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Thin Film Thermocouples for High Temperature Measurement

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INTRODUCTION

Thermocouples are devices primarily used for measuring temperature. Their discovery by Seebeck in 1822 was based on the findings that an electric current will flow in a closed circuit composed of two dissimilar conductors when their two junctions are kept at different temperatures. In fact, the thermocouple is a transducer which converts thermal energy into electrical energy. By careful control of the composition and metallurgical condition of the conductors and control of the reference junction temperature, a precise temperature measurement can be made of the second junction. In fact, platinum-rhodium thermocouples are used as the standard for temperature measurements above the melting point of antimony. The pattern of using a thermocouple for high temperature measurement is also followed when using thin films. In fact, the problems of contamination from the atmosphere or contacting surfaces and that of variable stresses on the conductors are considerably more troublesome with thin films than with wires. The contamination problem can be related both to the very high surface to volume ratio and short diffusion distances of the films. The residual stress problem can be primarily related to the substrate compatibility of the thin film and the rigors of the deposition process.

The thin film thermocouple (TFTC) has numerous advantages as a solid surface temperature measurement sensor. First, the extremely low mass, 10^{-4}g for a 2x2mm junction, creates a very modest disturbance of heat transfer on the surface. For most practical measurements this change of thermal mass or thermal conductance of the measured part is insignificant. The change in convective heat transfer to the surface is also extremely small since the 1μm film is below the dimensional scale of most convective heat transfer applications. However, there can be a change in radiative heat transfer, as well as in the emissivity of the surface. This can be minimized by the engineering design of the measurement. The use of coatings over the thin film thermocouple can alleviate this problem. For example, if the temperature of the surface of an aluminum oxide body is needed the platinum alloy thermocouple may be covered with a thin film of aluminum oxide to more nearly match the emissivity of the part. It is clear that the minimization of thermal disturbance using thin film thermocouples is much simpler than working with wire thermocouples or other contact devices. The small mass also leads to a rapid response and a measurement which is representative of the surface to be measured and this will be described below.

The excellent thermal characterization of the surface including a direct electrical signal dependent on that temperature is a significant advantage when compared to optical measurements which are modified by emissivity changes, transmission losses, and surrounding radiation reflections. Therefore, it is often best to calibrate an optical measurement with a direct (thermocouple or resistance thermometer) measurement.

The aforementioned advantages have led to numerous research and development programs for thin film thermocouples as well as critical applications. Some of the earliest work with thin film thermocouples was of a design which included concentric cylindrical thermoelements which are joined by an electroplated thin film normal to the cylinder and parallel to the surface to be measured (1). This design unfortunately does disturb the heat transfer through the part to be measured. The design has been used to measure gun barrel temperatures and some attempts have been made to measure diesel engine cylinder surface temperatures. However, this paper is intended to address thin film thermocouples in which each element is a deposited thin film on the surface to be measured. Early work in England (1966) by Marshall et al. (2) on TFTC's described the use of evaporated films of nickel, iron, copper, constantan, Chromel*, and Alumel*. Although these thin film thermocouples did not give bulk values of the Seebeck coefficient electric power, the results were consistent with film thicknesses of greater than 2500Å and Ni-Fe pairs were reproducible to $\pm 2°C$ at 250°C.

In Japan, Koike et al. in 1968 (3) were measuring the thickness dependence of the thermal electric force in evaporated Bi-Ag and Sb-Ag couples. They were able to obtain consistent results at 0.5μm thickness. During the early 1970's aircraft gas turbine engine companies in the U.S., including Pratt and Whitney (4,5), were interested in using thin film thermocouples to measure surface temperatures of first stage turbine blades and vanes. This key application led to a focus for much of the work in the United States since goals could be set for performance that could not be achieved by any other means.

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*The use of trade names does not imply any recommendation or endorsement of any commercial equipment or materials by NIST.

Some basic work was continued; Olson and Downey (6) were studying the aging effect of copper films on the Seebeck coefficient and Hill and coworkers (7) were studying the effect of physical vapor deposition parameters on the TEP of Mo-Ni. It was clear that consistent and reliable thermocouples would require a development of fabrication and application technology.

Activities at the National Institute of Standards and Technology (formerly NBS)

Our program at NIST was begun in 1982 with a project to study the fabrication and properties of the insulating oxide between the thermocouple and base metal at temperatures up to 1000C. I would like to describe highlights from our findings. The first project, sponsored by NASA, concentrated on improving the insulating properties of the oxide between the type S thin film thermocouples (Pt + Pt10%Rh) and gas turbine engine first stage blade and vane materials (8). Earlier results at Pratt and Whitney by Dils (4), Grant (5) and others had established the feasibility of using the thin film platinum alloys under the harsh conditions immediately downstream of the combustor in the gas turbine engine. The super alloys chosen for this hardware (MAR M200 + Hf* for the blades and MAR M509* for the vanes) were both protected by a MCrAℓY coating which develops an impure aluminum oxide protective layer on high temperature exposure to air. We found this thermal oxide to be inadequate to survive the electrical fields of the thermocouple without significant current leakage and explored the use of a sputtered $A\ell_2O_3$ layer for added insulation. A schematic class section of the thin film sensor is given in FIG 1. The oxide layer which is at least 2 μm thick is composed of a mixed thermal oxide plus a pure sputtered $A\ell_2O_3$. It was found that surface preparation was critical to insure a void free smooth oxide which would maintain 10-100KΩ at 1000°C. The difference between the mixed thermal oxide and pure alumina sputtered oxide was also measured using X-ray photoelectron spectroscopy (XPS) (8). In FIG 2 the presence of NiO was identified in the top 50Å of the thermal oxide. The Ni ($2p_{3/2}$) peak is indicated for both the metallic and oxide binding energy. NiO has typically 10^{-2}Ωcm resistivity at 1000°C (9). The sputtered oxide also demonstrated superior insulating properties in XPS studies, as indicated in FIG 3 where the higher binding energy of the O(1s) core level is identified with the sputtered oxide. This shift is partially associated with a charging shift prevalent in good insulating oxides.

The key tests were performed by measuring the resistance of the oxide layers at temperature and FIG 4 presents the results of some of those tests. All of these oxides have more than 1μm of sputter oxide on the thermal oxide. The resistivities of samples C24 and D2 in the figure are adequate at 1000°C (over 200KΩ). The thermal oxide on sample C24 was grown on an electron beam evaporated NiCoCrAℓY coating on the nickel based super alloy MAR M509 and B16 had FeCrAℓY and MAR M200 + Hf. Both of these combinations were adequate with the sputtered $A\ell_2O_3$ at 1000°C and indicated a self healing tendency as shown in FIG 4. It should be noted that the output of the thin film thermocouple was only 83% of the expected value of the bulk alloys.

The second NIST project, which was sponsored by the U.S. Department of Energy's ECUT program on thin film thermocouples, was intended to investigate how this technology might be used for measuring cylinder temperatures of diesel engine (10). These engines normally have cast iron cylinders and heads and it was necessary to develop a lower temperature process to form the insulating oxide. FeCrAℓY coating alloys were used with oxidizing treatments at 800-900C rather than the 1000-1100C used with the nickel and cobalt based alloys and thicker sputtered $A\ell_2O_3$ ($2\mu m$) was needed. Good insulating properties were obtained on several iron based alloys as indicated in FIG 5 where the resistance of sample G2 was 400KΩ at 850°C.

One of the most interesting recent developments in internal combustion engines is the ceramic-lined insulated engine. The intent here is to insulate the combustion chamber, thereby achieving higher specific power and lower specific fuel consumption, while eliminating the need for liquid cooling. A critical design parameter for this engine is the knowledge of the cylinder and head surface temperatures. We have been studying some of the critical materials problems related to using thin film thermocouples to solve that measurement problem (11). The best ceramic liners for both the head and the cylinders have proven to be plasma sprayed oxides. This technology combines the ease of fabrication, thermal properties, and reliability which can lead to significant improvements in diesel engines (12). The use of thin film thermocouples to solve this measurement problem appears to be appropriate. Their advantages of not disturbing the heat transfer to and from the surface, high temperature combustion chamber compatibility, and rapid response capability seem ideally suited to this problem. The environment is harsh; rapid cycling at 60 Hz to 900°C on an oxide surface while being blasted with soot and ash is a test of the adherence of any thin film. Our early studies at NIST to find a base metal thin film thermocouple which was stable at these temperatures were unsuccessful. The nisil-nicrosil thermocouple, which generally has the best high temperature stability in air among the base metals

(13), would not maintain a stable output in the thin film form due to oxidation at 900C (11). Therefore, we concentrated on developing a technique to maximize the adherence of platinum alloy thermocouples on the plasma sprayed oxides. Presently the best insulating oxide for the diesel engines is the plasma-sprayed partially stabilized zirconia of approximately 2mm thickness. Two techniques were developed. A sputtered bond coat of a reactive metal was placed between the ZrO_2(Y) and the platinum alloy. This reactive metal, less than 1% of the weight fraction, bonded to the ZrO_2(Y) with its native oxide on one side and to the noble metal on the top with a metallic bond. The success of this approach is depicted by the adhesion strength test results given in TABLE 1. The layers are deposited subsequently in the clean sputtering atmosphere at 0.3 Pa of argon at 99.999% purity with a pair of planar magnetrons and tested with an epoxy pull tab tester. The most consistent and best bond coat was found to be chromium which yielded room temperature bond strengths of greater than 50MPa, (fracture strength of the ceramic). A second successful technique was developed which included ion beam sputtering of the oxide surface just before and during the first 10 nm of platinum alloy deposition.

The preliminary testing was performed on monolithic ceramic bars and ZrO_2(Y) plasma sprayed steel bars, but the critical testing was performed in a diesel engine. This project was sponsored by the U.S. Department of Energy and the National Aeronautics and Space Agency and performed by engineers and scientists from Integral Technologies Inc., Purdue University and NIST. The objective was to measure the inside surface temperature of an operating diesel engine and the results of such tests have been published in a U.S. Society for Automotive Engineering Technical Paper (12) and presented at a Combustion

Institute Meeting (14). The sensor plug with its thin film thermocouple was inserted through the wall of the fourth valve completely simulating the thermal properties of the engine wall. A schematic drawing of the sensor plug is shown in FIG 6. Notice the sputtered thin film thermocouple on the cylinder wall surface and the wire thermocouple touching the back side of the ceramic liner enable accurate heat transfer measurements.

Some of the conclusions of this heat transfer measurement program were: 1) A set of heat flux data was obtained in a direct injection diesel engine coated with zirconia; 2) the heat flux was consistently diminished as the wall temperatures rose due to the insulation. This finding contradicts some earlier conclusions based on less precise measurements, and 3) since both the mean heat flux and peak heat flux were reduced, insulation can be expected to decrease specific fuel consumption and increase exhaust energy recovery potential. This latter effect is due to the reduced cooling losses.

Although the calculations of temporal response characteristics of the thin film thermocouple (12) indicated microsecond sensitivity for this application, we at NIST have attempted to measure the transient thermal response (15). We used an ArF excimer laser (193 nm) with a pulse width of 12 ns as a pulsed heat source for the platinum alloy and gold sputtered thin film thermocouple junctions of 3-6μm thickness. The substrates were chosen to represent widely differing thermal conductivities, including fully dense alumina circuitboard, plasma sprayed ZrO_2(Y), and a fibrous, low density insulator (MIN K2000)*. The experiment consisted of measuring thermocouple output following pulsed irradiation. A typical thermal response/decay curve is given in FIG 7 for the $A\ell_2O_3$ substrate. The limiting response of the electronics indicated a heating output response of the 4μm thick junction in the range of $1\mu s$. The cooling curve was used in the paper by Burgess et al. (15) to calculate the thermal diffusivity of the three substrate materials and their calculated values agree with those determined by other techniques.

The successes in the use of sputtered thin film platinum alloy thermocouples for measurements up to 1000°C has indicated numerous application possibilities. The fabrication technique is not limited to thermocouple materials which are available in wires since the structural functions of the thermocouple system can be accomplished with the substrate material. An interesting recent development is that of forming transparent thermocouples. We at NIST have investigated the system of indium oxide-indium tin oxide (ITO) (16). This system provides useful electrical conductivity for the thermocouple circuit, in fact, we have sputter deposited 9% ITO with $2 \times 10^{-4}\,\Omega cm$ resistivity. The optical transmission of the films was 70-90%, so that applications for thermally mapping lenses, mirrors, and photo detectors appear feasible. The thermoelectric potential of two sputtered thin film In_2O_3-ITO thermocouples is presented in FIG 8. The Seebeck coefficients of these couples are a powerful 0.1 mV/°C, which permits the variation of tin content in the legs to optimize optical and electrical properties as well as stability.

Current and Future Trends

The interest in the insulated diesel engine is continued in the U.S. Department of Energy Heavy Engine Program and at the NASA Lewis Research Laboratory. Further development is underway at Purdue University, ITI, and at NIST along the lines described above. NASA Lewis is also sponsoring work at UCLA related to high temperature thermocouples. Budhani et al (17) have reviewed the problems and prospects for use of thin film thermocouples in gas turbine engines and Prakash et al (18) have described the UCLA work in developing thin film thermocouples for SiC and Si_3N_4 applications. In France, Godefray and coworkers (19) are also studying PtPdAu alloys for use in turbine engines.

Novel applications for thin film thermocouples have been reported in the last few years. An IBM study by Tong et al (20) has investigated the use of Pt-Ir thin film thermocouples for monitoring instantaneous temperatures during electronic device processing. They found a 60 ns response time up to 790°C for the pure Pt-Ir couple. Kuo et al (21) at Syracuse University have used an copper-constantan TFTC to develop a miniature vacuum pressure gauge. They find that their device can be used over a wide range of measurements and can be incorporated easily with other integrated circuits. In Sicily, at the Instituto Dipartmentale di Fisica, Baeri and his coworkers (22) have made time resolved temperature measurements of pulsed laser irradiated germanium using TFTC's. Using an iron-constantan thin film protected with 1.3μm of Ge, they confirmed the thermal models for laser annealing, measuring up to 700°C with the high output thermocouple. Liebert and coworkers (23) at NASA Lewis have used TFTC's as high temperature (635°C) heat flux gauges to measure the Stanton number for convective heat transfer. Because of the minimal disturbance of the boundary layer temperatures, the NASA scientists were able to achieve experimental values within the calculated uncertainty of the measurement system.

The development of thin film thermocouples over the last few years has been exciting and has proved very useful. The broad range of applications related to surface temperature and heat transfer measurements has confirmed the early predictions. Their small size, convenient output, precision, and durability under harsh environmental conditions have carved out a niche in accurately determining temperatures where no other method was satisfactory.

Each application does require special considerations. The almost limitless combinations possible with fabrication techniques, such a sputter deposition, is both an excellent opportunity and a requirement for careful engineering. A review and analysis of some of the complexities of thin film thermocouples were made by Laugier (24) in 1980. He pointed out some of the problems related to residual stress and other thermal effects. There is also no question that the small thickness of the TFTC complicates the effects of chemical reactions with the substrate, coatings, and the atmosphere. Simple guidelines used for wire thermocouples are not adequate. Other complications arise during fabrication, where impurities can easily be introduced in the film which will affect its subsequent performance. Most publications indicate that the Seebeck coefficient of the TFTC was not equal to that of the bulk material and the explanations are usually inconclusive. The usual approach is to calibrate the individual TFTC and this is sometimes difficult. Accurate calibration can be obtained only if the thin film elements extend from the reference junction to the measuring junction.

It is apparent that the technology for application of the thin film thermocouples will expand and the number of applications will grow. It is also important that reliable standards and test methods be developed in order to insure confidence in the validity of TFTC measurements.

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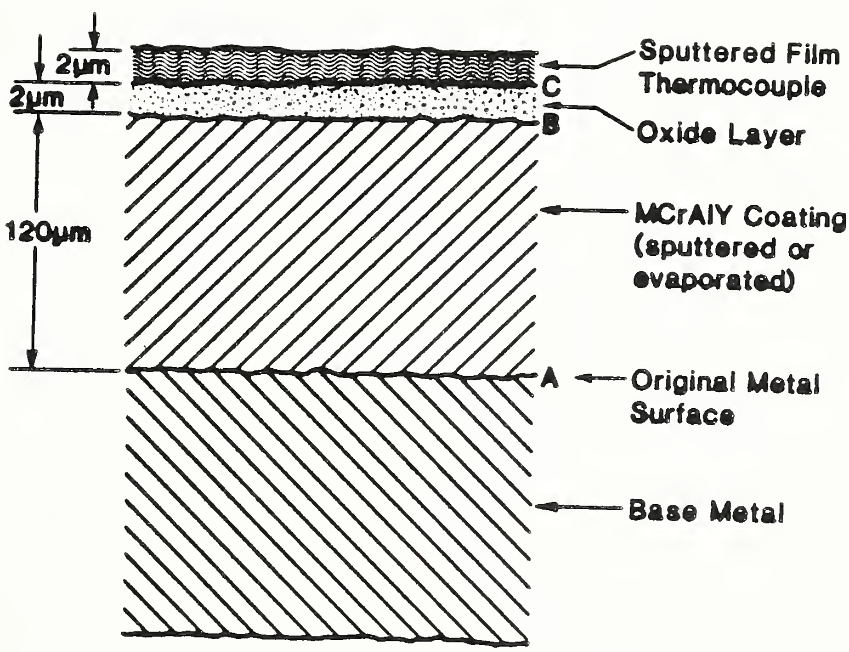
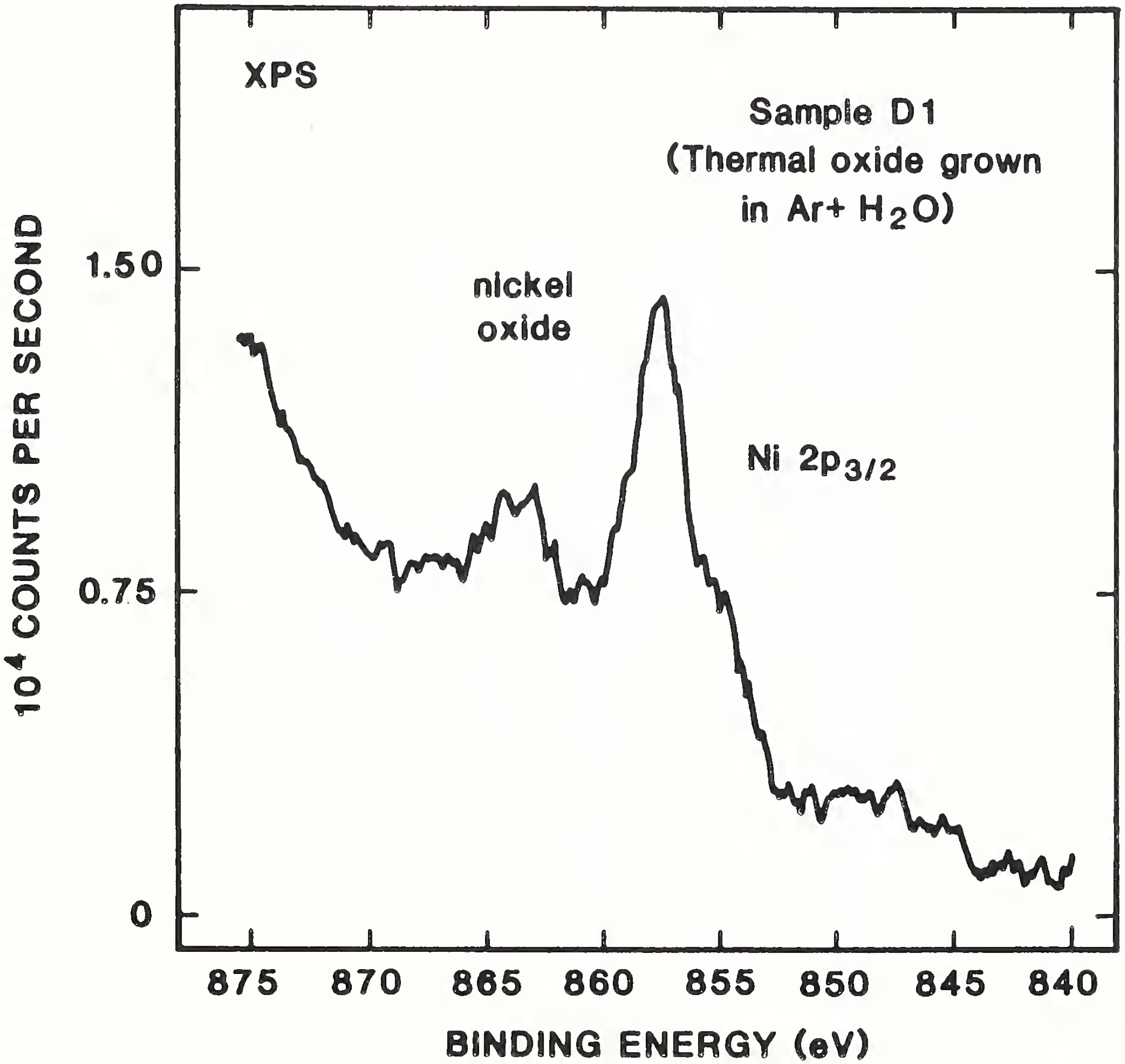
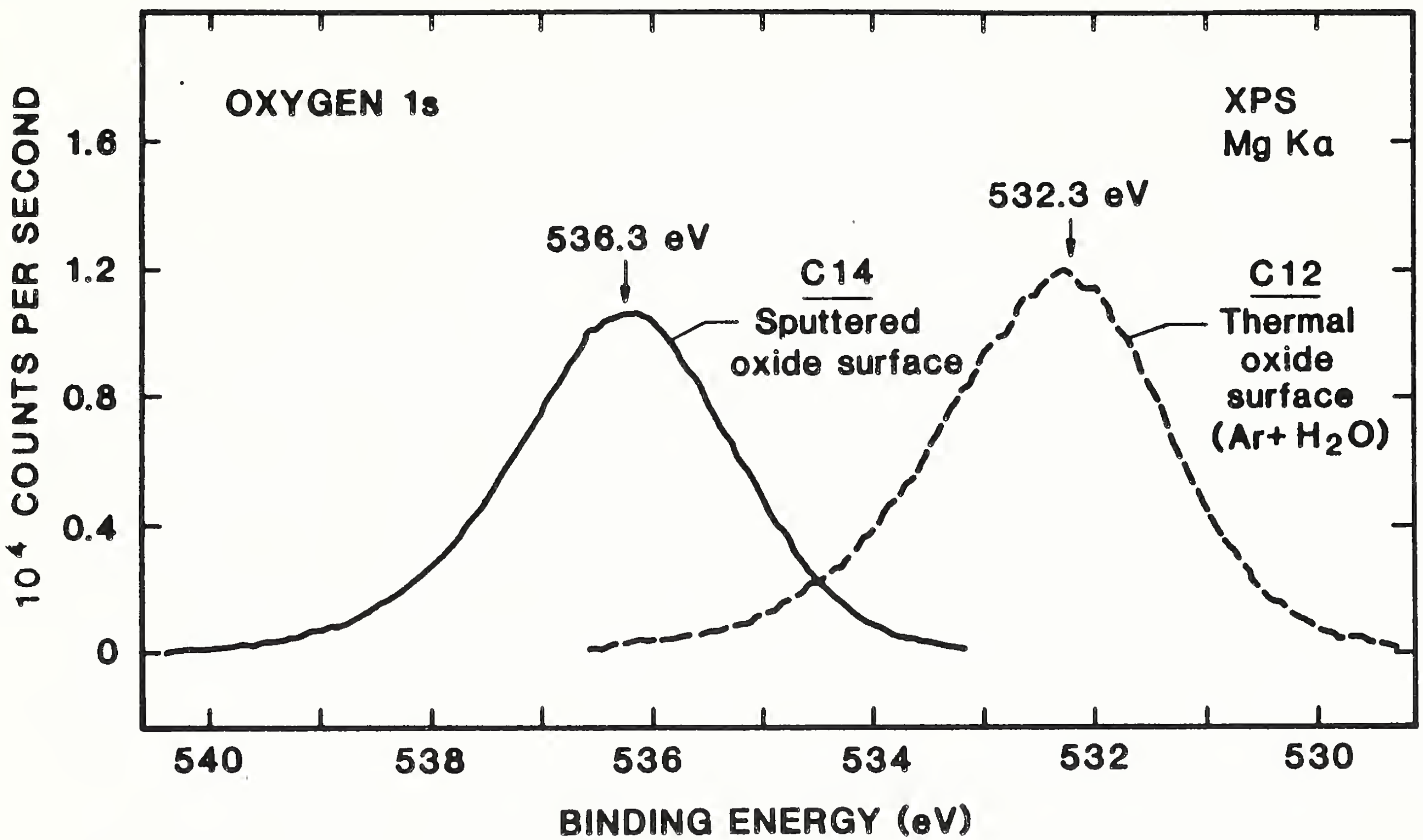


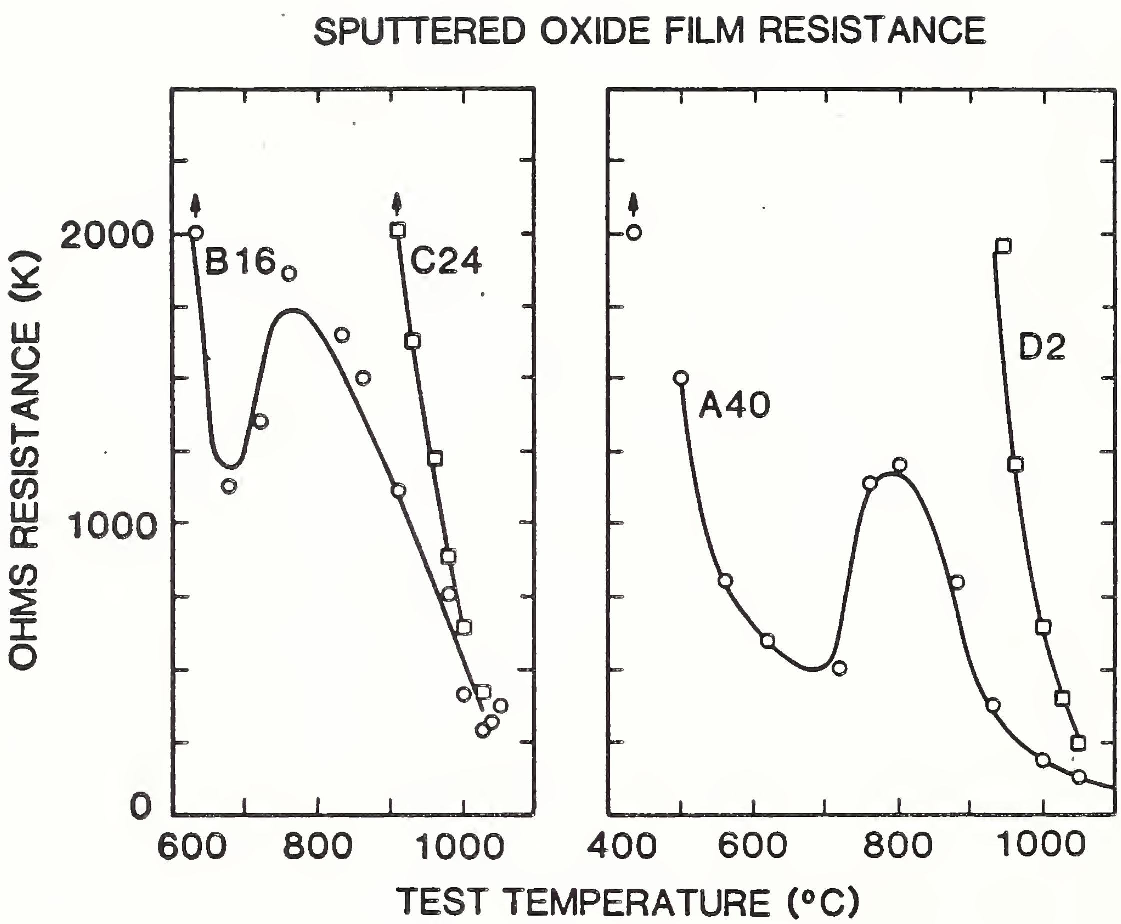
1. Schematic cross section of thin film thermocouple on gas turbine engine blade.



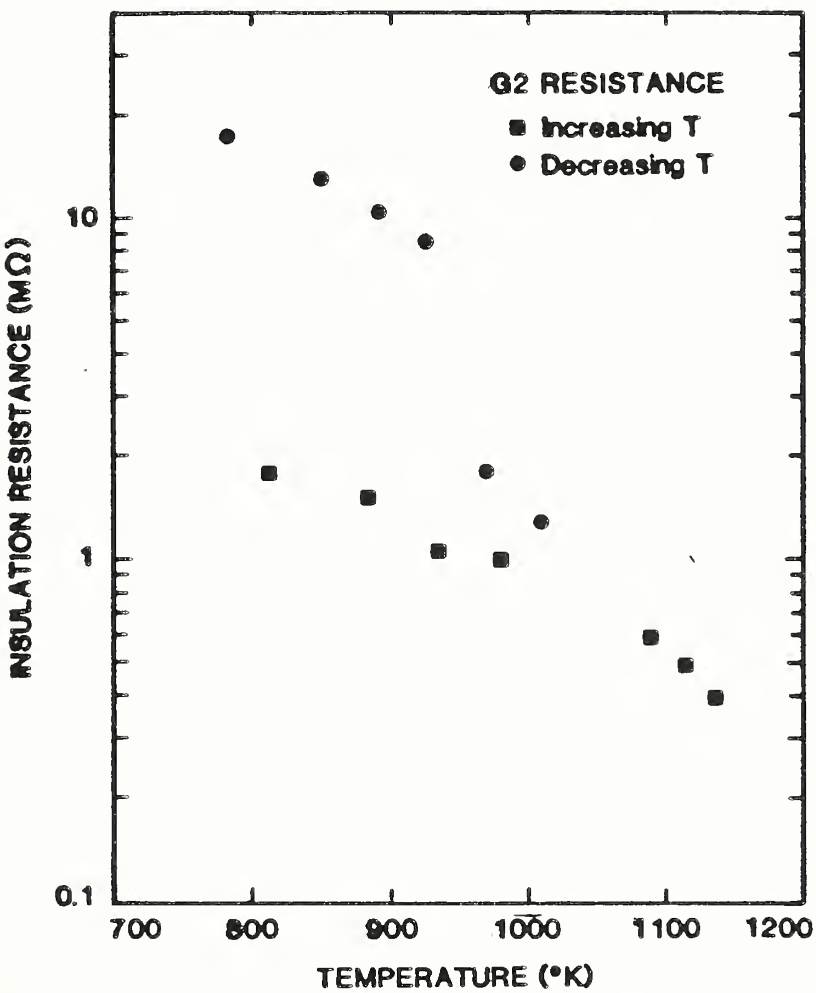
2. XPS nickel 2P(3/2) core level region indicating the presence of oxidized nickel in the surface aluminum oxide.



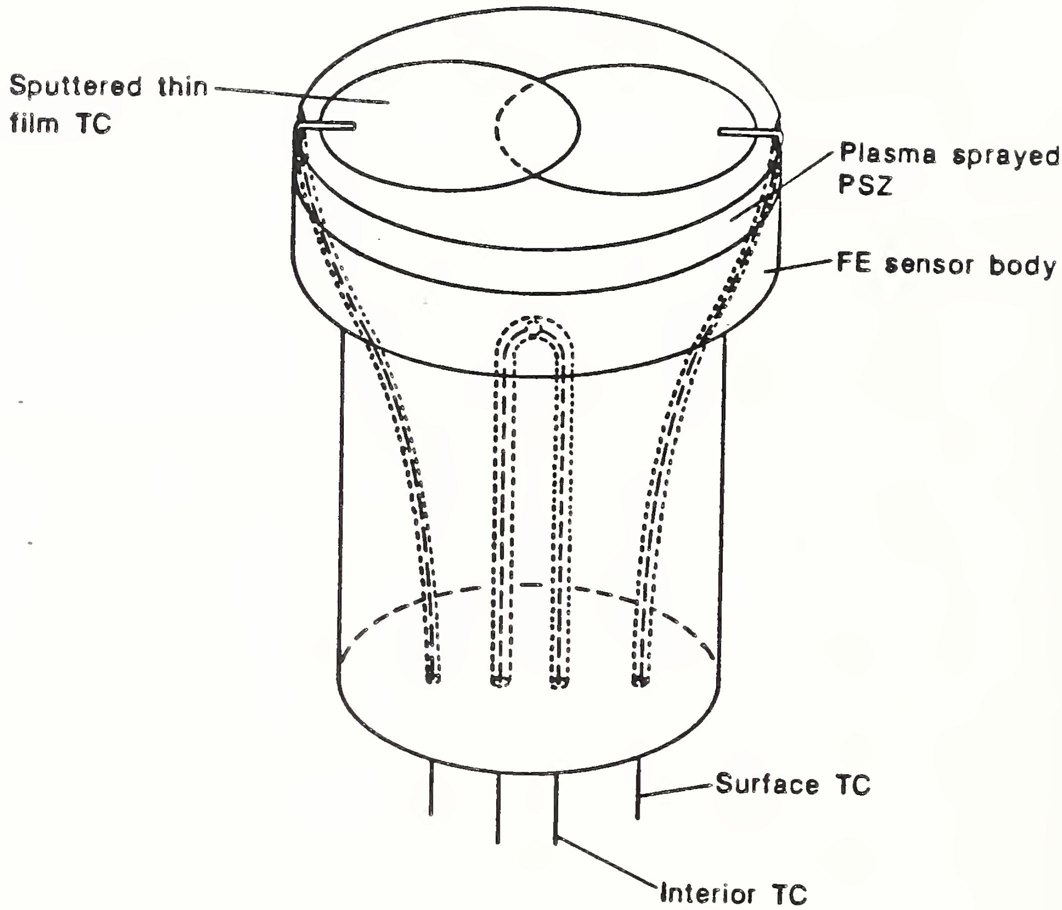
3. Oxygen 1s XPS core levels of thermal and sputtered oxides. The shift to the higher binding energy may result from charging.



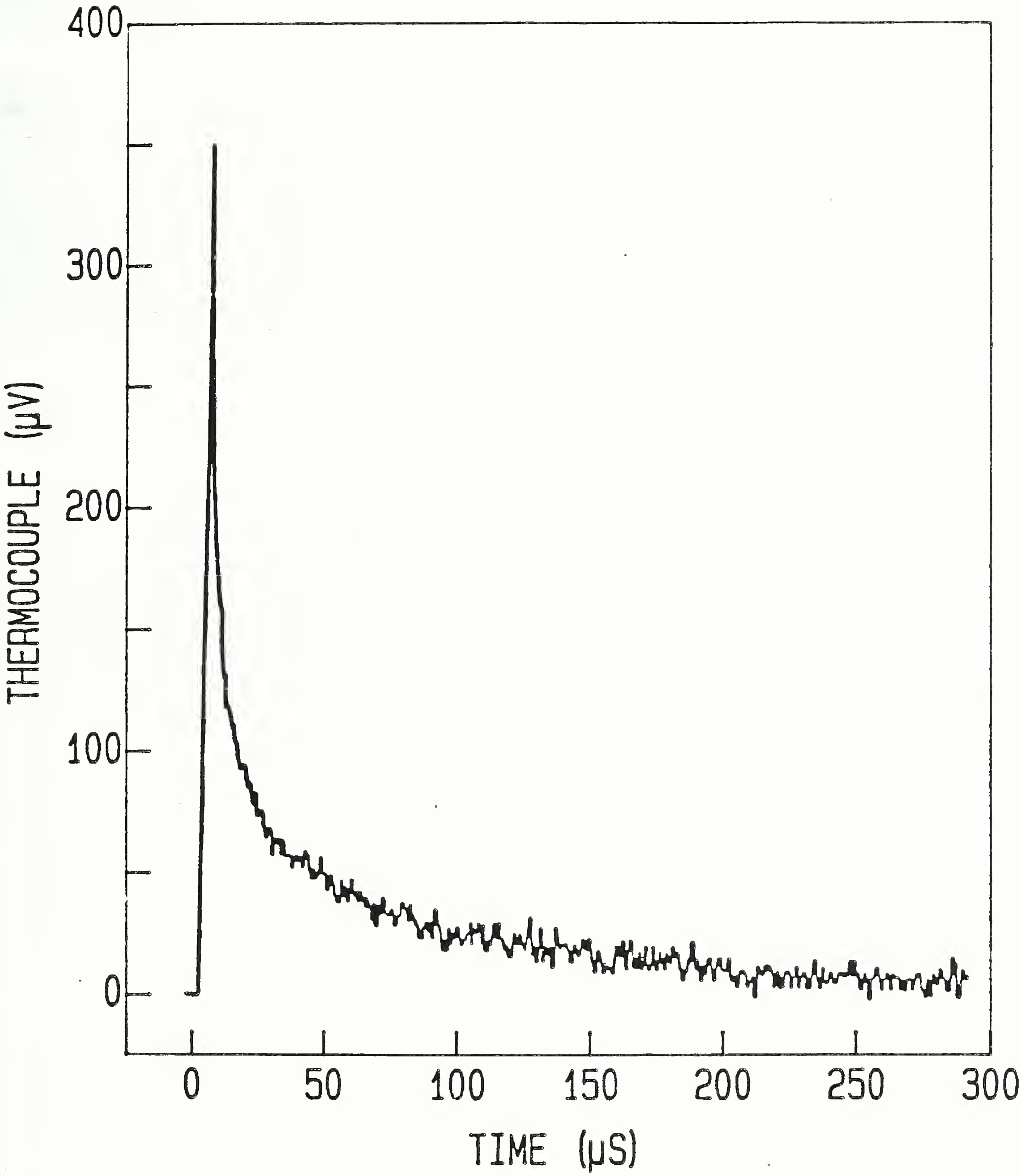
4. Resistance of sputtered oxide film on nickel and cobalt based superalloys as a function of temperature. Substrates A40 and B16 were thermal oxides of FeCrAℓY and C24 and D2 were thermal oxides of NiCoCrAℓY.



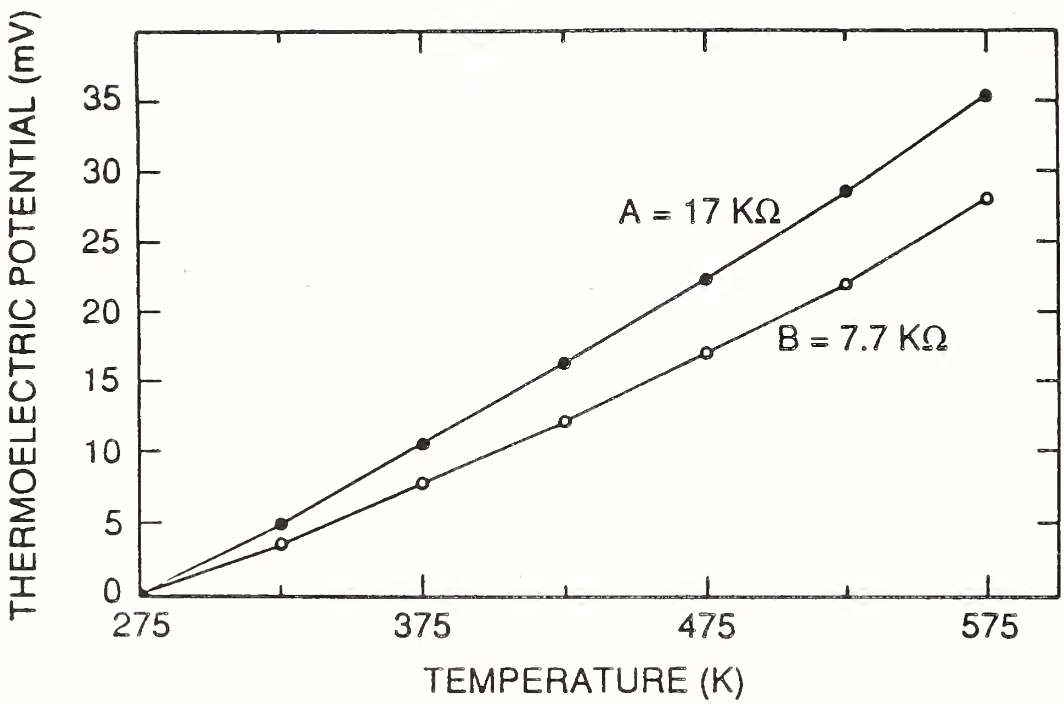
5. Electrical resistance of combined oxides on FeCrAℓY on 4340 steel alloy.



6. Schematic drawing of sensor plug for heat transfer in diesel engine cylinders.



7. Typical thermocouple output of laser pulse irradiated type S junction.



8. Thermoelectric potential of sputtered In_2O_3-ITO thin film thermocouple.

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☐ 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)

Thin film thermocouples have unique capabilities for measuring surface temperatures at high temperatures (above 800K) under harsh conditions. Their low mass, approximately $2x10^{-5}$ g/mm permits very rapid response and very little disturbance of heat transfer to the surface being measured. This has led to applications inside gas turbine engines and diesel engines measuring the surface temperature of first stage turbine blades and vanes and ceramic liners in diesel cylinders.

The most successful high temperature (up to 1300/K) thin film thermocouples are sputter deposited from platinum and platinum 10% rhodium targets although results using base metal alloys, gold, and platinel will also be presented. This paper reviews the fabrication techniques used to form the thermocouples, approaches used to solve the high temperature insulation and adherence problems, current applications, and test results using the thin film thermocouples. In addition a discussion will be presented on the current problems and future trends related to applications of thin film thermocouples at higher temperatures up to 1900K.

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

insulating oxides; platinum alloys; sputtering; thermocouples; thin films; vacuum deposition

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