozzle for these respective operations.

H. Coupons, Sample Parts

There are no established, reliable, non-destructive tests to determine the quality of thermal spray ceramic coatings. Neither the mechanical integrity nor the adherence of the coating, the two most important factors in the long term, successful performance of the coatings, can be determined nondestructively. Thus, the quality of the coatings depends upon a tight control of composition and processing variables in a certifiable manner and the periodic destructive sectioning of coatings to monitor their microstructure.

Coatings that are destructively analyzed must be deposited at the same time in the same manner and have all of the same characteristics as the coatings on production components. They can be deposited on two types of surfaces; flat or contoured tabs and actual sample components. The nature of the part being coated and economics determine which type of destructive sample is used and how often.

When flat or contoured tabs are used they should be essentially the same substrate material and be processed in exactly the same manner as the part.

They should be located in relation to the part being coated so that the plasma torch can traverse directly from the part's surface to the tab's surface with no opportunity for a change in the deposition conditions to occur. The tabs should be representative of the contour of the part being coated, but do not have to conform exactly to the part's surface contour. The temperature of the tab should be as close to that of the part as is possible.

When actual components are used to provide destructive samples, the economics have to be considered as well as the geometry of the part. For most diesel engine components, periodic use of an engine valve can be considered to be an adequate representation of coating quality. The generally larger, flatter surfaces of the piston crowns and fire decks of the cylinder heads that are coated can be represented by a valve face coating.The frequency of use of the tabs and components for destructive quality assurance specimens will be discussed later. After coating, all samples should be visually inspected for consistency of color and surface texture and the presence of cracks and delaminations.

GUIDANCE SUMMARY

- Both tabs coated at the same time, in the same manner, and at the same traverse speed as the production components being coated and actual, representative components should be used for visual inspection and destructive, quality control analysis.

I. Metallographic Analysis

The metallographic analysis of ceramic thermal barrier coating systems is the only reliable method for determining their characteristics and quality. There are no reliable, reproducible, non-destructive tests (NDT) to determine their strength, bonding to the substrate, porosity, presence of defects, or even thickness. This is especially true for thin ceramic coatings. Microscopic analysis of cross sections is used to determine the levels of the material and process variables that determine the nature of the coating on a specific part. The deposited microstructure is a function of the materials sprayed, the thermal spray equipment settings and the tooling used to position the plasma gun in relation to the part. It is the only absolute way to monitor the quality of the coating. Such factors as: thickness, porosity, structural uniformity, cracks, delaminations, unbonded areas, bond coat oxidation, foreign material contamination, unmelted particles and phase distribution are only discernible by destructive metallographic cross sectioning and microscopic examination.

The selection of cross section locations for microscopic examination should be based on the contours of the surface being coated. When tabs are used, the center area of the tab is an appropriate location. When actual components are used, two to four locations across the surface that represent significant changes in the part's surface orientation to the plasma gun are

appropriate locations. For example, on a typical bowl shaped valve face, specimens should be prepared from the flat, outer rim, the lip area of the bowl and the center of the bowl. Acceptable, non-acceptable microstructures of the coating for a specific part should be a part of the procurement documents.

The preparation of coating cross sections for microscopic examination should be a precise operation. The coating system consists of two parts, a metallic bond coat and a porous ceramic top coat, each of which has different responses to cutting and polishing operations. In particular, the porous ceramic coating can be extensively modified from its as-deposited or after service condition by the forces applied to it by the metallographic cutting and abrasive polishing actions. The actual, as deposited porosity of the ceramic can be modified because the cutting or polishing operations can pull out pieces of ceramic by fracturing the thin, membrane-like walls between the pores. When these "pullouts" occur the coating appears to be more porous and less uniform in the metallogical evaluation than it is on the production part. The resulting appearance can be cause for rejection of the coating when, in fact, the coating was satisfactory.

The use of precise, reproducible, mild cutting and polishing technique is imperative to prevent variable, incorrect microscopic observations from being made. The samples for microscopic examination can be vacuum impregnated with clear, cold mount epoxy resin prior to cutting and polishing to prevent pullouts from occurring. Hand polishing techniques in conjunction with a final machine polishing using a vibratory polisher can be used for the preparation of coatings. However, the skill of the metallographic mount preparer, particularly his ability to apply the same level of force to the surface at each polishing step, specimen after specimen, is critical. To eliminate the dependence on the technician's technique there is a trend toward using machine polishing for all steps after the cutting operation.

Figure 1 is a polished and etched specimen of a zirconia ceramic thermal barrier coating system that has been properly prepared and photographed. There is essentially no evidence of areas of pullout in the ceramic, each element of the material system, ie. the base metal cast iron, the metallic bond coat and the ceramic coating, is clearly defined and the interfaces between each layer are discernible. All coating cross sections analyzed should have at least this level of metallographic quality.

A detailed cutting and polishing schedule should be prepared and followed meticulously. Table 1 is a recommended procedure that utilizes hand polishing prior to final machine polishing to prepare the cross section of the specimen.While small variations from this procedure can be tolerated, if they are consistently performed, the procedure in Table 1 has been demonstrated to result in a highly reproducible surface for microscopic examination. The use of vacuum impregnation of the specimen with clear, cold mount epoxy resin provides additional assurance of metallographic reproducibility.

Because coating quality monitoring is primarily dependent on microscopic observations, it is important to periodically assess the reproducibility of the

metallographic procedures. Comparisons of mounted cross sections prepared by different technicians and by different laboratories should be made on a regular basis.

The number of destructive metallographic examinations to make during the establishment of the coating system for a particular part and during on-going quality assurance operations should be established at the beginning of the coated part's history and rigidly adhered to. It should be part of the prescribed quality control procedures for the part.

GUIDANCE SUMMARY

- Destructive metallographic analysis should be used as the primary method to initially establish the characteristics of and monitor the on-going quality of production coatings.

- A detailed metallographic specimen preparation schedule should be used for all cutting and polishing operations.

- Periodic monitoring of the reproducibility of metallographic procedures should be carried out.

I. Quality Control Program.

The summation of all of the elements for the use of ceramic thermal barrier coatings on diesel engine combustion zone components should be embodied in a quality control program that is established for each part coated by each plasma spray coating supplier. Each program should be developed with the coating supplier and should form the basis for his performance over the procurement life of the part. It should consist of three basic elements:

1. Definition of the coating composition, physical characteristics, application process powder, and quality control procedures.

2. Qualification of each coating supplier for each part.

3. Production quality control and assurance procedures.

Coating Material and Process Definition - The composition of each of the coating's layers, their thicknesses, porosity and other required characteristics should be defined. The various steps in the application of the coating, ie. the preparation of the base metal, masking, the spraying parameters, required handling and traversing equipment and all other elements of the operation should be established. A detailed quality control plan should be developed that encompasses material composition control, qualification of the coating procedures, visual and dimensional inspection and periodic, destructive

metallographic examination. All elements of the procurement of the coatings on each individual part, including final packaging and shipping instructions, should be established before any production part coating operations are initiated.

Qualification of the Supplier - A formal qualification procedure should be carried out to assure that each supplier will produce acceptable coatings on each part on a production basis before he is permitted to coat any production components. The preparation and approval of detailed operation procedures including all positioning and plasma spray equipment settings should be required. The skill of each person who will operate the equipment should be demonstrated. The procedure should consist of the spraying and destructive microscopic examination of components and tabs that conform to the established microstructure standards. The determination that the monoclinic phase content is something less than 10% of the ceramic coating by x-ray diffraction analysis is recommended, but not required. Once the procedures and operators are accepted the coating supplier should certify that all components were coated in accordance with the documented procedure and qualified machine operators.Any changes should be approved before being incorporated.A set of "frozen process" Process Operations Sheets should be prepared and incorporated into the quality control plan.

Production Quality Control Procedures - A visual and dimensional inspection procedure should be carried out. The uniformity of each coating layer's location, surface texture, color, amount of speckling and edge condition should be defined and determined for each individual part. Any required dimensions should be checked using micrometers and eddy current analysis, as appropriate.

A destructive metallographic analysis schedule should be established for both tabs and sample components. Tabs produced at the same time as the components should be examined at the beginning of each production shift, whenever a new powder lot is started, whenever a different equipment operator starts to spray components, and at other times deemed necessary. Sample components should be prepared and destructively analyzed at least once a day during production operations. The destructive samples should be microscopically analyzed and accepted before production components are sprayed. Care should be taken to not have operators prepare tabs and sample components in advance of actual production times. Stock piling of sprayed samples that are subsequently analyzed during selected production periods, ie., each shift or day defeats the purpose of the quality control activity.

While economics should be a factor in the scheduling of destructive analysis operations, it should not pre-empt the necessary sampling to assure quality. Since ceramic coatings cannot be inspected using non-destructive testing techniques, adequate destructive analysis is vital to an effective quality control plan.

The quality control plan should require complete documentation. All thermal spray powders should be certified to a specification. The detailed grit blasting, plasma gun and part positioning and plasma spraying machine settings should be documented. Adherence to the established settings should be certified to by each operator for each production shift. A copy of the process sheets, if necessary with the actual machine settings, should be made available to the user.

GUIDANCE SUMMARY

- The required characteristics of the coating system on each part should be defined in procurement documents.
- A formal qualification procedure should be completed for each part by each coating supplier prior to coating any production components.
- A schedule of destructive metallographic examinations should be established for each part during its production run.

LISTING OF GUIDANCE SUMMARIES

A. Ceramic Coating Composition.

- Use only 8 wt % Y_2O_3-ZrO_2 ceramic coating on engine components where No. 2 diesel oil is the fuel.
- Do not use fuels that contain vanadium in engines containing ceramic coated combustion zone components at this time.

B. Ceramic Coating Thickness and Microstructure.

- Ceramic coating thickness should be controlled in the range 0.010 - 0.015 in. (0.25 - 0.4 mm).
- Porosity in the ceramic coating should be evenly distributed and in the range 10 - 15%.
- Precise metallographic polishing techniques should be used in quality control procedures. A recommended procedure is contained in Section I.

C. Metallic Bond Coat.

- A bond coat of composition NiCoCrAlY or NiCrAlY that is 0.003 - 0.007 in. (0.08 - 0.18 mm) thick should be used between the structural alloy and the ceramic coating.

D. Ceramic Powder Characteristics.

- Use only pre-alloyed powders prepared by either 1) sintering and crushing or 2) spray drying and plasma sintering process

- Use ceramic coatings prepared from powders whose composition, particle size distribution, appearance, and handling and packaging have been specified and certified.

- The bond coat powders are best pre-alloyed, spherical, i.e., gas atomized powders that should have the same quality control procedures as the ceramic coating powders.

E. Base Metal Grit Blasting and Cleaning.

- Use a detailed grit blasting and cleaning schedule for preparing the substrate surface for coating deposition and have it certified by the coating suppliers in the form of "frozen process" Process Operation Sheets as part of their quality control plan.

F. Plasma Spraying

- Use an automated control system that integrates the plasma spray gun, the powder feeder and the gun to part positioning.

- Mask the surfaces in the spray path that should not be coated.

- Establish system settings for each part geometry during a qualification period that are determined from the destructive metallographic analysis of the deposited coating.

- Document all details of the system settings in "frozen process" Process Operation Sheets and require coating suppliers to certify to their continued use as part of their quality control plan.

G. Robots

- Use of a programmed robot to position the plasma gun and, wherever possible, the grit blast nozzle for these respective operations.

H. Coupons, Sample Parts

- Both tabs coated at the same time and in the same manner as the production components being coated and actual, representative components should be used for visual inspection and destructive, quality assurance analysis.

I. Metallographic Analysis

- Destructive metallographic analysis should be used as the primary method to initially establish the characteristics of and monitor the on-going quality of production coatings.

- A detailed metallographic specimen preparation schedule should be used for all cutting and polishing operations.

- Periodic monitoring of the reproducibility of metallographic procedures should be carried out.

J. Quality Control Program

- The required characteristics of the coating system on each part should be defined in procurement documents.

- A formal qualification procedure should be completed for each part by each coating supplier prior to coating any production components.

- A schedule of destructive metallographic examinations should be established for each part during its production run.

Table 1

Metallographic Preparation Technique

A. Coated components that have experienced engine service will be covered with oil and deposits which should be removed to the extent that the underlying coating can be visually inspected and sample regions can be selected. A stiff wire brush and kerosene may be used. Smaller components can be ultrasonically cleaned in kerosene as well.The kerosene can be removed after cleaning by rinsing with acetone.This cleaning treatment should not harm an adherent coating; however, loosely attached coating may be removed.The degree of cleaning necessary will likely be different for each component.

B. Samples are cut from the coated components using a SiC cut-of wheel with continual water lubrication. In the case of piston crown and cylinder head coatings, a band saw may be used to remove a manageable piece of material from the bulk.This piece may then be cut with a SiC wheel to obtain the sample. The cut surface of the sample should be at least 1/4 in. from any band saw cut. Clamping directly onto the coating to be examined should be avoided.

C. Cut specimens are ultrasonically cleaned in kerosene and then in acetone to remove oil and engine deposits from coating surface and pores. Samples are dried with hot air and placed in a ring for mounting. Place under a vacuum of around 25 mm Hg and hold for 1 or 2 minutes. Mix epoxy resin, which has been heated to between 50°C and 60°C with the hardener. The hardener epoxy ratio should be slightly higher than that recommended. Fill mould with epoxy while maintaining vacuum. Hold vacuum for an additional 2 minutes and then release. Repeat vacuum. Remove sample mold from chamber and leave to cure 12 hours.

D. Specimens are ground and polished as follows:

1. 180 grit SiC, horizontal grinding wheel with water lubrication.Grind to remove approximately 0.06 in. of material.

2. 240 grit SiC, horizontal grinding wheel with water lubrication.Grind to remove approximately 0.03 in.

3. 320 grit SiC, horizontal grinding wheel with water lubrication. Grind till 240 marks removed.

4. 600 grit SiC, horizontal grinding wheel with water lubrication. Grind till 320 marks removed.

5. Polish samples with 0.3 micron alumina suspended in distilled water using a silk cloth on a slowly turning polishing wheel. Polish until 600 grit lines are removed from mount, coating, and substrate materials (2 to 5 minutes).

6. Examine the sample under a microscope and note the density of voids. Final polishing is done in a vibrating automatic polisher with the same combination of 0.3 micron alumina and silk cloth used in Step 4. Remove and examine samples approximately every hour to determine if voids are diminishing. Photographs are helpful in determining this. If convenient, examine the same location after each period. Discontinue polishing when the apparent density of voids no longer decreases.

E. Cast iron substrates may be etched with 3% Nital for good bond coat/substrate contrast.

Appendix B

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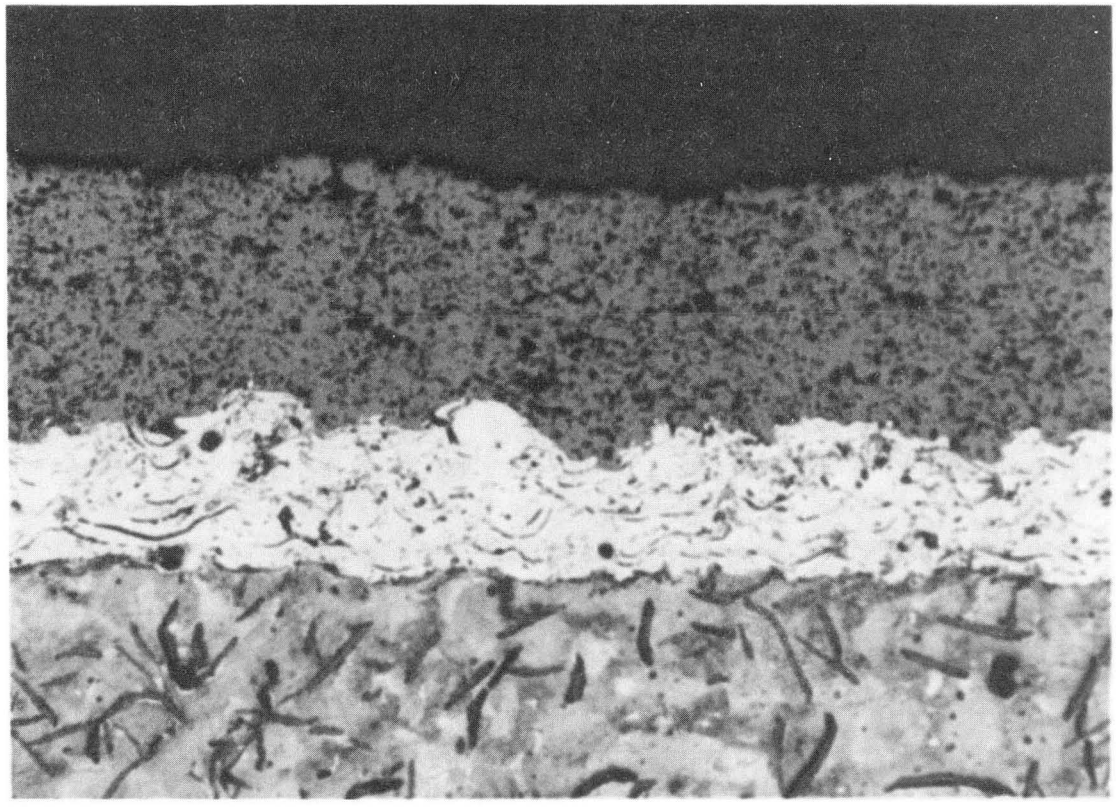
Authors: Kamo, R.; Assanis, D.
Publication: American Society of Mechanical Engineers, January 22-25, 1989, Houston, Tx.; ASME, New York, NY, USA ICE13 6p

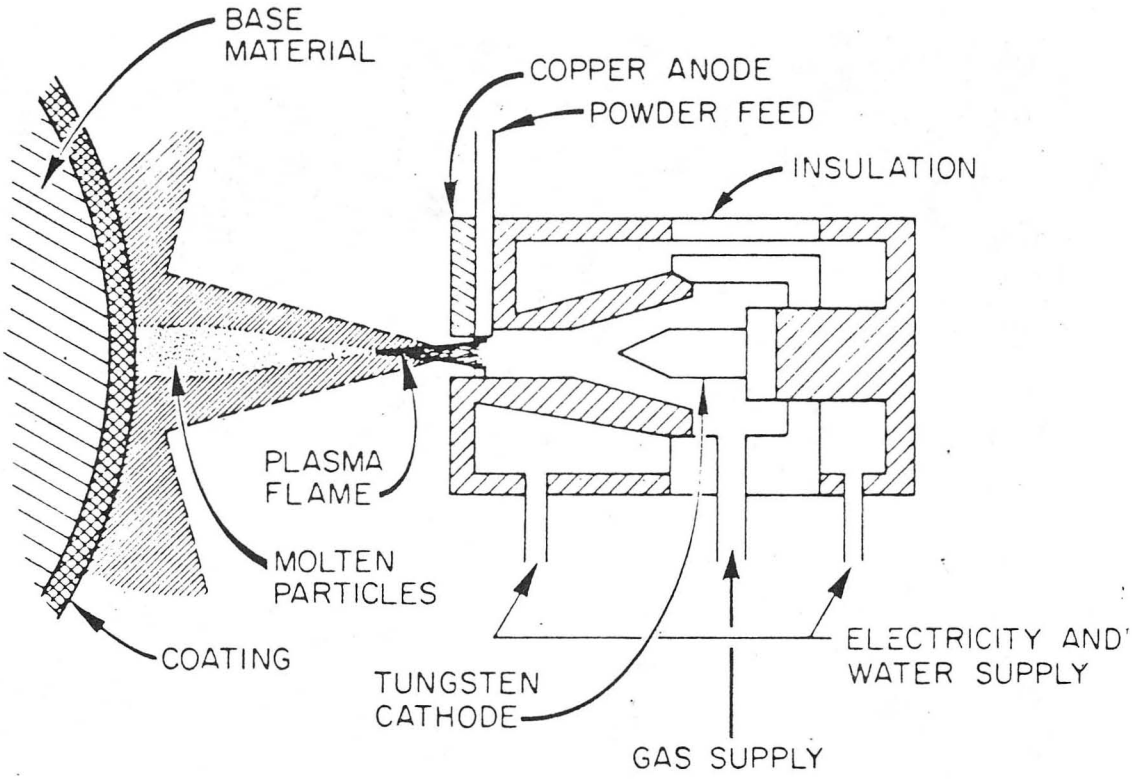
108. Title: COMPOSITE WEAR-RESISTANT CERAMIC COATINGS FOR ADVANCED DIESEL ENGINE APPLICATIONS
Author: Trott, C.R.; Murthy, A.K., Rutkowski,D.E.
Publication: Ceram. Eng. Sci. Proc., 10[9-10]1269

109. Title: EXPERIMENTAL INVESTIGATION OF THE HEAT TRANSFER IN INTERNAL COMBUSTION ENGINES WITH UNSULATED COMBUSTION CHAMBER WALLS
Author: Woschni, G.
Publication: Proceedings of the International Centre for Heat and Mass Transfer Ser. 26.; Hemisphere Publ Corp, New York, NY p 53-65, 1989



Thermal barrier coating structure

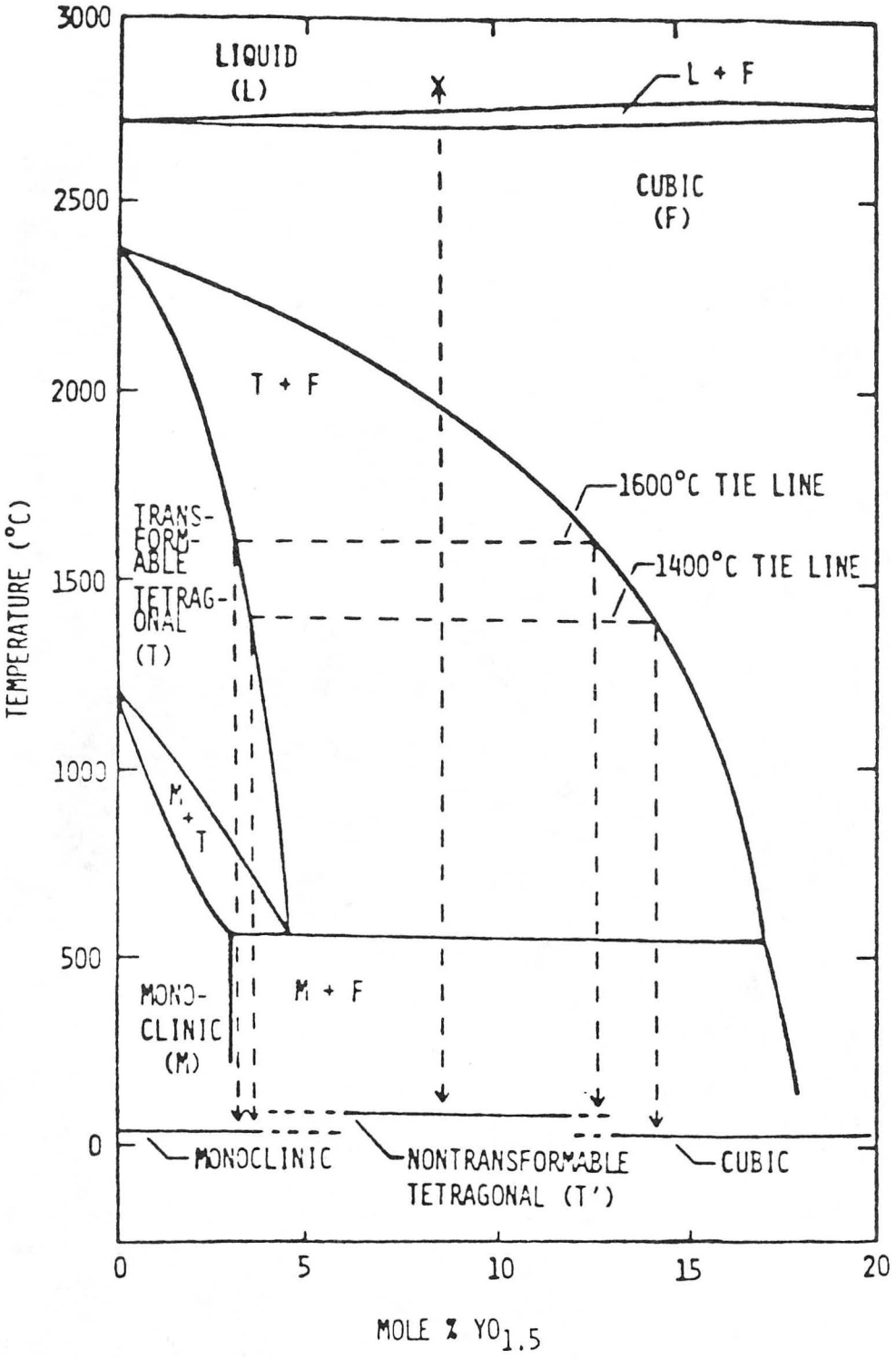
Figure 1



XBL 858-3216

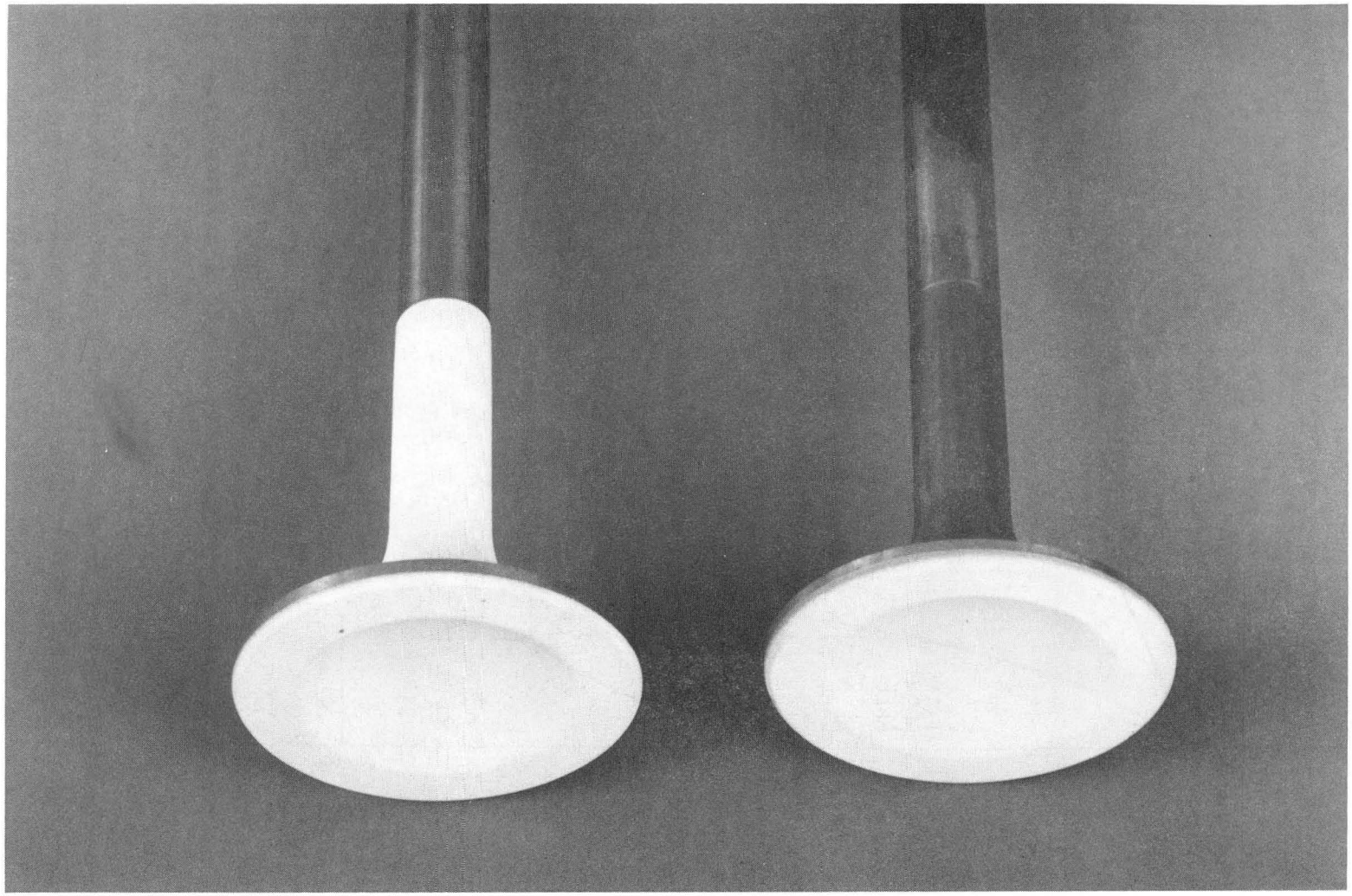
Typical plasma spray gun

Figure 2



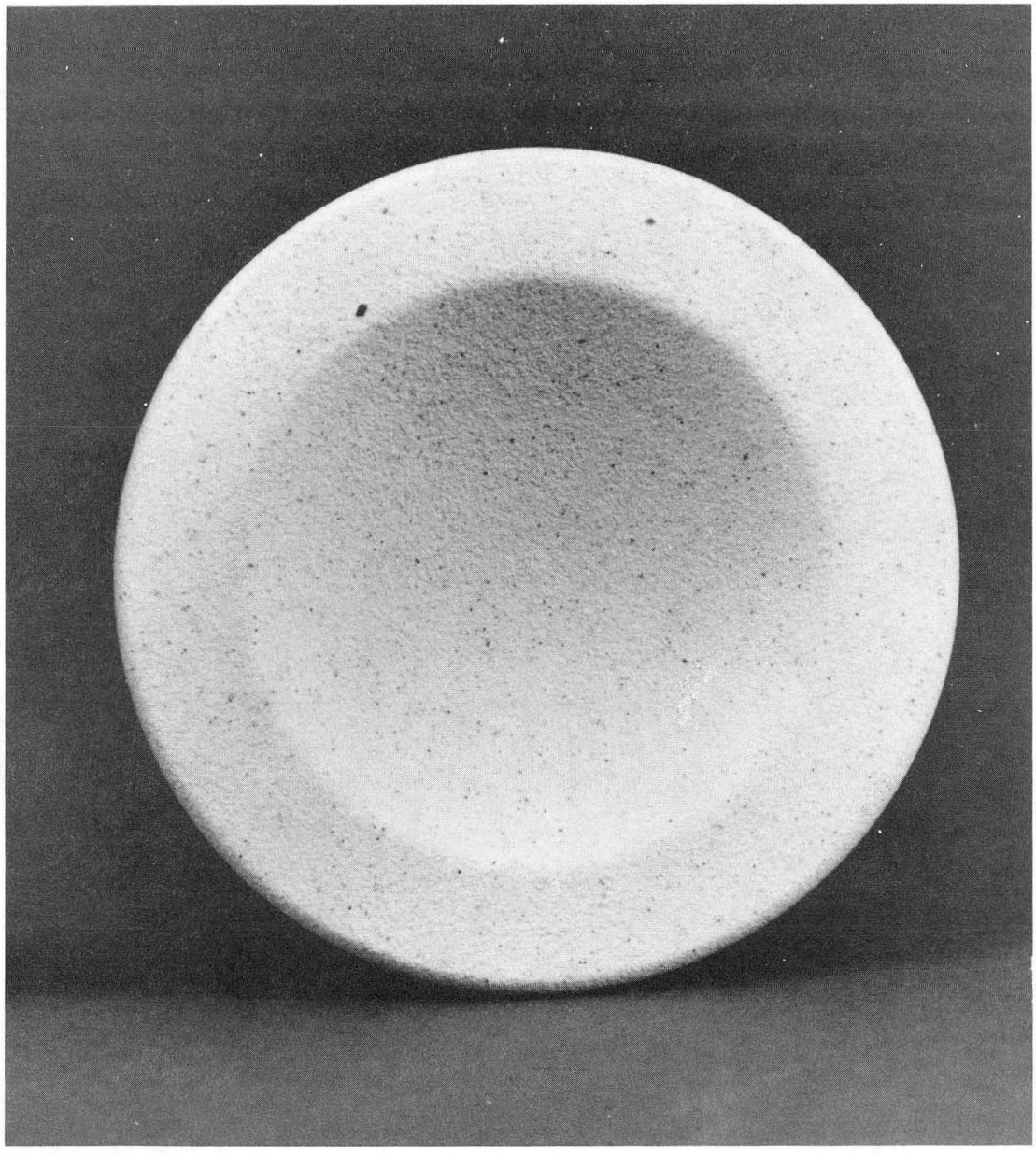
Low yttria region of ZrO_2-$YO_{1.5}$ phase diagram

Figure 3



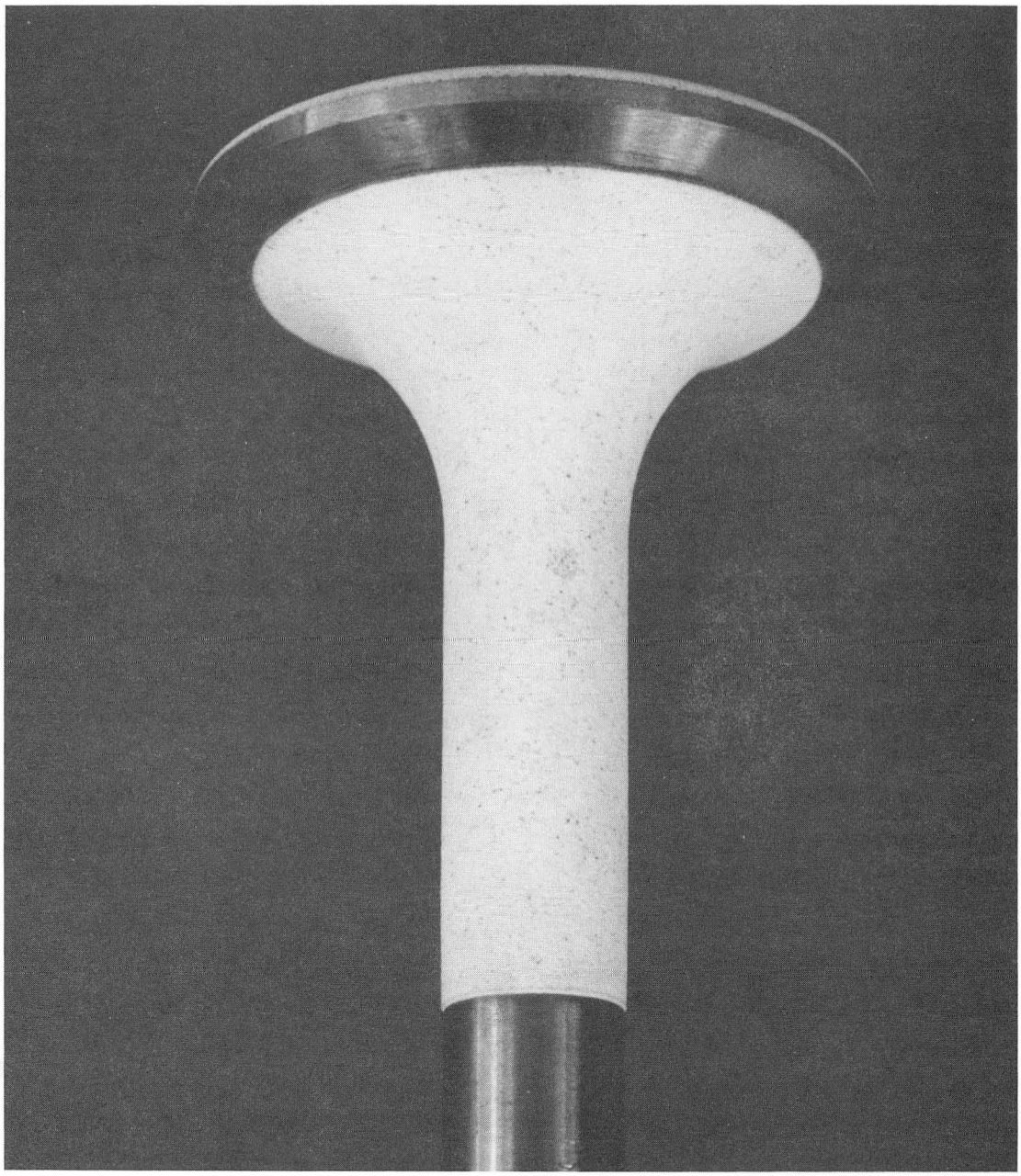
Supplier A coated valves

Figure 4



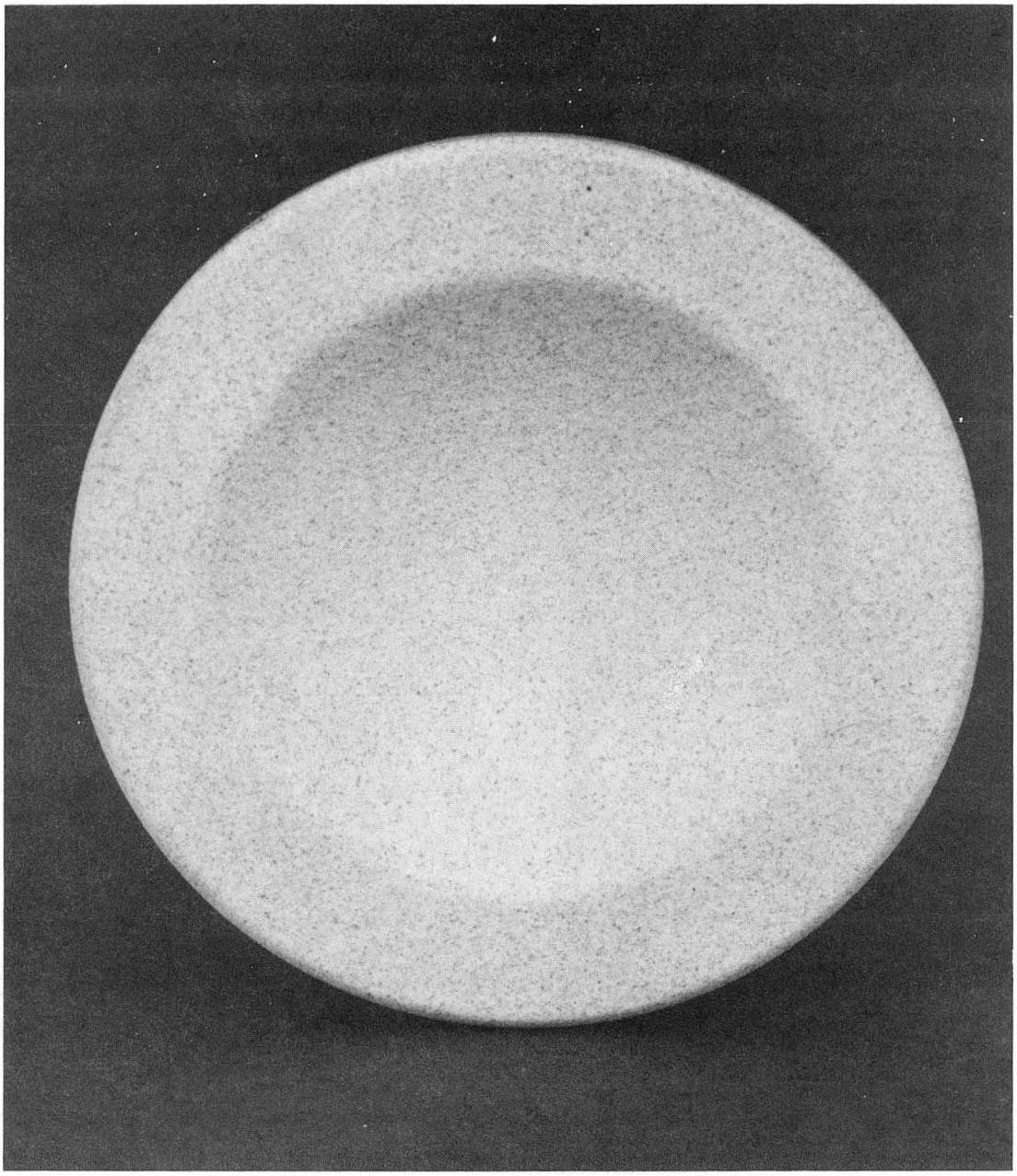
Supplier A valve face

Figure 5



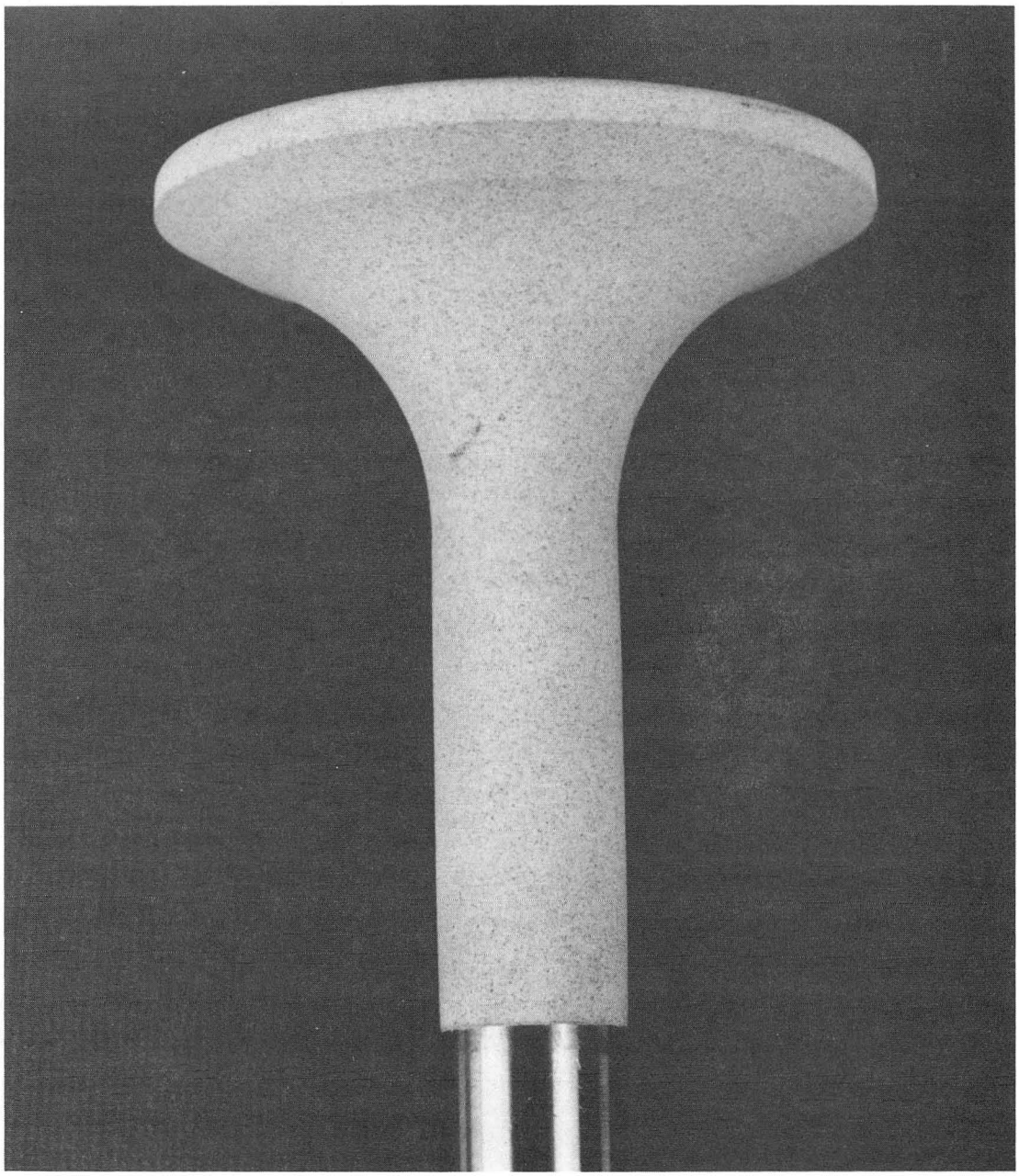
Supplier A valve tulip stem

Figure 6



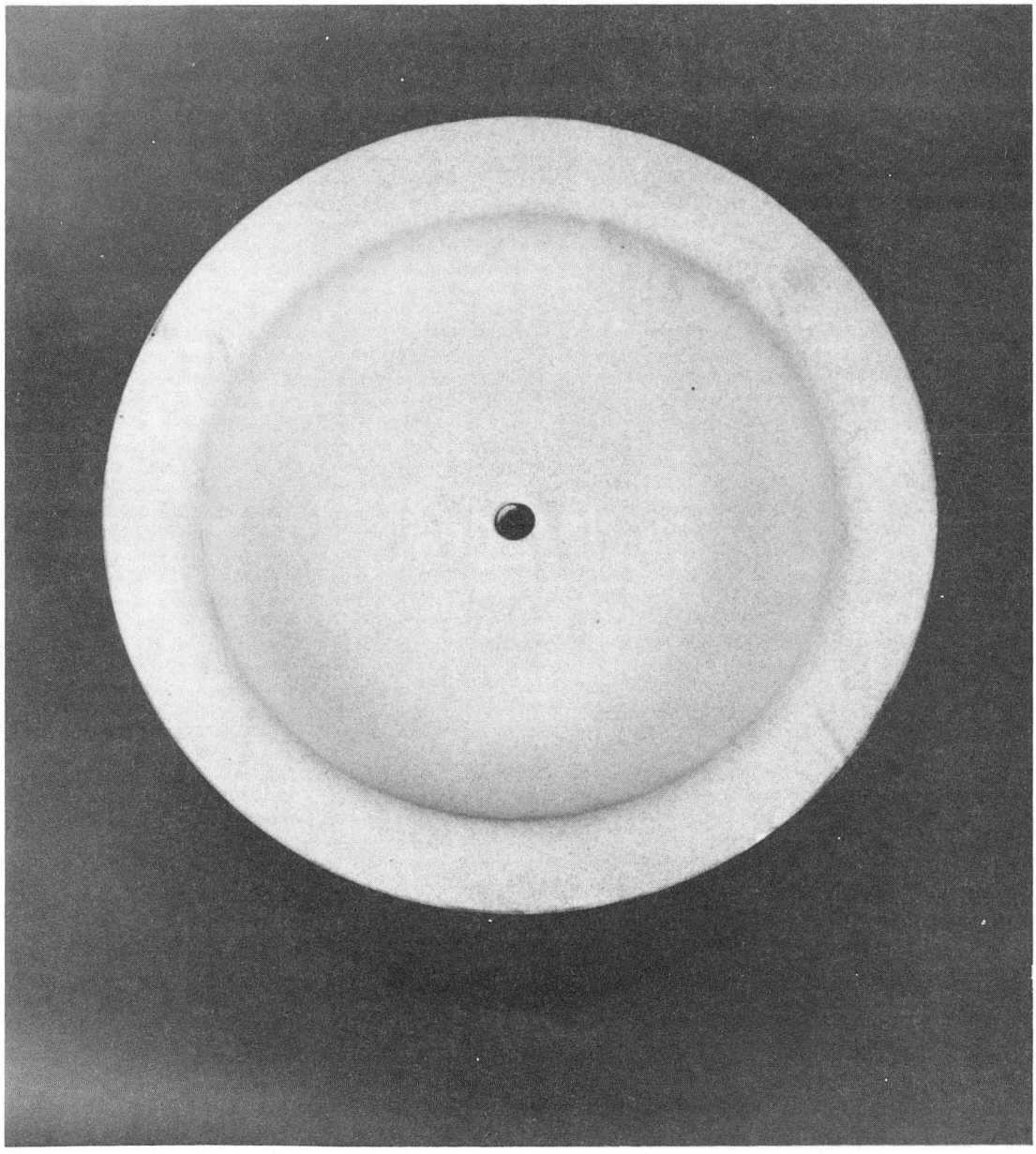
Supplier B valve face

Figure 7



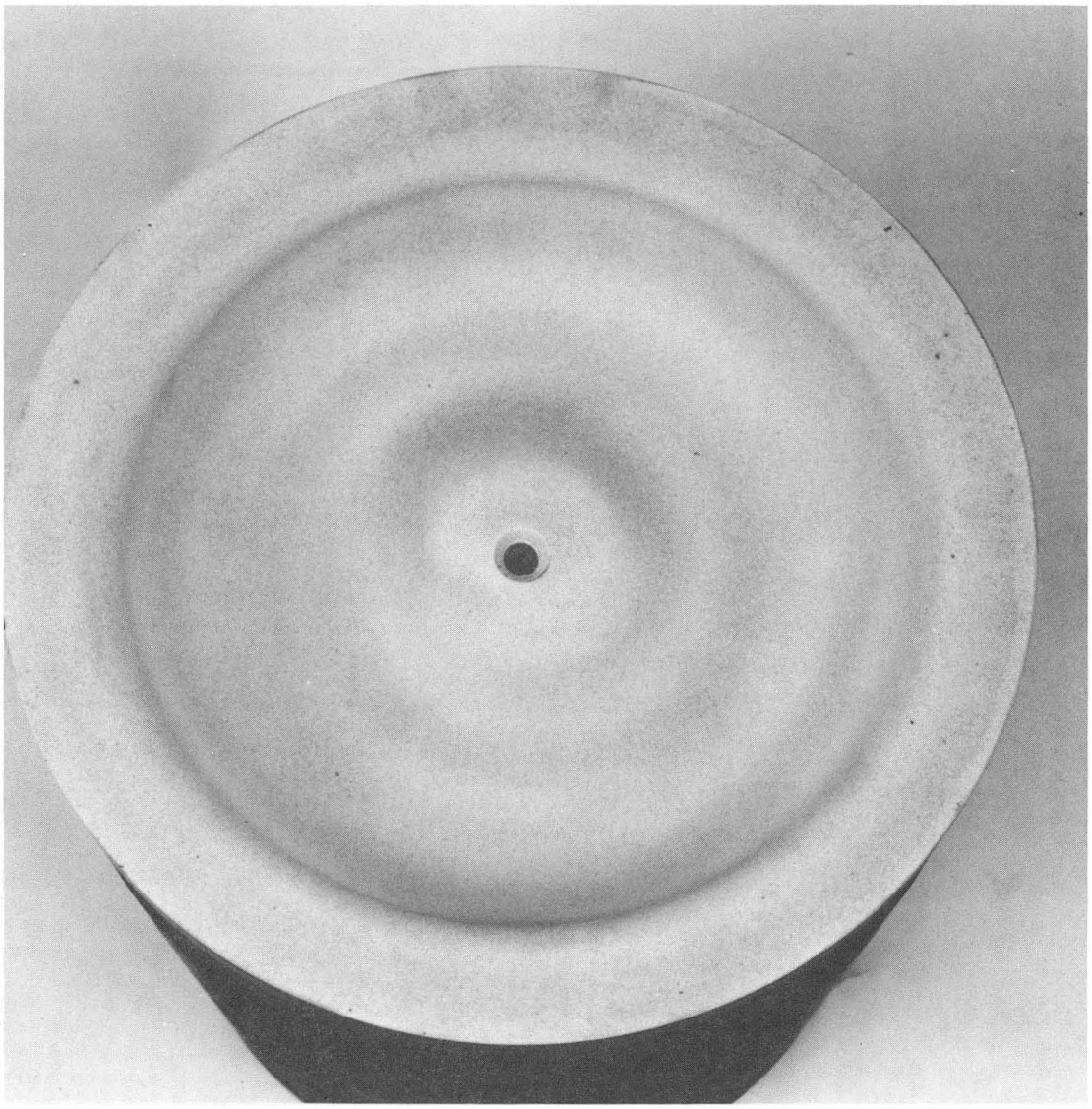
Supplier B valve tulip stem

Figure 8



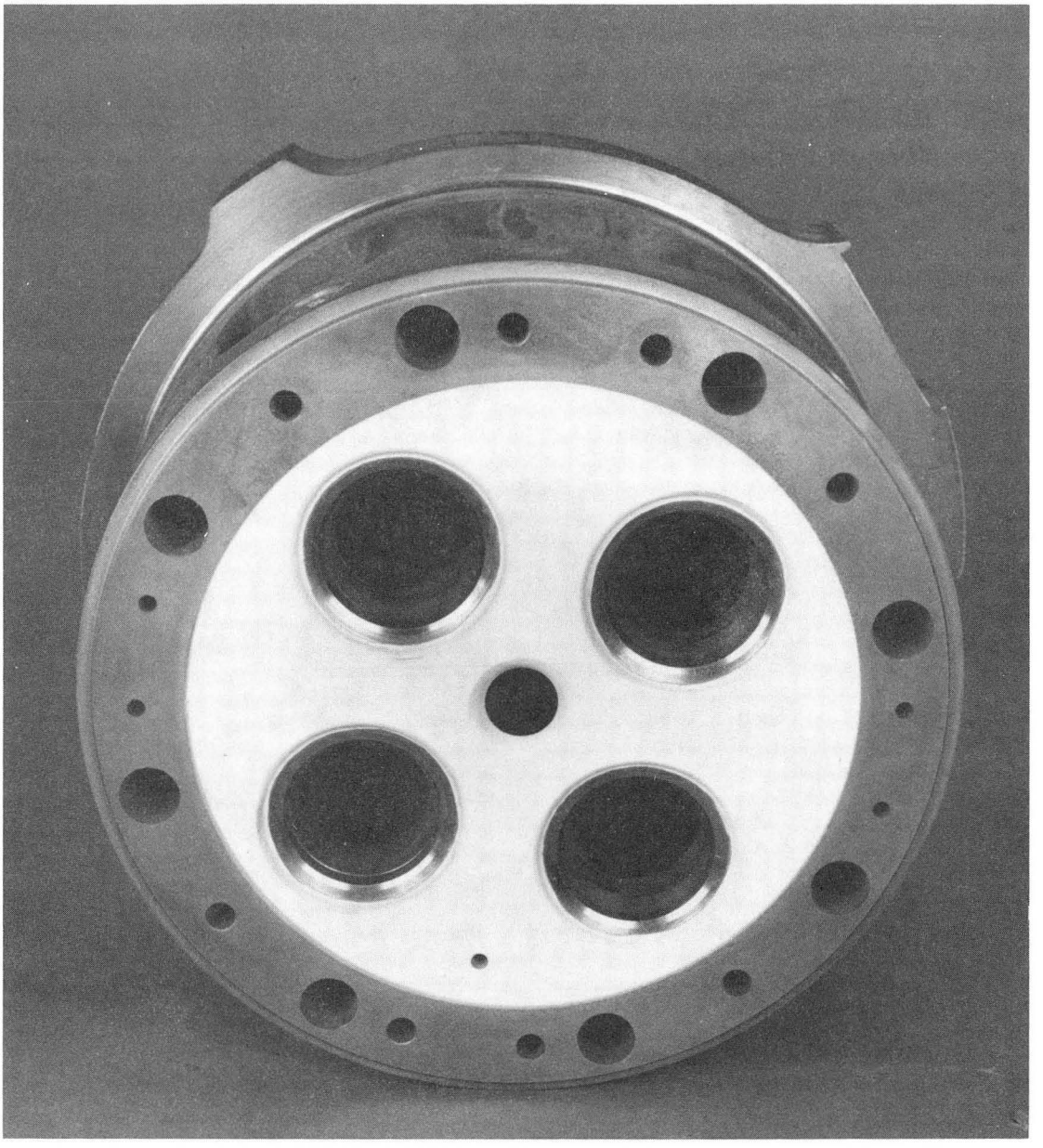
Supplier A piston crown

Figure 9



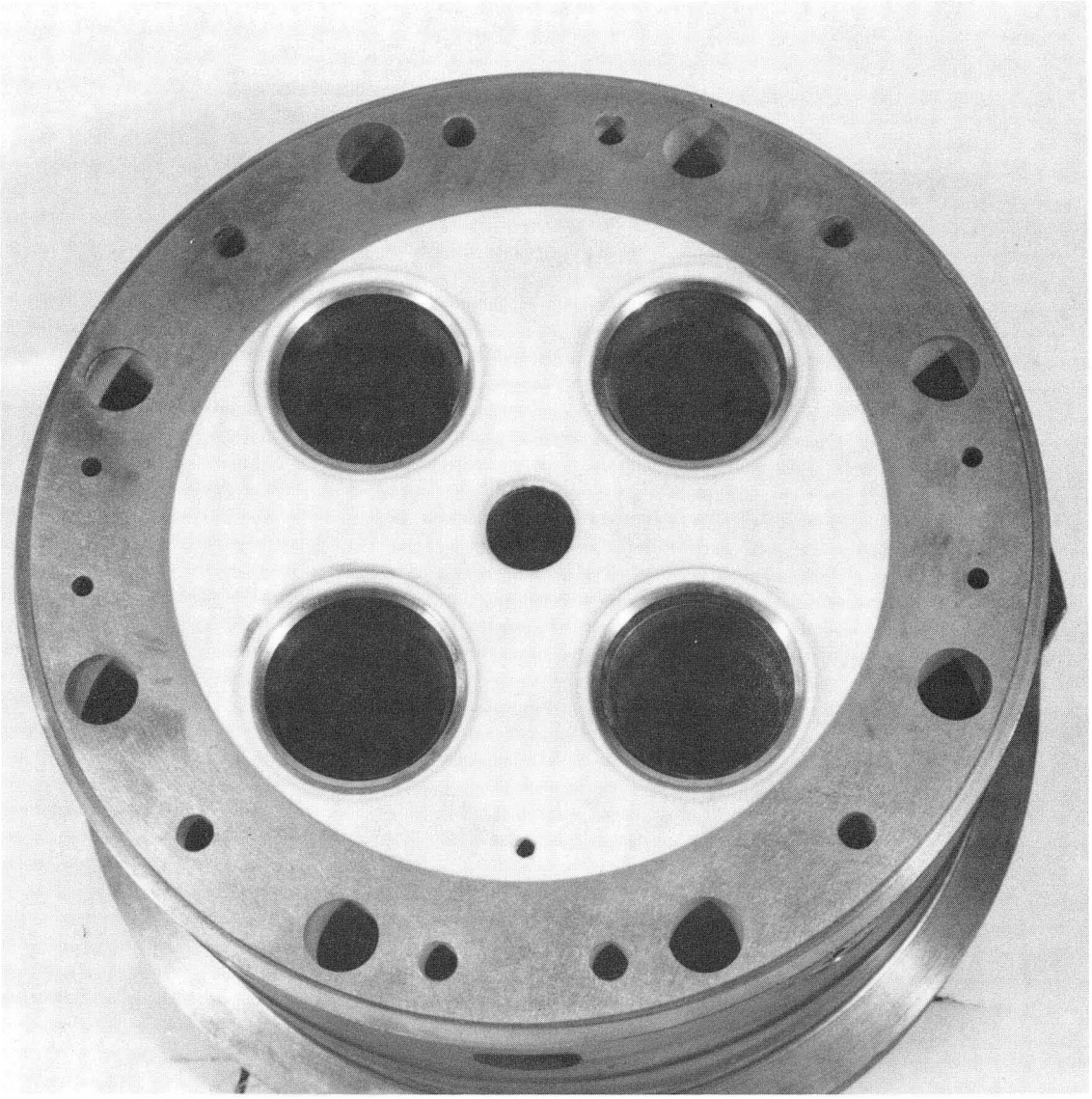
Supplier B piston crown

Figure 10



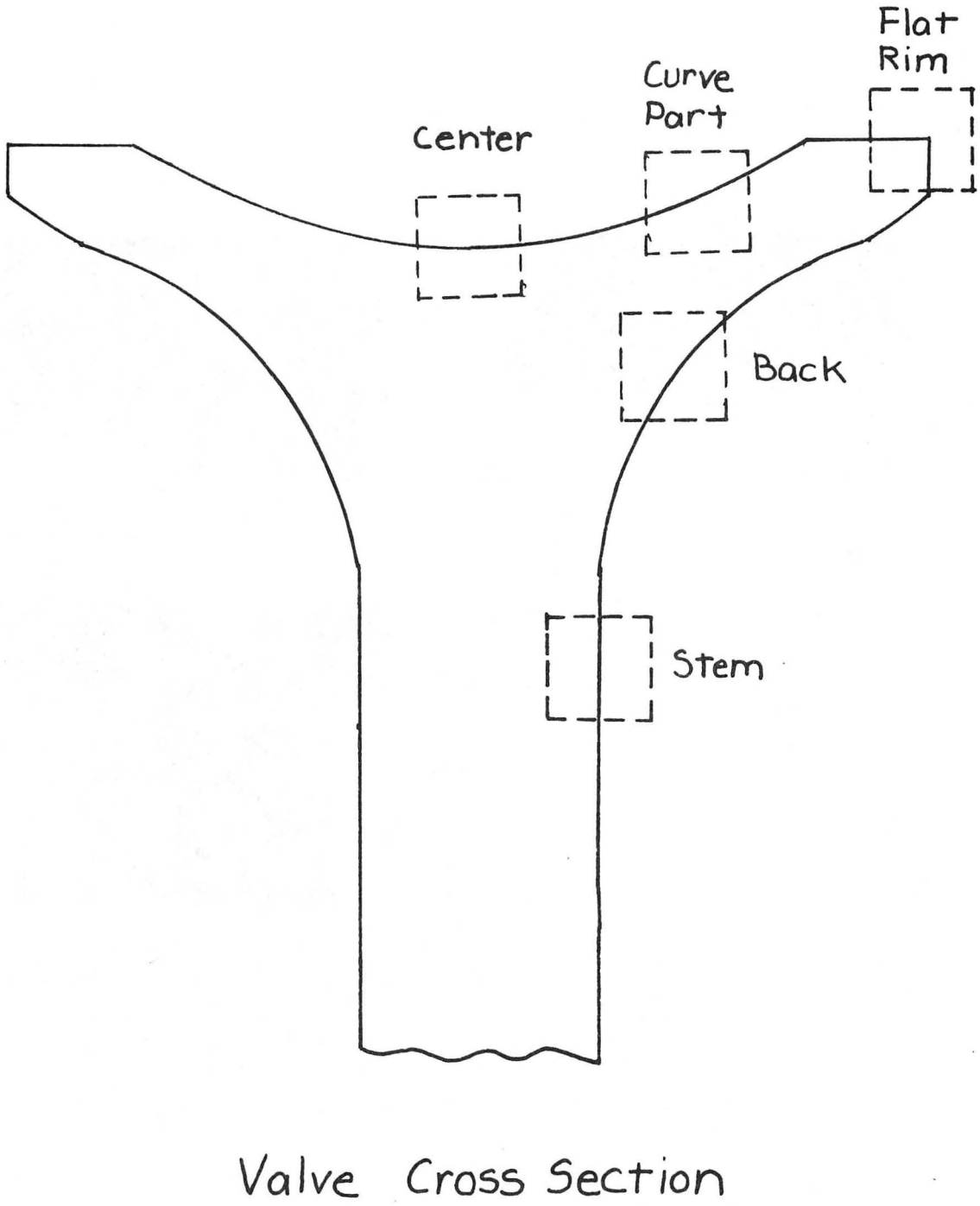
Supplier A cylinder head

Figure 11



Supplier B cylinder head

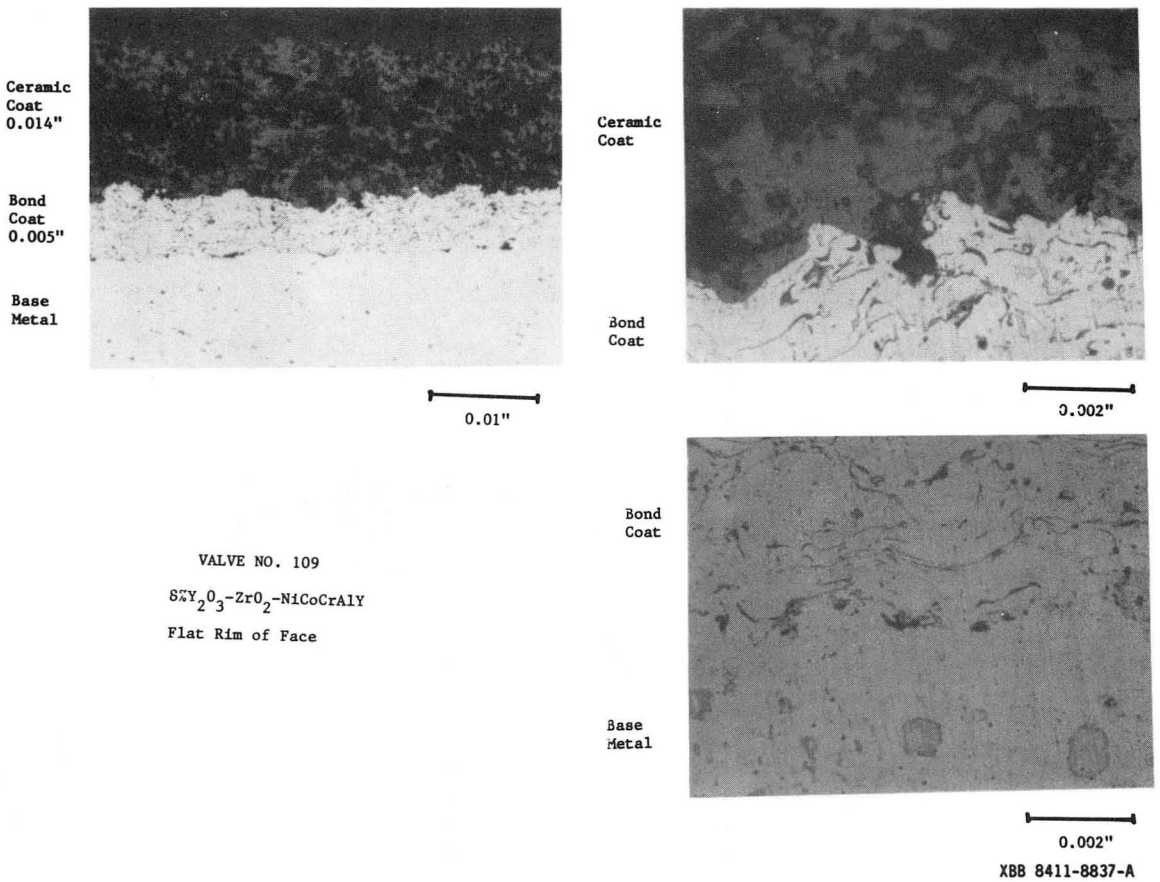
Figure 12



XBL 851-1068

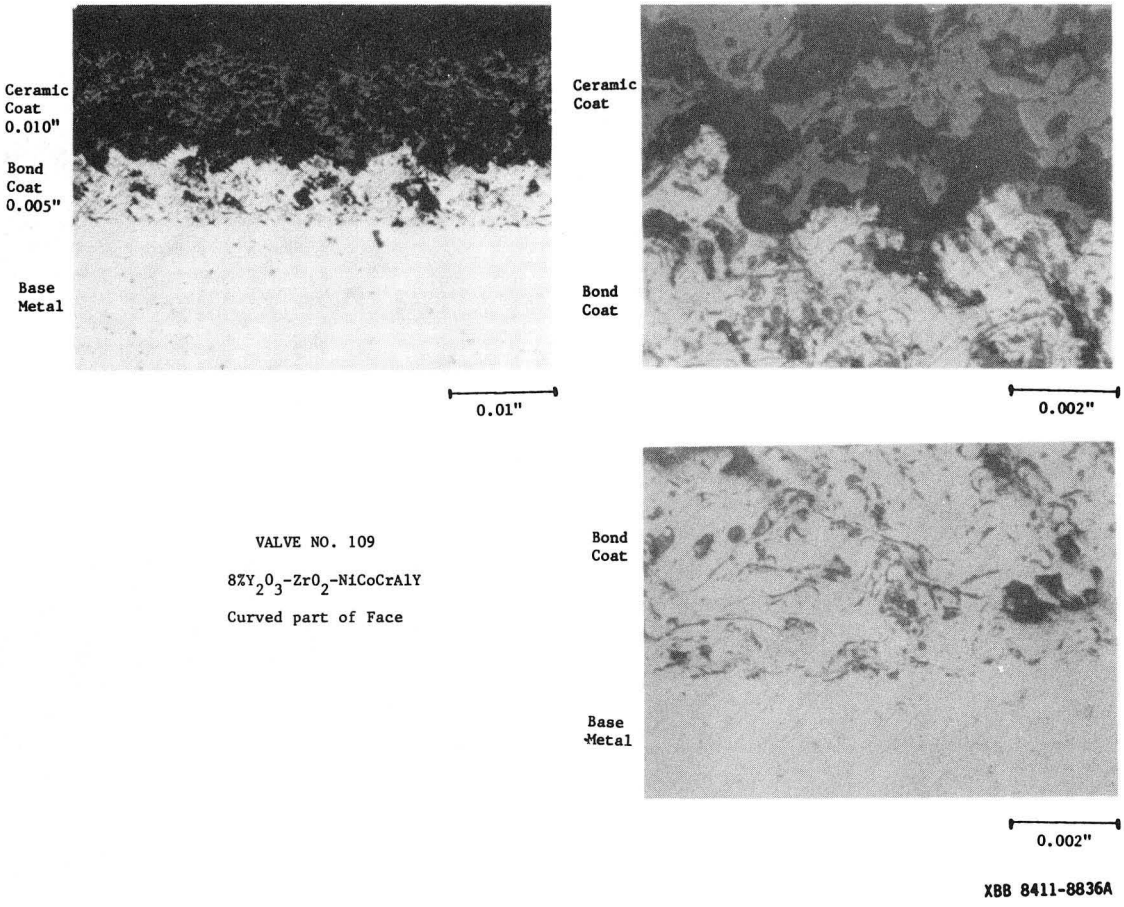
Sketch of valve showing micrograph specimen locations

Figure 13



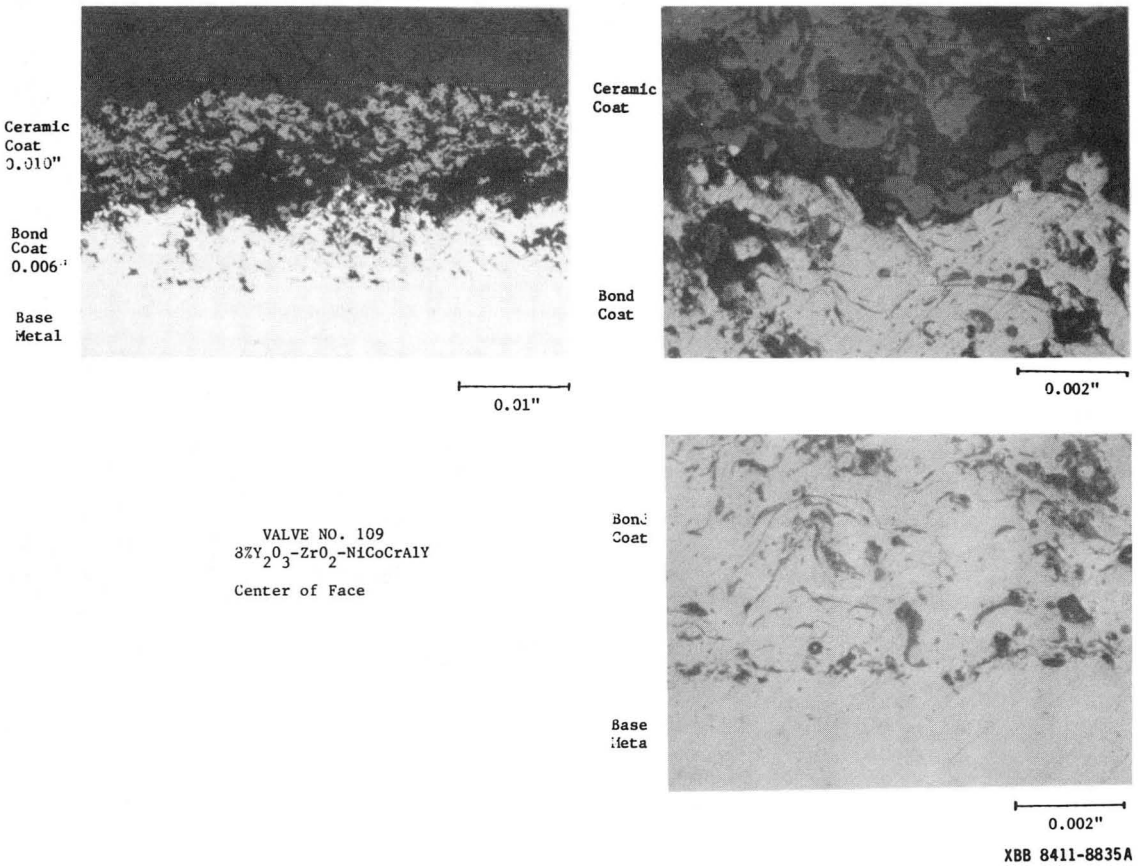
Supplier A coating - Valve No. 109 - flat rim of face

Figure 14



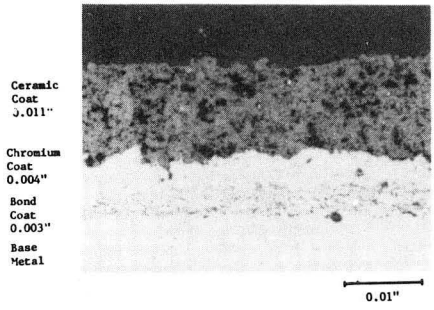
Supplier A coating - Valve No. 109 - part of face

Figure 15



Supplier A coating - Valve No. 109 - center of face

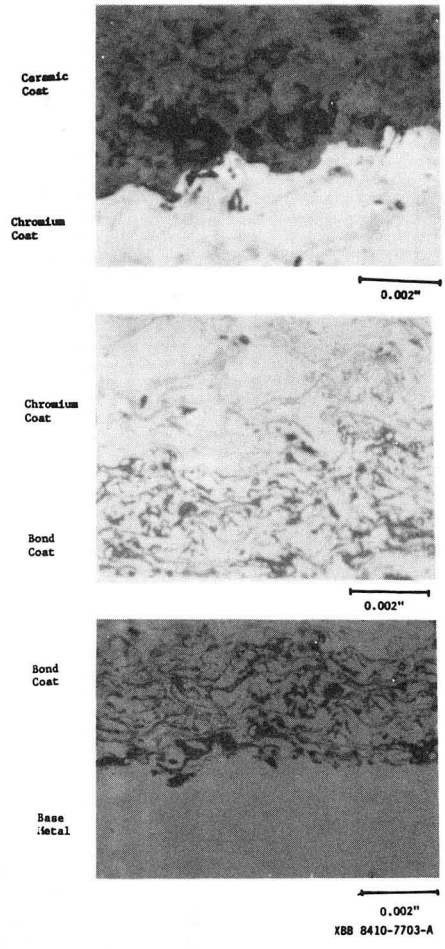
Figure 16



VALVE NO. 34

22% $MgO-ZrO_2-Cr-NiCrAlY$

Flat Part of Rim

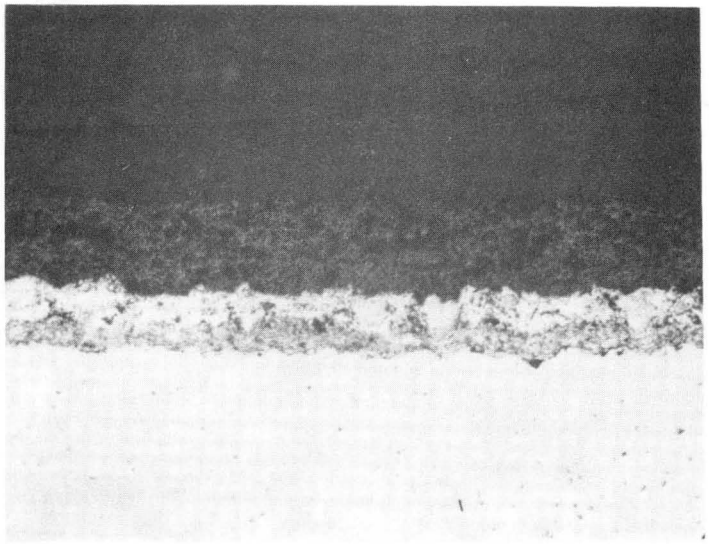


Supplier B coating - Valve No. 34 - flat rim of face

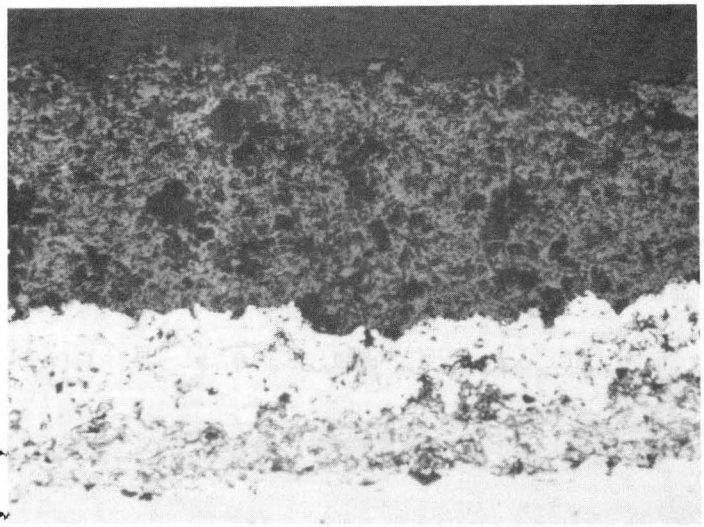
Figure 17

EUROCON ENGIN
VALVE NO. 34

22% $MgO-ZrO_2-Cr-NiCrAlY$



Curved Part of Face 0.05"

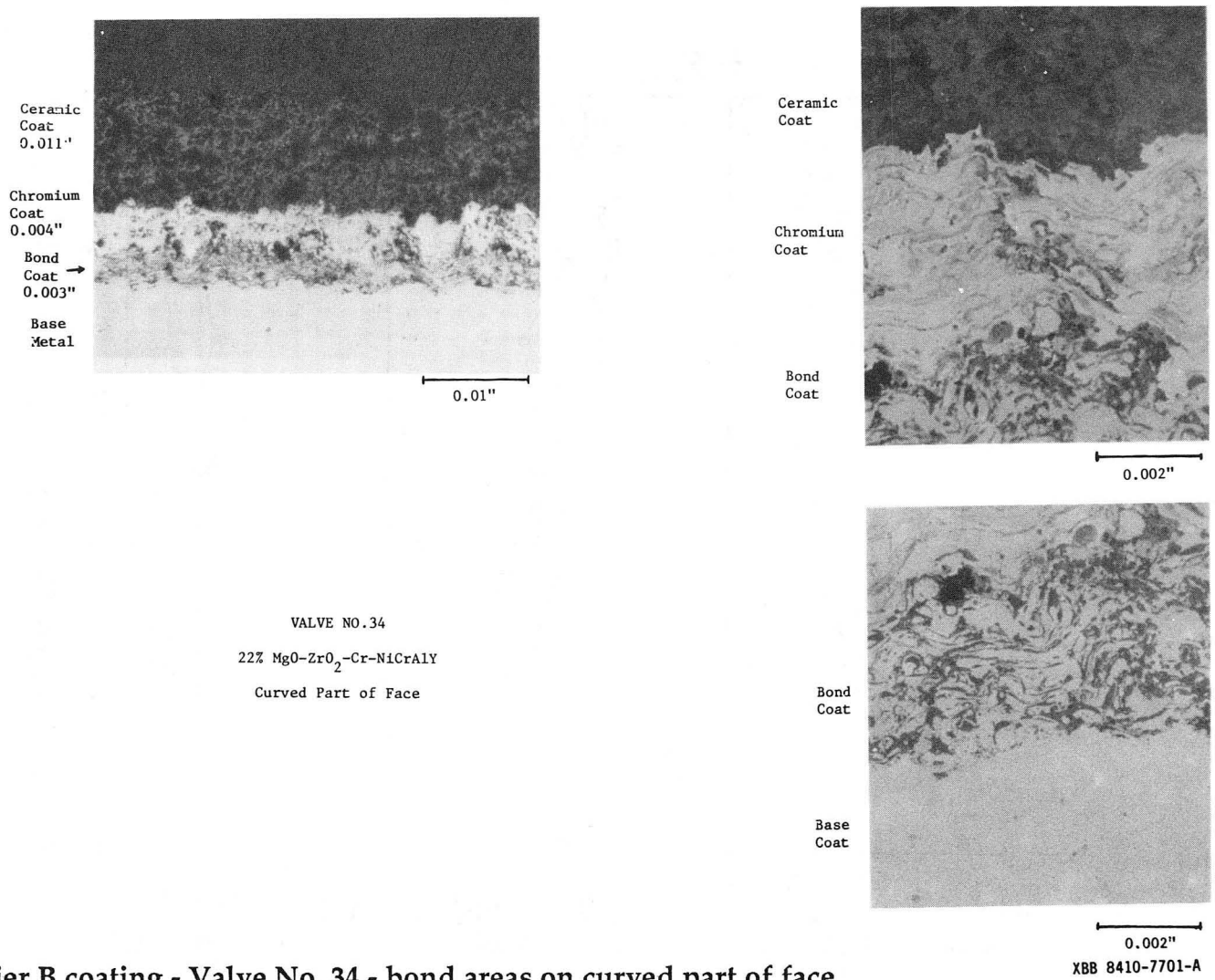


Center of Face 0.01"

XBB 8410-7697

Supplier B coating - Valve No. 34 - center and curved parts of face

Figure 18



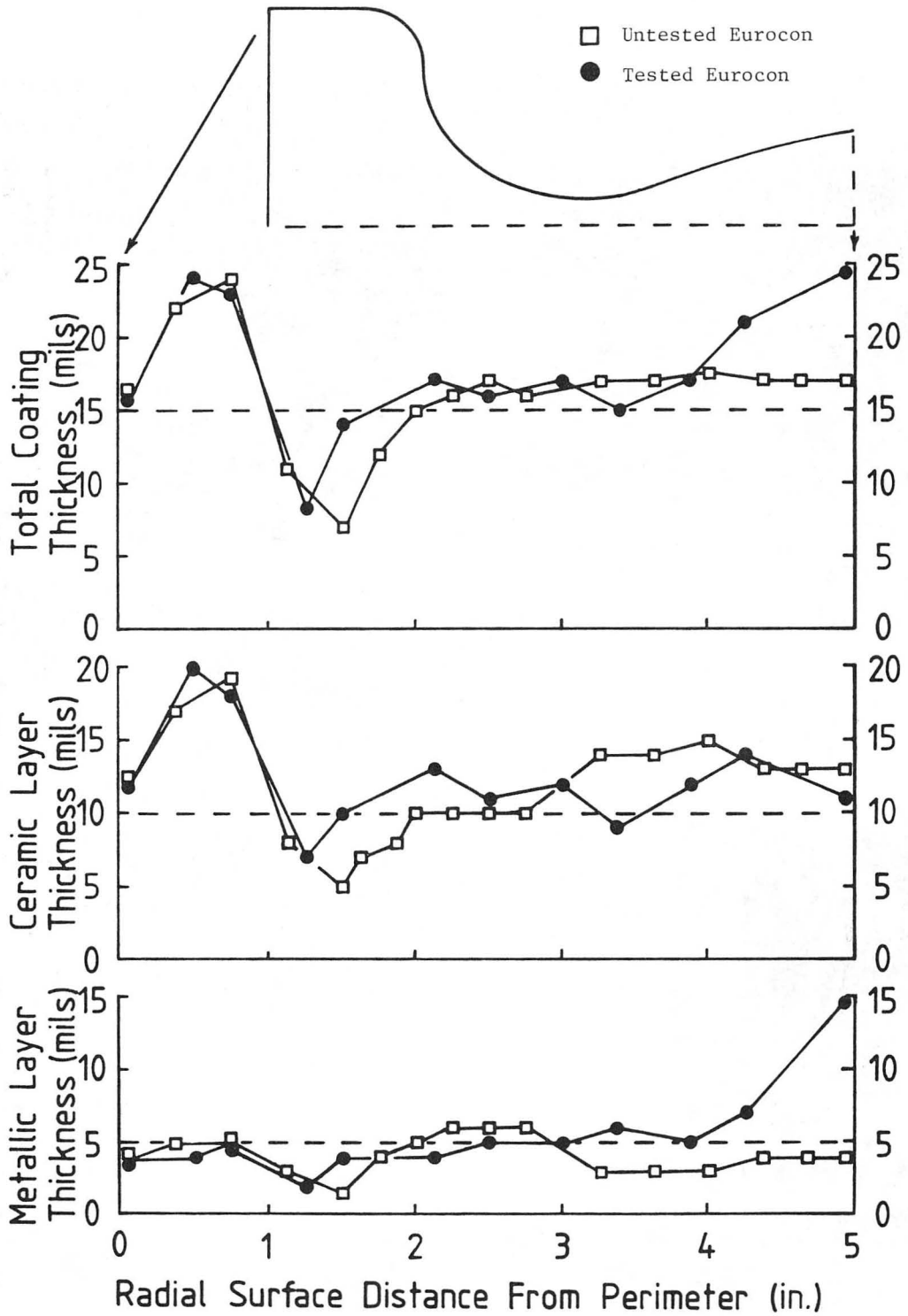
VALVE NO.34

22% $MgO-ZrO_2$-Cr-NiCrAlY

Curved Part of Face

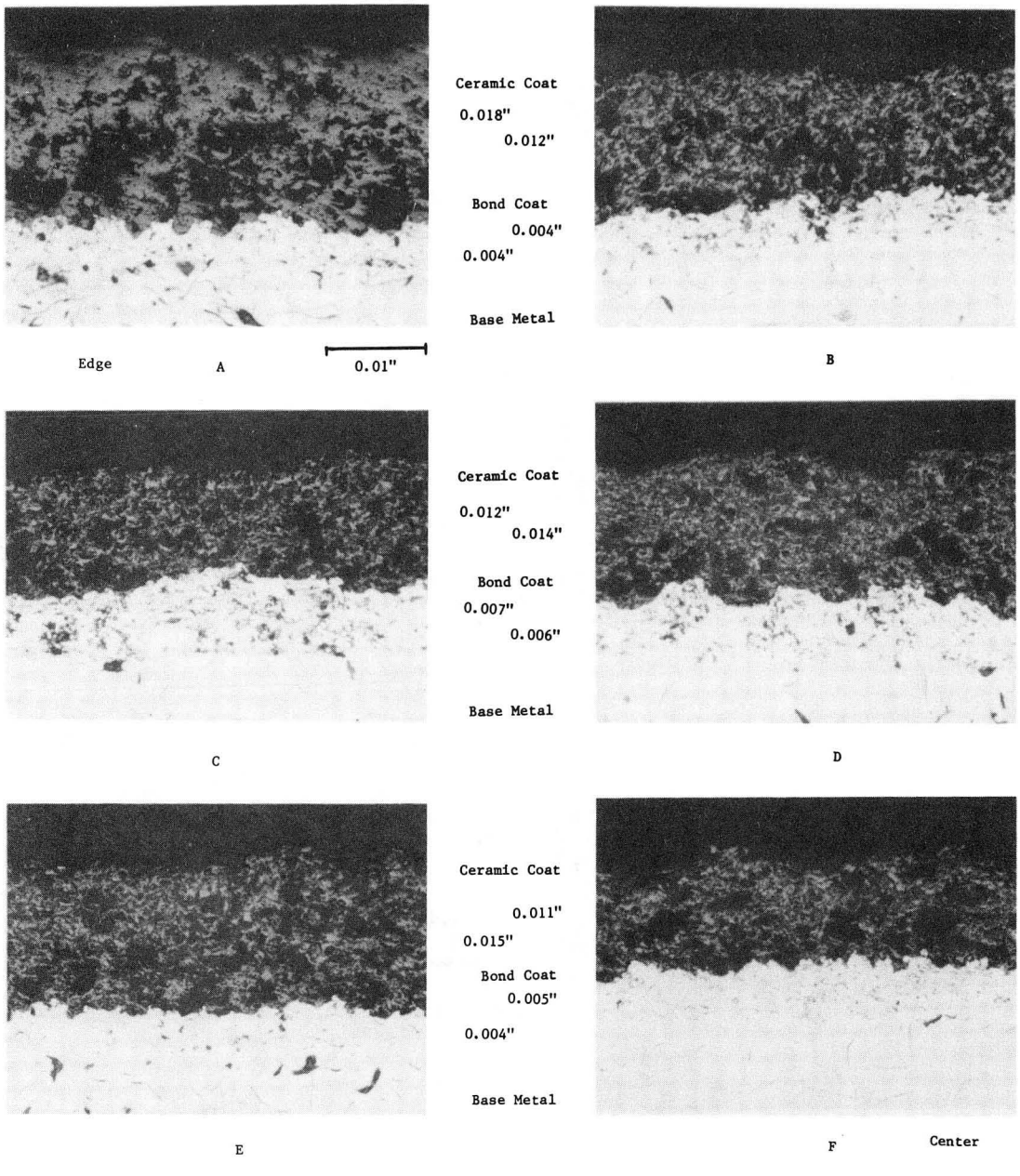
Supplier B coating - Valve No. 34 - bond areas on curved part of face

Figure 19



Supplier B piston crown coating thickness profile

Figure 20



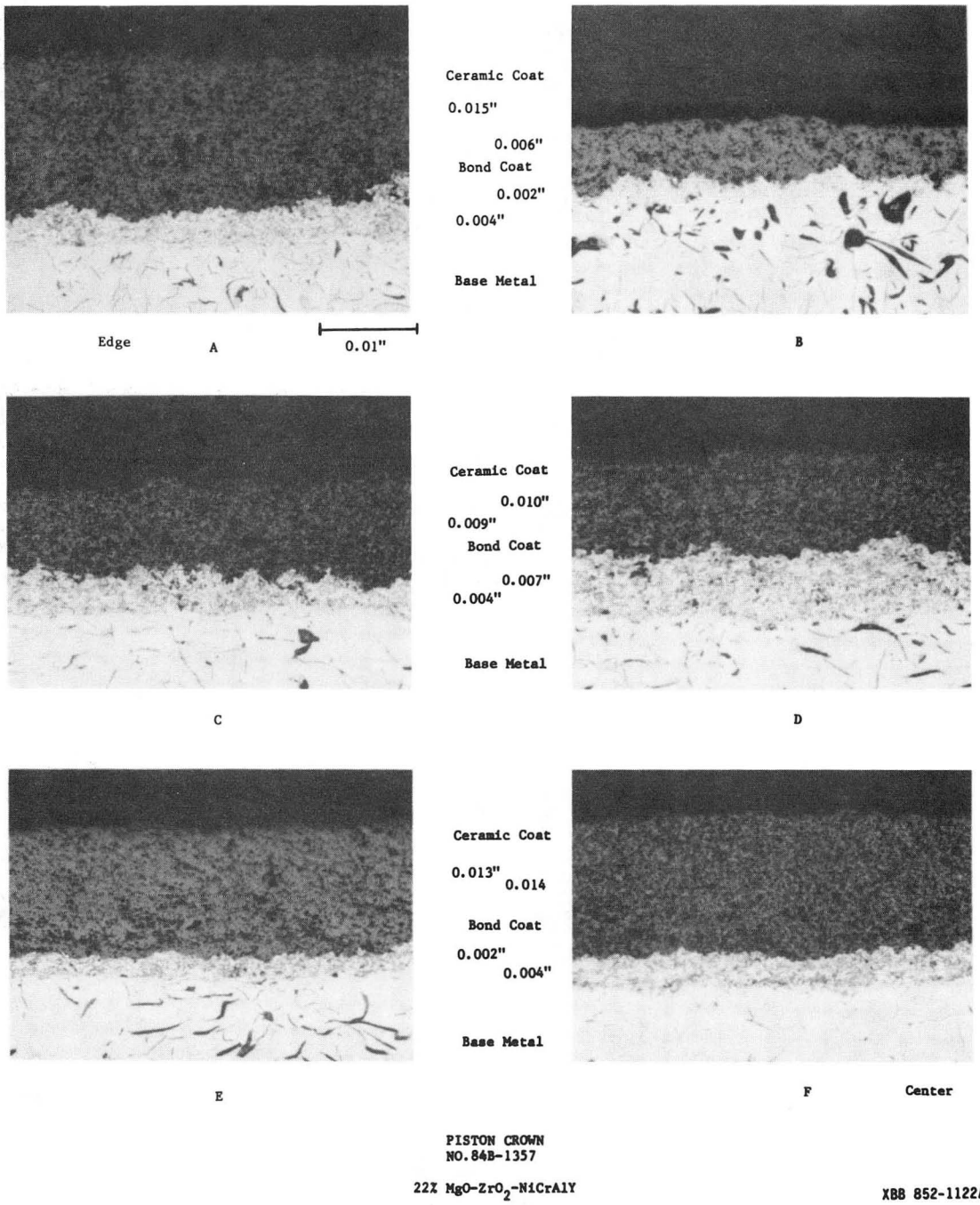
PISTON CROWN
NO. 84B-1465

8% Y_2O_3-ZrO_2-NiCoCrAlY

XBB 852-1121A

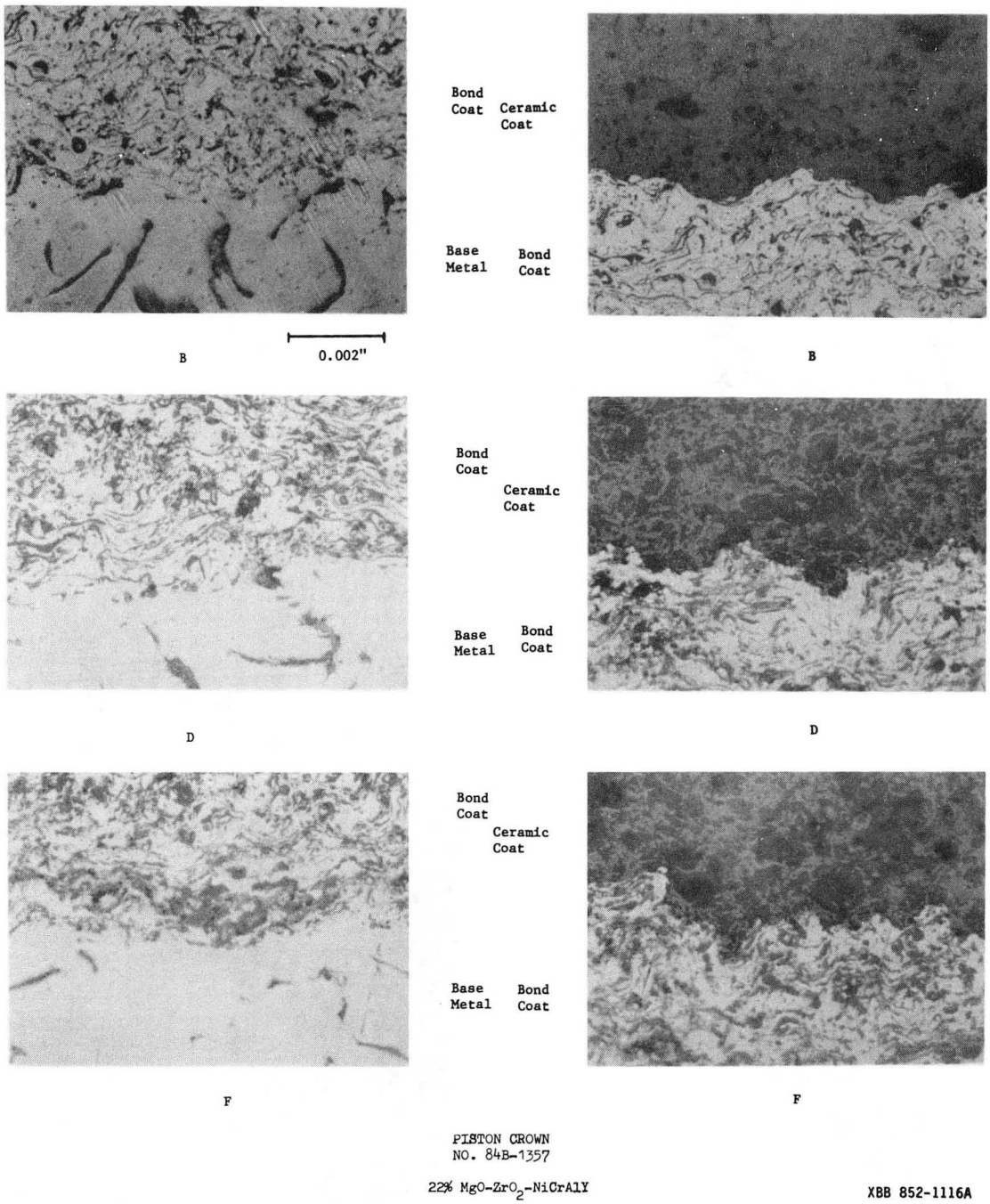
Supplier A coating - Piston Crown No. 84B-1465

Figure 21



Supplier B coating - Piston Crown No. 84B-1357

Figure 22



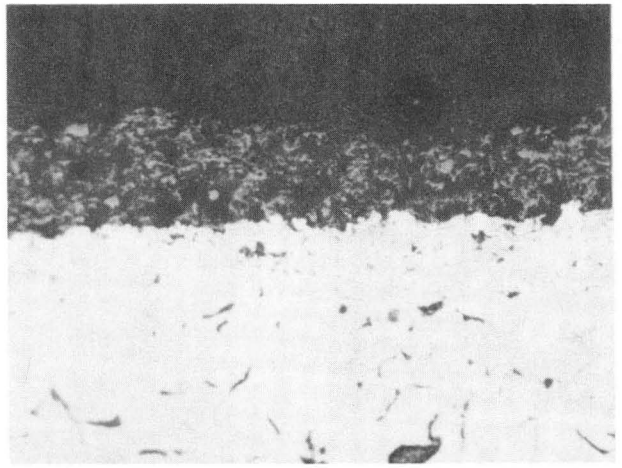
PISTON CROWN
NO. 84B-1357

22% $MgO-ZrO_2$-NiCrAlY

XBB 852-1116A

Supplier B coating - bond areas - Piston Crown 84B-1357

Figure 23



Ceramic Coat

0.007"

0.007"

Bond Coat

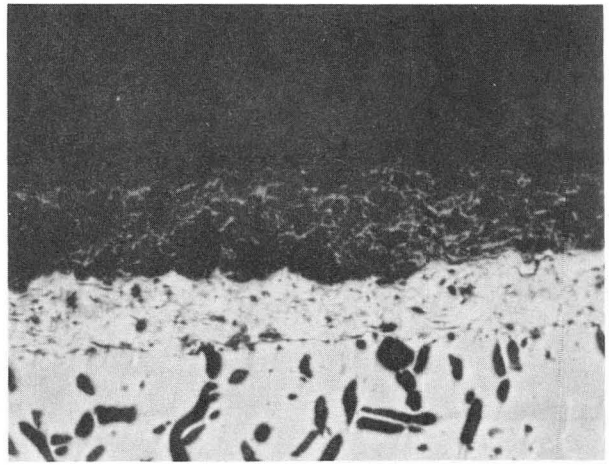
0.005"

0.005"

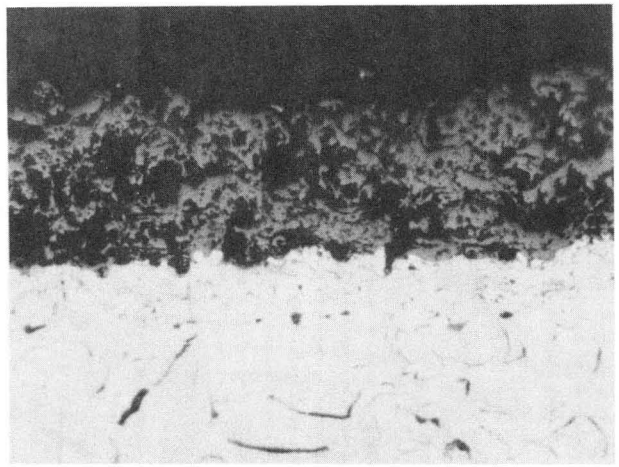
Base metal

X

0.01"



Y



Ceramic Coat

0.011"

Bond Coat

0.004"

Base Metal

C

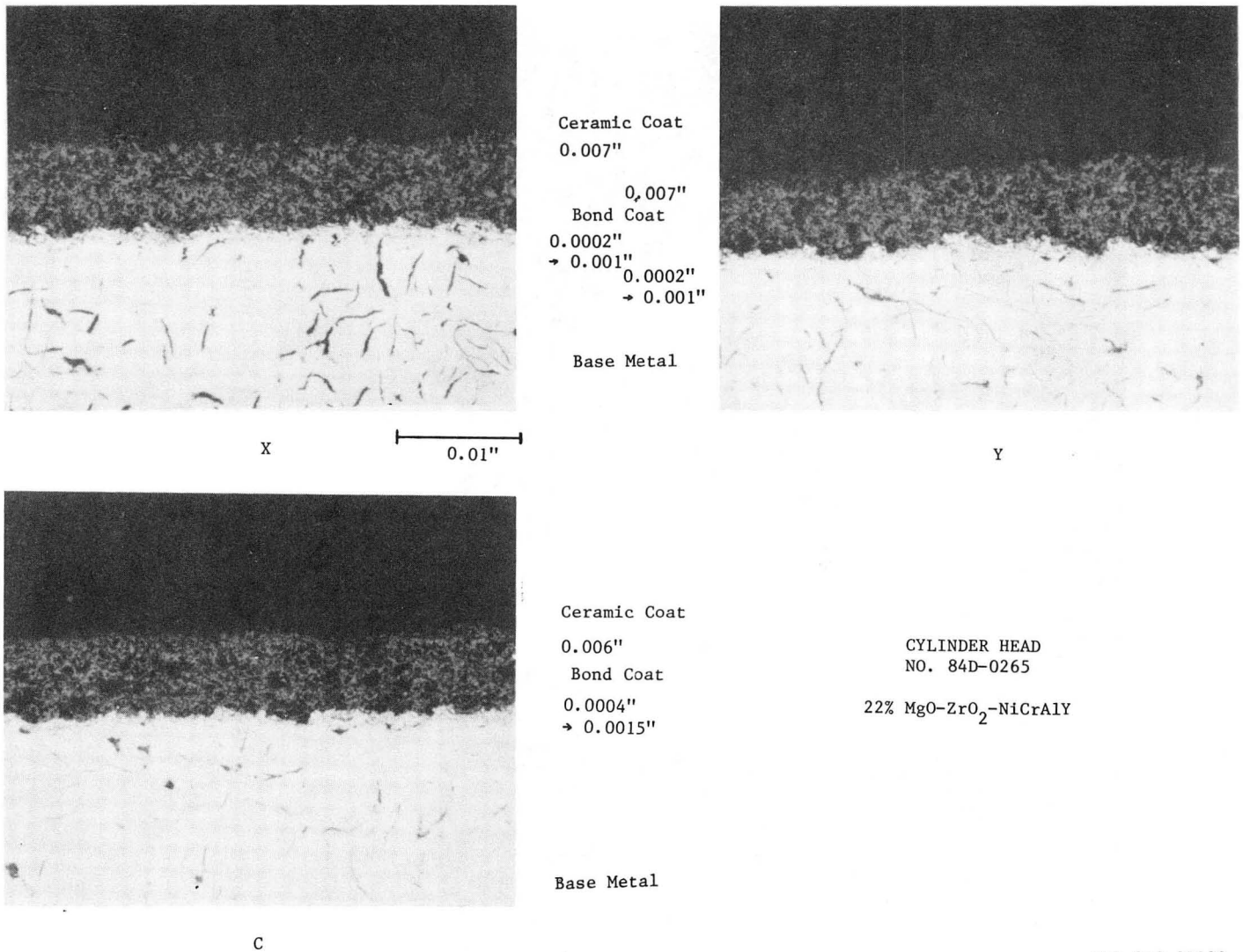
CYLINDER HEAD
NO. 84C-2775

8% Y_2O_3-ZrO_2-NiCoCrAlY

XBB 852-1118A

Supplier A coating - Cylinder Head No. 84C-0265

Figure 24



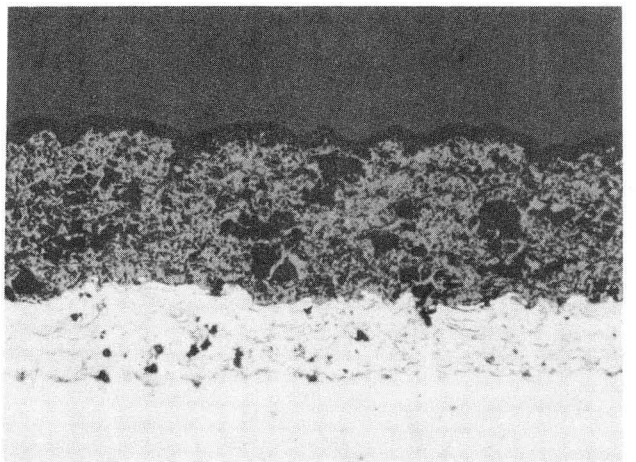
Supplier B coating - Cylinder Head No. 84D-0265

Figure 25

CBB 855-4006 A

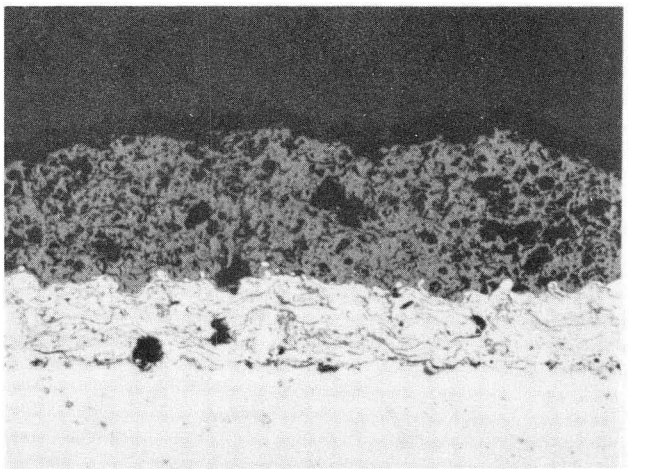
Supplier A coated valve face after 500 hours engine test

Figure 26

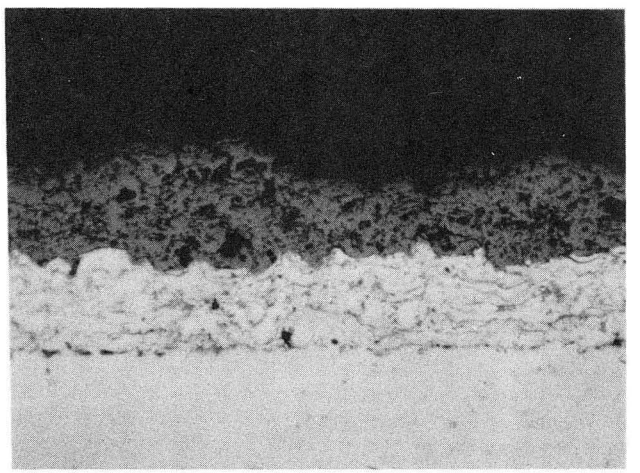


A

0.01"



B



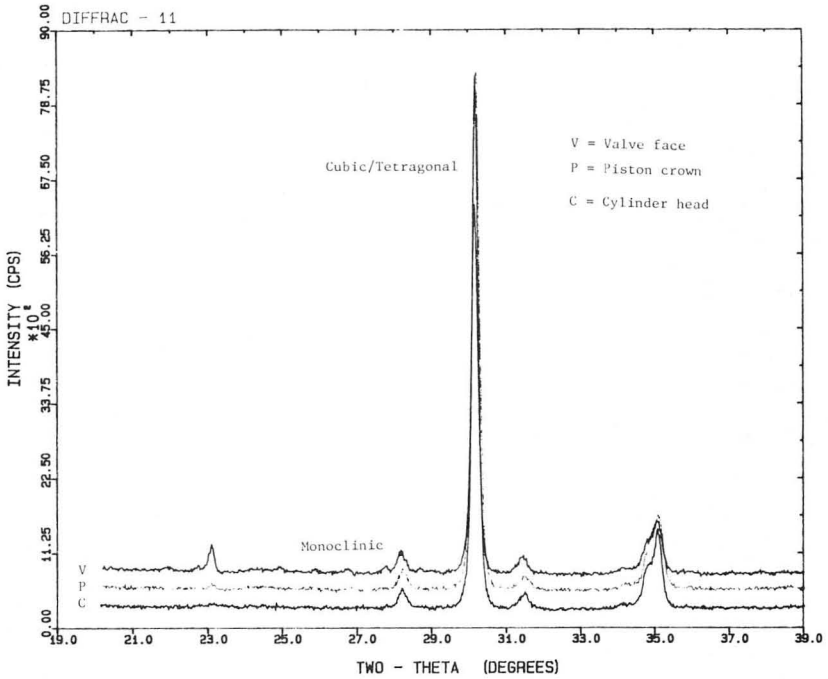
C

TCC valve face coating cross sections.

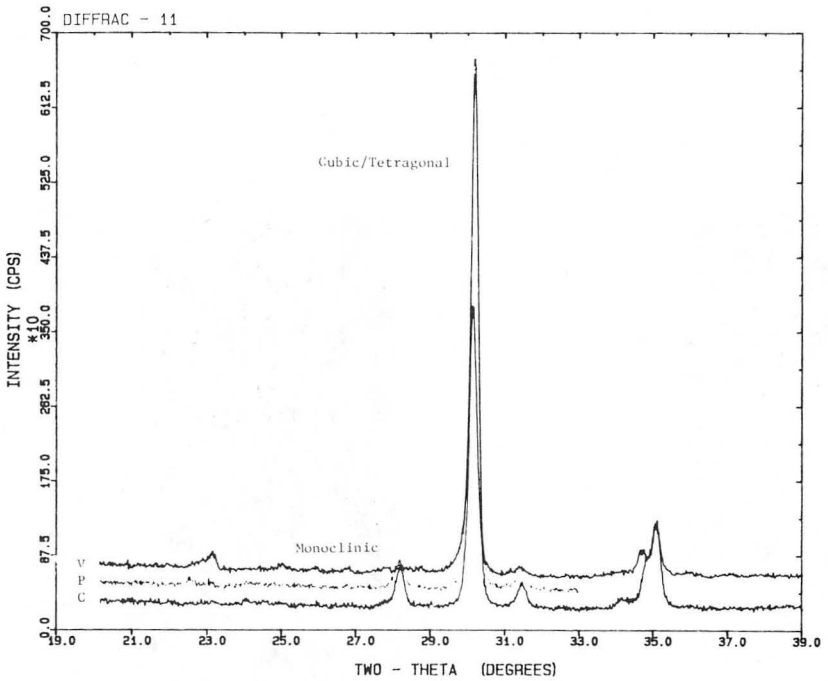
XBB 8510-8077

Supplier A valve face coating cross sections

Figure 27



Untested TCC component coatings' x-ray diffraction pattern

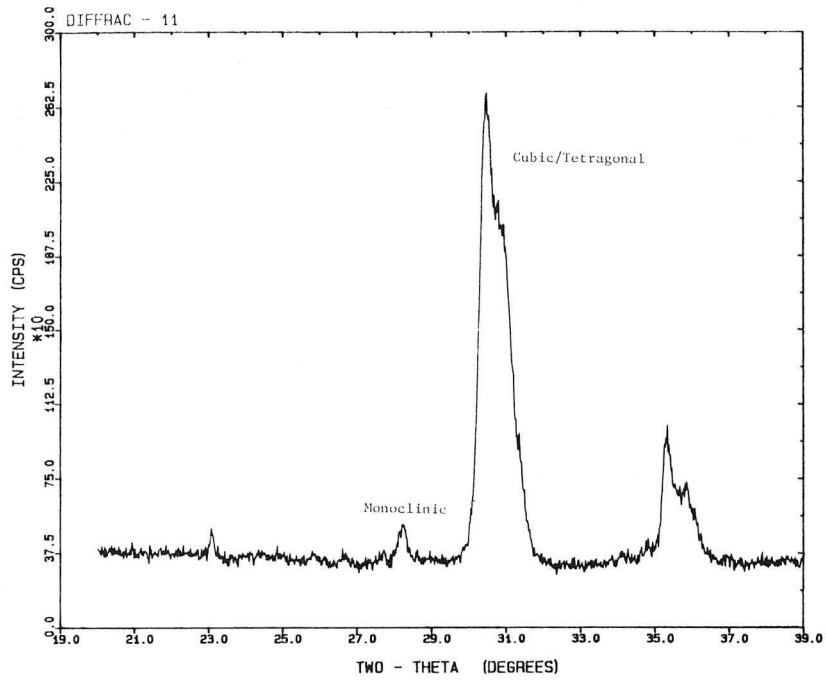


Tested TCC component coatings x-ray diffraction pattern

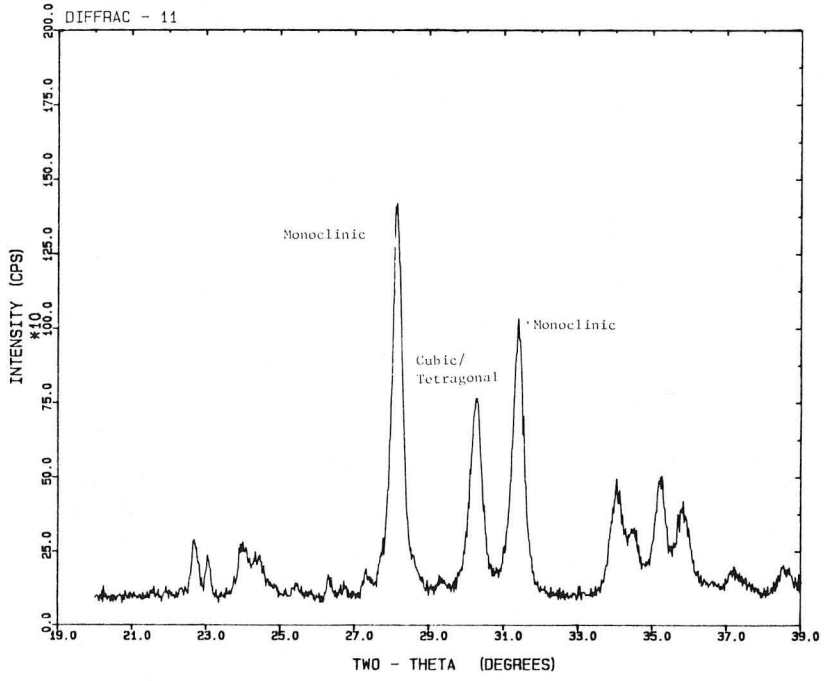
XBL 8510 4146

X-ray diffraction peaks of 8 Wt.% Y_2O_3-ZrO_2 coating (A) before and (B) after testing

Figure 28



Untested Eurocon valve face coating x-ray diffraction pattern

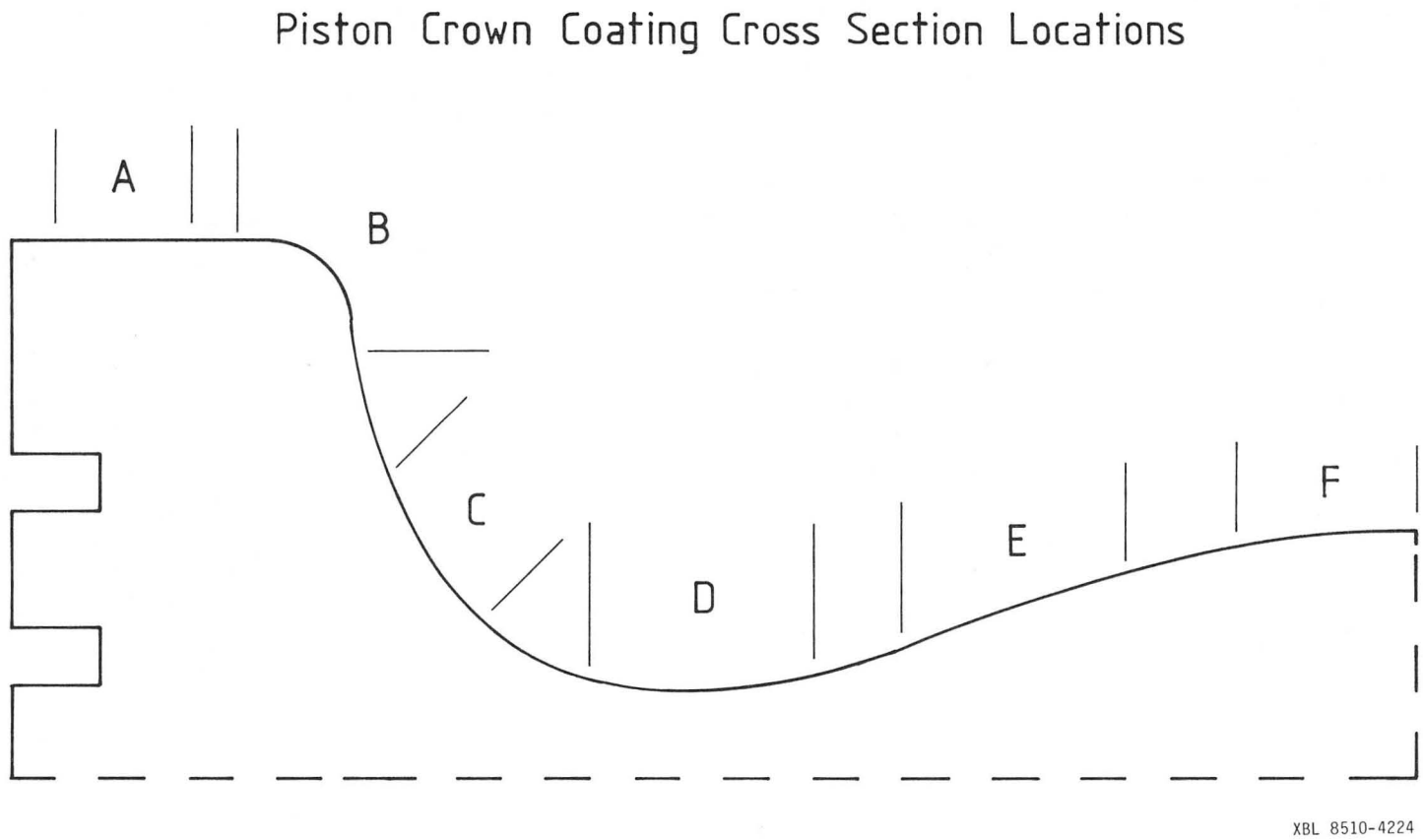


Tested Eurocon valve face coating x-ray diffraction pattern

XBL 8510 4145

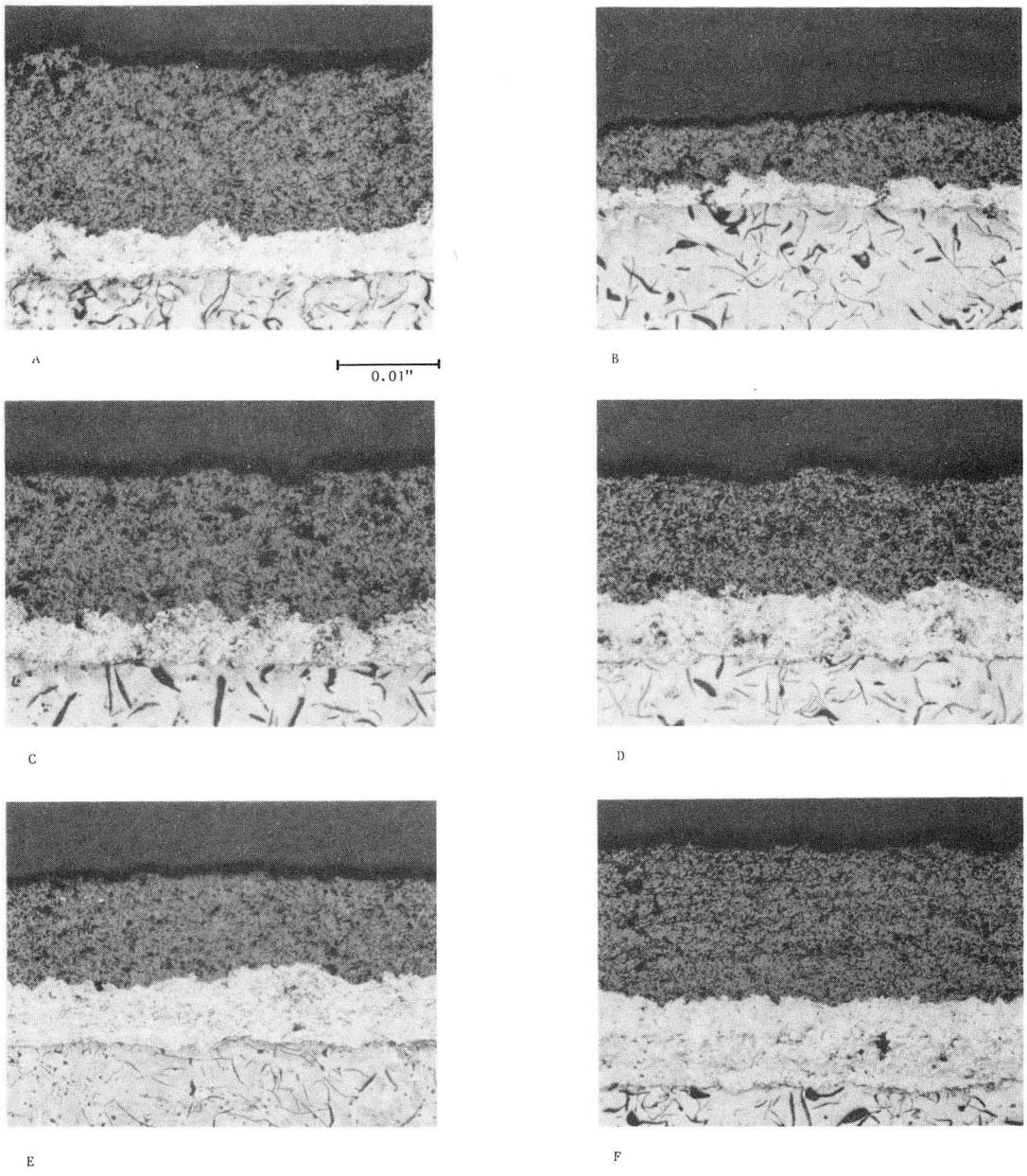
X-ray diffraction peaks of 22 Wt.% $MgO-ZrO_2$ coating untested and tested

Figure 29



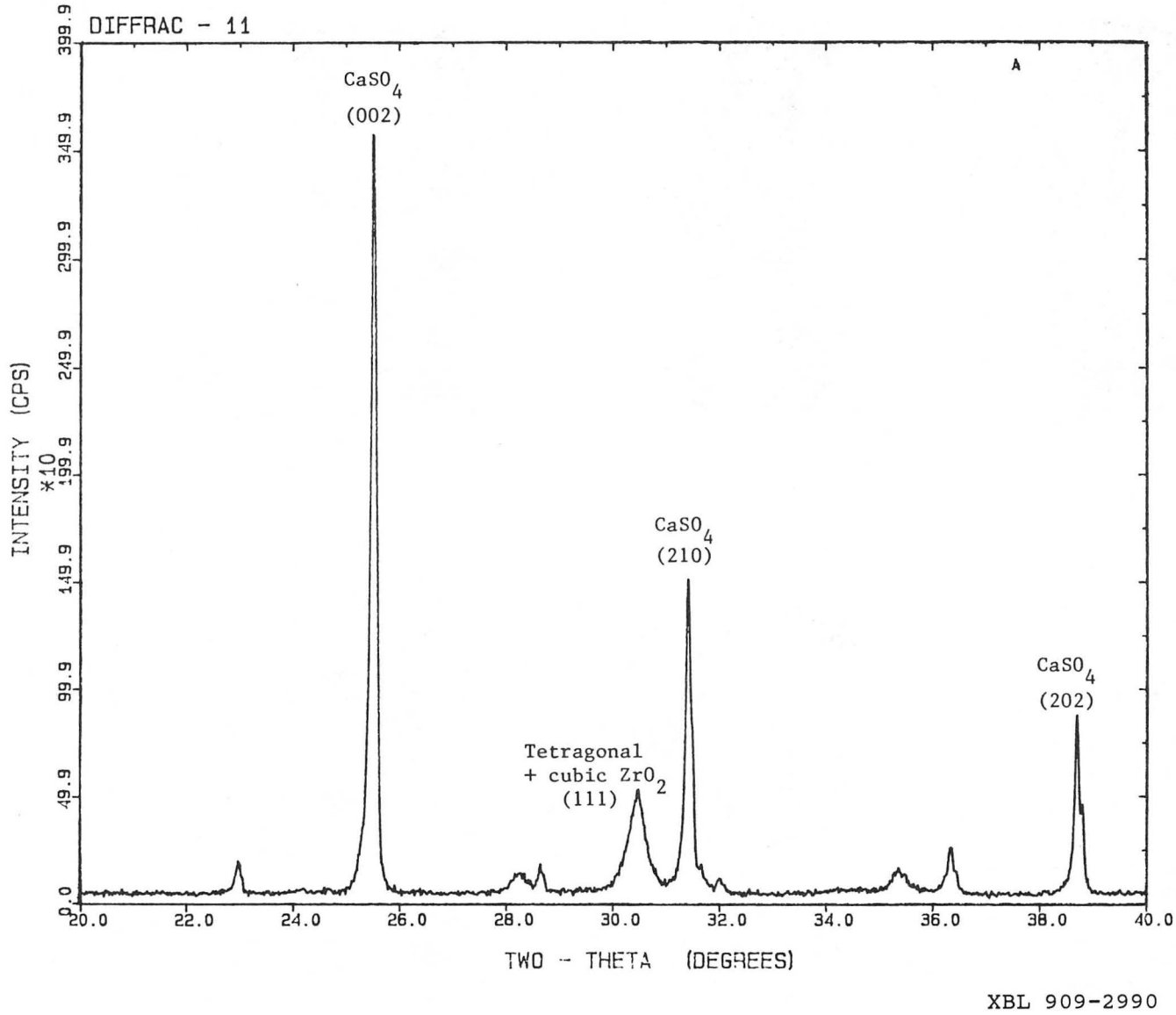
Sketch of one-half of the piston crown showing locations at which micrographs were taken

Figure 30



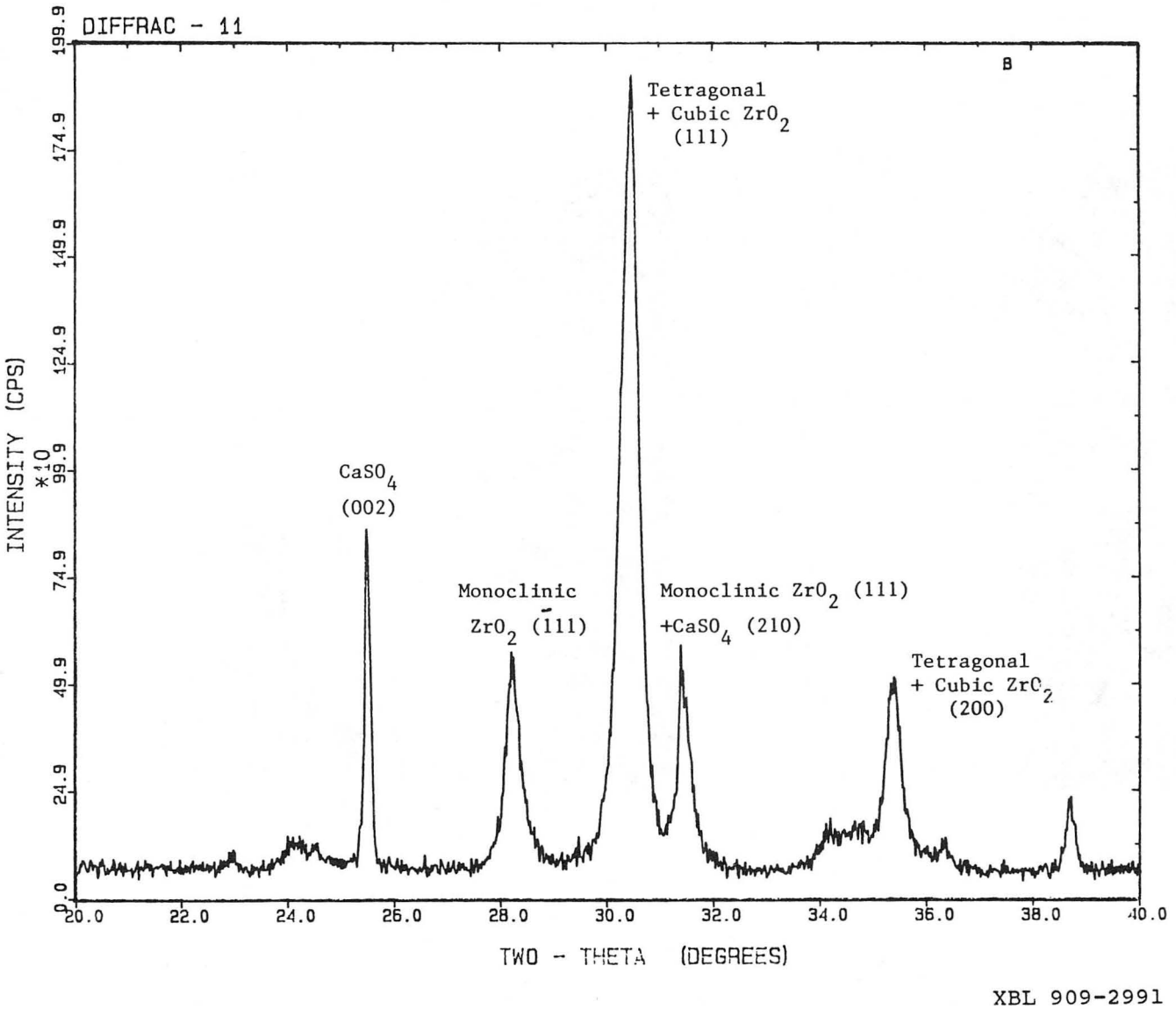
Cross section of the 22 wt.% $MgO\text{-}ZrO_2$ piston crown coating at the locations indicated in Figure 30

Figure 31



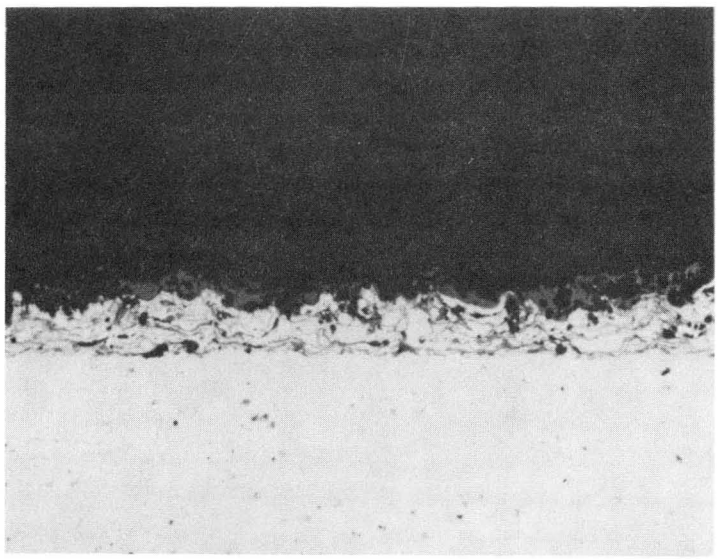
X-ray diffraction peaks of Supplier B coating, uncleaned

Figure 32

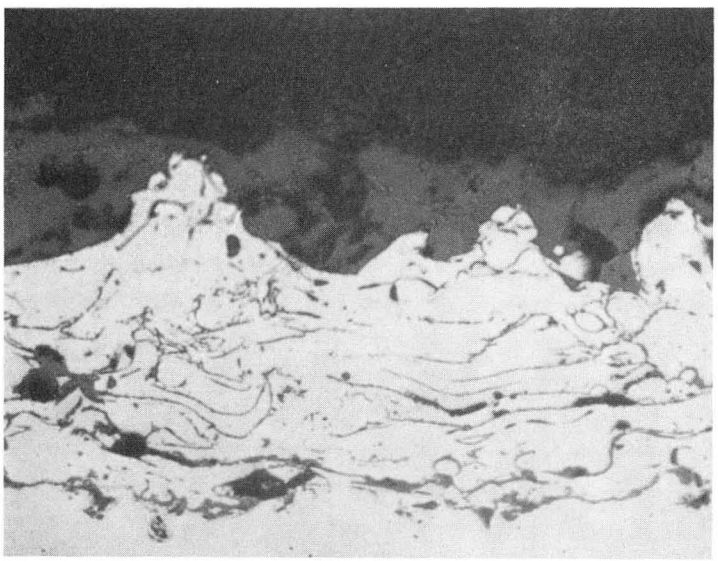


X-ray diffraction peaks of Supplier B coating, cleaned

Figure 33



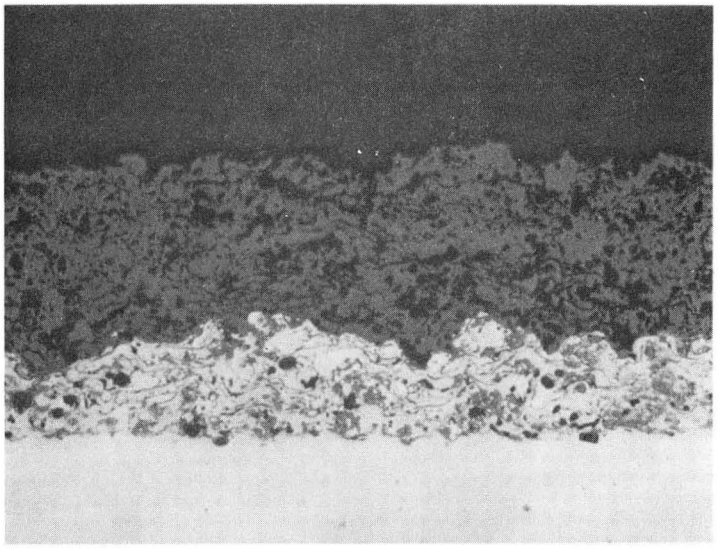
(a) 200 μm



(b) 50 μm

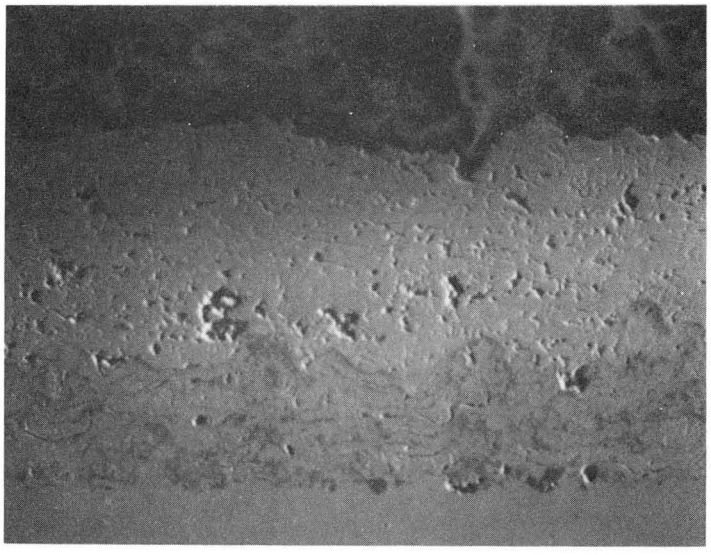
Post-service Supplier A valve coating; Valve No. 90

Figure 34 XBB 867-5820



(a)

200 μm

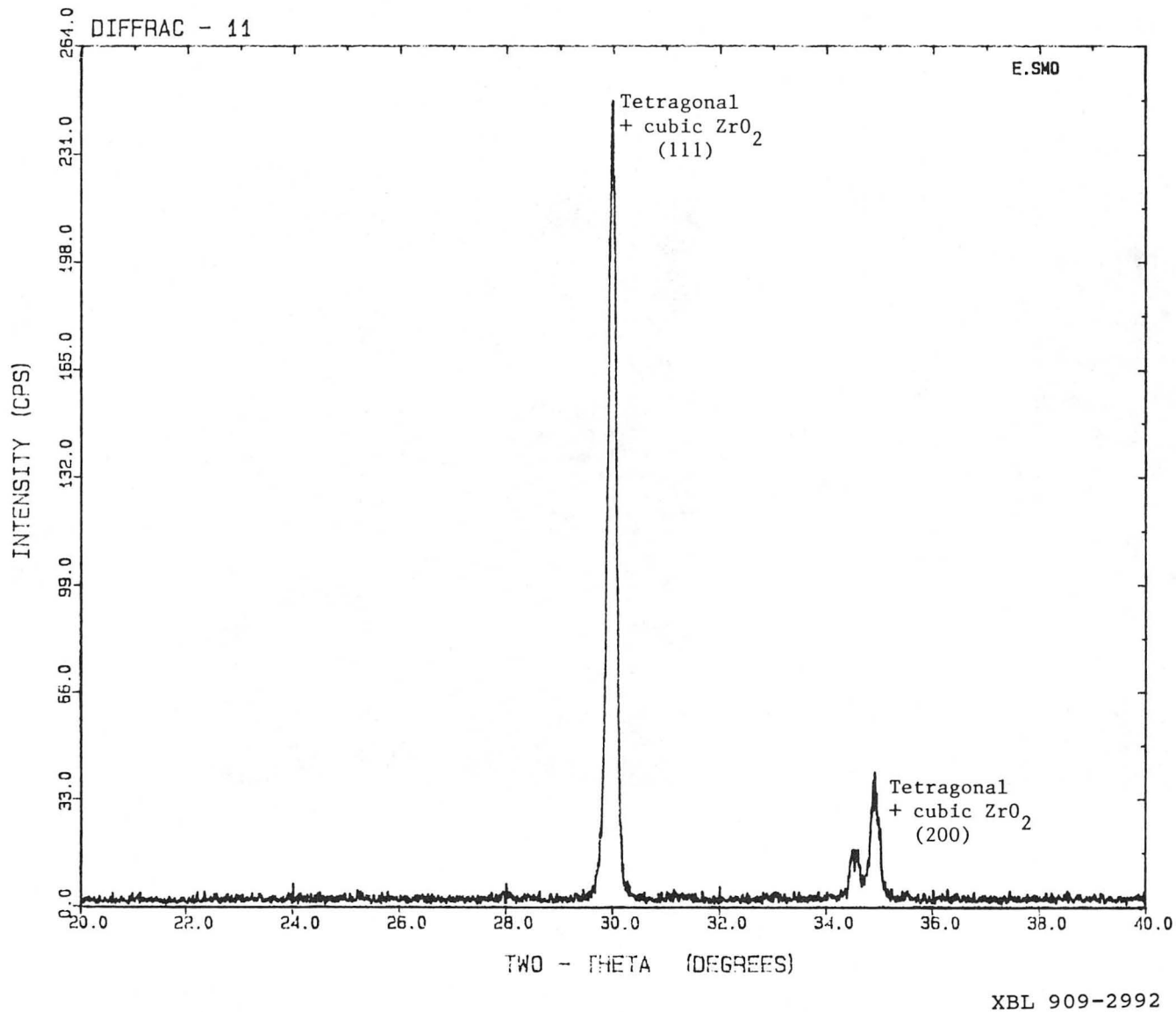


(b)

Post service Supplier A valve coating; Valve No. 99.

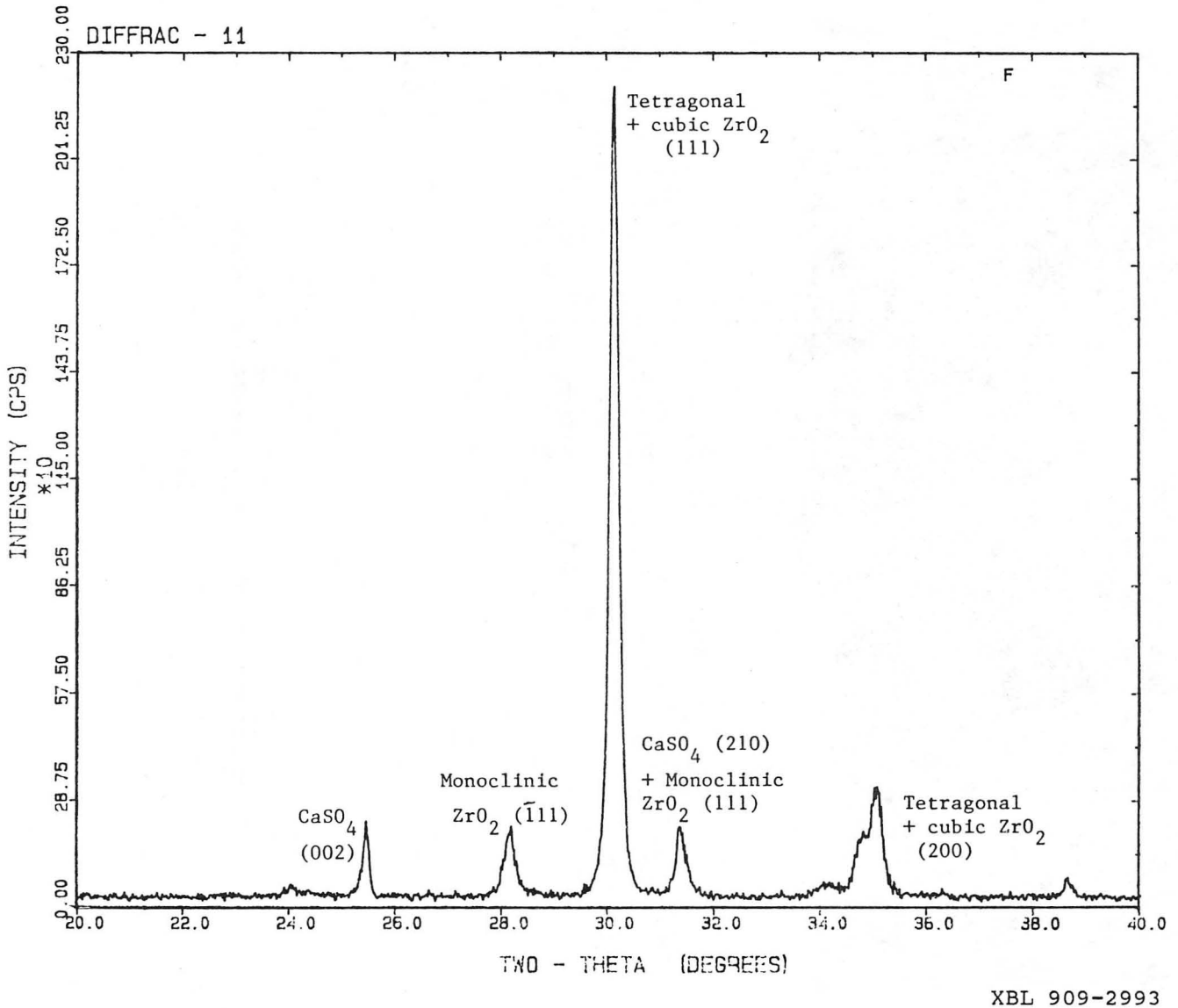
XBB 867-5818

Figure 35



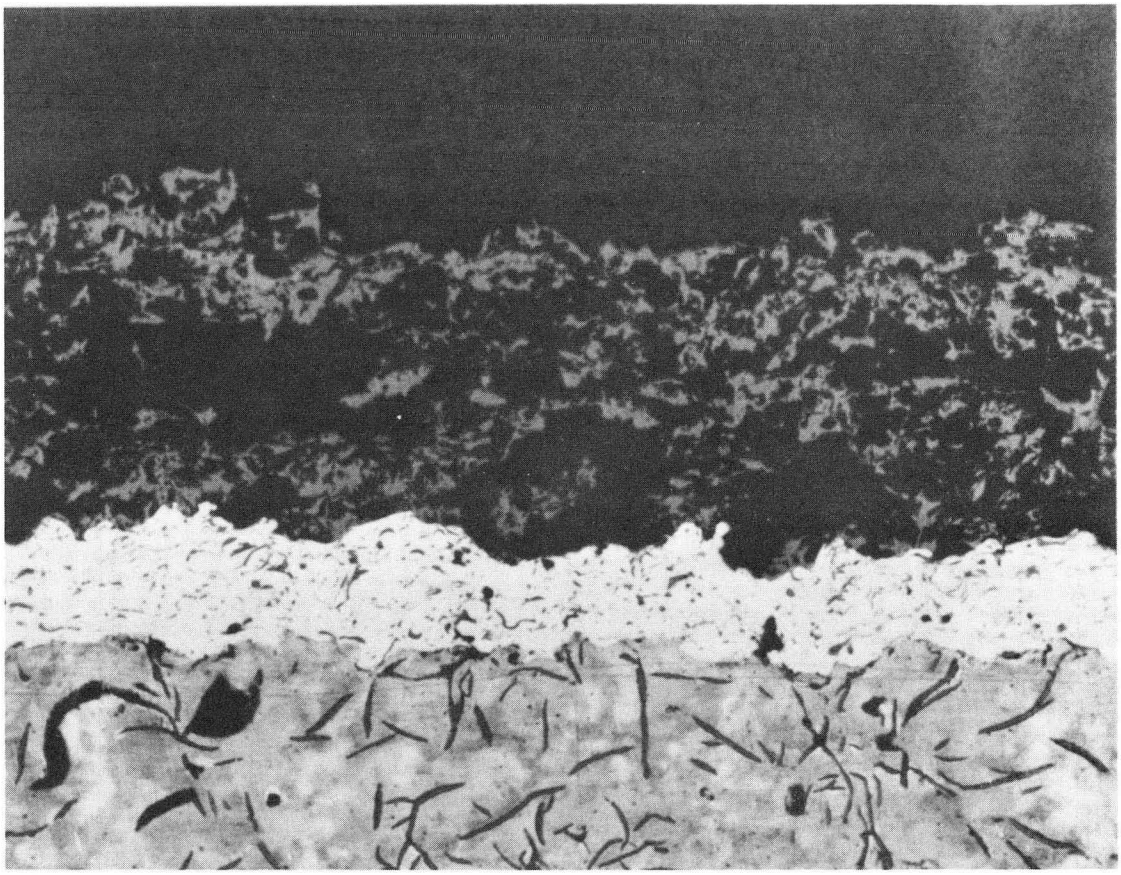
X-ray diffraction peaks of Supplier A coating; Valve No. 99.

Figure 36



X-ray diffraction peaks of Supplier A coating; Valve No. 90.

Figure 37

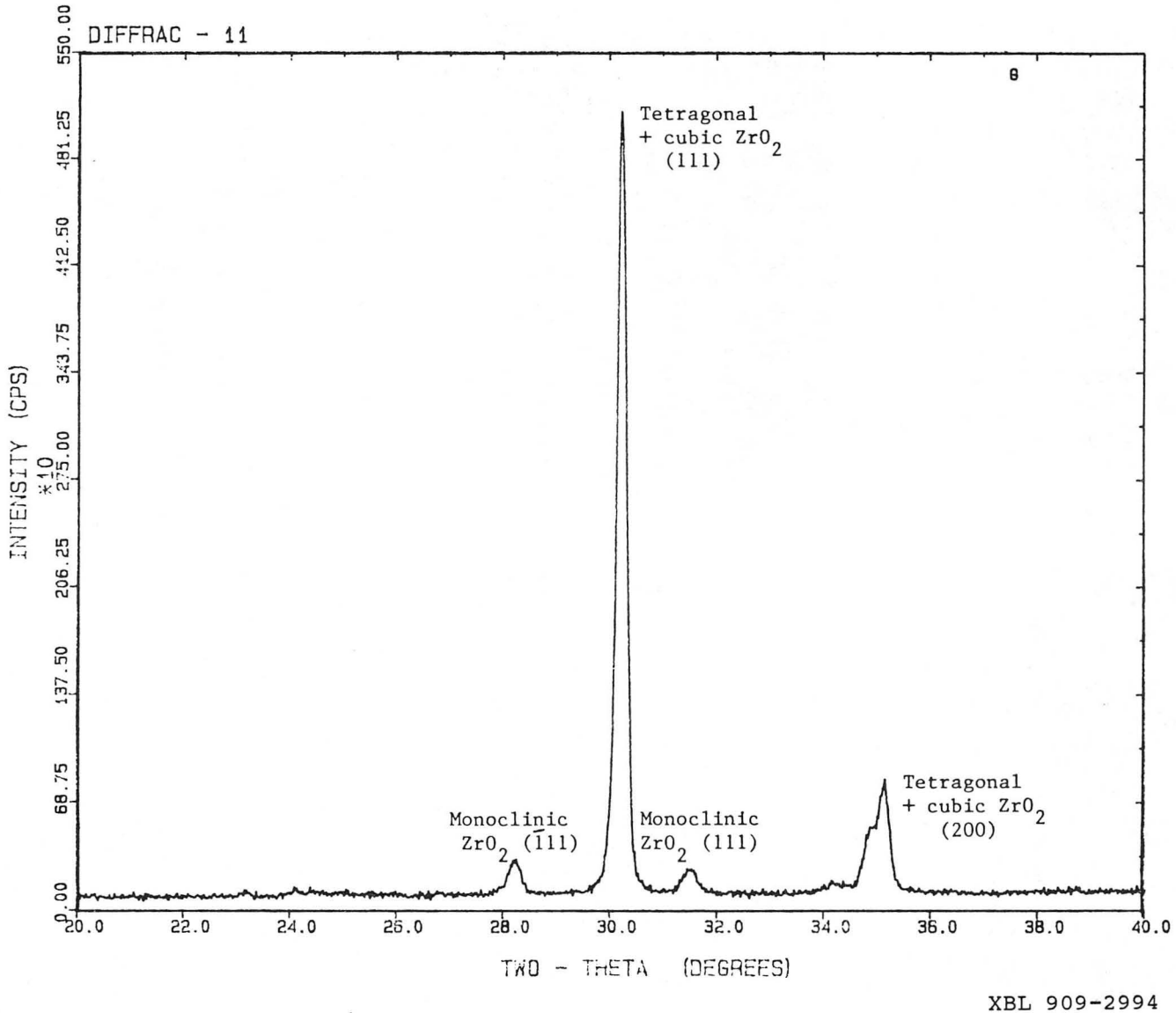


200 μm

Post service Supplier A piston crown coating.

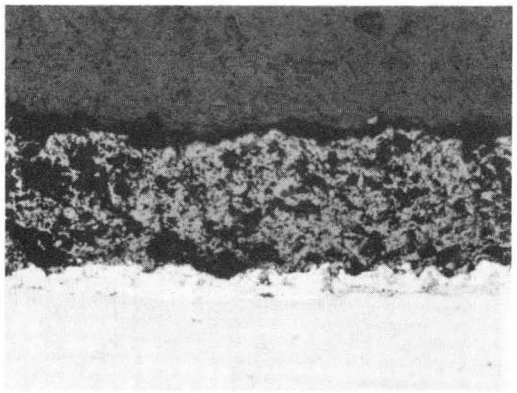
Figure 38

XBB 867-5816

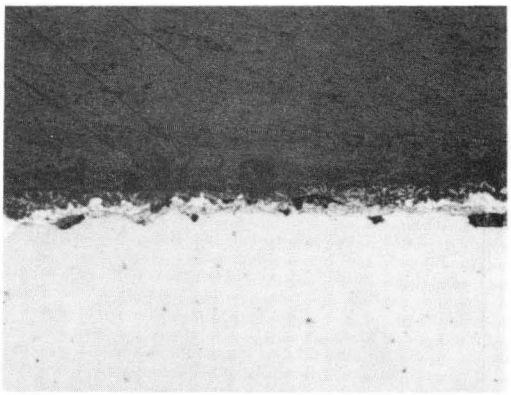


X-ray diffraction peaks of Supplier A piston crown

Figure 39



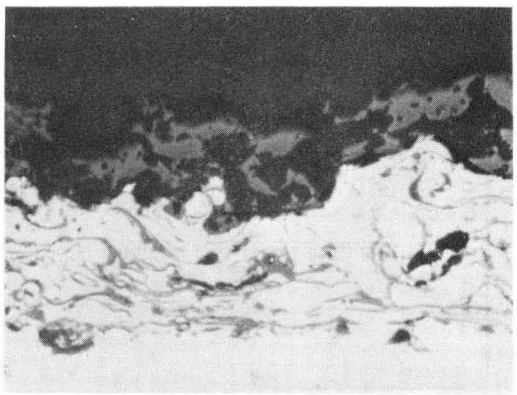
200 μm



(b)

200 μm

As-applied and post-service Supplier D valve face coatings.



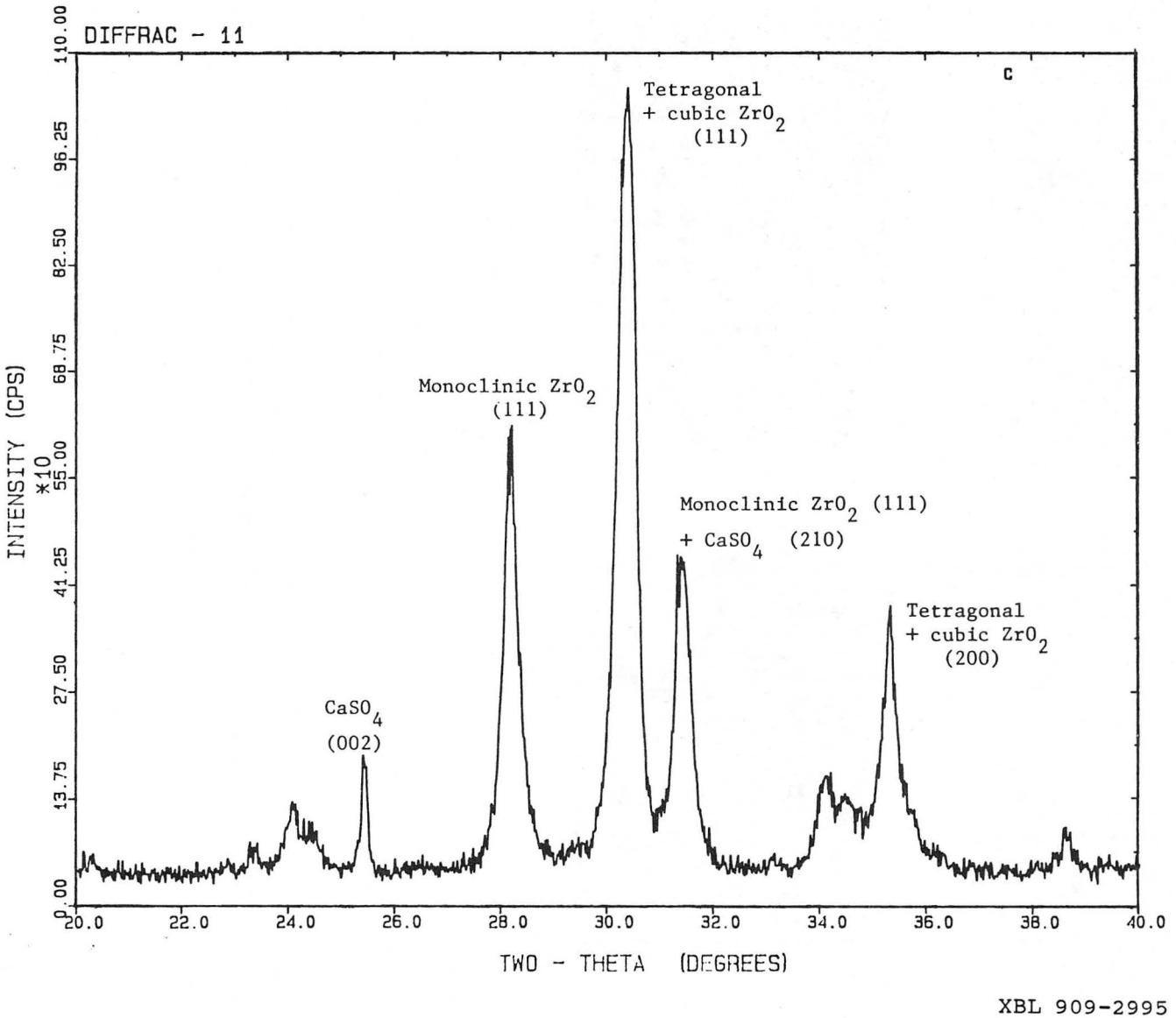
(c)

50 μm

XBB 867-5815

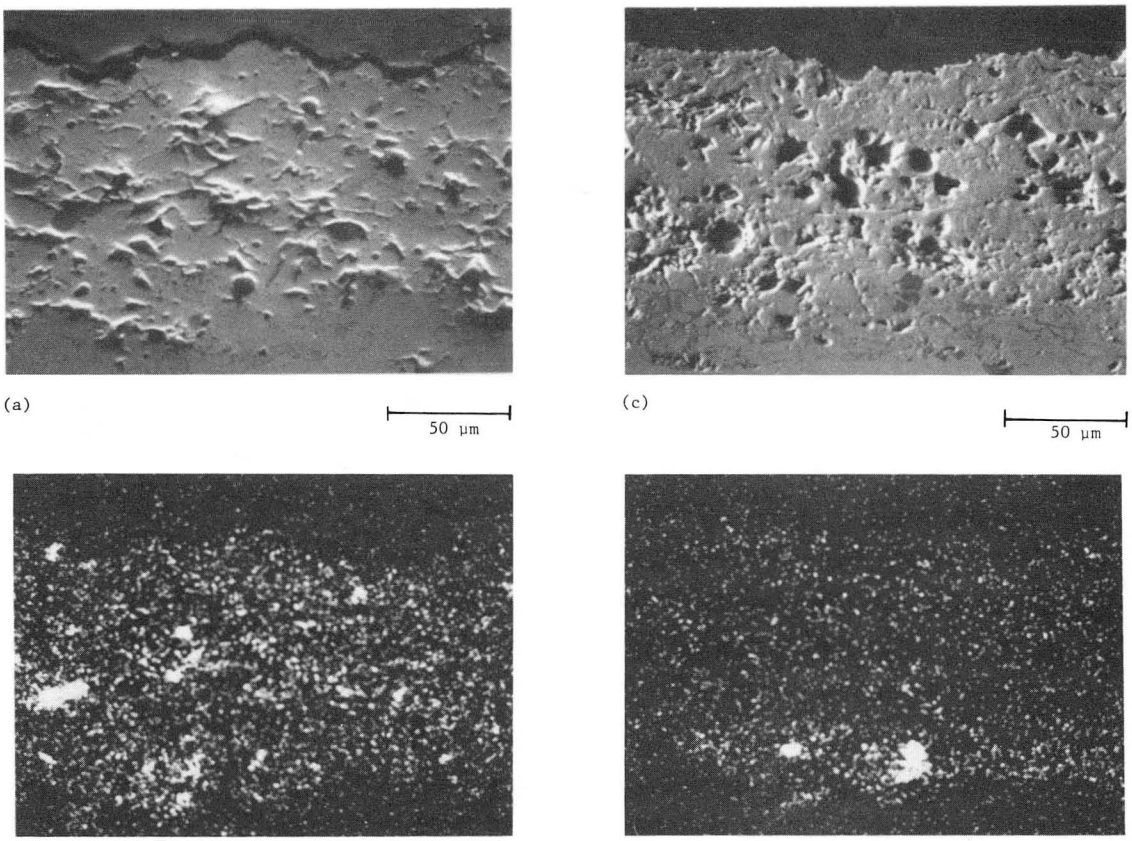
As-applied and post-service Supplier B valve face coatings

Figure 40



X-ray diffraction peaks of Supplier B coatings, after testing

Figure 41

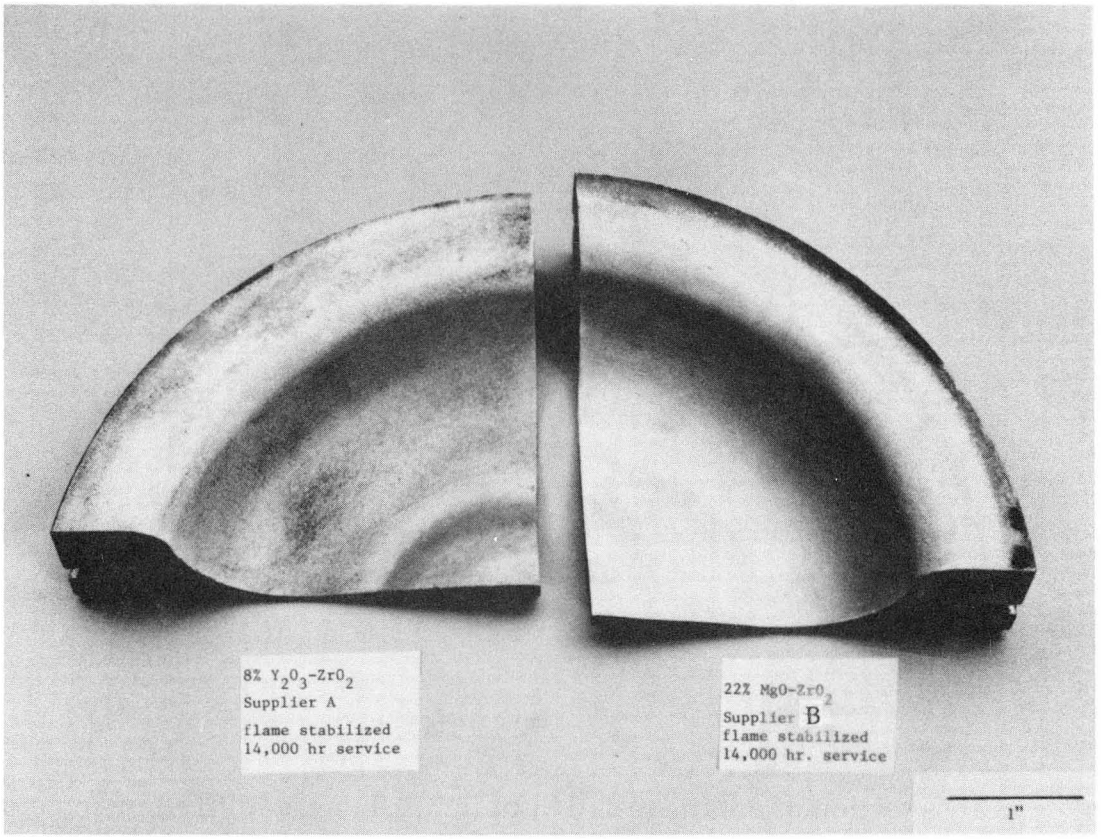


MgO distribution in as-applied and post-service Supplier D valve face coatings.

XBB 867-5821

MgO distribution in as-applied and post-service Supplier B valve face coatings

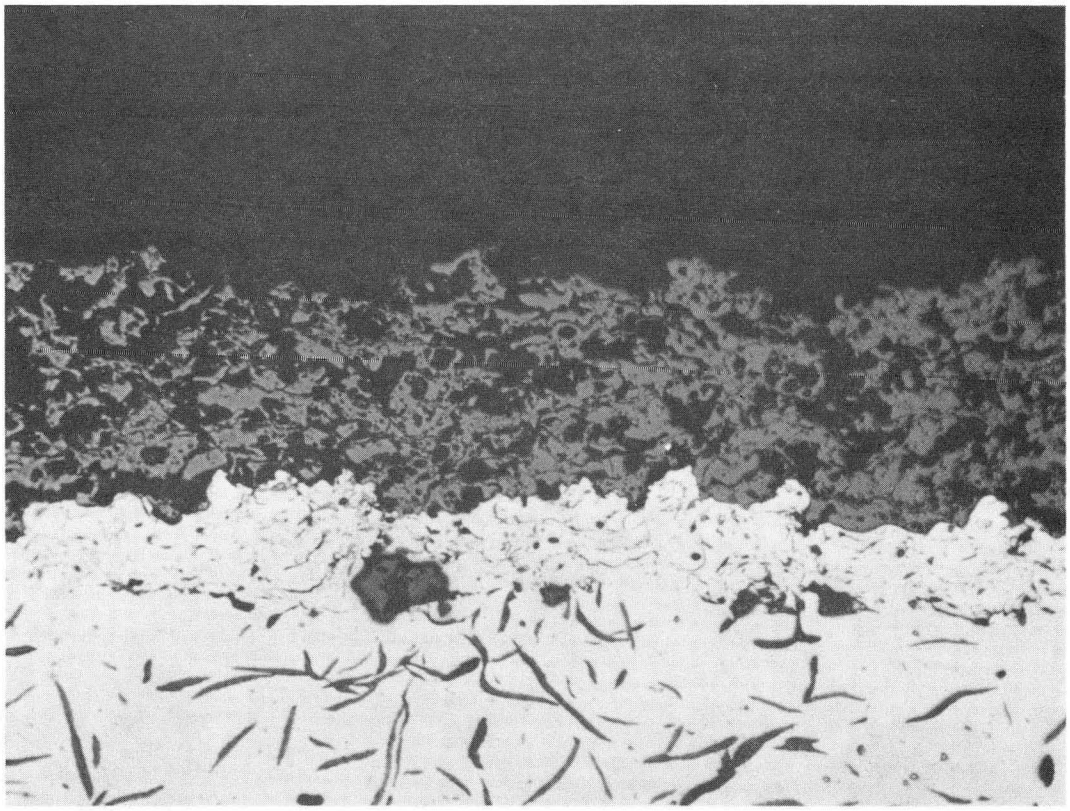
Figure 42



XBB 875-4130A

Supplier A (left side) and Supplier B coated piston crown after 14,000 hours engine service

Figure 43



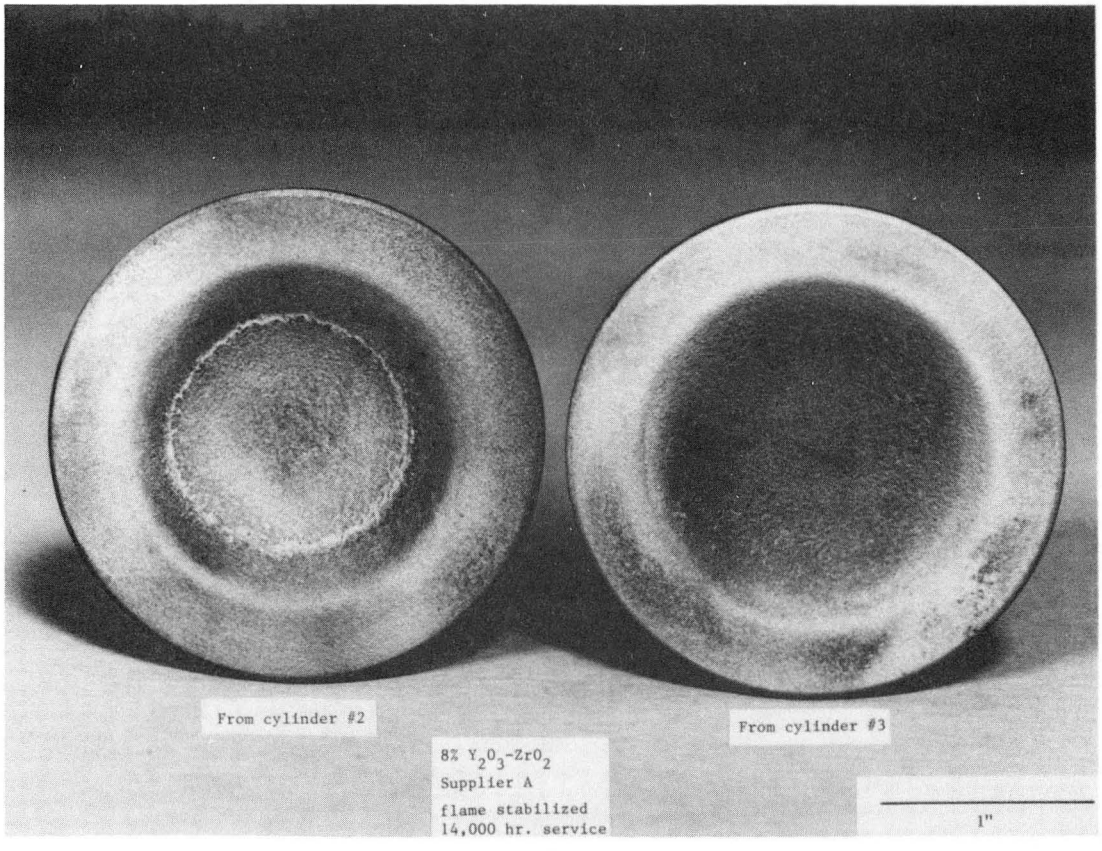
8% Y_2O_3-ZrO_2

0.01"

Cross section of engine tested Supplier A flame stabilized piston crown coating.

Figure 44

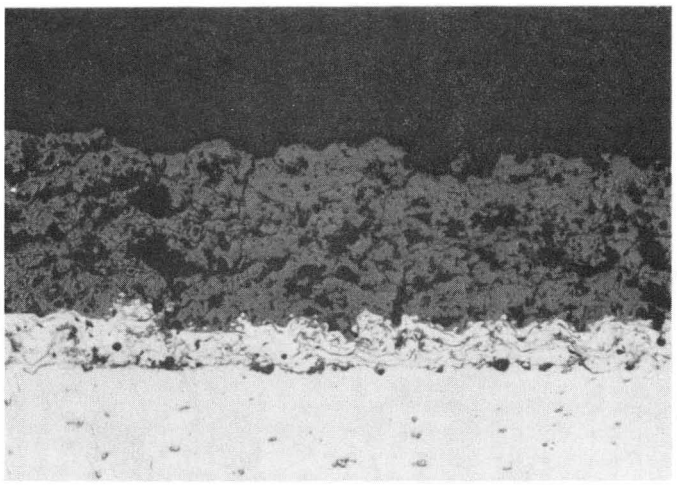
XBB 877-5703



XBB 875-4126A

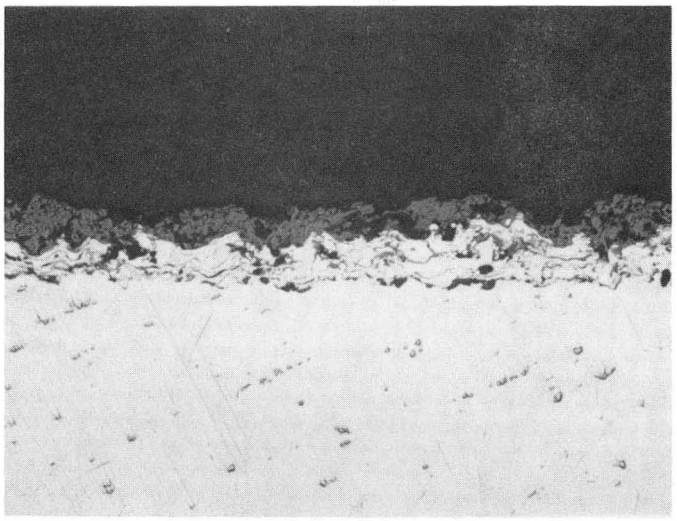
Engine tested Supplier A flame stabilized valve face coatings from cylinder 2 (left) and 3

Figure 45



(A) Valve Center

0.01"



(B) Valve Rim

8% Y_2O_3-ZrO_2

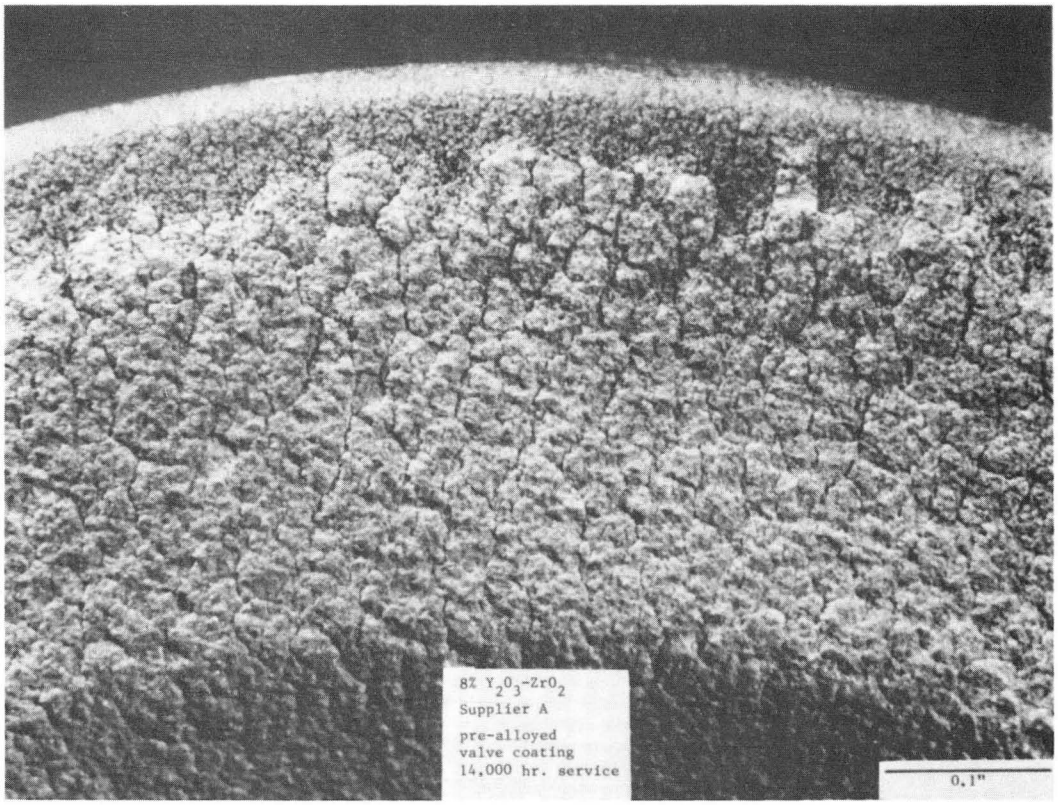
Cross sections of engine tested Supplier A flame stabilized valve face coating from Cylinder No. 2

Figure 46 XBB 877-5704

XBB 875-4128A

Engine tested Supplier A pre-alloyed valve face coating from Cylinder No. 2 (left) and No. 3

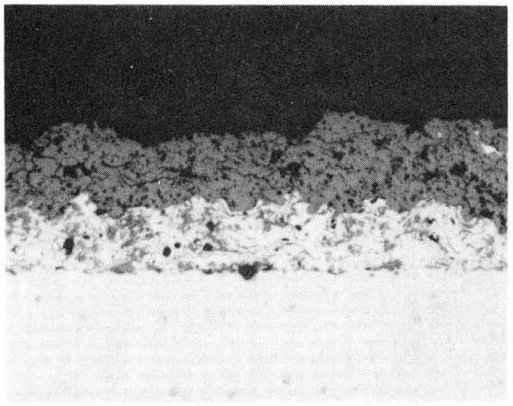
Figure 47



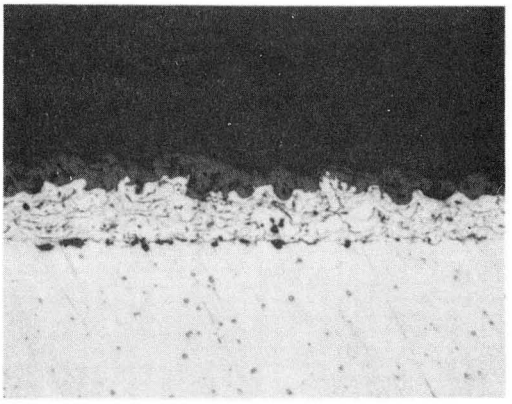
XBB 875-4123A

Macroscopic view of ZrO_2 coating segmentation

Figure 48



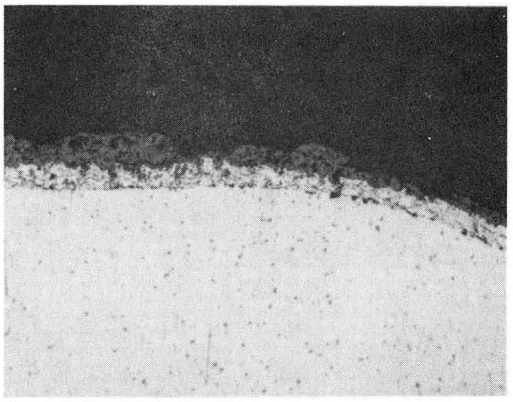
(A) 0.01"



(B) 0.01"

8% Y_2O_3-ZrO_2
Supplier A

pre-alloyed
valve coating
14,000 hr. service



(C) 0.025"

XBB 877-5705

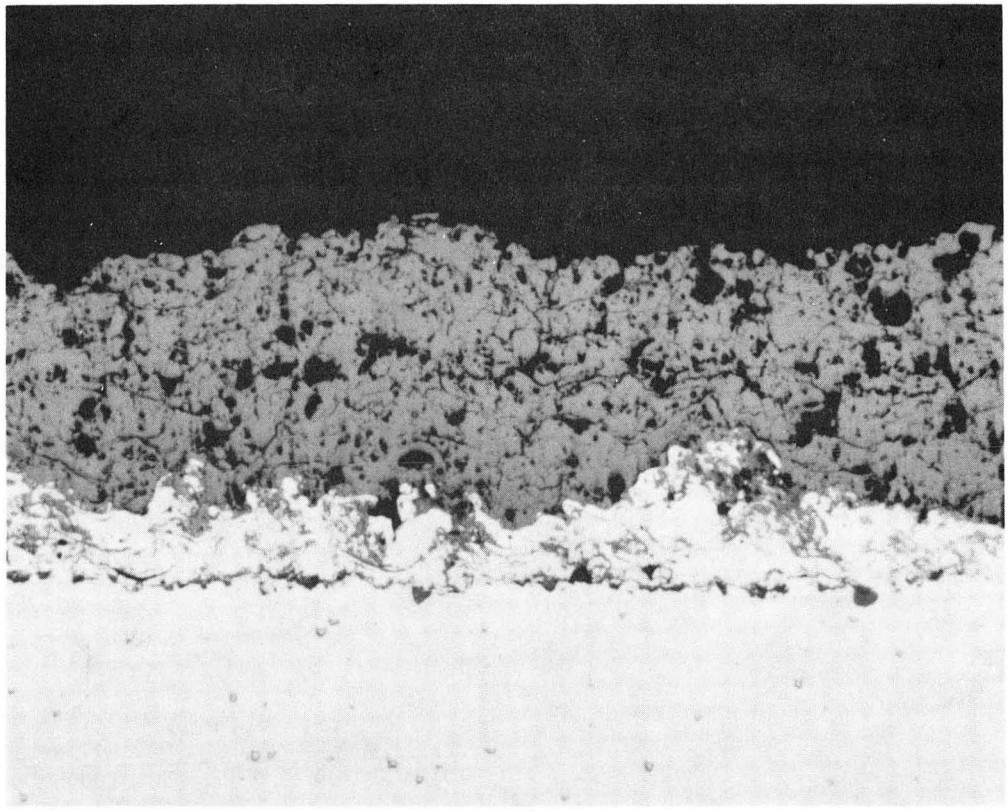
Cross section of engine tested Supplier A pre-alloyed valve face coating Cylinder No. 3 (A) coating in cup region (B) coating on rim (C) transition between cup and rim regions.

Figure 49

XBB 875-4132A

Engine tested Supplier A pre-alloyed valve stem coating (partially covered by $CaSO_4$ layer)

Figure 50

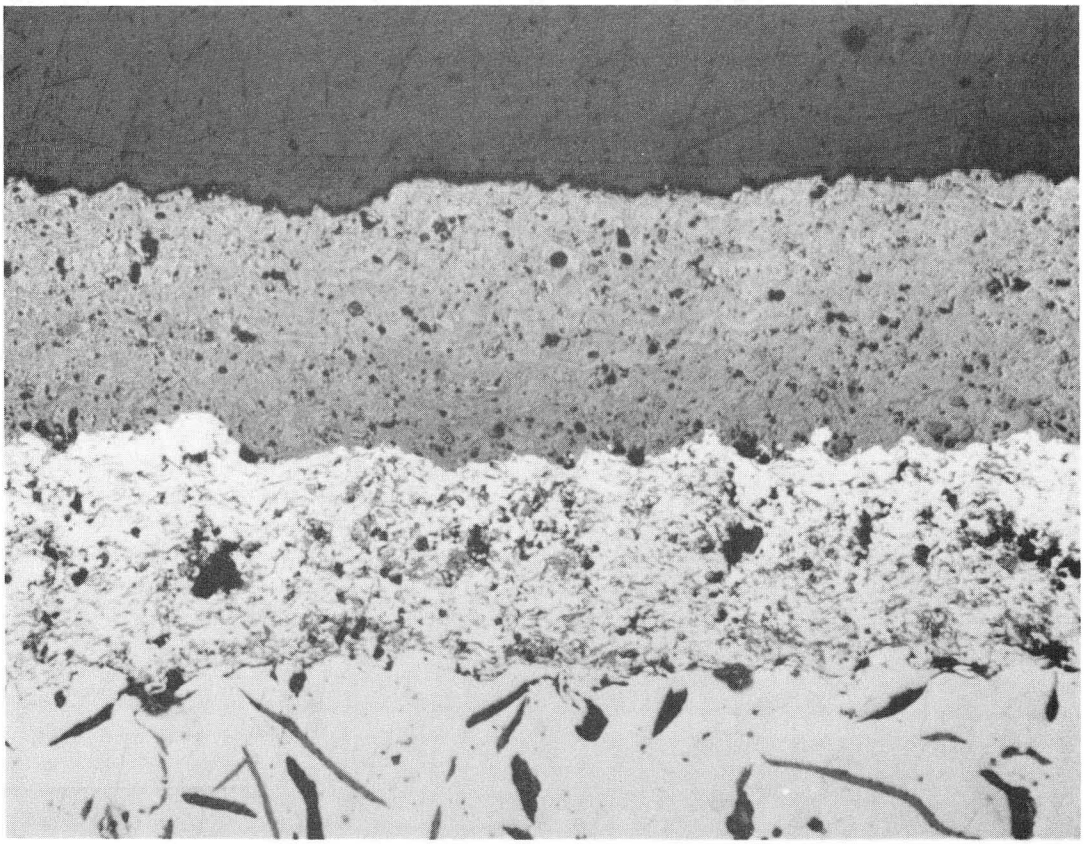


8% Y_2O_3-ZrO_2 0.01"

Cross section of engine tested Supplier A pre-alloyed valve stem coating

Figure 51

XBB 877-5706



22% $MgO-ZrO_2$ 0.01"

Cross section of engine test Supplier B piston coating

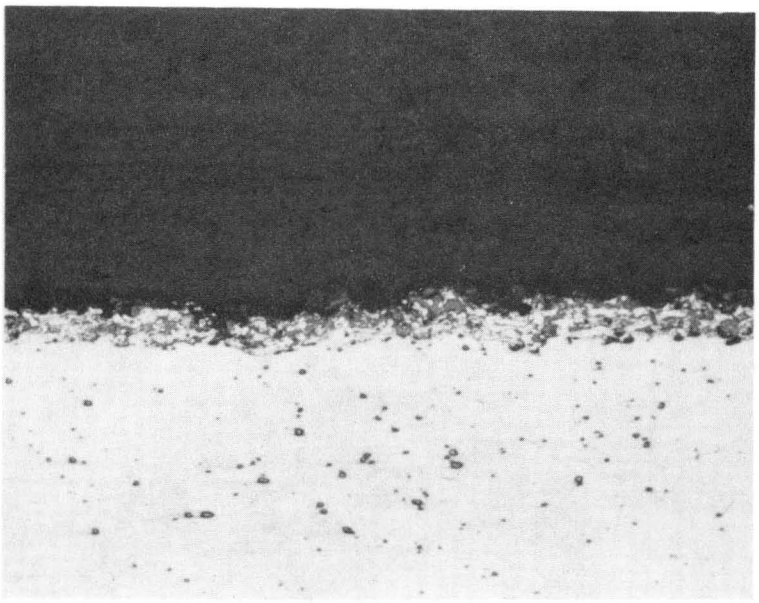
Figure 52

XBB 877-5707

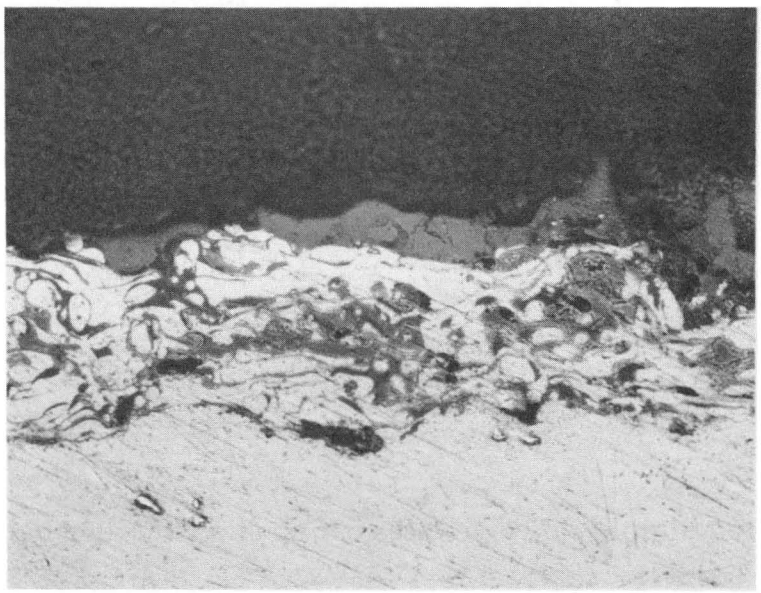
XBB 875-4125A

Engine tested Supplier B valve face coating showing the absence of a ceramic layer

Figure 53



(A) 0.01"

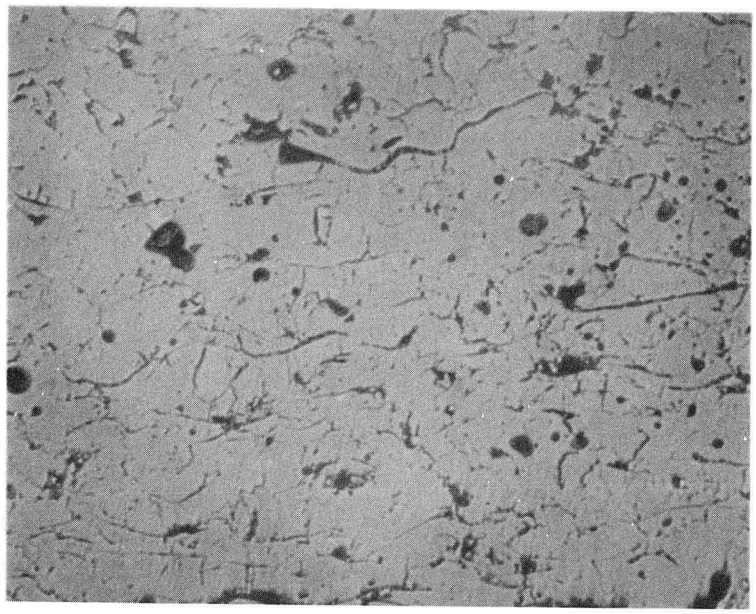


(B) 22% $MgO-ZrO_2$ 0.002"

Cross sections of engine tested Supplier B and A valve face coating

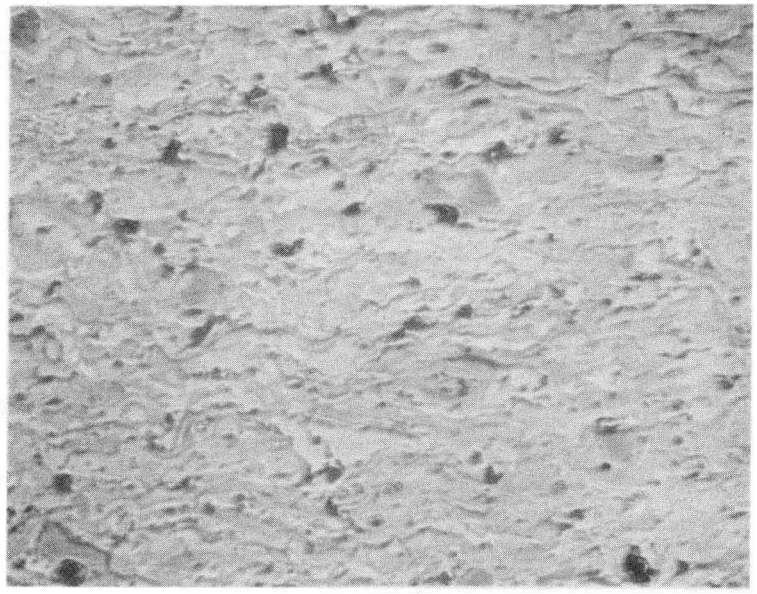
Figure 54

XBB 877-5708



(A) Supplier A 8%Y_2O_3-ZrO_2

0.0025"

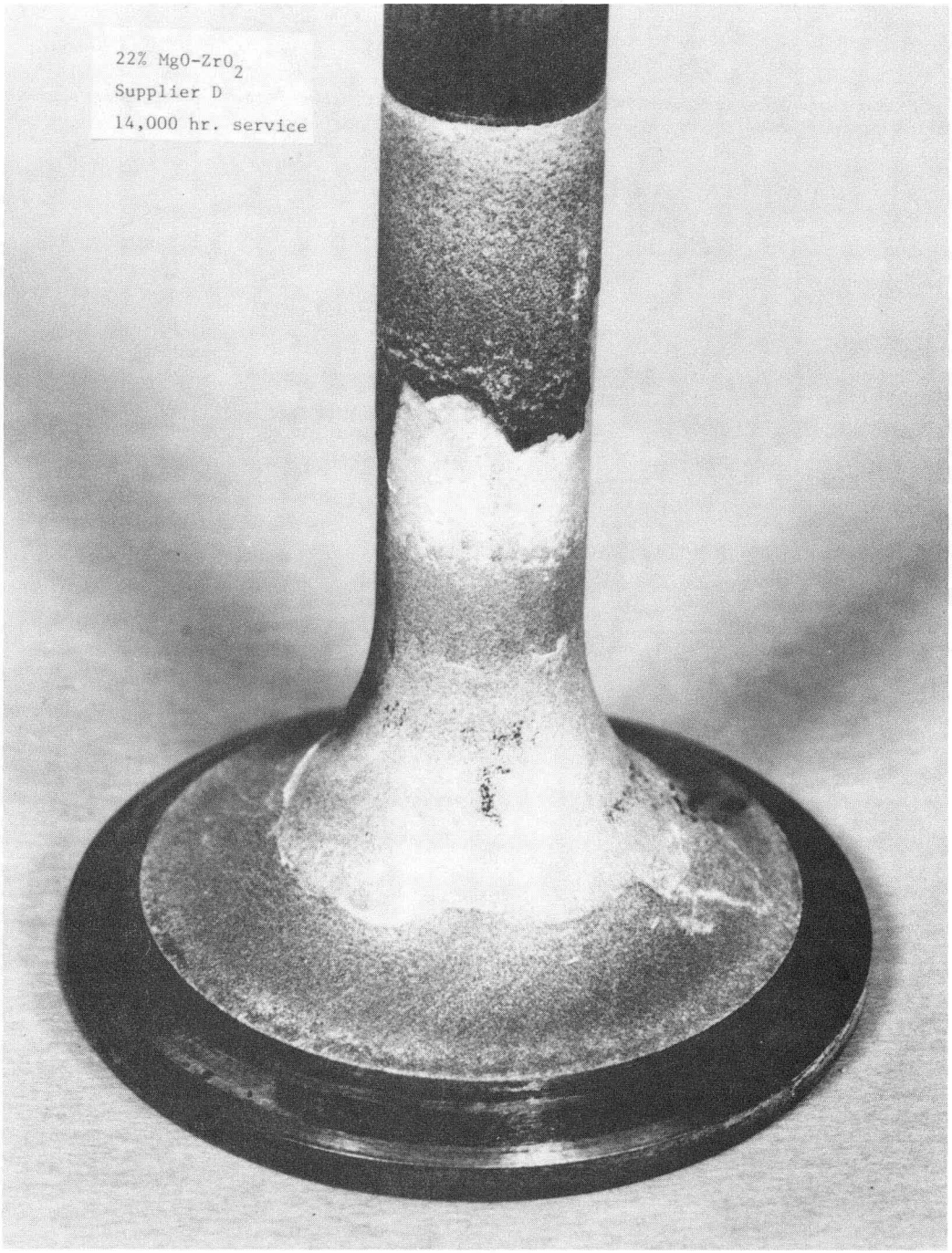


(B) Supplier B 22%MgO-ZrO_2

Cross section of the as-applied Supplier B and A zirconia layers

Figure 55

XBB 877-5709



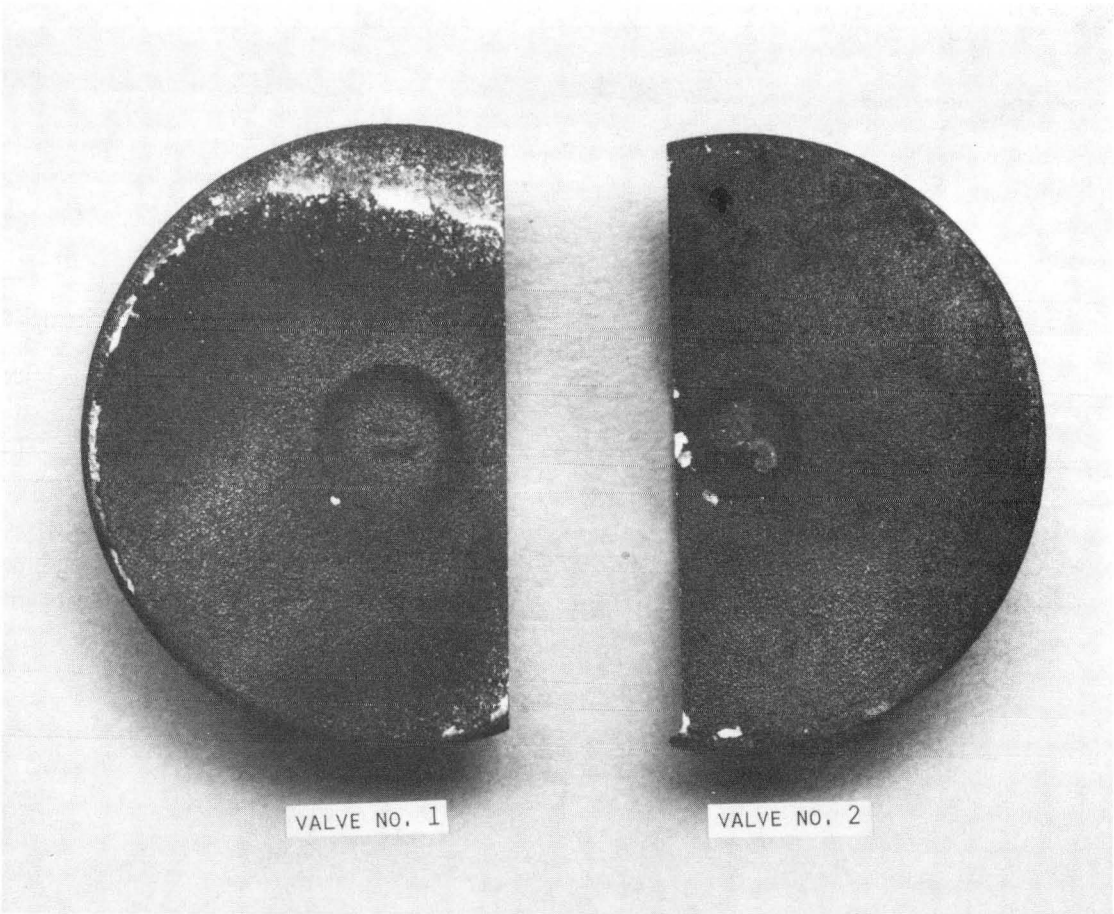
XBB 875-4131A

Engine tested Supplier B valve stem coating showing partial zirconia loss

Figure 56

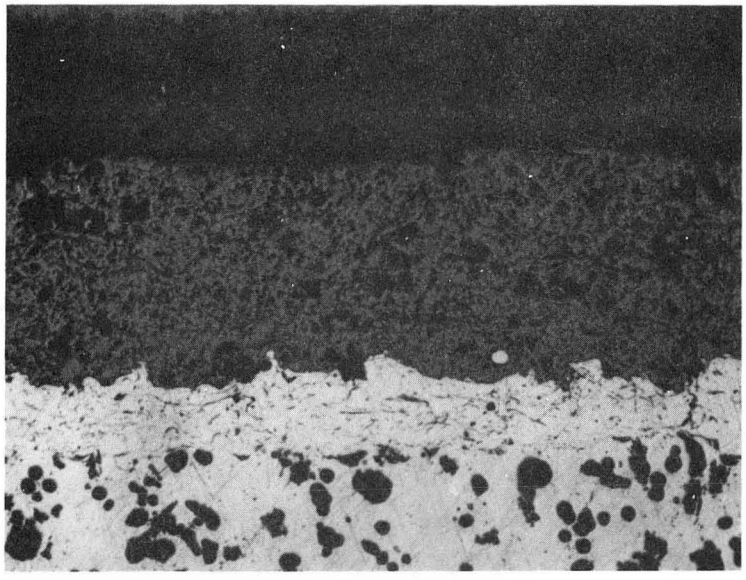
Coated piston crown after small bore diesel engine test

Figure 57



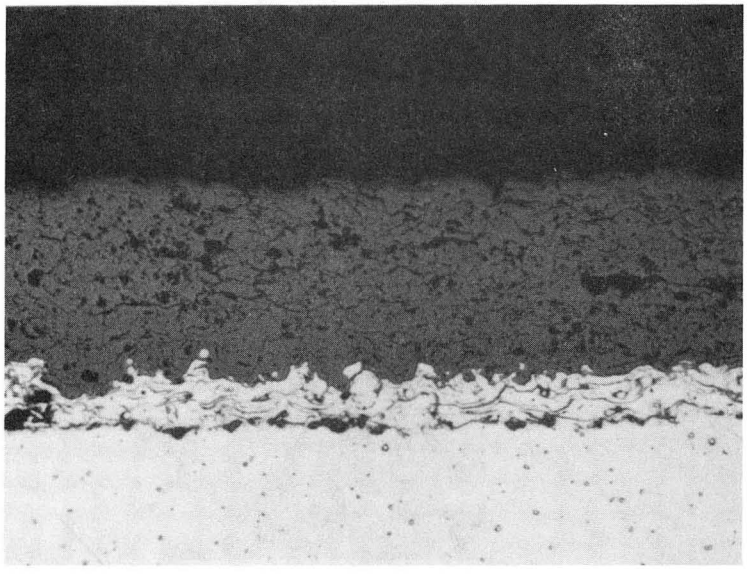
Surface of valves 1 and 2 after small bore diesel engine test

Figure 58



(A) Typical Piston Coating Cross Section

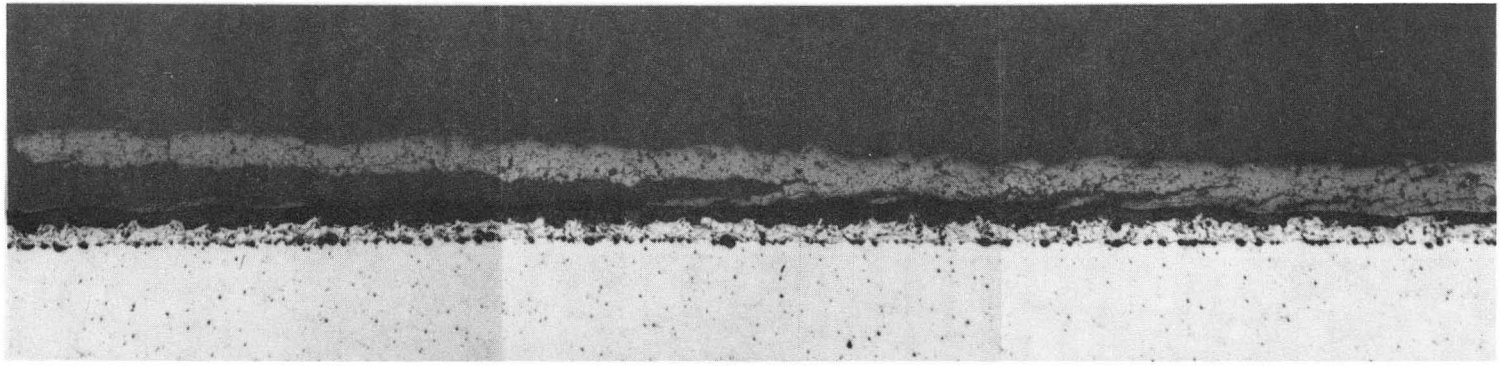
0.010"



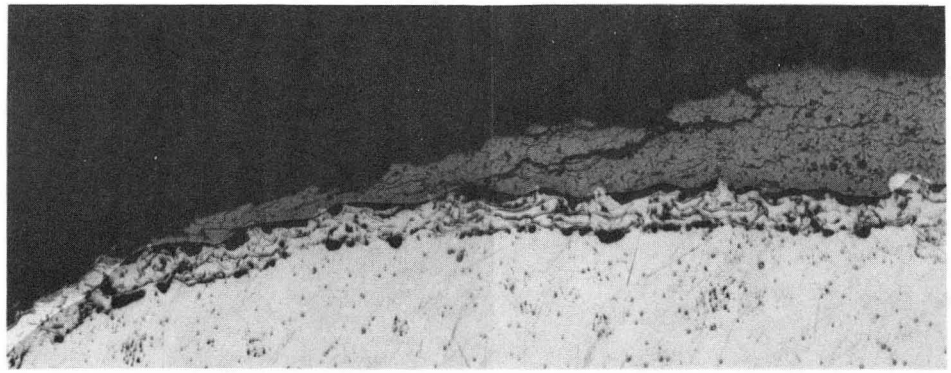
(B) Typical Valve Coating Cross Section

Cross sections of piston crown and valve face after testing

Figure 59



(A) Near Edge of Valve #1 0.020"



(B) Edge of Valve #2 0.010"

Delaminated coating area on valve faces

Figure 60

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