MASTER

Laboratory Evaluation of Ceramic Coatings for Diesel Exhaust Valves

**Eaton Corporation
Engineering & Research Center
Southfield, Michigan 48076**

November, 1980

**U.S. Department of Energy
Office of Coal Utilization
Division of Heat Engines and Heat Recovery**

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LABORATORY EVALUATION
OF CERAMIC COATINGS FOR
DIESEL EXHAUST VALVES

Final Technical Report
DOE Contract No. DE-ACO3-79ET15320

Prepared By

David H. Scharnweber
Dennis T. Vukovich
Eaton Corporation
Engineering & Research Center
26201 Northwestern Highway
Southfield, Michigan 48076

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Prepared For

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Program Manager - John Fairbanks

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ABSTRACT

Diesel engine exhaust valves coated with zirconia and calcium silicate ceramic coating systems, developed by the Central Institute for Industrial Research, Oslo, Norway, were laboratory fixture tested to assess bond strength and structural integrity under representative mechanical and thermal stress conditions. The results indicate the zirconia coating systems are worthy of additional evaluation in a medium or high speed industrial/utility diesel engine.

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INTRODUCTION

Diesel engines in the United States have been operated almost exclusively on light distillate petroleum fuel, such as No. 2 diesel fuel, or on natural gas. The hottest diesel engine component, the exhaust valve, operates at temperatures just below the threshold of aggressive hot-corrosion with these fuels. Due to a large fuel cost differential, Europeans typically operate medium- to low-speed diesel engines on residual fuels. The severity of hot-corrosion attack on European diesel exhaust valves and pistons markedly increased after the 1973 "Yom Kippur War" as the refineries extracted more of the quality fuels in their processing, resulting in poorer quality residual fuels with higher levels of hot-corrosion related impurities. The Norwegian Shipowners Association supported the Central Institute for Industrial Research in Oslo to address the problem. Their solution was a series of coatings which have increased low-speed and medium-speed diesel exhaust valve life by a factor of three in marine use operating on low grade residual fuels.

The Department of Energy (DOE) has a major role in encouraging the earliest transition to nonpetroleum or alternative fuels. Coal as a liquid or gas is a prime alternative fuel candidate based on vast coal resources in the U.S. and the efforts underway developing coal-derived fuels. Diesel engine operators' concern is for economically advantageous operation which is environmentally acceptable. Thus, the least expensive coal-derived fuels will be evaluated for diesel engine compatibility. Engine durability will be a major concern. Coal-derived liquid fuels will have a significantly hotter flame due to the lower H/C ratio compared with No. 2 diesel fuel. As a result, combustion zone components will run about 38°C (100°F) hotter, which would enhance hot-corrosion. Some of the known aggressive hot-corrosion elements are anticipated in coal-derived fuels. Also, engine intake air, particularly around coastal areas, introduces a wide range of hot-corrosion active salts. Carbonaceous particulates may introduce an erosion problem on liners, pistons, and exhaust valves. Erosion and hot-corrosion have a synergistic effect, resulting in considerably more attack than the individual effects. This hot-corrosion/erosion problem could be greatly reduced by expensive fuel upgrading. Thus, it is prudent that the DOE support the evaluation of ceramic type coatings that could enhance diesel engine durability with coal-derived fuels and encourage their early use.

This contract is part of an overall DOE effort to assess the Norwegian coating technology in order to determine its potential for diesel engine operation on residual fuels, coal-derived fuels and other candidate alternative fuels.

OBJECTIVE

The objectives are to evaluate the mechanical integrity and properties of ceramic coatings on diesel engine exhaust valves under laboratory conditions. Specific evaluation includes assessing coating integrity under seat/face impacts, valve head flexure and thermal gradients representative of the medium- to high-speed industrial/utility diesel engine valve environment. The coatings evaluated were developed by the Central Institute for Industrial Research and supplied under a cooperative DOE agreement with that activity.

CONCLUSIONS

The zirconia coatings demonstrated sufficient resistance to seat face wear, head flexural fatigue, and thermal cycle shock to justify additional coating integrity evaluation testing in a firing engine. The major area of continued concern is coating seat face wear and the insulation effect of the zirconia seat face coating on valve temperatures.

The calcium silicate coating did not demonstrate sufficient performance to warrant future engine testing. The calcium silicate coating repeatedly failed in thermal cycle shock testing. Calcium silicate coating on the fillet area demonstrated good resistance to head flexural fatigue. The calcium silicate seat face coating wear test results were inconclusive due to insufficient coating thickness.

RECOMMENDATIONS

It is recommended that exhaust valves plasma sprayed with zirconia coating systems be tested in a high-speed, heavy-duty diesel engine. Testing should involve engine operation with standard distillate fuel, residual fuel grades, and appropriate alternative fuels. The issue of coating integrity on the seat face and its effect on heat flux should be of major importance.

DISCUSSION

The three test fixtures utilized for this program, seat face wear, structural fatigue, and thermal cycle, were designed to separate the three stress environments to facilitate independent evaluation of each. It was felt that valve coatings could be more effectively screened because if a coating was rated a failure at this level of test evaluation, the probability of failure in an operating engine environment would be high because of the synergistic effect of stress input and material response.

The number of introduced variables in coating composition, thickness, and area coverage versus the number of test valves precluded any seat face wear or structural fatigue wear tests of zirconia coatings with each of the three different stabilizers: yttria, magnesia, and calcia. Fortunately, it was possible to test zirconia coatings with the three different stabilizers in the thermal cycle test; accordingly, the results did not detect a performance difference between the three stabilizers. It would be expected that the primary significance of the stabilizers could best be tested on a corrosion oriented test fixture or in actual engine testing. The two different zirconia coating thicknesses did not produce any differentiating effect in any of the fixture tests.

The seat face wear tests were run at room temperature and evaluate mechanical impact strength and the wear resistance of the coatings. The applied thickness of the calcium silicate coatings were insufficient to allow proper machining preparation of the seat face. For seat face wear and structural fatigue fixture testing, it was decided to test valves that had a partial remaining calcium silicate coating, in an attempt to gain some insight into the coating's performance. The fact that some of the calcium silicate coating left on the seat face after machining remained on the seat face after testing suggests that this coating may have some wear resistance potential.

The structural fatigue test fixture was operated at room temperature to singularly evaluate fatigue of the fillet and head top coatings and assess seat face scrubbing wear that result from head flexure. The number of coating variables also resulted in a somewhat different procedural approach to the structural fatigue test, because in most cases only one valve was available for a given coating type, thickness, and area coverage. Therefore, the maximum load was increased in incremental steps in an attempt to search for a coating failure threshold without inducing structural failure of the valve. It is, of course, more desirable to run a greater number of samples to establish a stress/cycles-to-failure characteristic. However, because no coating failures were encountered, the structural fatigue test results indicate good adherence strength of the zirconia and calcium silicate coatings to the valve head top surface and fillet areas during head flexural strain. The resultant seat face scrubbing wear resistance for the zirconia coatings was acceptable. The previously mentioned

insufficient applied coating thickness of calcium silicate precluded any conclusive evaluation of seat face scrubbing wear.

Of the three subject test fixtures, the thermal cycle test fixture has the least correlation to actual engine conditions. However, it is very effective for relative comparisons. The superior performance of the zirconia coatings over calcium silicate in the Thermal Cycle Shock test is significant. It should be noted that in order to ensure a significant coating thickness for thermal cycle testing, the seat face of the calcium silicate coated valves were not machined. This fact should not affect the results since the valve is not seated during this test.

The significance of the several valves tested with Stellite F coatings is not emphasized, because it is not a ceramic and it is a known reliable seat face overlay material. However, it should be noted that the plasma sprayed Stellite F coatings received from NCIIR were more porous than the Stellite facing found on current Eaton production valves.

Any further evaluation of ceramic coatings for exhaust valves, especially zirconia, should further address seat face wear resistance and the coating's thermal insulation effect on overall valve temperatures. The issue of whether or not to coat the seat face would depend on the particular residual fueled engine environment in question. If ceramic coating on the valve seat face results in unacceptable valve temperatures due to reduced heat flux through the valve seating interface, internal valve cooling techniques could solve the problem. However, it should then be considered whether an effective internal valve cooling and/or insert seat cooling approach might preclude the need for corrosion resistant coatings. Seat abrasion and deposit control, of course, would still need to be addressed.

**PREPARATORY EFFORTS
PRIOR TO
COATING APPLICATION**

1. PREPARATORY EFFORTS PRIOR TO COATING APPLICATION

1.1 Valve Nomenclature

There is no industry-wide standard for engine poppet valve nomenclature. The nomenclature presented in Figure 1-1 was used for this contract.

1.2 Test Valve Identification

The contract effort involved two current production poppet type exhaust valves and are referred to as valve type A and valve type B. The valve material designators are per SAE J775a specifications.

1.2.1 Valve Type A

This valve is the P/N 5100437 exhaust valve for the Detroit Diesel Allison Series 92 two-stroke cycle diesel engine. The valve has a two-piece welded construction. The valve head material is SAE HEV-3 nickel based super alloy and the valve stem is SAE HNV-3 Silchrome 1 martensitic steel. The valve seat face has a 0.5 mm (0.02 in.) minimum thickness facing of SAE VF-2 Stellite 6 cobalt based chromium tungsten alloy overlay. The descriptive valve dimensions are illustrated in Figure 1-2.

1.2.2 Valve Type B

This valve is the P/N 145701 exhaust valve for the Cummins NH/NT series four-stroke cycle diesel engine. This valve is also a two-piece welded construction. The valve head material is SAE EV-4 chrome-nickel austenitic alloy steel and the valve stem is SAE NV-5 medium carbon alloy steel. The valve seat face has a 0.9 mm (0.035 in.) minimum thickness facing of SAE VF-2 (with the exception of 6.0% max iron) Stellite 6 overlay alloy. The descriptive valve dimensions are presented in Figure 1-3.

1.3 Valve Coating Envelope Definition

It was decided not to thin the valves to compensate for coating thickness. This decision was based on the following: the maximum nominal coating thickness would only be 0.5 mm (0.020 in.) and the test fixtures could readily accept the additional thickness; the engine configurations could be readily adapted to accommodate the coating, and it was desired to give the tested ceramic coating the maximum structural support possible.

1.4 Valve Material/Coating Compatibility

The valve materials were reviewed with the NCIIR coating source and it was determined that material compatibility was not a problem.

1.5 Valve Seat Insert Determination

With the concurrence of NCIIR, it was decided that respective production valve seat inserts would be used and that no ceramic coating would be applied to the insert seats. The standard production valve seat inserts for both valve types A and B are made from SAE VF-3 material with a hardness of R_C 35-48 and R_C 45-55 respectively.

1.6 Machine Load Socket For Fatigue Test

For the structural load valve fatigue test, a spherical socket is machined in the valve head to accept the load application ball. The socket dimensions for valve types A and B are presented in Figure No. 1-4. There was some concern whether to machine the sockets before or after coating application. It was decided to machine sockets in two of each valve type prior to coating. The remaining one of each valve type would be machined after coating. This procedure would allow a comparison on this issue. It was subsequently found that machining the socket before or after coating application had no affect on the results.

1.7 Thermocouple Installation Method

In typical valve thermocouple installations, a slot is machined down the outside of the valve stem in which the wires are routed to drilled location holes in the valve head. The stem slot is then filled with a high temperature epoxy sealer. At the time the valves had to be sent to NCIIR, no information regarding how far the coating would extend up the valve fillet had been received. It was decided not to risk machining thermocouple location holes through the ceramic coating; therefore, it was decided to install the thermocouple probe in holes electron discharge machined (EDM) down the center of the valve stem. The hole depth was controlled from the valve head top surface. The thermocouple installation hole configuration for valve types A and B are shown in figure 1-5. Chromel-alumel thermocouples with an exposed junction and inconel sheath were used. The thermocouple junction was held in contact with the hole bottom surface by means of retention collar located at the top of the valve stem.

1.8 Analytical Temperature Estimate

A computer finite element temperature prediction analysis was conducted on each valve type to assist the selection of maximum valve temperatures for the thermal cycle test. These analyses consisted of utilizing existing Eaton valve finite element models with a new layer of elements added to represent the ceramic coating. The revised element mesh for valve types A and B are shown in Figures 1-6 and 1-7. For both models, a coating thickness of 0.2 mm was used on the seat face and 0.5 mm on the head top, margin, and fillet.

At the time these temperature analyses were conducted, NCIIR was in the process of re-evaluating their coating thermal conductivity values. Therefore, the calculations were run with two selected zirconia thermal conductivity (k) values of 4.2 and 0.42 W/mK. The 4.2 W/mK value was found in a previous published report by NCIIR (Ref. 1.10.1). The 0.42 W/mK value is a lower limit value used in previous work at Eaton. At the time of these temperature analyses, Eaton was not aware that a calcium silicate coating would be introduced.

The valve environmental parameters, gas temperature, film heat transfer coefficient, etc., were selected from the engine of each respective valve type. For valves without internal cooling, the maximum temperature occurs at the center of the valve head at or near the valve top surface. Therefore, the temperature of interest was at the node nearest the thermocouple contact point located at the 1.5 mm reference position defined in Section 1.7. This thermocouple location is the closest practical to the valve maximum temperature point.

1.8.1 Valve Type A Computer Analysis Results

	<u>Temperature at 1.5 mm Reference Location</u>
No Coating	860 K (1089°F)
Zirconia Coating, k = 4.2 W/mK	863 K (1096°F)
Zirconia Coating, k = 0.42 W/mK	870 K (1107°F)

1.8.2 Valve Type B Computer Analysis Results

	<u>Temperature at 1.5 mm Reference Location</u>
No Coating	873 K (1114°F)
Zirconia Coating, k = 4.2 W/mK	876 K (1118°F)
Zirconia Coating, k = 0.42 W/mK	878 K (1121°F)

The reference location temperature increased slightly with decreasing thermal conductivity of the coating due to the insulation effect of the zirconia coating on the valve seat face. In a typical exhaust valve environment, the vast majority of the heat flux into the valve head from the combustion chamber is transferred out of the valve through the valve seat face/insert seat interface when the valve is seated.

1.9 Valve Coating Source

Twenty-four (24) valves of types A and B were procured. Eleven (11) valves of each type were EDM machined for thermocouple installation. Twenty (20) of each valve type, of which ten had thermocouple holes and two had spherical sockets, were sent for ceramic coating application to:

Norwegian Central Institute
for Industrial Research (NCIIR)
c/o Dr. Ingard Kvernes
Forskningssv 1
P.B. 350 Blindern
Oslo 3, Norway

Coating composition, thickness, and valve areas to be coated were decided by NCIIR. NCIIR's efforts were carried out under terms of a separate contract with the U.S. Department of Energy. (Contract No. DE-AC03-79ET15324).

1.10 References

- 1.10.1 Ingard Kvernes and Karl Petter Lillerud, Ceramic Coatings on Diesel Engine Components, Norwegian Central Institute for Industrial Research, Oslo, Norway. Final Report to U.S. Department of Energy under Contract No. ET-78-X-01-4288, December 7, 1979, page 4.

Figure 1-1
VALVE NOMENCLATURE

Figure 1-2

DESCRIPTIVE VALVE DIMENSIONS

VALVE TYPE A

Figure 1-3

DESCRIPTIVE VALVE DIMENSIONS

VALVE TYPE B

VALVE TYPE	SPHERICAL RADIUS mm	CENTER DEPTH mm
A	6.4	2.1
B	9.6	3.2

Figure 1-4

SPHERICAL SOCKET MACHINED IN VALVE HEAD
FOR FATIGUE TEST LOAD APPLICATION BALL

Figure 1-5
THERMOCOUPLE INSTALLATION HOLE

Figure 1-6
FINITE ELEMENT MESH-VALVE TYPE A
COATING INDICATED BY SHADED ELEMENTS

Figure 1-7

FINITE ELEMENT MESH-VALVE TYPE B
COATING INDICATED BY SHADED ELEMENTS

PREPARATORY EFFORTS

PRIOR TO VALVE TESTING

2. PREPARATORY EFFORTS PRIOR TO VALVE TESTING

2.1 Coated Valve Identification

Twenty coated valves of each type A and B (40 total valves) were received from NCIIR in two separate shipments. The valve lot consisted of five different top coating specifications, two top coating thicknesses, and two different degrees of area coverage. The bond coating specification remained constant. This was more variables than Eaton was anticipating; therefore, the effectiveness of the test plan was somewhat compromised. The as-received valve serialization indicating the coatings, thickness, and valve areas covered is presented in Figure 2-1.

2.2 Valve Seat Face Machining

Except for valve B-1 which was left with as-received machining, the seat faces were machined to a total indicated runout of 0.038 mm (0.0015 in.) or less and a surface finish of 0.76-1.0 μ m (30 to 40 in.) R_a . Grinding was done with a Norton 39C60-H-8VK, Crystolon grinding wheel without coolant. The calcium silicate coated valves had insufficient coating thickness for proper seat face preparation. Therefore, the calcium silicate coated valves scheduled for thermal cycle testing did not have the seat faces machined so as to retain maximum coating thickness.

2.3 Coated Valve Dimensional Inspection

The coated valves were dimensionally inspected for seat face angle, seat face runout, seat face surface finish, margin thickness and diameter, concentricity, straightness, and roundness of the stem and head. Except for the dimensions obviously affected by the coating thickness, the plasma coating application process did not produce any dimensional warpage.

2.4 Test Fixture Description and Adaptation

The following three valve test fixtures were adapted to accommodate this test program.

2.4.1 Valve Seat Face Wear Test Fixture

The valve Seat Face Wear Test Fixture is comprised of a rigid structure which provides mounting surfaces for the valve seat insert and loading actuator. Photographs of the Seat Face Wear Test Fixture are shown in Figure 2-2. The insert seat was distorted or the seat width narrowed to increase contact stress and accelerate wear rates.

The valve is actuated by a servo-controlled electrohydraulic actuator with LVDT type displacement and strain gage type load feedback systems. The test valve is cyclically lifted and seated on the insert seat in a sawtooth waveform with controlled maximum seating force, seating velocity, displacement, and cycling frequency. The test is conducted at room temperature.

2.4.2 Valve Structural Fatigue Test Fixture

The Structural Fatigue Test Fixture is a closed-loop electrohydraulic system which provides sinusoidal cyclical compressive load application on the head of a continuously seated valve. Photographs of the Structural Fatigue Test Fixture are shown in Figure 2-3. The fixture utilizes LVDT type displacement and strain gage type load feedback systems for test control. The load is applied through a 12.7 mm (0.50 in.) (valve type A) or 19.0 mm (0.75 in.) (valve type B) diameter steel ball and spherical socket machined in the valve head. The test parameters are minimum load, maximum load, and cycle frequency. This test produces head flexure to evaluate fatigue and seat face scrubbing wear. The test is intended to represent the gas pressure loading on the valve head from the engine combustion process.

2.4.3 Valve Thermal Cycle Test Fixture

The Thermal Cycle Test Fixture automatically cycles the valve between a natural gas burner heat source and a compressed air jet cooling source to produce a desired temperature gradient. Photographs of the Thermal Cycle Test Fixture are shown in Figure 2-4. The test parameters are minimum and maximum temperatures and cycle time. The thermocouple used for test temperature control is located in the valve head as described in Section 1.7 and Figure 1-5.

VALVE SERIAL NUMBER	S/S	T/C	COATING TYPE - AREA COVERED - THICKNESS*	
			HEAD TOP & MARGIN	SEAT FACE & FILLET
A-1,B-1			ZrO ₂ + 25% MgO (0.4 mm)	ZrO ₂ + 25% MgO (0.4 mm)
A-2,B-2			ZrO ₂ + 25% MgO (0.4 mm)	ZrO ₂ + 25% MgO (0.4 mm)
A-3,B-3			ZrO ₂ + 25% MgO (0.4 mm)	Not Coated
A-4,B-4			ZrO ₂ + 25% MgO (0.4 mm)	Not Coated
A-5,B-5	X		ZrO ₂ + 25% MgO (0.4 mm)	Not Coated
A-9,B-9			ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)	ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)
A-14,B-14		X	ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)	ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)
A-15,B-15		X	ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)	Not Coated
A-16,B-16		X	ZrO ₂ + 20% Y ₂ O ₃ (0.4 mm)	Not Coated
A-17,B-17		X	ZrO ₂ + 5% CaO (0.4 mm)	Not Coated
A-6,B-6			ZrO ₂ + 25% MgO (0.4 mm)	Stellite F
A-7,B-7			ZrO ₂ + 25% MgO (0.2 mm)	ZrO ₂ + 25% MgO (0.2 mm)
A-8,B-8			ZrO ₂ + 25% MgO (0.2 mm)	Stellite F
A-10,B-10	X		ZrO ₂ + 25% MgO (0.2 mm)	CaSiO ₃ (Thick. Not Given)
A-18,B-18		X	ZrO ₂ + 25% MgO (0.2 mm)	CaSiO ₃ (Thick. Not Given)
A-19,B-19		X	ZrO ₂ + 25% MgO (0.4 mm)	CaSiO ₃ (Thick. Not Given)
A-20,B-20		X	ZrO ₂ + 25% MgO (0.2 mm)	CaSiO ₃ (Thick. Not Given)
A-21,B-21		X	ZrO ₂ + 5% CaO (0.4 mm)	CaSiO ₃ (Thick. Not Given)
A-22,B-22		X	ZrO ₂ + 5% CaO (0.2 mm)	CaSiO ₃ (Thick. Not Given)
A-23,B-23		X	ZrO ₂ + 5% CaO (0.2 mm)	CaSiO ₃ (Thick. Not Given)

S/S - Spherical head socket for Fatigue Test

T/C - Thermocouple installation hole

* - Nominal coating thickness values given by NCIIR

Except for the Stellite F coatings, all coatings had a 0.1 mm nominal thickness bond coat of Ni-20% Cr-6% Al-0.1% Y.

Figure 2-1
Valve Coating System Identification
As-Received Coated Valves From NCIIR

Fig. 2-2 Valve Seat Face Wear Test Fixture

Fig. 2-3 Valve Structural Fatigue Test Fixture

Fig. 2-4 Valve Thermal Cycle Test Fixture

VALVE TEST PROGRAM

3. VALVE TEST PROGRAM

3.1 Valve Test Procedure & Conditions

3.1.1 Seat Face Wear Test

The test valve is cyclically lifted off and seated on an insert seat that has excessive runout or a narrowed seat width to increase contact stress. The seat runout and width are recorded with each valve in the subsequent Test Results section. A sawtooth wave form was used to control valve motion. The face wear tests were run at room temperature with a 3560 N (800 lb.) maximum seating force, 0.76 mm (0.030 in.) displacement, 15 Hz frequency, and a 120 mm/sec (4.7 in/sec) valve seating velocity. The valve does not rotate during this test. The test term target for this test is six million total cycles. The valves were visually inspected at one-half million cycle intervals for the first two million cycles and at one million cycle intervals thereafter.

3.1.2 Structural Fatigue Test

The continuously seated valve is cyclically loaded at a frequency of 20 Hz on a sinusoidal waveform between a 111 N (25 lbs.) minimum load and a selected maximum load. The maximum loads used were a multiple of a reference load defined by the product of maximum combustion pressure times valve head area. This reference load is 12,000 N (2700 lbs.) for valve type A and 22,200 N (5000 lbs.) for valve type B. The seat inserts for the A type valves had a 1.98 mm (0.078 in.) seat width and 0.038 mm (0.0015 in.) seat runout. The seat inserts for the B type valves had a 1.88 mm (0.074 in.) seat width and 0.038 mm (0.0015 in.) runout. These seat width and runout values are within production limits for each respective valve. Because of the more than expected number of coating compositions, thicknesses, and area coverage variables introduced by the coating source versus the limited number of test valves, a complete fatigue matrix test was not possible. Therefore, running variations were made in an attempt to locate failure thresholds in most cases with only one sample. The maximum term for the test was six million cycles. The valves were visually inspected at one-half million cycle intervals.

3.1.3 Thermal Cycle Test

Based on the results of the Section 1.8 Analytical Temperature Analysis and previous Eaton analytical and thermocouple test data, the Thermal Cycle Base Test parameters were set at, 477 K (400°F) minimum temperature, 893 K (1150°F) maximum temperature, and a cycle time of five (5) minutes. For a more severe Thermal Cycle Shock Test, the cycle parameters were 477 K (400°F), 978 K (1300°F) and 2.5 minutes. Therefore, the Thermal Cycle Shock Test thermal gradients were approximately twice as severe as the first level. The tests were run on a temperature control basis and the cycle temperature/time profile was triangular with equal heating and cooling gradients. Some difficulty was encountered in maintaining the 2.5 minute Thermal Shock cycle time with the B type valves. To assess an even higher maximum temperature, one B type valve was tested with a minimum and maximum temperature of 477 K (400°F) and 1088 K (1500°F) and a cycle time of 6.5 minutes which was the lowest attainable time.

3.2 Valve Test Results

3.2.1 Seat Face Wear Test Results

The following eight valves were tested per procedures and conditions outlined in section 3.1.1, except for Valve A-2 which was tested on a special heated fixture. The insert seat width and total indicated runout (TIR) are listed for each test. For reference, the new production seat width for valve types A and B are 1.98 mm and 1.59-3.18 mm, respectively. The maximum production runout for both A and B type valves is 0.051 mm.

Table 3-1

Valve No.	Coating Type On Seat Face	<u>Insert Seat</u>		Total Test Cycles	Photograph Figure No.
		<u>Width</u> mm	<u>TIR</u> mm		
A-12	Not Coated	1.98	0.178	6 x 10 ⁶	3-1
A-1	ZrO ₂ + MgO	1.98	0.178	9.5 x 10 ⁶	3-2
A-2	ZrO ₂ + MgO	1.98	0.025	2 x 10 ⁶	3-3, 4-27
A-19	CaSiO ₃	1.98	0.178	6 x 10 ⁶	3-4, 4-7
B-24	Not Coated	1.04	0.203	6 x 10 ⁶	3-5
B-2	ZrO ₂ + MgO	1.04	0.203	6 x 10 ⁶	3-6, 4-23D
B-7	ZrO ₂ + MgO	1.85	0.038	6 x 10 ⁶	3-7
B-21	CaSiO ₃	1.85	0.038	4 x 10 ⁶	3-8

Results

- Valve A-12: For these test conditions, no abnormal seat face wear characteristics were encountered. See photograph in Figure 3-1.
- Valve A-1: The magnesia stabilized zirconia coating remained intact. See photograph in Figure 3-2.
- Valve A-2: Because of the success of the room temperature tests, it was decided to test this magnesia stabilized zirconia coated valve on a heated wear test fixture located at the Eaton Engine Components Division in Battle Creek, Michigan. This test, which is mechanically similar to the room temperature test, was run with a 644-699 K (700-800 degrees F) seat insert reference temperature, which for an uncoated valve represents a maximum metal temperature of 921 K (1,200 degrees F). Inspection after completion of the prescribed two million cycles revealed that the zirconia coating had been completely worn off the seat face and severe zirconia spalling occurred on the margin. See photographs in Figures 3-3 and 4-27. The significance of this test result is inconclusive due to a valve/fixture lateral misalignment problem that occurred during the test.
- Valve A-19: During machining, approximately one-half of the bond coat was exposed over the seat face area because the applied calcium silicate coating thickness was insufficient to allow proper seat face preparation. Some of the calcium silicate still on the seat face remained on after the test. See photograph in Figure 3-4 and seat face SEM surface examination in Figure 4-7.
- Valve B-24: For these test conditions, no abnormal seat face wear characteristics were encountered. See photograph in Figure 3-5.
- Valve B-2: The seat width was narrowed to increase contact stress. At first, the resulting wear groove was thought to be a failure; however, subsequent analysis revealed that the magnesia stabilized zirconia coating was still present in the wear groove. See photographs in Figures 3-6 and 4-23D.

Valve B-7: Because the results of valve B-2 were first thought to be a failure, the seat width and TIR for this test were set within production limits to establish a threshold. The magnesia stabilized zirconia coating remained intact without distress. See photograph in Figure 3-7.

Valve B-21: The test was terminated due to loss of all calcium silicate coating on the seat face. A major portion of the seat face calcium silicate coating was lost during preparation grinding because the applied coating thickness was insufficient. The remaining calcium silicate wore off. See photograph in Figure 3-8.

3.2.2 Structural Fatigue Test Results

The eight valves listed on the following page were tested per procedures and conditions outlined in Section 3.1.2. Additional valve to valve test condition variations are also noted with each respective valve.

Table 3-2
Structural Fatigue Test Results

Valve No.	Coating Type		Maximum Load N	Total Test Cycles	Photograph Figure No.
	Head Top & Margin	Seat Face & Fillet			
A-9	ZrO ₂ + Y ₂ O ₃	Not Coated	13,300	3 x 10 ⁶	3-9, 4-11
			17,800	2 x 10 ⁶	
			22,200	1 x 10 ⁶	
			26,700	361,800 6.4 x 10 ⁶	
A-10	ZrO ₂ + MgO	CaSiO ₃	13,300	1.4 x 10 ⁶	3-10
A-7	ZrO ₂ + MgO	ZrO ₂ + MgO	13,300	3 x 10 ⁶	3-11, 4-8
			17,800	3 x 10 ⁶ 6 x 10 ⁶	
A-8	ZrO ₂ + MgO	Stellite F	13,300	3 x 10 ⁶	3-12
			17,800	3 x 10 ⁶ 6 x 10 ⁶	
B-9	ZrO ₂ + Y ₂ O ₃	Not Coated	22,200	3 x 10 ⁶	3-13
			35,600	1.7 x 10 ⁶ 4.7 x 10 ⁶	
B-1	ZrO ₂ + MgO	ZrO ₂ + MgO	13,300	2 x 10 ⁶	3-14
			22,200	4 x 10 ⁶ 6 x 10 ⁶	
B-10	ZrO ₂ + MgO	CaSiO ₃	22,200	3 x 10 ⁶	3-15, 4-13
			26,700	2 x 10 ⁶	
			31,100	1 x 10 ⁶	
				6 x 10 ⁶	
B-8	ZrO ₂ + MgO	Stellite F	22,200	3 x 10 ⁶	3-16
			26,700	3 x 10 ⁶ 6 x 10 ⁶	

Results

- Valve A-9: This baseline valve, without seat face and fillet coating, was taken in incremental maximum load steps to structural fatigue failure of the valve. A chordal crack in the valve head resulted in the head top yttria stabilized zirconia coating breaking away in one major piece with the separation occurring at the zirconia coating/bond coating interface. See photographs in Figures 3-9 and 4-11.
- Valve A-10: A test fixture control failure resulted in a massive force overload that produced structural failure of the valve after 1.4×10^6 cycles. The relative toughness of the calcium silicate fillet coating is noteworthy when considering the massive longitudinal strain. The magnesia stabilized zirconia coating on the head top, margin, and approximately one-half of the seat face was broken off at the zirconia/bond coat interface. See photograph in Figure 3-10.
- Valve A-7: The magnesia stabilized zirconia coating remained intact without distress. See photographs in Figure 3-11 and seat face SEM surface examination in Figure 4-8.
- Valve A-8: The magnesia stabilized zirconia head top coating remained intact without distress. As would be expected, the Stellite F seat face coating also remained intact. See photograph in Figure 3-12.
- Valve B-9: This baseline valve, without seat face and fillet coating, was taken in incremental maximum load steps to structural fatigue failure of the valve. The yttria stabilized zirconia head top coating, for the most part, remained on the valve. See photograph in Figure 3-13.
- Valve B-1: The magnesia stabilized zirconia coating remained intact without distress. The seat face finish was left as received from NCIIR. See photograph in Figure 3-14.
- Valve B-10: Proper dimensional seat face machining resulted in approximately ten percent exposure of the NiCrAlY bond coat due to insufficient applied thickness of the

calcium silicate coating which was subsequently measured to be 0.1 mm. Some of the remaining calcium silicate seat face coating stayed intact. The magnesia stabilized zirconia head top coating remained intact. See photographs in Figure 3-15 and seat face coating SEM surface characterization in Figure 4-13.

Valve B-8: The magnesia stabilized zirconia head top coating remained intact without distress. Again as expected, the Stellite F seat face coating also remained intact. See photograph in Figure 3-16.

3.2.3 Thermal Cycle Test Results

The fourteen valves listed on the following page were tested per procedures and conditions outlined in Section 3.1.3.

Table 3-3
Thermal Cycle Test Results

Valve No.	Coating Type		Maximum Cycle Temp. K	Total Test Cycles	Test Time Hours	Photograph Figure No.
	Head Top & Margin	Seat Face & Fillet				
A-24	Not Coated	Not Coated	977 S	2143	100	
A-14	ZrO ₂ + Y ₂ O ₃	ZrO ₂ + Y ₂ O ₃	894 B	1334	100	
A-14	ZrO ₂ + Y ₂ O ₃	ZrO ₂ + Y ₂ O ₃	977 S	2338	101	3-17, 4-18
A-20	ZrO ₂ + MgO	CaSiO ₃	977 S	1928	78.5	3-18, 4-21
A-21	ZrO ₂ + CaO	CaSiO ₃	977 S	1104	65.0	3-19
A-18	ZrO ₂ + MgO	CaSiO ₃	894 B	1329	101	3-20
A-23	ZrO ₂ + CaO	CaSiO ₃	894 B	1698	106	3-21
B-25	Not Coated	Not Coated	894 B	1237	101	
B-14	ZrO ₂ + Y ₂ O ₃	ZrO ₂ + Y ₂ O ₃	894 B	164	12.4	3-22
B-15	ZrO ₂ + Y ₂ O ₃	Not Coated	894 B	1242	105	3-23
B-19	ZrO ₂ + MgO	CaSiO ₃	894 B	1685	100	
B-19	ZrO ₂ + MgO	CaSiO ₃	977 S	1199	86.7	3-24
B-18	ZrO ₂ + MgO	CaSiO ₃	977 S	828	56.0	3-25
B-17	ZrO ₂ + CaO	Not Coated	1088 S	988	104	3-26, 4-20

B = Thermal Cycle Base Test

S = Thermal Cycle Shock Test

Results

- Valve A-24: For these test conditions, no abnormal valve distress was encountered.
- Valve A-14: The yttria stabilized zirconia ceramic coating remained intact without distress after 100 hours of Thermal Cycle Base testing and a subsequent 100 hours of Thermal Cycle Shock testing. See photographs in Figure 3-17 and SEM surface examination in Figure 4-18.
- Valve A-20: Thermal Cycle Shock testing was terminated after 78.5 hours due to spalling of the calcium silicate coating at the seat face/fillet interface. The magnesia stabilized zirconia coating remained intact without distress. See photographs in Figures 3-18 and 4-21.
- Valve A-21: Thermal Cycle Shock testing was terminated after 65.0 hours due to spalling of the calcium silicate coating at the seat face/fillet interface. The calcia stabilized zirconia coating remained intact without distress. See photograph in Figure 3-19.
- Valve A-18: Completed 101 hours of Thermal Cycle Base testing without any distress of the magnesia stabilized zirconia head top coating or calcium silicate seat face and fillet coating. See photograph in Figure 3-20.
- Valve A-23: Completed 106 hours of Thermal Cycle Base testing without any distress of the calcia stabilized zirconia head top coating or calcium silicate seat face coating. See photograph in Figure 3-21.
- Valve B-25: For these test conditions, no abnormal valve distress was encountered.
- Valve B-14: Thermal Cycle Base testing was terminated after 12.4 hours due to spalling of the yttria stabilized zirconia coating in the area of the valve top surface and adjacent margin. The coating fracture occurred at the zirconia coating/bond coating interface. Subsequent analysis indicated that porosity at the zirconia/bond coat interface contributed to this early failure. See photographs in Figures 3-22 and 4-26.

- Valve B-15: Completed 105 hours of Thermal Cycle Base testing without any distress of the yttria stabilized zirconia head top coating. See photograph in Figure 3-23.
- Valve B-19: Completed 100 hours of Thermal Cycle Base testing without any distress of the magnesia stabilized zirconia or calcium silicate coatings. Subsequent Thermal Cycle Shock testing was terminated at 86.7 hours due to spalling of the calcium silicate coating at the seat face/fillet interface. See photograph in Figure 3-24.
- Valve B-18: Thermal Cycle Shock testing was terminated after 56.3 hours due to spalling of calcium silicate coating at the seat face/fillet interface. See photograph in Figure 3-25.
- Valve B-17: Completed 104 hours of a special case Thermal Cycle Shock test, in which the maximum temperature was increased to 1088 K. The calcia stabilized zirconia head top coating remained intact without distress. See photograph in Figure 3-26 and SEM surface examination in Figure 4-20.

Fig. 3-1 Valve A-12 Seat Face Wear Test

Fig. 3-2 Valve A-1 Hot Seat Face Wear Test

Fig. 3-3 Valve A-2 Seat Face Wear Test

Fig. 3-4 Valve A-19 Seat Face Wear Test

Fig. 3-5 Valve B-24 Seat Face Wear Test

Fig. 3-6 Valve B-2 Seat Face Wear Test

Fig. 3-7 Valve B-7 Seat Face Wear Test

Fig. 3-8 Valve B-21 Seat Face Wear Test

Fig. 3-9 Valve A-9 Structural Fatigue Test

Fig. 3-10 Valve A-10 Structural Fatigue Test

Fig. 3-11 Valve A-7 Structural Fatigue Test

Fig. 3-12 Valve A-8 Structural Fatigue Test

Fig. 3-13 Valve B-9 Structural Fatigue Test

Fig. 3-14 Valve B-1 Structural Fatigue Test

Fig. 3-15 Valve B-10 Structural Fatigue Test

Fig. 3-16 Valve B-8 Structural Fatigue Test

Fig. 3-17 Valve A-14 Thermal Cycle Test

Fig. 3-18 Valve A-20 Thermal Cycle Test

Fig. 3-19 Valve A-21 Thermal Cycle Test

Fig. 3-20 Valve A-18 Thermal Cycle Test

Fig. 3-21 Valve A-23 Thermal Cycle Test

Fig. 3-22 Valve B-14 Thermal Cycle Test

Fig. 3-23 Valve B-15 Thermal Cycle Test

Fig. 3-24 Valve B-19 Thermal Cycle Test

Fig. 3-25 Valve B-18 Thermal Cycle Test

Fig. 3-26 Valve B-17 Thermal Cycle Test

**MICROSTRUCTURAL ANALYSES
OF MATERIAL**

4. MICROSTRUCTURAL ANALYSES OF COATINGS

4.1 Method of Analyses

Characterization of coated surfaces and qualitative analyses of coating materials were accomplished using an AMR-1200A Scanning Electron Microscope (SEM) with a Kevex Elemental Dispersive X-Ray Spectrum Analyzer (EDS). Photomicrographs of coating surfaces and a representative EDS spectrum are presented in this discussion. Included are as-received valve samples and samples after fatigue testing, face wear testing, thermal cycle base testing, thermal cycle shock testing, and heated face wear testing.

Each valve was given an SEM examination after testing except in cases where similar results were obtained during testing or similar failure mechanisms were observed. In such cases one valve representative of the set was analyzed.

4.2 Valve Coatings As Received

Surface characteristics of the four as-received coatings are shown in Figure 4-1. $\text{ZrO}_2 + 25\% \text{MgO}$ and $\text{ZrO}_2 + 20\% \text{Y}_2\text{O}_3$ have a similar surface appearance. $\text{ZrO}_2 + 5\% \text{CaO}$ appears to have less voids than the other two zirconia coatings. Of the two coatings, calcium silicate is the more coarse coating and contains larger voids than the zirconia coatings.

Representative EDS spectra of the three zirconia coatings are given in Figure 4-2, 4-3, and 4-4. The spectra show that the specified stabilizing elements are present in each respective zirconia coating. Figure 4-5 is the EDS spectra for the calcium silicate coating.

Cross sections of an as-received type A valve are shown in Figure 4-28. The view shows the mechanical bonding of NiCrAlY to the valve head material and the bonding of zirconia to NiCrAlY. The cracks and delamination shown in Figure 4-28A were formed during metallurgical sample preparation.

Porosity was found at the NiCrAlY/valve head interface of valve B-14. It is presumed that the porosity was formed during the application of the yttria stabilized zirconia and the NiCrAlY base coatings (Figure 4-29A). This conclusion is based on the observation that valve A-14 does not contain porosity when coated to the same thickness (0.4 to 0.9 mm). The porosity in valve B-14 destroyed the bond integrity of the coating and could account for the reduced performance. Valve B-14 is further discussed in Section 4.3.2.

The zirconia coating thickness on the valve head top surface was observed to be greater at the center and to taper off close to the value given by NCIIR at the head circumference. This variation was considerably greater on type A valves. A typical example of this condition is shown in the Figure 4-28B sectional photograph of untested valve A-14, where the zirconia thickness varied from 1.0 mm near the center to 0.43 mm near the circumference. The head top surface coating thickness variations are likely due to the manual application technique with the valve rotating about its longitudinal axis. As previously mentioned, the calcium silicate seat face coating thicknesses were insufficient to allow proper preparation machining. After test, sectional inspection of valves A-18, A-20, A-23, and B-19, where the calcium silicate seat face coating was not machined for thermal cycle testing, the calcium silicate seat face coating thickness was measured to be 0.1 mm.

With the zirconia coated valves, the NiCrAlY bond coat nominal thickness was 0.1 mm. For the calcium silicate coated valves, the NiCrAlY bond coat nominal thickness ranged from 0.05 mm to 0.1 mm.

4.3 Valve Coatings After Testing

4.3.1 Unfailed Valve Coatings

Figures 4-6 through 4-13 show ceramic coated valve seat faces that survived the Face Wear test. During this test seat face material is transferred to the ceramic coated seat, and some crushing of the ceramic occurs. Wear debris accumulates in the porosity of the ceramic coated valves. The seat face of valve A-1 had a dark gray ring on the seat face after testing. An EDS spectrum of the wear debris shows that the wear print is seat insert material (Figure 4-9). The presence of cobalt in the spectrum confirms that an SAE VF-3 seat insert material was used during the face wear test.

Coarser wear debris deposits formed on valves A-7, B-1, and B-10 are shown in Figures 4-8, 4-12, and 4-13, respectively. As one would expect, the X-ray spectra (Figures 4-10, 4-14, and 4-15) show that the debris contains tungsten and cobalt, both of which are contained in the seat insert.

Figure 4-7 shows that the NiCrAlY bond coating was exposed during the grinding of valve A-19. However, this valve survived 6×10^6 face wear test cycles with no major damage to the seat face area. It appears, therefore, that a combination

of calcium silicate and exposed NiCrAlY bond coating did not alter the wear properties of the seat face.

Figure 4-11 shows that the wear mechanism of a metal seat face is similar to that of a ceramic. This figure shows wear debris in the valleys of the grooves from the machining of the seat face.

The thermal Cycle Base testing and Thermal Cycle Shock testing do not significantly alter the surface structure of calcia, magnesia, and yttria stabilized zirconia coatings. Comparison of Figures 4-16 through 4-20 with Figure 4-1 indicates that the surface appearance of the zirconia was not changed during thermal testing. Thus, it can be assumed that the zirconia coatings will tolerate the thermal loadings with no apparent loss of performance.

4.3.2 Failed Valve Coatings

Valves A-20 and B-19 showed evidence of chipping and spalling of the calcium silicate coated fillets during the Thermal Cycle Shock test. Examination of the fracture (Figures 4-21 and 4-22) indicates that the coating failed as a result of cleavage fracture in the calcium silicate. In both cases shown the calcium silicate failed within the material and not at the base coat/ceramic or base coat/valve boundary.

Grooving was observed on valve B-2 during the Face Wear test. This condition is a result of reduced seat insert contact area. Figure 4-23 shows that the zirconia seat face coating was not completely penetrated during testing. The discoloration observed in the wear groove was originally thought to be full penetration and failure but was after identified as insert material (Figures 4-24 and 4-25).

The zirconia coating on the head top of valve B-14 spalled after 12.5 hours of Thermal Cycle Base testing. The coating failed at the NiCrAlY/zirconia interface. Valve A-14 was coated with the same yttria stabilized zirconia as valve B-14 and had approximately the same thickness. Valve A-14 survived 100 hours of Thermal Cycle Shock testing, and no coating failures were observed. The Thermal Cycle Shock test is considered more severe than the Thermal Cycle Base test.

Porosity was found at the coating interfaces of valve B-14 (Figure 4-29A). It is believed that the porosity contributed to the short life of valve B-14. Since valve A-14 survived a more severe test, it is believed that coating misapplication rather than coating material failure reduced the performance of valve B-14.

A. ZrO₂ + 25% MgO

B. ZrO₂ + 20% Y₂O₃

C. ZrO₂ + 5% CaO

D. CaSiO₃

**Fig. 4-1 S.E.M. Surface Characteristics of
Deposited Ceramic Coatings, 900x**

Figure 4-2 EDS of ZrO_2 + 25% MgO Coating

Figure 4-3 EDS of $\text{ZrO}_2 + 20\% \text{Y}_2\text{O}_3$ Coating

Figure 4-4 EDS of ZrO_2 + 5% CaO Coating

Figure 4-5 EDS of CaSiO_3 Coating

Fig. 4-6 Valve A-1 $\text{ZrO}_2 + \text{MgO}$ Seat Face After 9.5×10^6 Face Wear Test Cycles Showing Wear Debris, 900x

Fig.4-7 Valve A-19 CaSiO_3 Seat Face After 6×10^6 Face Wear Test Cycles. Shows NiCrAlY Base Coating Exposed During Grinding, 40x

Fig. 4-8 Valve A-7 $\text{ZrO}_2 + \text{MgO}$ Seat Face After 6×10^6 Fatigue Test Cycles, 900x

Figure 4-9 EDS of Wear Debris on the Seat Face of Valve A-1

E.T.N.

DE-AC03-79ET15320

300106A72B

PR= 500S 500SEC 0 INT

U=8192 H=20KEV 1:30 AQ=20KEV 10

Figure 4-10 EDS of Wear Debris on the Seat Face of Valve A-7

Fig. 4-11 Valve A-9 Showing an Uncoated Seat After 6.4×10^6 Fatigue Test Cycles, 1000x

Fig. 4-12 Valve B-1 $ZrO_2 + MgO$ Seat Face Showing Mechanical Wear Debris Deposits After 6×10^6 Fatigue Cycles, 65x

Fig. 4-13 Valve B-10 $ZrO_2 + MgO$ Seat Face After 6×10^6 Fatigue Test Cycles. Light Area Are Bond Coating Exposed During Seat Grinding, 400x

Figure 4-14 EDS of Wear Debris on the Seat Face of Valve B-1

Figure 4-15 EDS of Wear Debris on the Seat Face of Valve B-10

A. Fillet: CaSiO_3 , 900x

B. Head Top: ZrO_2 + MgO , 900x

Fig. 4-16 Valve A-18 After 100 Hours of Thermal Cycle Base Test

A. Fillet: CaSiO_3 , 900x

B. Head Top: ZrO_2 + CaO , 900x

Fig. 4-17 Valve A-23 After 105 Hours of Thermal Cycle Base Test

A. Fillet: $\text{ZrO}_2 + \text{Y}_2\text{O}_3$, 1000x

B. Head Top: $\text{ZrO}_2 + \text{Y}_2\text{O}_3$, 900x

Fig. 4-18 Valve A-14 After 100 Hours of Thermal Cycle Base Test Plus 100 Hours of Thermal Cycle Shock Test

Fig. 4-19 Valve B-15 $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ Head Top After 105 Hours of Thermal Cycle Shock Test, 900x

Fig. 4-20 Valve B-17 $\text{ZrO}_2 + \text{CaO}$ Head Top After 104 Hours of Thermal Cycle Shock Test, 900x

A Fillet: CaSiO_3 ,900x

B. Seat Face: Flaking of CaSiO_3 ,80x

C. Head Top: ZrO_2 + 25% MgO , 900x

D. Seat Face: Cleavage Fracture of CaSiO_3 ,900x

Fig. 4-21 Failure Analysis of Valve A-20 After 78 Hours of Thermal Cycle Shock Testing

A. Fillet and Seat Face: CaSiO_3 , 900x

B. Fillet: Cleavage Fracture of CaSiO_3 In Spalled Area, 900x

C. Head Top: $\text{ZrO}_2 + 25\% \text{MgO}$, 900x

Figure 4-22, Failure Analysis of Valve B-19 after 100 hrs. of Thermal Cycle Base Test + 87 hrs. of Thermal Cycle Shock Test.

A. Seat Face: Area 1 (Right), 900x

B. Seat Face: Wear Groove (Area 2), 50x

C. Seat Face: Area 2 (Above Right) in Wear Groove, 1000x

D. Seat Face Cross Section, 12x

E.T.N

DE-AC03-79ET15320

300106B2B

PR= 500S 500SEC 0 INT

V=8192 H=20KEV 1:30 AQ=20KEV 10

Figure 4-24 EDS of Flat Areas in the Wear Groove of Valve B-2

Figure 4-25 EDS of Valleys in the Wear Groove of Valve B-2

A. Spalled ZrO₂, 3x

B. Fracture Along the NiCrAlY to ZrO₂ Interface, 65x

Figure 4-26, Failure Analysis of Valve B-14 Head Top after 12.5 Hours of Thermal Cycle Base Test

A. Seat Face Showing a Zr Map

B. Seat Face Showing Wear

Figure 4-27, Failure Analysis of Valve A-2 after 2x10⁶ Cycles of Heated Seat Face Wear Test

A. Coating Layers

B. Zr Dot Map Superimposed Over Layer Section

**Fig. 4-28 Cross Section of Untested Valve
A-4 ZrO_2 + MgO Head Top Coating Over
NiCrAlY Bond Coat**

A. Valve B-14 $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ Over NiCrAlY Bond Coat

Fig. 4-29 Cross Section Examination Illustrating Various Observed Coating Interface Boundary Characteristics

B. Valve B-1 $\text{ZrO}_2 + \text{MgO}$ Over NiCrAlY Bond Coat. Black Area is Mounting Material