NBSIR 85-3110

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U.S. DEPARTMENT OF COMMERCE
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ABSTRACT

The feasibility of fabricating thin film thermocouples on internal combustion engine hardware was investigated. The goal was to find a procedure that would be useful for the measurement of the metal temperature of valves, valve seats, combustion chamber surfaces, cylinder walls, and piston heads during engine operation.

The approach pursued was to coat the engine hardware material with an aluminum-containing, oxidation-resistant ferrous alloy (FeCrAlY) which forms an oxide layer with good electrical resistance. This thermal oxide was coated with a thin layer of reactively sputtered aluminum oxide and sputtered thin film type S thermocouple legs of platinum and platinum plus 10% rhodium. This project was used to investigate the materials problems related to obtaining good adhesion in the metal metal-oxide-oxide-metal laminate and the electrical insulating properties of the oxide. Thermal oxidation, reactive sputtering of Al_2O_3 and platinum alloy sputtering were investigated using optical microscopy, x-ray photoemission spectroscopy (XPS), laminar adhesion testing, and the evaluation of high temperature electrical properties.

A successful method for fabricating thin film thermocouples on internal engine materials was developed. Adherent, electrically insulating aluminum oxide with a type S thermocouple was produced on a 10 cm long stainless steel bar. The fabrication techniques and results of tests run on that bar as well as numerous small test coupons are presented.

I. INTRODUCTION

The development of the internal combustion engine has led to higher and higher efficiencies in both the Otto-cycle and diesel-cycle engines. However, further improvements in efficiencies could be attained with better control of the combustion and heat transfer processes within the combustion chamber and cylinder. Improved engine diagnostics inside the cylinder have been found to be a potentially major contribution to this improved technology for energy efficiency[1]. In response to this need, DOE has a major ECUT project which focusses primarily on non-contact, optical, engine diagnostics.

One of the critical measurements for these diagnostics relates to temperature of the cylinder, valve, and piston surfaces. These measurements have been made with recessed thermocouples; however, the size of the thermocouple and the associated heat transfer to the bead has led to uncertainties in the measurement which can be reduced by further miniaturization of the thermocouple. A new technology related to thin film thermocuples is being developed which reduces these uncertainties and reduces any disturbances to the gas dynamics near the surface of the material. This technology is under development by NASA sponsored projects at United Technology Corporation[2,3] and NBS[4] and includes thin film thermocouples and strain gauges for gas turbine engines. For these applications, type S thermocouple materials (platinum and platinum plus 10% rhodium) are applied to nickel and cobalt based gas turbine alloys with suitable protective and insulating intermediate layers. The gas turbine engine application requires temperature measurements up to 1300K in combusting gas environments.

This approach appears to be suitable for internal combustion engine thermometry of valves, valve seats, combustion chamber walls, and piston heads. The required bonding, materials compatibility, electrical performance problems must

be solved, however, to obtain a feasible working system with internal engine structural materials. Perhaps the most critical problem area is the fabrication of an electrically insulating layer between the base metal and the elements of the thermocouples. This layer must not only electrically isolate the metal components but must also provide for bonding and joining the system into a temperature measuring device less than five micrometers in thickness. The insulating layer was also found to be the critical performance limitation for gas turbine engine sensors. A schematic diagram of the thin film thermocouple is given in Figure 1.

Three base alloys were chosen to represent the internal engine combustion chamber materials. They include a cast iron (1177); a low alloy, high temperature ferritic steel (4340); and a high temperature austinitic steel (347). These iron-based alloys represent the variety of iron-based alloys used in engines with respect to carbon content, crystal structure, native oxide, and alloying content and indicate the feasibility of attaching thin film thermocouples to almost any iron-based engine alloy. The compositions of the alloys are given in Table I.

The insulation layer chosen consists primarily of Al_2O_3. This material has been found to be useful in the nickel and cobalt base alloy systems and has outstanding dielectric and adhesion properties in thin films. The stability of Al_2O_3 in oxidizing and reducing hot gases is important and superior to chromium oxides. Nickel and iron oxides do not have adequate electrical insulating properties and aluminum oxide has the advantage of superior growth rates in oxidizing atmospheres on iron-based alloys. This has led to the study and development of aluminum containing iron- and nickel-based alloys for extreme high temperature alloys. Studies by Grace and Seybolt[5], Gulbransen and Sudres[6], Sargusa and Lee[7], and, more recently, Boggs,[8] have explored the kinetics of

aluminum oxide scale formation on iron-aluminum-chromium alloys and lead to a well established technology for high temperature coating alloys. Similar work with nickel and cobalt aluminum-containing alloys has led to the development of those high temperature coatings for gas turbine engines. The most recent work by Hagel[9], Sprague et. al.,[10], Rao et. al.,[11], Smeggil and Bornstein[12], and Pettit[13] has led to the incorporation of yttria for coating adhesion and stability and has established the state of the art in high temperature oxidation resistance for base metals.

We have chosen the FeCrAlY alloy as a coating material for the internal engine parts in order to secure a high quality Al_2O_3 base for the insulating layer and for its compatibility with iron based alloys. The composition of iron plus 18% chromium, 11% aluminum, and 1% yttrium supplies sufficient aluminum for appropriate oxide growth kinetics to form scales 1-2 μm thick. This oxide scale is not generally adequate for electrical insulation because of inhomogeneities and must be augmented with sputtered Al_2O_3. This approach has proved to be superior in the gas turbine engine alloy work[2,3]. Imperfections in the thermal oxide include growth habits other than film growth which leads to gaps in the insulating layer and oxide growth which is not Al_2O_3. The thermal oxide is a good base for sputtered Al_2O_3 to promote adhesion and the pinhole defects in the sputtered layer are normally protected by the thermal oxide.

In summary, the materials approach is to coat three internal engine iron-based alloys with FeCrAlY; thermally produce Al_2O_3; sputter Al_2O_3; and sputter the type S (platinum and platinum plus 10% rhodium) thermocouple legs on the oxide. The emphasis of this project is to develop, evaluate, and analyze the feasibility of this approach for temperature measurement of internal combustion engine combustion chamber hardware. The fabrication approach included

producing thermal oxide films and sputtered oxide and metal films. The evaluation approach included mechanical (adhesion) testing of the films, thermal cycling, and electrical testing of the insulation. The analysis included optical microscopy and surface analysis with X-ray photoemission spectroscopy.

II. EXPERIMENTAL PROCEDURE

A. Materials

The three internal combustion engine alloys chosen were 1177 gray cast iron, 4340 low alloy heat resistant steel, and 347 austinitic stainless steel. Their compositions are given in Table I. These alloys were chosen after consulting with DOE contractors and major engine producers to be typical for the types of alloys used in commercial engines. The gray cast iron was obtained from the NBS Standard Reference Materials supply and has been used by engine manufacturers for that purpose. The 4340 and 347 alloys were obtained from standard commercial sources. FeCrAlY coatings for the alloys were obtained commercially and were produced by vacuum sputtering. The coating supplier has a long history of producing this type of coating for turbine engine research and development. All other materials processing was carried out in house.

B. Cleaning and Finishing

The as-received coated alloys were ground and polished through a -600 mesh silicon carbide paper. Some surface roughness is important for adhesion[4] and although both the -600 mesh finish and a subsequent shot peening of 50 μm Al_2O_3 spheres were used, no advantage for either finish was indicated. The cleaning procedure included ultrasonic degreasing in acetone followed by methyl alcohol and deionized water rinses.

C. Thermal Oxidation

Thermal oxidation was performed in a silicon carbide resistance-heated tube furnace in which atmospheres of dry argon, argon plus 4% hydrogen, and air were used. The hydrogen bearing gas enabled the suppression of iron, nickel, and chromium oxide formation when producing the alumina film. The procedure of using a very low oxygen partial pressure for the early stages of aluminum oxide film formation was developed by Grant et. al.[2] and promotes a better electrical insulating thermal oxide with NiCoCrAlY. In this study, dry argon (P_{O_2} = 1.0 Pa) was used in the initial oxidation heat treatment. After the initial thin oxide is formed, all oxidation was performed in air. Although previous work[4] included oxidation at 1275-1350K, lower oxidation temperatures of approximately 1175K were used to prevent coarse oxide formation with the iron-based alloys. Thermal oxide films of approximately 1 μm were produced as the base for the sputtered oxide.

D. Sputtered Films

In-house sputtering included the reactive sputtering of Al_2O_3 and RF magnetron sputtering of platinum and platinum 10%-rhodium thermocouple alloys. The sputtering was accomplished using a 60 cm diameter vacuum sputtering chamber and a 3000 watt RF generator at 13.56 MHz, an impedance matching box, and a 5 cm diameter planar magnetron. A quartz oscillator thickness gauge was used to monitor the deposition during sputtering and a mass spectrometer was used for residual gas analysis. Bottled 99.999% pure Argon and 99.99% pure oxygen were used as the sputtering gases. Typical parameters for platinum and platinum +10% rhodium sputtering were: target to substrate distance 15-25 cm; initial vacuum $4\text{-}15\times10^{-5}$ Pa; argon sputtering pressure 0.14 Pa; 250 watts power; deposition ranges 0.4-0.8 nm per sec metal; and RF impedance 50 ohms. The reflected power

was less than 1%. Typical parameters for reactive sputtering of Al_2O_3 were: 99.99% aluminum target; target to substrate distance - 15 cm, initial vacuum $4x10^{-5}$ to $1.4x10^{-4}$ Pa; argon was less than 1%. Typical residual gas and the mass spectrometer indicated the following pressures: $H_2O = 10^{-4}$, $Ar = 10^{-6}$, $O_2 = 10^{-5}$, $CO-N_2=3x10^{-5}$, $CH_4=5x10^{-6}$ Pa. The thickness of deposition was checked by weight gain on the sample and monitored on a glass slide. The glass slide is also a convenient way to insure the stoichiometry of the Al_2O_3 since any problems affect the transparency of the deposit. Thickness of the Al_2O_3 deposits was also checked using interferometers with thallium illumination which indicated fringes at step heights of 0.27 μm.

E. Thermal, Mechanical, and Electrical Testing

Several thermal, mechanical and electrical tests were used to evaluate the adhesion, stability, electrical performance, and overall suitability of the aluminum oxide coatings and platinum-platinum rhodium thermocouple films. They included a mechanical adhesion test, electrical insulation and dielectric performance-at-temperature test, and a thermal cycling stability test. The adhesion test employed a commercial Sebastian* adhesion tester which operates by pulling an epoxy bonded tab from the bonded film. These tests are reported directly as a shear strength of the fiber bond or strength up to 70 MPa (10,000 psi).

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*Certain commercial equipment, instruments, and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendtion or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

The electrical insulation and dielectric test is performed using a test jig in an air atmosphere furnace. The 2 cm x 2 cm test coupon is held with platinum and platinum-10% rhodium connections to the thin film thermocouple electrodes and heated to approximately 1200K. The output voltage and resistance with a one volt potential are monitored between the Pt and Pt/Rh thin film and between the thin film and substrate (ground) while heating the test coupon. This test detects any premature dielectric breakdown of the insulator and any instability of the thin film sensor. Although the test cannot insure the stability of the thermocouple emf since the entire thin film thermocouple is at virtually one temperature, it does detect increases in resistance or deterioration mechanisms such as oxidation of rhodium during high temperature exposure.

The thermal cycling test is also performed on the 2 cm square test coupon by cycling the coupon to approximately 1200K. The heating cycle is generated by a gas fired torch in 120 seconds and cooling to below 100°C is also accomplished in less than 5 minutes. Temperatures were measured with a carefully placed thermocouple and by optical pyrometry. Both techniques for measurement underestimate the maximum temperature of the thin film itself which tends to develop hot spots as defects are generated. This test detects adhesion problems as well as overall film stability under harsh environmental conditions.

Thin film thermocuples were produced with 10 cm length on long bars to measure output voltages between the hot and cold junctions. These test bars were placed through the wall of the furnace with the hot junction and the cold junctions monitored with type S reference grade thermocouples. A drawing of the test bar is presented in Fig. 2. Cold junction connections were made with copper thermocouple extension wire.

F. Analytical Characterization Techniques

Analytical techniques have been applied to characterize various aspects of the layers, surfaces and interfaces present in the thin film thermocouple devices. The overall objective was to identify the most desirable methods for each fabrication step. Characterizations were carried out to document the quality of the insulating aluminum oxide layer, the degree of metal diffusion into the aluminum oxide, and the amount and type of near-surface impurities. The X-ray photoemission spectroscopy (XPS or ESCA) measurements were made on a Leybold-Heraeus spectrometer to determine surface contamination and composition. This information relates to the adherence and electrical properties of the thin films. The presence of iron and chromium in the thermal oxide are also indicators of the need for controlled atmospheres during oxidation.

III. RESULTS

A. Thermal Oxidation

A thermal oxide, primarily aluminum oxide, was grown on all of these samples which were coated with FeCrAlY. This technique has been used successfully for nickel and cobalt based superalloy substrates[4]; however, those alloys permit heat treatments in the 1300-1350K temperature range. Attempts at employing those high temperatures in air oxidation with cast iron (1177) and low alloy high temperature steel (4340) indicated the base alloy could not survive the heat treatment even when coated with FeCrAlY. Excessive oxidation ruined the samples. Oxidation was also attempted in argon plus 4% hydrogen which suppresses oxidation of metals other than aluminum and yttrium. These samples had little weight gain but the oxide spalled and later attempts to coat with sputtered oxide indicated little or no adherence of the sputtered coating. Because of

these results, further oxidation of specimens was carried out in the temperature range of 1100-1200K. Even at these lower temperatures, the cast iron samples did not form good clean oxides. The quality of the oxide can be judged by its color since Al_2O_3 is transparent and white while iron, nickel, and deleterious chromium oxides are colored. The microscopic appearance at 500X is also a strong indication of flaws in the insulating layer. Pits, mounds, inclusions, cracks, and discolorations which can be seen at 500X are strong indications of electrical problems in the insulation. For this reason, all samples were inspected at 500X after each step in the fabrication; i.e., polishing, oxidation, sputter oxide coating, and platinum film deposition.

Surface polishing and cleaning is an important parameter in preparation of samples for thermal oxidation and sputter coating. A smooth even substrate is required to prevent uneven oxide growth and aids in the development of a smooth strong oxide film free from electrical flaws. However, it has been found[2,3,4] that a smooth Al_2O_3 oxide surface does not promote adherence of the platinum alloy films. Two general approaches which have had some success in the past were employed. One includes a fine polish (with 1 μm diamond abrasions) followed by 50 μm glass shot peening and the second is to finish with -600 mesh silicon carbide wet polishing. This later treatment leaves parallel ridges as exhibited in Fig. 3 (sample G3b) after thermal oxidation. The 50 μm shot peening leads to a surface after thermal oxidation as exhibited in Fig. 4. We found that the -600 mesh polish surface (Fig. 3) on sample G3b was generally more dependable in avoiding short circuits and in promoting adhesion of the sputtered films and was the technique used for most of the sample coupons.

Optimization of the heat treatment to form the thermal oxide on the FeCrAlY coating was intended to generate a uniform film at least 0.5 μm thick and preferably over 1.0 μm thick. The oxidation was initiated with some samples in

high purity argon to suppress the formation of iron oxide but no significant difference was noted between those samples and the samples oxidized completely in air. Oxidation in air at 1173K (900°C) required at least 50 hours to obtain approximately 1 μm of oxide. We calculated the oxide thickness from weight gain on samples which were completely covered with FeCrAlY and considered that estimate to be ±20% or better. Interferometry of oxide films was also used to verify film thicknesses.

Numerous attempts were made during this project to fabricate the sputtered deposited laminates without the oxidized FeCrAlY intermediate layer but they failed to yield an adherent platinum film on the sputtered Al_2O_3. Thermal Al_2O_3 is also produced for turbine engine blades and vanes using pack cementation processes involving the addition of aluminum to the base alloy followed by oxidation and this may well be a successful approach. It is also likely that the NiCoCrAlY and CoCrAlY coatings used for gas turbine engine hardware would also be suitable for forming the thermal oxide. In fact, we have had superior results using NiCoCrAlY compared to FeCrAlY with nickel and cobalt alloy substrates[4].

In summary, the successful thermal oxide formation used in this project involved coating the iron base structural alloys 4340 and 347 with FeCrAlY followed by air oxidation at 1173-1200K for 50-75 hours. In order to obtain adequate adhesion of platinum alloy films, a 600 mesh polishing was used which yielded the proper surface roughness for adhesion.

The aluminum oxide coating has a much lower coefficient of thermal expansion than the iron base alloys. This difference is approximately $9x10^{-6}K^{-1}$ related to the 347 alloy and $8x10^{-6}K^{-1}$ related to the 4340 alloy. A change of 800K in the substrate temperature would therefore lead to a strain differential of 0.7%. Since the cross sectional area of the films

is negligible compared to the substrate, this strain must be accommodated by the film. The Al_2O_3 thermal oxide films are in compression when cooled from the oxidizing temperature and no doubt some cracking does occur. This situation is complicated by the sputter deposition of an Al_2O_3 film at low temperatures (~300K) which is in compression as deposited. A second heating of the assembly then relieves the compression force and generates tensile stresses in the oxide. These complex residual stress patterns appear to receive better accommodation with the undulating surfaces of Fig. 3 and 4 than is apparent on the smoother surfaces as shown in Fig. 5 (Sample E8) where tensile cracks damage the oxide. With the smooth surface, the stresses appear to build up over long distances and cause large tensile cracks which ruin the electrical properties.

B. Sputtered Thin Films

The thin film thermocouples are composed of various layers approximately 1-4 μm thick. Their electrical performance requires an insulator of high dielectric performance to prevent breakdown and high resistance (>10KΩ) over distances of approximately 3 μm. Therefore, the insulator must be pore free and free of 3 μm diameter defects that would affect the electrical properties. As was mentioned in the Introduction, aluminum oxide is an excellent choice for the insulator and reactive vacuum sputtering has been found to be a useful way of achieving these properties. Similarly, the platinum and platinum-rhodium alloy films must have excellent electrical properties. Thin film deposition of platinum group metals can be achieved by numerous means such as electroplating, electron beam coating, slurry and sinter techniques, electrophoresis, electroless deposition, etc., but the sputtering technique has been found by the electronics industry to be preferred for its reproducibility. The metal films of the thermocouple must be uniform, strong, ductile, adherent, stable, and durable. The

sputtering technique has been used in the aircraft engine industry and can be commercialized with confidence because of its use by many vendors.

Reactive sputtering of aluminum oxide has been described by Berry[14]. The development of RF sputtering enabled the production of non-metallic films leading to unique capabilities of this technique. The Al_2O_3 sputtered film can be produced using an aluminum target or an alumina target since the RF field does not require a conducting target. Since the bombarding and ejected species are almost completely of atomic form both targets are similar in practice. To achieve Al_2O_3 in the substrate film oxygen must be present in the sputtering atmosphere which reacts with the deposited film as it is built up. In fact, with oxygen present in the sputtering atmosphere, an aluminum target is rapidly oxidized so that both aluminum and alumina targets have similar surfaces. Aluminum targets are to be preferred because of the ease of fabrication and superior heat transfer characteristics.

The technique for deposition of the Al_2O_3 insulating film was planar magnetron DC sputtering. This technique was pioneered by Nowicki[15] at Honeywell for metal-oxide-semiconductor (MOS) devices and is superior to chemical vapor deposition (CVD) because of the better control of residual stresses. The magnetron has the added advantage of high deposition rates and therefore greater promise as a commercial technique. In this investigation, high purity aluminum was used in preference to the 6061 alloy used by Nowicki to avoid contamination by silicon and magnesium. The presence of magnesium may, in fact, promote better adhesion[17] but was not investigated in this work.

Experimental investigations of sputtering rates, atmospheres, target to substrate distances, and power levels were used to optimize coating purity, smoothness, and adhesion. Purity is judged by the level of optical clarity and absences of color. Smoothness is verified with the optical microscope, and

adhesion was measured with an adhesion tester. The best quality films were produced using 400 watts on a 5 cm diameter target of 1100 aluminum at 15 cm target to substrate distance. The pressure of the sputtering atmosphere of 90% argon, 10% oxygen, was 2×10^2 Pa to optimize the film. Typical sputtering rates were 0.3-0.6 nm per second so that a 3 μm film required two hours to deposit. A typical good sputtered film is shown in Fig. 6. At 500X, the coating is colorless, clear, and appears to have 1-2 μm hills which are a reproduction of the thermal oxide topography. Each coating is made on a glass slide in addition to the test coupon. The coatings on the glass slide were used to evaluate the clarity, thickness, and smoothness.

Thickness of the coating is an important parameter and three methods were used for its measurement. During the coating, the rate and accumulation are measured using a calibrated quartz oscillating crystal. Weight gain was measured on each sample and glass slide. The weight gain was calculated using estimates of the covered area and some allowance had to be made for wrap around coating on unmasked areas. The weight gain estimate of thickness is probably within 20% of the true value. The third method used for confirmation of thickness employed an optical interferometer.

X-ray photoemission spectroscopy was used to determine the composition of the surface oxides. Two thermally oxidized surfaces were examined: one oxidized in air (E4) and one in argon plus 4% hydrogen (E7). The wide energy range scan of E4 is presented in Fig. 7. The peak at 533.7 eV binding energy originates from the 1s electron level of oxygen, the 120 eV peak is from the aluminum 2s level, the 77 eV peak is from the aluminum 2p electrons, and the peak at 286.8 eV derives from carbon 1s electrons. Two important observations can be made from this wide scan of E4 which is air oxidized FeCrAlY on a 4340 substrate. First: the carbon peak which remains after 2 hours of sputter cleaning

indicates a contamination problem which could affect both adhesion and electrical properties. Second: The absence of any Fe or Cr peaks indicates that the thermal oxide formed in air is almost entirely Al_2O_3. Narrow XPS scans for iron and chromium were made between 733 and 708 eV for Fe2p and between 595 and 575 eV for Cr2p. These peaks were hidden in the noise and rough calculations based on earlier work indicate chromium concentration at less than 0.2% and iron at less than 0.05%.

The reduction in the concentration of surface carbon during sputter cleaning by a factor of one half was accompanied by the doubling of the aluminum peak whereas no significant change in the oxygen peak was measured after the sputter cleaning. Estimations of the Al to O ratios indicated the oxide was low in Al ($Al_{1.5}O_3$ compared to the Al_2O_3 stoichiometric composition) which could result from carbon contamination, possibly in the form of CO.

The other samples studied with XPS included E7, which had a thermal oxide produced at 1175K in argon plus 4% hydrogen on 4340 and FeCrAlY and E8, which had 3 μm of sputtered Al_2O_3 on an air thermal oxide of FeCrAlY. The wide scan for E7 is presented in Fig. 8. The carbon peak before cleaning was not nearly so pronounced and is very small after 1 hr of sputter cleaning. Some interference with the aluminum 2p peak is caused by 4f photoemission from platinum which also results in small binding energy peaks at 611,519,331,318 and 40 eV. The aluminum 2s to oxygen 1s peak ratio indicates an approximate ratio of $Al_{2.5}O_3$. This is not considered strong enough evidence to propose an off-stoichiometric aluminum oxide. The iron peaks from $Fe2p_{3/2}$, $Fe2p_{1/2}$ and Fe (A) at 726, 714 and 644 eV, respectively, are weak as is the 579 eV binding energy peak from $Cr2p_{3/2}$, but they are much clearer than any of these features for the E4 sample measurements. Estimations indicate 0.3% Cr and 0.1% Fe in sample E7. The platinum presence was related to remnants of an

electrode on the oxide surface. The E8 wide scan XPS is given in Fig. 9. This sample has the sputtered Al_2O_3 and Fig. 9 is representative of the sample after 1 hr of sputter cleaning. This sample would not be expected to have iron or chromium and does not. Carbon contamination (287 eV) is also less than the other two samples analyzed. The approximate calculated ratio of the aluminum to oxygen ratio is represented by $Al_{2.3}O_3$; however, the true composition is almost certainly closer to stoichiometric. An interesting side effect is the charging shift on the sputtered Al_2O_3 which is approximately 2.7 eV higher in E8 compared to the thinner thermal oxide of E4, exhibiting the better insulating quality of E8.

In summary, neither air oxidized nor $Ar+H_2$ oxidized FeCrAlY indicated much iron or chromium in the oxide surface. The iron (0.1%) and chromium (0.3%) on E7 may be visible due to pores in the thin oxide. The absence of Fe and Cr relates to the faster oxidation rate of the aluminum and the extremely low diffusion coefficients of Fe and Cr in Al_2O_3. In addition, it is evident that carbon contamination is significant, especially in the air oxidized E4.

Platinum and platinum-10% rhodium films for the thermocouples were also deposited using planar magnetron vacuum sputtering. The best films were made using a target to substrate distance of 15-20 cm, 200-250 watts, 0.14 Pa argon sputtering gas and electrically grounded substrates. The target materials were pure 10 cm discs approximately 0.3 cm in thickness. The deposition rates were approximately 0.6-0.8 nm per second and no significant difficulties were encountered in obtaining good quality coatings which were generally mirror smooth on the glass slide and reproduced the surface topography of the test coupon. Adhesion and durability of these coatings is discussed below.

The masking for the thermocouple pattern was accomplished using 0.12 mm thick steel shim stock. This material is easy to cut and provided the necessary

resolution of the thermocouple patterns and electrode required. Simple spring clamps could be used to provide masking for thermocouple legs of 1 mm width.

C. Adhesion of Sputtered Layers

One of the critical properties for the thin film thermocouple assembly is adhesion of the oxide and platinum alloy thin films. A summary of the results of the adhesion testing is presented in Table II. This table also summarizes the heat treatments and sputtered oxide thicknesses. Good adhesion properties were attained when the FeCrAlY coatings were polished but had sufficient surface roughness (600 mesh polish or 50 μm shot peening) and the sputtered oxide was less than 4 μm thick. A problem with the thicker oxide is illustrated in Fig. 10 where the 4.8 μm thick sputtered Al_2O_3 spalled (E8). Other problems with adhesion seem to relate to oxidation in argon plus 4% hydrogen at a high temperature (1310K) as evidenced by E5 and too thin a thermal oxide such as E3 which was oxidized at 1073K. The adhesion problem with the thin thermal oxide is related closely to the fact that we seem to need the 0.5-1.0 μm thermal Al_2O_3 as a good substrate for sputtered Al_2O_3. Although several attempts were made with all three substrate alloys to eliminate the oxidized MCrAlY from the procedure, no dependable procedure was developed.

To recapitulate the results given in Table II, E1 was oxidized at an excessively high temperature. E2T (top) was sputtered with Al_2O_3 before the thermal treatment and adhesion was good on the -600 mesh surface finish. E2B (bottom) also had good adhesion of both the oxide and platinum films using the standard heat treatment at 1175K followed by sputtering. E3 was heat treated at a low (1075K) temperature and the smooth sputtered oxide did not yield good platinum adherence. E4 and E6 had good adherence. E5 was oxidized in argon plus 4% H_2 at high temperatures (1315K) and the adherence was adequate. E7 which was oxidized in argon plus hydrogen at 1175K and had a thin oxide which

was smooth but had only fair adhesion (17 MPa) on the platinum. E8 had poor adhesion of the platinum on the smooth oxide which cracked on thermal cycling. E9 had no FeCrAlY and together with E10 and E16 had adequate adhesion of the sputtered oxide but poor adhesion of the platinum. We did not find the proper thermal oxidation conditions and sputtering conditions for the cast iron series (Table II) to insure good adhesion of platinum.

The "G" series evaluation of 347 alloy plus FeCrAlY are also given in Table II. The only adhesion problems with the sputtered oxide was on G6T (top) on which two layers were sputtered and the top layer had only fair adhesion. Adhesion of the platinum on G8 was poor. This was also noted on the other sample (E8) which had been oxidized in argon for the first 20 hours at 1175K followed by air oxidation. This treatment seems to produce a smoother sputtered oxide which tends to crack on cooling (Fig. 5). G5T which had two sputtered layers also had an adhesion problem with the platinum. Fast thermal cycling was used to uncover adhesion problems that may relate to thermal excursions in engine applications. The test included heating the 1.8 cm square test coupon to 1175K four times from near room temperature. The heating took less than two minutes and cooling took less than five minutes. Samples E2, F2, G3, and G8 were subjected to this test and all survived without delamination. Some small (1 mm) perforations were generated by hot spots on the E2 and F2 samples caused by the uneven heating of the torch.

D. Electrical Properties

Electrical properties were tested on the thin films to measure the insulating quality of the oxide and the thermocouple output. The test coupons and procedures were described in the Experimental Procedure section. Samples which passed the room temperature test for resistance between the platinum thin film and substrate (ground) were measured for resistance in an air atmosphere furnace

up to approximately 1100K. The small test coupons which had both adherent platinum thin films and no room temperature shorts include E7, E8, G2, G4T, G4B and G7. The resistance of a 3-4 μm aluminum oxide film would be expected to drop to the 10KΩ range at approximately 800-900K according to data in Samsanov's Oxide Handbook[18] and a correlation with that data had been observed with the oxide films on the nickel and cobalt based superalloys[4]. Typical data for these samples is presented in Figs. 11 and 12. Fig. 11 displays the data for the oxide electrical resistance versus temperature of sample E7. At temperatures below 800K, the resistance was greater than 500KΩ and above that temperature the resistance falls with increasing temperature to approximately 20KΩ at 1200K. This behavior is similar to that predicted[18] and indicates the superior quality of Al_2O_3 as a high temperature electrical insulator. An interesting behavior pattern was observed with sample G2 (Fig. 12). With this test as well as the G4T, G4B, and G7 tests, the electrical resistance dropped with increasing temperature but on cooling the sample had higher resistance than on heating. In fact, this "self-healing" characteristic of the aluminum oxide on FeCrAlY is important for its use as a high temperature oxidation protective coating. The exposure of the FeCrAlY at high temperatures to air leads to a protective film of adherent Al_2O_3. This behavior was also noted in the thin film thermocouple work described by Kreider, et. al.[4] for FeCrAlY coatings on cobalt and nickel-based substrates but not with the NiCoCrAlY coatings. The interaction of the thermal oxide and the sputtered oxide coating is complex and suggests the possibility of improving the insulating field by heat treatments after fabrication. The electrical tests on the small coupons confirmed that the best fabrication procedure included a -600 mesh finish on the FeCrAlY followed by air oxidation at 1175-1200K and the sputter coating of at least 3 μm of Al_2O_3.

This procedure lead to adherent platinum films which were well insulated from the substrate.

Ten centimeter long bars (Fig. 2) were tested for thermocouple output voltages as a function of temperature. Adhesion of the platinum and platinum-rhodium thin films was a problem, especially on those bars which did not have the oxidized FeCrAlY base for the sputtered layers. Sample H3, however, did establish the feasibility of the approach. It was fabricated using the preferred approach and the performance is displayed in Fig. 13. The figure is used to compare the e.m.f. output of the thin film thermocouple to the difference between two reference grade type S thermocouples stationed at the hot junction and extension wire connections of the thin film thermocouple. One problem related to this comparison is that the reference thermocouples do not measure exactly the metal temperature of the bar and they are affected by their surroundings more than the thin film thermocouple. A second important problem relates to the exact composition of the sputtered thin film thermocouple which determines its calibration. In fact, the test cannot be considered an accurate calibration of the thin film thermocouple but only a demonstration of feasibility of the approach. Nevertheless, the comparison in Fig. 13 indicates rather good agreement and the slope of the data is within 20% of 1.0 which would be expected for platinum and platinum plus 10% rhodium. The sputtering procedure may have affected the composition of the coatings.

IV. SUMMARY AND CONCLUSIONS

The feasibility of fabricating thin film thermocouples on internal combustion engine hardware was investigated. The goal was to find a procedure that would be useful for the measurement of the metal temperature of valves, valve seats, combustion chamber surfaces, cylinder walls, and piston heads during

operation. The ferrous alloys investigated included a gray cast iron (1177), a ferritic, low alloy, high temperature steel (4340), and an austenitic stainless steel (347).

In order to insulate the thermocouple elements from the engine hardware, aluminum oxide was chosen. Al_2O_3 has been demonstrated to have the best high temperature electrical insulating properties and can be fabricated as a thin film both by thermal oxidation and by reactive sputtering. A combination of both film production techniques was found to be necessary to obtain both good insulating and good adhesion properties.

In order to obtain good oxide film properties, a sputtered film of FeCrAlY was employed which provides a very compliant high temperature base for the oxide and thermocouple thin films. The FeCrAlY also forms an adherent, pure aluminum oxide film on thermal oxidation which is suitable as a base for the thin film thermocouple. The best oxidation conditions which were compatible with the coated 4340 and 347 alloys included an air firing at approximately 1200K for 50 hours. This treatment yielded a thin (0.5-1.5 μm) film of pure Al_2O_3 as determined by XPS. The best surface condition of the FeCrAlY prior to oxidation was found to be a clean -600 mesh polished finish. This approach led to adherent sputtered Al_2O_3 and platinum alloys.

A 3 μm sputtered Al_2O_3 film was found necessary for electrical insulation of the thermocouple. Rf reactive sputtering of aluminum in 10-20% oxygen atmospheres was used to produce successful (adherent and electrically insulating) films. The adherence was measured to be typically 70 MPa which permits thermal cycling to 1200K on the iron alloy substrates. Electrical properties of the films were also measured at temperatures up to 1200K. XPS was used to confirm the purity of the film and optical microscopy was found to be a valuable tool in monitoring fabrication of both the thermal and sputtered oxide films.

Thin film sputtered platinum and platinum-10% rhodium was used to form the thermocouple and a thickness of 2 μm is recommended. This thickness is required for durability but is limited by the adhesion properties. The electrical properties of these films were measured as 10 cm thermocouples on substrate bars and compared to reference grade type S thermocouples. The performance demonstrated the feasibility of the approach for measuring metal temperatures in internal combustion engines using iron-based alloys.

V. RECOMMENDATIONS

The MCrAlY coating described in this report requires an additional coating step and a high temperature heat treatment which significantly complicates this procedure for the production of thin film thermocouples. If a method for directly applying the insulating layer and thin film thermocouple were developed, the technique would be considerably more attractive. The present problems of this approach relate to adherence of the precious metal thin film thermocouple and breakdown of the oxide insulation. The adherence problems might be solved by employing techniques used in ceramic joining such as thin film metalizing with molybdenum and by using base metal thermocouple materials such as type K or other combinations. Other insulating materials may be better for the automotive engine since the maximum temperature capability is not as high as that required for gas turbine engines. For example, SiO_2 has good insulating properties and good sputter deposited layers can be produced which should be adequate for internal combustion engine hardware. In addition, the control of substrate temperature and electrical bias could lead to an improvement of oxide integrity.

It is recommended that a technique be explored for applying thin film oxides and thermocouple materials to both ferrous and aluminum alloy engine

hardware. This project would include the use of reactive metal films to improve bonding, new oxides including SiO_2 and new thermocouple alloys. Substrate temperature and bias control would be used to improve the oxide and bonding also. The goal of this project would be to develop an inexpensive thermal sensor technology for current internal combustion engine valves, valve seats, combustion chambers, cylinder walls, and piston heads.

VI. ACKNOWLEDGMENTS

This project was sponsored by the Office of Energy System Research, Energy Conversion and Utilization Technologies (ECUT) Program, U.S. Department of Energy under interagency agreement number DE-A105-830R21375 through the Oak Ridge National Laboratory, operated by Martin Marietta Energy Systems, Inc. The authors wish to thank Dr. Joseph Carpenter of Oak Ridge National Laboratory and Dr. James Eberhardt of the ECUT Program for their help and guidance in this project. Also, we would like to thank Edward Farabaugh for his help with the Xray photoemission spectroscopy studies and James Allen and James Melvin for their help in fabrication and testing.

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Table I. Composition of Substrate and Coating Alloys in weight percent, [balance is Fe]

	Cr	Ni	Mn	Si	C	Other	Other
1177	1.4	3.0	0.37	0.9	2.7	1.5 Mo	0.6 P
4340	-	1.8	0.7	0.2	0.4	0.25 Mo	0.8 Co
347	18	11	2.0	1.0	.08	1.0 Nb+Ta	
FeCrAlY	18	-	-	-	-	11 Al	0.7 Y

Table II. Adhesion and Thin Film Parameters

Sample	Oxidation Temp/Time K/hrs	Thermal Oxide Thickness μm	Sputter Oxide Thickness μm	Adhesion Strength Strength MPa	Comments
E1	1350/65	-	-		Coarse Oxide
E2T	1175/24	-	5	>70 >70 (Pt)	Sputter before heat treatment
E2B	1175/24	-	4	>70 28 (Pt)	Thermal cycling
E3	1075/24	-	3	>70 0 (Pt)	smooth, thin thermal oxide
E4T	1175/24	-	4	>63	Pt shorted
E5T	1360/66	-	-	50	oxidized in Ar + 4% H_2
E5B	1360/66	-	1	33	
E6	1175/42	-	2.5	>70	
E7	1175/24	-	4	20 27 (Pt)	Oxidized in Argon + 4% H_2
E8	1175/24	-	4	50 0 (Pt)	Oxidized in argon, air
E9	-	-	4	38	No FeCrAlY
E10	-	-	1.7	64 0 (Pt)	No FeCrAlY
F2T	-	-	3	35	No oxidation heat treatment
F4	1075/24	-	-	-	Uneven oxide
F8	1175/42	-	2	-	Uneven oxide
G1	1175/24	1.0	-	>70	Ar + 4% H_2
G2T	1190/62	2	3.2	-	
G2B	-	2	3.2	68	
G3T	1190/50	0.6	2.0	65	Grit Blasted

Table II. (Cont.)

Sample	Oxidation T°K/hrs	Thermal Oxide μm	Sputter Oxide μm	Adhesion Strength MPa	Comments
G3B	-	0.6	3.2	70 70 (Pt)	Thermal cycle test
G4T	1190/50	0.8	3.0	>70 (Pt)	Grit blasted
G4B	-	0.8	4.0	-	
G5B	1175/50	0.5	1+5	69 0 (Pt)	two sputtered oxide layers
G6T	1175/50	0.5	1+4	14	two sputtered layers, smooth
G7T	1180/65	0.8	2	25 (Pt)	
G8B	1175/50	0.5	4	58 (Pt) <1 (Pt)	Oxidized in argon, air

Table III. Thin Film Thermocouple Test

Reference T/C mv	Junction T/C mv	Difference mv	Difference T(K)	Thin Film T/C* mv	Thin Film T/C* T(K)-273
.58	.09	.49	78	.22	60
1.28	.33	.95	140	.47	96
1.80	.48	1.32	186	.72	129
2.35	.65	1.70	230	1.03	168
3.12	.95	2.17	283	1.38	210
4.22	1.33	2.89	361	1.94	273
5.00	1.65	3.35	410	2.42	325
5.95	2.00	3.95	471	2.95	383
6.76	2.42	4.34	511	3.17	406

*0.14 mv added for 298°K cold junction

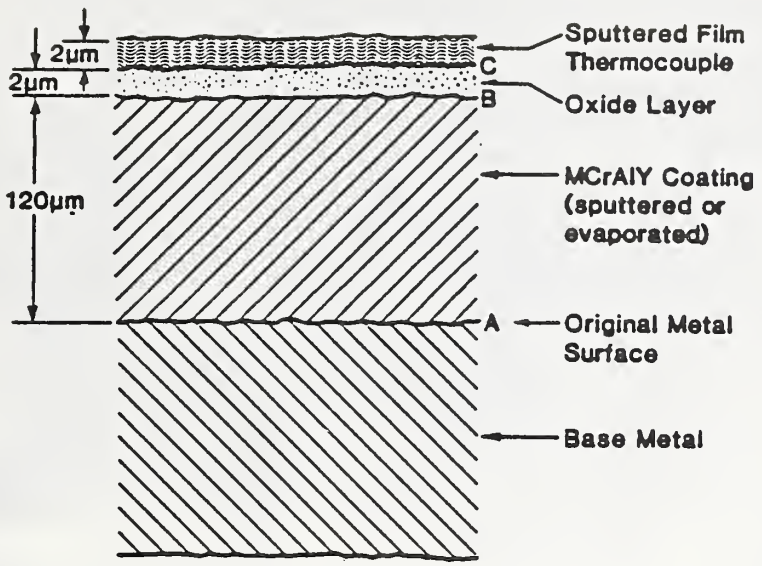

Figure 1. Schematic cross section of thin film sensor

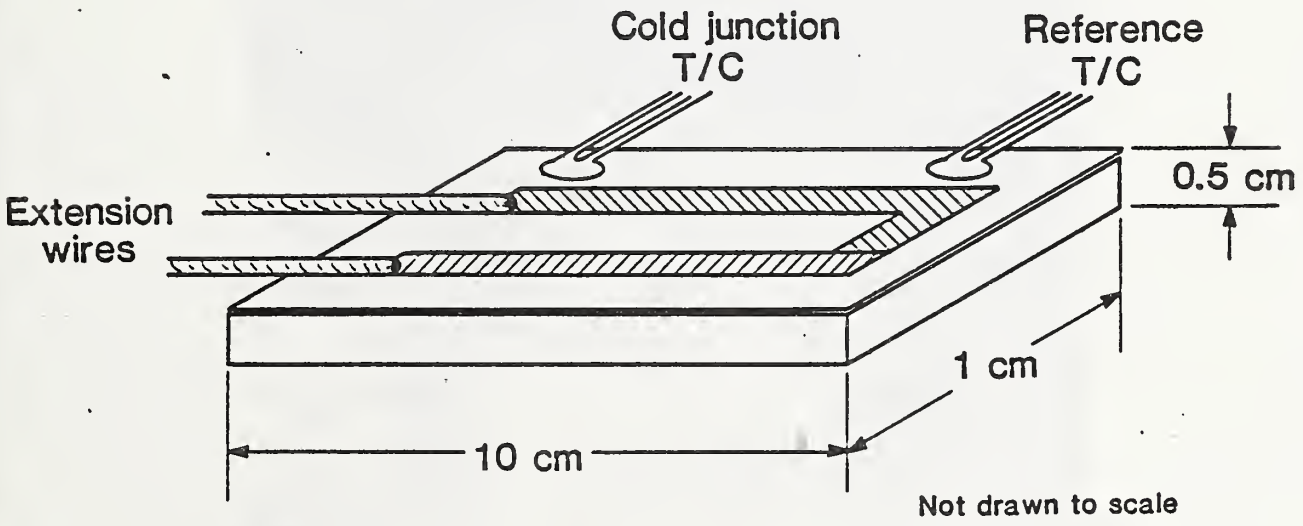

Figure 2. Thin film thermocouple test bar

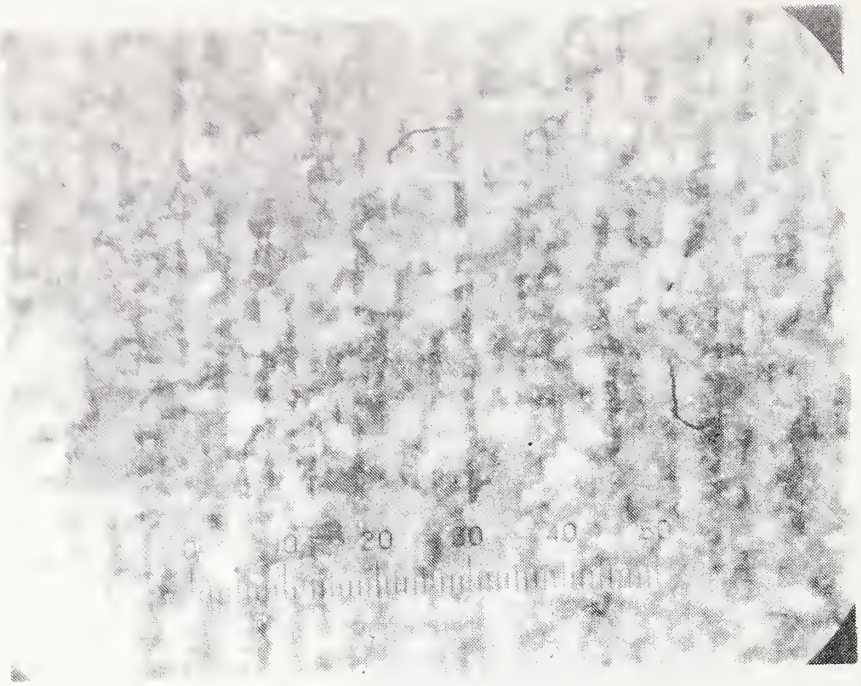

Figure 3. Thermal oxide of G3b - FeCrAlY
has -600 mesh polish - 500x

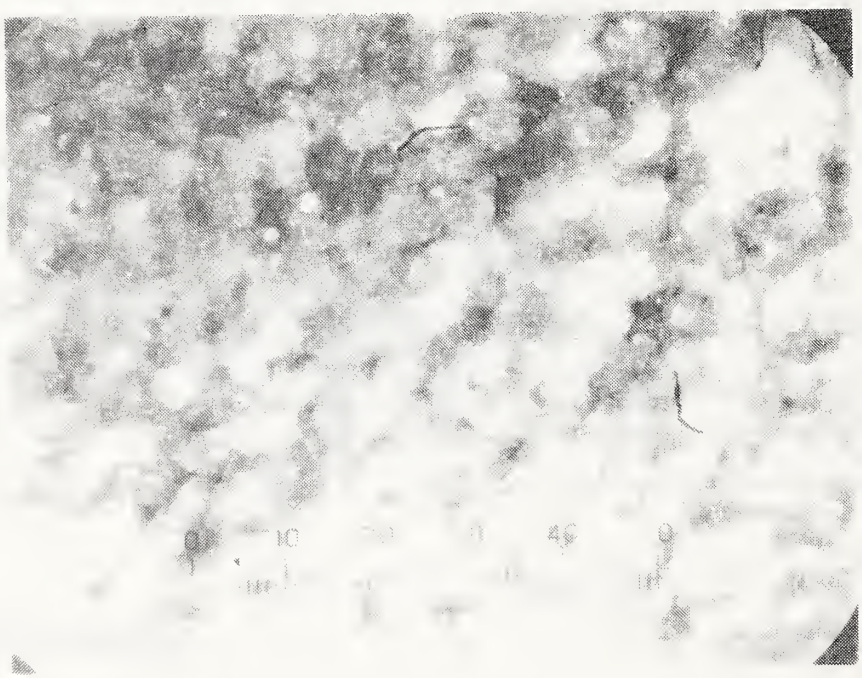

Figure 4. Thermal oxide of G3T - FeCrAlY
has shot peened finish - 500x

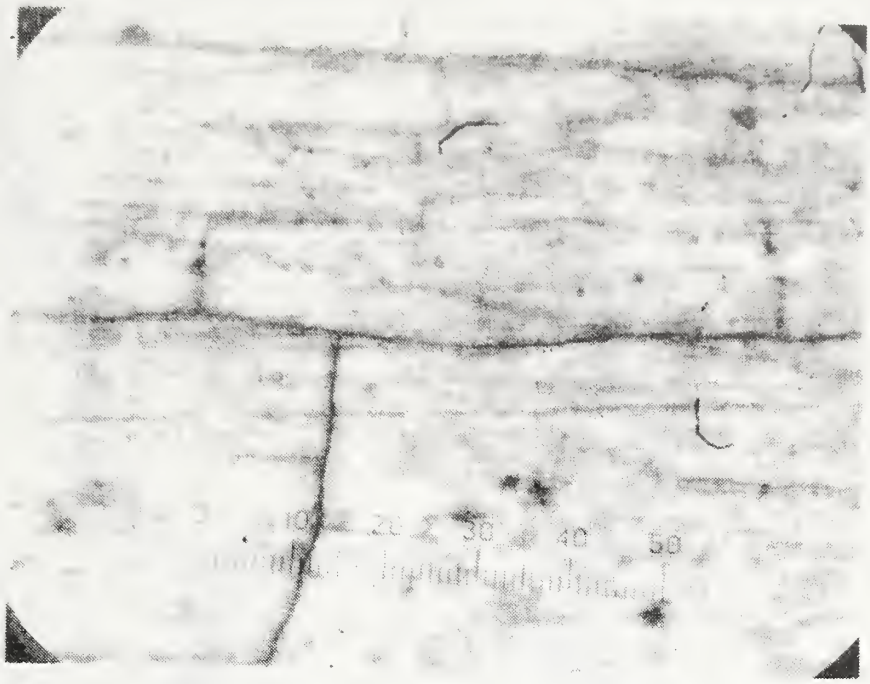

Figure 5. Cracked oxide of E8 - 500x

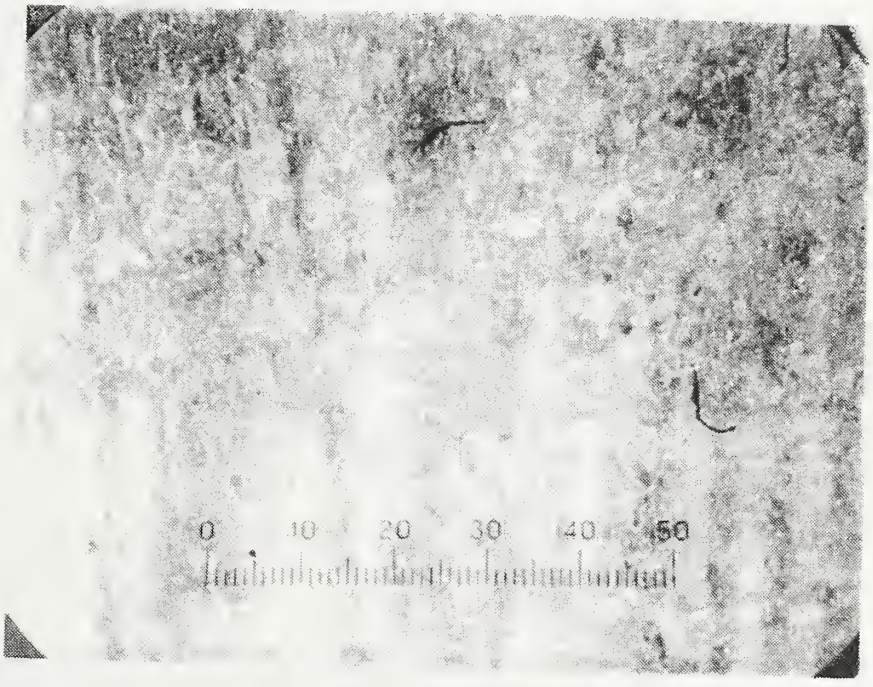

Figure 6. Sputtered oxide of G4T - 500x

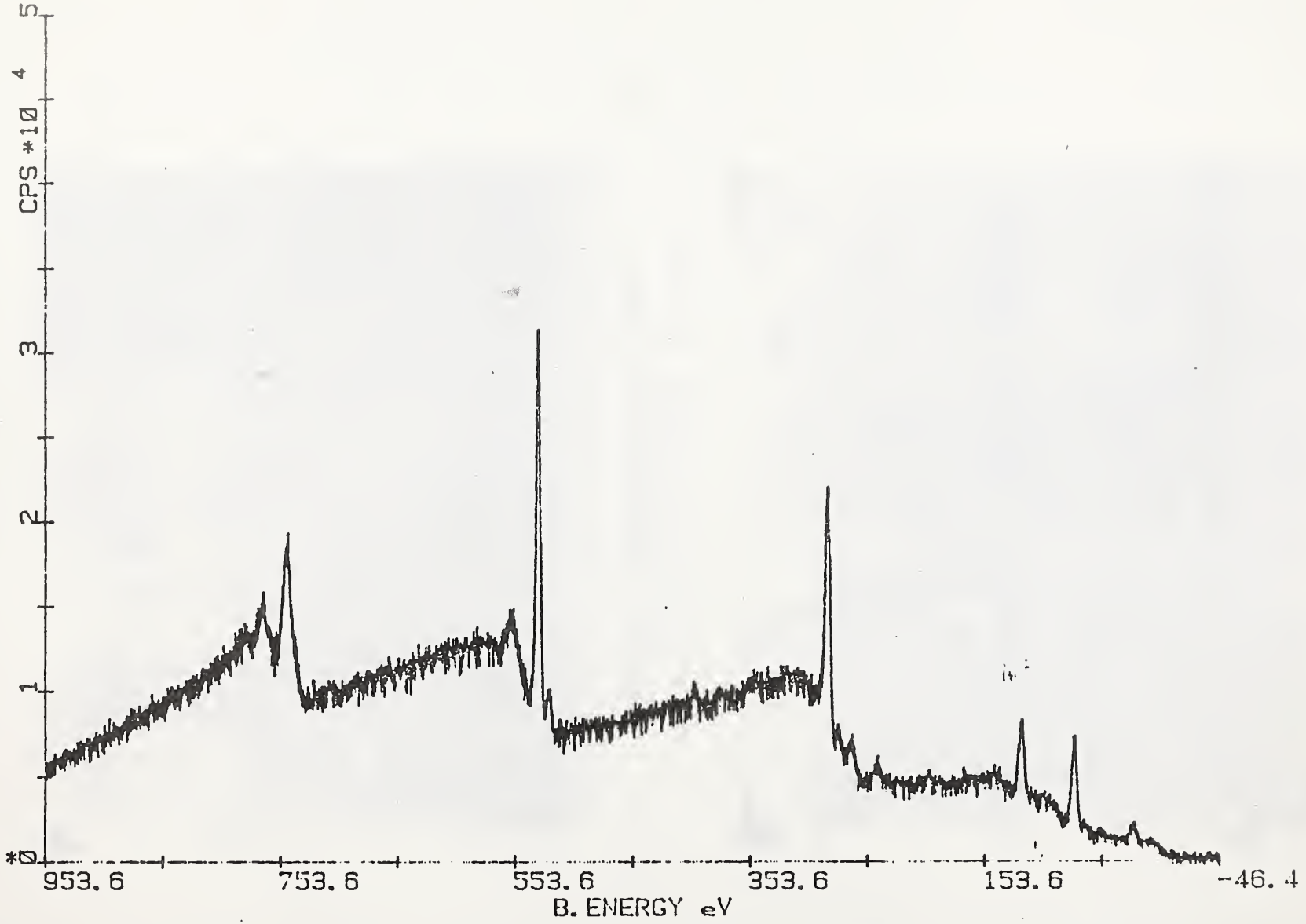

Figure 7. XPS binding energy scan of E4 thermal oxide (air)

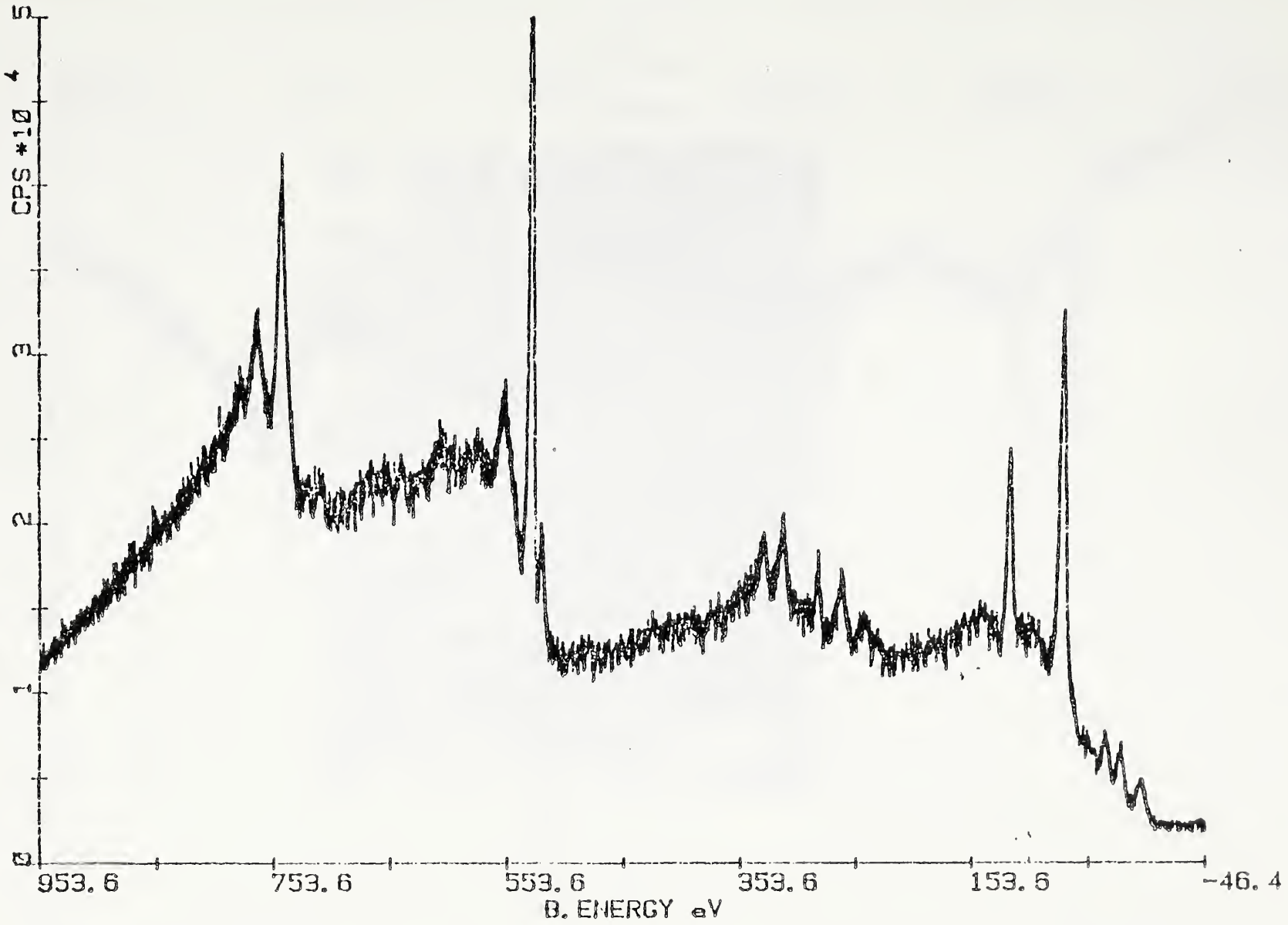

Figure 8. XPS binding energy scan of thermal oxide ($Ar+H_2$) on E7

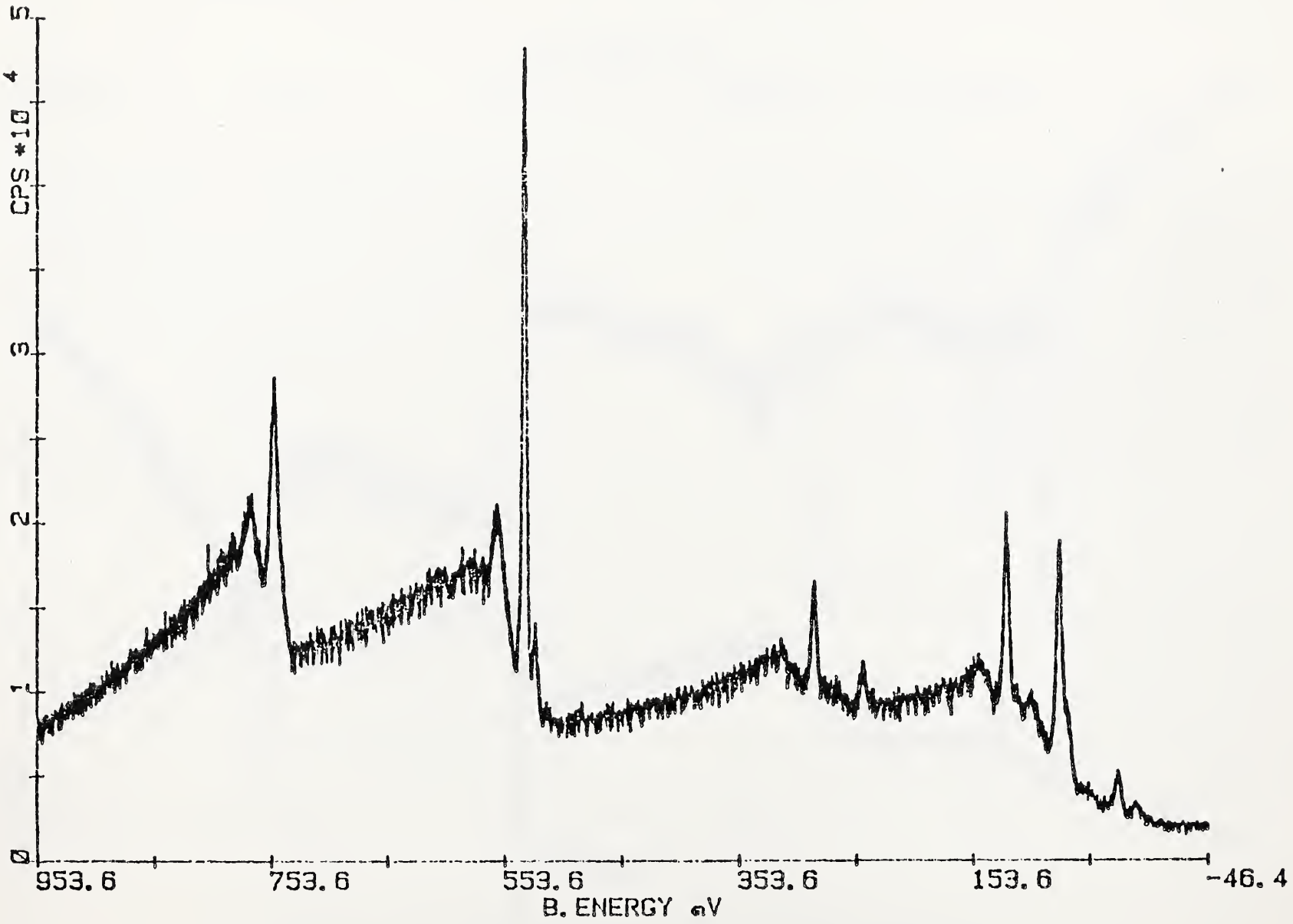

Figure 9. XPS binding energy scan of sputtered oxide on E8

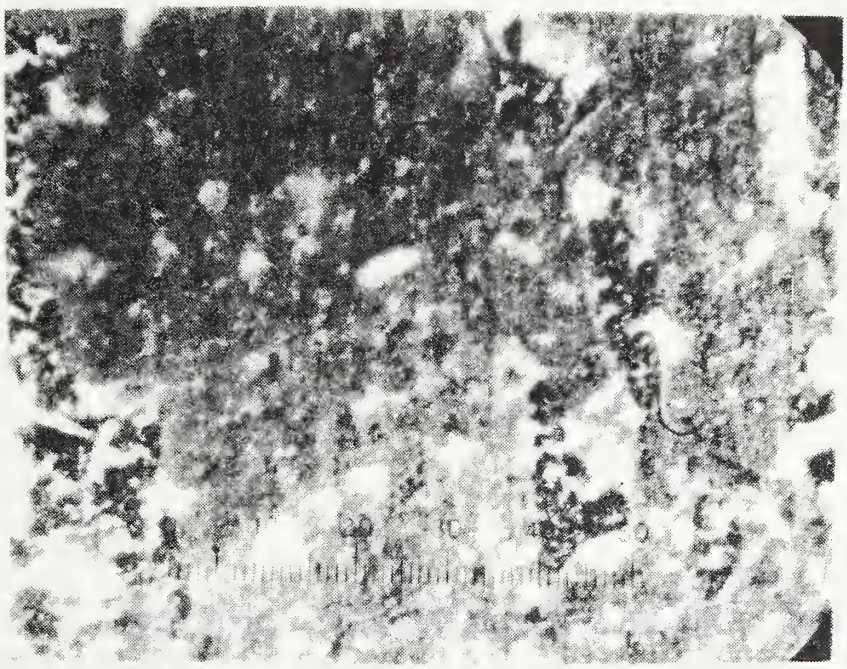

Figure 10. Spalled sputtered oxide on G6 - 500x

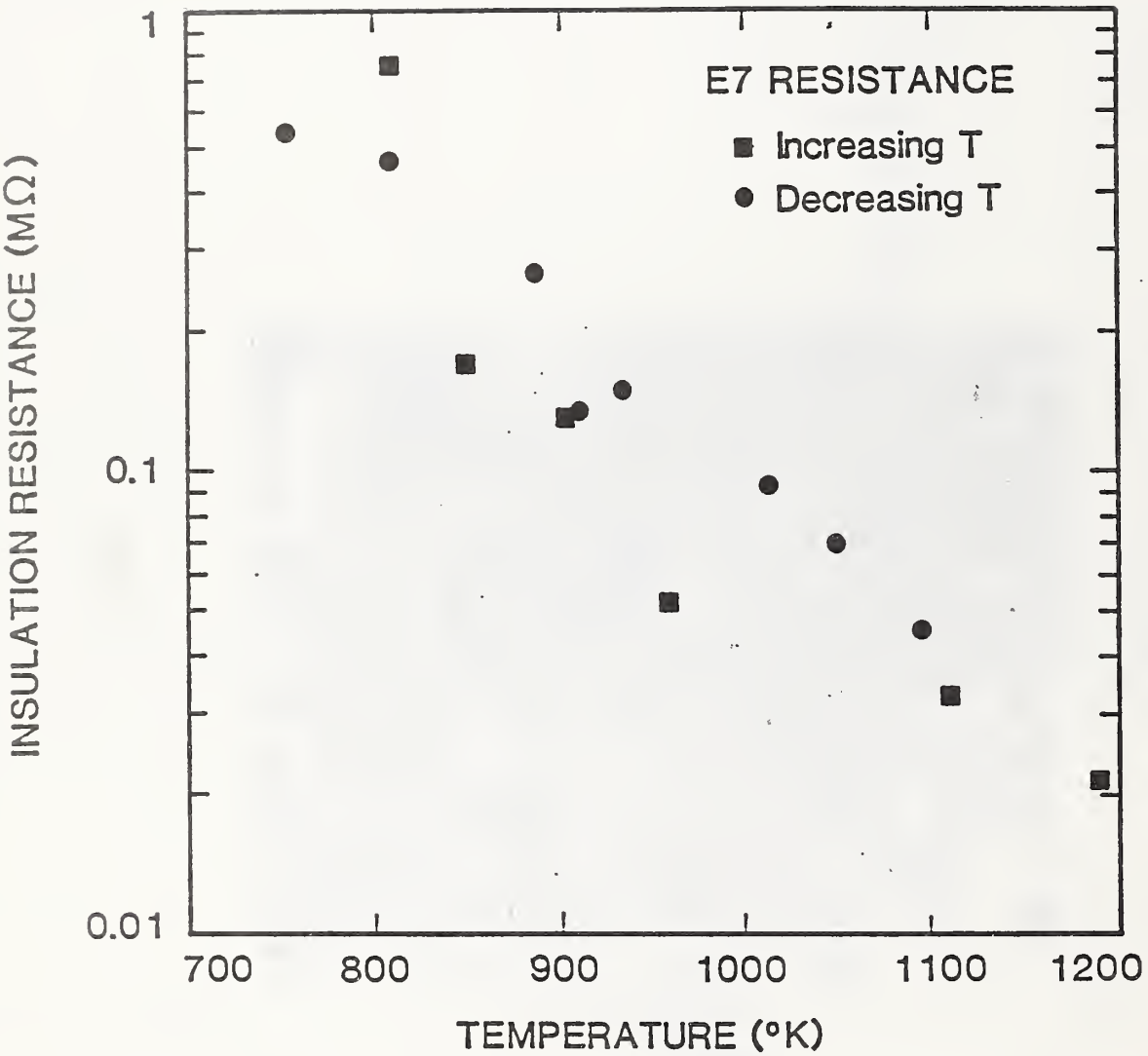

Figure 11. Electrical resistance as a function of temperature of E7

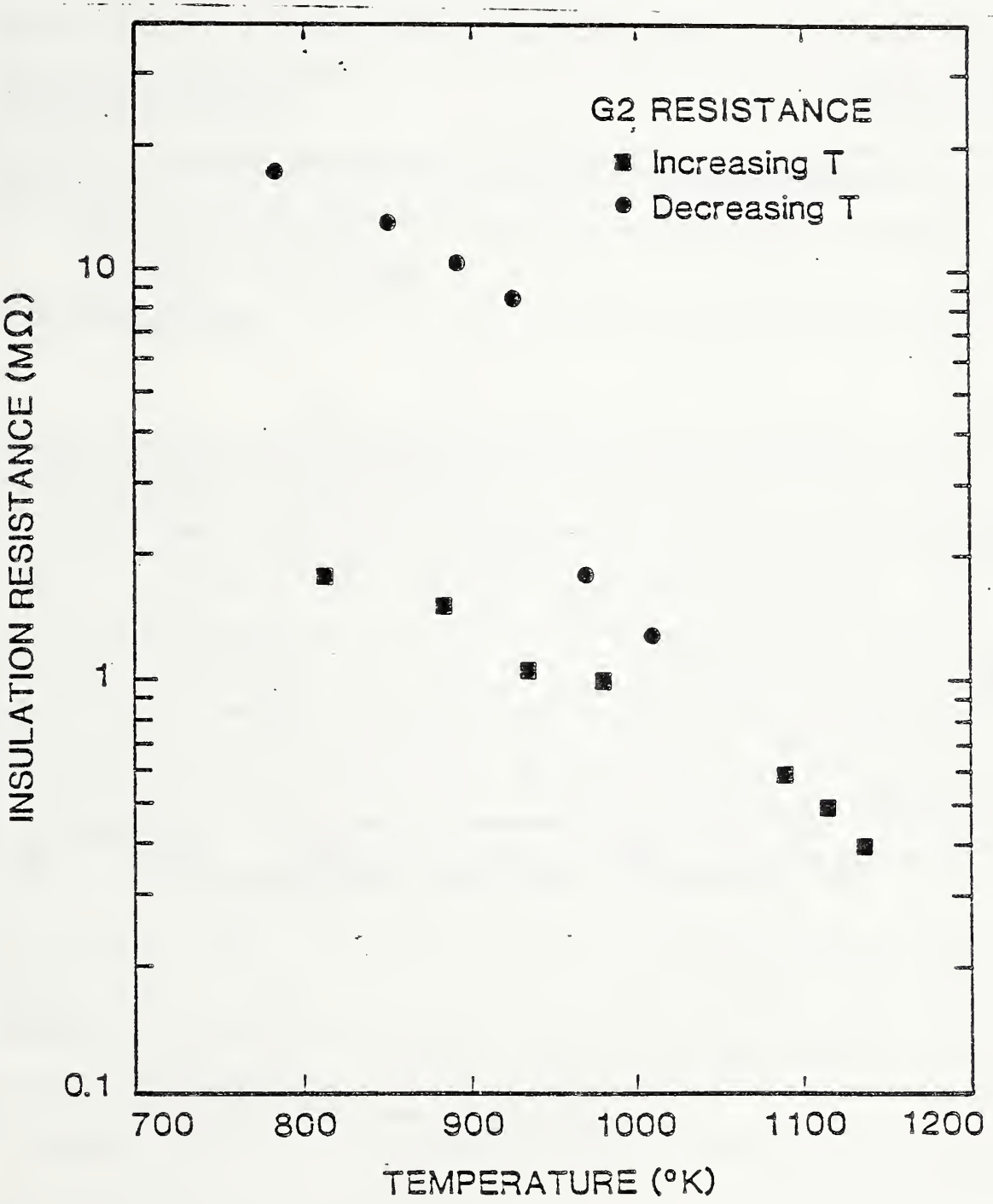

Figure 12. Electrical resistance as a function of temperature of G2

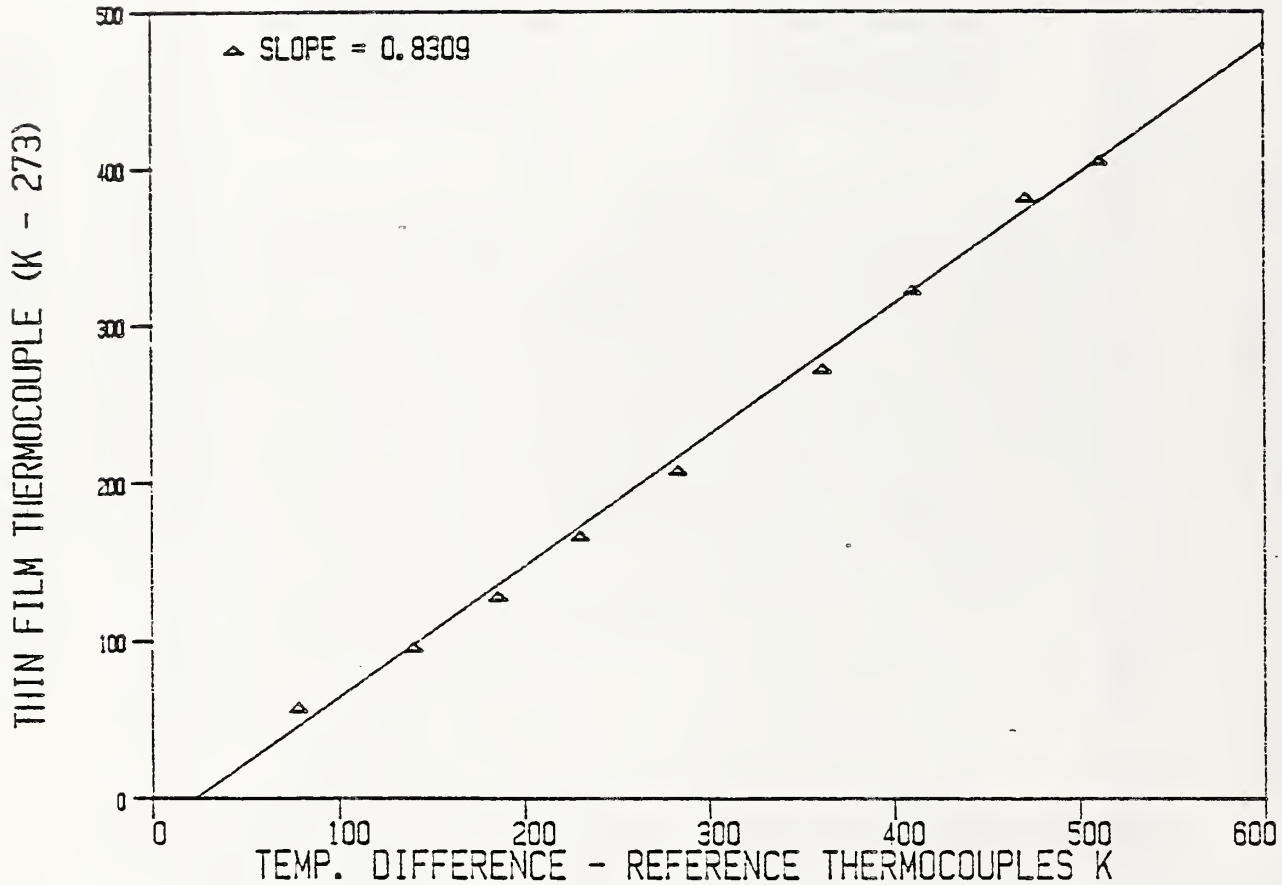

Figure 13. Thin film thermocouple test

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U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. NBSIR 85-3110	2. Performing Organ. Report No.	3. Publication Date February 1985

4. TITLE AND SUBTITLE

INTERNAL COMBUSTION ENGINE THIN FILM THERMOCOUPLES

5. AUTHOR(S)

Kenneth G. Kreider and Stephen Semancik

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

DE-A105-830R21375

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

Energy Conversion and Utilization Technologies (ECUT) Program
Department of Energy
Washington, D.C. 20585

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 feasibility of fabricating thin film thermocouples on internal combustion engine hardware was investigated. The goal was to find a procedure that would be useful for the measurement of the metal temperature of valves, valve seats, combustion chamber surfaces, cylinder walls, and piston heads during engine operation.

The approach pursued was to coat the engine hardware material with an aluminum-containing, oxidation-resistant ferrous alloy (FeCrAlY) which forms an oxide layer with good electrical resistance. This thermal oxide was coated with a thin layer of reactively sputtered aluminum oxide and sputtered thin film type S thermocouple legs of platinum and platinum plus 10% rhodium. This project was used to investigate the materials problems related to obtaining good adhesion in the metal metal-oxide-oxide-metal laminate and the electrical insulating properties of the oxide. Thermal oxidation, reactive sputtering of Al_2O_3 and platinum alloy sputtering were investigated using optical microscopy, x-ray photoemission spectroscopy (XPS), laminar adhesion testing, and the evaluation of high temperature electrical properties.

A successful method for fabricating thin film thermocouples on internal engine materials was developed. Adherent, electrically insulating aluminum oxide with a type S thermocouple was produced on a 10 cm long stainless steel bar. The fabrication techniques and results of tests run on that bar as well as numerous small test coupons are presented.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

harsh environment measurements; internal combustion engine; oxide insulators; sputtering; temperature measurement; thermocouples

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14. NO. OF PRINTED PAGES

41

15. Price

$8.50