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A Final Report for:

CHEMICAL VAPOR DEPOSITION OF TURBINE THERMAL BARRIER COATINGS

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NASA/John H. Glenn Research Ctr.
21000 Brookpark Rd.
Lewis Field
Cleveland, OH 44135

Prepared by:

Victor E. Haven

Submitted by:

Spire Corporation
One Patriots Park
Bedford, MA 01730-2396

PROJECT SUMMARY

Ceramic thermal barrier coatings extend the operating temperature range of actively cooled gas turbine components and increase engine efficiency. Performance of present yttria-stabilized zirconia (YSZ) coatings is limited by the material's microstructure, which is determined by deposition method. The goal of this Phase II Small Business Innovation Research project was to extend Phase I research which indicated that metalorganic chemical vapor deposition (MOCVD) can produce YSZ coatings which could improve thermal barrier material through better control of the ceramic film microstructure.

During Phase II, Spire Corporation's MOCVD reactor was extensively modified and used to deposit YSZ coatings on turbine blade material coupons provided by a major manufacturer of jet engines. Coating composition, crystal structure, and response to elevated temperatures were characterized. Although major technical problems with the reactor prevented variations of deposition conditions over a wide range, stoichiometric zirconia coatings with yttria fractions from 0 to 14% were deposited on coupons previously coated with an oxygen barrier layer. Difficulties with the MOCVD reactor prevented formation of YSZ coatings thicker than about 50 micrometers, thus precluding deposition of the 125 micrometer thickness needed for thermal barriers for gas turbine blades. A Spire-proprietary technique was also tested and found to deposit thin (1 to 2 micrometers), adherent, highly crystalline YSZ coatings. These coatings may have potential as a nucleation layer for oxide coatings that are subsequently deposited by MOCVD.

Although the project was unsuccessful in developing a superior thermal barrier coating, considerable information was gained on the formation of zirconia and yttria coatings by MOCVD. The reactor problems, mainly control of reagent partial pressures, flow patterns in the deposition zone, and substrate heating, provide design information that will be valuable for any future efforts to deposit thick, adherent, uniform, thermal barrier coatings. Finally, the concept of using a thin, highly crystalline YSZ interface layer between the oxidation protection layer and the thick thermal barrier coating has enough potential to be subject of further investigation.

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1. PROJECT OBJECTIVES

1.1 Overall Objective

Ceramic thermal barrier coatings extend the operating temperature range of actively cooled gas turbine components and increase jet engine efficiency. Performance of existing plasma-sprayed or electron-beam physical-vapor-deposited (EB-PVD) stabilized-zirconia coatings are limited by the material's microstructure, which is determined by deposition method. The overall objective of this program was to employ metalorganic chemical vapor deposition (MOCVD) of yttria-stabilized zirconia (YSZ) coatings to improve performance through better control of the ceramic film microstructure. Variation of process parameters in MOCVD can independently alter the rate of nucleation and crystal growth, permitting microstructure variation from fine grained, to columnar, to epitaxial crystal orientation. Realization of MOCVD's potential to optimize barrier-coating structure could lead to higher performance for future aero propulsion systems.

1.2 Technical Objectives

The technical objectives of Phase II were to deposit and test MOCVD thermal barrier coatings on coupon samples and gas turbine blades at maximum operating temperatures. This demonstration would be a convincing initial step toward achieving the overall objective of the research.

1.2.1 Phase I Research

Phase I research identified two technical deficiencies to be addressed to optimize MOCVD parameters. These problems were: (1) low vapor pressure of the yttrium source relative to the zirconium source, and (2) an inability to heat the substrate to be coated to arbitrarily high temperatures without causing gas phase interactions. The first problem must be resolved to adjust the yttria content to the correct value, nominally 7%, and the second problem must be resolved to produce an optimized crystal structure in the thermal barrier coating itself. Specific milestones to solve these problems and achieve the technical objective were:

- Choice of yttrium precursor
- Optimization of reactor configuration
- Demonstration of strongly adherent coating
- Demonstration that a coated coupon survives exposure to turbine temperatures in an oxidizing environment, including multiple cycles and thermal shock.
- Demonstration of coating uniformity on a scrap turbine blade.
- Demonstration that a coated turbine blade survives multiple thermal cycling, thermal shock, *etc.* in a simulated turbine environment.

1.2.2 Phase II Work Plan -

The technical effort was initially divided into thirteen tasks:

1. Set up and test modified MOCVD reactor
2. Acquire and test deposition rates for new yttrium source compound
3. Deposition of thin film YSZ on trial substrates to verify composition and structure.

4. Deposition of YSZ to full thickness on test substrates
5. Initial specimen testing
6. Failure analysis
7. Process optimization
8. Preliminary deposition on turbine blades fro uniformity
9. Sample preparation for burner rig testing of blades
10. High temperature testing of actual coated blades
11. Failure analysis of blades
12. Analyses and recommendations
13. Reporting

As discussed in Section 2.11, technical difficulties during Phase II research necessitated a revised statement of work plan, which was followed during the final months of the program.

2. WORK CARRIED OUT

2.1 Section Overview -

The goal of this program was to demonstrate a cost effective technique for depositing ceramic thermal barrier coatings of yttria stabilized zirconia (YSZ) on turbine blades. Thickness of the films was to be 125 -150 microns with a yttria content of 7%.

Metalorganic chemical vapor deposition (MOCVD) was used as the coating deposition technique. The yttria and zirconia precursors were yttrium (thd) and zirconium T butoxide. The source chemicals were purchased from INORGTECH.

Sections 2.2—2.14 describe in detail the work carried out in each of the program quarters.

2.2 First Quarter Work

Progress during this first quarter was very slow. The contract started ahead of initial planning so that the deposition reactor required was not available until the second quarter of the program. Also, the key technical personnel at the subcontractor were on maternity leave, and Spire's request for a proposal to initiate placing of the subcontract was also delayed one quarter.

The principal investigator had discussions with furnace design engineers for the modification of the reactor. Spire's proposed concept for deposition in a cold wall system, with coaxial tubes cooled by air flow in the outside portion and with heating of the part by infrared radiation through the cooled walls, was judged to be a very high technical risk and an unproven design.

Reevaluating the RF power requirements for an induction heated reactor were quite favorable. Initial estimates, as proposed, assumed tens of kilowatts would be required to heat the bars. However, after a more thorough look at the requirements, it was determined that approximately one kilowatt would be needed to heat the test bar to the required deposition temperature of 750°C.

Considering this fact, it was decided to go ahead and build an RF heated reactor. A 2.5 kW RF supply was ordered and plans commenced to build the reactor.

2.3 Second Quarter Work

During the second quarter of the program the reactor used in Phase I was modified. Changes to the gas handling system were made to allow for better source distribution. Figure 1 shows a schematic diagram of the reactor gas distribution. Also, the RF generator was received and installation took place. An RF coil was wound and installed around the quartz reactor tube.

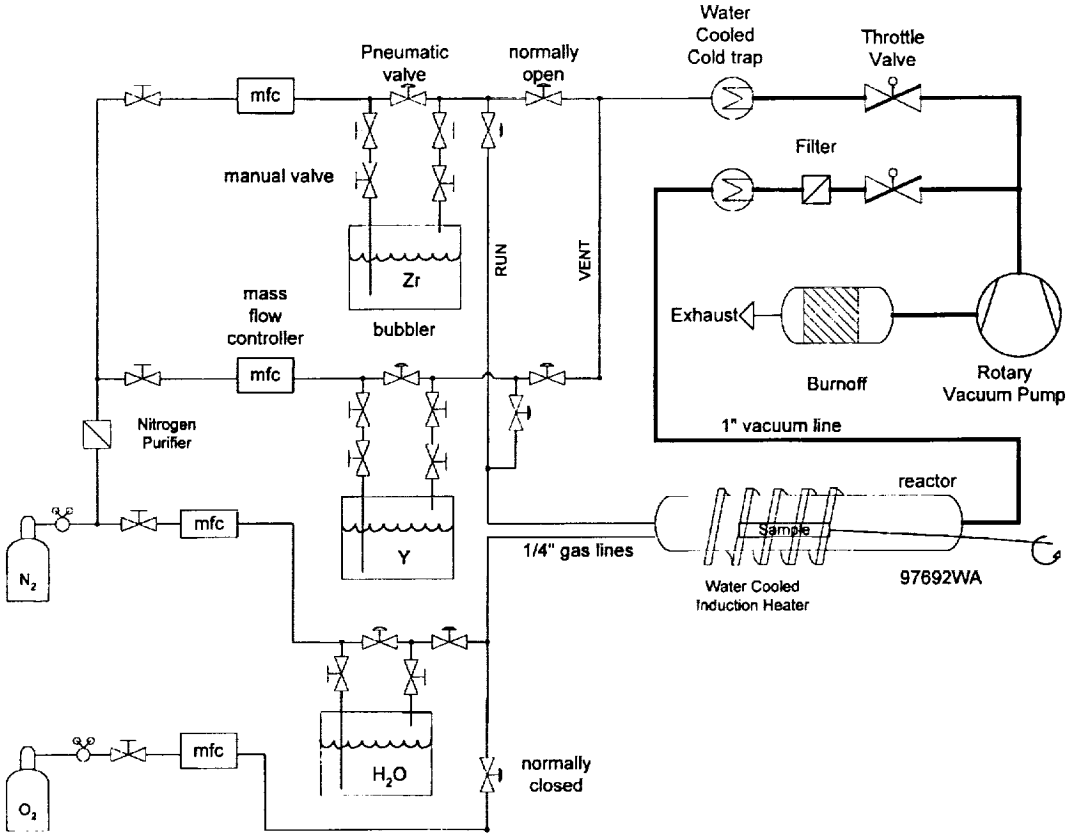


Figure 1 Schematic diagram of gas flow control system for MOCVD reactor.

The reactor was tested to assure the test bars could be sufficiently heated. Figure 2 shows the test bar being induction heated. The sample is glowing yellow-orange, indicating a temperature of about 800°C; actual run temperature is nominally 750°C, measured with an optical pyrometer. An estimated emissivity of the steel bar of 0.3 was used for the measurement.

Sources for both zirconium and yttrium were installed and made ready for deposition experiments. Deposition experiments were planned but a vacuum pump motor failure delayed the work.

The subcontract to Pratt & Whitney was placed, and their work began to prepare bond-coated, aluminide test pieces for deposition and subsequent burner rig experiments.

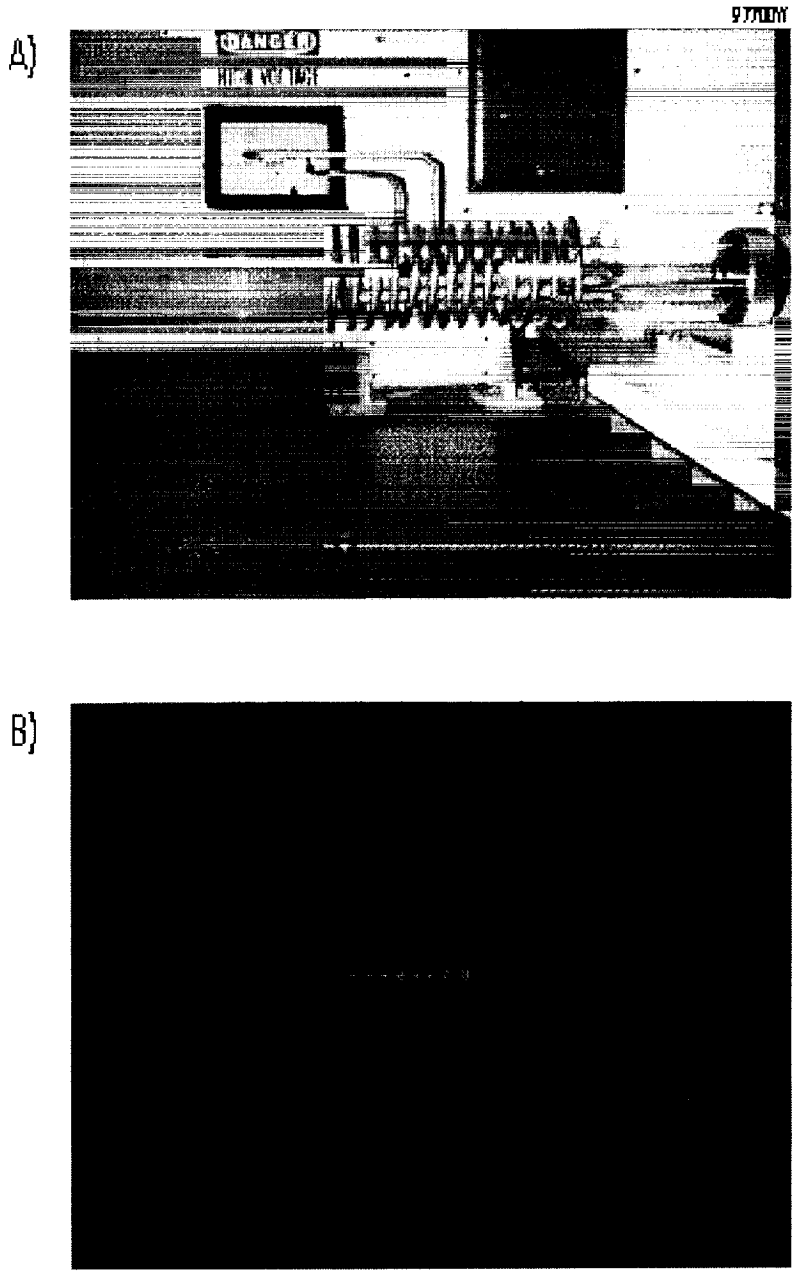


Figure 2 **Picture of RF heated reaction chamber (A) in normal lighting, and (B) in the dark with only the glow of the heated sample bar visible.**

2.4 Third Quarter Work

Spire made good progress during the third quarter. The pump problem was repaired and zirconia films were deposited in the modified reactor.

Initial test runs were made to determine starting point deposition conditions and to investigate potential reactor problems. Stainless steel bars (manufactured in the Spire machine shop) were used for these evaluation runs. Various deposition conditions were investigated as outlined in Table 1.

Table 1 Initial deposition conditions.

Parameters						
Zr Flow (cc) @ 60°C	Y Flow (cc)	Y Temp. (°C)	O_2 Flow (cc)	Main Ar Flow (cc)	Reactor Pressure (torr)	Bar Temp. (°C)
20 -200	80 - 200	135 - 175	100 - 1000	100 - 1000	10 - 50	675 - 775

During the deposition experiments, it quickly became apparent there was a problem with the RF heating. Whenever O_2 was added to the reactor while the RF was on and the chamber pressure was below 10 torr, a plasma would form. The plasma was especially intense at the stainless steel coupling used to hold the test piece to a support rod. A new coupling was fabricated using an insulating material (boron nitride) and installed. The new coupling reduced the plasma to a small area around the threaded inserts securing the rod. The plasma was far enough downstream from the deposition area to allow the experiments to continue.

The best deposited films were ten microns thick, deposited in one hour. The thickness of the coating along the test bar was ascertained from interference fringes along the rod. Zirconia thin films are transparent and produce these fringes. The coating thickness was graded almost linearly with distance along the rods, becoming thinner as it moved away from the injection point of the reactor. The reactor walls were quickly coated with a thick white powder deposit. A sample of the powder and a test stainless steel bar from the same deposition run were analyzed by energy dispersive spectroscopy (EDS). The powder sample indicated a yttrium-to-zirconium ratio of 12.6 to 87.4 atomic percent. However, EDS done on the test bar only indicated the presence of Zr.

After EDS data was analyzed, reactor conditions were adjusted to arrive at the desired yttrium-to-zirconium ratio of 7 to 93%. During the run the Y source ran out or the bubbler clogged and experiments were put on hold so repairs could be made.

2.5 Fourth Quarter Work

In the fourth quarter, the Y source was changed and lines cleaned, readying the reactor for deposition runs. The reaction chamber was modified to improve thickness uniformity as a function of distance along the rod. A quartz cone was added to funnel the gas flow onto the test rod (Figure 3). A few thin test runs of ZrO_2 were run to determine what effect the cone had on uniformity. The uniformity was improved but not substantially.

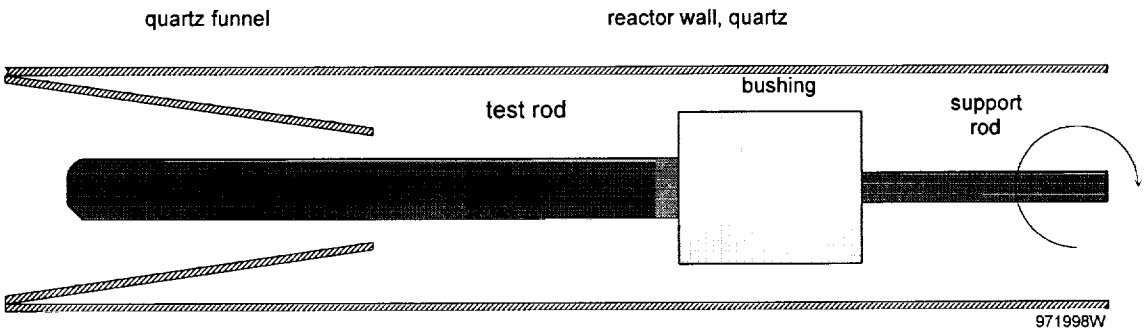


Figure 3 Diagram of reactor showing placement of flow controlling cone

Following the uniformity study, runs to optimize the yttrium-to-zirconium ratio commenced. However, reactor problems deterred progress on this front. Some of the problems encountered were clogged Zr, and Y feed and vent lines, the return of RF plasma in the deposition zone, Zr, and Y source contamination. The numerous problems were traced to plumbing leaks found at VCR fittings inside the high temperature oven. It is believed these leaks were caused by the fittings being repeatedly thermally cycled each time the oven was cooled and reheated for deposition. VCR fittings are known to loosen under these circumstances. The loose fittings most likely allowed air and water vapor to enter the gas handling system, oxidizing the sources and clogging lines and bubblers. The fittings were tightened and reactor leak checked. A decision was also made to keep the source oven temperature fixed at the elevated temperature to minimize thermal cycle fitting loosening.

Also during this quarter the subcontractor prepared test rods with the special alloy bond coat for high temperature testing. These rods were received by Spire, but were held until the reactor was running better.

2.6 Fifth Quarter Work

Plagued by the aftermath of fourth quarter problems, only small progress was realized in this quarter. New sources, unexpectedly contaminated last quarter, were ordered. Long lead times for the sources limited time to perform experiments. Once the new sources arrived, they were installed and work began. A small piece of Silicon was mounted to the end of a bar with silver epoxy. Deposition conditions (Table 2 below), believed to be the best to date were run. The silicon sample from the run was measured using EDS and showed near correct stoichiometry, with 10% yttrium-oxide in zirconium oxide (desired amount is 7%). See Figure 4.

Table 2 Deposition conditions for EDS sample pictured in Figure 4.

Reactor Temp	Y Flow	Y Temp.	Y Press.	Zr Flow	Zr Temp.	Zr Press.	O_2 Flow	Reac. Press.	Deposit Time
675°C	*200 cc /min*	*160°C*	*10 torr*	*20cc*	*60°C*	*10 torr*	*500cc /min*	*4 torr*	*2 hours*

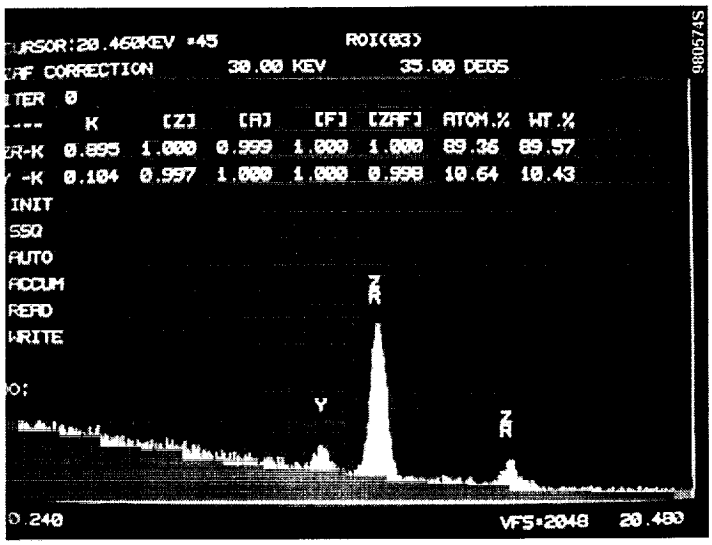


Figure 4 **EDS spectrum of sample showing nearly correct stoichiometry, with 10% yttrium-oxide in zirconium oxide (desired amount is 7%).**

2.7 Sixth Quarter Work

Reactor problems again hindered any real progress in the sixth quarter. The Y source continued to clog and deposits in the Zr vent line shut the reactor down on numerous occasions. Much of the time in this quarter was spent repairing the reactor.

However, even with the problems, thick coatings of zirconia were deposited on a test rod. Initially, the coating was thicker near the "front" of the test piece, closest to the gas inlet in the MOCVD coating system. Turning the test piece end-to-end halfway through the coating cycle resulted in a more uniform coating along the length. Coatings thickness was a maximum of 30 microns. Uniformity was fair over most of the sample, but in some areas adhesion was poor.

The sample was sent to Pratt & Whitney for analysis. Microphotographs of the coating are shown in Figure 5a-d.

2.8 Seventh Quarter Work

Most of this quarter was spent in re-optimizing the coating process after repairing the reactor problems from last quarter. The pressure was increased to reduce the plasma and its deleterious effects. The temperature and flow of the gases were adjusted so that the rod was preferentially coated. At the conclusion of this quarter we had a coating of about half the desired thickness on the test sample. The yttrium content of sample shown in Figure 6 is 10 ±1 atomic percent.

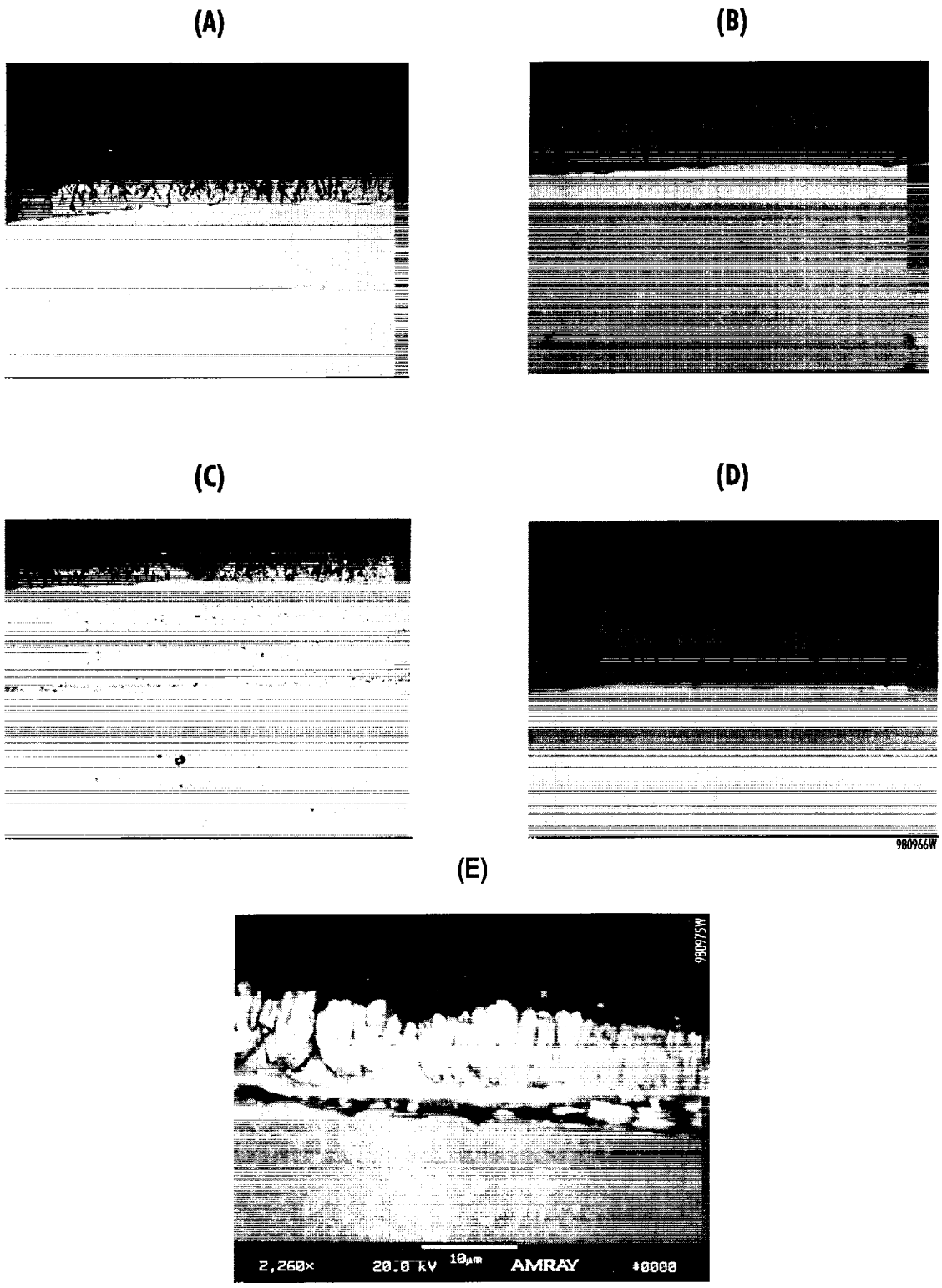


Figure 5 a) Low magnification micrograph of a more uniform part of the ceramic coating. b) High magnification of a uniform part of the ceramic coating. c) Low magnification photo of a less uniform part of the ceramic coating. d) High magnification photo of a less uniform part of the ceramic coating; and e) high magnification image of 10 micron CVD zirconia film.

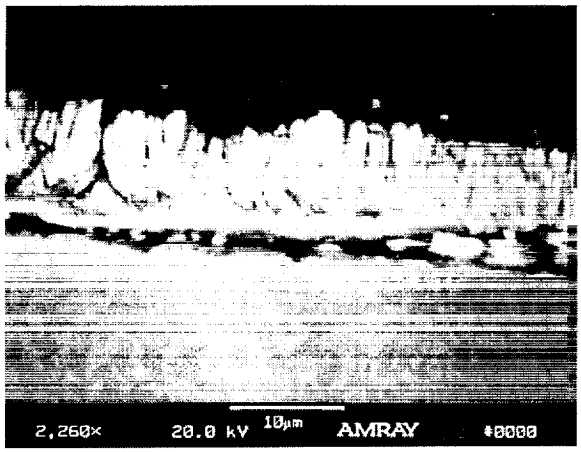


Figure 6 **High magnification photo of cross section of yttria zirconia coating.**

2.9 Eighth Quarter Work

During this quarter, thick coatings of yttria-stabilized zirconia were deposited on a test rod. The coating thickness was made more uniform through optimization of the RF coil to more uniformly heat the test piece. Unfortunately, the adherence of this coating was not good. The bar (sample 5) was sent to Pratt & Whitney for testing, but unfortunately some of the coating was scored and scratched off during shipping. Figure 7 a and b shows the test bar coating as received by Pratt & Whitney.

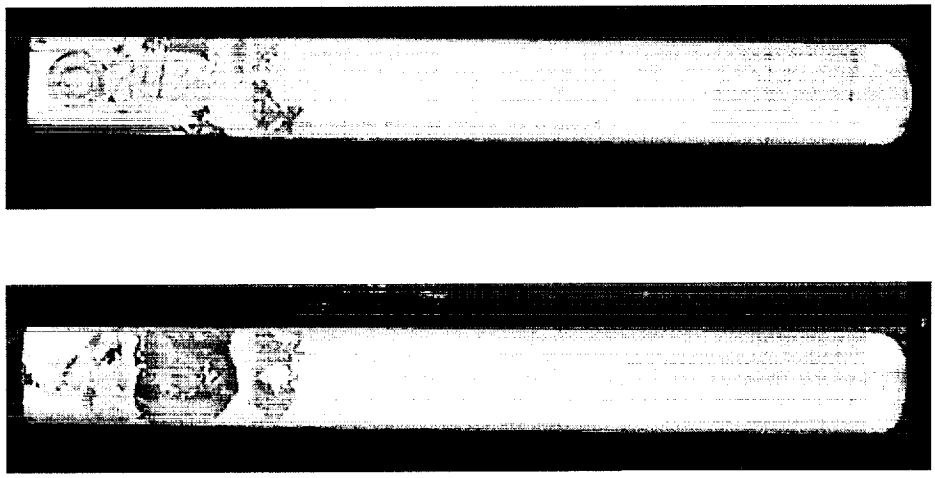


Figure 7 **(a) Leading edge image of Spire sample #5 test bar in as received condition.**
(b) Trailing edge image of Spire sample #5 test bar in as received condition.

Pratt & Whitney examined sample #5 by SEM. Analysis shows that the average yttrium content (taken at four locations around the bar, 2.5 inches from the bottom) is 14 ± 3%. The amount of yttrium present appears to be consistent around the perimeter of the test bar. The thickness of the coating taken from a sample 2.5 inches from the butt is 16.62 ± 4.92 μm or 0.65 ±0.19 mils. This is substantially below the target of a five mil thick coating.

The microstructure of the test bar is shown in Figure 8a-h. The columnar structure of the yttria stabilized zirconia coating seems to be disturbed in a three micron layer near the ceramic/ bond coat interface as seen in Figure 8h.

A short thermal anneal experiment was conducted to try and improve the adhesion of the films. Preliminary results of the experiment indicated that sintering the films at high temperature improved the adhesion. This issue is discussed in more detail in the next section.

Due to the many technical problems, Spire asked for a program extension. This extension was granted in early 1999 and was extended through September 1999.

2.10 Ninth Quarter Work

During the ninth quarter, Spire performed YSZ deposition and high temperature anneals in an attempt to improve the adhesion of the films. Two types of annealing experiments were performed. In the first experiment, one hour open air oven anneals were performed at 950°C after each 10 microns of YSZ deposition. In a second experiment, one test bar from experiment one was annealed at 1200°C in a diffusion tube with a mixture of N_2 and air. A summary of the experiments are shown in Tables 3 and 4.

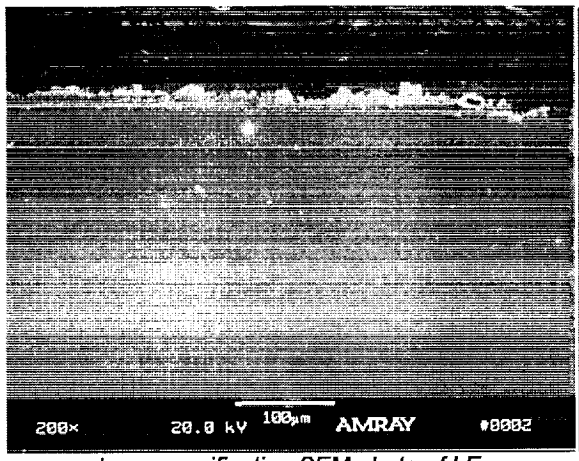
As can be seen from the Tables 3 and 4, high temperature annealing did not change the appearance of the films and did not improve the adhesion properties. Also, it appears that the thickness of the films, regardless of deposition time, are self-limiting around 50 microns, indicating the film is not adhering after 50 microns of deposition. It appeared that the thickness limit was related to the formation of powdery material on the reactor wall.

In January 1999, the Principal Investigator (Anton Greenwald) left the company. This limited further technical work during the quarter. All technical work stopped after the above experiments and a program reevaluation was initiated.

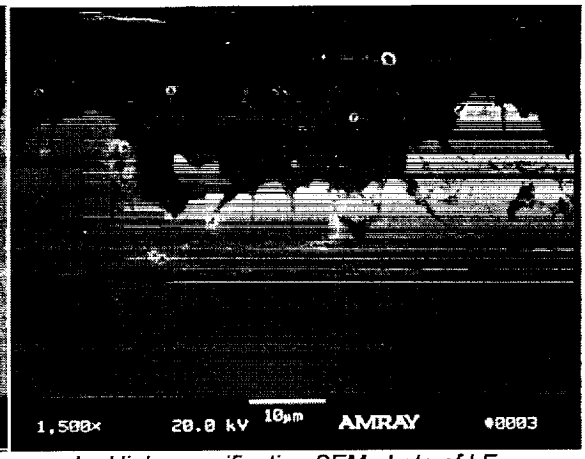
2.11 Tenth Quarter Work

During this quarter, Spire reevaluated program goals, technical progress to date, remaining funds, and determined a course of action which would most likely lead to good YSZ coatings.

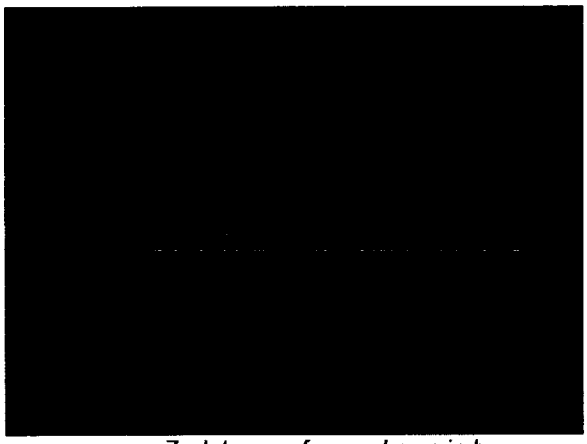
Technical issues relating to film adhesion were discussed with Ms. Sue Meier at Pratt & Whitney. One most probable cause of the poor adhesion was agreed to be depositing the film at too low a temperature. Ms. Meier believed that a temperature of approximately 1000°C-1100°C is required to achieve adherent, hard films.



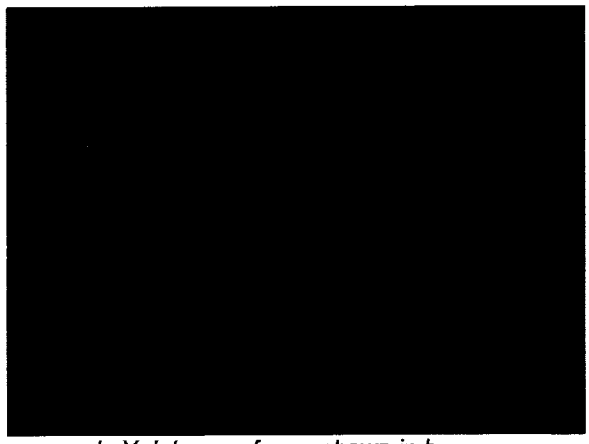
a. *Low magnification SEM photo of LE.*



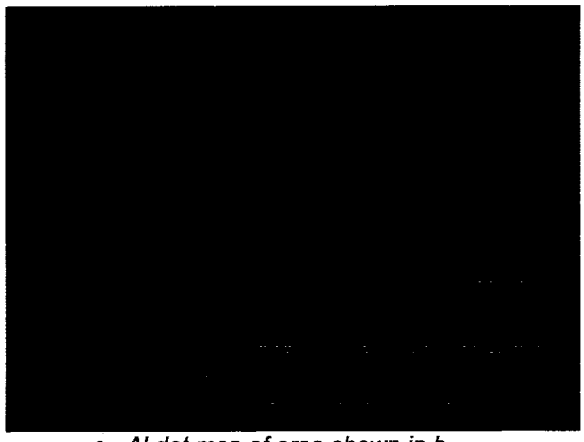
b. *High magnification SEM photo of LE.*



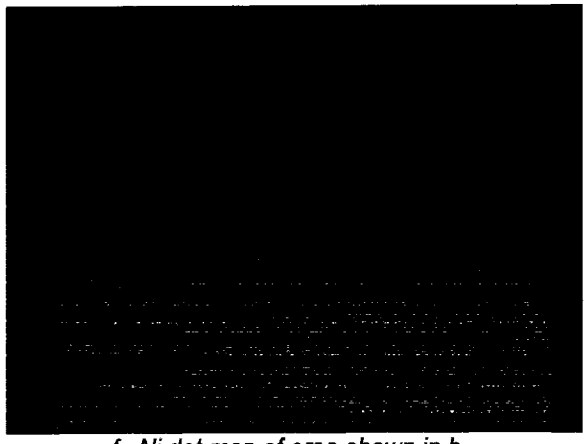
c. *Zr dot map of area shown in b.*



d. *Y dot map of area shown in b.*

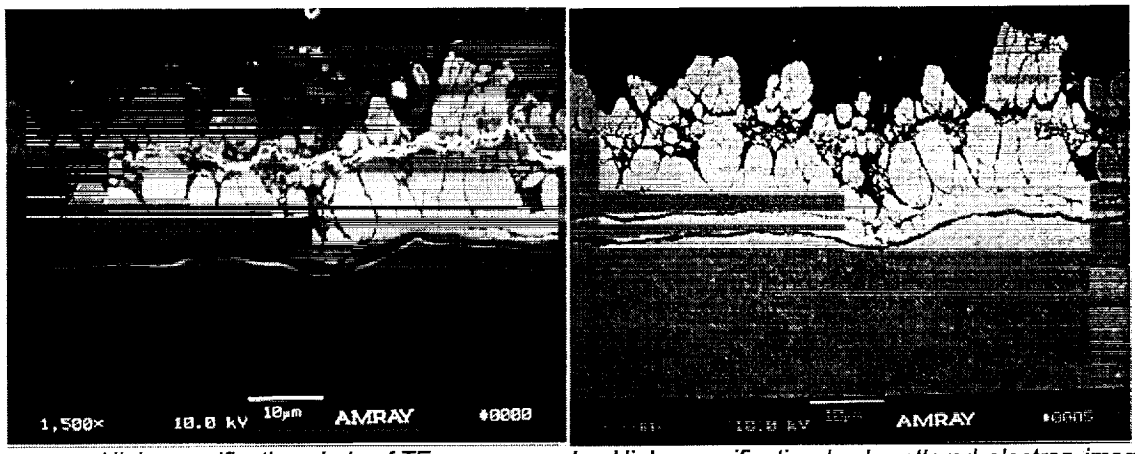


e. *Al dot map of area shown in b.*



f. *Ni dot map of area shown in b.*

Figure 8 Microstructural analysis of Spire sample #5.



g. High magnification photo of TE.

h. High magnification backscattered electron image of TE.

Figure 8 Microstructural analysis of Spire sample #5. (concluded)

Table 3 Summary of Annealing Experiment #1

MOCVD Deposition Cycle #	Thickness (μm)	Appearance After Deposition	Oven Anneal Temperature (° C)	Anneal Time (Hrs.)	Appearance After Anneal
1	10-15	Whitish, powder like	950	9	No change
2	25-30	Whitish, powder like	950	8	No change
3	35-40	Whitish, powder like, looks thicker and a little rough	950	9.5	No change
4	40-45	Whitish, powder like	950	8	No change
5	50-55	Whitish, powder like	950	8	No change
6	50-55	Whitish, powder like	950	8	No change. Film thickness appears to be self limiting around 50 microns. Also, film scrapes off easily.

Table 4 Summary of Annealing Experiment 2.

Process Lot #	Sample ID #	Anneal Temperature (°C)	Anneal Gas	Results
6163	85	1200	50% N2, 50% Air	Film still appears whitish in color, very little change from before anneal. Film scrapes off easily.

Using these facts, a revised statement of work was generated requesting a reallocation of subcontract funds and a change to the statement of work. The revised statement of work is summarized below. Also, a request was made to change the principal investigator from Anton Greenwald to Victor E. Haven (See Spire memo dated 22 April 1999, attn: Mr. Jon Schultz).

2.12 Revised Statement of Work

First, to address the deposition temperature problem, an upgrade to the RF heating system will be made to allow deposition temperatures to 1000°C-1100°C. The current system uses a 2.5 kW RF generator which only heats the bars to between 600-800°C. The 2.5kW generator will be replaced with a 5 kW generator and will allow heating to well over 1000°C. Also, the RF coil will be modified to improve coupling efficiency to the bar.

To address the problem of low deposition rate caused by reaction tube wall deposition, the reactor tube will be redesigned to allow more of the reactant to flow over the bar and will incorporate reaction tube wall cooling. The tube wall temperature will be controlled at a level cool enough to limit the decomposition of the chemicals and at the same time hot enough to reduce condensation of the reactants. It is estimated that the wall temperature will be maintained between 100-300°C . The reaction tube will either be cooled using fluid (water, alcohol, oil) or with forced air using high flow blowers around the reaction tube.

The following are the tasks and improvements required for the deposition of thick films of yttria-stabilized zirconia (YSZ) suitable for turbine blade coatings:

2.12.1 Task 1 - Reactor Modifications

1A Design and procure new reaction tube (bell jar)
1B Specify and procure reconditioned 5 kW RF generator (trade in 2.5kW unit)
1C Design modified gas handling/injection system for improved reactant delivery
1D Order new metalorganic sources.

2.12.2 Task 2 - Reactor Setup

After the reactor modifications have been designed and the parts are in-house, the reactor will be setup. The following tasks will be performed.

2A Install new reaction tube (bell jar) and modified cooling system
2B Install RF generator and remake RF coil
2C Install redesigned gas injection plumbing to allow for more efficient injection of the reactants
2D Clean plumbing, install gas dryers, leak test, heat tape gas lines.

2.12.3 Task 3 - Test Hardware

When reactor is assembled the following tests will be performed:

3A Test RF radiation for safety

3B Test heating capability, determine that 1000°C deposition temperature can be achieved, modify as required.

2.12.4 Task 4 - Plan and Perform Experiments

4A Plan experiments and deposit about 10 films with different flow conditions for composition and growth rate tests. RBS, SIMS and other techniques as applicable, will be used to determine composition and thickness.

4B Deposit 10 micron films on 4 test bars, test composition and adhesion

4C Deposit 50 μm films on 2 test bars, test composition, adhesion and send to Pratt & Whitney for testing.

4D If Task 4C yields good material, deposit 100-125 micron films on 2 bars and send to Pratt & Whitney for testing.

4E If time allows, repeat task 4D with minor deposition conditions and send to Pratt & Whitney for testing

2.12.5 Task 5 - Reports and Deliverables

Monthly or quarterly (as requested by NASA) and final report will be prepared.

2.13 Eleventh Quarter Work

During this quarter, Spire negotiated a revised statement of work with P&W and sent a signed modified contract to NASA on July 21, 1999. The new completion date is December 31, 1999.

Work on the reactor commenced immediately after contract approval. All designs were completed, parts ordered and ninety percent of the reactor modifications were completed. The following is a summary of tasks completed in the eleventh quarter.

2.13.1 Tasks Completed

A larger, 5kw RF generator was ordered, tested and installed on the reactor. Heating tests were performed at the RF vendor's facility before accepting the unit, with a stipulation that the unit will heat a test bar to over 1000°C. The unit had little trouble heating a bar to over 1100°C (measured with an optical pyrometer), in approximately 5 minutes. Figure 9 is the bar on test at the RF vendor's facility.

A new gas injection manifold was designed, fabricated and installed on the reactor. The improved manifold has three inlets. One for the Zr precursor, one for the Y precursor and a third for the main push line and O_2 source. All lines are injected separately into the reaction chamber to minimize gas phase reactions and oxide formation which can clog lines, a persistent problem during this program.

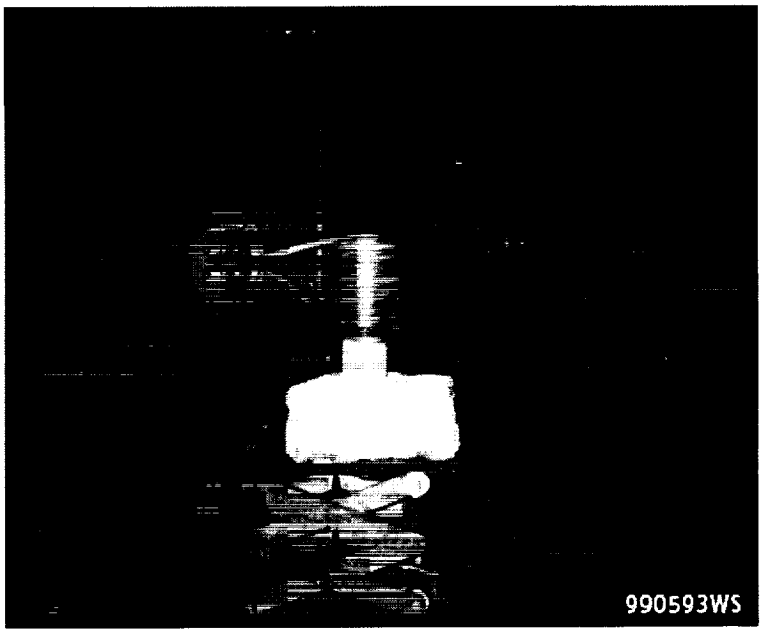


Figure 9 Bar during heating test at RF vendor's facility

The reactor plumbing was modified to reduce dead space and to allow for better purging between runs, and to reduce pre-reaction deposits. Two pressure monitors (Baratrons) were added to the MO bubblers so the pressure could be monitored during the runs. Air blowers were added to keep the quartz reactor walls cool to minimized deposits. In addition, all MO and main lines were rerouted to go through a N_2 purifier. This was done to keep carrier gas clean to minimize MO source contamination, another problem encountered in the past. Figure 10 shows the modified reactor plumbing.

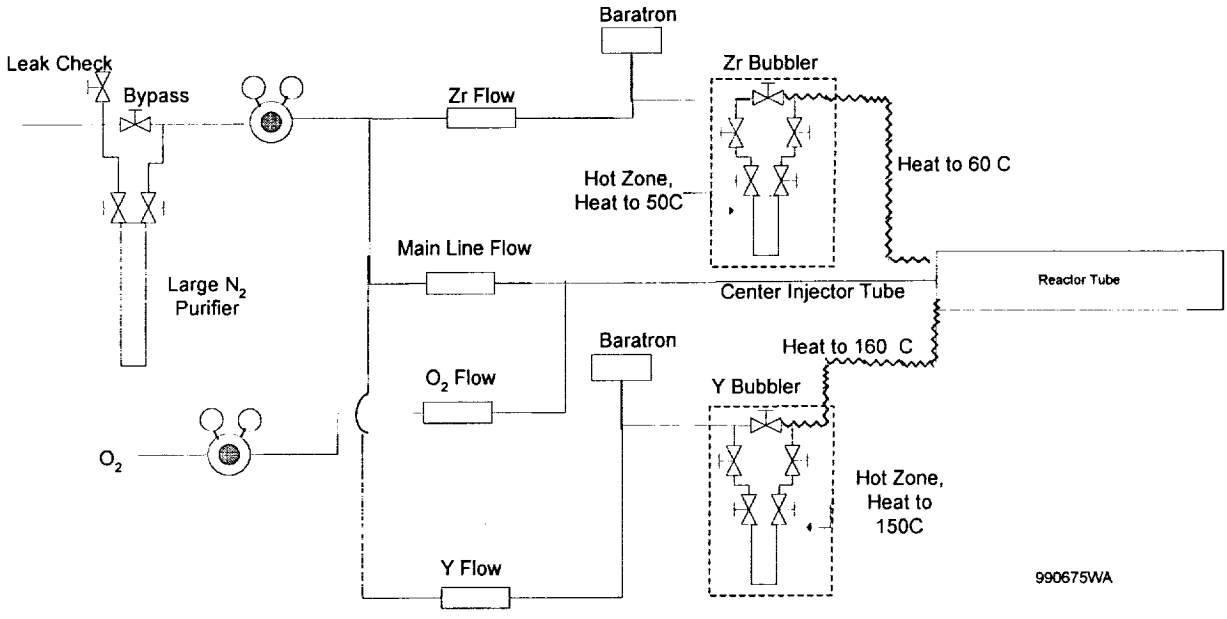


Figure 10 Modified reactor plumbing

2.14 Twelfth Quarter Work

In this quarter, remaining hardware changes were completed, as outlined below, and deposition experiments began.

Completed hardware changes:

- Leak checked plumbing
- Made new RF coil for better coupling to the test bar
- Installed new Y and Zr sources
- Wired pressure sensors (Baratrons) and displays
- Installed reaction tube cooling blowers
- Installed rebuilt vacuum pump

2.14.1 Deposition Experiments

For the initial experiments, stainless steel test bars (made in the Spire shop) were used. The first experiments run were to determine heating capability of the system and to calibrate roughly the optical pyrometer reading versus RF power settings. RF power settings for high and low temperature ranges were calibrated, 1050-1080°C and 930-960°C, respectively.

After the temperature was calibrated, initial deposition conditions were chosen to determine the zirconia deposition rate. (See Table 5.)

Table 5 Initial zirconia deposition conditions to determine deposition rate.

Reactor Pressure (torr)	Zr flow(cc)@ 50°C	Main flow N_2 (cc)	O_2 Flow (cc)	Deposition Temperature (°C)	Deposition Time (min.)
48	20	400	500	1080	60

A stainless steel test bar was loaded and reactor pumped down to 48 torr. When all flows and pressures were stabilized, the Zr bubbler valves were opened. Immediately, Zr source liquid started to enter the reactor tube, covering the bottom portion of the tube; the run was aborted. The Zr source was removed and weighed; 30 grams of Zr still remained, so the source was reinstalled and leak-checked. The reaction tube was removed, cleaned, and reinstalled.

Again, with caution, the test run was initiated. This time everything performed well and deposition took place as expected. Within minutes of starting the deposition, the reactor walls were covered with a white deposit. The bar was examined after one hour of deposition and had a bronze color with a rainbow pattern (Figure 11). SEM and EDS done on the film indicate the film is less than 5 microns thick, determined by the relatively strong peaks from the stainless steel rod (Fe, Cr), as compared to the Zr peak. Figure 12 is an EDS scan of the film, and

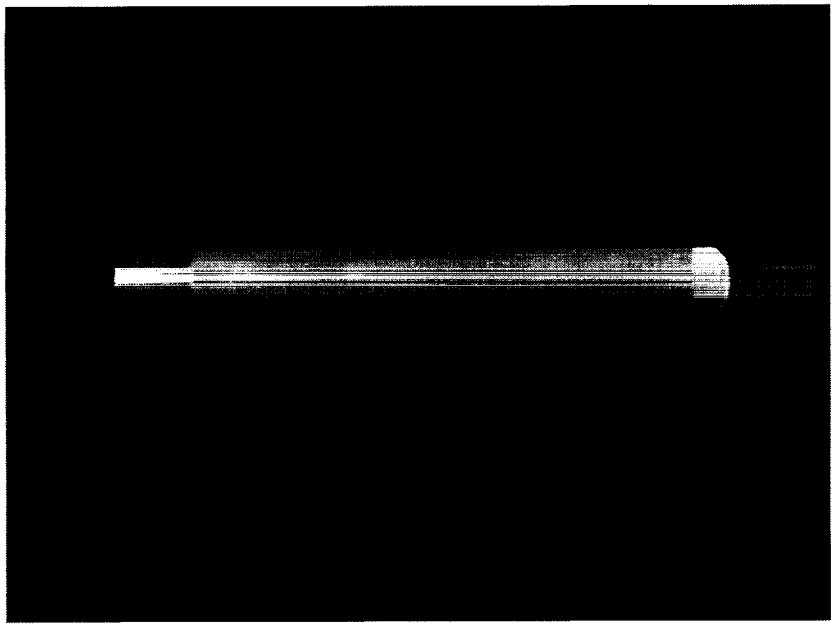


Figure 11 **Photograph of zirconia film deposited using conditions from Table 5.**

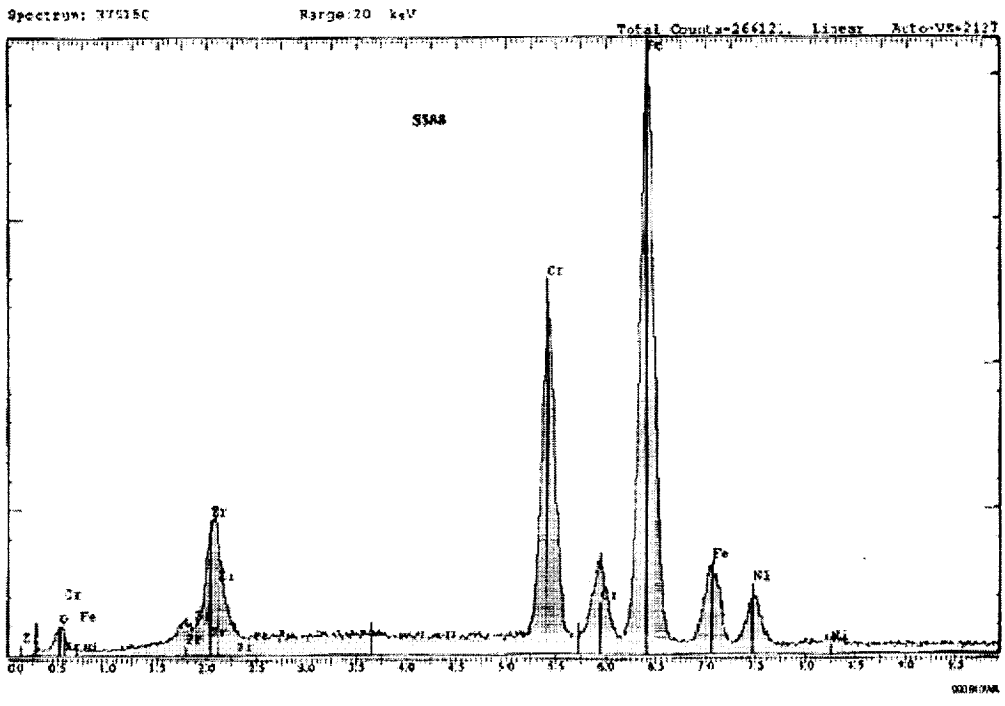


Figure 12 **EDS of thin zirconia film deposited using conditions from Table 5.**

The run in Table 5 above was repeated a second time with identical results. A third run was made using the conditions from Table 5 except the deposition temperature was maintained at 960°C. The film from this run was even thinner then the other two runs.

One additional run was attempted using similar flow conditions. However, the Zr bubbler clogged during heating and the run was aborted.

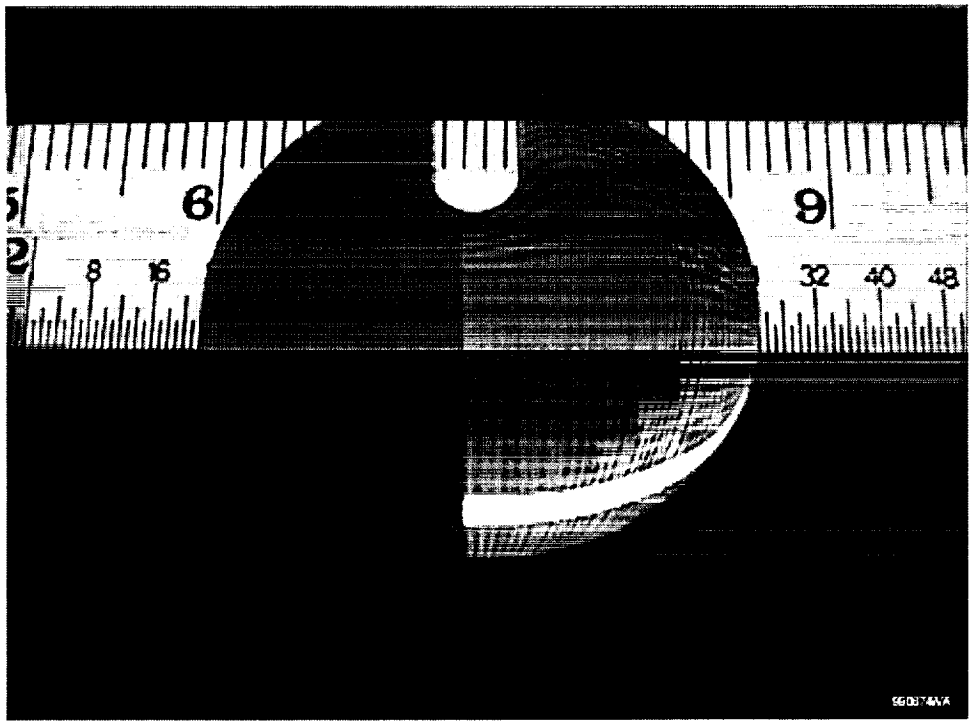
The outcome of these experiments was very disappointing. All modifications to the reactor to improve the deposition rate and film properties did not improve the results. The deposition rate is still very slow and not sufficient for efficiently depositing thick films. Also, the plumbing modifications did not help the clogging problems encountered numerous times during this program.

Experiment with Highly Crystalline Nucleation Layer - A preliminary experiment was conducted to evaluate the possibility of using a new deposition process, developed for other applications at Spire, to form a nucleation layer for thermal barrier coatings. Oxide coatings formed by Spire's proprietary process are generally thin, highly crystalline, and have been demonstrated to be strongly adherent to several different materials, including Co-Cr-Mo superalloys, stainless steels, titanium, and Ti-6A-4V alloy.

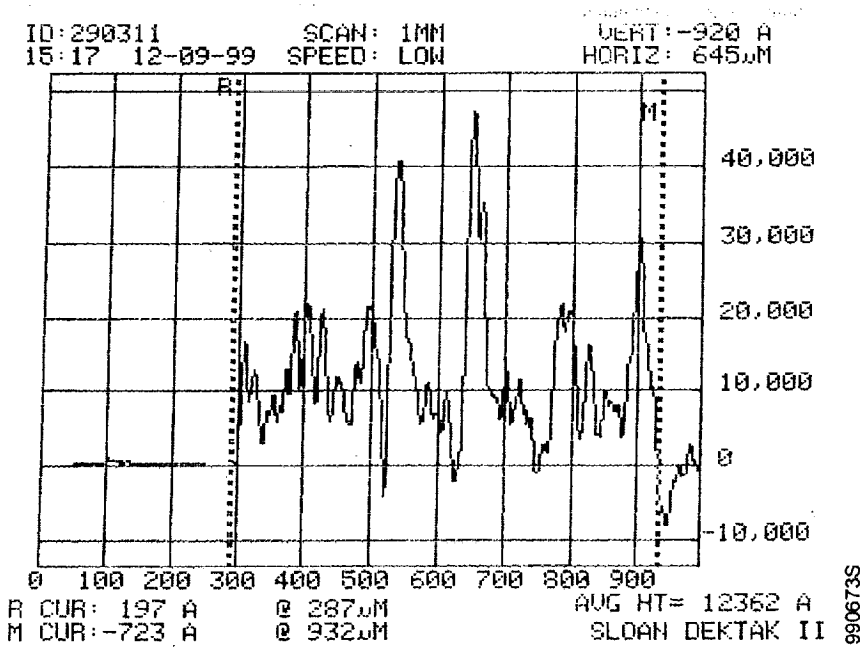
Figure 13a shows an example of the YSZ coating deposited by the proprietary process on a polished Co-Cr-Mo (ASTM F-799) coupon. The coating was applied on half of the coupon so that a thickness measurement could be made with a Dektak IIA surface profilometer. Figure 13b is a 1 mm profilometry trace across the coated and uncoated boundary, indicating that the polycrystalline coating has an average thickness of about 1.2 microns. (It should be noted that the apparently negative values of the trace in Figure 13b are due to overshoot of the profilometer's diamond stylus.) Based on tape adhesion and scratch tests, the YSZ coating by the proprietary process is very adherent and was judged to show promise as the interface between the oxidation barrier and thermal barrier coatings for turbine blades.

Theorizing that the slow MOCVD deposition rate could be caused by poor nucleation on the surface of the test bars, the Spire process was used to deposit a highly crystalline layer of Zr oxide, yttria-stabilized with approximately 10% Y_2O_3, on one Pratt & Whitney bar (SP55). Figure 14 is an SEM micrograph of the bar after one deposition cycle of the Spire process, showing that the surface was fully covered with no evidence of flaking.

The proprietary process was repeated 8 times with a 1000°C anneal of 50% mixture of O_2 and N_2 between each deposition. The resulting film thickness after the eight cycles is approximately 5 microns. Figure 15 is an SEM micrograph of the 8 cycle film, showing a morphology similar to that of the initial layer. Figure 16 is an EDS analysis of the film following the depositions. The EDS spectrum indicates a thin film of Zr oxide with about 10% Y_2O_3. The thickness of the film was deduced from the strong Ni, Co, Cr, and Al peaks generated by the underlying Pratt & Whitney anti-corrosion layer of NiCoCrAlY, as compared to the relatively weak Zr and Y peaks from the Spire-deposited top film.



(a)



(b)

Figure 13 **(a) Co-Cr-Mo alloy coupon with yttria-stabilized zirconia coating deposited on half of its polished surface. (b) Surface profilometery trace across coating boundary indicating average thickness of about 1.2 microns.**

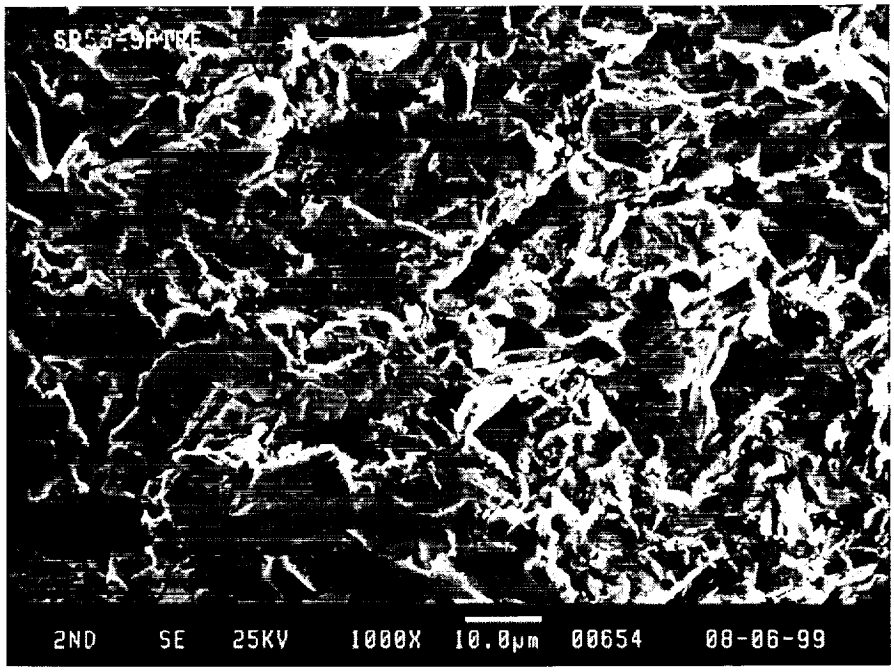


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Figure 14 **SEM Micrograph of Zr oxide, Y stabilized film deposited with Spire proprietary process.**

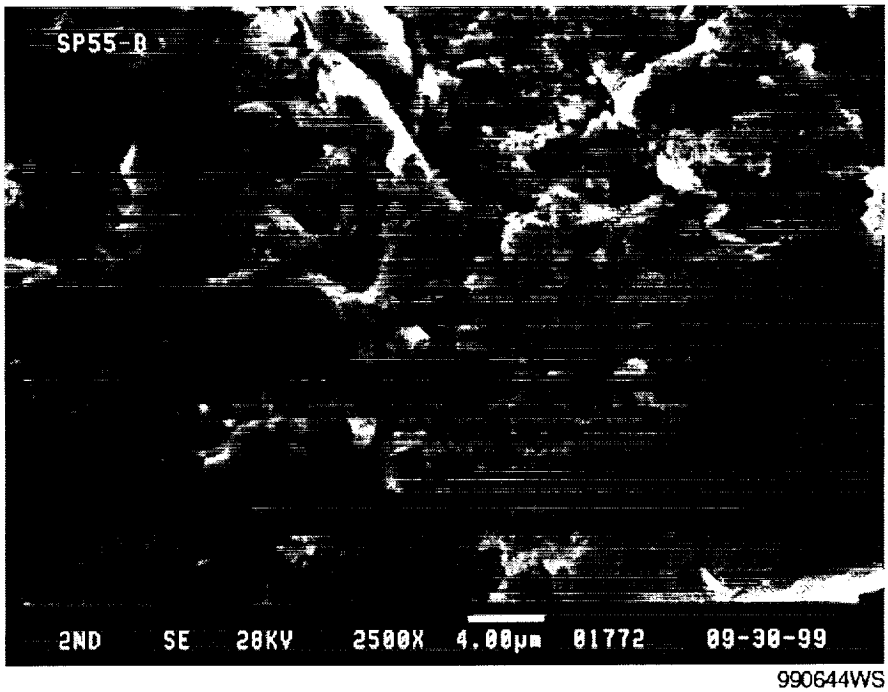

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Figure 15 **SEM micrograph of 8 cycle Y stabilized Zr film deposited using the Spire proprietary process.**

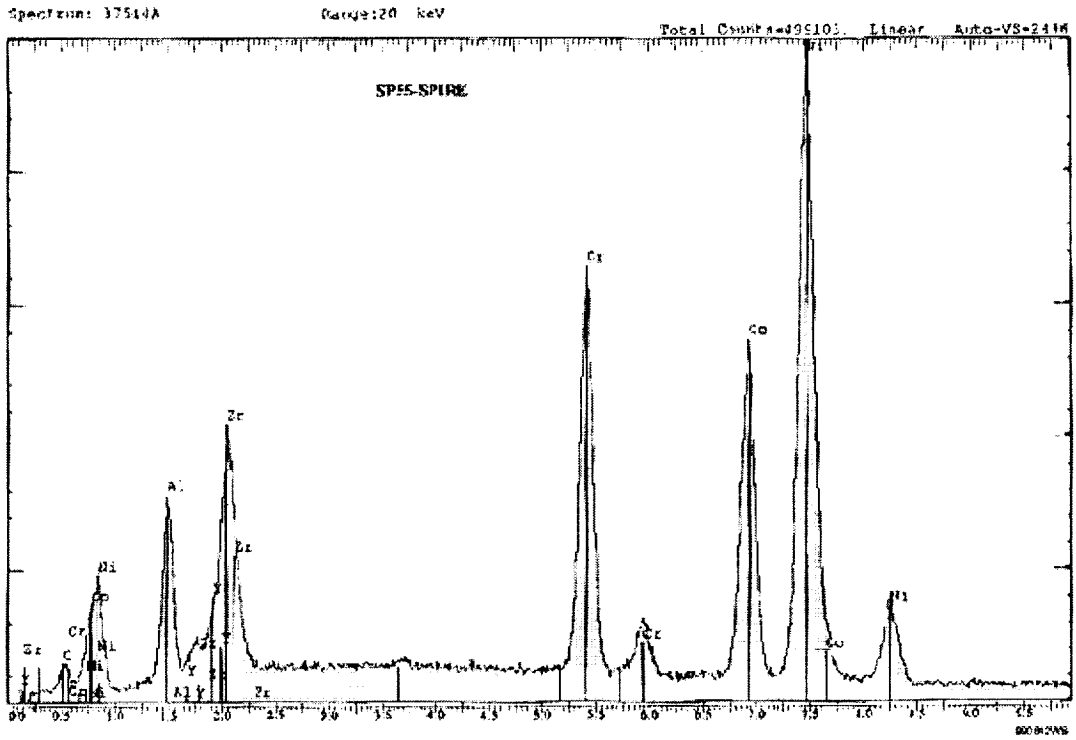

Figure 16 **EDS Spectrum of 8 cycle Y stabilized Zr film deposited using the Spire proprietary process.**

MOCVD Deposition Attempt on Crystalline Nucleation Layer - A final MOCVD deposition was attempted using the bar with the 8 cycle, Spire proprietary coating as the nucleation layer. The Zr source, which had clogged from the previous run, was replaced with a new source, and the test bar loaded into the reactor. Flow conditions for depositing yttrtia-stabilized Zr oxide were determined and the reactor was heated to 1070°C. Oxygen was turned on and the Zr bubbler was opened. Again, some liquid instantly appeared in the reaction chamber. This time only a small amount was visible so the run was continued. The Y source was opened and flow set. However, pressure began to build up in the Y line after five minutes. The Y bubbler by-pass was opened and the pressure stabilized, indicating a blockage in the Y bubbler. The run was continued using just Zr oxide. However, after about five minutes the Zr source liquid in the tube (flammable solvent) ignited violently; blowing the reactor end cap off the tube. At this point the reactor was shut down and a decision was made for both technical and safety reasons to terminate all MOCVD work.

Following the mishap, the reactor was disassembled and decontaminated. All sources were returned to vendor.

3. RESEARCH FINDINGS OR RESULTS

Although YSZ coatings with nearly correct stoichiometry were deposited on various substrates, it is quite evident from the work performed during this program that MOCVD, using the Zr T-Butoxide and Y THD sources, is not an option for depositing thermal barrier coatings on turbine blades. The low vapor pressure of the sources makes the transport properties unfavorable for depositing thick films in a timely or cost-effective process. Also, operating the sources at a low pressure and high temperature, required for transport, causes many other problems, such as line clogging and source contamination/degradation.

There are other metalorganic sources now available which might lead to better results. Some potential sources that have been reported with favorable results (Journal of Material Research, Ref. Vol. 14, No 1 Jan 1999) are $Zr(acac)_4$ and $Zr(dpm)_4$ (acac=acetylacetonate; dpm=dipivaloylmethanate) as well as a new, highly volatile, air-and moisture-stable Zr precursor, $Zr(tfacen)_2$ (tfacen=bis-trifluoracetylacetone-ethylenediminate).

The preliminary experiments with coatings deposited by Spire's proprietary process indicated that thin layers (1 to 2 microns) of YSZ could be formed on hard metal substrates and that the coatings were highly crystalline and adherent. Based on these observations, a multiple-layer coating, with intervening annealing cycles, was attempted, although with only a small additional build-up of coating material. Use of the crystalline YSZ as a nucleation layer for further build-up by MOCVD was not sufficiently tested to determine its true potential, although the good adhesion and uniform surface coverage shown by the 1 to 2 micron YSZ layer provides a basis for optimism. Development of better MOCVD techniques would allow a good test of this approach.

4. POTENTIAL APPLICATIONS FOR THE PROJECT RESULTS IN A PHASE III FOR NASA PURPOSES AND FOR COMMERCIAL PURPOSES

The importance of gas turbines for aeropropulsion, marine, and stationary power plants was the major technological motivation of this SBIR project to develop better thermal barrier coatings for turbine blades by metalorganic chemical vapor deposition. Based on experience with deposition of electronic materials such as gallium arsenide, oxide coatings formed by MOCVD should have highly consistent stoichiometry, excellent crystal quality, and adhesion properties that are potentially better than those formed by plasma spray, conventional CVD, or vacuum evaporation. These coatings, when applied to turbine blades, should improve turbine performance by allowing higher temperature, longer lifetime operation.

Although the project was unsuccessful in developing a superior thermal barrier coating, considerable information was gained on the formation of zirconia and yttria coatings by MOCVD. The problems encountered with the reactor, mainly control of reagent partial pressures, flow patterns in the deposition zone, and substrate heating, lead to YSZ coatings in which composition, thickness, and thickness uniformity were difficult to establish. The strides made in overcoming these problems are all valuable for any future efforts to deposit thick, adherent, uniform, thermal barrier coatings. Finally, the concept of using a thin, highly crystalline YSZ interface layer between the oxidation protection layer and the thick thermal barrier coating has enough potential to be subject of further investigation.

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Spire Corporation
One Patriots Park
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13. ABSTRACT *(Maximum 200 words)*

Ceramic thermal barrier coatings extend the operating temperature range of actively cooled gas turbine components, therefore increasing thermal efficiency. Performance and lifetime of existing ceramic coatings are limited by spallation during heating and cooling cycles. Spallation of the ceramic is a function of its microstructure, which is determined by the deposition method.

This research is investigating metalorganic chemical vapor deposition (MOCVD) of yttria stabilized zirconia to improve performance and reduce costs relative to electron beam physical vapor deposition. Coatings are deposited in an induction-heated, low-pressure reactor at 10 microns per hour. The coating's composition, structure, and response to the turbine environment will be characterized.

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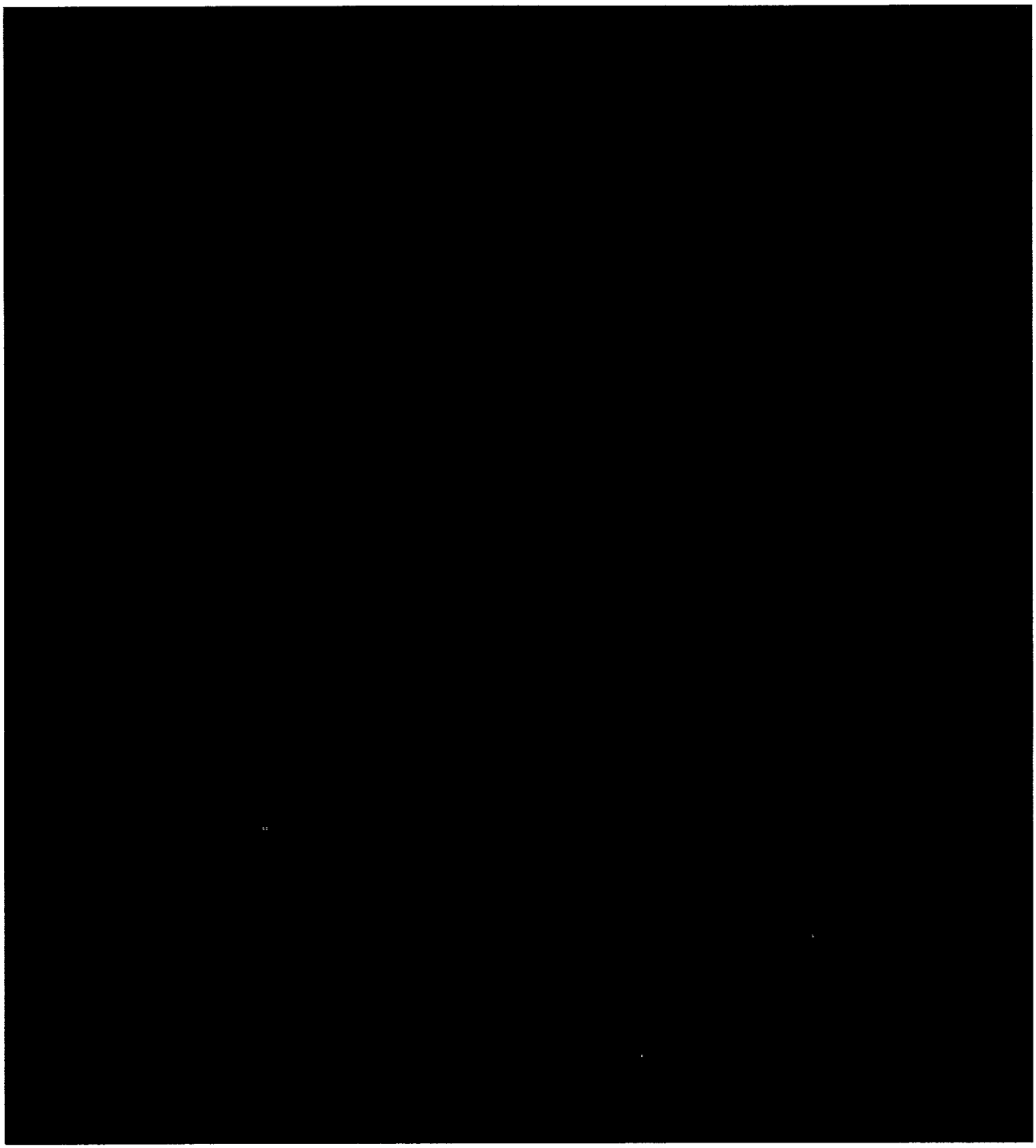

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