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Development of Sputtering Process to Deposit Stoichiometric Zirconia Coatings for the Inside Wall of Regeneratively Cooled Rocket Thrust Chambers

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Thermal barrier coatings of yttria stabilized zirconia and
zirconia-ceria mixtures were deposited by rf reactive sputtering.
Coatings were 1-2 mils thick, and were deposited on copper
cylinders intended to simulate the inner wall of a regeneratively
cooled thrust chamber.   Coating stoichiometry and adherence
were investigated as functions of deposition parameters.

Modest deposition rates (~ 0.15 mil/hr) and subambient
substrate temperatures (~80°C) resulted in nearly stoichiometric
coatings which remained adherent through thermal cyles between -196
and 400°C.   Coatings deposited at higher rates or substrate
temperatures exhibited greater oxygen deficiences, while coatings
deposited at lower temperatures were not adherent.   Substrate
bias resulted in structural changes in the coating and high
krypton contents; no clear effect on stoichiometry was observed.

DEVELOPMENT OF SPUTTERING PROCESS TO DEPOSIT STOICHIOMETRIC ZIRCONIA COATINGS FOR THE INSIDE WALL OF REGENERATIVELY COOLED ROCKET THRUST CHAMBERS

INTRODUCTION

Planned regeneratively cooled thrust chambers consist of an inner wall surrounded by cooling channels cut in an outer containment structure. The inner wall, usually copper or nickel, is subjected to the coolant (liquid hydrogen) on its outer surface and the hydrogen-oxygen flame on its inner surface. The severe temperature gradient, together with the cyclic nature of the thrust chamber operation, limit the useful life of the inner wall. Both erosion and thermal fatigue contribute to failure.

The application of a thermal barrier coating to the inner surface of the wall was expected to reduce the temperature gradient and thus the amplitude of the thermal fatigue strain. Such a coating would also reduce erosion, since suitable materials are much harder than the wall material. The principal problem in the application of such a coating is maintaining adherence during the severe and rapid thermal cycles experienced by the thrust chamber wall. The cause of the problem is the mismatch in thermal expansivity between candidate barrier materials and copper or nickel.

In a previous program,[1] an attempt was made to accommodate the expansivity mismatch by use of a graded composition interlayer. The interlayer consisted of nickel and stabilized zirconia, which were sputter deposited in a stepless gradient from pure

nickel to pure zirconia. A small thickness of zirconia completed the coating. Although these coatings remained adherent in laboratory thermal cycles, they crazed and spalled after a few firing cycles of the thrust chamber test section.[2] This behavior appeared to be related, at least in part, to the nonstoichiometry of the zirconia, which resulted in swelling upon oxygen pickup during the high temperature portion of the cycle.

The objectives of the present program were, therefore, to determine the influence of deposition parameters on stoichiometry of the zirconia; and to investigate the adherence of stoichiometric zirconia coatings to the copper wall. Deposition parameters known or expected to control the Zr/O ratio were:

1) deposition rate

2) partial pressure of oxygen in the sputtering atmosphere

3) substrate temperature

4) substrate electrical potential (bias)

Insofar as they control the microstructure and stress state of the zirconia coating, these parameters are also expected to influence the adherence of the coating even within the range of values which result in stoichiometric zirconia. Additional factors affecting adherence were the use of a bonding layer and the thermal expansivity of the zirconia, which was varied by alloying witn ceria.

EXPERIMENTAL PROCEDURE

Coatings were deposited in a radio-frequency triode sputtering apparatus which is shown schematically in Figure 1. This apparatus was developed from that used in a previous program[1] by the addition of a directly cooled substrate capable of operation at cryogenic temperatures, and the additional shielding and power supply necessary for applying a radio-frequency bias to the substrate.

Sputtering targets were prepared by plasma spraying yttria stabilized zirconia or zirconia*-ceria mixtures on stainless steel tubular supports.

A typical deposition was performed as follows: The apparatus was evacuated to 10^{-7} torr and backfilled with a dynamic atmosphere of research grade krypton at 2-3 mtorr. The substrate was brought to the specified temperature and then cleaned by ion etching. Finally, the deposition proper was begun by applying radio-frequency power to the target. Oxygen was added to the sputtering atmosphere beginning at various points during the period in which the target power was increased to its specified value. Although it was desired to control the partial pressure of oxygen, the quantity actually controlled was the oxygen flow rate, since the residual gas analyzer output was subject to radio-frequency interference. Calibrations performed with no radio-frequency power (i.e. either no target power or a metal

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*The same yttria-stabilized zirconia was used in the mixtures.
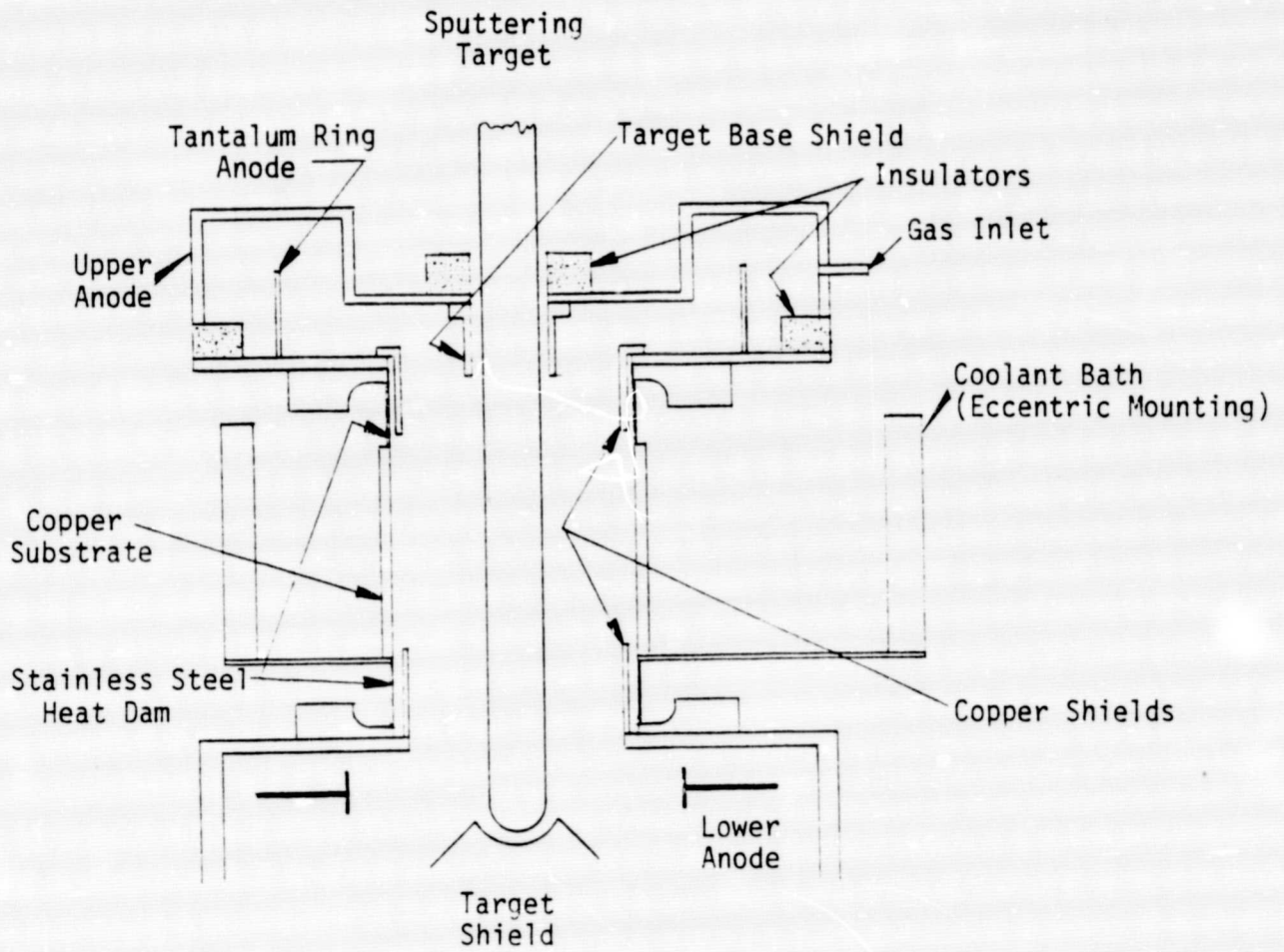
FIGURE 1.   Schematic arrangement of sputtering apparatus used in this work.

target with direct current power) indicated that the two standard cubic centimeter per second flow rate produced a net partial pressure of 1.4×10^{-3} torr or about 30% of the total sputtering pressure. The partial pressure of oxygen was about 70% when the sputtering system was turned off. This flow rate and partial pressure had been found to be the maximum the apparatus would tolerate for useful periods. Since it was also known that the range of other parameters resulting in stoichiometry expanded with increasing oxygen partial pressure, this flow rate and pressure was used in all experiments.

Coated substrates were sectioned for evaluation by x-ray diffraction, x-ray fluorescence, and scanning electron microscopy. Continuous ring samples were subjected to two types of thermal cycle. The first consisted of slowly heating from room temperature to some elevated temperature and cooling back to room temperature. This cycle was repeated with $100^{\circ}C$ increments until coating failure occurred or to $600^{\circ}C$, where rapid oxidation of the copper substrate occurred. The second type consisted of rapid cycles between liquid nitrogen and an elevated temperature, the latter again being increased by $100^{\circ}C$ steps until coating failure or $600^{\circ}C$. The first type of thermal cycle permitted oxidation of off-stoichiometry coatings, while the latter emphasized thermal shock.

Selected rings were scribed with gauge marks, and cut between the marks. Remeasurement of the gauge mark spacing indicated the stress in the deposit prior to sectioning.

RESULTS AND DISCUSSION

The deposition parameters, coating thickness and character
are shown in Table I. The depositions are described individually
in the following sections.

A. EXPERIMENTAL DEPOSITIONS AND DEPOSIT CHARACTERIZATION
Experiments 13 and 14

The effect of substrate temperature on the stoichiometry
and adherence of stabilized zirconia was investigated in
the first group of experiments. A coating (Exp. 13)
deposited at -196°C (liquid nitrogen temperature) experienced
flaking from the edges of the coated area upon opening the
apparatus. It appeared that some of the flaking had
occurred prior to opening the apparatus, but after deposition
was completed (since the bare copper substrate was exposed
where flaking occurred). It is inferred that flaking
occurred during the warming from -196°C to room temperature.

The flakes were translucent and pale yellow in color.
This was taken as evidence of their nearly stoichiometric
composition, in accordance with our previous experience
with oxides.[3] The deposit on the substrate shields,
which were near room temperature during deposition, was
black and opaque. This agrees with the results of the
previous contract[1] and indicates the beneficial effect
of subambient substrate temperature in approaching stoichiometry
of sputter deposited oxides.

TABLE I. DEPOSITION CONDITIONS AND DEPOSIT CHARACTER

Experiment No.	Substrate Temp °C	Target††	Target Power (watts)	Bias Power (watts)	Deposit Thickness (mils)	Comments
13	-196	ZrO_2	700	0	0.4	Not adherent at room temperature. Pale yellow color.
14	-80	ZrO_2	930	0	0.6	Adherent. Medium yellow color.
15	15	ZrO_2	1120	406	N/A	Powdery structure, removable by rubbing surface.
16	15	ZrO_2-CeO_2	1150	400	N/A	"
17	-196*	ZrO_2-CeO_2**	1700	600	N/A	" " "
18	-80/ -44	ZrO_2	1450	300	0.2†	Nonadherent. Black, rough surface. Powdery structure, removable by rubbing surface. Darker grey color.
19	-80	ZrO_2	1350	0	0.4	Adherent, pale grey color.
20	-80	ZrO_2	750	0	0.9	Adherent, darker grey color.
21	-80	ZrO_2	850	0	1.5	Titanium underlayer. Adherent, yellow-amber color.
22	-196	ZrO_2	800	0	2.0	Titanium underlayer. Debonded upon exposure to air. Yellow color.
23	-80	ZrO_2-CeO_2	800	0	1.8	Titanium underlayer. Adherent, yellow-amber color.

*Coolant containment lost during run, completed at elevated temperature.
**Target coating spalled during run.
†Adherent underlayer portion.
††Yttria stabilized zirconia was used in all cases.

7

A stabilized zirconia coating (Exp. 14) deposited at $-80^{\circ}C$ (obtained with dry ice and methanol) was adherent when examined at room temperature. It remained adherent during a thermal cycle between room temperature and $-196^{\circ}C$.

Flakes removed from the coating by thermal cycling between wider temperature limits were translucent but a darker yellow color than those deposited at liquid nitrogen temperature. The color difference was partly attributed to the greater coating thickness (0.9 vs. 0.5 mil) and partly due to a greater deviation from stoichiometry. The microstructure of the deposit is shown in Figure 2. The columnar structure has an apparent diameter of 0.3 micron.

An attempt was made to quantitatively assess the deviation from stoichiometry by lattice parameter measurements immediately after deposition and again after annealing at $900-1000^{\circ}C$ in air. The anneal was presumed to result in sufficient oxygen pickup to achieve stoichiometry; the magnitude of the change in lattice parameter would then indicate the magnitude of the previous deviation from stoichiometry. Lattice parameters were also measured after a vacuum anneal at $900^{\circ}C$, which produced a large oxygen deficiency. Samples turned black after this anneal, but remained translucent.

The results of these measurements (Table II) indicate the unsatisfactory nature of the techniques. Although the data for Exps. 13 and 14 are consistent with the color
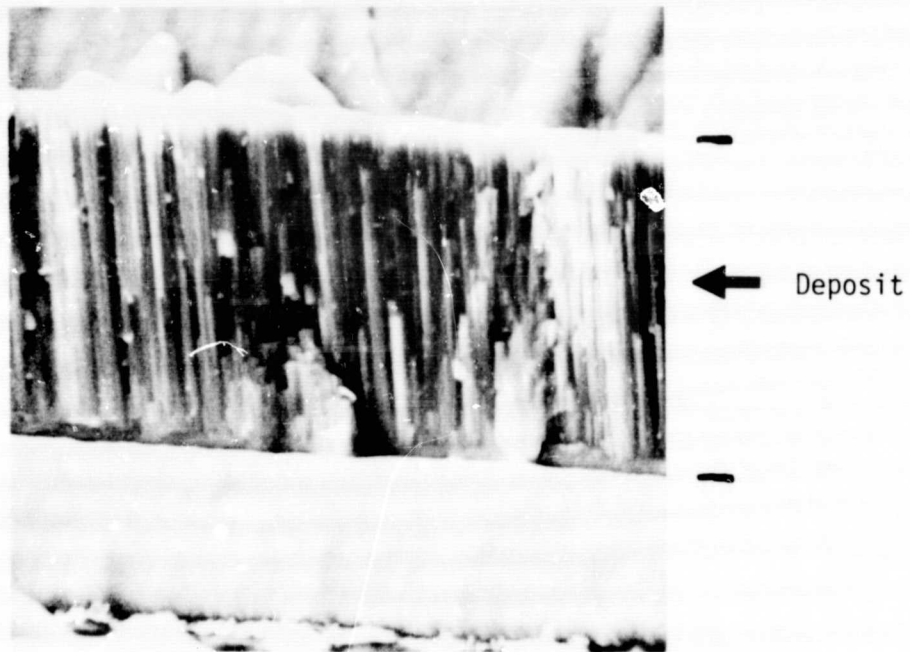
— Deposit

FIGURE 2. Microstructure of zirconia (#14) sputter deposited
at -80°C and 930 watts. Cross-section prepared by
fracturing deposit. Scanning electron micrograph.
4000X

9

TABLE II. LATTICE PARAMETERS OF ZIRCONIA DEPOSITS IN THE AS-DEPOSITED CONDITION, AND AFTER HEAT TREATMENT AT 900°C IN VACUUM AND IN AIR.

Sample	Lattice Parameter, Angstroms		
	As-Deposited	Air HT	Vac HT
13	5.115	5.113	5.152
14	5.020	5.049	5.180
15	5.122	5.114	5.158
16	5.223	5.185	5.077
Sputtering Target	5.200	5.200	5.064

differences, the changes in the lattice parameters of other samples were inconsistent in sign and magnitude. Therefore, the method was abandoned, and deviations from stoichiometry were assessed by color and light transmission. While this method is qualitative, it is sensitive, and in the absence of cationic composition changes between specimens, is expected to be reliable.

Experiments 15 and 16

In the next pair of depositions, a radio-frequency (rf) bias was applied to the substrates. The rf power was controlled to maintain a dc voltage between -40 and -45 volts on the substrate. This resulted in about 30% of the deposited atoms being resputtered from the substrate, as determined by the measured reduction in the specific deposition rate. The target power was increased to maintain a similar net power level. The substrate was cooled with cold water ($\sim 10^{o}C$) to simplify the rf shielding required by the bias application. A stabilized zirconia target was employed for the first deposition; the second used a target consisting of 50% stabilized zirconia - 50% ceria.

In both depositions, the coating consisted of a dark grey underlayer with a loosely bonded surface layer of yellow powdery nature. The microstructure of the underlayer was significantly different from that of unbiased coatings in that the columnar structure was absent (Figure 3). The features observed in Figure 3 are believed to originate in
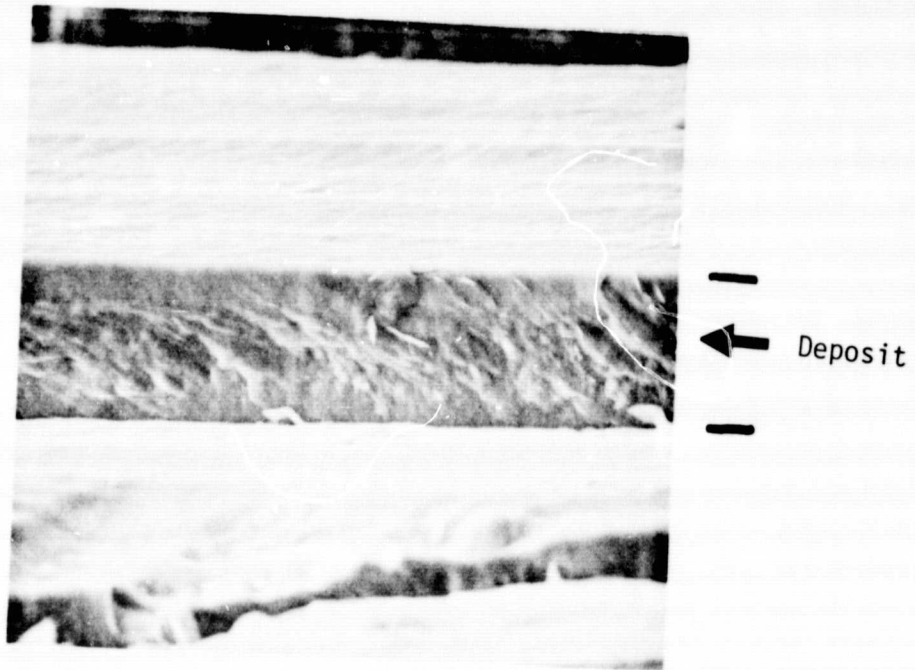
FIGURE 3. Microstructure of zirconia-ceria (#16) sputter deposited at $10^\circ C$ and 1100 watts, with -45 volt, 400 watt bias. Scanning electron micrograph. 2000X

the fracture process used for specimen preparation and only indirectly reflect the growth structure. Although no grain structure is visible, the material was fully crystalline with a grain size of > 500 Å, as indicated by the absence of line broadening in the x-ray diffraction pattern. The nature of the powdery portion of the coating can be observed in Figure 4 (arrow) as an open structure which flaked and curled during deposition. No changes in deposition parameters occurred between the early and late portions of the experiment to account for the change in coating microstructure.

The application of bias to the substrate also increased the degree of preferred orientation, with {111} planes tending to lie in the plane of the deposit.

The coatings were removed from the substrate and analyzed by x-ray fluorescence for krypton, the principal constituent of the sputtering atmosphere. Although it was not possible to prepare standards, the raw data suggested a krypton content about four times greater than in unbiased deposits. Similar increased in krypton content have been observed in Al_2O_3 sputter deposited under bias.[3]

The zirconia-ceria deposit (Exp. 16) was found by x-ray diffraction to be a single phase fcc solid solution of the components, with a lattice parameter of 5.271 Å. Ceria and stabilized zirconia are fcc with lattice parameters of 5.348 and 5.086, respectively. The solid solution decomposed into the equilibrium pure phases at about $250^{\circ}C$

FIGURE 4. Surface of deposit of Figure 3, showing flake structure
believed to correspond to powdery outer layer of deposit.
Scanning electron micrograph. 350X

when heated in a scanning calorimeter. The reaction was not accompanied by macroscopically visible changes, i.e. cracking, curling, etc.

Experiments 17 and 18

The effect of substrate bias on coating stoichiometry was not clear from experiments 15 and 16, due to the mixed character of the coatings. Therefore, the next pair of experiments combined the bias application with the subambient substrate temperature. No useful results were obtained from experiment 17, due to a loss of substrate cooling. The loss was not detected until completion of the experiment, since the entire substrate and coolant container were enclosed by the rf ground shield. Experiment 18 was begun with a $-80^{o}C$ substrate temperature, but was completed with a $-44^{o}C$ temperature when a leak occurred, forcing a change from dry ice/alcohol to a calcium chloride brine. The coating was similar in character to those described above.

Since the negative effects of rf substrate bias were not mitigated by reduction of the substrate temperature, and since the reliability of the apparatus when set up for the combination of subambient substrate temperature and rf bias left much to be desired, no further experiments in this direction were performed.

Experiments 19 and 20

The coatings produced in the above experiments were too thin for significant measurements of adherence, but

were judged sufficiently close to stoichiometry for the intended thermal (i.e. nonoptical, nonelectronic) application. Therefore the next group of experiments was aimed at producing 1.0 - 1.5 mil thick coatings. First, an attempt was made to increase the deposition rate in order to obtain the desired thickness within one 8-hour shift. Experiment 19 was prematurely terminated by the formation of an insulating coating on the upper anode. The coating made it impossible to maintain the sputtering plasma in the target-substrate annulus. The coating was pale grey in color, indicating that the higher deposition rate had resulted in a greater oxygen deficiency. Further experiments were therefore limited to target powers of ~ 800 watts.

Two measures were taken to avoid the anode-insulation problem. A shield was installed around the base of the target (see Figure 1) to reduce the amount of sputtered material reaching the anode chamber. Additional anode surface in the form of a ring of tantalum sheet was provided; it was expected that the exterior surface of this ring would not be coated and that the ring would prevent sputtered material from reaching the anode chamber well.

Although the target-base shield was fabricated of copper, and was bolted to a water-cooled surface, it was heavily oxidized after experiment 20. The zirconia deposit was more deficient in oxygen than the previous one, in

spite of the reduced target power. This was attributed to the gettering action of the shield, which reduced the partial pressure of oxygen in the system.

The shield was removed for subsequent experiments. The tantalum anode ring by itself was found to be sufficient to preserve anode function for the desired duration of deposition.

Adherence testing of the above specimens (described in a later section) indicated that the bond strength was inadequate for the intended application, even with coating thicknesses less than specified (0.002 ± 001 inch). The character of the debonding and the near-stoichiometric nature of the coatings implied that a closer approach to stoichiometry would not significantly improve adherence. Therefore an additional bonding mechanism was sought via an interlayer between the copper substrate and the zirconia deposit.

B.   INTERLAYER

Unless a movable shutter is located between the target and substrate until the substrate is ion cleaned and the target is brought to a steady state surface condition (i.e. pre-sputtering), some form of interlayer exists between the substrate and the deposit. The character of this interlayer depends on the details of the ion cleaning, the geometry of the apparatus, and the way in which the target is brought to a steady state. The former factors

were fixed in the present work, and the latter was primarily controlled by the point in time when oxygen was added to the sputtering atmosphere.

The interlayer material deposited prior to the addition of oxygen was substoichiometric zirconia, as indicated by its opacity and black color. The thickness of this layer varied from approximately zero (when oxygen was added as target power was first applied) to a calculated 0.01 mil, when oxygen was added after the target was brought to full power.

Since this substoichiometric interlayer had no discernable effect on adherence of the zirconia, although it was itself more adherent than the balance of the coating (see adherence section), a discrete metallic interlayer was investigated.

In previous work,[4] a titanium interlayer was found to produce a very strong bond between a copper deposit and a Cervit[®] substrate, i.e. the fracture surface was in the Cervit rather than at the interface. Based on this experience, titanium was employed as an interlayer in the following experiments.

The titanium for the interlayer was deposited on the zirconia target in a separate experiment, using the same apparatus but in the reverse direction. The titanium target, which nested inside the copper substrate was then

removed and the system was re-evacuated for the zirconia deposition. The final thickness of the titanium interlayer was ~ 1 μm, as can be seen in Figure 5.

Experiments 21 - 23

Of the final three experiments, two utilized -80°C substrate temperatures; one with a stabilized zirconia target and one with a 50/50 mixture of zirconia and ceria. The third, experiment 22, repeated the earlier use of a -196°C substrate temperature, with the addition of the titanium underlayer. It was hoped that the titanium would overcome the spalling previously observed upon warmup from this substrate temperature. However, any contribution of the titanium to the bond strength was overwhelmed by the increased stress resulting from the greater coating thickness. The deposit spalled over ~ 40% of its area upon warmup, and the remaining deposit spalled upon exposure to room air over a 30-minute period. This result confirmed the earlier experiment, 13, and ruled out the use of the -196°C substrate temperature.

The -80°C deposits, Exps. 21 and 23, were adherent and met the specified thickness requirement. Flakes removed from the substrate by thermal cycling were dark grey and opaque; however, removal of the substoichiometric layer in acid resulted in a pale amber, translucent character similar to earlier deposits formed at -80°C. These deposits were selected for shipment to NASA. Their microstructures are shown in Figures 5 and 6.
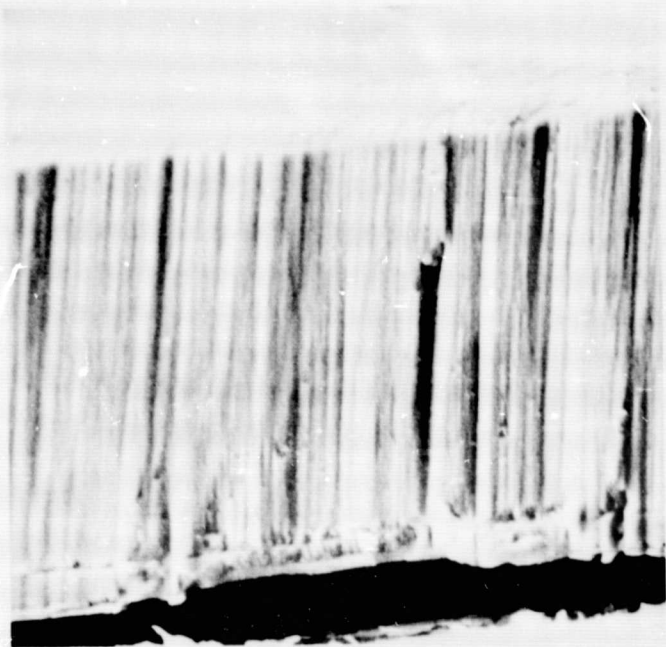
FIGURE 5. Microstructure of zirconia-ceria (#21) sputter deposited at $-80^{\circ}C$ and 850 watts over titanium underlayer. Scanning electron micrograph. 2000X
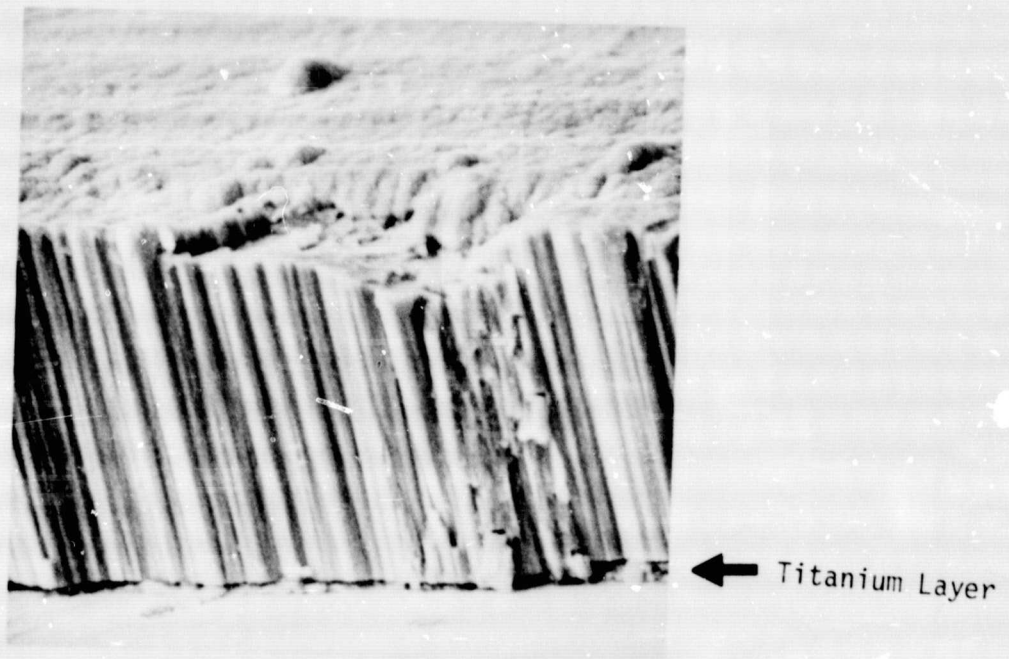
←— Titanium Layer

FIGURE 6. Microstructure of zirconia-ceria (#23) sputter deposited
at -80°C and 800 watts over titanium underlayer. Scanning
electron micrograph. 2000X

C. ADHERENCE OF THE ZIRCONIA DEPOSITS

The deposits produced in the investigation of substrate temperature and bias effects (Exps. 13-18) were not subjected to formal adherence tests by programmed thermal cycling. Their differences in thickness, stoichiometry, and structure effectively precluded such testing. Their adherence was qualitatively determined by single thermal cycles between room temperature and liquid nitrogen, by examining and mechanically probing cut edges, etc. This work indicated that the substoichiometric interlayer had no influence on adherence of the main portion of the coating, that substrate bias did not improve adherence (of the coherent portion of the deposit), and that adherence was inversely related to coating thickness. The latter observation was consistent with the circumferential strain measurements obtained by slitting coated rings, which indicated a strain proportional to coating thickness. The anticipated dependence of strain on deposition parameters was not large enough to be reliably separated from the thickness effect.

The debonding process was generally initiated at either a cut edge of the sample or at the edge of the coating as defined by the substrate shield (see Figure 1). Coatings with an appreciable thickness of substoichiometric zirconia (i.e. those in which the introduction of supplementary oxygen was delayed until full target power was attained) generally debonded in two stages. The first stage consisted

of the majority of the coating thickness flaking, leaving behind an opaque, dark grey or black layer. The flakes were translucent and yellow to amber depending on deposition conditions. The second stage, which was not always observed, consisted of flaking of the opaque layer, exposing the copper substrate.

The adherence of the later series of deposits (19-23) was evaluated by slow cycles between room temperature and an elevated temperature, and fast cycles between liquid nitrogen and elevated temperature, as described in the Experimental Procedure section. These tests were intended to separate oxygen deficiency effects from pure thermal shock effects. The location and character of the debonds were noted as well as the temperature of occurrence. The results are shown in Table III.

The performance of Sample 19 is attributed to the small coating thickness relative to the other samples. The absence of failure at $600^{o}C$ in the slow cycle for this sample, and the similar failure temperatures in slow and fast cycles for the other samples, is taken to indicate that the coatings are sufficiently close to stoichiometry for their intended use.

The performance of Exp. 21 was significantly better than that of Exp. 20, in spite of the much greater coating thickness of the former. The difference, which consisted of partial rather than total area debonding, and the greater temperature required to produce failure, is attributed to the titanium interlayer.

TABLE III. ADHERENCE OF ZIRCONIA COATINGS AS MEASURED BY THERMAL CYCLING

Experiment No.	Peak Temperature of Failure Cycle*		Failure Characteristics
	Slow Cycle	Fast Cycle	
19	600+ (no failure)	600	Debonded to copper on quenching from $600^{\circ}C$; had crazed slightly at $600^{\circ}C$
20	400	300	Debonded to copper on heating; actual sample temperature ~ $320^{\circ}C$ in slow cycle
21	400	400	Slow cycle: partial area debond to Ti layer on cooling from $400^{\circ}C$. Fast cycle: parital area debond to Ti layer at $400^{\circ}C$.
22	Not cycled; debonded to copper on initial warmup to room temperature		
23	300	300	Slow cycle: debonded to Ti layer at ~ $250^{\circ}C$ on heating. Fast cycle: debonded to Ti layer on heating to $300^{\circ}C$.

*In the slow cycle, samples were furnace heated from ambient to elevated temperature and furnace cooled. In the fast cycle, samples were placed in a preheated furnace and then quenched in liquid nitrogen. In both, the elevated temperature was incremented by $100^{\circ}C$ in each subsequent cycle. The cycle in which failure occurred is identified by its maximum temperature.

The zirconia-ceria coating (Exp. 23) was somewhat less adherent than the stabilized zirconia (Exp. 21). This was unexpected, since the 50-50 mixture has a thermal expansivity ($10-11 \times 10^{-6}/^{\circ}C$) much closer to that of copper ($16 \times 10^{-6}/^{\circ}C$) than that of stabilized zirconia ($7-8 \times 10^{-6}/^{\circ}C$). Although the actual bond strength should be similar, the lesser stress generated on thermal cycling by the smaller expansivity mismatch was expected to result in improved performance.

The fact that the failure temperature coincided with the temperature of the decomposition of the metastable phase suggests that the reaction was responsible for the failure. The probable mechanism would be volume change associated with the decomposition. This assignment could be verified by changing deposition conditions to produce the equilibrium two-phase structure directly, however the required changes are unfavorable; i.e. increased substrate temperature (loss of stoichiometry) or reduced deposition rate (problem of electron source life).

The level of adherence of the zirconia deposits in this study was much less than that observed in the previous study[1] which employed graded composition interlayers. The difference is attributed principally to the greater thickness of the zirconia in the present work, which was 1.5 - 1.8 mils vs. approximately 0.1 mil in the previous study, i.e. the total thickness of the coating was ~ 3.5 mils, but only the outermost layer was substantially pure

zirconia. It appears that the graded composition interlayer, which is expected to provide some degree of thermal insulation and erosion resistance, is a necessary component of a sputter deposited zirconia coating on copper.

SUMMARY AND CONCLUSIONS

Thermal barrier coatings of yttria stabilized zirconia and zirconia-ceria mixtures were deposited on cylindrical copper substrates by rf reactive sputtering. The stoichiometry and adherence of the coatings were examined as functions of sputtering parameters, principally substrate temperature and bias, and deposition rate.

It was found that stoichiometry was approached (i.e. the oxygen deficiency diminished) as the substrate temperature and/or the deposition rate was decreased. The lowest temperature $(-196^{o}C)$ produced the most nearly stoichiometric coating, but was not usable since the coating debonded from the substrate upon warming to room temperature. Also, the coating was sensitive to moisture pickup from atmospheric humidity.

Deposits formed at $-80^{o}C$ were adherent, insensitive to atmospheric humidity (or liquid phase water) and had somewhat greater oxygen deficiency.

The application of an rf bias to the substrate during deposition resulted in an increase in krypton content, and an altered microstructure. Biased coatings consisted of an initial layer with a noncolumnar microstructure, and a final layer of a noncoherent powdery nature. The transition between these layers

could not be associated with any change of deposition parameters during the run. Bias had no significant effect on stoichiometry.

Variables other than substrate temperature which affected coating adherence were coating thickness, composition, and presence of a titanium interlayer. As expected, thinner coatings were more adherent. Zirconia-ceria coatings were less adherent than zirconia coatings, possibly due to the decomposition of the metastable single phase formed during deposition. Although not clearly separated in a single variable experiment, the titanium interlayer did appear to favorably influence adherence of the zirconia coating.

The level of adherence obtained in this study was significantly less than that obtained in previous work with graded composition interlayers. Part of the difference is attributed to the greater thickness of zirconia (factor of 10) in the present work; the rest to the strain distribution capability of the graded composition interlayer.

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