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SUMMARY

The Gas Research Institute (GRI) has sponsored a study of the durability of advanced material combinations in gas-fuelled reciprocating engines. Under contract to GRI, Adiabatics, Inc. designed and directed a phase II study which was designed to test valves and valve seat inserts of various material combinations, for 1000 hours in a Cummins GTA-855 engine. Components were specially made or coated commercially. The engine tests were conducted by Engineering Test Services in Charleston, South Carolina. Subsequently, an analysis of the wear characteristics of the valve and valve seat inserts was conducted by the Tribology Group at the National Institute of Standards and Technology (NIST).

The valves were coated with superalloys (Stellite 1, Stellite 6 or Tribaloy 800), while the valve seat inserts were made of GTE/Eaton hipped silicon nitride, Norton/TRW sialon, or the metal alloy Eatonite. The industry standard valve/seat pair, Stellite 1/Eatonite, was used to provide a baseline for the study.

The engine test, scheduled for 1000 hours, was interrupted after 417 test hours due to a failure of a baseline valve. The engine was partially rebuilt, salvaging test parts whenever possible and the test was resumed. At 581 hours, an accidental engine overspeed caused an additional test failure that lead to the termination of the test. A decision was made to proceed with the wear analysis without further engine testing.

Post test analysis carried out at NIST concentrated on wear measurements of the valve/seat pairs and chemical analysis of the lubricant and specimens. **Examination of the specimens revealed that severe wear occurred for each of the inlet valves, caused primarily by plastic deformation and lack of lubrication. The exhaust valves showed much less wear. The presence of carboneous deposits on the wear surfaces, formed by oxidized oil and combustion products, probably protected the valves.** The best intake valve/seat combination was Stellite 6 coupled with sialon, while the most effective exhaust valve/seat combination was Tribaloy 800 coupled with silicon nitride. No measurable wear was detected on either the silicon nitride or sialon valve seat inserts. The superalloy coated valves suffered significantly less wear than the baseline case, thus the advanced material combinations appear to represent a distinct improvement above those normally used by the industry.

Chemical analysis of crankcase oil removed from the engine during the test demonstrated that significant oxidation had occurred. Evidence of condensed phase oxidized organic material near the contact and lubricant additive components in the worn region of several valves, confirmed that some lubricant was getting to the valve/seat interface during engine operation. Bench wear tests conducted on silicon nitride with degraded lubricant at high temperature exhibited increased wear, compared with tests carried out using new oil. Further laboratory wear tests on silicon nitride/superalloy material pairs are recommended, to isolate the effects of lubricant chemistry and operating environment on the wear of these advanced material combinations.

Note

Certain commercial equipment, instruments, or materials are identified in this report in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Wear Mechanisms of Valves and Valve Seat Inserts in a Gas-Fired Reciprocating Engine

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Objective:

To quantitatively measure wear and to identify the dominant wear mechanisms experienced by selected valve and valve seat insert combinations during operation in a natural gas-fueled reciprocating engine.

Introduction:

Increasing environmental concerns are prompting engine designers to examine alternative fuel sources, such as natural gas. An initial study carried out by the Southwest Research Institute[1] (SwRI), under contract to the Gas Research Institute (GRI), concluded that valve and valve seat wear remain a critical barrier to the more widespread use of natural gas engines. High temperatures and lack of lubrication in the upper cylinder, due to the absence of high molecular weight species in the gaseous fuel, were the primary causes of wear. The current project forms part of the ongoing GRI study directed towards increasing the durability of gas-fueled reciprocating engines. The eventual goal is to achieve 40,000 hours of operating between major engine overhauls. Previous work, denoted phase 1, carried out by the Adiabatics Inc. in conjunction with GRI, examined the use of advanced materials to reduce wear[2]. Engine tests for that work were conducted at the Southwest Research Institute, with a Cummins GTA-855 natural gas engine for 300 hours, using valves that had been plasma-coated with Stellite 1 and Stellite 6, coupled with silicon nitride valve seat inserts. Stellite 1 was also combined with Eatonite as a baseline for comparison. The use of silicon nitride eliminated wear of the valve seats, at a cost of accentuated wear on the metal counterface of the valve. The overall wear rate for the system was significantly less than that measured for Eatonite valve seat inserts, which were considered to be the industry standard. The Tribology group at the National Institute of Standards and Technology (NIST) carried out post-test analysis of the valve components[3]. The dominant wear mechanism on the valve coating was established to be impact fracture and corrosion, with some evidence of low cycle fatigue.

Because of the substantial reduction in wear, demonstrated with Stellite 6 coated valves coupled with silicon nitride, a second test phase was initiated. The purpose of this phase, was to further test the most promising material combinations from phase 1, as well as a new material pair, over an extended test duration of 1000 hours.

Engine Test Program

The alloys used to coat the valve faces for the second phase of the engine durability test were Stellite 6 and Tribaloy 800. As in the previous test, Stellite 1 was included as the industry standard coupled with an Eatonite valve seat. The remaining valve seat inserts were sialon (Norton/TRW) sintered at atmospheric pressure and HIPPED AY-6 silicon nitride (GTE/Eaton). The approximate composition (in wt %) of the metal alloys used in the valve coatings and Eatonite valve seat inserts are given in Table 1.

Table 1: Approximate Compositions (in wt. %) of the Metal Alloys Used

Alloy	B	C	Co	Cr	Fe	Mn	Mo	Ni	Si	W
Stellite 1	0.1	2.4	45.5	30.5	3.0	1.0	1.0	3.0	1.0	12.5
Stellite 6	-	1.15	57.4	27.7	3.0	1.0	1.0	3.0	1.15	4.5
Tribaloy 800	-	0.08	47.5	17.5	1.5	-	28.5	1.5	3.4	-
Eatonite 2	-	2.4	10.0	29.0	8.0	0.5	-	34	1.0	15.0

The engine durability test used a six cylinder Cummins GTA-855 natural gas engine, operating at 330 HP (250 kW) @ 1800 RPM for 11 hours, with an intermittent one hour cycle of 375 HP (280 kW). After 417 hours into the planned 1000 hour test, No. 2 cylinder head suffered extensive damage due to failure of the baseline valves. The engine was partly rebuilt and testing resumed at a continuous engine load of 330 HP. After 581 hours component failure caused the engine to overspeed, resulting in further damage and termination of the test.

The fuel used throughout the test was natural gas, with the chemical composition shown in Table 2 and an energy content of 1021 BTU/ft^3 @ Standard Temperature and Pressure (STP). It may be noted that trace concentrations of sulfur containing compounds are present in the gas. Formation of sulfuric acid from these compounds may result in corrosive wear of susceptible components, during prolonged operation.

Table 2: Composition of Natural Gas Fuel

Constituent	Conc.(±0.1%)	PPM
Methane	97.9	-
Propane	0.1	-
Nitrogen	0.3	-
Ethane	1.1	-
CO_2	0.46	-
N-Pentane	0.03	-
N-Butane	0.02	-
I-Butane	0.02	-
Hydrogen Sulphide	-	0.0126
Residual Sulfur	-	0.0475
Mercaptan Sulfur	-	0.0
Sulfide Sulfur	-	0.0

The engine oil used was Mobil Pegasus 485. This is a commercially available lubricant especially formulated for use in natural gas engines. The oil was replaced every 250 hours and samples were taken at selected intervals throughout the test cycle. The initial 250 hours, during which break-in occurred, was the only period covering a complete oil change interval without engine failure. Table 3 shows the engine run times for which samples of used oil were available for post-test analysis.

Table 3: Oil Samples Removed From Gas Engine

Sample No.	Engine Hours	Oil Hours	
1	6	6	
2	50	50	
3	100	100	
4	125	125	
5	250	250	
6	258	8	*
7	375	125	
8	443	25	**
9	553	136	
10	581	164	

* Oil was changed after 250 hours
** Engine was rebuilt after 417 hours

The NIST received the oil samples and the ten sets of valves and valve seat inserts from Adiabatics Inc. Each valve and seat was identified by a two digit number reflecting the source of that part as given in Table 4. The first number indicates the head from which the valve came (1, 2 or 3), the second indicates the valve position within that head (1 to 8). This is illustrated in Fig. 1.

Table 4: Material Cross Reference

Location	Valve Material	Seat Material	Intake (I) Exhaust (E)	
1-3	Tribaloy-800	Sialon	I	
1-4	Tribaloy-800	Sialon	E	
1-7	Stellite-6	Sialon	E	
1-8	Stellite-6	Sialon	I	
2-3	Stellite-1	Eatonite (Base)	I	*
2-4	Stellite-1	Eatonite (Base)	E	*
3-3	Tribaloy-800	AY-6 Si_3N_4	I	
3-4	Tribaloy-800	Ay-6 Si_3N_4	E	
3-7	Stellite-6	AY-6 Si_3N_4	E	
3-8	Stellite-6	AY-6 Si_3N_4	I	

* The baseline valve/seat pairs were replaced at 417 engine hours.

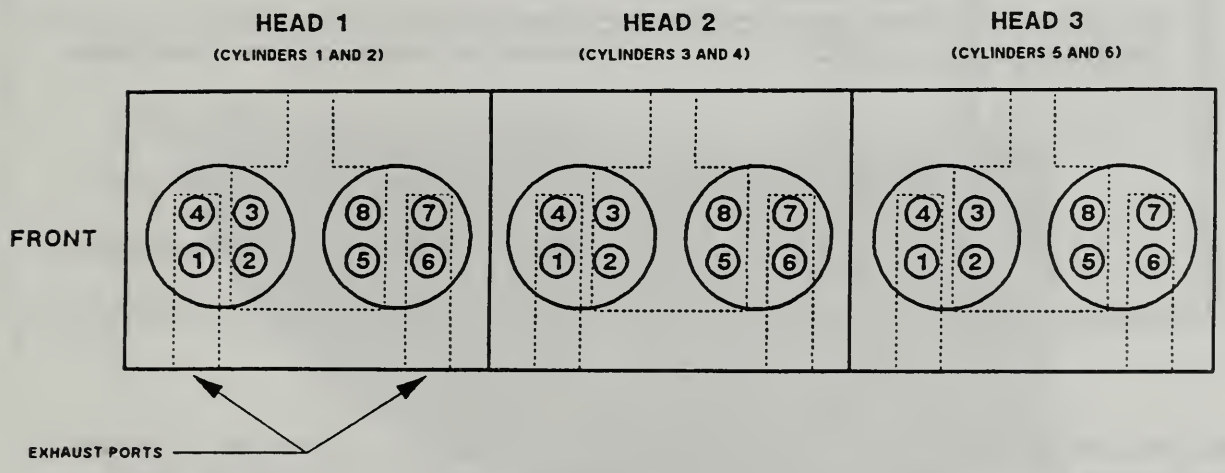


Fig. 1. Location of the Valves and Cylinders (Firedeck view)

Technical Approach

A major objective of the present work was to accurately quantify the amount of wear experienced by each component. Equally important however, was the definition of the limiting wear mechanism, as this would identify the most important issues for further investigation. Both the valve/seat pairs and samples of used crankcase oil were analyzed, using the techniques presented in Table 5 below.

Table 5: Summary of analysis and performance measurements used for this study

Subject	Technique		Purpose
Valve/Seat	SEM, EDX, Profilometry	}	Examination of wear scar
	FTIR, Raman	}	Chemical composition of deposits
	Hot hardness	:	Effect of temperature on hardness
Dissolved deposits	IR, GPC-GFAA	}	Chemical composition of deposits
Lubricant	TFOUT	:	Oxidation stability of lubricant
	IR	:	Oxidation state of lubricant
	Metals analysis	:	Metal content of used lubricant
	Wear tests	:	Effect of lubricant oxidation on wear

The worn surfaces of the valves were examined using a Scanning Electron Microscope (SEM) and three dimensional profilometry, to provide both qualitative and quantitative information about the wear scar. Deposits present on the valve face were analyzed using Gel Permeation Chromatography - Graphite Furnace Atomic Absorption (GPC-GFAA), Energy Dispersive X-ray analysis (EDX), Transmission Infrared microscopy (IR), reflection micro-focused Fourier Transformed Infrared spectroscopy (FTIR), and micro-focused time resolved Laser Raman spectroscopy. Knowledge of the composition of the valve deposits provided by these tests can be used in evaluating the wear mechanism. Hot hardness tests were also carried out on the plasma coating, to determine the effect of temperature on material strength.

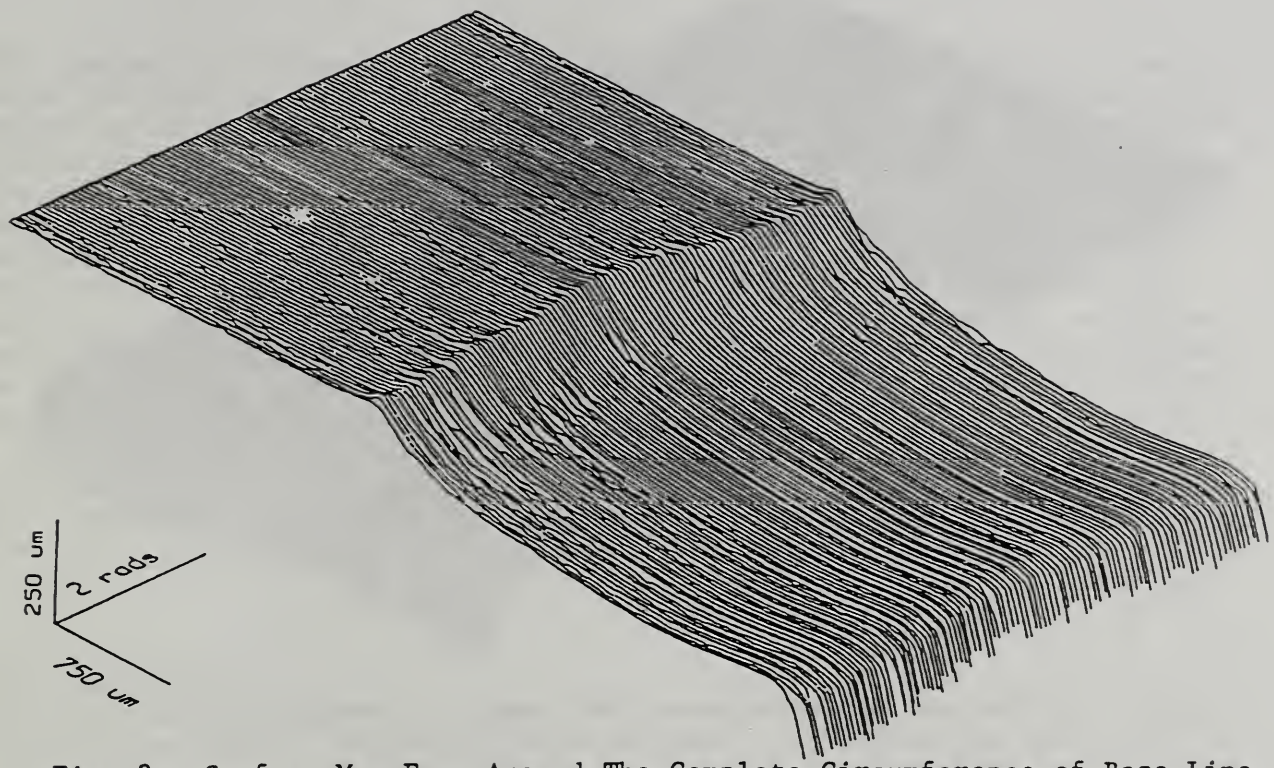


Fig. 2: Surface Map From Around The Complete Circumferance of Base Line Valve 2-3.

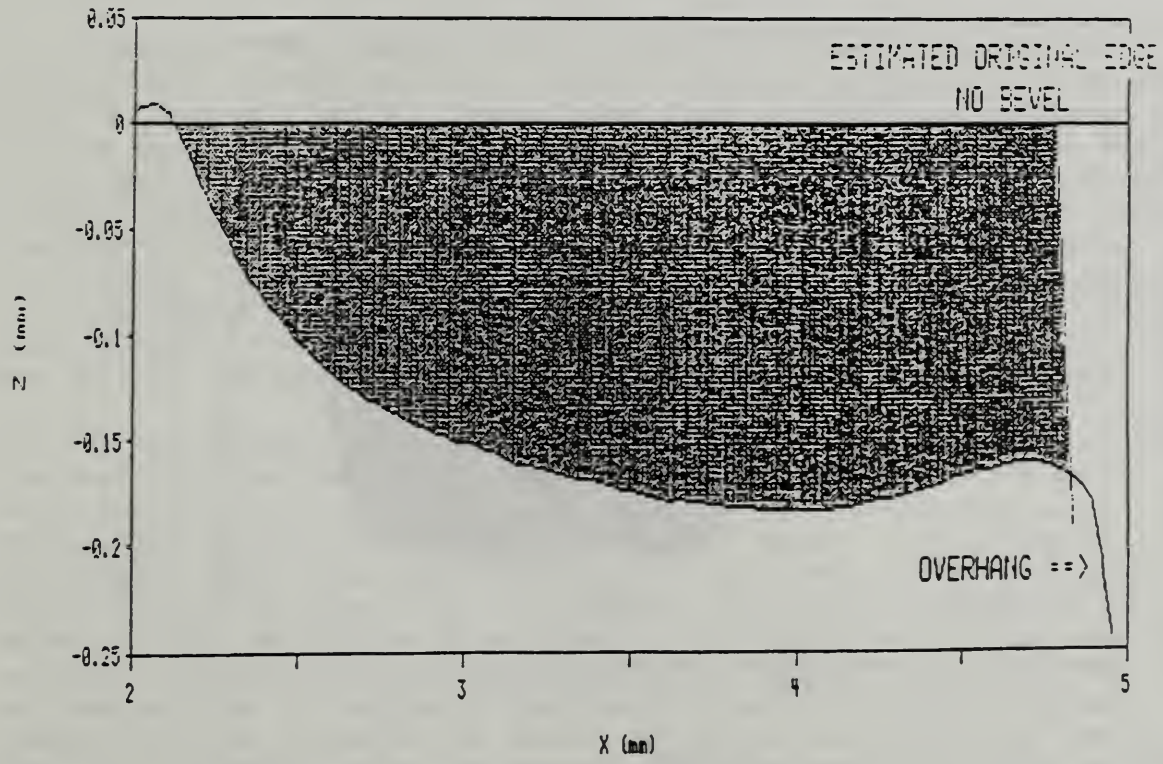


Fig. 3: Average Cross Section of Wear Track on Valve 2-3.

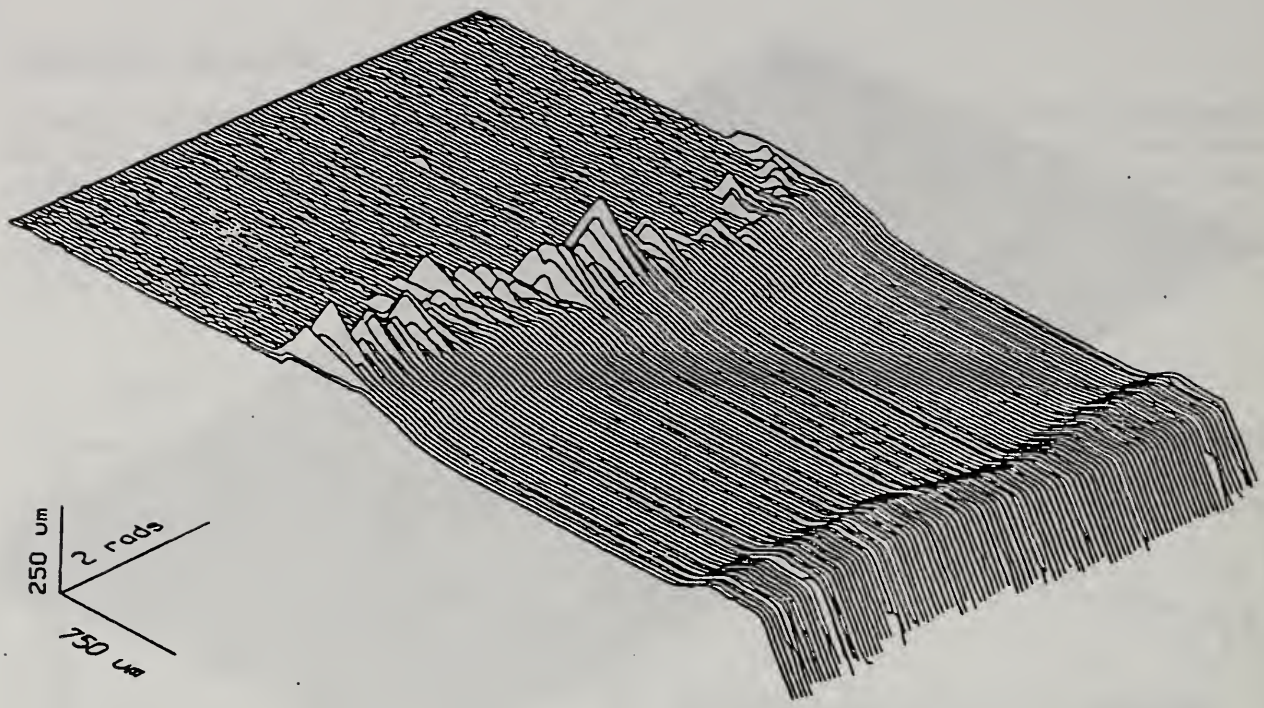


Fig. 4: 3-D Surface Map From Around The Complete Circumferance of Valve 1-7.

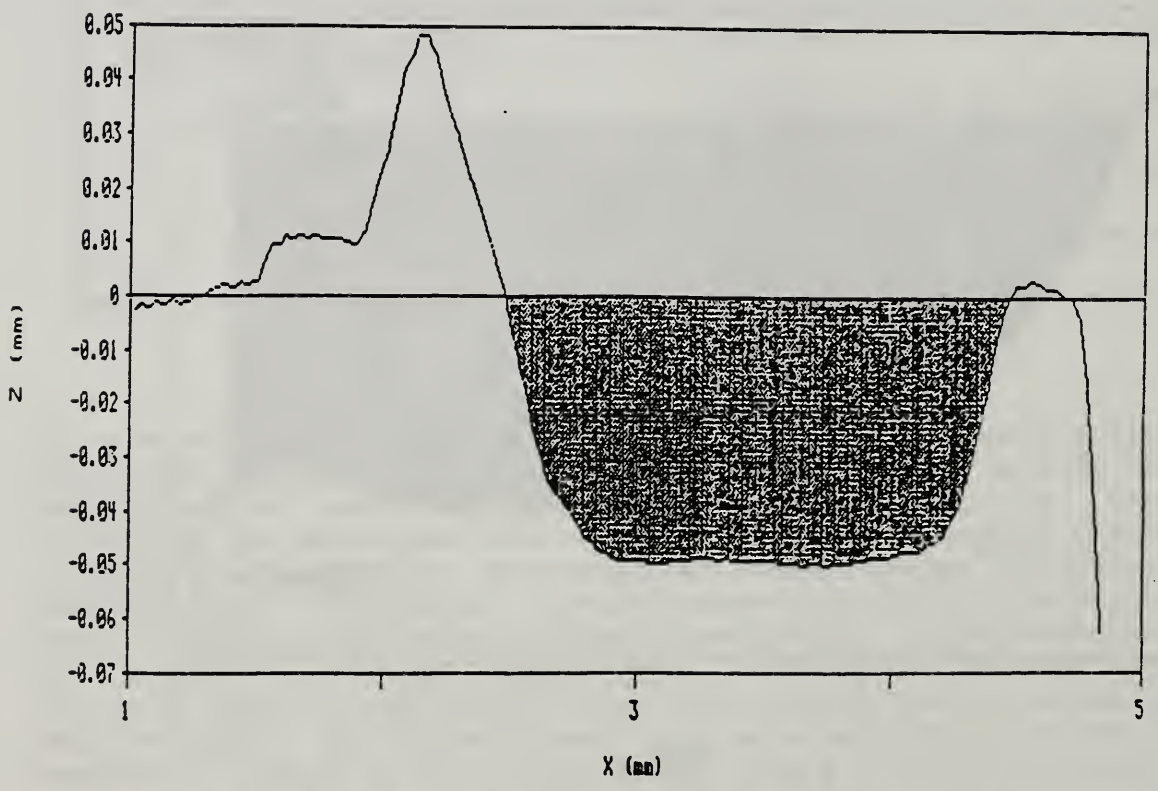


Fig. 5: Average Cross Section of Wear Track on Valve 1-7.

The Cummins GTA 855 engine does not provide oil seals on the valve stem, so some lubricant may migrate to the valve/seat contact during operation. The volume of lubricant which passes the valve guides is expected to be limited mainly by over-pressure present at the valves, created by the turbocharger and exhaust back pressure. Specimens of the degraded lubricant were evaluated using the Thin Film Oxidation Uptake Test (TFOUT), IR and Metals Analyses. Finally, wear tests were carried out on silicon nitride with both new and used crankcase oils, at various temperatures. These tests provide critical information relating to the effect of lubricant oxidation on wear for advanced materials. Examination of the used oils concentrated on the first 250 hour oil change cycle (Table 3), which is the only period uninterrupted by mechanical failure.

A compilation of the data collected using these techniques is provided in the appendices. Selected graphs and figures will also be used throughout the text to highlight particular points of interest.

Wear Measurement

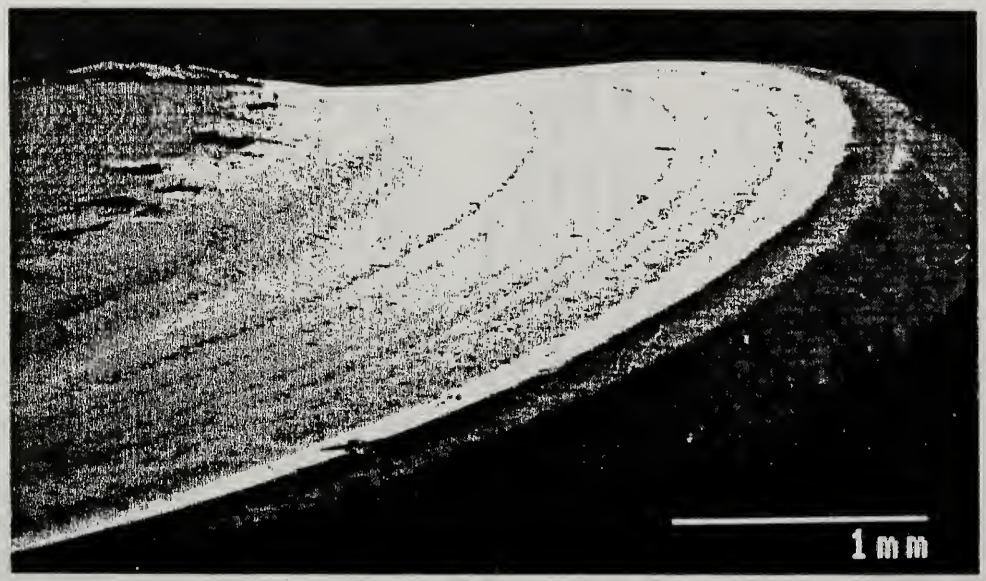
To accurately define the wear volume for each of the material pairs, the three dimensional surface mapping technique developed at NIST[4], was applied to both the valves and valve seat inserts. A jig was designed and built to rotate the specimens in discrete increments. This allowed a series of profiles to be taken in a radial direction, around the complete circumference of the part to provide a 360° scan.

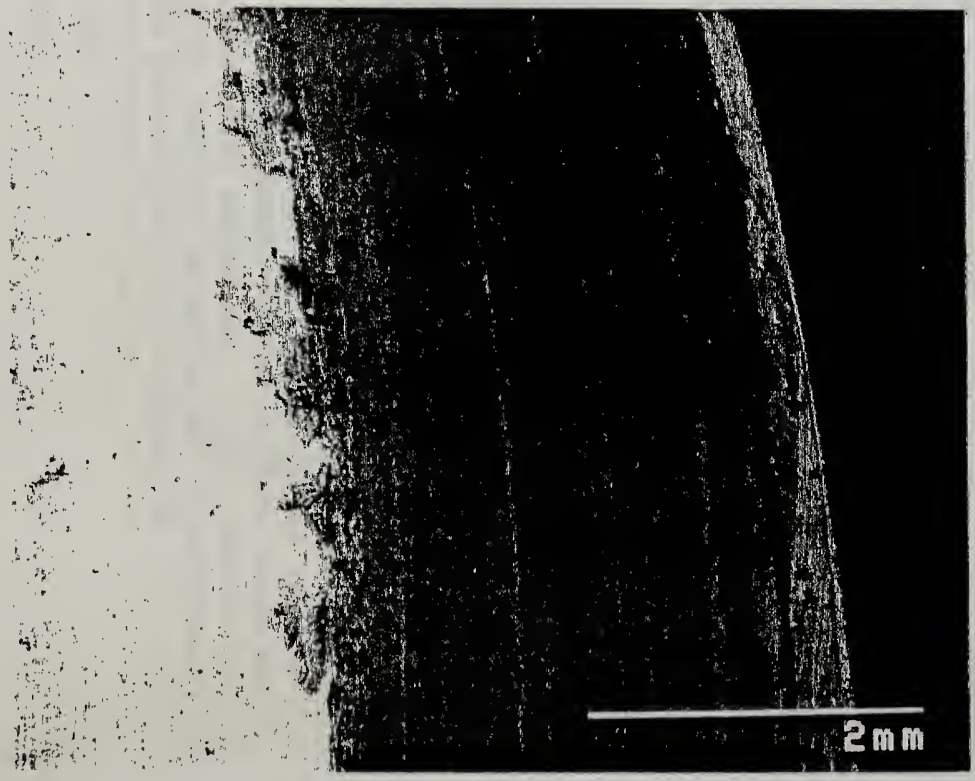
To facilitate visual analysis of the wear scar, these radial surface profiles were transformed into a pseudo-cartesian coordinate system as shown in figures 2 and 4. Traces taken from the remaining specimens are plotted in appendix 1. Each individual trace represents a radial profile across the contact area, with the valve stem located at the left of the figure. Each surface map depicts one complete revolution of the valve, so that the first and last traces come from the same point. To further simplify the data, the average wear scar profile for each of the valves was calculated from the surface traces in the 3-D wear maps, as depicted in Figs. 3 and 5. This view shows the average shape of the wear scar around the valve. Profile maps for all of the valves are presented in appendix 2.

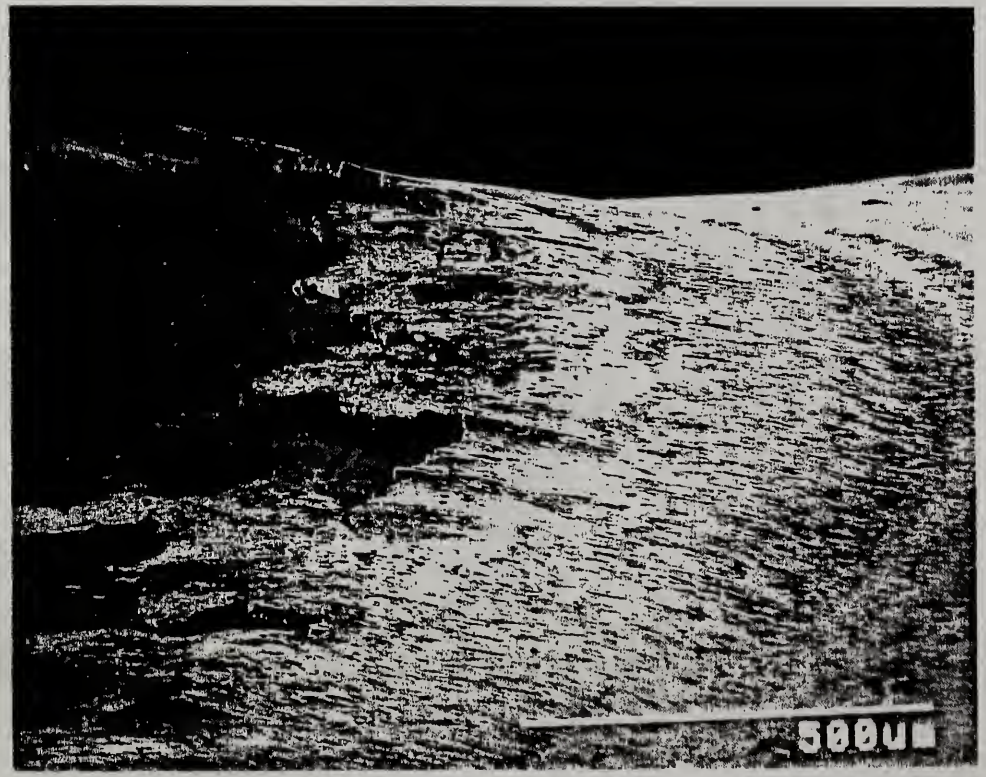
Wear of the ceramic valve seat inserts was negligible, thus the contour of the wear scars on the mating valves corresponds to the profile of the unworn seat. For the baseline case, however, due to the combined deformation of both the valve and valve seat insert, wear is biased towards the outside edge, completely removing the outer bevel from the intake valve as illustrated in Figs. 2 & 3. An interesting feature visible on several valves, is the deposition of material at the inside edge of the wear scar, as shown in Figs. 4 & 5. Examination of this deposit using the SEM microscope (Fig. 6) indicated that severe plastic flow had occurred, resulting in the extrusion of metal from inside the contact to form the lip. It is possible that the extreme conditions produced by the accidental

Fig. 6

STELLITE-6 EXHAUST VALVE
(vs. SIALON)



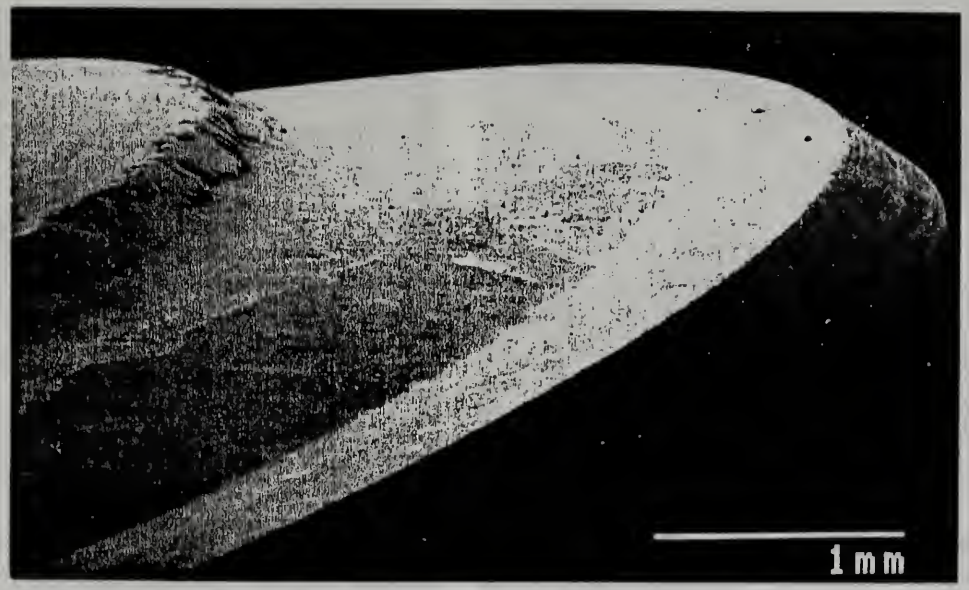


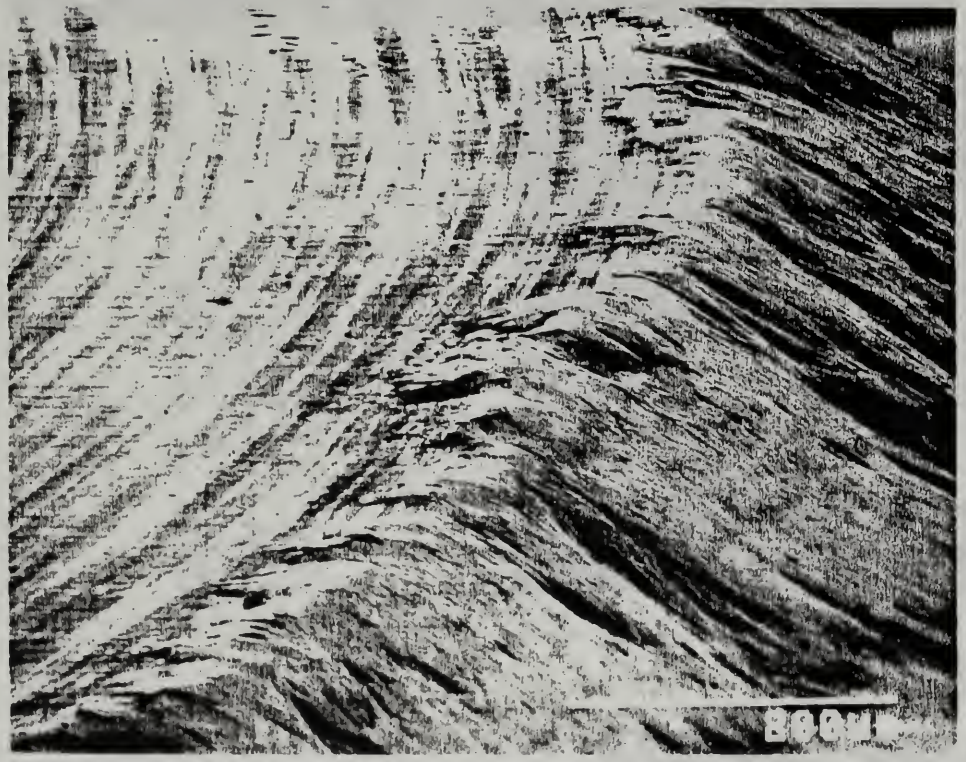


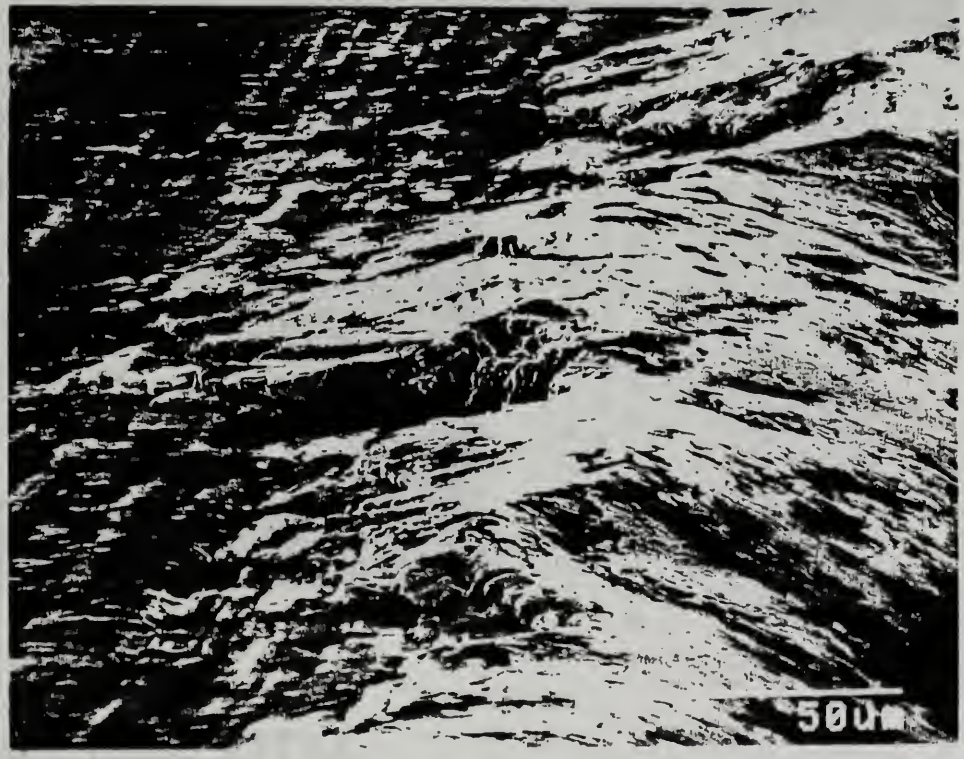
TRIBALOY-800 INTAKE VALVE

(vs. SIALON)

Fig. 7

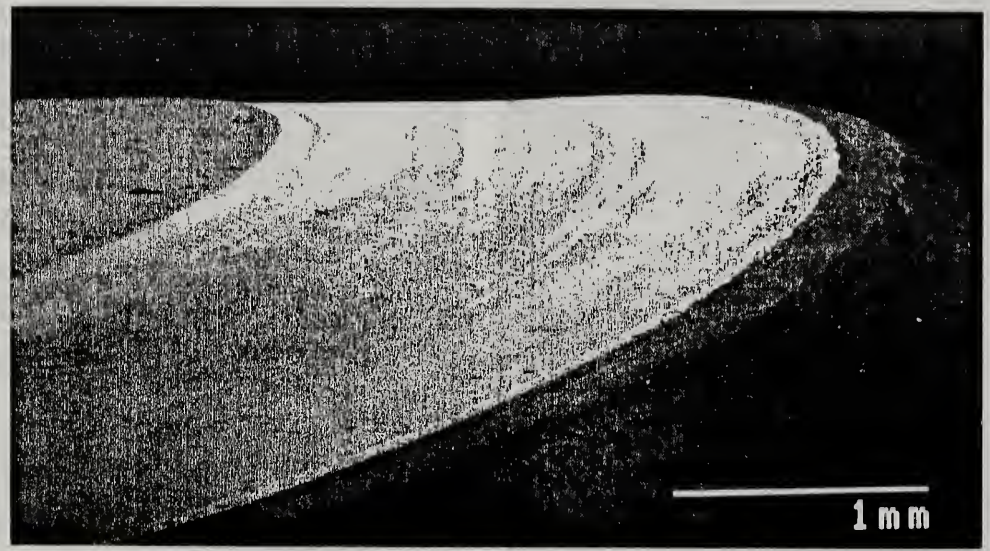


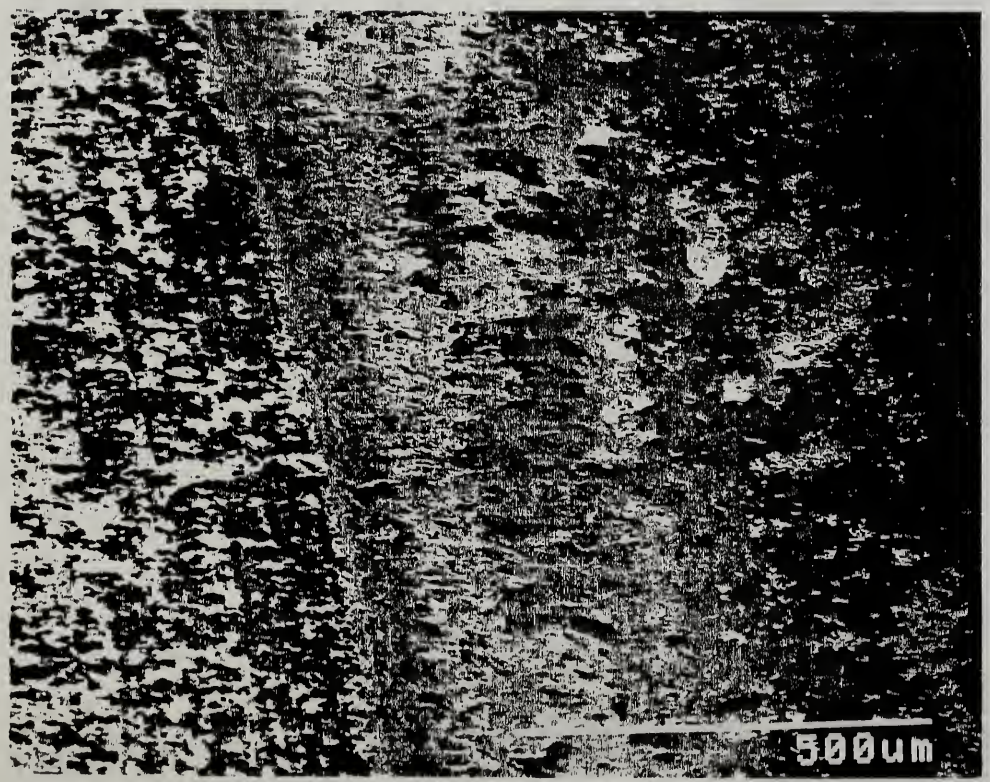




TRIBALOY-800 EXHAUST VALVE
(vs. SIALON)

Fig. 8





overspeed which prematurely concluded the engine test contributed in a significant way to generating the damage. Similar features are visible on the Tribaloy 800 inlet valve shown in Fig. 7. In contrast the Tribaloy 800 exhaust valve shown in Fig. 8 has a relatively smooth and unworn surface by comparison. Note the layer of deposit which is clearly visible on the valve face.

By comparing the average profiles from the worn surfaces (shown in appendix 2) with those of new valves, a quantitative measurement of the material removed was obtained. The results are summarized in Fig. 9 to allow comparison between the different material combinations.

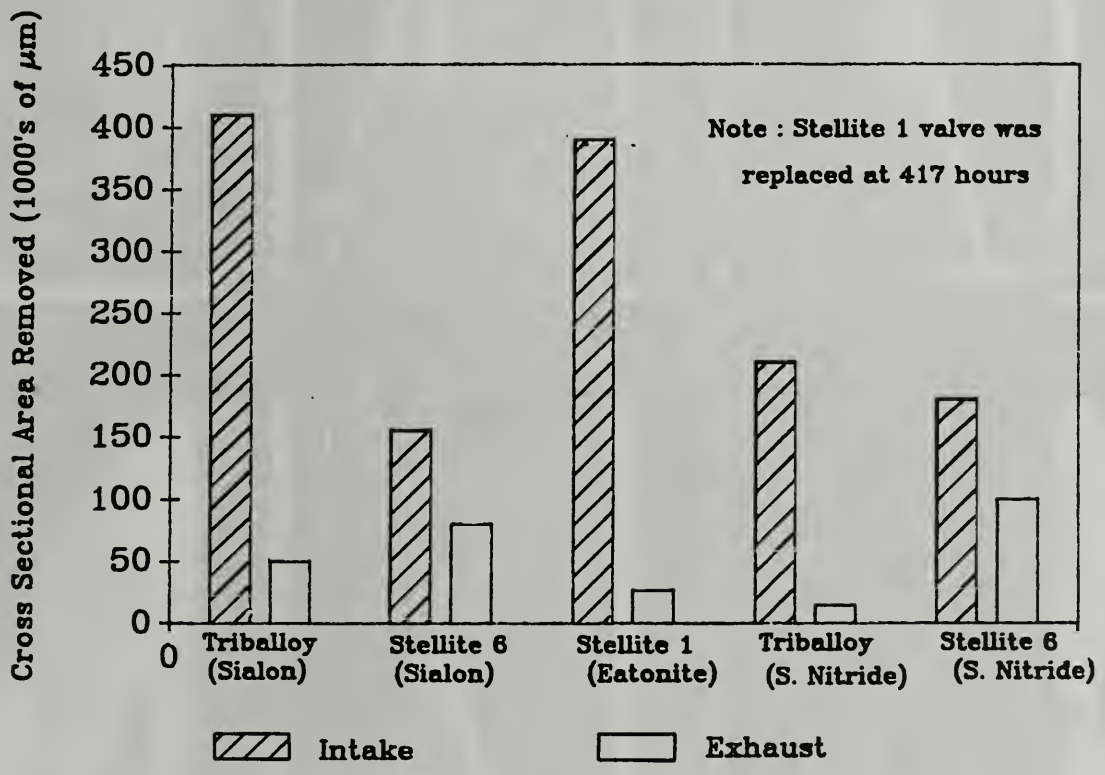


Figure 9: Comparison of Wear Volume of Different Valves/Seat couples

The Stellite 1/Eatonite couple were replaced after 417 test hours and hence only experienced 164 hours of operation. Despite this the wear volume was still comparable to that of the remaining valves, which remained in the engine for the entire 581 hours. Therefore, all of the advanced materials tested are more durable than the baseline materials, which are the current

Fig. 10

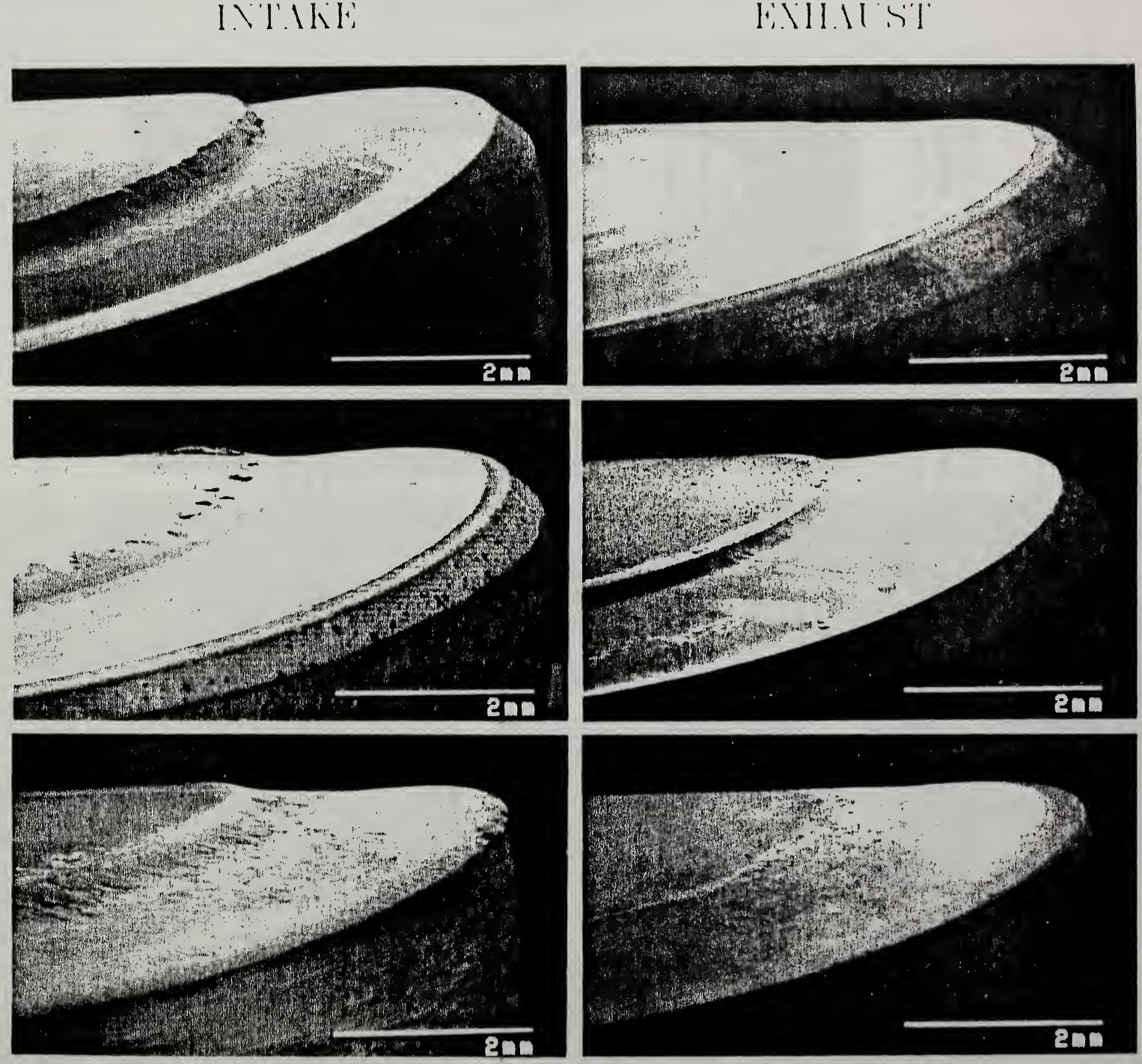
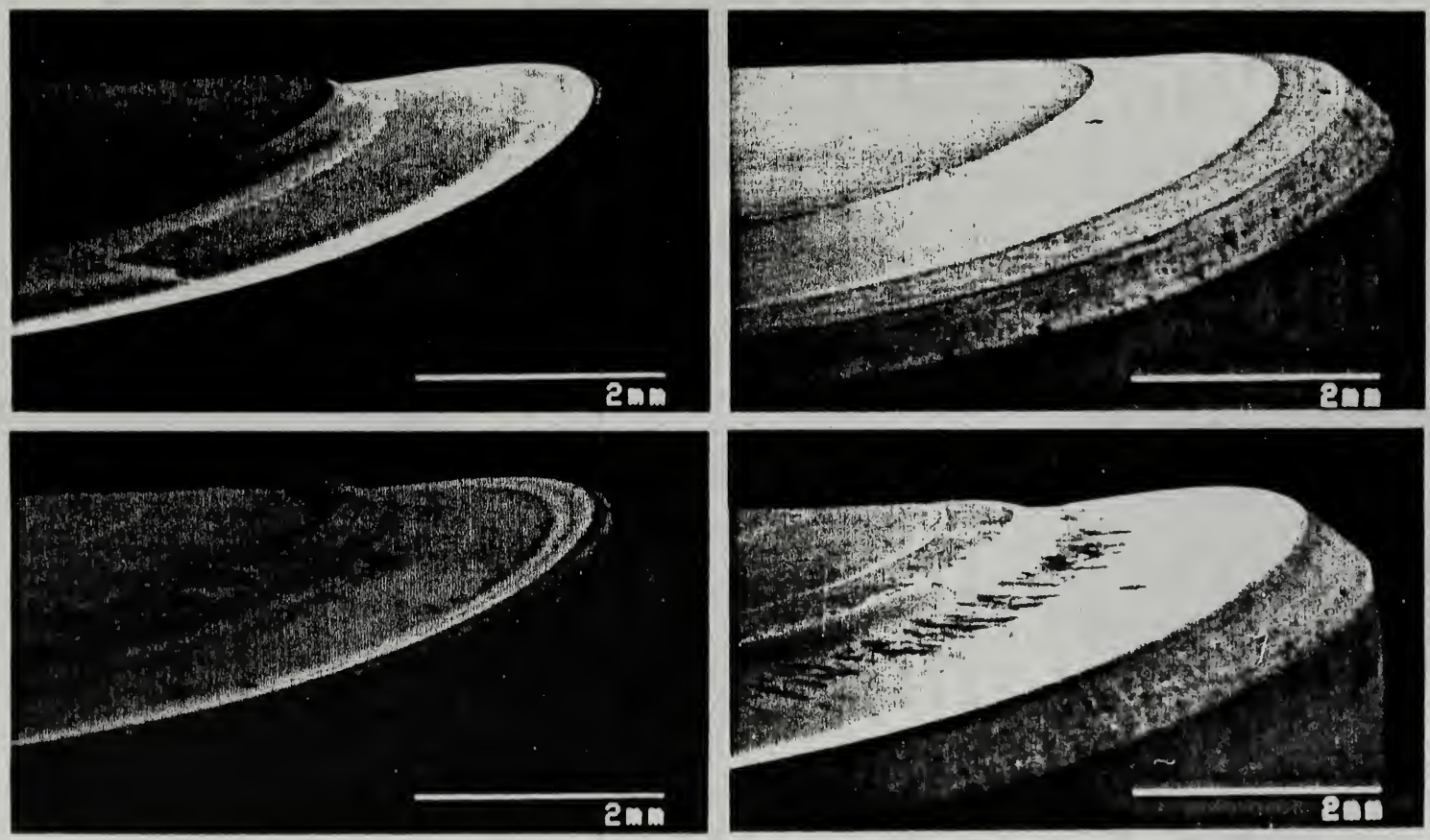

INTAKE
EXHAUST
TRIBALOY 800
(vs. SIALON)
STELLITE-6
(vs. SIALON)
STELLITE-1
(vs. EATONITE)
2mm
2mm
2mm
2mm
2mm
2mm

Fig. 11


INTAKE
EXHAUST
TROBALOY-800
(vs. AY-6Si3N4)
STELLITE-6
(vs. AY-6Si3N4)
2mm
2mm
2mm
2mm

industry standard. Tribaloy 800 run against a silicon nitride seat was the most successful exhaust valve material, but was marginally less effective than Stellite 6/sialon when used as an intake valve. The results from this test indicate that material combinations which produce low wear as inlet valves are not necessarily successful as exhaust valves. The optimum solution may require different material combinations, depending on whether the valve is to be used as an intake or an exhaust. For each of the material combinations used, the wear rate of the intake valves is much greater than that of the exhaust. This is contrary to the normal result for gasoline and diesel engines, where additional lubrication of the intake valves is provided by additives or by the high molecular weight species present in the fuel.

Photographs of the worn surfaces from each of the valves are shown in Figs 10 and 11 for comparison. All of the Stellite 6 and Tribaloy 800 valves coupled with ceramic seat inserts are smooth and free of pitting, although gross plastic flow has taken place towards the inside of the seat on the intake valves. The surface of the Stellite 1 valve is rough by comparison, probably because the Eatonite counterface is relatively soft compared to ceramic, hence compliance is not confined to the valve face.

Hot Hardness tests were conducted in an attempt to explain the observed wear characteristics of the various materials. The hardness of each of the valve facings is plotted in Fig. 12, as a function of temperature. For the range of temperatures examined Tribaloy 800 is considerably harder than either Stellite 1 or 6. However, in the present test no direct correlation exists between hot hardness and wear, indicating that perhaps other parameters such as fatigue strength, fracture toughness, and surface chemical reactivity may be important. Further detailed laboratory tests are necessary to examine this result.

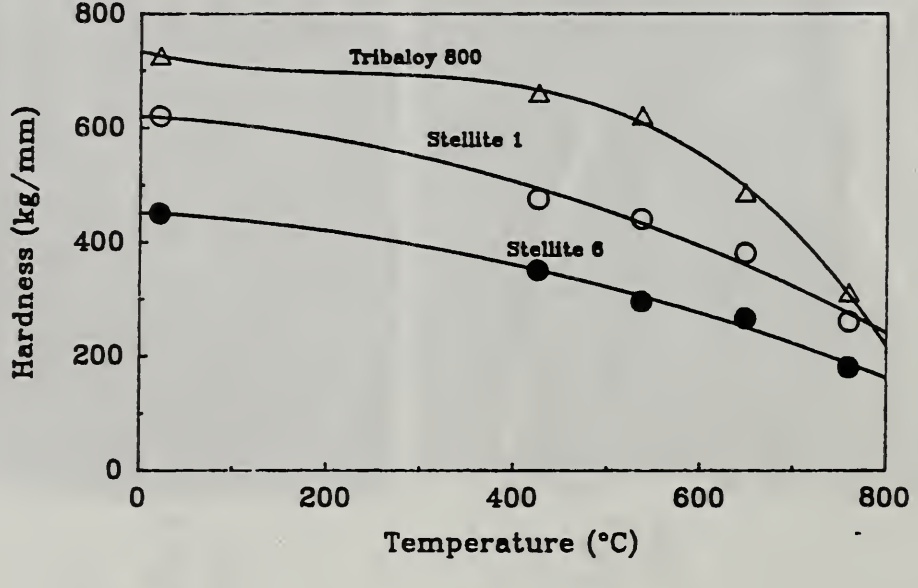


Figure 12: Hot Hardness of Alloy Materials

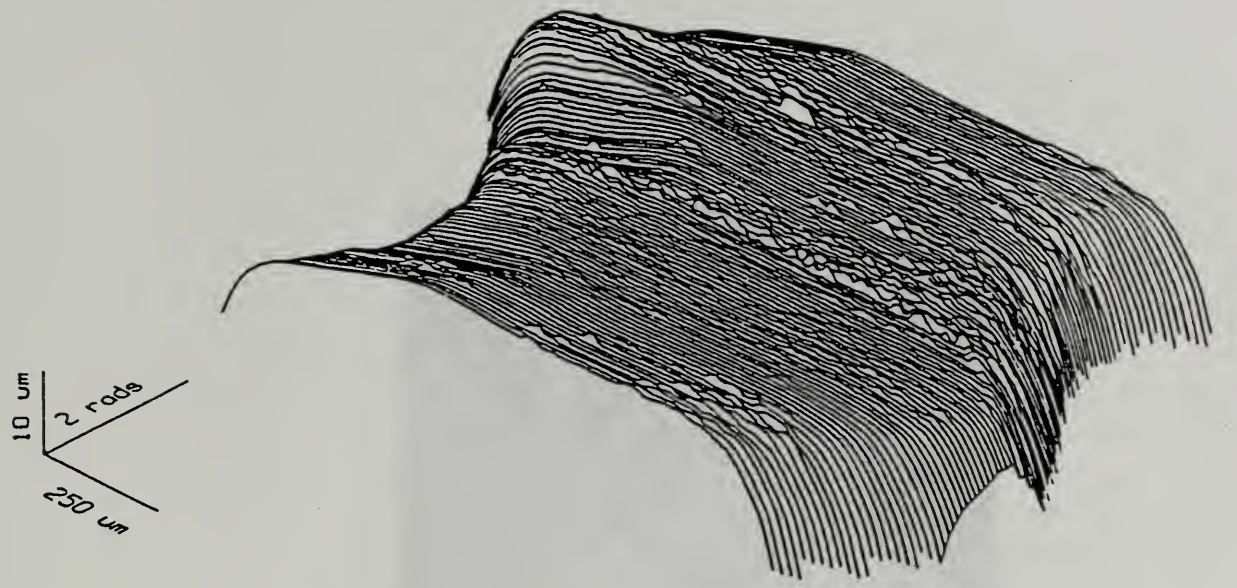


Fig. 13: 3-D Profile From Si_3N_4 Exhaust Seat (3-7).

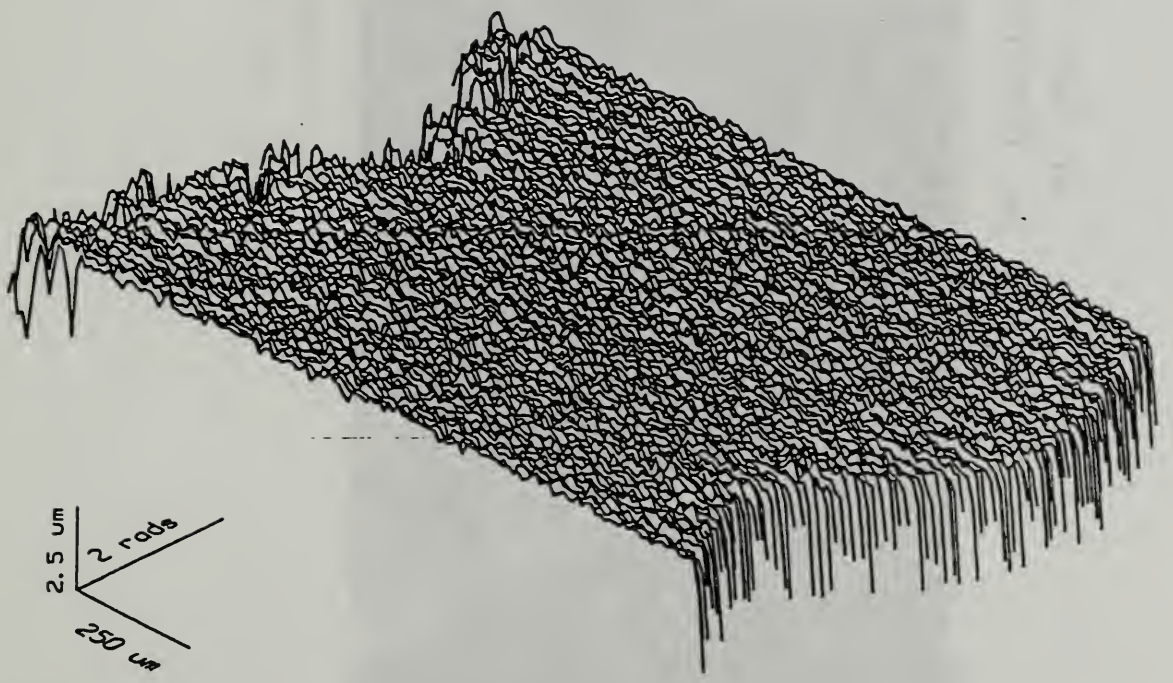


Fig. 14: 3-D Profile From Unworn Si_3N_4 Seat (Note Vertical Magnification).

Fig. 15

AY–Si_3N_4 INTAKE SEAT
(vs. TRIBALOY–800 VALVE)

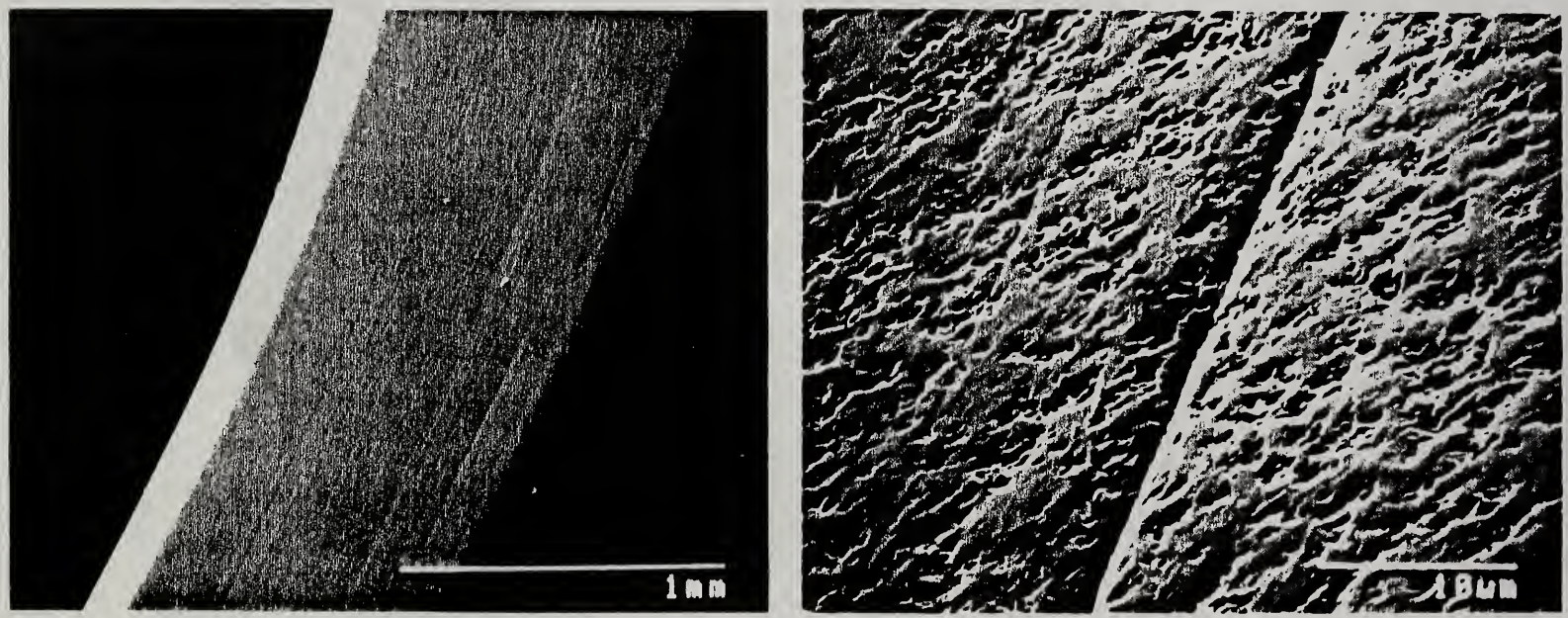
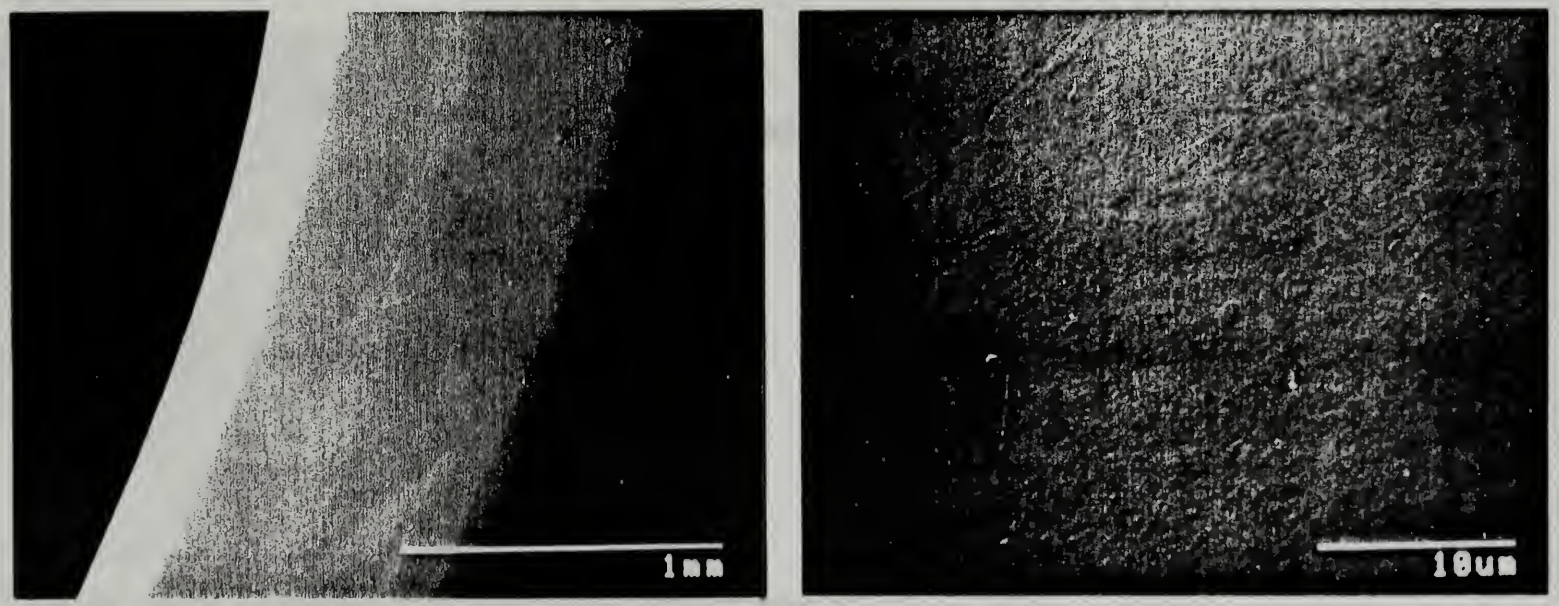


Fig. 16

AY–Si_3N_4 EXHAUST SEAT
(vs. STELLITE–6 VALVE)



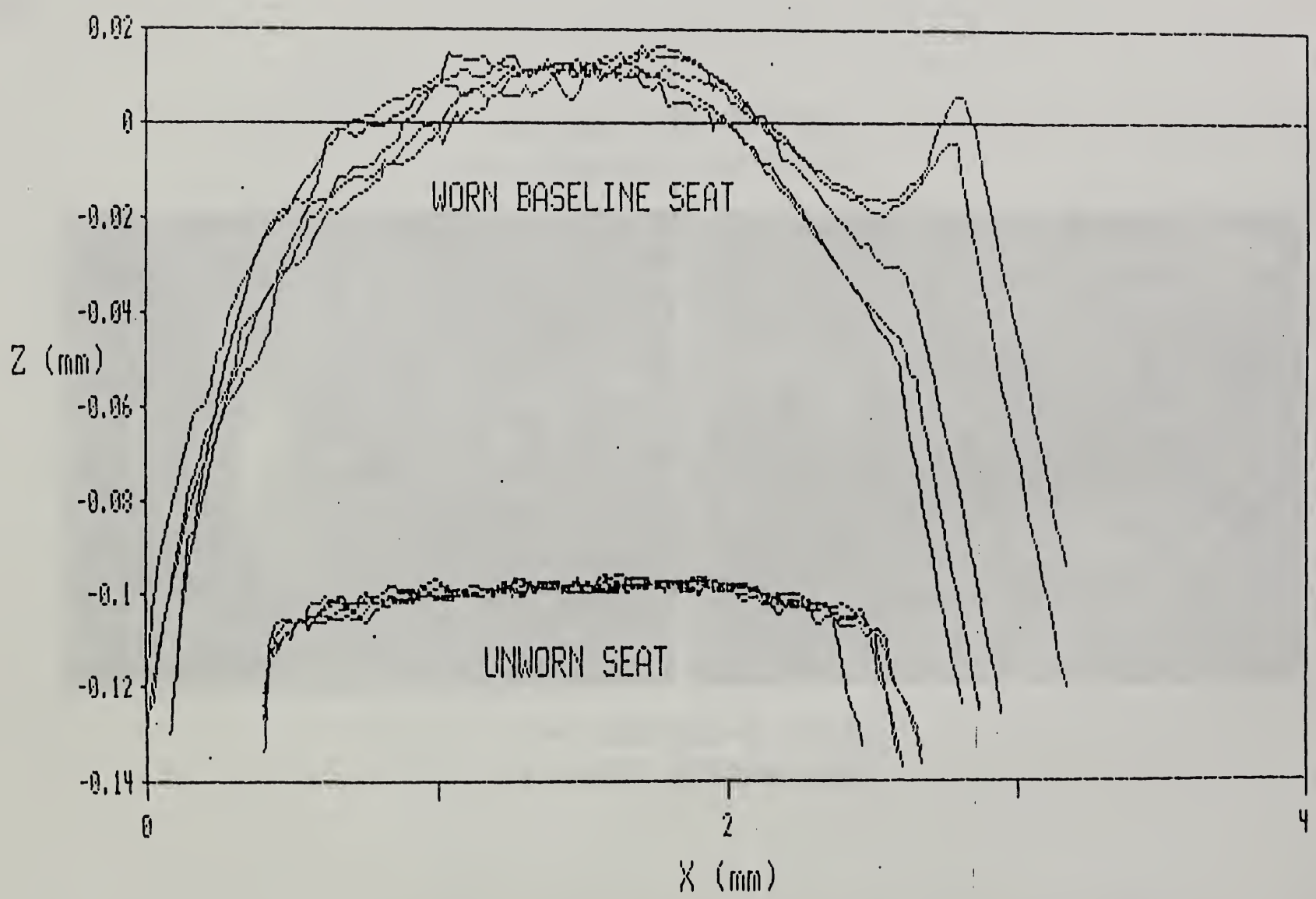
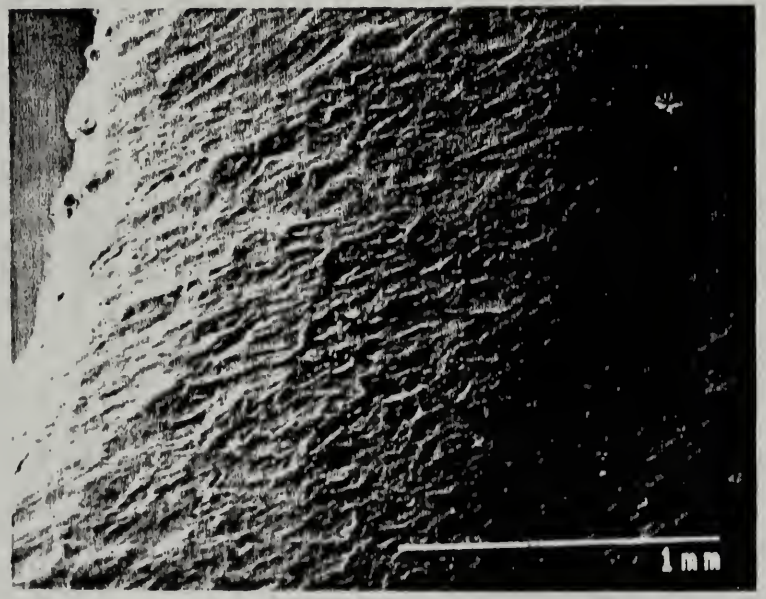


Figure 17: Profiles from both worn and unworn eatonite (baseline) valve seats (Note that the profile of the unworn seat is displaced downwards for clarity.)

Fig. 18

EATONITE INTAKE SEAT



EATONITE EXHAUST SEAT

Figures 13 and 14 show surface profiles taken from around the contact area on both used and unused ceramic seat inserts. The dimensions of the used ceramic seat inserts were still within the tolerances originally specified, so no quantifiable wear had taken place. The only visible evidence of wear was a slight bevelling of the normally sharp corners at the upper and lower edges of the seat. Photomicrographs taken using the SEM show some minor pitting of the silicon nitride seat used in conjunction with Tribaloy 800, as shown in Fig. 15. Although insignificant when compared to the wear on the metallic counterface, this phenomenon may effect the long term durability of the seat insert. No such pitting is visible when silicon nitride is coupled with Stellite 6 (Fig. 16), probably due to the lower hardness of that superalloy (Fig. 12). A selection of profiles from around the worn surface of the baseline (Eatonite) seat are plotted in Fig. 17, along with the profile of an unworn seat for comparison. During the 164 hours that the metallic seat was in the engine, substantial deformation of the contacting surface occurred, which may lower the valves effectiveness. Furthermore, the topography of the seat is not consistent around its circumference, possibly resulting in a poor seal as the valve rotates. Photographs of the worn surface from both the inlet and exhaust Eatonite seat inserts (Fig. 18) show that this deformation was caused by plastic flow and material removal. Thus, the topography of all the metallic surfaces examined (both valves and seat inserts) is dominated by plastic deformation, which precludes the observation of the effects of other wear processes. If the severe plastic flow was indeed caused by the overspeed condition, mechanisms such as chemical degradation, may have a significant effect on the surfaces under normal operation.

Lubricant Degradation

Samples of used engine oil were analyzed for the presence of metals and oxidation products using Inductively Coupled Plasma (ICP) analysis and Infrared (IR) Absorbance spectroscopy respectively. These analyses were conducted to determine the level of severity to which the lubricant was subjected.

The results of the metals analysis are presented in Table 6. The metals in the upper portion of the table relate to the trace metals that might come from wearing components in the engine such as the valve coatings. One exception is molybdenum, which is sometimes used as part of an antifriction/antiwear package. Most of these metals remained at a steady low value throughout the test. Iron, however, increased from 28 to 58 ppm during the first 250 hours of the test. After the 250 hour oil change iron dropped to 9 ppm, then rose to 24 ppm, and stayed near this level for the rest of the test. These values for iron are relatively minor and do not indicate a tremendously high wear or corrosion situation. In addition, iron is present in many parts of the engine. It is therefore difficult to attribute even a large jump in iron concentration to a problem with a single engine component such as a valve coating. Copper and lead values appear to rise initially, however, after the 250 hour oil change, they remain at low, steady values. Usually, increases in these two metals are

Table 6: Results of Total Metals Analysis

Engine Hours	6	50	125	250	258	375	443	453	581
Element	Parts Per Million								
Aluminum	2	2	2	1	0	1	0	1	1
Chromium	1	2	1	2	0	0	0	1	1
Copper	5	6	10	30	5	9	4	6	5
Iron	28	32	40	58	9	24	18	31	27
Lead	8	8	14	16	0	0	0	3	5
Molybdenum	0	0	0	0	0	0	4	11	17
Nickel	0	0	0	0	0	0	0	0	0
Silicon	6	5	5	4	0	1	2	3	3
Tin	2	1	1	2	0	0	4	4	4
Barium	7	6	8	8	1	1	2	10	25
Boron	6	1	2	2	1	1	3	27	132
Calcium	956	976	1032	1007	1102	1214	1130	1190	1212
Magnesium	40	4	5	6	1	3	11	156	467
Phosphorous	366	338	336	309	271	309	302	481	787
Zinc	307	272	285	282	307	362	376	616	1024
				*			**		

* Oil was changed after 250 hours
** Engine was rebuilt at 417 hours

associated with wear and/or corrosion of the copper-lead bearings used in the engine. The values observed do not indicate a problem.

The lower portion of the Table shows elements usually attributed to the lubricant formulation. Barium, Magnesium and calcium are blended into the lubricant as part of the detergent/dispersant package, while zinc and phosphorous are components of the anti-wear additives. Boron could be associated with either the antiwear components or the detergent/dispersant package. Many of the components associated with the lubricant formulation seem to increase near the end of the test. To examine this more closely, metals associated with the lubricant formulation (including molybdenum) are plotted as a function of engine operation time, in figure 19. In order to plot the data on a single graph, the concentration of several metals were re-scaled by dividing by ten. These metals are noted in the legend as (x10) values. All of the metals plotted except calcium have a sudden increase toward the end of the test. These increases range from doubling (P, Zn, Mo) to over an order of magnitude increase (B, Ba, Mg). This behavior is quite unusual and may reflect either a problem developing in the lubricant, or a sampling difficulty combined with precipitation of selected additives in the oil.

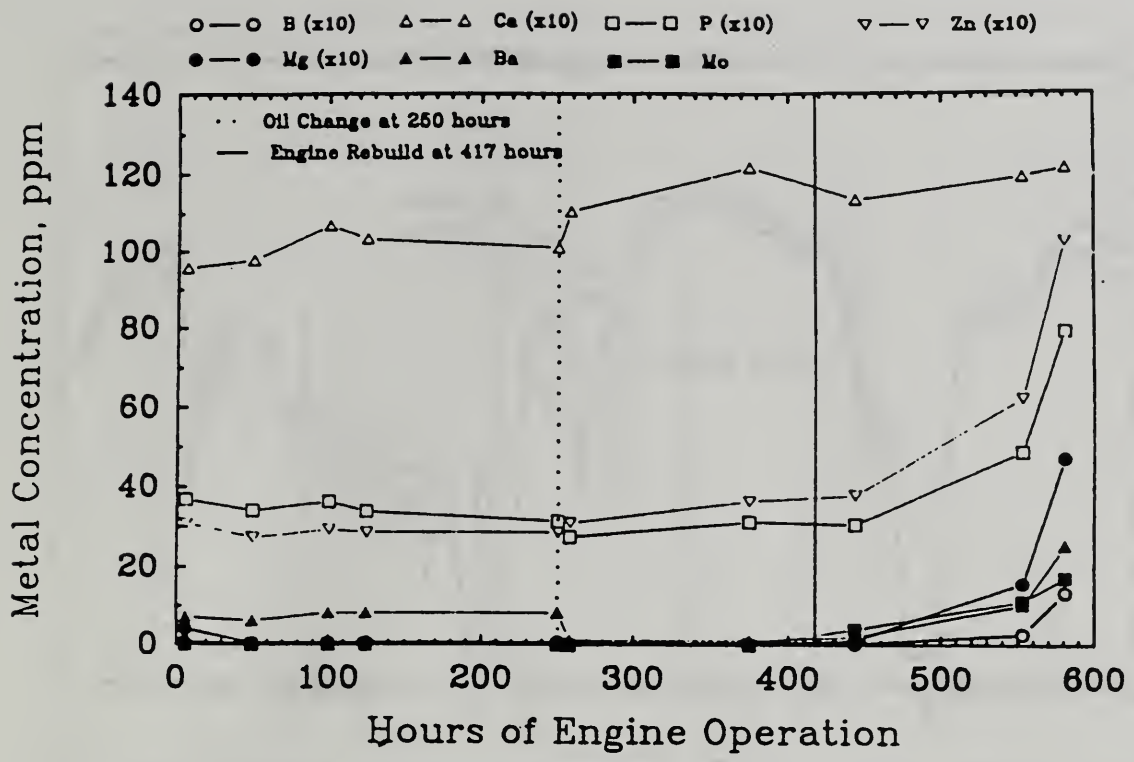


Fig. 19: Trace Metal Analysis of Used Engine Oil.

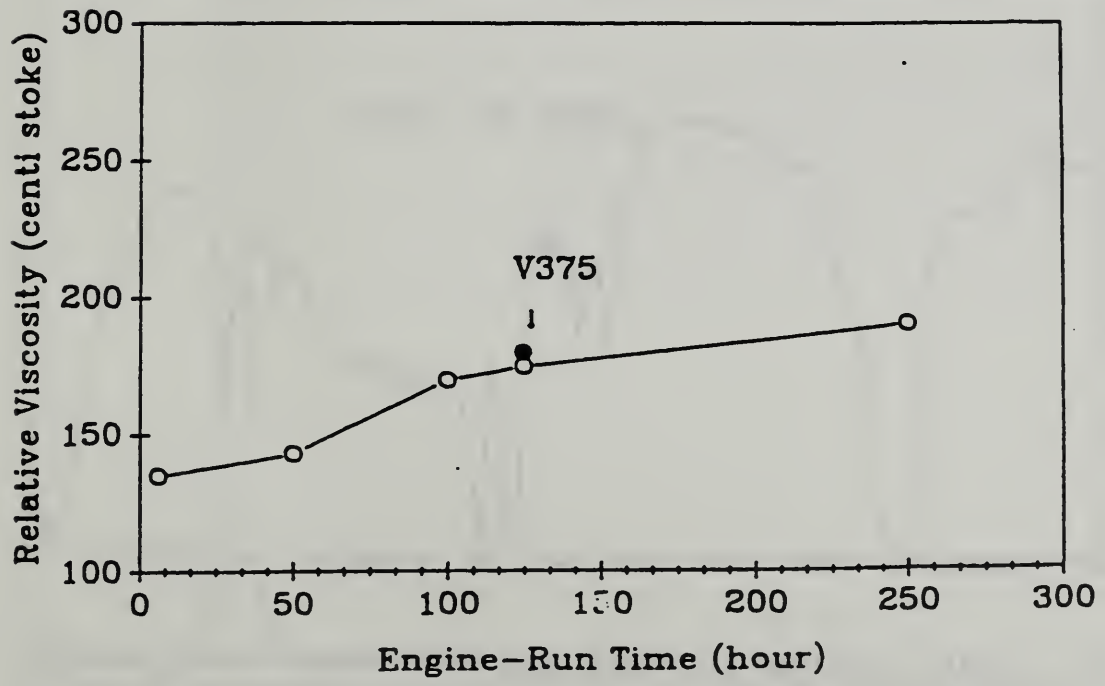


Fig. 20: Relative Viscosity of Pegasus-485 as a Function of Engine-run Time.

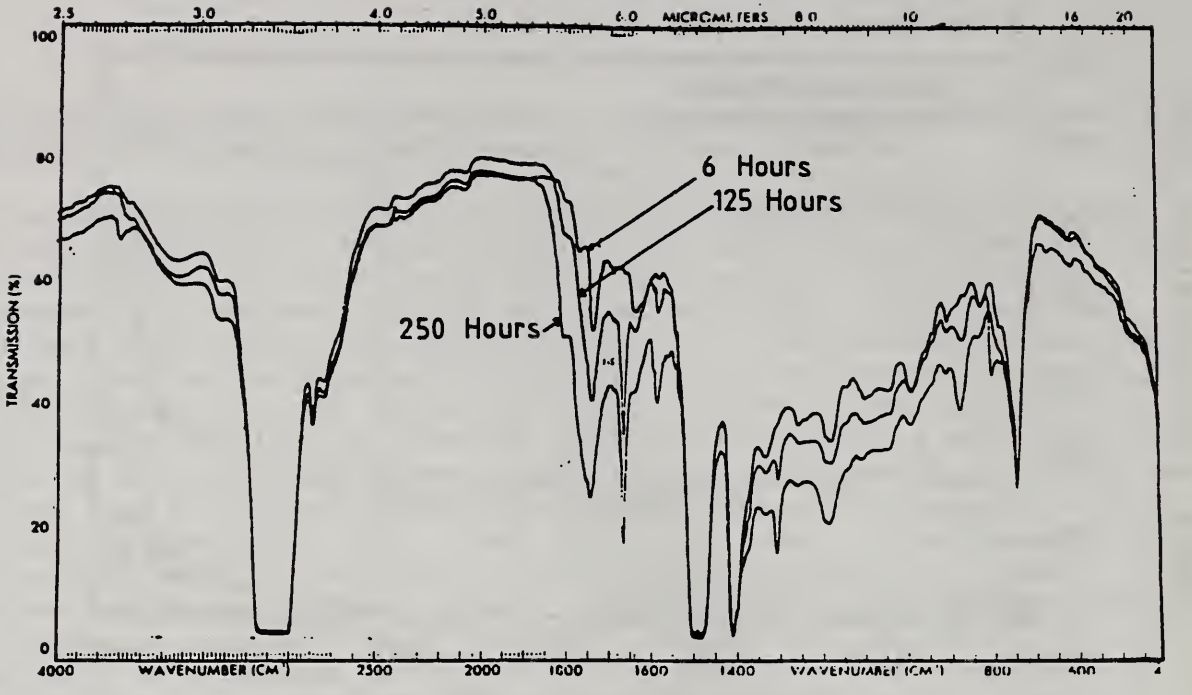


Fig. 21: IR Spectra for Used Engine Oils From First 250 Hour Oil Change Cycle.

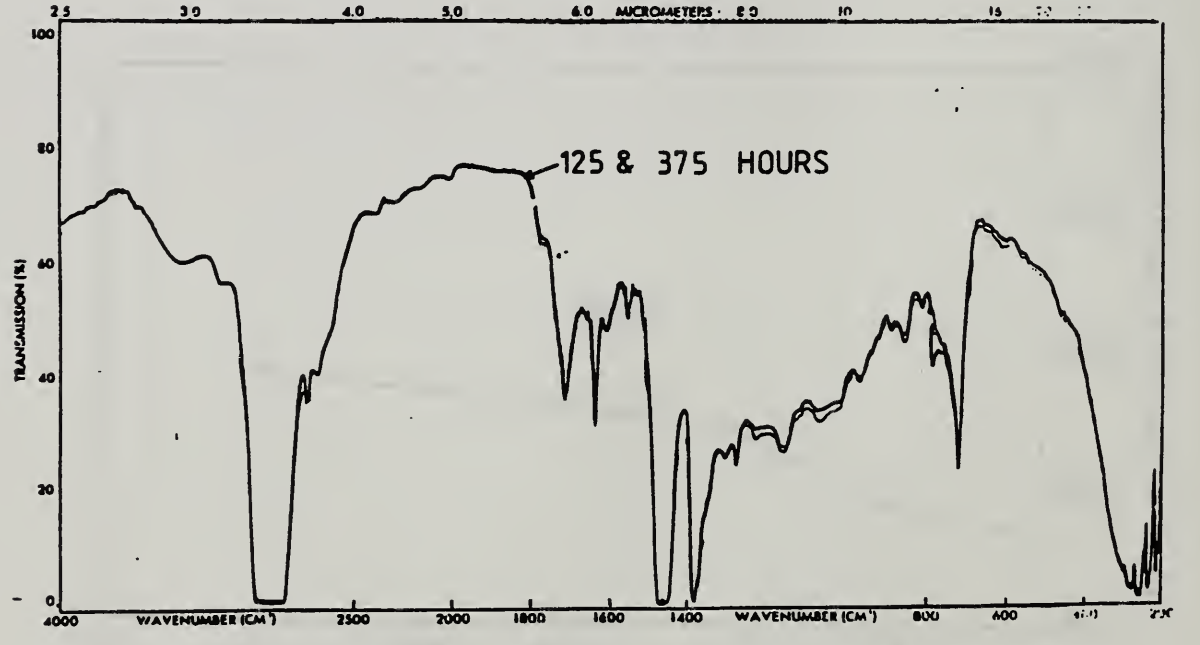


Fig. 22: Engine Oils From First and Second Oil Change Cycles Compared Using IR Analysis.

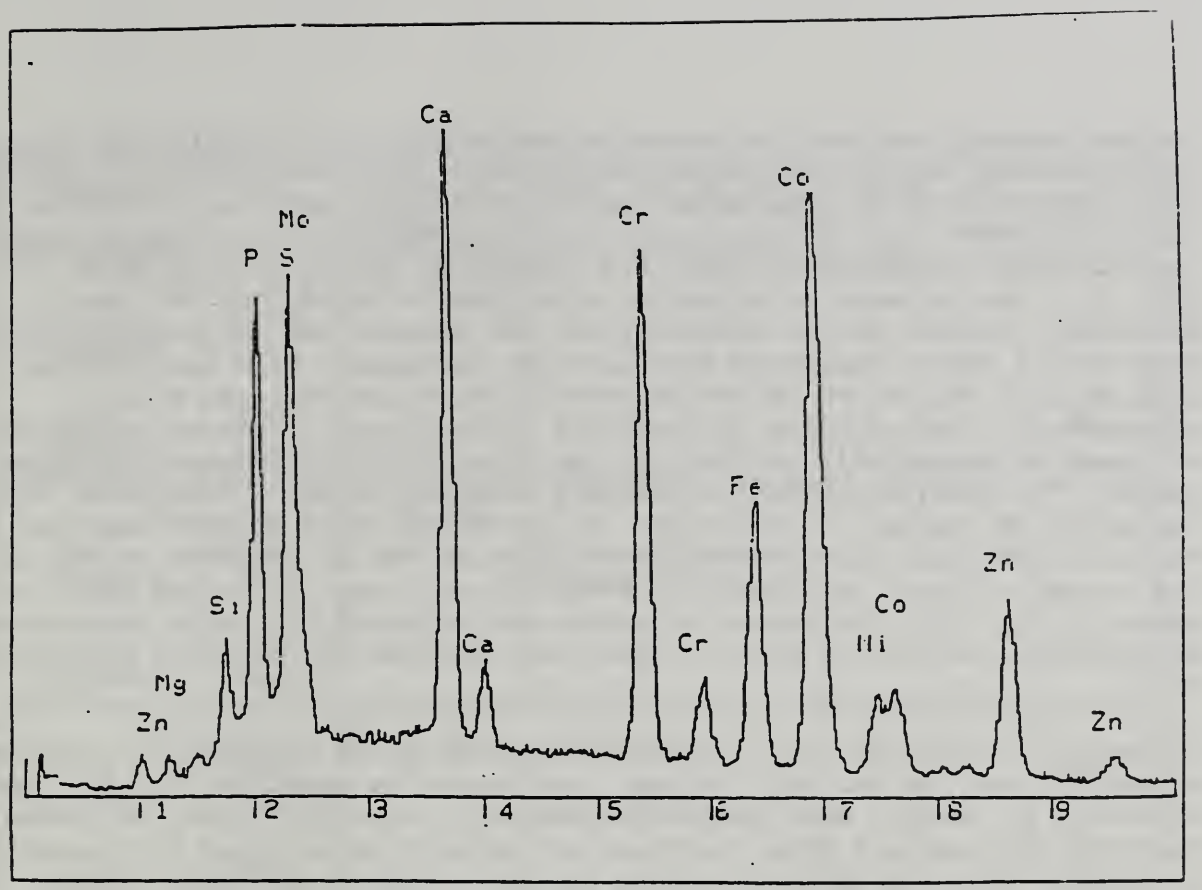


Fig. 23: EDX Analysis of Triballoy-800 Intake Valve (Vs. Sialon Seat)

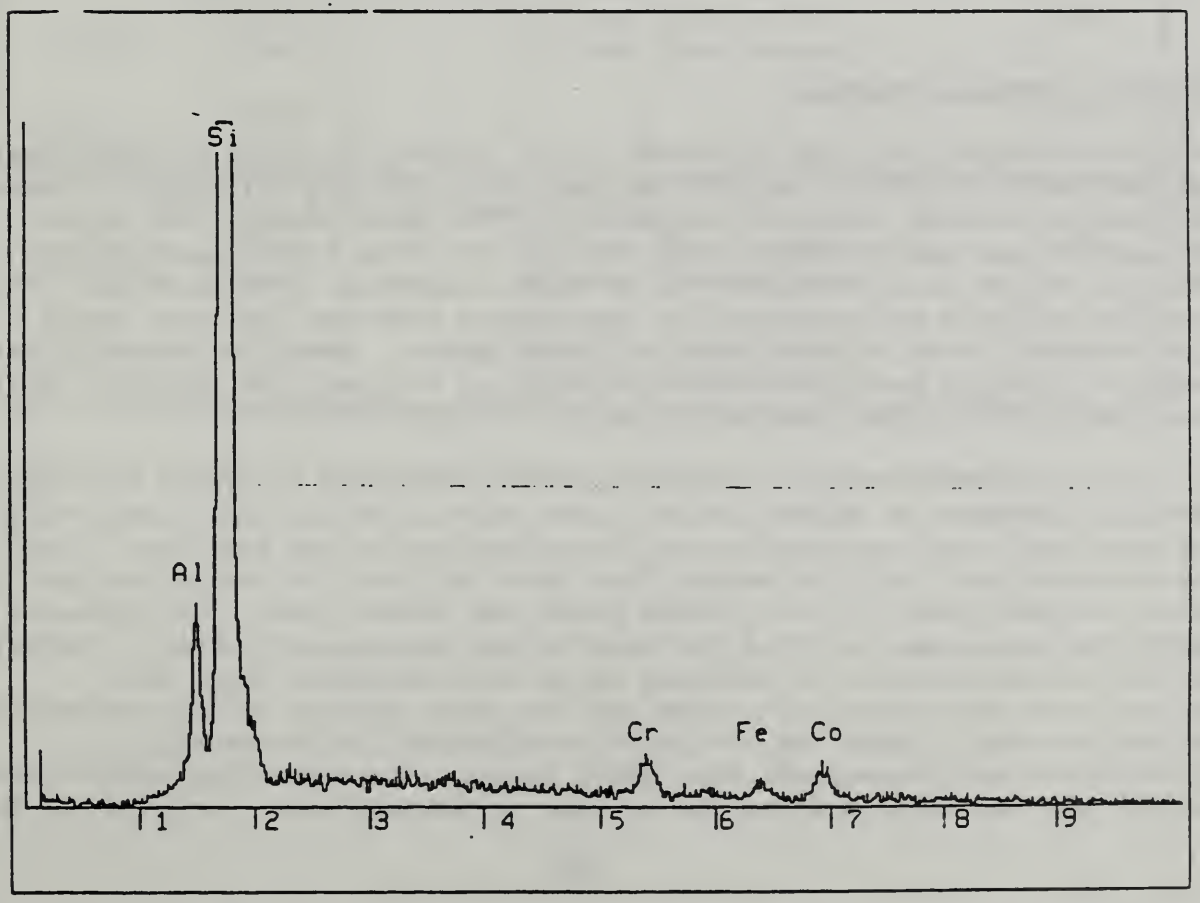


Fig. 24: EDX Analysis of Sialon Intake Seat (Vs. Stellite-6 Valve)

IR spectroscopy was used to determine the severity of oxidation on the oil. Qualitatively, all of the samples exhibited significant amounts of carbonyl (C=O) and nitro (N=O) absorbance which reflects oxidation and nitration of the lubricant. This is most easily seen with the series of samples taken from the engine before the first oil change (at 250 hours), as shown in Fig. 21. The increase in oxidation with time is evident as the test proceeds. Because of the complexity of the samples and the possibility of band shifts due to component interactions, two peaks, 1710 and 1635 cm^{-1} were used to follow the oxidation attributed to carbonyl and nitro absorbances. The addition of fresh oil at the change interval brings the oil back to essentially the initial low level of IR absorbance for these peaks. The level of oxidative severity seems to be quite consistent from one phase of the test to the next. As an example, the IR spectrum from 125 hours of the first oil interval is the same as the IR spectrum of the from the second 125 hour interval (375 hours of total engine running time) as shown in Fig. 22. The levels of oxidation indicated by the IR spectra are significant, but not as high as have been observed for severely degraded oils.

Oxidation of the used oil is also reflected by a 40% increase in lubricant viscosity over the initial 250 hour test cycle, as shown in Fig. 20. The viscosity of the 375 hour sample is denoted by a solid circle, and shows that the 125 hour oil from the first oil cycle is equivalent in viscosity to the 125 hour oil from the second oil cycle (375 hours total engine operation). The lubricant does not appear to have experienced any oxidative "break point" commonly associated with failing lubricants.

Surface Chemical Analysis

Surface chemical analyses performed on the valves and seats included Energy Dispersive X-ray (EDX) analysis (as part of an SEM system), micro-focussed reflection Fourier Transform Infrared (μ-FTIR) spectroscopy, and micro-focussed Raman spectroscopy. EDX analysis provided a semi-quantitative measure of the near surface ($\approx$ 10 μm depth) elemental concentration. Since the EDX analysis was performed in conjunction with the SEM, very small (micrometer) sized regions could be investigated. Raman spectroscopy was used to identify specific chemical species on and near the surface. μ-FTIR was used to determine chemical structures on the surfaces.

A typical EDX spectrum of a valve surface is provided in figure 23. Iron, cobalt, chromium and nickel are from the valve coating itself, but calcium, phosphorous, zinc, and sulfur are from additives in the lubricant. The observation that additive metals find their way onto the valve surface confirms that some oil does indeed reach the contact area. The presence of additive metals was verified for both intake and exhaust valves. Analysis of the ceramic valve seat surfaces using this technique (Fig. 24), established that chromium, cobalt and iron were present on certain portions of the contact. These are the major constituents in the metallic counterface and demonstrate that metal transfer was occurring between the valves and the ceramic seats due to lack of lubrication. Variation in the

Location	Area.	Graphitic Carbon	SiO_2	Fe_3O_4	$PO_4^=$	$SO_4^=$	M-O Bond	Wear Vol.
Tribaloy 800 Vs. Sialon								
1-3 (intake)	Stem							400
	Seat	✓						
1-4 (Exhaust)	Stem		✓				✓	50
	Seat	✓	✓				✓	
Stellite 6 Vs. Sialon								
1-8 (Intake)	Stem		Strong Fluorescence					150
	Seat		Strong Fluorescence					
1-7 (Exhaust)	Stem				✓	✓		75
	Seat		✓				✓	
Stellite 1 Vs. Eatonite (Baseline)								
2-3 (Intake)	Stem							400
	Seat		Strong Fluorescence					
2-4 (Exhaust)	Stem		✓				✓	25
	Seat	✓					✓	
Tribaloy 800 Vs. Silicon Nitride								
3-3 (Intake)	Stem		Strong Fluorescence					200
	Seat		Strong Fluorescence					
3-4 (Exhaust)	Stem				✓	✓	✓	25
	Seat	✓						
Stellite 6 Vs. Silicon Nitride								
3-8 (Intake)	Stem		Strong Fluorescence					175
	Seat		Strong Fluorescence					
3-7 (Exhaust)	Stem		Strong Fluorescence					75
	Seat		Strong Fluorescence					

Table 7: Results From Laser Raman Analysis of Valve Deposits

composition and volume of deposit around the contact area was noticed on several valve seat inserts. The cause of this variation is unclear, but may be related to either the gas flow pattern through the valve port, or blow-by through a badly seated valve during compression and combustion cycles.

Raman spectroscopy could only be applied to half of the specimens due to strong fluorescence on some samples. Of the samples that were analyzed, evidence was found for various amounts of graphitic carbon, SiO_2, phosphate, sulfate, and M-O bonds where M represents various metals (i.e. an oxide layer). Individual spectra are presented in appendix 4, and data are summarized in Table 7. It is difficult to draw many conclusions with this data because the technique was only successful for half of the samples, however some trends may be seen. Specifically, these results indicate that a correlation may exist between the presence of graphitic carbon and metallic oxides and the low wear rate achieved by specimens 1-4, 1-7 and 3-4. This is consistent with evidence in the literature that both of these substances are known to provide some surface protection under certain conditions. Furthermore, valve 1-7 which experienced greater wear than the remaining exhaust valves has no measurable graphitic carbon present on the surface. The presence of phosphate and sulfate compounds on the surface of some of the samples supports previous EDX evidence that lubricant reached the valve face during operation. The reason for the variation in the composition of the deposits observed between the valves is unclear, although the conditions prevailing within each cylinder immediately before conclusion of the test may have been a contributing factor. It would be worthwhile to carry out analysis on further specimens, both to obtain a better statistical average and to observe deposits formed under normal operating conditions.

FTIR analysis of the deposits on the valves and seats was unable to find any conclusive reaction products other than oxidized organic compounds with infrared absorbance in the carbonyl and hydroxy group regions. These absorbances are normal for oxidation products expected to contain a complex mixture of carboxylic acids, aldehydes, and alcohols.

Chemical Analysis of Solvent Extraction of Valve Deposits

In order to further analyze the deposits on the valves, a solvent extraction was carried out on each of the valves. Tetrahydrofuran (THF) was used to dissolve some of the deposits from each of the valves. Part of the extract was used for dispersive transmission infrared (IR) spectroscopy and part was used for Gel Permeation Chromatography (GPC).

In order to obtain IR spectra, the samples had to be evaporated almost to dryness to remove most of the THF solvent that would interfere with the analysis. This sample was then cast onto a cell and the rest of the solvent evaporated. IR spectra obtained using this procedure confirmed the previous finding of FTIR - that the dissolved component of the deposit contained a complex mixture of oxidized organic compounds containing carbonyl and hydroxyl groups.

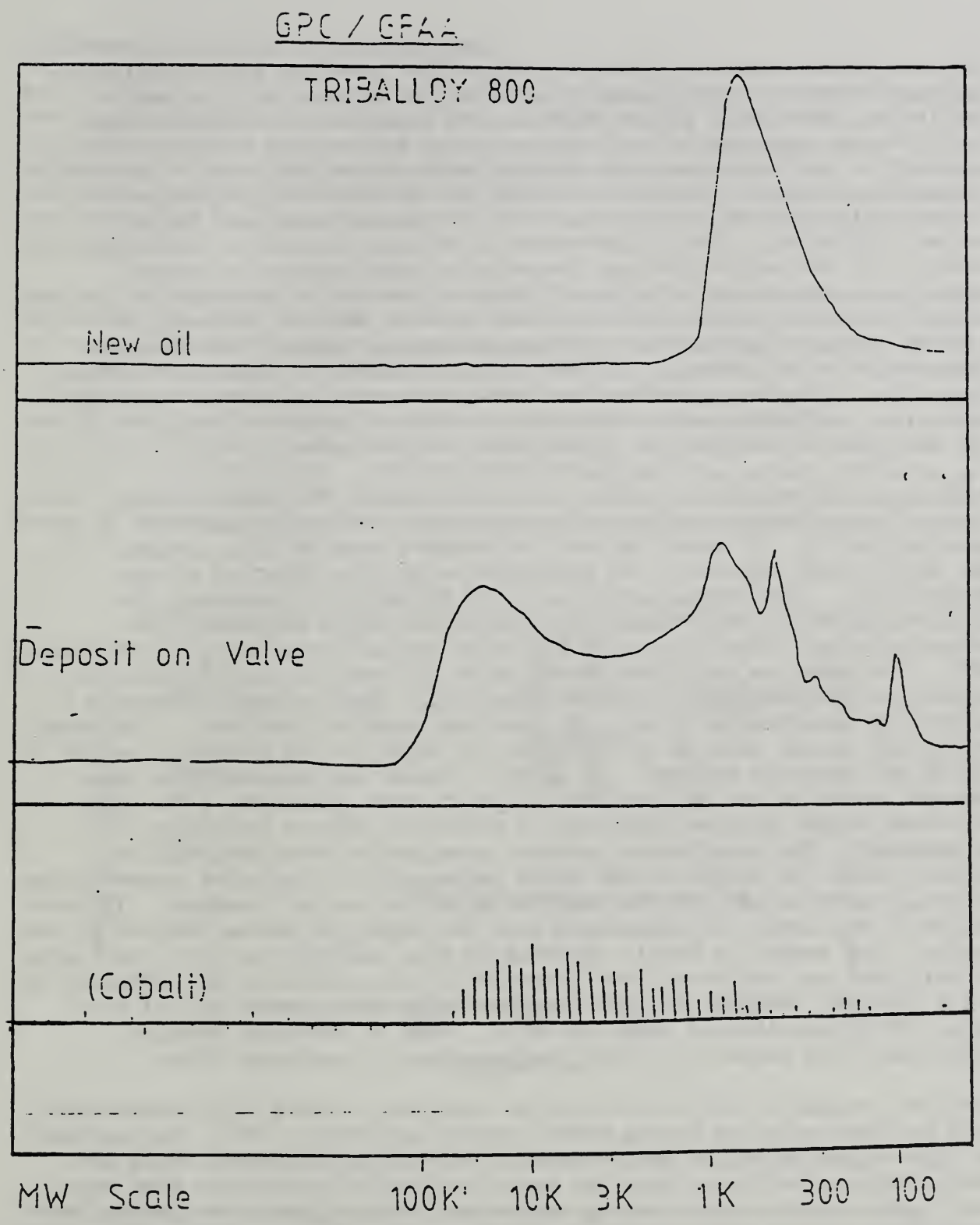


Fig. 25: GPC/GFAA Analysis of Deposits Dissolved From The Surface of Triballoy 800 Valve

GPC is a liquid chromatographic technique that provides semi-quantitative information on the molecular size distribution of species in a sample. Applied to lubricants, it can indicate the approximate molecular weight distribution of lubricant oxidation products and provide insight on the severity of the environment to which a lubricant is subjected. One unique capability of the GPC apparatus at NIST is the ability to determine the concentration of metals associated with species eluting from the GPC column[5] (GPC-GFAA). This information is valuable because it indicates the severity of the metal-lubricant interaction with respect to surface corrosion. Many metals will react chemically with the lubricant to produce metalo-organic compounds. To a limited extent, this is necessary to provide adequate lubrication. In some instances however, the chemical interaction is too strong, and the lubricant serves to chemically attack the surface, leading to corrosion of the surface and a loss of structural integrity. GPC-GFAA analysis has the capability of determining whether or not the chemical interaction is adequate, or corrosive.

Samples of THF extracted deposit were subjected to GPC-GFAA analysis. A representative example of the results obtained using this analysis is provided in Fig. 25, which relates to deposits removed from specimen 1-3. The upper trace represents the molecular weight distribution of the original oil. The maxima occurs at ≈ 500 MW which is reasonable for a lubricating oil of this viscosity. The second trace represents the molecular weight distribution of the valve deposit from valve 1-3 (Tribaloy 800). The peaks on the right hand side of the spectra are compounds of similar molecular weight as the original oil. They probably represent a mixture of entrained original lubricant and oxidized lubricant. The large, broad peak to the left of the original oil peak is high molecular weight (≈ 20,000 MW) reaction product. In general, these are considered to form through oxidation and condensation-polymerization reactions. The high molecular weight observed indicates a relatively severe oxidizing environment. The lower trace contains a series of GFAA analyses for cobalt, where the height of the spike represents the relative concentration of cobalt associated with the selected molecular weight compound. In this instance, the cobalt is associated with the higher molecular species in the sample. The amount of cobalt observed in this analysis is quite low (parts per million) and indicates that corrosion of the cobalt by the lubricant is not a problem. Similar GPC-GFAA analyses were conducted on all of the other THF extractions of valve deposits. None of the other samples contained large amounts of cobalt metalo-organic compounds either.

Lubricant oxidation and polymerization reactions require high temperatures, such as those existing during normal engine operation. Thus, the presence of high molecular weight species on the valves, as determined using GPC-GFAA analysis, indicates that the deposits found on the valves must have been formed in the engine during operation. This supports the contention that some oil must have reached the valve head during operation, either by descending the valve stem, or as vapor produced by lubricant evaporating from the cylinder walls.

Performance Testing of Used Lubricant

Analytical tests (IR, viscosity, and metals) have indicated that oxidation and degradation of the lubricant has occurred during engine operation. One important question that arises is what effect does this change have on the performance of the lubricant? Specifically, what is the effect on the oxidation stability and antiwear capability of the oil? These questions were addressed by conducting oxidation and wear tests on the used lubricant.

The Thin Film Oxidation Uptake Test (TFOUT - ASTM D4742, 1989) measures the oxidation induction time of the lubricant under conditions which simulate the high-temperature oxidation processes in reciprocating engines. This test was carried out on a selection of oils from the initial 250 hour cycle in order to determine whether the oxidation stability of the oils had been significantly affected by its use in the engine. Samples of used oil taken at 100 and 250 hours were examined using TFOUT and the results compared to the unused oil (Fig. 26). The oxidation induction time after 100 hours of engine use is only 25% of that for the new oil, therefore engine operation seems to have significantly reduced the oil's oxidation stability.

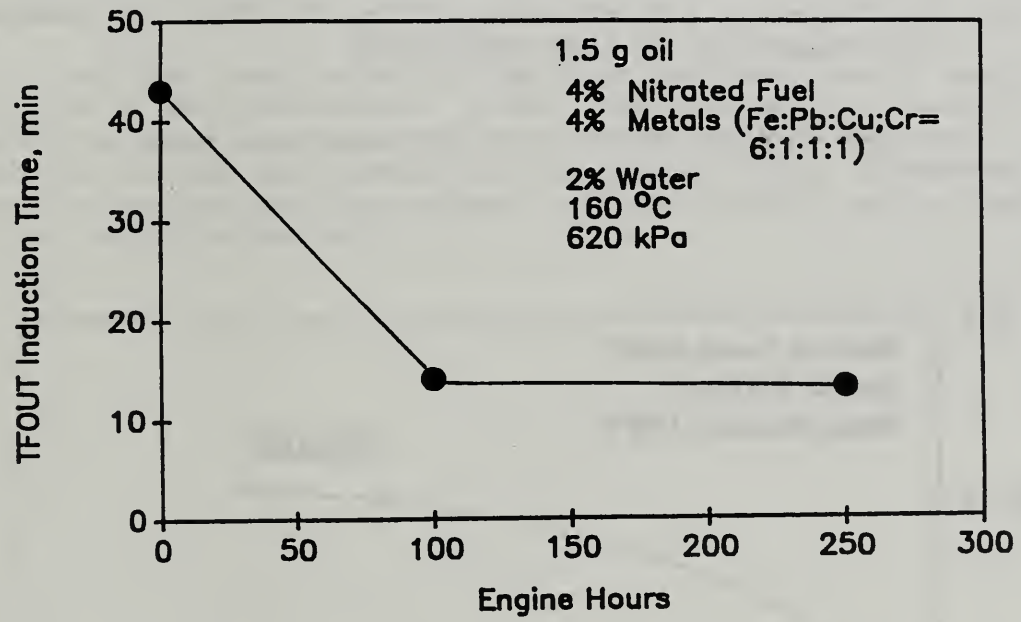


Figure 26: Results of TFOUT tests on new and used engine oils

The effect of lubricant degradation on wear was assessed by conducting ball-on-three-flat tests[6] on the used lubricant. Silicon nitride was used as the wear substrate since this was one of the important components in the valve/insert assembly. Test parameters are outlined in Table 8.

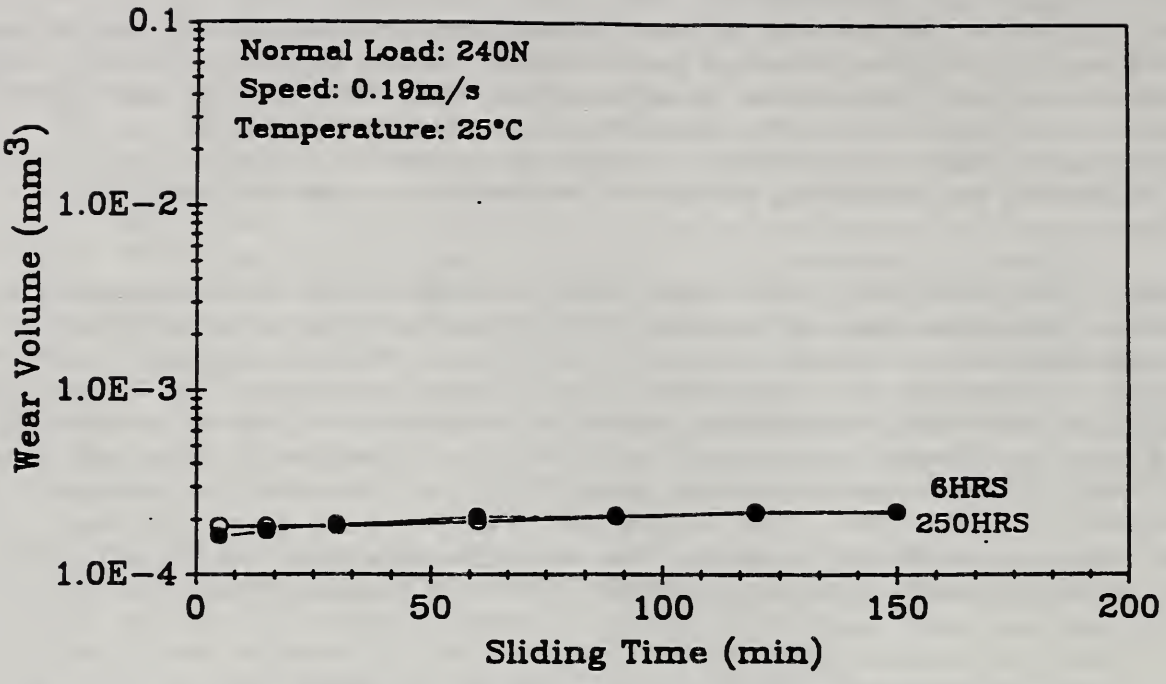


Fig. 27: Wear Valume as a Function of Sliding Time for Si_3N_4 Lubricated With Pegasus-485 at Room Temperature.

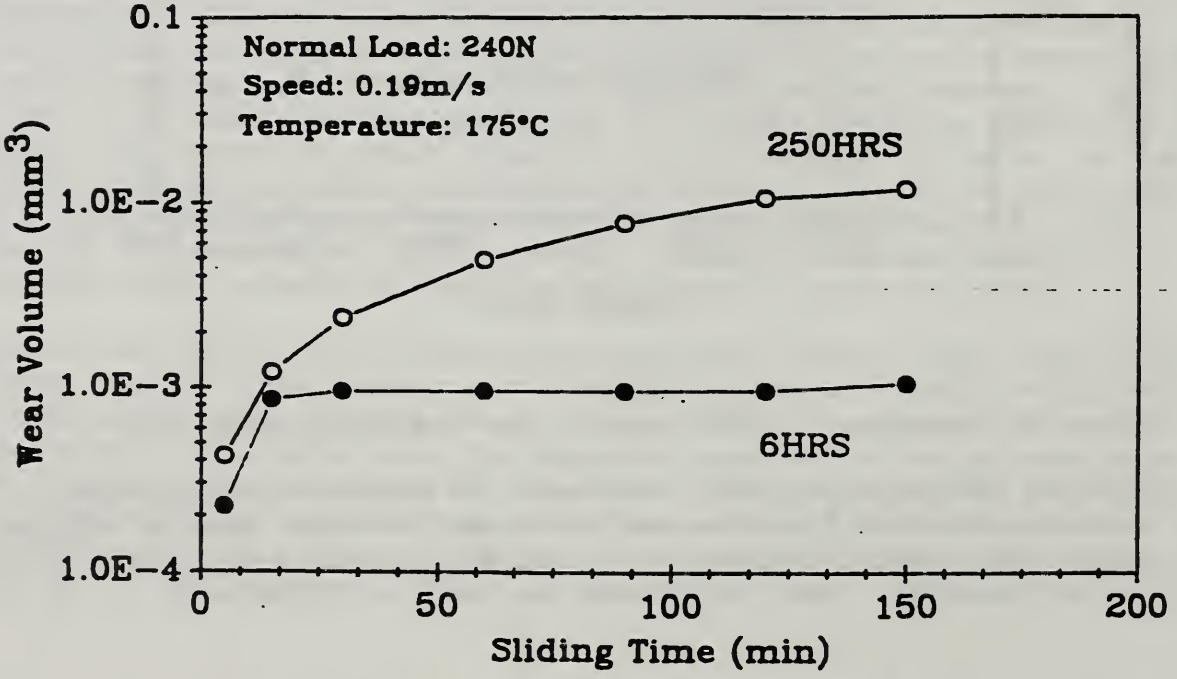


Fig. 28: Wear Volume as a Function of Sliding Time for Si_3N_4 Lubricated With Pegasus-485 at Elevated Temperature.

Table 8: Parameters Used During Wear Test

Parameter	Value	Units
Material	NBD-100	-
Normal load	240	Newtons
Temperature	25	Centigrade
	175	Centigrade
Speed	500	RPM
	(0.19)	(m/s)
Duration	0 - 150	Minutes

For tests carried out at 25°C lubricant degradation has little effect on wear, as illustrated in Fig. 27. The two lines coincide almost exactly and little wear occurred over the complete test duration for either 6 hour or 250 hour oil. To gauge the effect of temperature on the wear process, the above tests were repeated at a bulk oil temperature of 175°C. The wear observed with both oils (Fig. 28) has increased above that measured at 25°C, however, the 250 hour used oil has significantly higher wear than the 6 hour oil.

This initial wear study serves to highlight the importance of lubricant degradation on wear performance. A more complete analysis would be necessary to fully understand the relationship between lubricant degradation and wear performance for the complete range of materials utilized in natural gas fired engines (silicon nitride, sialon, Stellite 1, Stellite 6 and Tribaloy 800).

Conclusion

The new material combinations tested represent a considerable improvement, on both intake and exhaust valves, when compared to the baseline valve/seat combination, which is the industry standard.

The best intake valve/seat combination was Stellite 6 coupled with sialon by Norton/TRW, although several other material combinations were within the range of experimental error. The most effective exhaust valve/seat combination was Tribaloy 800 coupled with silicon nitride by GTE Eaton.

Substantial wear occurred on each of the inlet valves, caused primarily by lack of lubrication and mechanical deformation of the metallic surfaces. Accidental overspeed which terminated the test may have been a contributing factor, although its net effect on the wear volume is unclear. Appreciably less wear was measured on the exhaust valves than on the intake valves. This appears to be due to the extra protection provided by a layer of deposit on the exhaust valve face.

The dimensions of the ceramic valve seats were still within the originally specified tolerance, so no measurable wear existed, representing a major improvement over the Eatonite (baseline) seats which were worn and had lost their original shape.

The results obtained from the present abbreviated engine test would suggest that improved lubrication is required at the valve seat. This is especially important for the intake valves. However, increased wear resistance in the valve materials would also alleviate the tribological problems at the contact, without creating the technological difficulties inherent in valve seat lubrication.

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APPENDICES

APPENDIX 1

3-D Surface Maps of Valve Faces

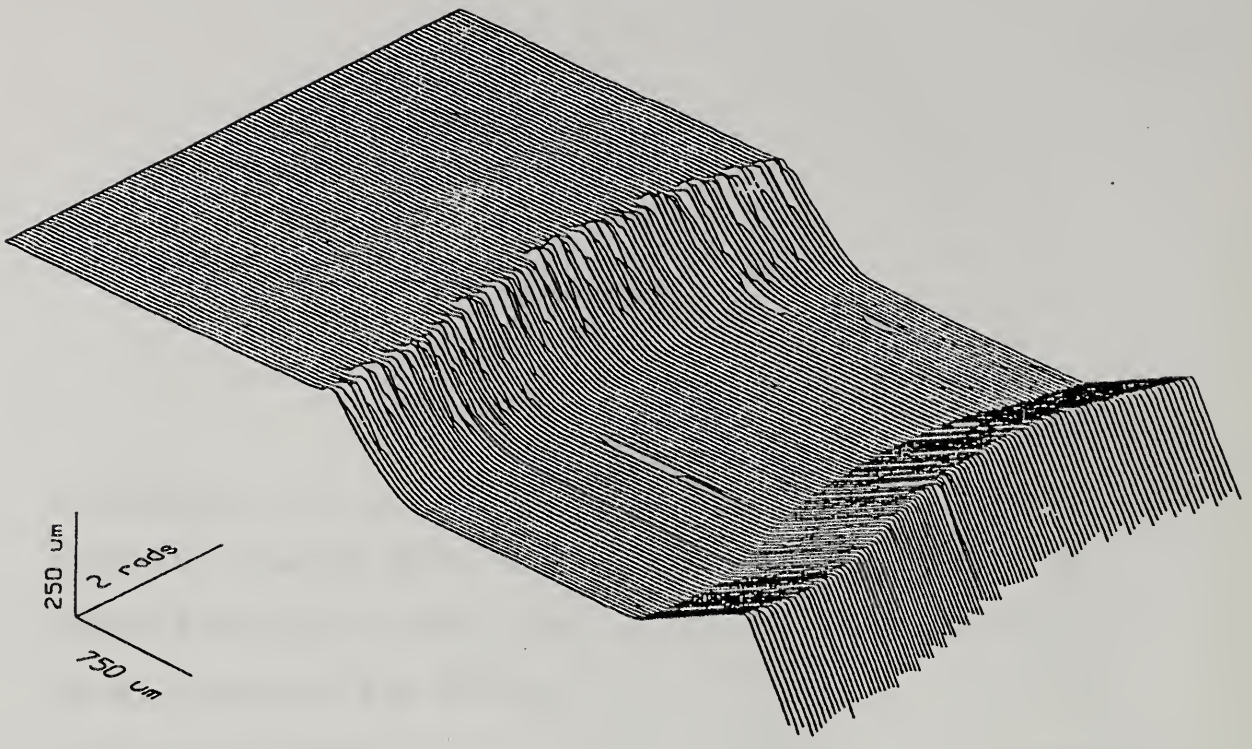

Fig. A1.1: Surface Map of Tribaloy 800 Inlet Valve (Vs. Sialon)

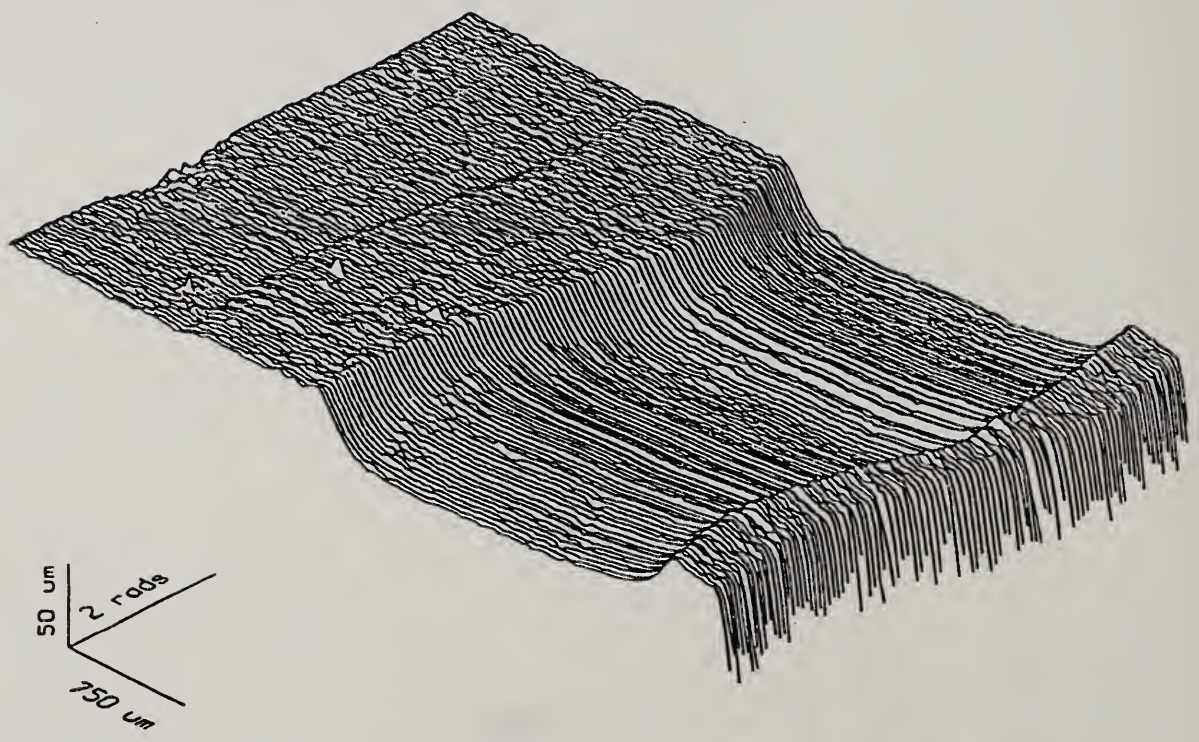

Fig. A1.2: 3-D Surface Map of Tribaloy 800 Exhaust Valve (Vs. Sialon)

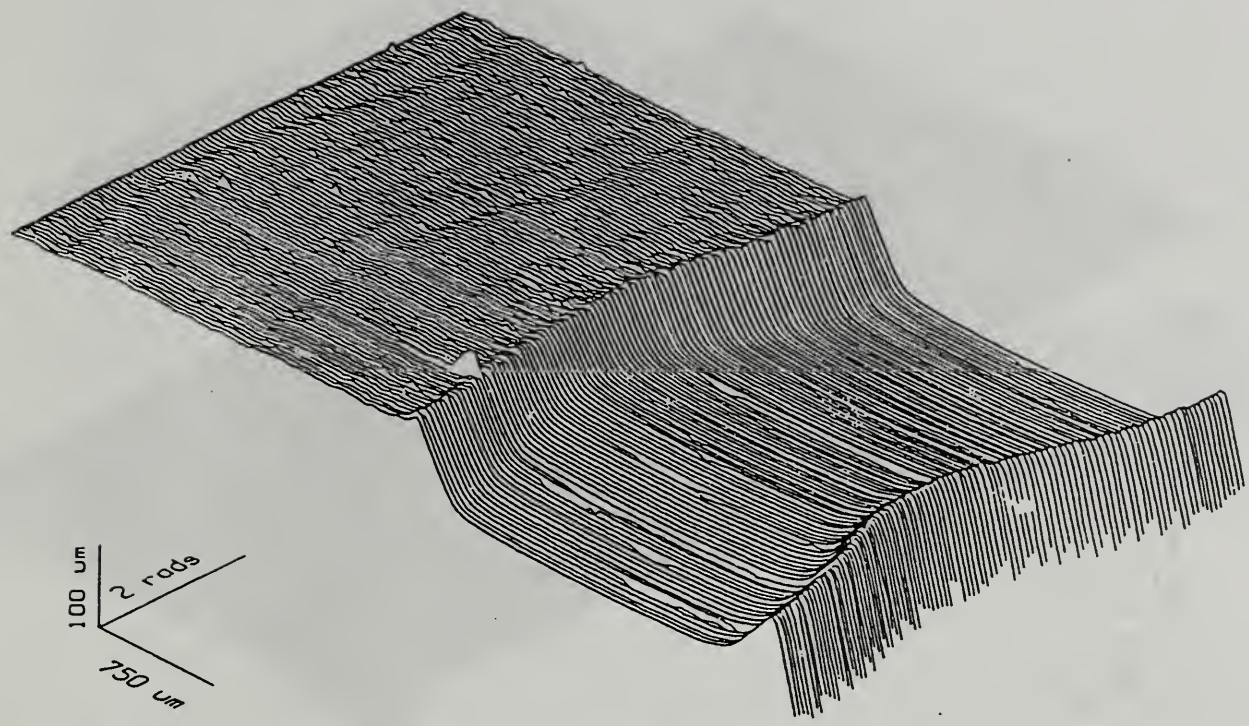

Fig. A1.3: 3-D Surface Map of Stellite 6 Inlet Valv e (Vs. Sialon)

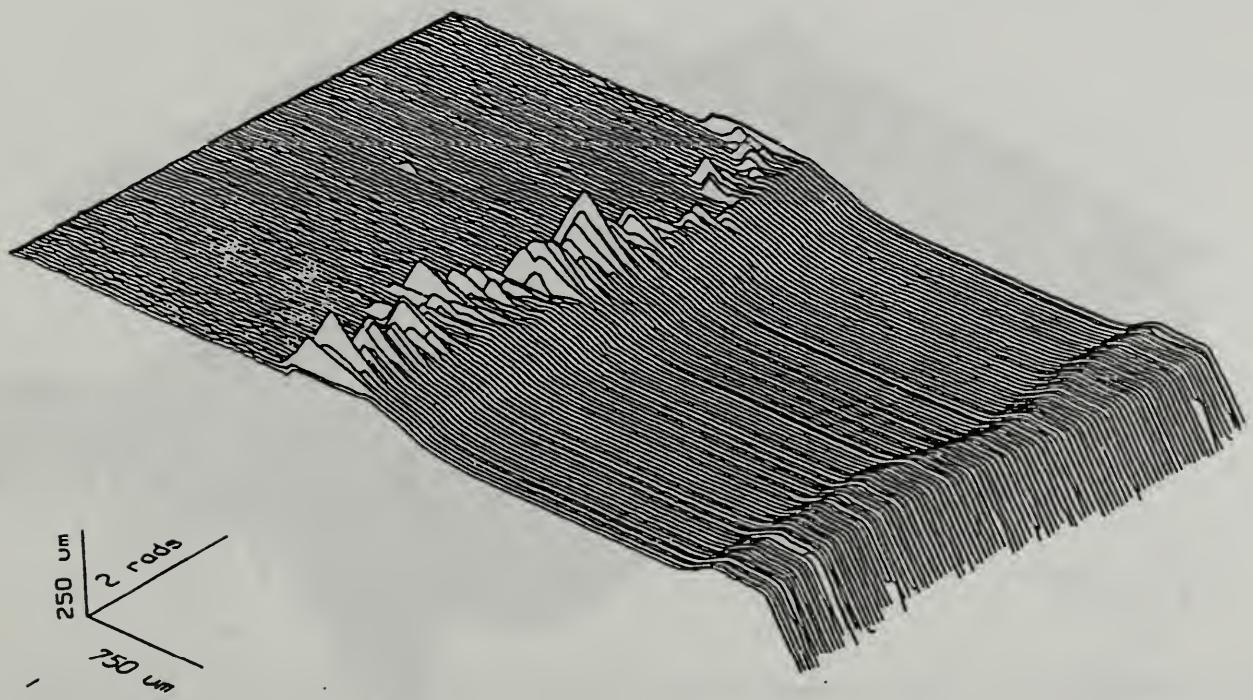

Fig. A1.4: 3-D Surface Map of Stellite 6 Exhaust Value (Vs. Sialon)

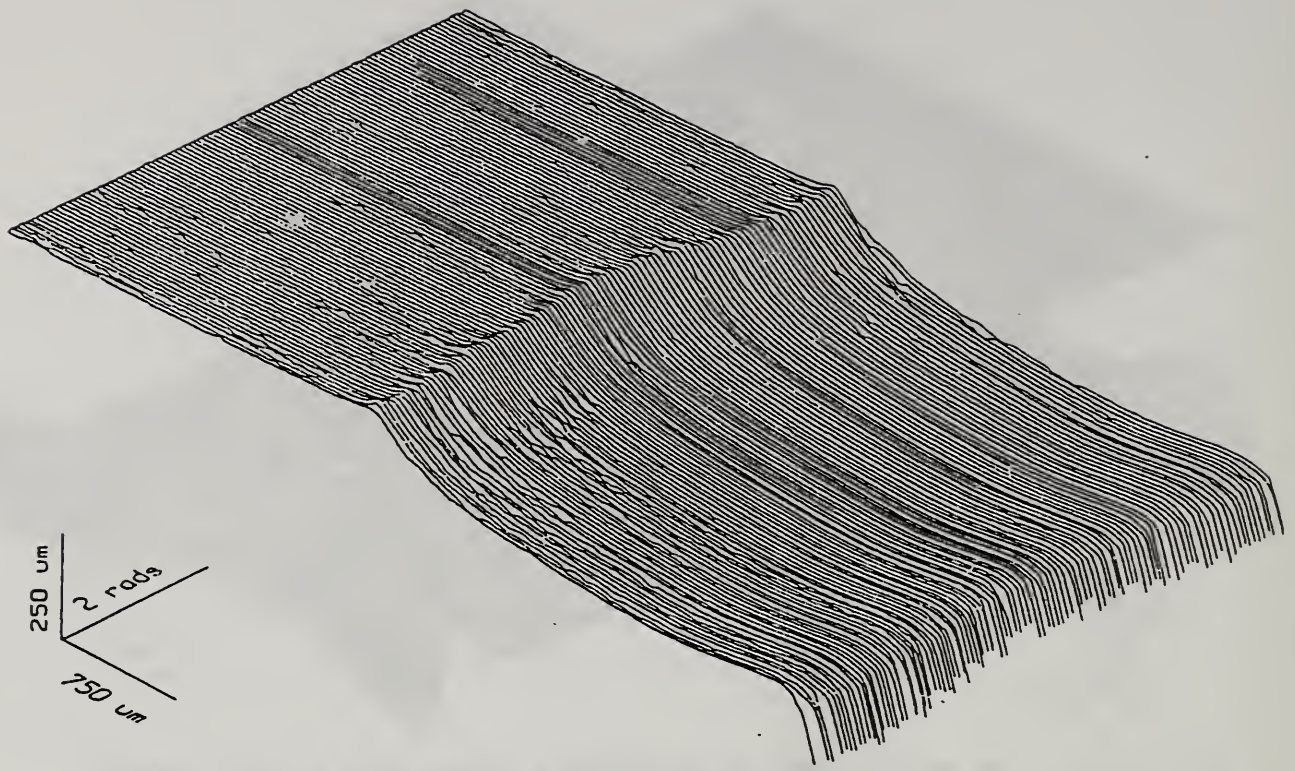

Fig. A1.5: 3-D Surface Map of Stellite 1 Inlet Value (Vs. Eatonite)

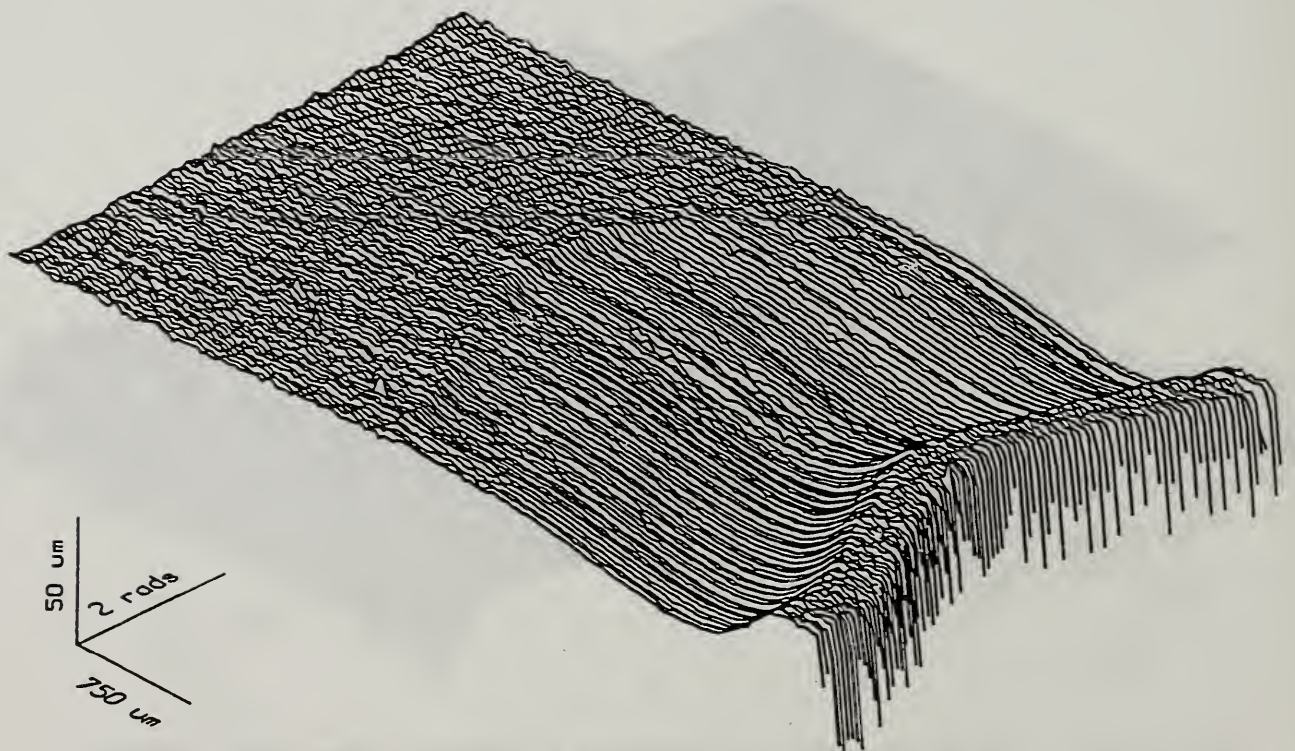

Fig. A1.6: 3-D Surface Map of Stellite 1 Exhaust Valve (Vs. Eatonite)

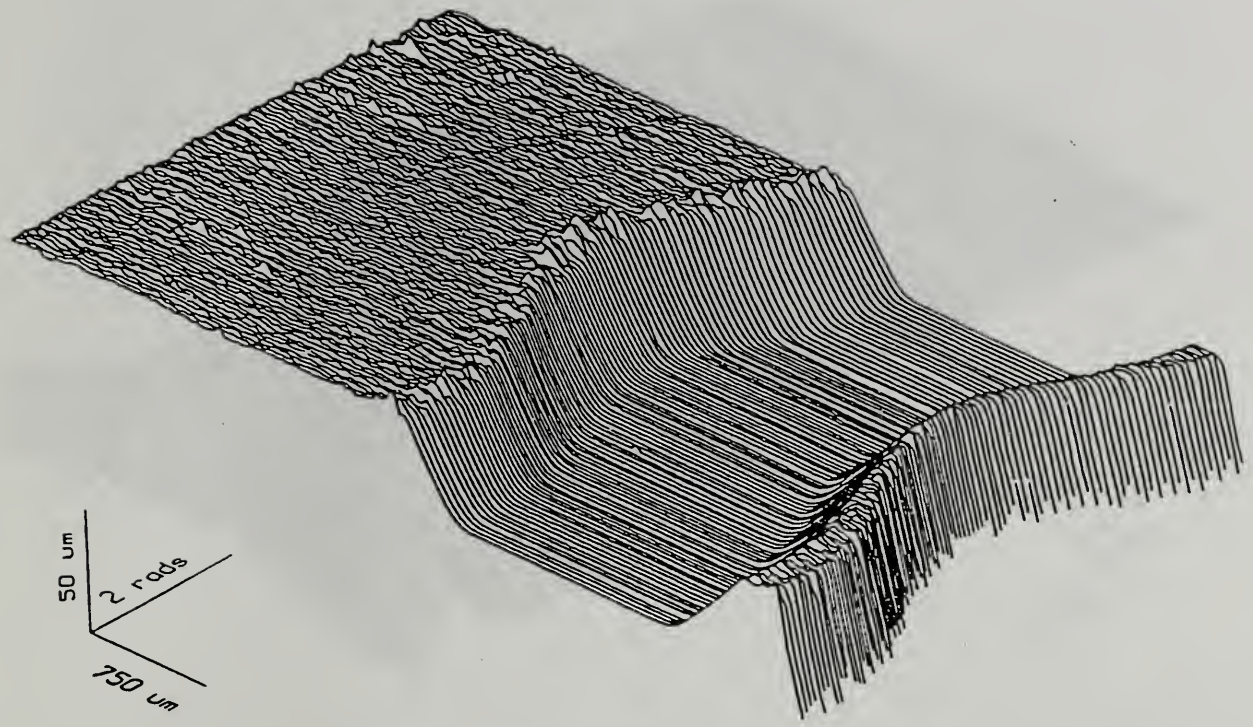

Fig. A1.7: 3-D Surface Map of Tribaloy 800 Inlet Valve (Vs. Silicon Nitride)

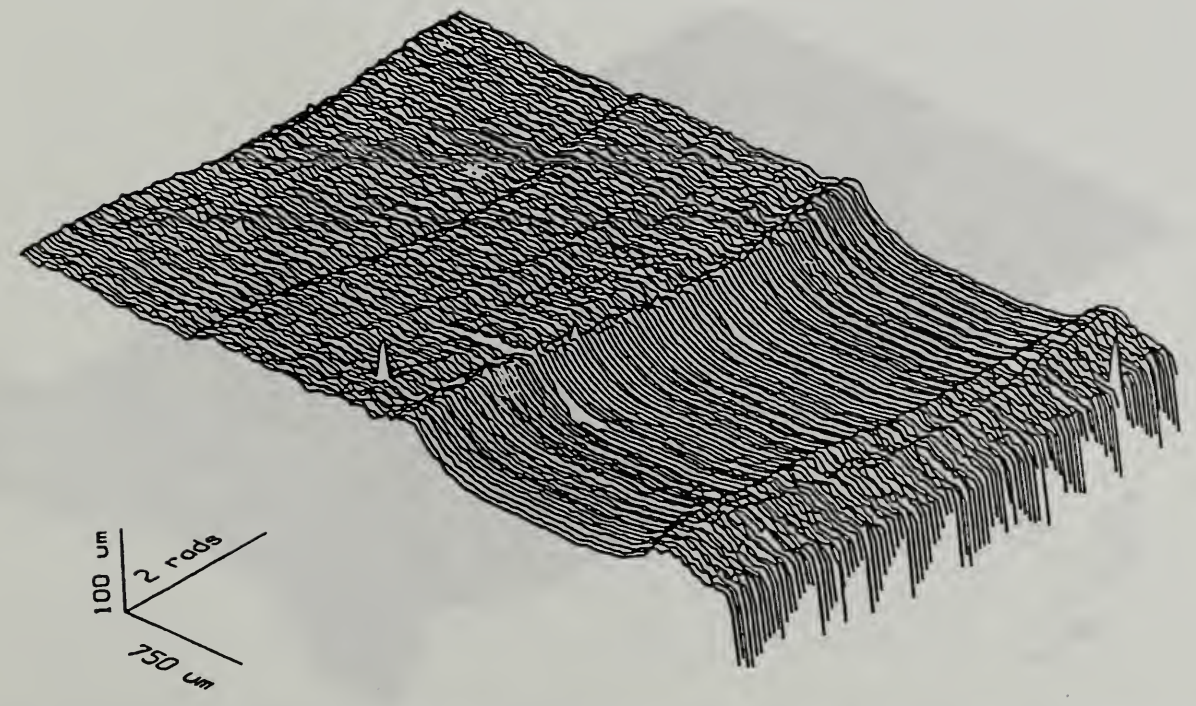

Fig. A1.8: 3-D Surface Map of Tribaloy 800 Exhaust Valve (Vs. Silicon Nitride)

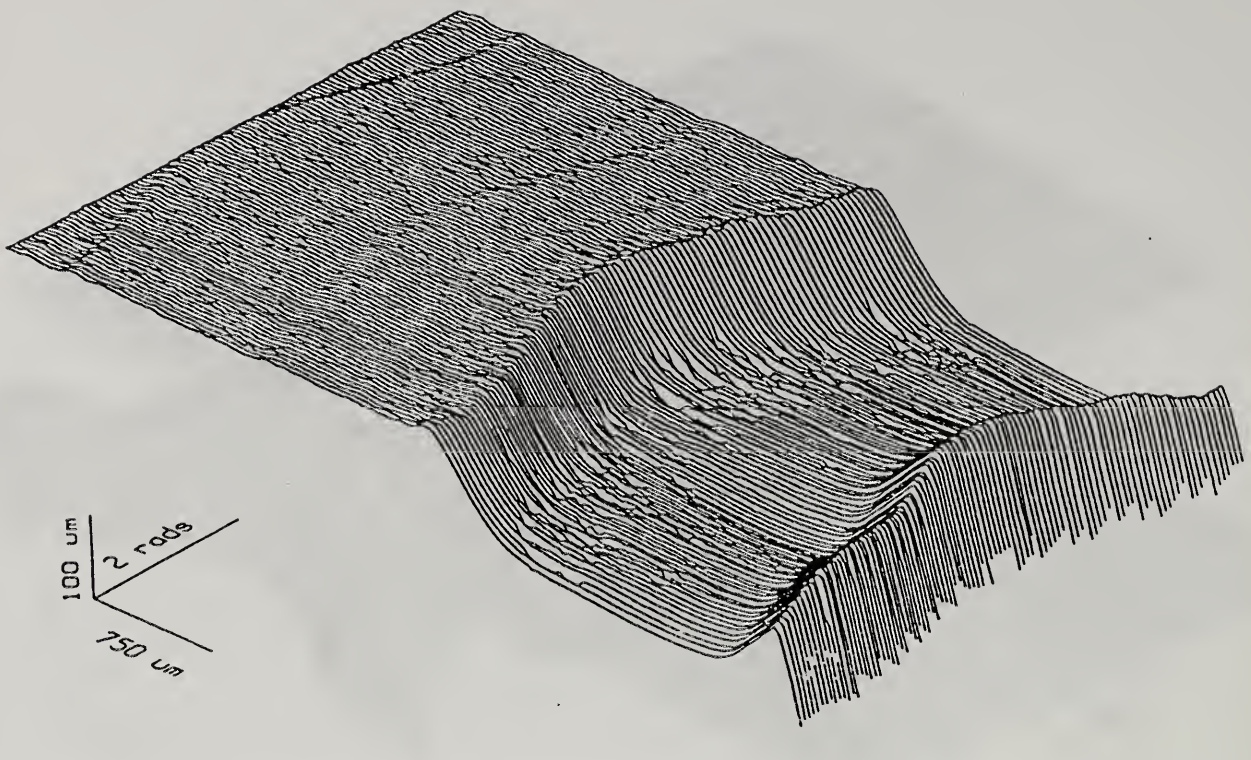

Fig. Al.9: 3-D Surface Map of Stellite 6 Inlet Valve (Vs. Silicon Nitride)

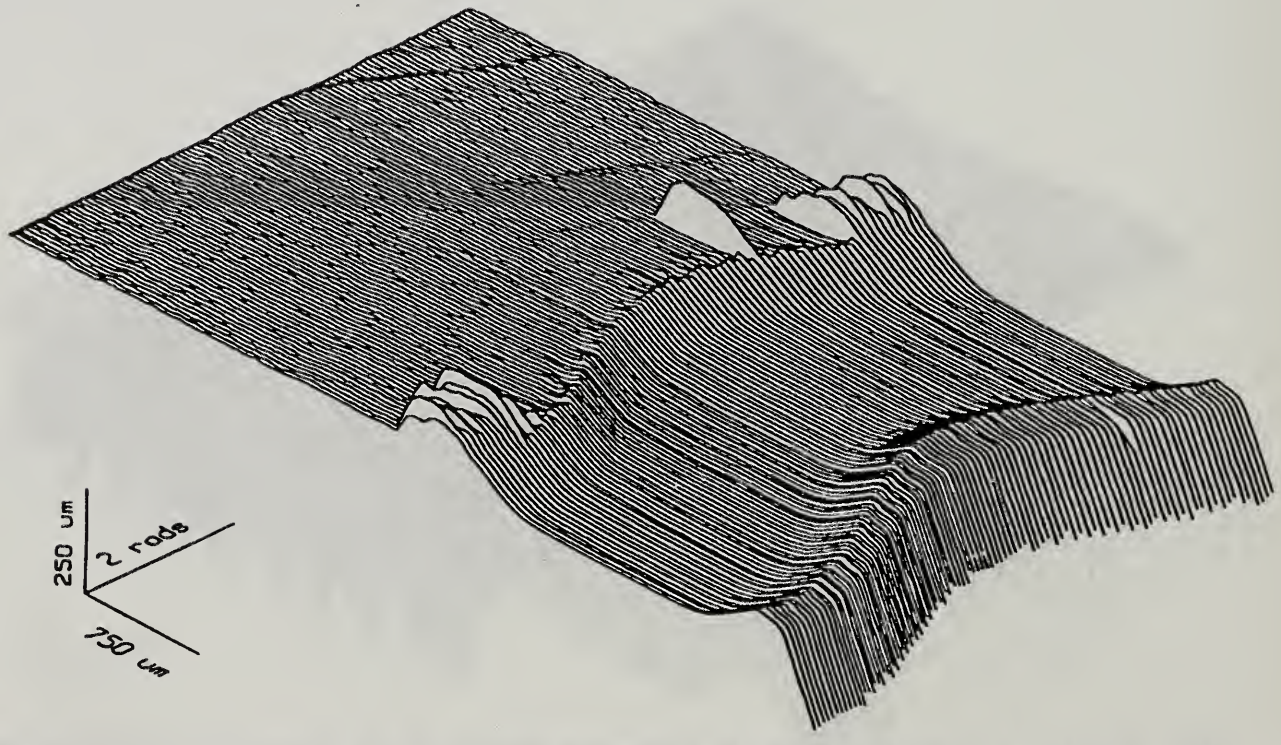

Fig. Al.10: 3-D Surface Map of Stellite 6 Exhaust Valve (Vs. Silicon Nitride)

APPENDIX 2

Averaged Profiles from Valve Faces

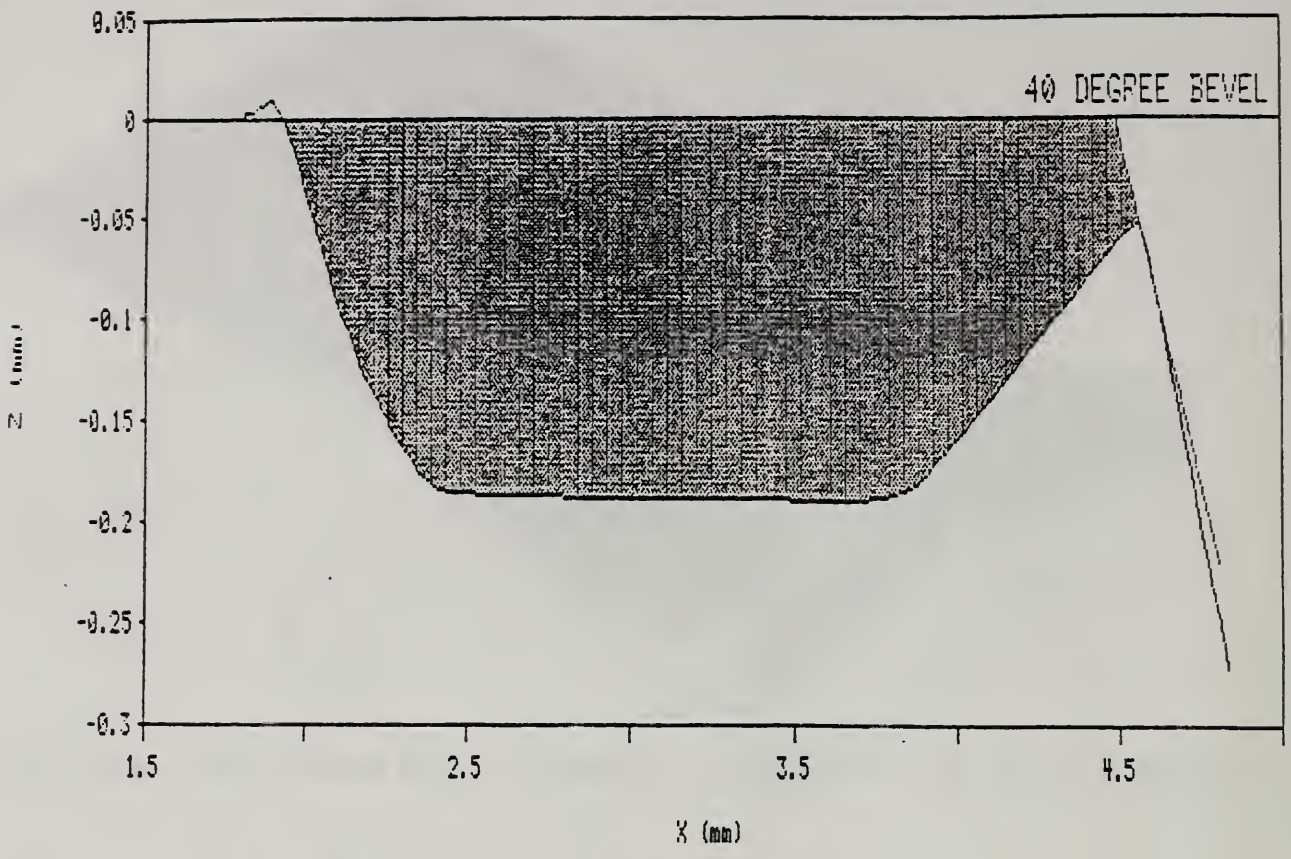

Fig. A2.1: Average Profile of Valve 1-3

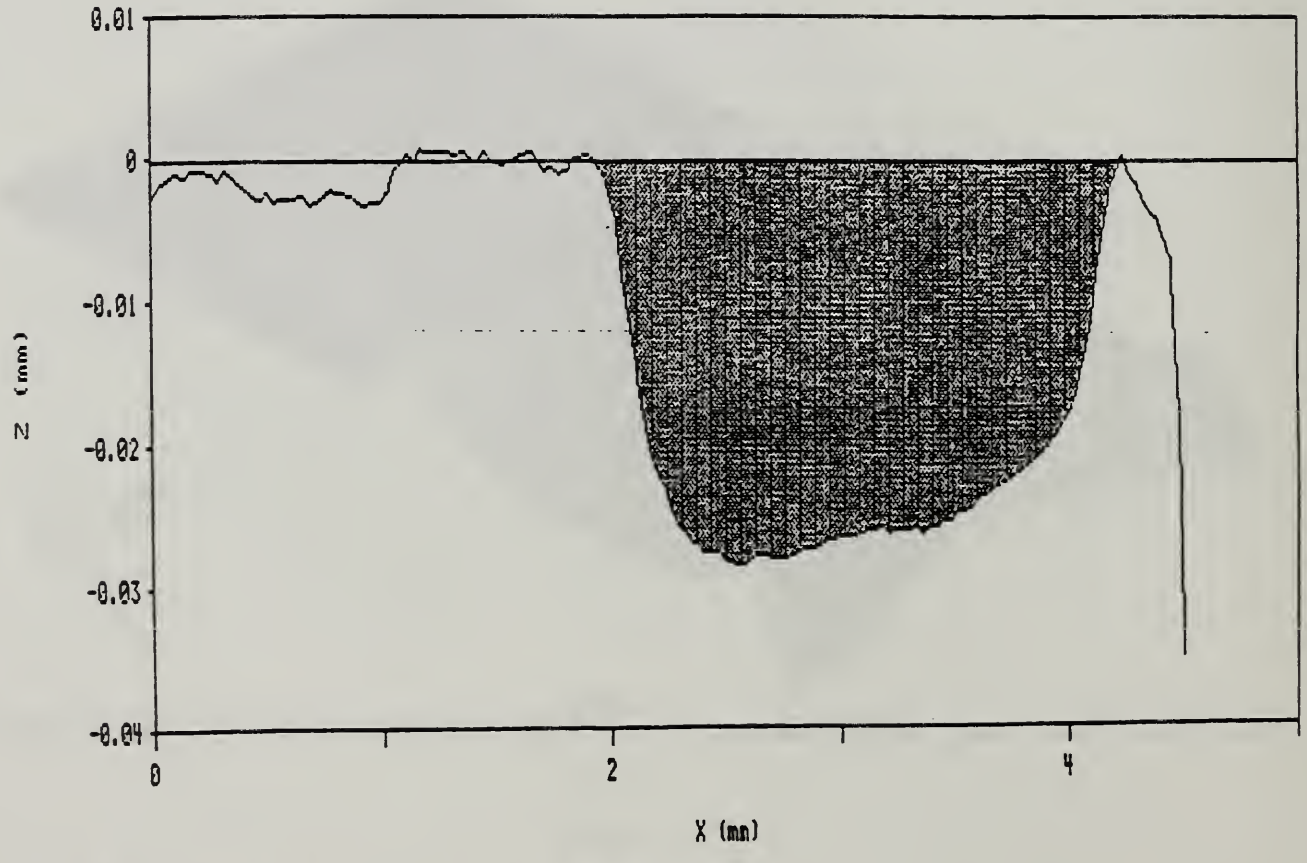

Fig. A2.2: Average Profile of Valve 1-4

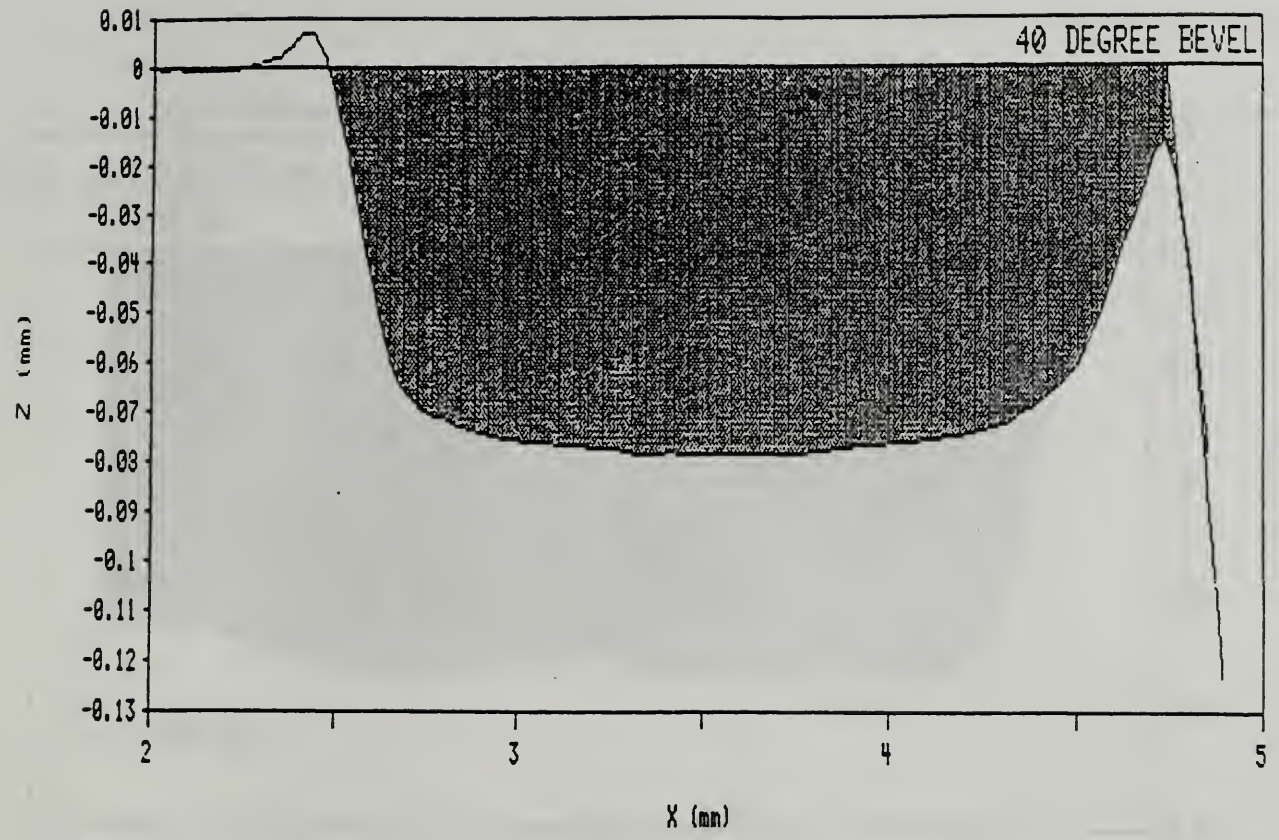

Fig. A2.3: Average Profile of Valve 1-8.

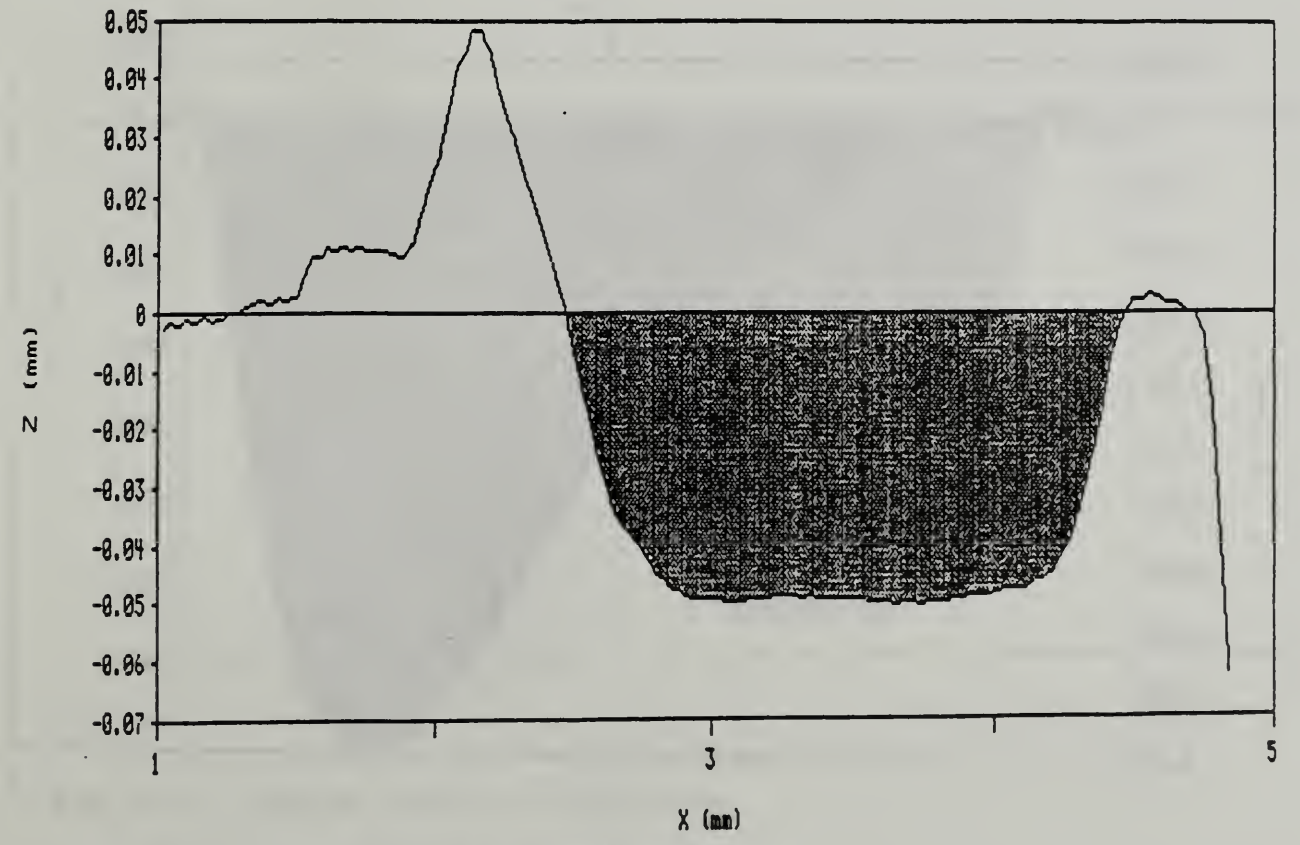

Fig. A2.4: Average Profile of Valve 1-8.

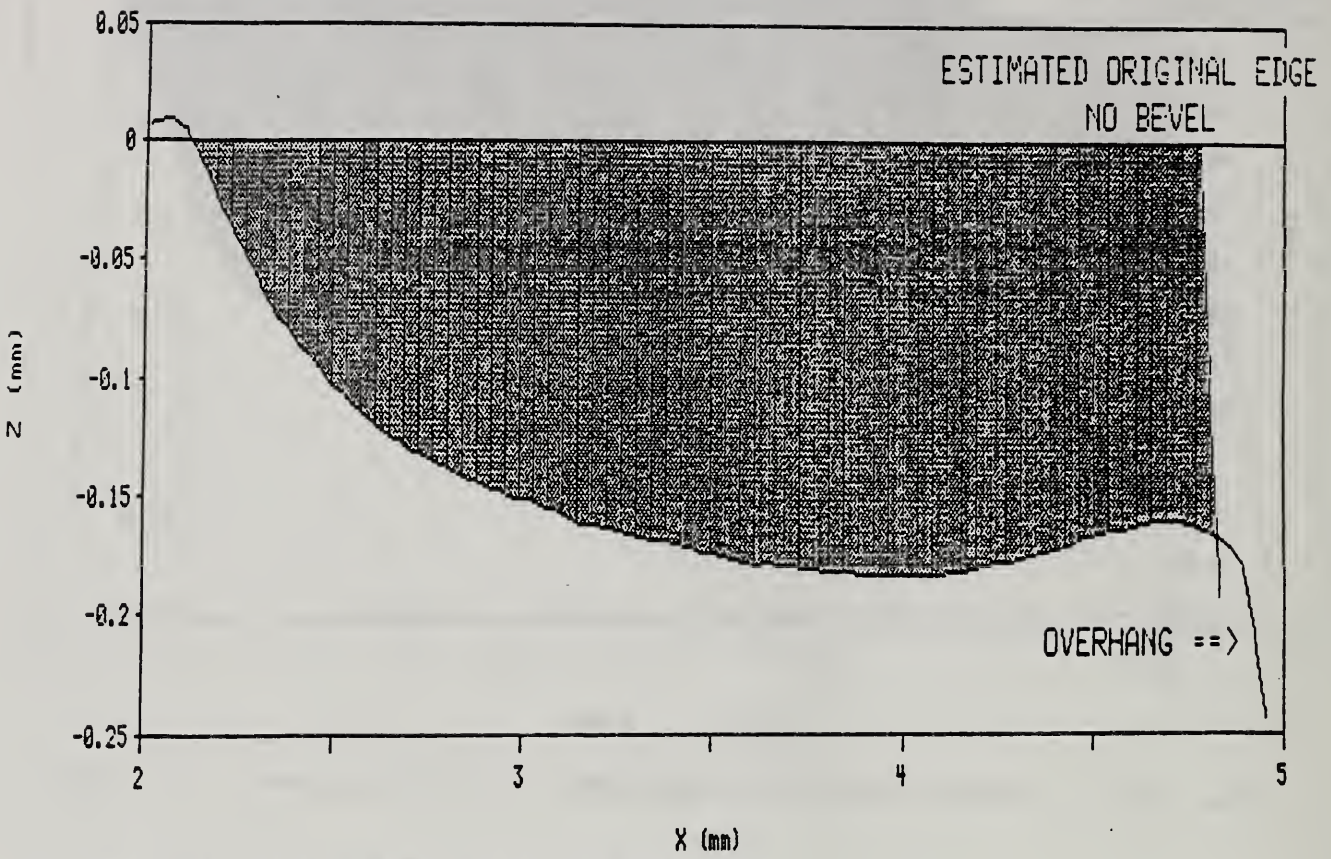

Fig. A2.5: Average Profile of Valve 2-3.

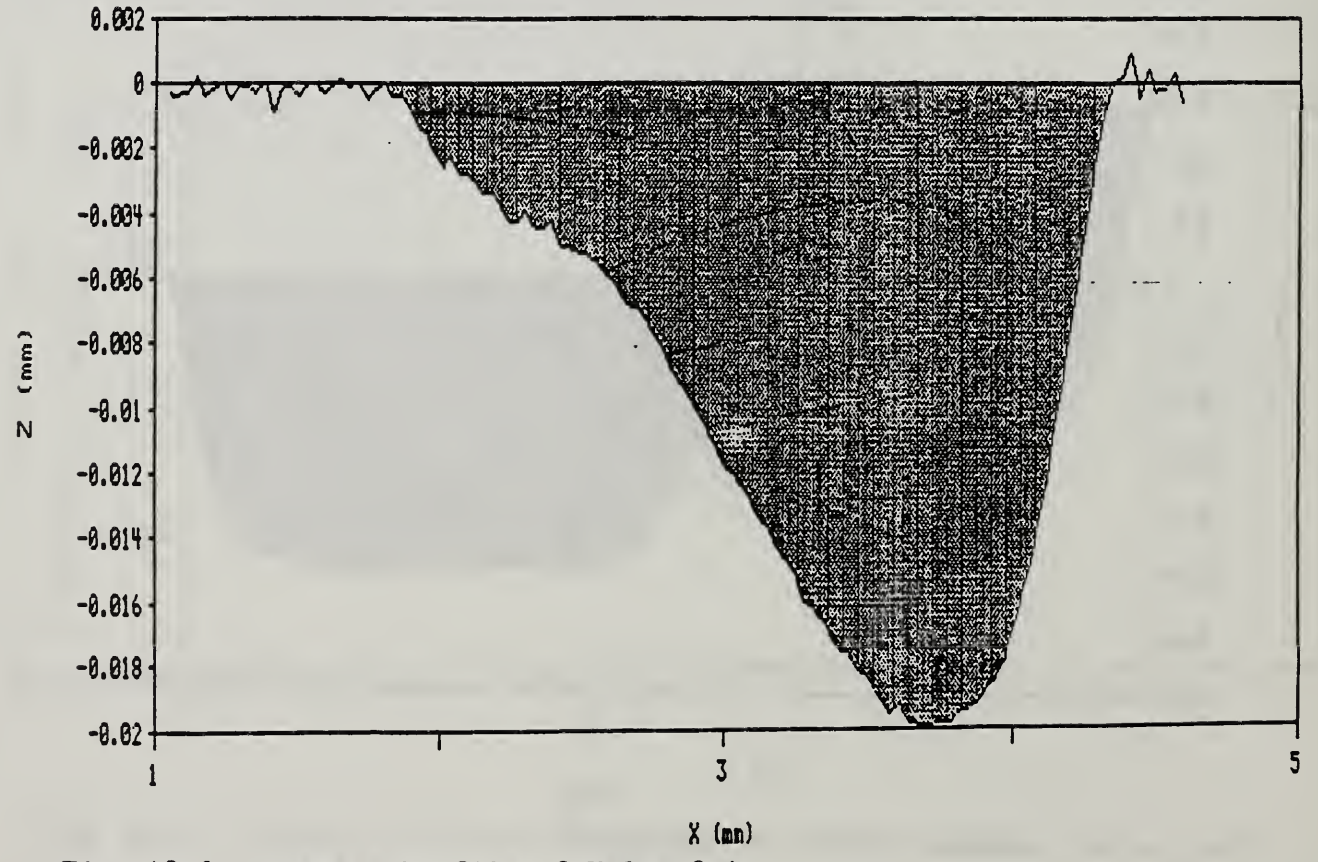

Fig. A2.6: Average Profile of Valve 2-4.

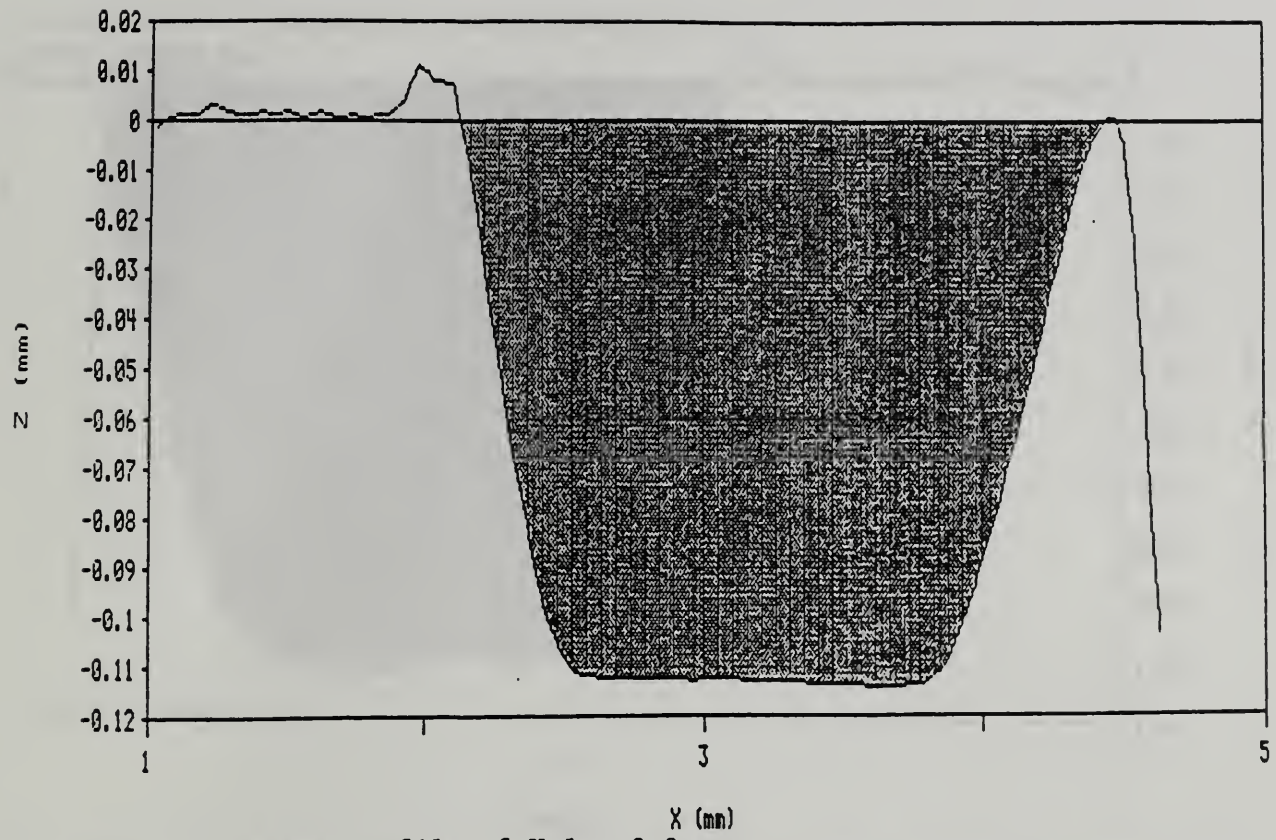

Fig. A2.7: Average Profile of Valve 3-3.

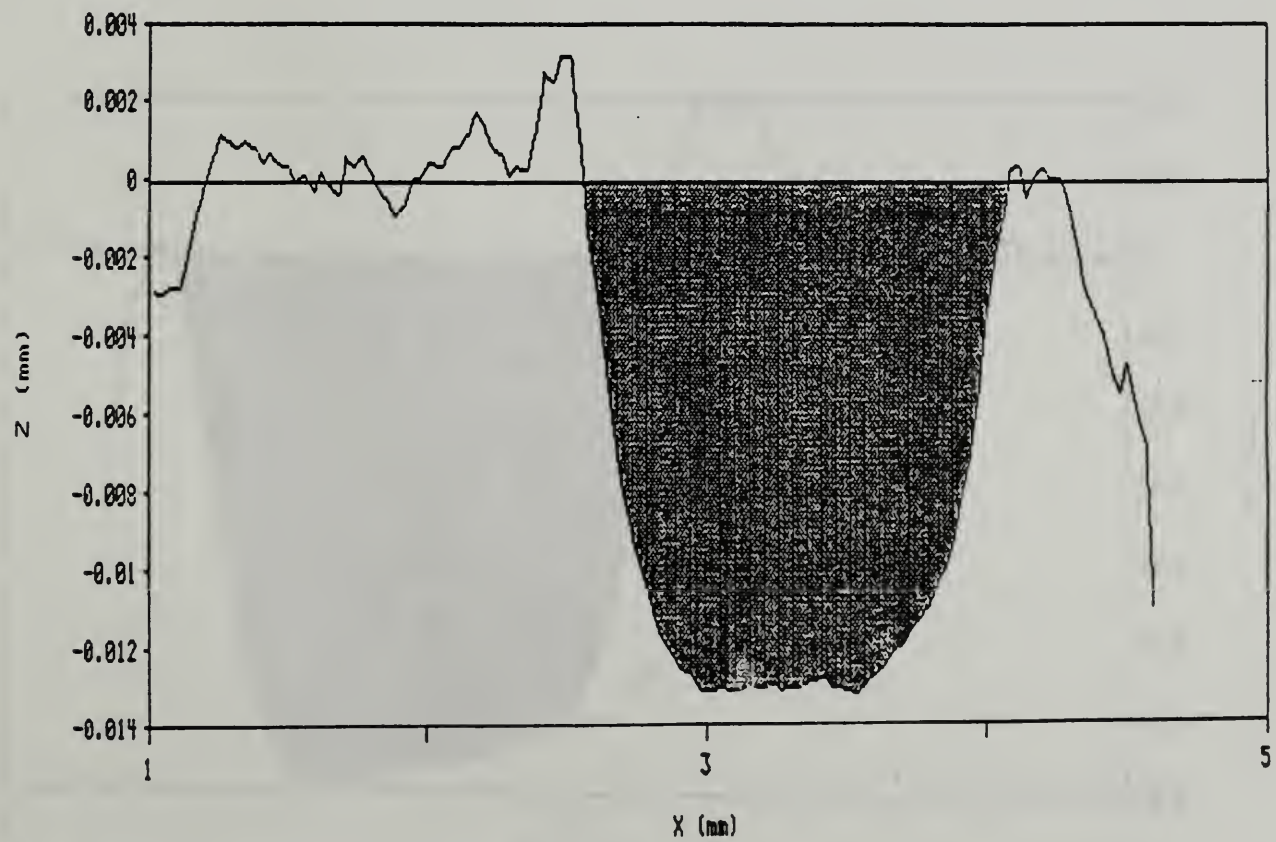

Fig. A2.8: Average Profile of Valve 3-4.

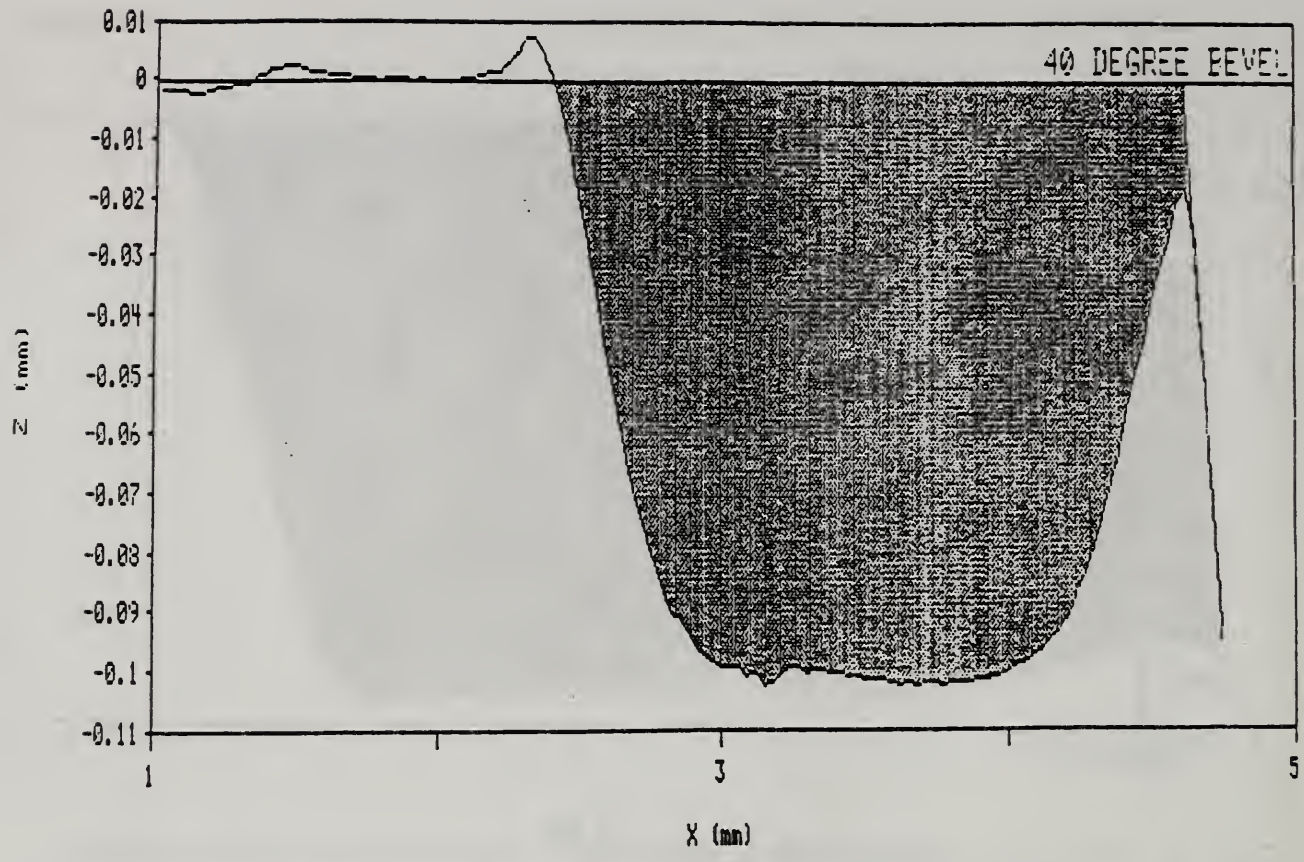

Fig. A2.9: Average Profile of Valve 3-8.

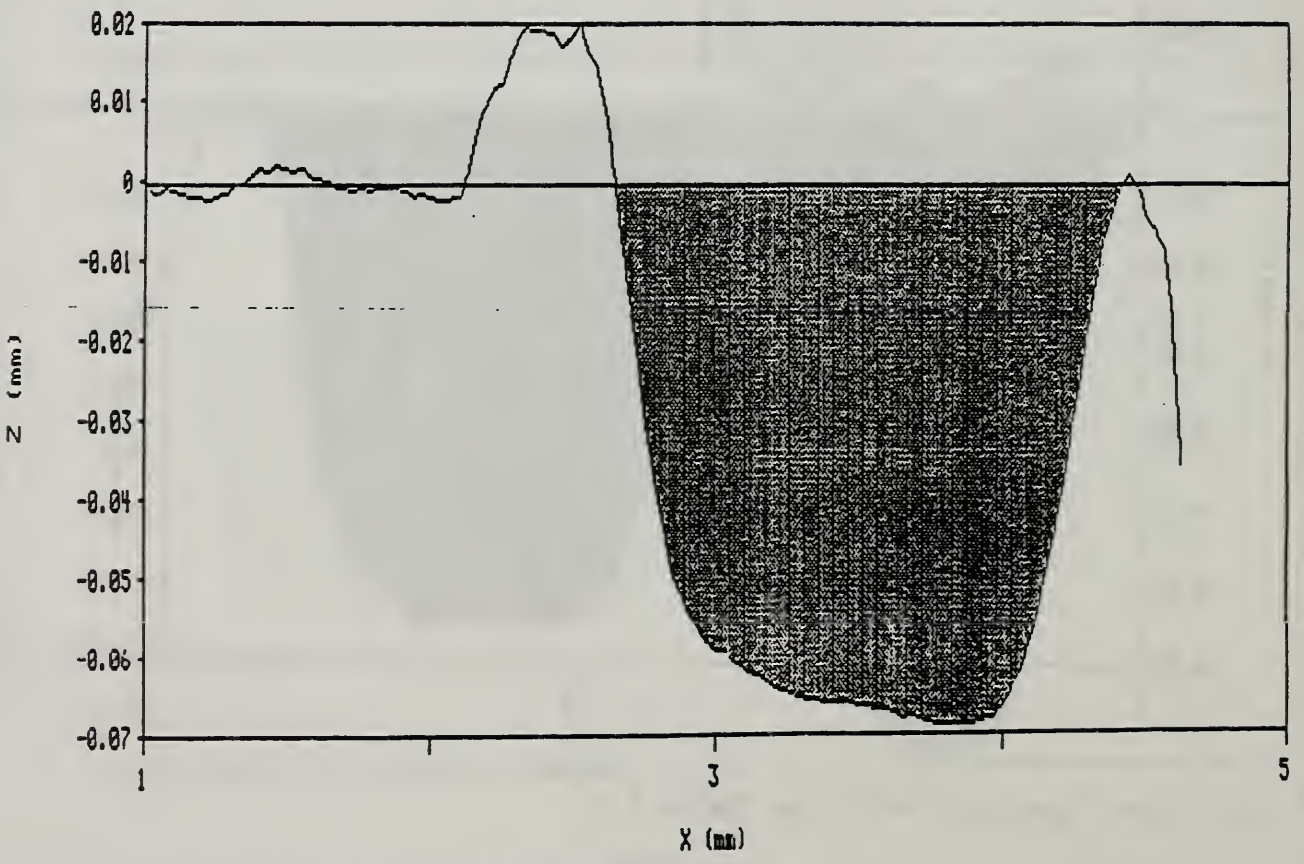

Fig. A2.10: Average Profile of Valve 3-7.

APPENDIX 3

Printout from Energy Dispersive Xray Analysis

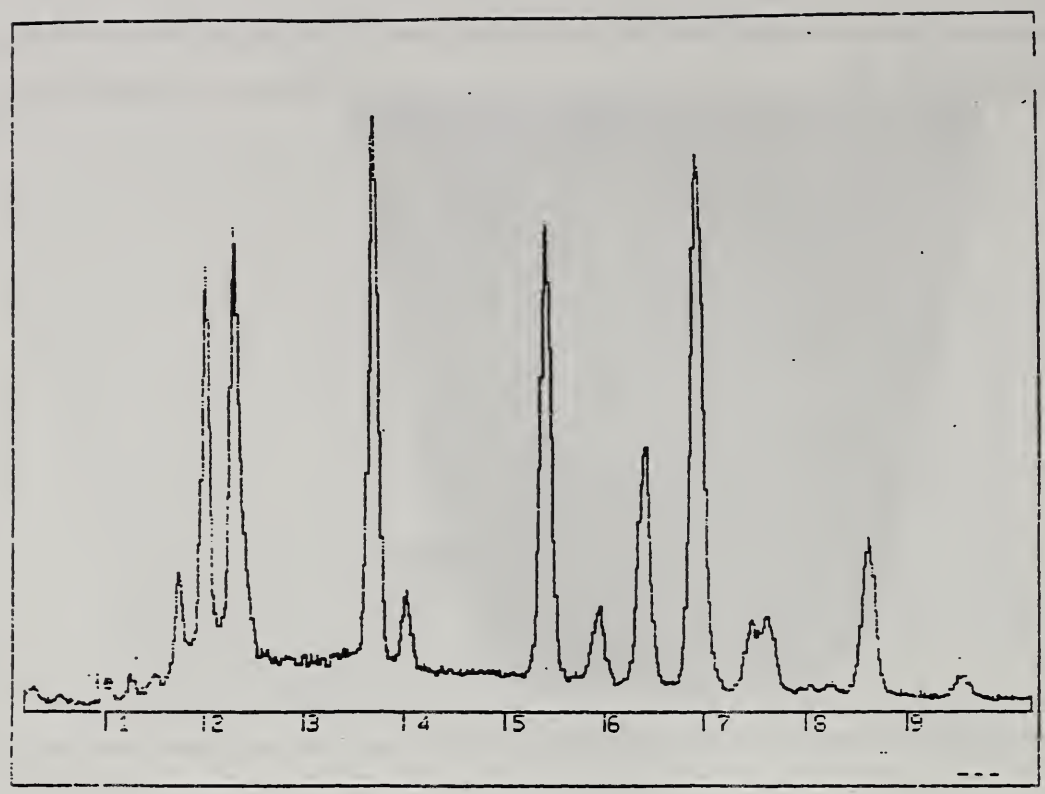

Fig. A3.1: EDX Analysis of Tribaloy-800 Intake Valve (Vs. Sialon Seat)

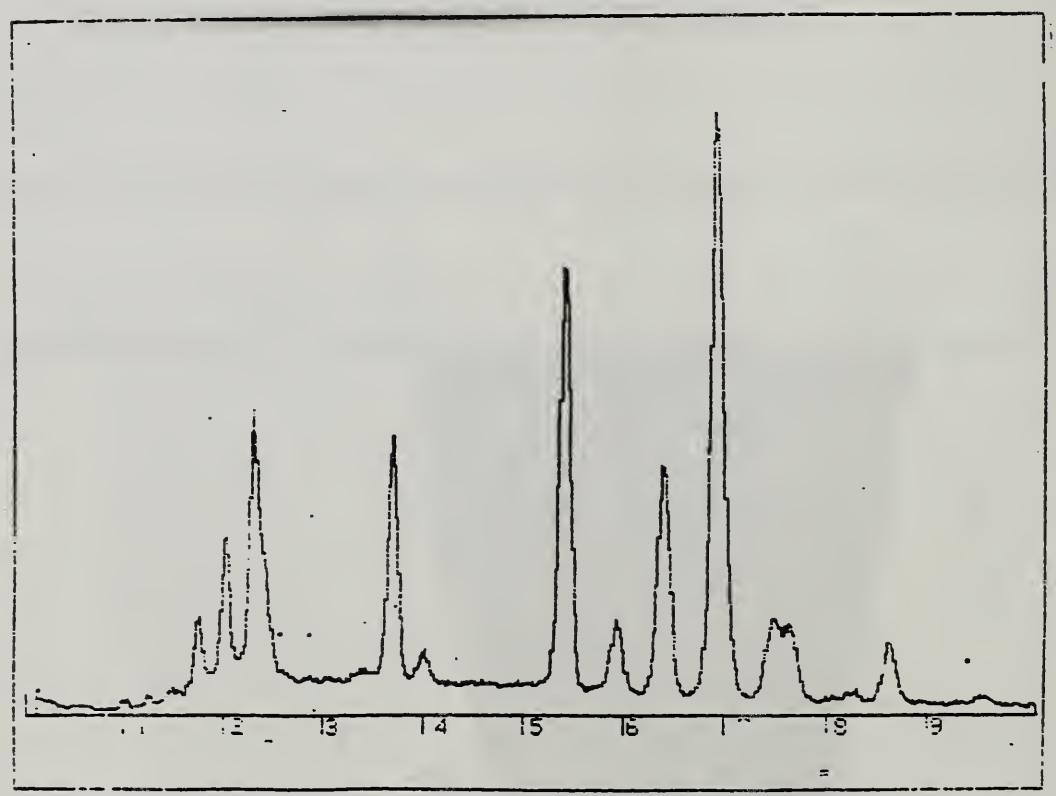

Fig. A3.2: EDX Analysis of Tribaloy-800 Exhaust Valve (Vs. Sialon Seat)

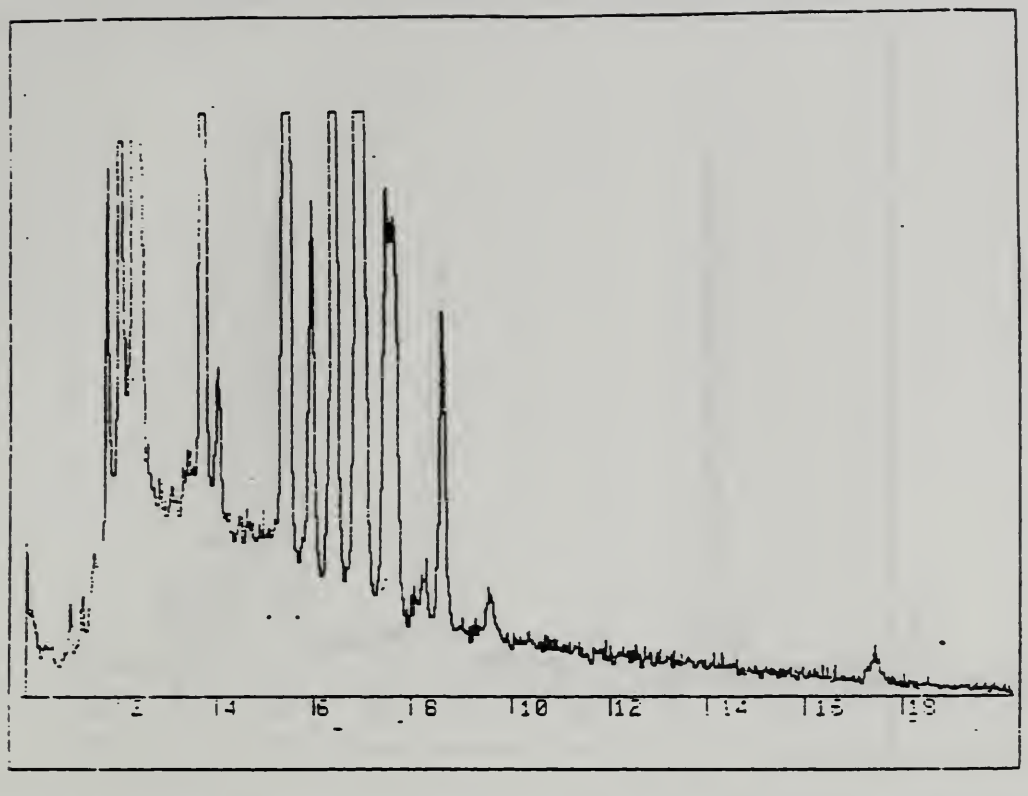

Fig. A3.3: EDX Analysis of Tribaloy-800 Exhaust Valve (Vs. Sialon Seat)

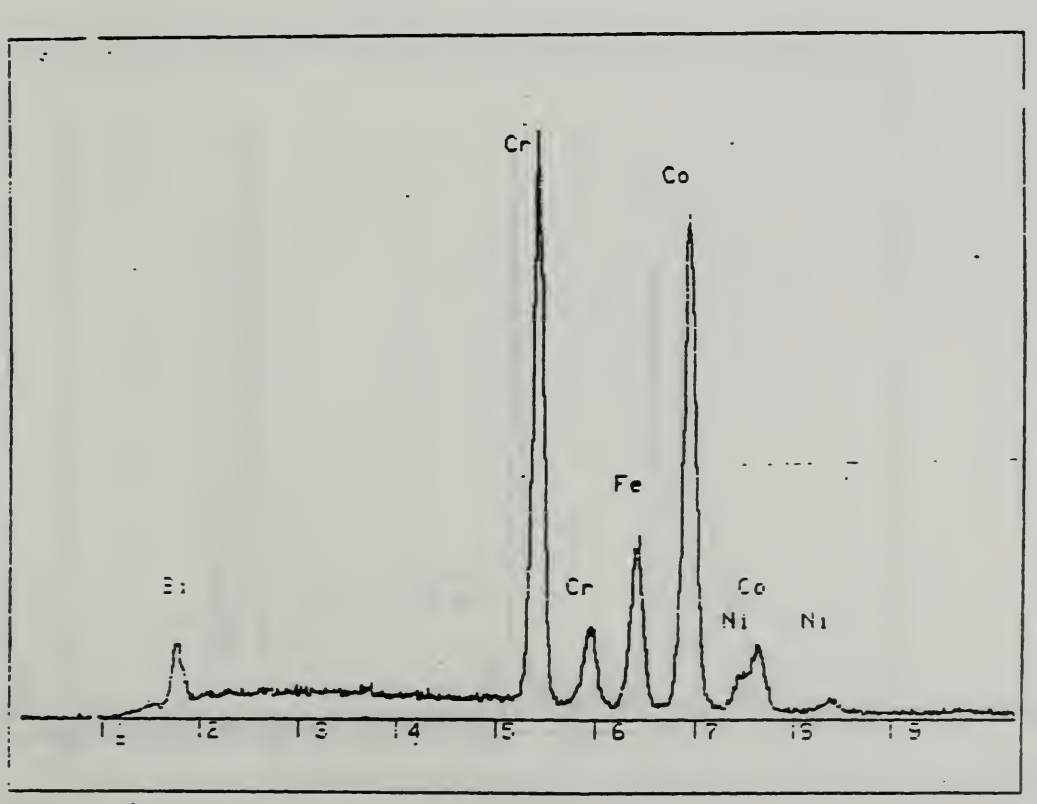

Fig. A3.4: EDX Analysis of Stellite 6 Intake Valve (Vs. Silicon Nitride Seat)

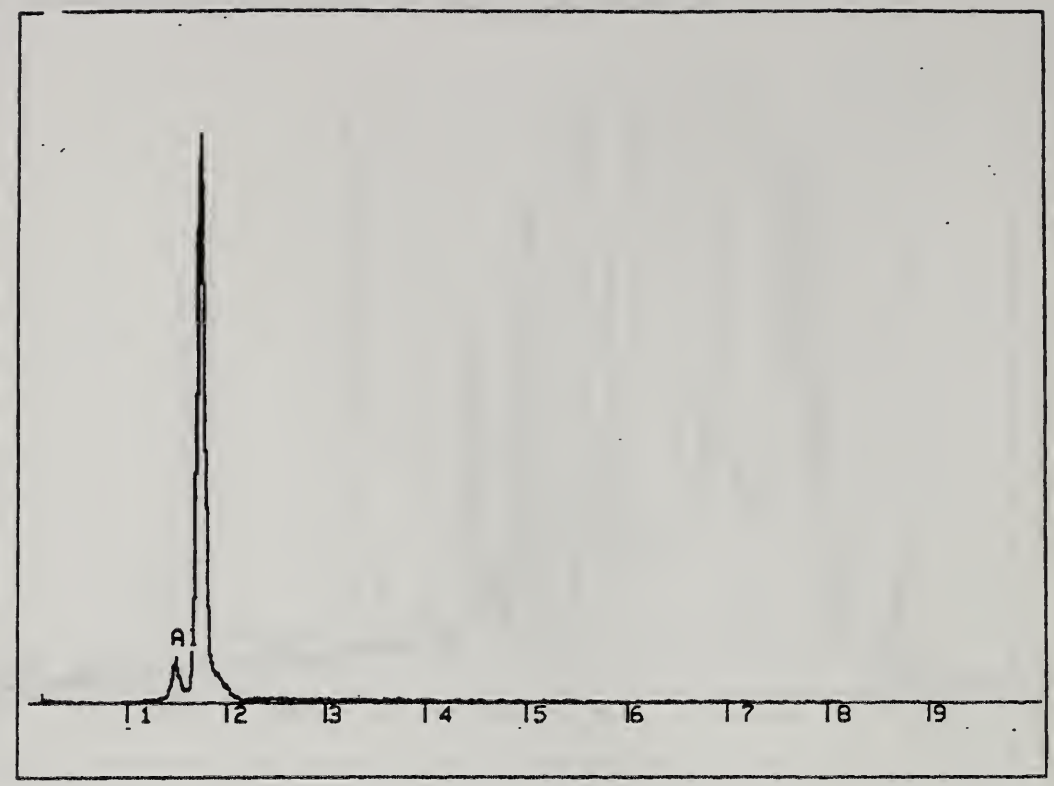

Fig. A3.5: EDX Analysis of Sialon Exhaust Seat (Vs. Stellite 6 Valve)

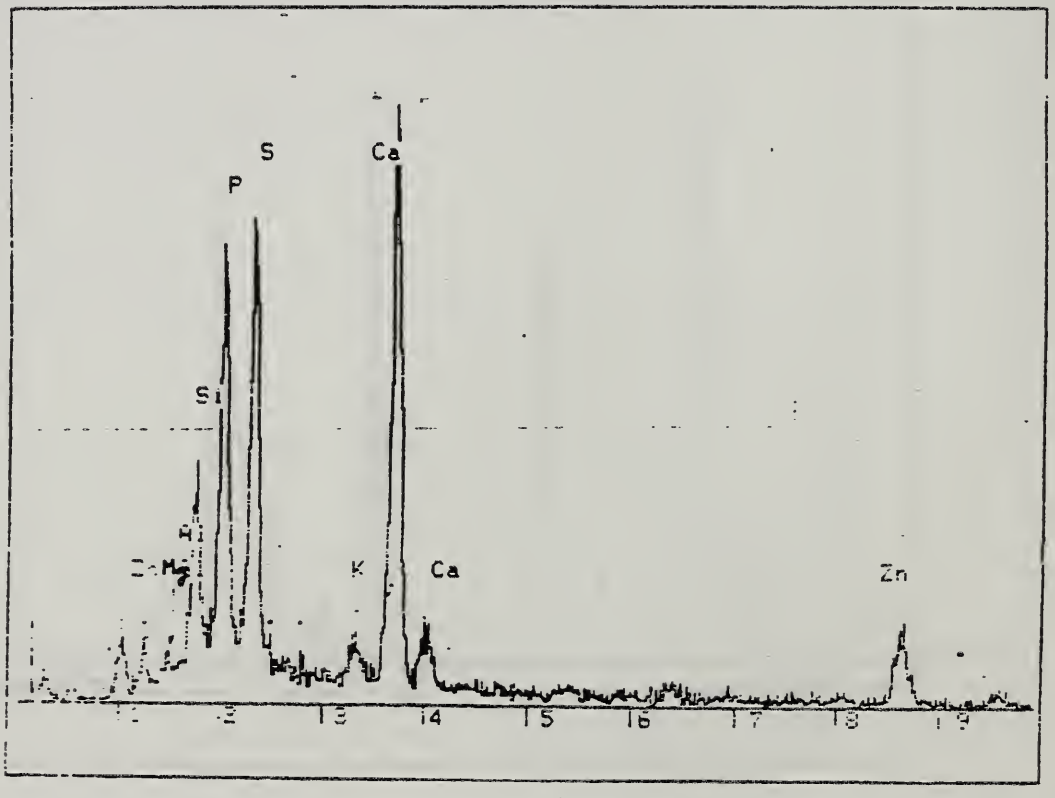

Fig. A3.6: EDX Analysis of Sialon Exhaust Seat (Vs. Stellite 6 Valve)

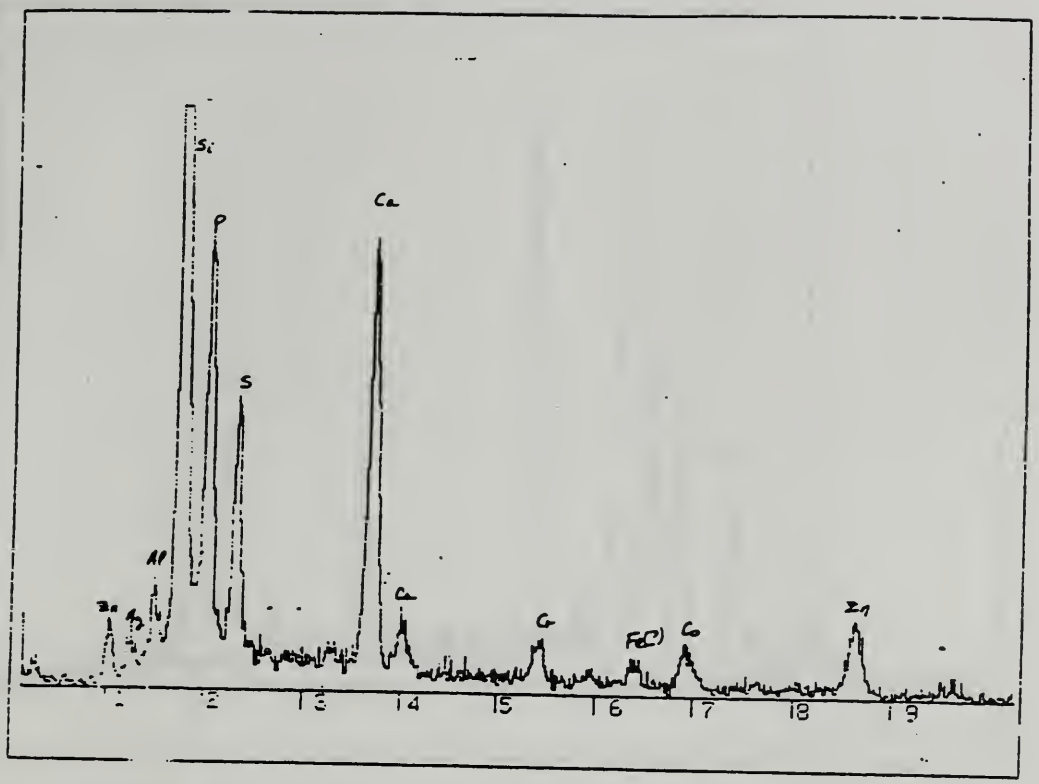

Fig. A3.7: EDX Analysis of Sialon Exhaust Seat (Vs. Stellite 6 Valve)

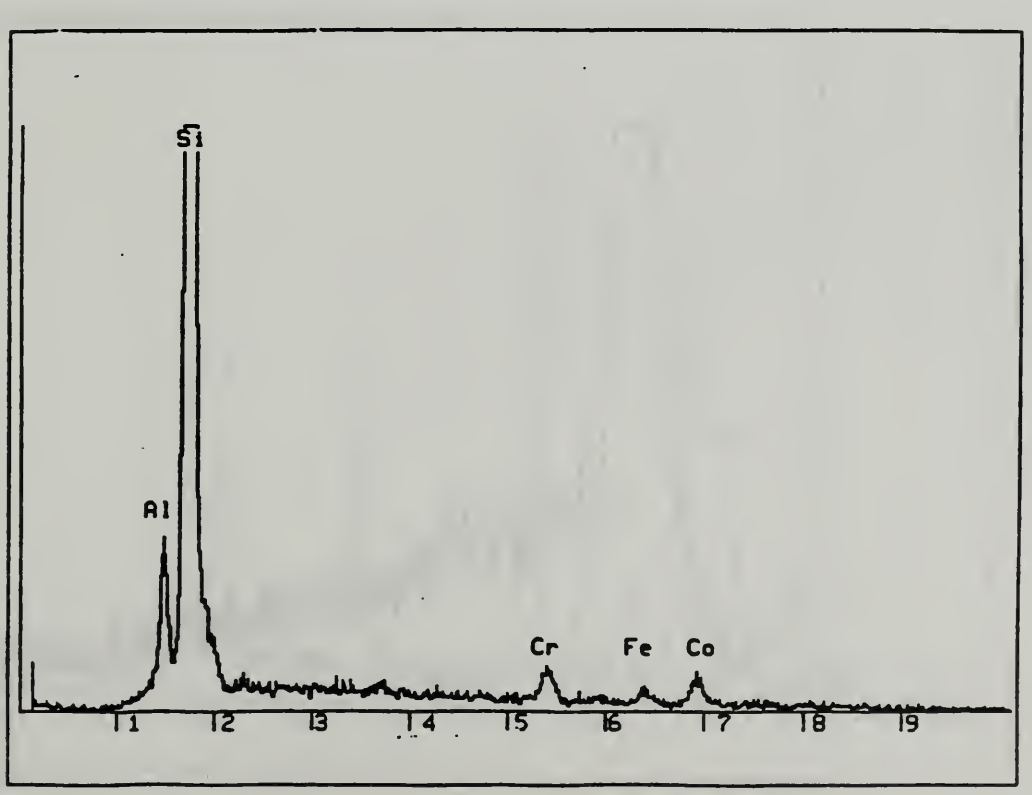

Fig. A3.8: EDX Analysis of Sialon Intake Seat (Vs. Stellite 6 Valve)

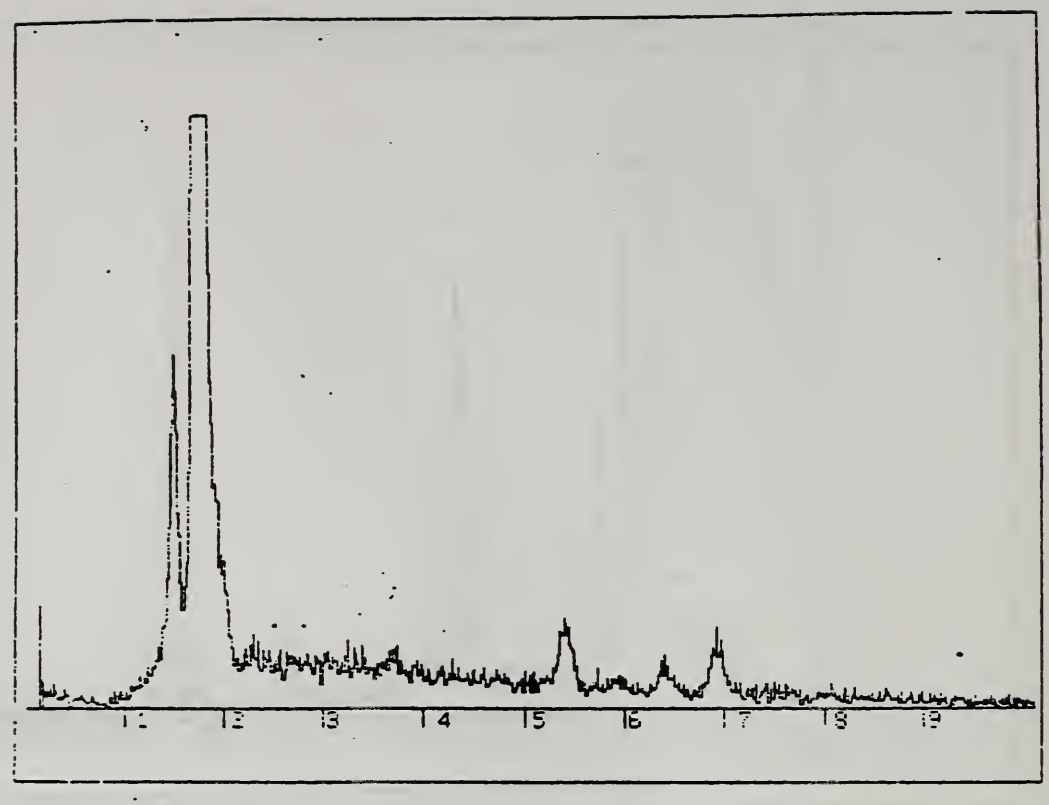

Fig. A3.9: EDX Analysis of Sialon Intake Seat (Vs. Stellite 6 Valve)

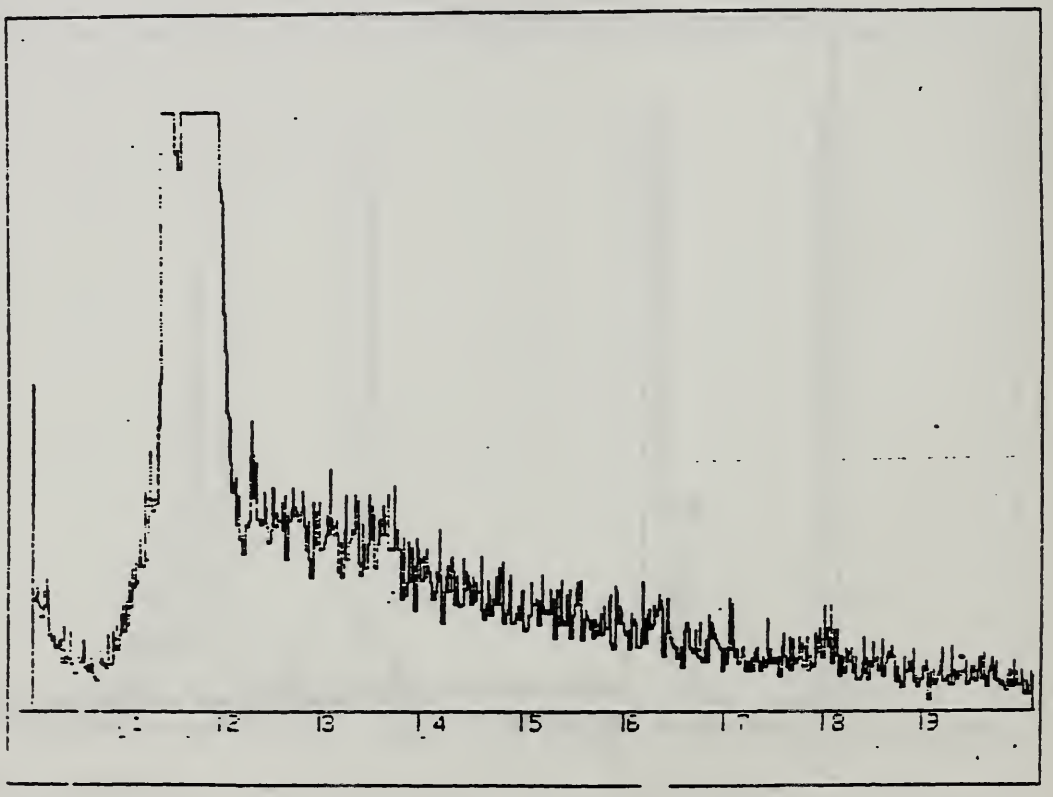

Fig. A3.10: EDX Analysis of Sialon Intake Seat (Vs. Stellite 6 Valve)

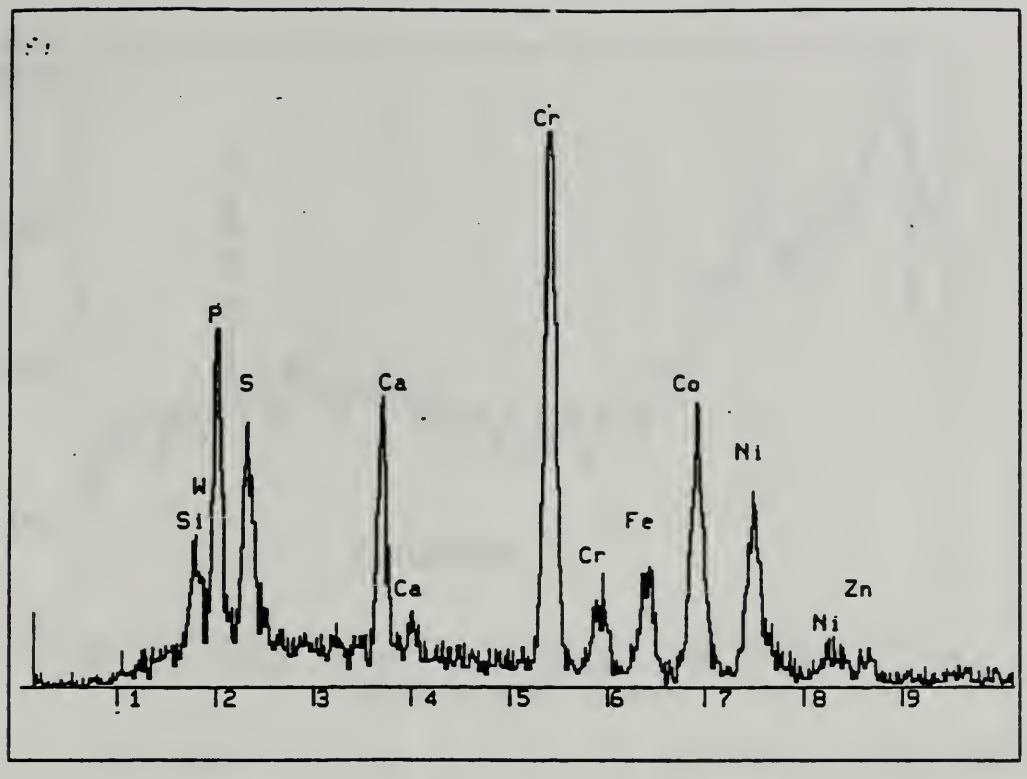

Fig. A3.11: Eatonite Exhaust Seat (Vs. Stellite 1 Valve)

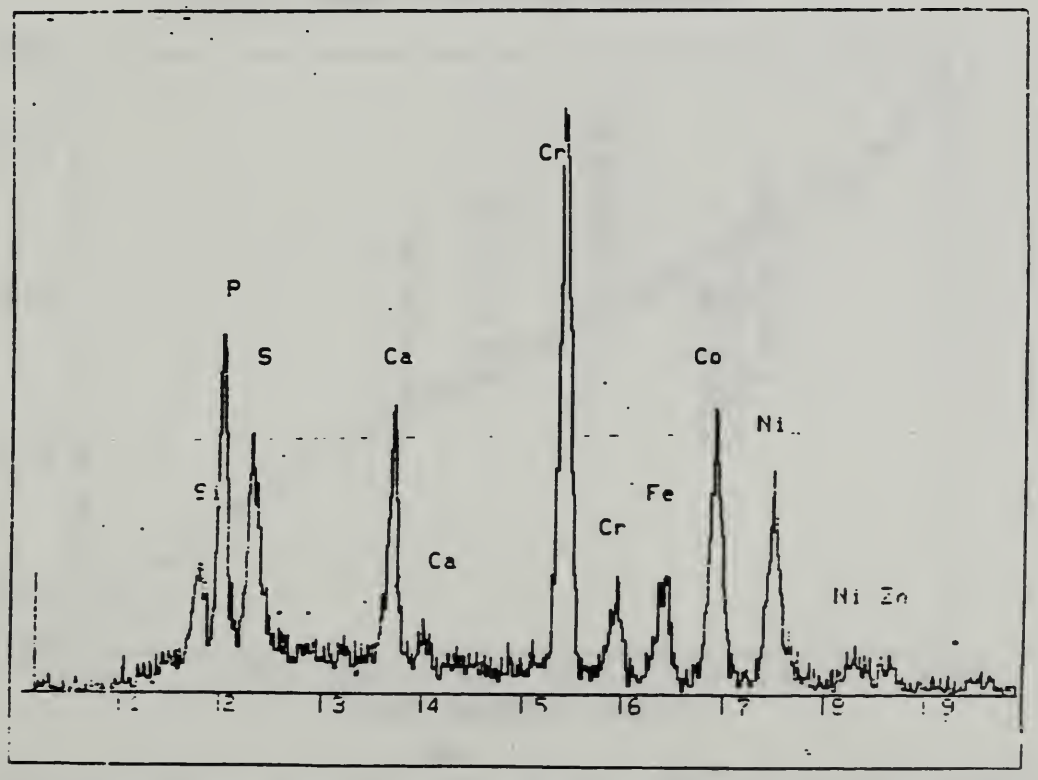

Fig. A3.12: Eatonite Exhaust Seat (Vs. Stellite 1 Valve)

APPENDIX 4

Printout from Laser Raman Analysis

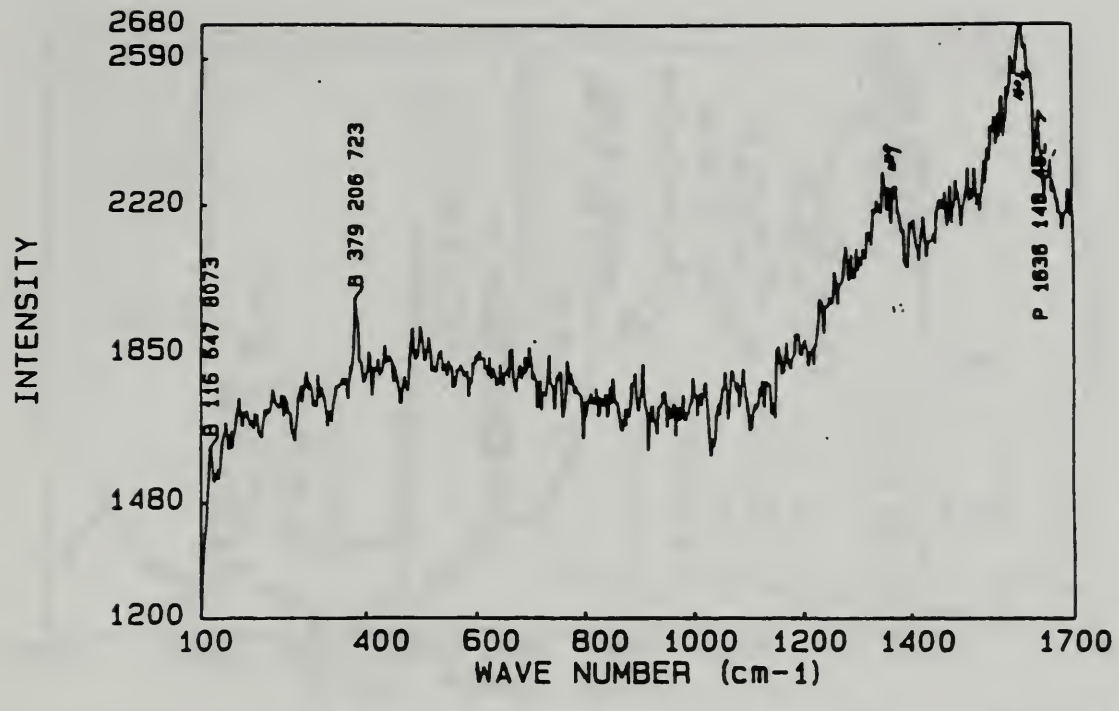

Fig. A4.1: Laser Raman Analysis of Deposit on Specimen 1-3 Near Wear Track.

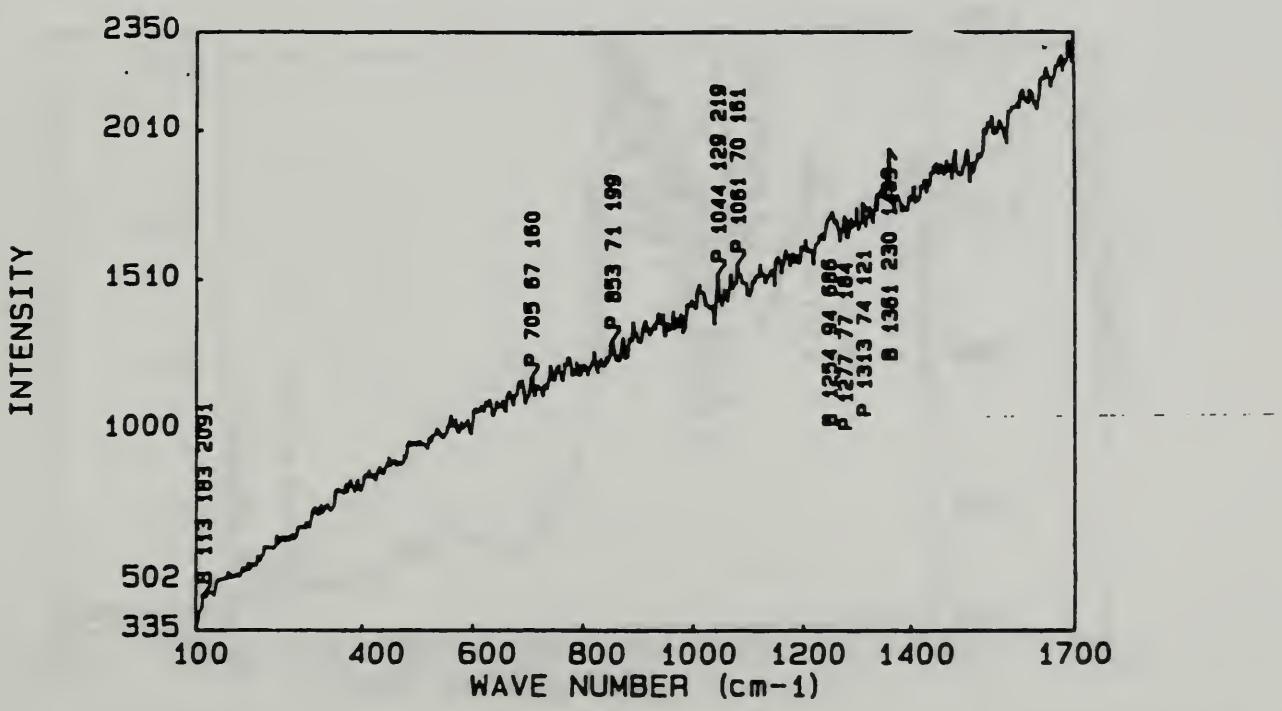

Fig. A4.2: Laser Raman Analysis of Deposit on Specimen 1-3 Near Valve Stem.

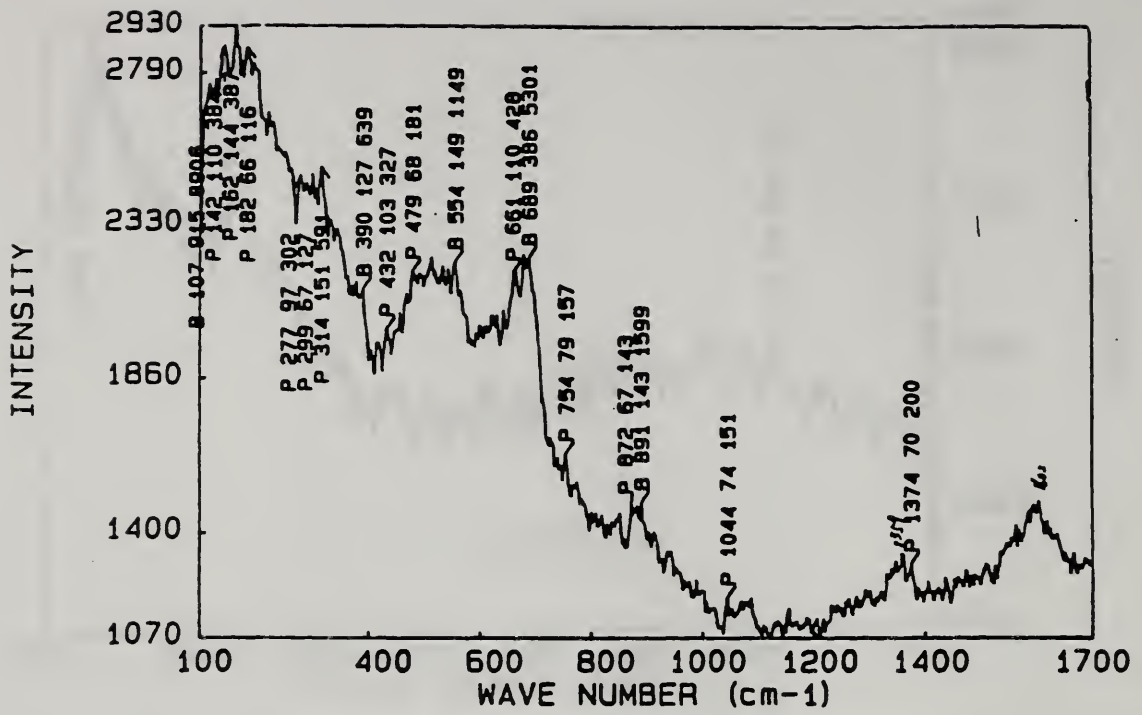

Fig. A4.3: Laser Raman Analysis of Deposit on Specimen 1-4 Near Wear Track.

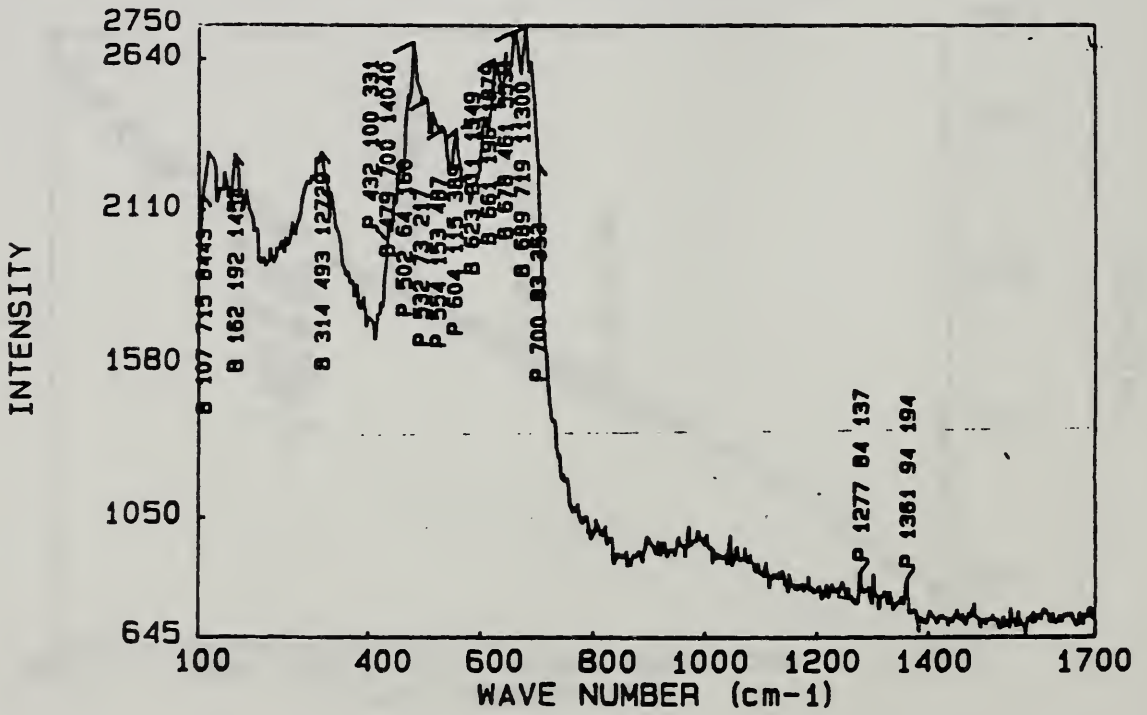

Fig. A4.4: Laser Raman Analysis of Deposit on Specimen 1-4 Near to Valve Stem.

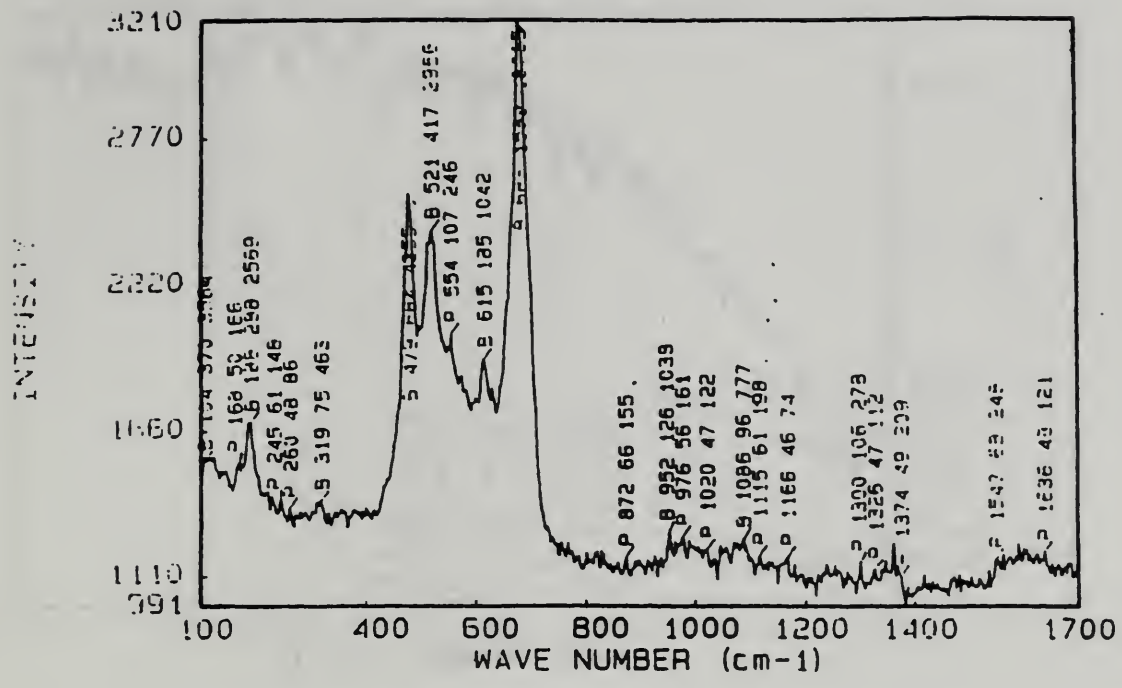

Fig A4.5: Laser Raman Analysis of Deposit on Specimen 1-7 Near Wear Track.

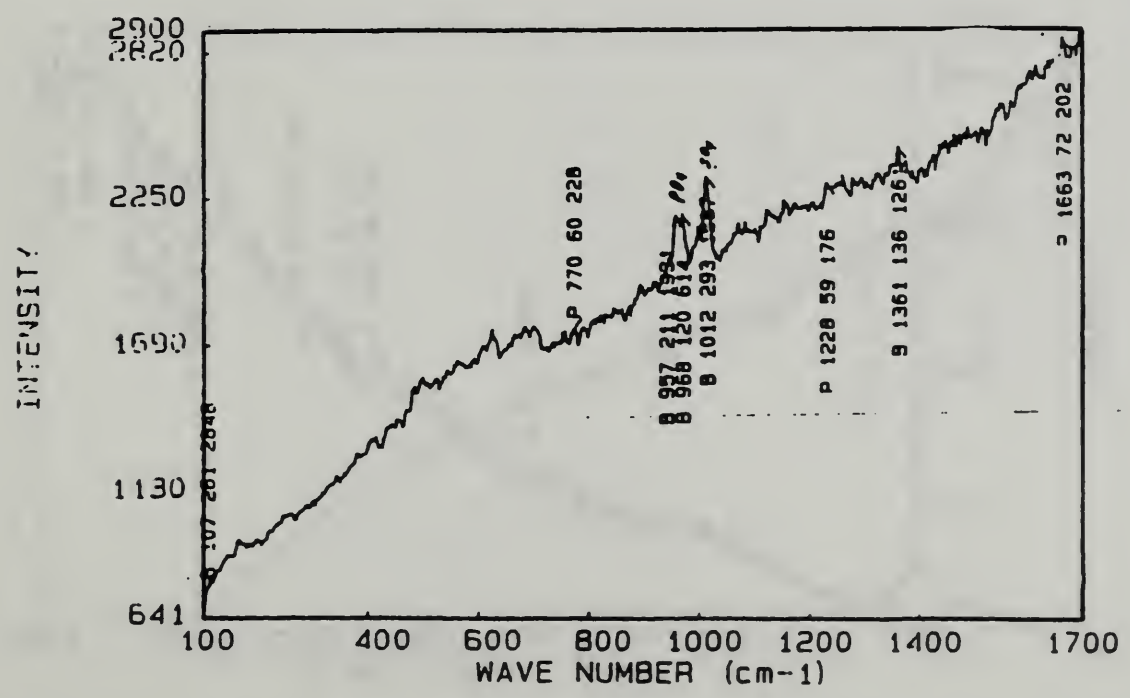

Fig. A4.6: Laser Raman Analysis of Deposit on Specimen 1-7 Near Valve Stem.

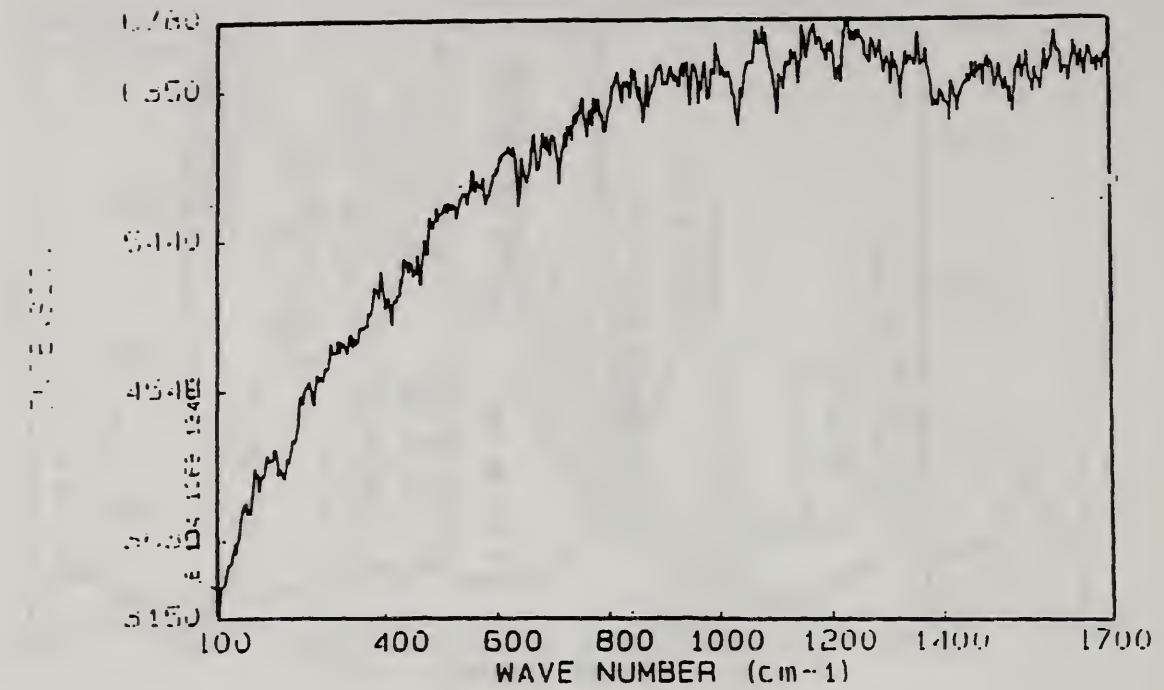

Fig. A4.7: Laser Raman Analysis of Deposit on Specimen 1-8 Near Wear Track.

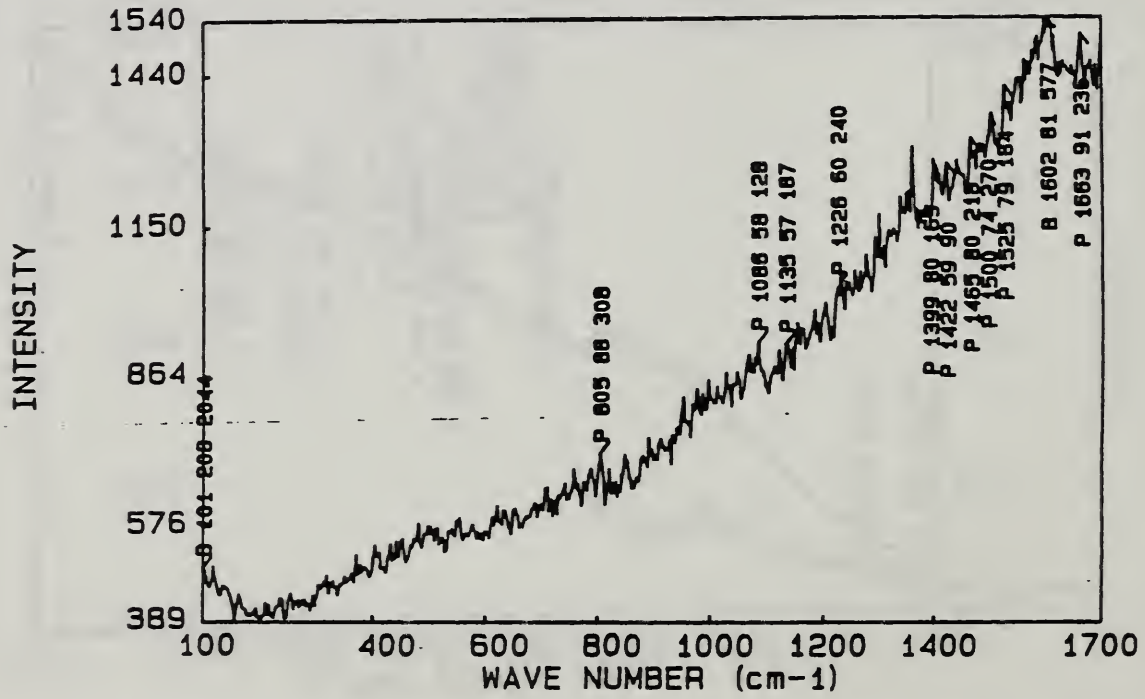

Fig. A4.8: Laser Raman Analysis of Deposit on Specimen 1-8 Near Valve Stem.

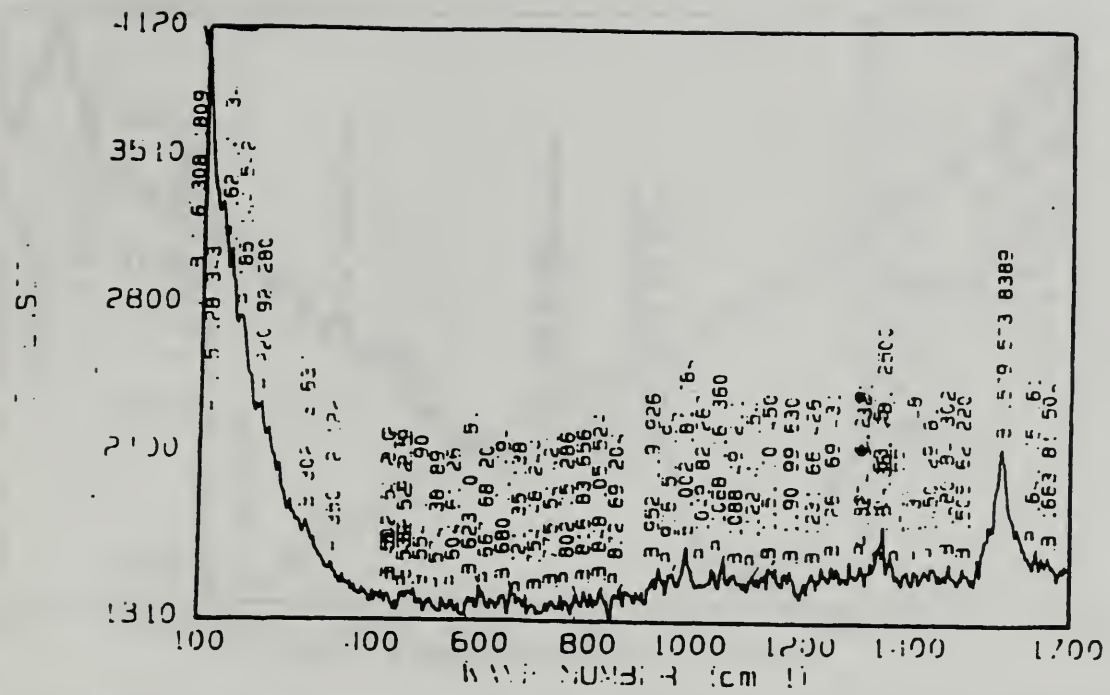

Fig. A4.9: Laser Raman Analysis of Deposit on Specimen 2-3 Near Wear Track.

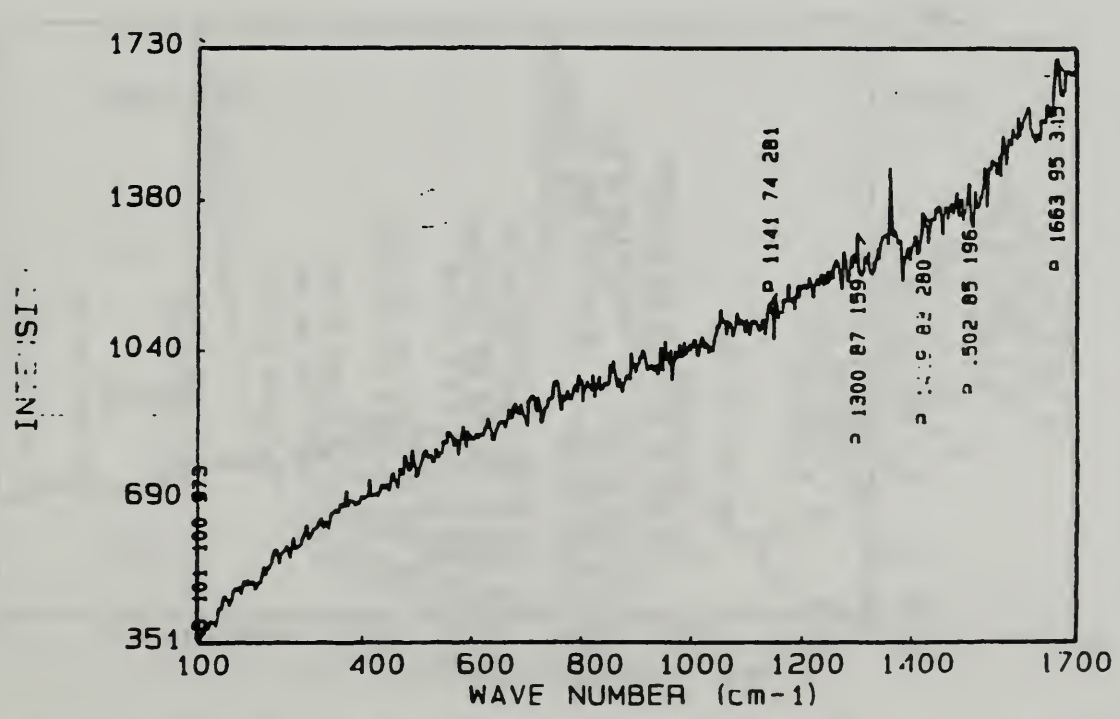

Fig. A4.10: Laser Raman Analysis of Deposit on Specimen 2-3 Near Valve Stem.

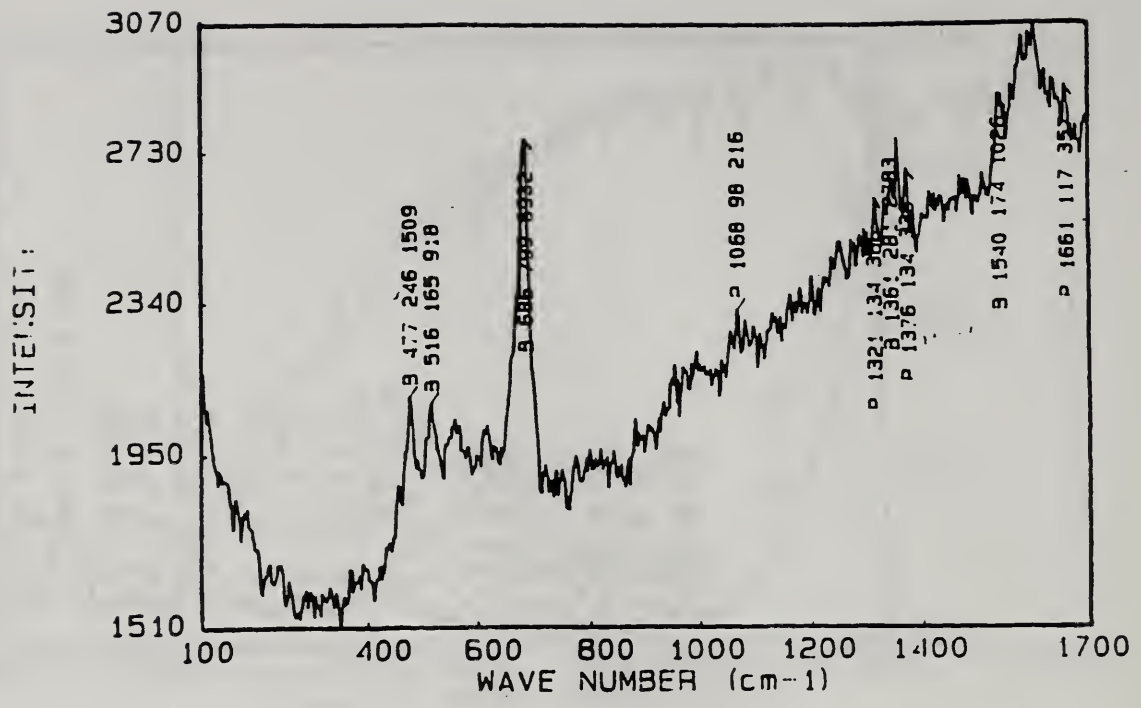

Fig. A4.11: Laser Raman Analysis of Deposit on Specimen 2-4 Near Wear Track.

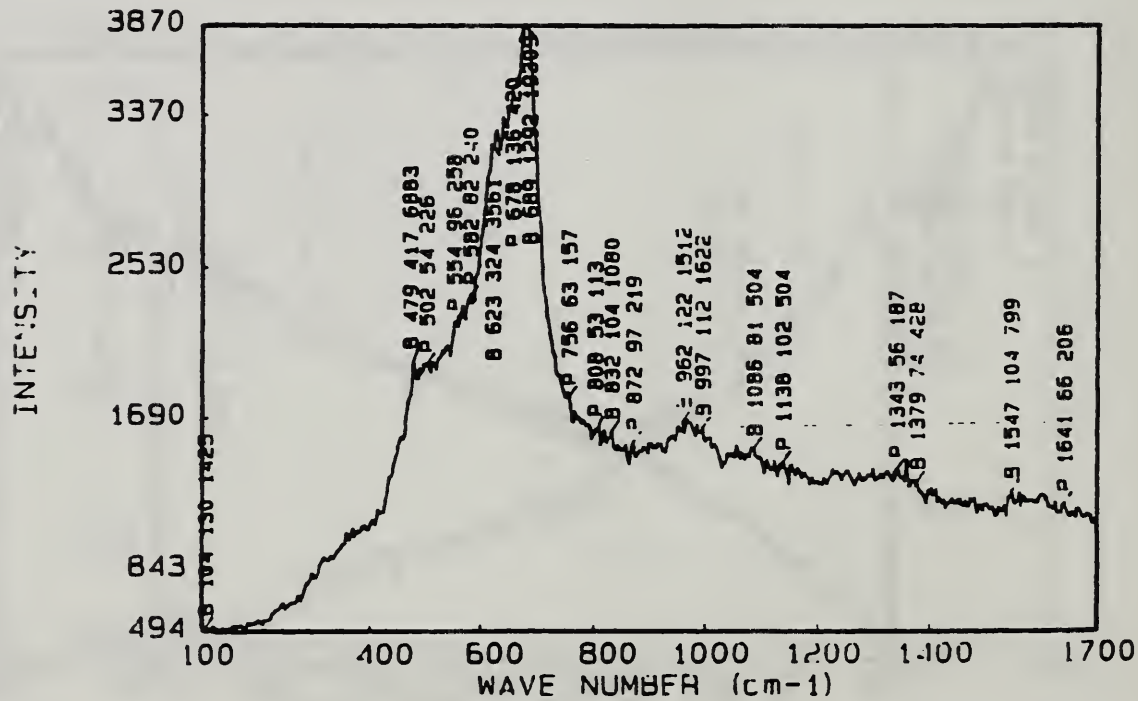

Fig. A4.12: Laser Raman Analysis of Deposit on Specimen 2-4 Near Valve Stem.

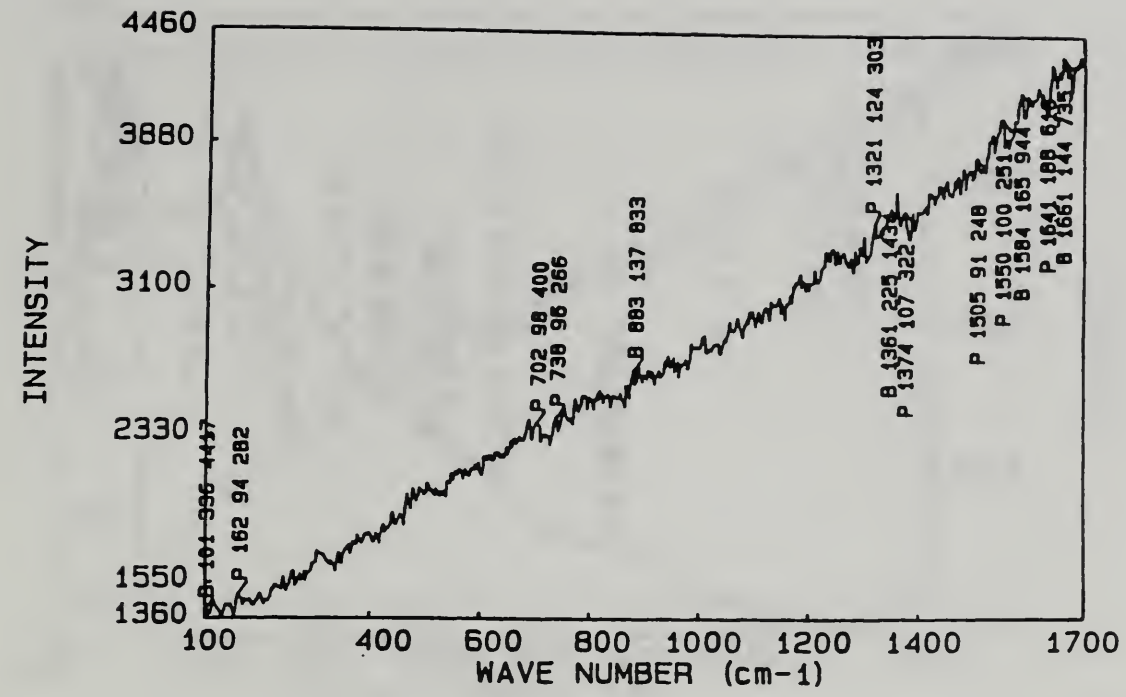

Fig. A4.13: Laser Raman Analysis of Deposit on Specimen 3-3 Near Wear Track.

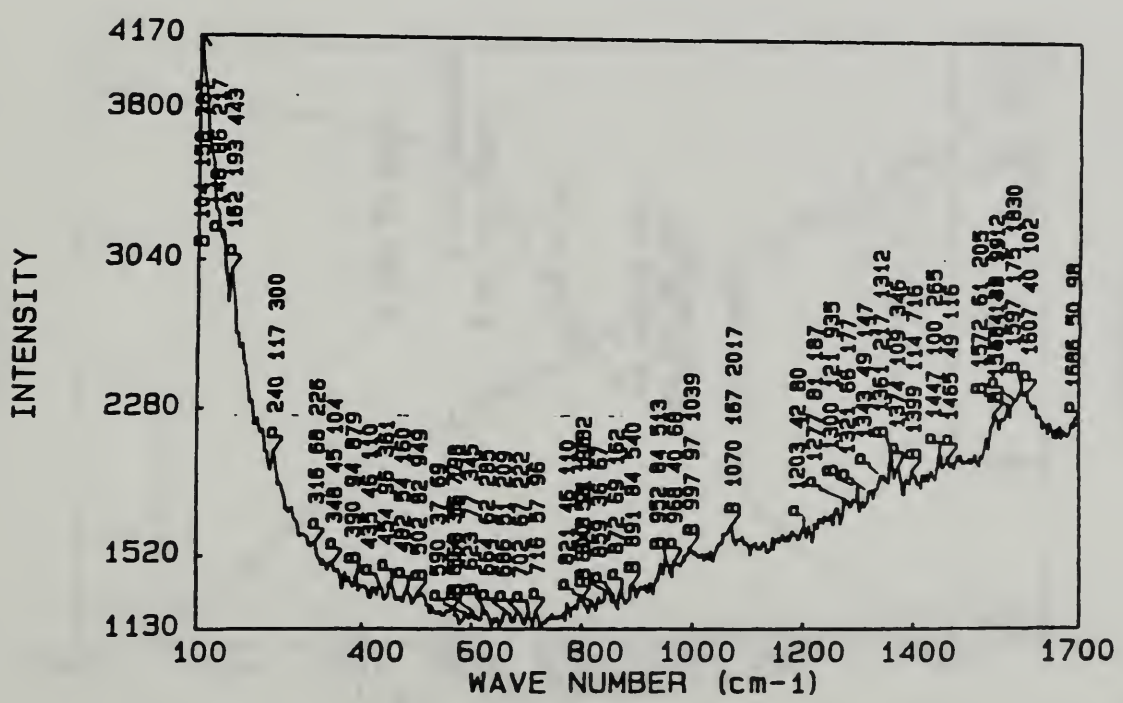

Fig. A4.14: Laser Raman Analysis of Deposit on Specimen 3-3 Near Valve Stem.

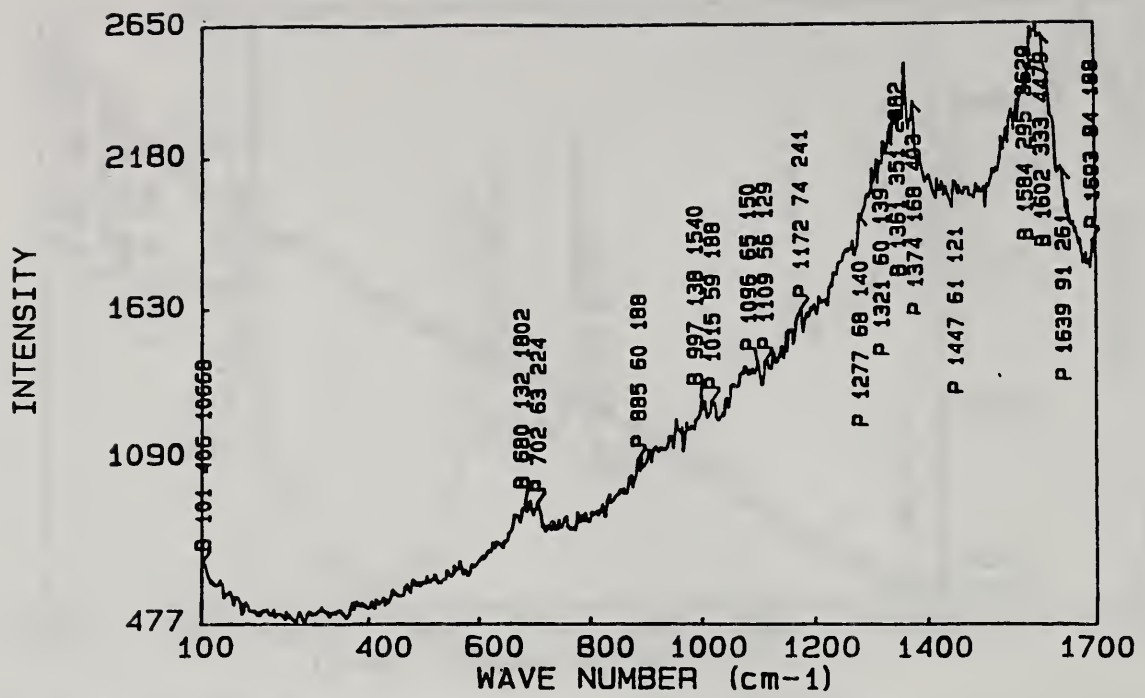

Fig. A4.15: Laser Raman Analysis of Deposit on Specimen 3-4 Near Wear Track.

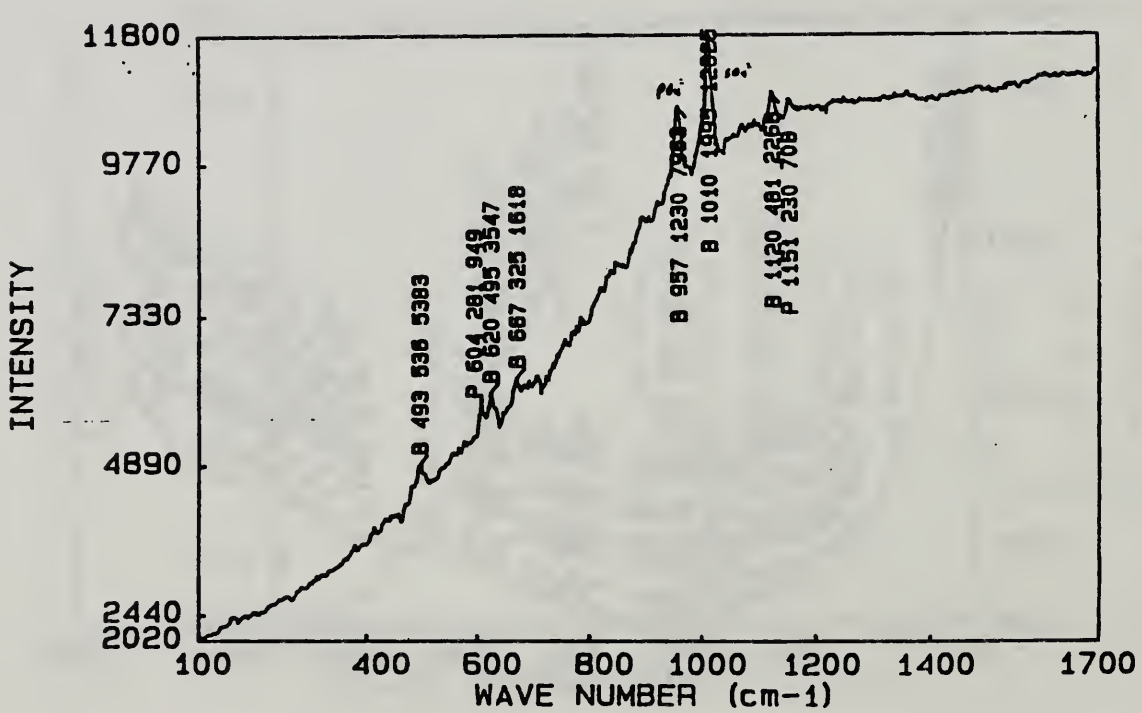

Fig. A4.16: Laser Raman Analysis of Deposit on Specimen 3-4 Near Valve Stem.

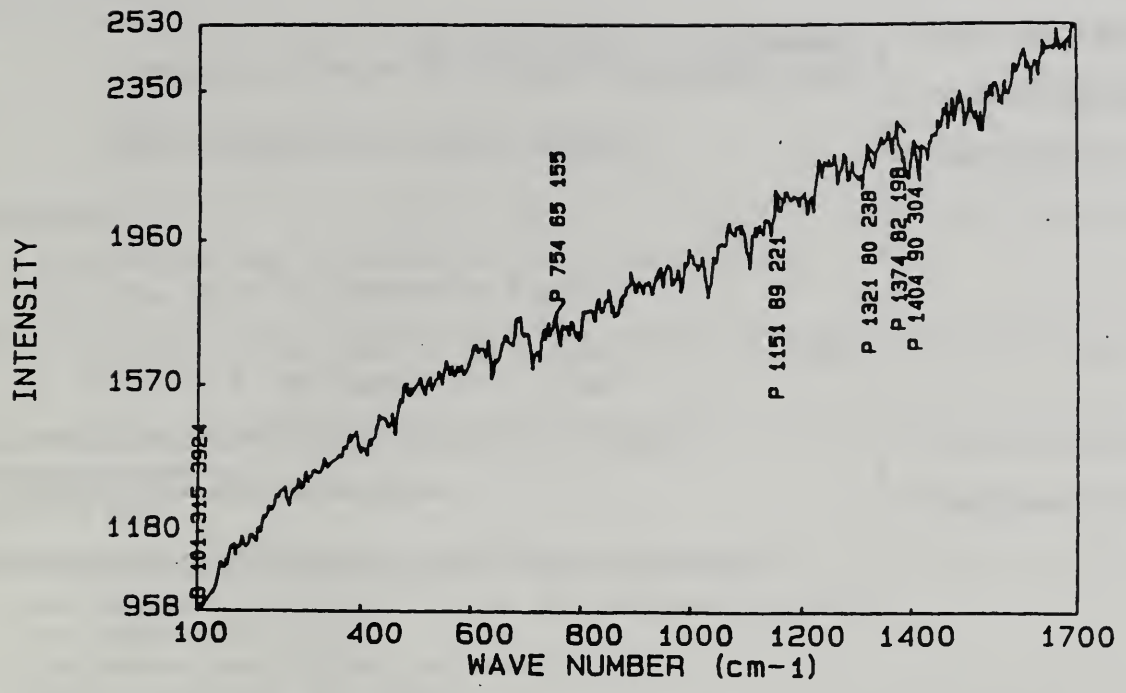

Fig. A4.17: Laser Raman Analysis of Deposit on Specimen 3-7 Near Wear Track.

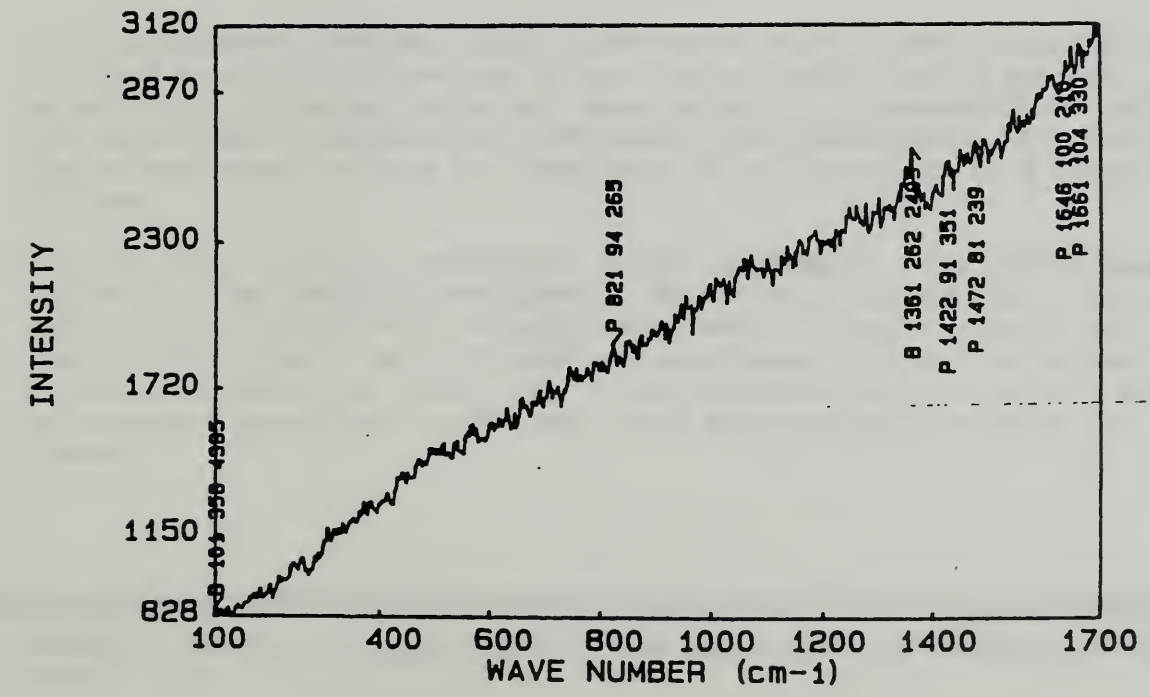

Fig. A4.18: Laser Raman Analysis of Deposit on Specimen 3-8 Near to Valve Stem.

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U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

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5. AUTHOR(S) P. I. Lacey, S. M. Hsu, R. S. Gates, S. Lee, L. Ives, C. Ku, P. Pei, Y. Wang, E. P. Whitenton, R. G. Munro

6. PERFORMING ORGANIZATION (IF JOINT OR OTHER THAN NIST, SEE INSTRUCTIONS)

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GAITHERSBURG, MD 20899

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Gas Research Institute, Center for Advanced Materials
410 Walker Building
The Pennsylvania State University
University Park, PA 16802

10. SUPPLEMENTARY NOTES

☐ DOCUMENT DESCRIBES A COMPUTER PROGRAM; SF-185, FIPS SOFTWARE SUMMARY, IS ATTACHED.

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

The Gas Research Institute (GRI) sponsored a study of the durability of advanced material combinations in gas fuelled reciprocating engines. A selection of valve/seat materials were tested in a Cummins GTA-855 engine. The engine test, scheduled for 1000 hours, was interrupted after 417 hours due to mechanical failure and terminated at 581 hours due to a second failure.

The wear rates and wear mechanisms of the components, were investigated by a team from the National Institute of Standards and technology. The post test analysis concentrated on wear measurement of the valve/seat pairs and chemical analysis of the lubricant and specimens, in order to determine the predominant causes for wear. All of the advanced materials tested appear to represent a distinct improvement above those normally used by the industry.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

ceramics; chemical; engine; seats; super alloy; test; tribology; valves; wear

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