

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A129292

**DIP PROCESS
THERMAL-BARRIER COATINGS
FOR SUPERALLOYS**

Final Report

March 1983

By: Ibrahim M. Allam and David J. Rowcliffe

Prepared for:

DEPARTMENT OF THE AIR FORCE
Air Force Office of Scientific Research (AFSC)
Bolling Air Force Base, DC 20332

Attention: Dr. A. H. Rosenstein

Contract F49620-81-K-0009

SRI Project PYU 2509

Approved for public release;
distribution unlimited.

DTIC
ELECTE
S JUN 13 1983 **D**
E

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025
(415) 326-6200
TWX: 910-373-2046
Telex: 334 486



DTIC FILE COPY

83 06 10 052

SRI International



DIP PROCESS THERMAL-BARRIER COATINGS FOR SUPERALLOYS

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DTIC

This technical report has been reviewed and is
Final Report approved for public release IAW AFR 190-12.
Distribution is unlimited.

MATTHEW J. KEMPER
March 1983 Chief, Technical Information Division

By: Ibrahim M. Allam and David J. Rowcliffe

Prepared for:

DEPARTMENT OF THE AIR FORCE
Air Force Office of Scientific Research (AFSC)
Bolling Air Force Base, DC 20332

Attention: Dr. A. H. Rosenstein

Contract F49620-81-K-0009

SRI Project PYU 2509

Approved by:

D. L. Hildenbrand, Director
Materials Research Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83- 0441	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DIP PROCESS THERMAL-BARRIER COATINGS FOR SUPERALLOYS		5. TYPE OF REPORT & PERIOD COVERED FINAL TECHNICAL 12-15-80 to 1-14-83
		6. PERFORMING ORG. REPORT NUMBER 2509
7. AUTHOR(s) IBRAHIM M. ALLAM AND DAVID J. ROWCLIFFE		8. CONTRACT OR GRANT NUMBER(s) F49620-81-K-0009
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI INTERNATIONAL 333 RAVENSWOOD AVENUE MENLO PARK, CALIFORNIA 94025		10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F/A2 2306/A2
11. CONTROLLING OFFICE NAME AND ADDRESS USAF, AFSC AIR FORCE OFFICE OF SCIENTIFIC RESEARCH Bldg. 410, Bolling AFB, DC 20332		12. REPORT DATE MARCH 1983
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 34
		15. SECURITY CLASS (of this report) UNCLASSIFIED
15a. DECLASSIFICATION DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Thermal barrier coatings Reactive metals Oxidation Selective oxidation Thermal cycling		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new concept of growing a ceramic-based thermal barrier coating on gas turbine alloys was investigated. This process involves hot dipping alloy substrates in low-melting cerium-nickel or zirconium-nickel eutectics. Cerium oxide (CeO_2) or zirconium oxide (ZrO_2) were then grown by selective oxidation to form an external thermal barrier layer above an inner composite (CeO_2 or ZrO_2 /substrate alloy) layer. The microstructure and chemical composition of the thermal barriers were studied as a function of composition of melts and		

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

substrates, dipping temperature and oxidation conditions. This evaluation has led to a good understanding of the factors that control the formation of desirable coatings and to the specification of the conditions to produce them.

ZrO₂-based coatings produced by this technique are dense, adherent, and more resistant to spallation than CeO₂-based coatings. The ZrO₂ barriers on a Co-Cr-Y alloy were completely successful in limited thermal cycling tests made in air between room temperature and 1000°C. The major cause of degradation of CeO₂-based coatings in similar tests was attributed to the oxidation of high concentrations of nickel and cobalt in the scale. Such inclusions are absent in the ZrO₂ barriers and arise in the CeO₂ barriers because of the higher growth rate of CeO₂. Approaches taken to slow the rate of growth of the CeO₂ and to improve its spallation resistance were not successful.

An important advantage of ZrO₂-based coatings over CeO₂-based coatings produced by this technique is that ZrO₂ grows totally as an overlay layer with little or no influence of elements from the substrate. In contrast, CeO₂-based coatings grow completely within the surface zone of the coated substrate, and thus their properties can be affected by substrate constituents.

Up to 5 wt% yttrium was added to the Zr-Ni coating melt in an attempt to stabilize zirconia in the cubic form. The yttrium appeared as uniformly distributed Y₂O₃ in the ZrO₂ outer layer. This suggests that higher levels of yttrium or higher processing temperatures are required.

The results of this program suggest that the dip process could be an important alternative approach to plasma spraying for producing thermal barrier coatings on superalloys.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



CONTENTS

	<u>Page</u>
PROFESSIONAL CONTRIBUTION.....	vi
INTRODUCTION.....	1
Background.....	1
Objectives.....	2
SUMMARY OF FIRST YEAR'S WORK.....	4
PROGRESS IN THE SECOND YEAR.....	6
Coating Technique.....	6
CeO ₂ -Based Coatings.....	8
Influence of Active Elements.....	8
Use of Substrate Alloys to Replace Nickel in the Ce-30% Ni Coating Melt.....	13
Zirconia-Based Coatings.....	14
SUMMARY AND CONCLUSIONS.....	23
RECOMMENDATIONS FOR FUTURE DEVELOPMENT.....	25
REFERENCES.....	26
PUBLICATIONS, PRESENTATIONS, AND PATENTS.....	27

ILLUSTRATIONS

Figure		Page
1	Schematic Diagram of Hot-Dipping Apparatus	7
2	Ce-Ni Phase Diagram	9
3	Elemental Distribution Across Coated MAR-M509 Following Hot Dipping and Annealing	11
4	Elemental Distribution Across a CeO ₂ -Based Coating on a MAR-M509 Substrate	12
5	Zr-Ni Phase Diagram	15
6	Elemental Distribution Across Coated Co-10%Cr-3%Y Substrate Following Hot Dipping and Annealing	17
7	Elemental Distribution Across ZrO ₂ -Based Thermal Barrier Coating on Co-10%Cr-3%Y Substrate	18
8	Microstructure of Thermally Cycled Co-10%Cr-3%Y Substrate Coated With ZrO ₂ /Y ₂ O ₃	21

PROFESSIONAL CONTRIBUTION

The individuals at SRI International with major responsibility for this program are as follows:

Principal Investigator: Dr. Ibrahim M. Allam

Program Manager: Dr. David J. Rowcliffe

The program was managed and directed for the Air Force Office of Scientific Research by Captain Steven Wax.

INTRODUCTION

Background

Ceramic thermal barrier coatings are needed in aircraft gas turbine engines to increase the thermal efficiency and extend the life of the coated components. In addition, coated components require less intricate cooling systems, thus reducing the complexity and costs of cooling configurations.

Stabilized zirconia is favored as a thermal barrier material, principally because of its low thermal conductivity,¹⁻³ and because its coefficient of thermal expansion is among the highest of most oxides,⁴ thus making it compatible with superalloys. However, the benefits obtained by applying any thermal barrier ceramic coating depend critically on its integrity (e.g., uniformity, porosity) and on its ability to remain adherent to metallic substrates. These properties are determined by the chemical, physical, and mechanical properties of the ceramic materials and, more important, by the method of application.

Over the past twenty years, plasma spraying has become the most common technique for applying thermal barrier coatings to aircraft combustors and afterburners. However, this technique has never produced a fully successful coating for turbine blades and vanes. The principal problems associated with the use of plasma-sprayed zirconia coatings are the loss of adhesion to the metallic substrates and the penetration of the coating by molten salts.

Large efforts were made to improve the performance of ceramic thermal barrier coatings, principally by introducing metallic bond coating underlayers and by modifying the composition of the coating itself. Other approaches involve the introduction of graded layers or multilayered coatings. All these approaches, however, resulted in only marginal improvements in the coating performance, and a fully acceptable thermal barrier coating still remains to be developed.

Over the past two years, SRI International has developed a new concept for applying ceramic coatings that is radically different from contemporary approaches. The new process involves the application of a thin layer of a low melting (cerium-nickel or zirconium-nickel) eutectic on a superalloy substrate by hot dipping. This is followed by conversion of the less noble component of the eutectic (cerium, or zirconium) into an external oxide layer, by selective oxidation in a controlled environment.

The first efforts to apply the concept of dip coating were described in an earlier report,⁵ and a detailed account of the work during the first year of this contract was presented in an interim report.⁶ The present report summarizes the earlier work and describes the major accomplishments of the second year of work on the application of cerium oxide and zirconium oxide as thermal barrier coatings for high temperature alloys.

Objectives

The overall objective of this program is to develop an oxide thermal barrier coating for superalloys by the hot dip process. The coating must be uniform, dense, adherent and free from metallic constituents. Two coating systems are considered: cerium oxide and zirconium oxide. The objectives of the first year were as follows:

- (1) Optimize processing conditions and properties of the dip coating on IN738.
- (2) Evaluate thermal oxidation resistance of the optimized coating under static and thermal cycling conditions and determine whether hot strength is degraded.
- (3) Using the optimized dip coating system for IN738, develop to a promising stage dip coatings for other superalloys, with primary emphasis on nickel-base superalloys.

The objectives of the second year are given below:

- (1) Modify the composition and microstructure of the oxide coating to produce an external CeO_2 layer free from metallic constituents, and improve the coating/substrate adhesion.
- (2) Determine whether an adherent ZrO_2 -based thermal barrier layer can be produced by the dip coating process.

SUMMARY OF FIRST YEAR'S WORK

The concept of growing oxide layers by selective oxidation was validated during an earlier exploratory program.⁵

To improve the coating quality, we studied a range of coating compositions applied to a number of Ni- and Co-based superalloys. It was also necessary to optimize the processing conditions for the four-step coating process to produce thin and crack-free duplex coatings. The first year of effort also included a preliminary evaluation of the oxidation behavior of optimized coatings under isothermal and thermal cyclic conditions.

The most significant results of the first year of work^{6,7} are summarized below:

- (1) Of the five compositions of the low-melting coating alloys, Ce-30% Ni performs the best.
- (2) The integrity of the duplex coating on cobalt-base alloy substrates (MAR-M509 and Co-25Cr-6Al-0.5Hf) is superior to that on nickel-base alloys (IN738 and Ni-25Cr-8Al-1Y). Coatings on MAR-M509 in particular are thin, adherent, crack free, and easily reproducible.
- (3) Hot dipping, annealing, and selective oxidation treatment of MAR-M509 produced a duplex oxide layer that is very promising as a thermal barrier. The outer scale is a continuous protective CeO₂ layer, and the inner layer is a subscale of CeO₂ matrix and unoxidized alloy islands. The microstructure of the duplex scale changes gradually toward the substrate into a fibrous CeO₂ network embedded in a matrix of the substrate alloy.
- (4) The outer scale and the subscale contain high levels of metallic nickel and cobalt incorporated during the rapid growth of CeO₂. The presence of both metals lowers the

oxidation resistance of the coating and weakens its adherence to the substrate.

- (5) The final step, recrystallization annealing, reduces the CeO_2 to the unstable Ce_2O_3 and allows solid state interaction between cerium oxides and other substrate constituents that lead to the formation of complex mixed oxides, i.e., $0.5(La_2O_3-Cr_2O_3)$, $0.5(Ce_2O_3-La_2O_3 \cdot Cr_2O_3)$, La_6WO_{12} , and $(La_6, Ce_6)WO_{12}$. Tungsten-containing oxides in particular are volatile at higher temperatures and their presence is considered deleterious to the coating. Recrystallization annealing has thus been eliminated from the coating process.
- (6) A model was proposed that describes the mechanism of oxidation during the formation of the duplex coating and accounts for the incorporation of nickel and cobalt in the barrier structure. Based on this model, approaches were devised to eliminate the incorporation of unwanted metals and to improve the performance of the coating.

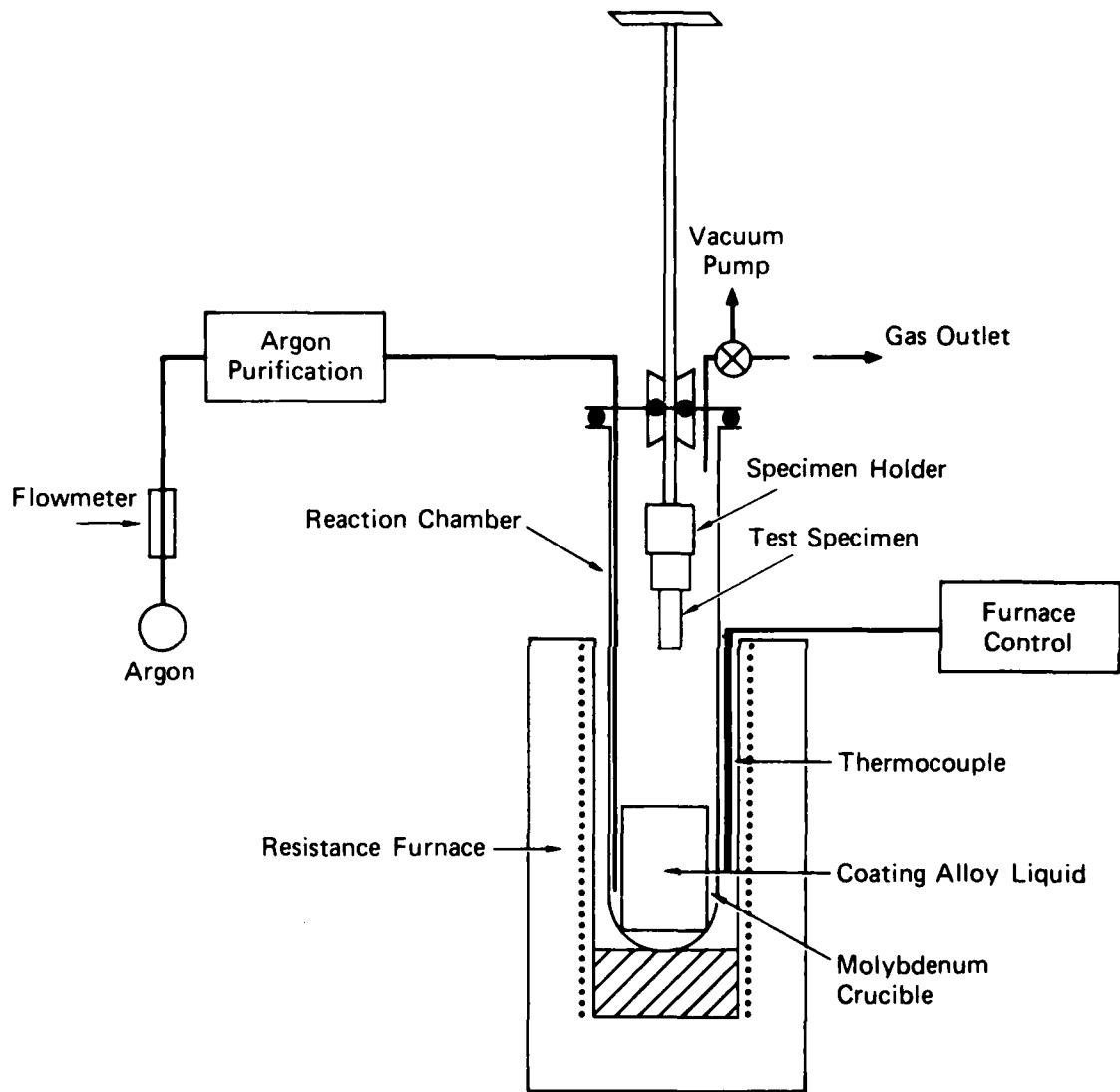
PROGRESS IN THE SECOND YEAR

This section is divided into three parts. The first describes the coating technique. The second describes efforts made to produce an adherent CeO_2 -based coating that is free from metallic constituents to resist the oxidizing environment. The third section describes efforts made to produce ZrO_2 -based thermal barrier coatings using the hot dip process.

Coating Technique

The hot dipping apparatus is diagrammed in Figure 1. It consists of a closed-end alumina reaction chamber in a vertical resistance furnace. The coating alloy is placed in a molybdenum or alumina crucible at the bottom of the reaction chamber, and superalloy test specimens are attached to a vertical stainless steel push-rod passing through a Cajon ultra-torr fitting. Before heating, the reaction chamber is evacuated (10^{-5} atm) and flushed with oxygen-free argon. The furnace is then heated under flowing argon to the required dip temperature. Test samples are lowered slowly into the molten alloy and submerged, typically for 1 minute, then withdrawn. The second step of the coating process consists of annealing the dipped samples to improve the bond between the coating and substrate.

The third step, selective oxidation, involves heating the coated samples in an appropriate gas mixture, for example of 1% CO -99% CO_2 in two stages--first at 600°C then at 800°C . At 600°C , the gas mixture provides an equilibrium oxygen partial pressure of $\approx 2 \times 10^{-21}$ atm. The dissociation pressures of NiO and CoO at the same temperature are 7.2×10^{-20} and $\approx 2.5 \times 10^{-21}$ atm, respectively. Hence little or no oxidation of Ni or Co is expected in the coating layer or within the interaction zone. Under these conditions, cerium oxidizes selectively into a thin external CeO_2 layer and a composite subscale layer that contain CeO_2



SA-8658-1

FIGURE 1 SCHEMATIC DIAGRAM OF HOT-DIPPING APPARATUS

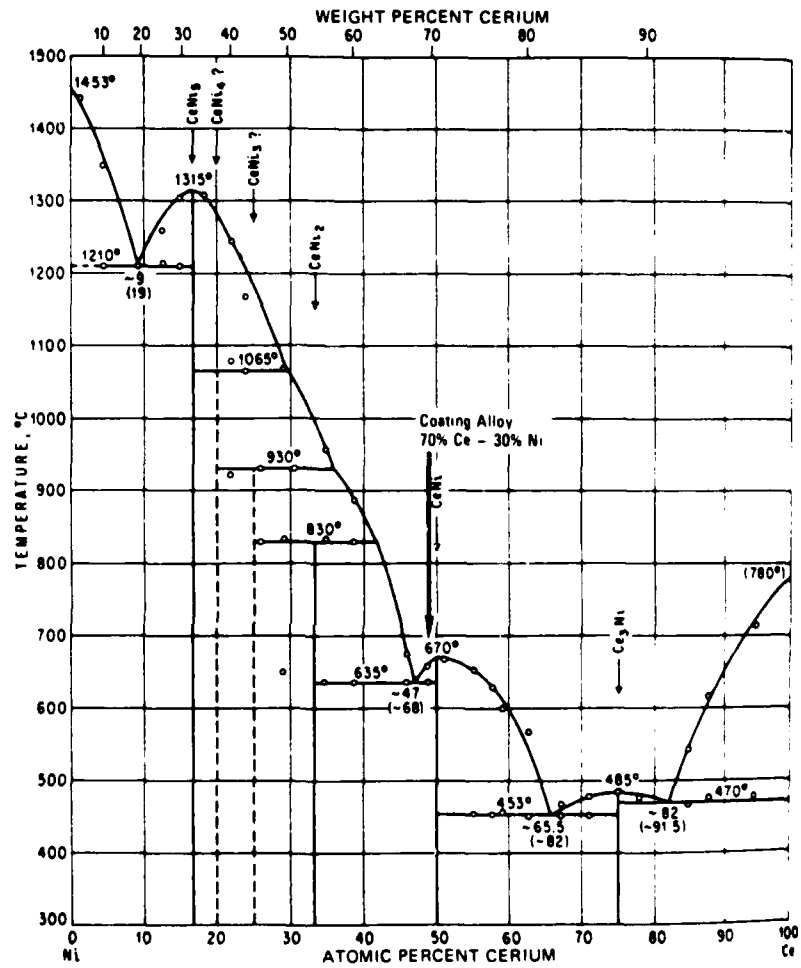
particles in the unoxidized alloy matrix. Further oxidation at 800°C ensures the complete conversion of cerium into cerium oxide.

At equilibrium, the Boudouard reaction $2\text{CO} = \text{C} + \text{CO}_2$ maintains a carbon activity of ≈ 0.063 at 627°C. Under certain conditions, this carbon activity can be high enough to form cerium carbide. Previous experiments showed that powdery cerium carbide formed at high ratios of CO to CO_2 if the oxidation temperature was kept below 600°C. This problem was prevented by using a mixture of hydrogen/water vapor/argon to provide an oxygen pressure low enough to selectively oxidize cerium without oxidizing nickel or cobalt in the coating layer. This gas mixture, at the appropriate temperature and composition was used to produce the ZrO_2 layers.

CeO₂-Based Coatings

Influence of Active Elements

Previous results^{6,7} indicated that the coating alloy Ce-30% Ni was particularly suitable for hot dipping because it has a relatively low melting temperature and the conversion of cerium to cerium oxide in the coating layer can be made within a short time at 600°C. Figure 2 shows the location of this alloy on the Ce-Ni phase diagram.⁸ It was found that the external CeO_2 thermal barrier layer contains large concentrations of metallic nickel and cobalt. The presence of both elements in the unoxidized form is particularly harmful because the subsequent growth of their oxides during testing disrupts the continuity of the external CeO_2 thermal barrier layer and causes severe spallation. It was suggested^{6,7} that metallic nickel and cobalt were incorporated in the CeO_2 layer because the rate of growth of CeO_2 is faster than the back diffusion of both metals away from the oxidation front. To avoid this problem, it was necessary to reduce the rate of growth of cerium oxide. The principal approach used this year to achieve this goal was to introduce into the coating melt small amounts of elements that are more active toward oxygen than cerium. The original alloy composition (Ce-30% Ni) was modified by adding 5% of one of the elements: yttrium, hafnium, magnesium, calcium, or aluminum. The active elements have a



SA-8658-11C

FIGURE 2 Ce-Ni PHASE DIAGRAM

higher affinity for oxygen than cerium and should oxidize preferentially on exposure to high temperature at low oxygen pressures. The concentration of these elements was chosen to be $\approx 5\%$ by weight for two reasons. First, the addition of up to 5% by weight of any of these elements is not expected to increase substantially the melting temperature of the coating alloy. Second, these elements should oxidize to form internal oxide particles in the coating ahead of the continuous CeO_2 layer. If the active element internal oxide particles are formed in a dense configuration, they may provide a barrier to the diffusion of oxygen and thereby reduce the overall growth rate of CeO_2 .

The superalloy MAR-M509 (10.3% Ni, 23.27% Cr, 7.25% W, 3.18% Ta, 0.63% Fe, 0.59% C, 0.24% Si, 0.43% Zr, 0.19% Ti, 0.05% Cu, 0.01% Mn and balance cobalt) was chosen as a substrate for the CeO_2 -dip coating because it provided the best coating compatibility with the CeO_2 -dip coating in comparison to other substrates.⁶

The results indicated that the introduction of active elements to the coating alloy produces no beneficial effects in the coating microstructure or properties. Following hot dipping and annealing, the microstructure and element distribution within the coating layer (cerium-rich zone) is essentially similar to that formed by hot dipping into coating melts that do not contain the additional active elements.

Figure 3 shows a typical cross section of MAR-M509 following hot dipping (and annealing) in the coating alloy Ce-25Ni-5Y. Yttrium is present right through the Ce-rich zone, at slightly higher-than-average concentration near the outer surface. The large islands in the middle zone are pure chromium rejected from the Ce-rich matrix, possibly because chromium is insoluble to any extent in cerium, and because cerium tends to form stable intermetallics with nickel and cobalt.

Figure 4 shows the microstructure and distribution of elements across the total cross section of the duplex thermal barrier coating following the conversion of cerium and yttrium into oxides. The analysis indicates that the presence of yttrium produces no change in

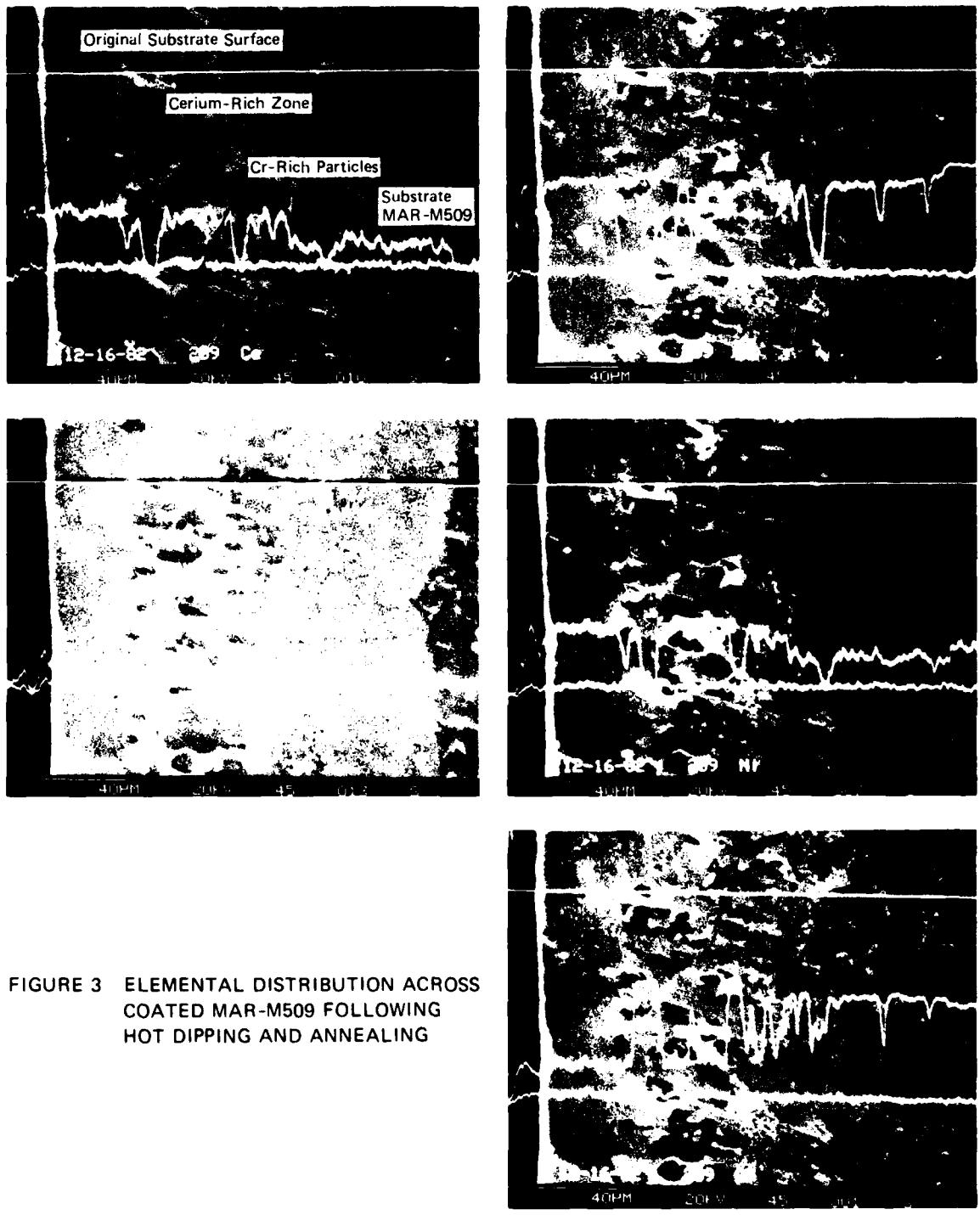


FIGURE 3 ELEMENTAL DISTRIBUTION ACROSS COATED MAR-M509 FOLLOWING HOT DIPPING AND ANNEALING

JP-2509-14

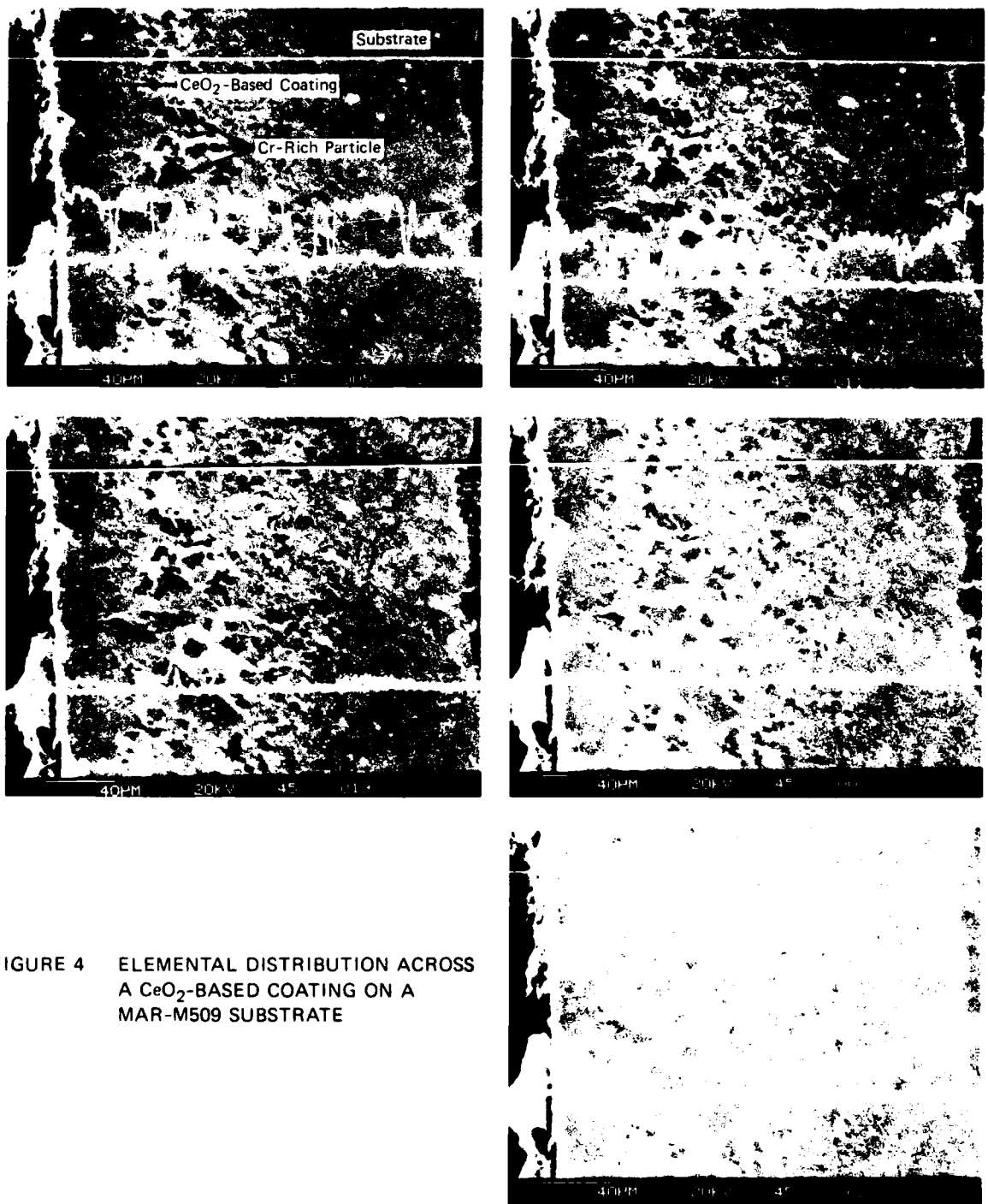


FIGURE 4 ELEMENTAL DISTRIBUTION ACROSS
A CeO₂-BASED COATING ON A
MAR-M509 SUBSTRATE

JP-2509-15

either the coating microstructure or the distribution of elements. The external layer remained unfavorably rich in nickel and cobalt.

Metallographic and EDAX examination of different cross sections from all active element modified coatings revealed the absence of any dense configuration of the active element external oxide particles as originally predicted. It appears that the active element oxidizes homogeneously with cerium to form a mixed oxide. Because of the absence of any physical obstacle (active element internal oxide particles) ahead of the interface between the rapidly inward-growing cerium oxide and the remaining Ce-rich metallic portion of the surface modified zone, the oxidation of cerium proceeds unhindered during the selective oxidation step until all cerium within the surface zone is converted into cerium oxide. This rapid conversion of cerium to oxide can overrun unoxidized nickel and cobalt in the vicinity of the interface and can entrap these elements in the external oxide layer.

Use of Substrate Alloys to Replace Nickel in the Ce-30% Ni Coating Melt

This approach involved the modification of the initial coating composition to provide a gradual change from an outer ceramic layer (CeO_2) to an inner oxide/metal layer where the metallic islands are similar in composition to the coated substrate. For example, the superalloy substrate MAR-M509 was hot dipped in a coating alloy made of Ce-37% MAR-M509. The ratio of cerium to nickel plus cobalt in this coating alloy is about 2.67, compared with a cerium-to-nickel ratio of about 2.33 in the original alloy (Ce-30%Ni). Hot dipping the alloy MAR-M509 in the new melt should produce an adherent coating that is chemically more compatible with the coated substrate than when the same substrate was dipped in the original coating alloy (Ce-30 Ni).

Several combinations of coating melts were applied on matching substrates. The results, however, were disappointing because of the failure of the oxide layer once cooled from the selective oxidation temperature. The oxide scale was very thick ($>1000 \mu\text{m}$), porous, and contained numerous cracks. These characteristics are probably related

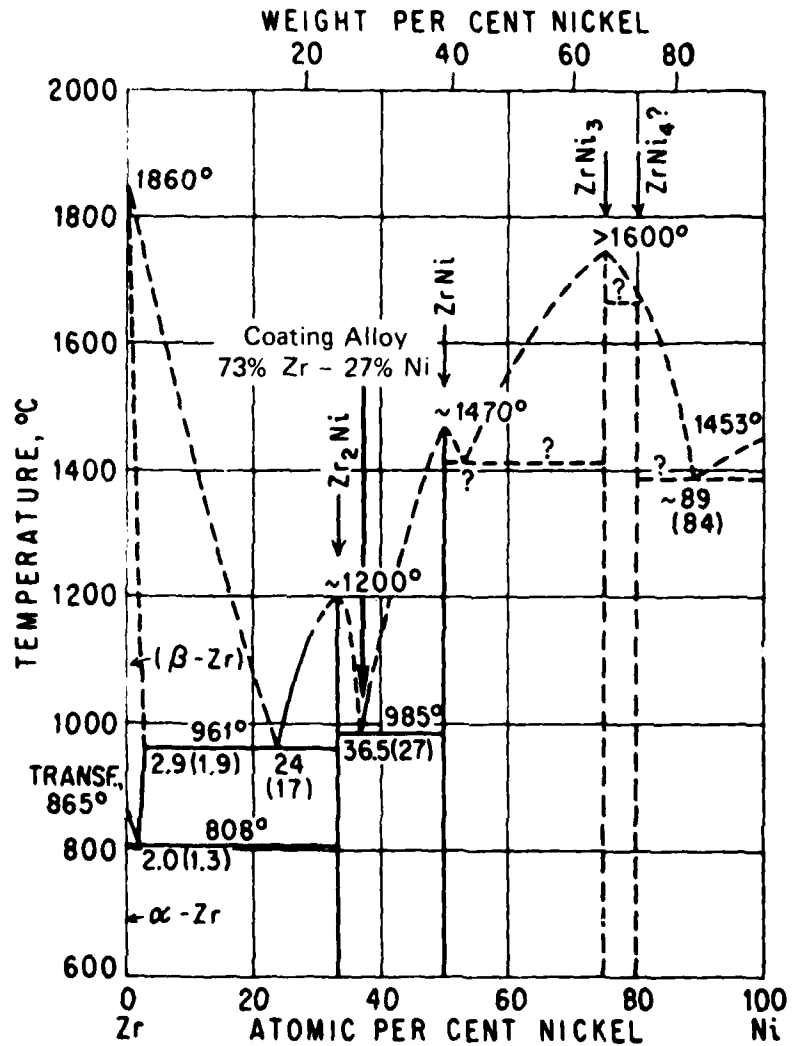
to the high melting point and consequently the high dipping temperature (>900°C), which led to a substantial diffusion of cerium into the base substrate. Attempts to improve the coating behavior by reducing the hot dipping and annealing temperatures were unsuccessful.

Zirconia-Based Coatings

We examined the concept of applying a ceramic thermal barrier coating by hot dipping an alloy substrate into a low melting eutectic, then selectively oxidizing the more active component, using the Zr-Ni system. This approach was taken for two reasons: (1) to determine whether dip coatings could be made successfully in another system and (2) to obtain information on coating formation and growth under different conditions in order to understand the difficulties with the Ce-Ni system.

Figure 5 shows the binary phase diagram of the system Zr-Ni. The coating alloy composition is Zr-25.65%Ni-5%Y by weight. Yttrium was added to the Zr-Ni coating alloy, primarily to provide a dopant to stabilize ZrO_2 in the cubic structure during the selective oxidation stage and also because there is some evidence that yttrium improves the adherence of plasma-sprayed ZrO_2 coatings. The ratio of Zr to Ni in this alloy is 2.7, which is similar to that of the $NiZr_2$ -NiZr eutectic composition. The 5%Y does not significantly alter the melting temperature of the Zr-Ni eutectic. The substrates were dipped at 1027°C.

Two substrate alloys have been examined so far, MAR-M509 and Co-10%Cr-3%Y. The results obtained indicate that the ZrO_2 -based coatings applied by this technique are highly adherent, uniform, and have very low porosity. A major difference between the ZrO_2 -based coatings and CeO_2 -based coatings using the hot dip technique is that virtually no diffusion zone forms within the substrate alloy when the ZrO_2 -based coating is applied. The coating layer is established externally on top of the substrate surface; thus its composition is not significantly altered by the substrate constituents.



JA-350583-109

FIGURE 5 Zr-Ni PHASE DIAGRAM

Figure 6 shows the EDAX-concentration profiles of different elements within the Zr-rich layer after hot dipping the substrate alloy (Co-10%Cr-3%Y) in the coating alloy, followed by an annealing treatment. The coating layer is about 150-160 μm thick with a relatively thin ($\approx 20 \mu\text{m}$) diffusion zone. Note that Cr is virtually nonexistent within the coating layer and that a relatively small amount of Co diffuses from the substrate right through the coating to the external surface.

Selective oxidation was conducted at 1027°C in a gas mixture of hydrogen/water vapor/argon with an appropriate composition to provide an oxygen partial pressure of about 10^{-17} atm. At this pressure, both nickel and cobalt are thermodynamically stable in the metallic form. The scale produced by this process consists of an outer oxide layer about 40 μm thick and an inner subscale composite layer of about 120 μm thick. The outer layer contains only ZrO_2 and Y_2O_3 . The subscale also consists of a $\text{ZrO}_2/\text{Y}_2\text{O}_3$ matrix, but contains a large number of finely dispersed metallic particles, essentially nickel and cobalt as shown in Figure 7.

Although nickel and cobalt were present uniformly within the outer region of the metallic coating after hot dipping and annealing and before the conversion of Zr and Y into oxides (Figure 6), they were virtually absent from this same region after the selective oxidation treatment (Figure 7). X-ray diffraction analysis of the surface of the sample shown in Figure 7 indicated that this outer oxide layer is formed exclusively of a mixture of monoclinic zirconia and yttria. It is evident that the final distribution of elements across the duplex coating layer and the subsequent oxide morphology are determined largely by the conditions of the final selective oxidation treatment.

The coated sample shown in Figure 7 was selectively oxidized at 1027°C, which is slightly above the melting temperature of the coating. We believe that oxidation proceeds as follows. The melt composition at the sample surface before the selective oxidation treatment consists largely of Zr, Ni, smaller concentrations of Y and Co, and a trace of Cr. Once oxygen is admitted at $P_{\text{O}_2} \approx 10^{-17}$ atm, Zr and Y atoms diffuse

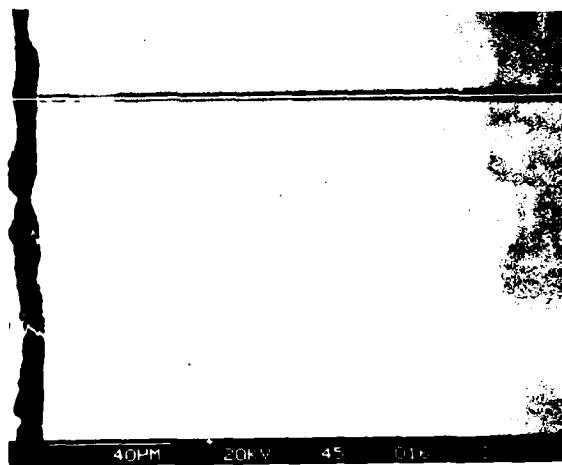
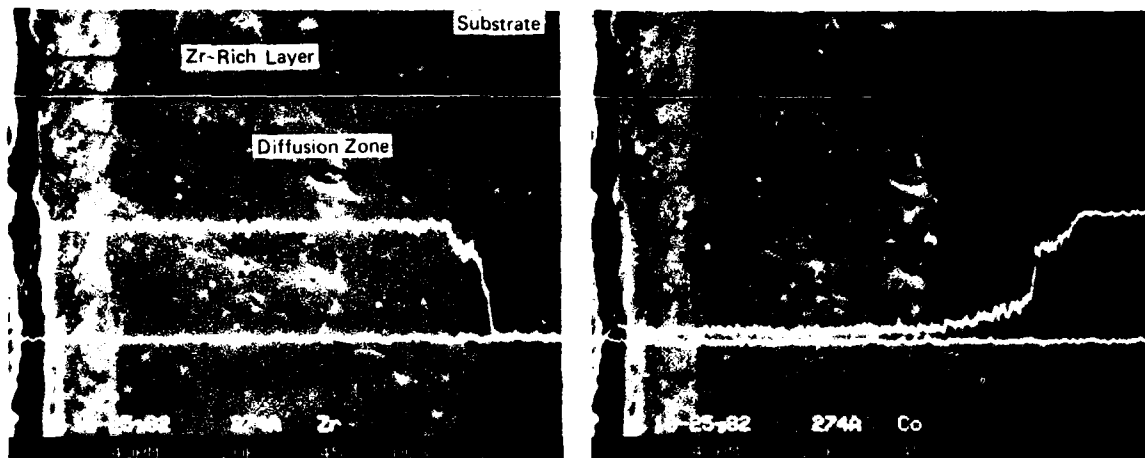


FIGURE 6 ELEMENTAL DISTRIBUTION ACROSS
 A COATED Co-10%Cr-3%Y
 SUBSTRATE FOLLOWING HOT
 DIPPING AND ANNEALING



JP-350683-110

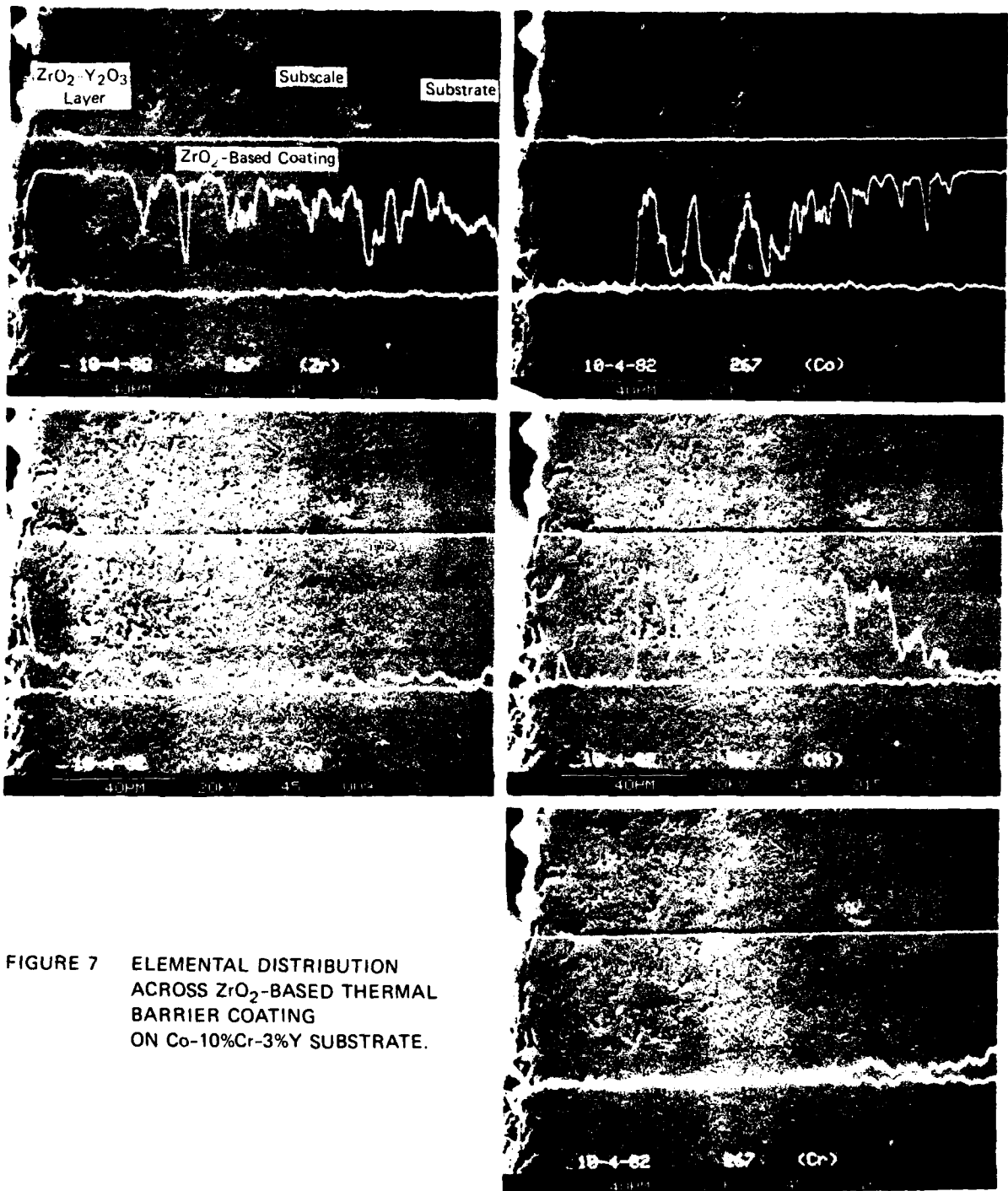


FIGURE 7 ELEMENTAL DISTRIBUTION
ACROSS ZrO_2 -BASED THERMAL
BARRIER COATING
ON Co-10%Cr-3%Y SUBSTRATE.

JP-350583-111

rapidly in the melt toward the outer oxygen/metal interface to form a solid ZrO_2/Y_2O_3 mixture. The more noble elements (Ni and Co) are then excluded from the melt and accumulate on the metal side of the interface. The depletion of Zr from this melt increases the nickel content of the alloy and renders it more refractory. Once the coating alloy solidifies, atoms of all elements in the remaining metallic part of the coating become less mobile than in the molten state, and further oxidation proceeds as a solid state reaction. The continued growth of the ZrO_2/Y_2O_3 layer promotes a counter-current solid state diffusion process in the metal side of the interface in which Zr and Y diffuse toward the interface, while nickel and cobalt diffuse away from the interface.

The profile presented in Figure 7 indicates that, under the external ZrO_2/Y_2O_3 layer, nickel and cobalt exist as small particles embedded in the subscale composite layer. The reason for their existence in such a distribution within a matrix of the ZrO_2/Y_2O_3 subscale is not well understood. It should be emphasized that the weight fraction of nickel present in the coating layer, before oxidation, amounts to about 25%, which corresponds to about 20% in volume fraction. This amount will increase in the subscale after the exclusion of nickel from the outer ZrO_2/Y_2O_3 external scale during selective oxidation. This substantial amount of nickel, added to cobalt diffusing from the substrate, is expected to remain trapped in the subscale layer of the coating during the completion of selective oxidation of Zr and Y.

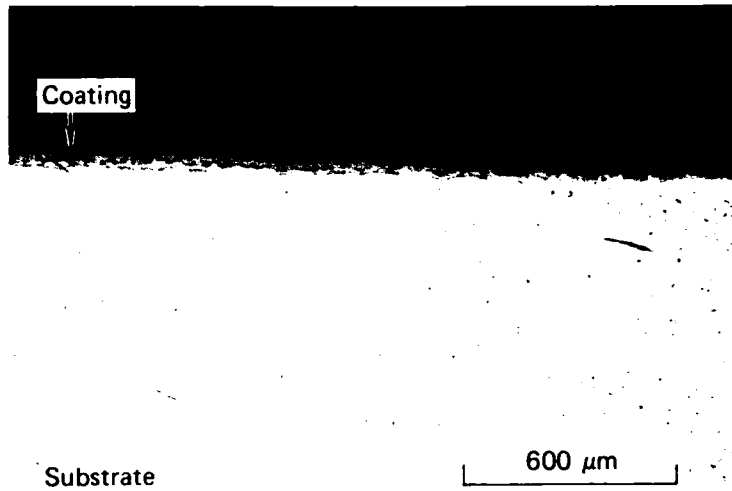
The configuration and distribution of nickel and cobalt within this zone is likely to be determined by the mechanism of oxidation of Zr and Y within the subscale zone. At least two possibilities exist:

- (1) The concentration of nickel and cobalt in the metal ahead of the interface becomes very high as a result of their exclusion from the ZrO_2/Y_2O_3 scale initially formed from the melt. Some back-diffusion of both elements in the solid state is likely to continue during further exposure, but the remaining portion of both elements may be overrun by the advancing oxide/metal interface.

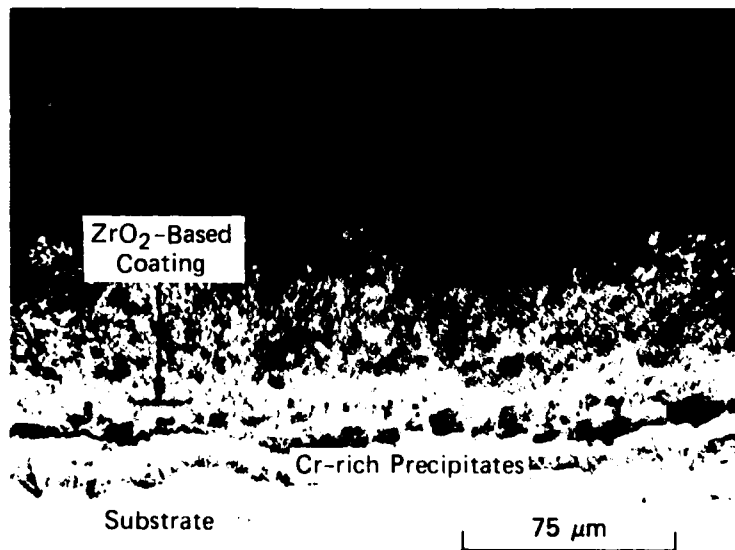
(2) A transition from internal to external oxidation occurs, as originally proposed by Wagner.⁹ After the initial formation of a ZrO_2/Y_2O_3 layer at the surface, ZrO_2 internal oxide particles may form ahead of the interface when the concentration of dissolved oxygen and zirconium exceeds the solubility product necessary for their nucleation. Then, these particles may partially block further Zr-O reaction because the diffusion of oxygen atoms to the reaction front (of internal oxidation) can occur only in the channels between the particles that were precipitated previously. Further reaction at the reaction front may occur either by sideways growth of the existing particles, which requires a very small supersaturation, or by nucleation of a new particle. The sideways growth of the particles can thus lead to a compact oxide layer, which can entrap metallic constituents existing within the same region.

In general, regardless of the mechanism involved in determining the morphology and distribution of the metallic particles within the subscale zone, the formation of such a ceramic/metallic composite layer between the outer ceramic layer and the inner metallic substrate is highly advantageous. This composite layer reduces the stresses generated from the mismatch in coefficients of thermal expansion of the outer ceramic coating and the inner metallic substrate.

Coating adhesion was evaluated by exposing of several test specimens to 10 thermal cycles between 1000°C and ambient temperature in air. The ZrO_2/Y_2O_3 coating on the alloy Co-10%Cr-3%Y remained completely adherent and showed no sign of spallation or cracking. Figure 8 shows a cross section of one of these surfaces after this test. The scale is completely pore-free. Careful metallurgical examination along the whole length of the specimen did not reveal any sign of cracking. Furthermore, microprobe analyses across this section showed that the distributions of Zr, Y, Ni, Co, and Cr are essentially the same as those samples that had not been cycled. Thus the elemental profiles in the thermally cycled samples are



(a)



(b)

JP-350583-112

FIGURE 8 MICROSTRUCTURE OF A THERMALLY CYCLED
Co-10%Cr-3%Y SUBSTRATE COATED
WITH ZrO₂/Y₂O₃ (a) X50 (b) X400

typified by those shown in Figure 7. The successful cycling of the coated Co-10%r-3%Y alloy is an important result because it is the first demonstration that the dip process can produce coating of high integrity.

A similar ZrO_2/Y_2O_3 coating applied to MAR-M509 spalled after the second cycle from 1000°C. The different behavior of the two coated alloys can be related to their compositions. It has been established that yttrium in the substrate increases the adhesion of plasma sprayed ZrO_2 ⁴ and the adhesion of oxides that grow by inward diffusion of oxygen, such as Al_2O_3 .¹⁰ Our results support this view, and it would be very valuable to determine the levels of yttrium in other substrate alloys that would improve the durability of thermal barriers produced by dip coating. These results also suggest that yttrium in the coating has little effect on bonding, probably because it is converted to yttria and is not located near the substrate interface.

X-ray analysis of the coating surface indicates the presence of monoclinic ZrO_2 and Y_2O_3 . It is likely that the selective oxidation temperature and the thermal cycling conditions are insufficient to allow the formation of Y_2O_3 -stabilized cubic zirconia. However, the phase diagram of the $Y_2O_3-ZrO_2$ system suggests that higher Y_2O_3 contents will cause the formation of cubic zirconia below 1200°C, which is a desirable working temperature for superalloys coated with thermal barriers.

SUMMARY AND CONCLUSIONS

SRI has developed a new concept for applying oxide thermal barrier coatings on high temperature alloys. Thin metal layers are produced by dipping superalloy substrates in low-melting point alloys in the Ce-Ni and Zr-Ni systems. The thermal barrier coating is formed by selectively oxidizing the reactive metal in the thin layer. The coating consists of a uniform external oxide layer and an inner composite oxide/metal layer.

The most important conclusion from the work so far is that dense adherent ZrO_2 thermal barrier coatings can be successfully applied on gas turbine alloys by the hot dip process. These coatings were undamaged in limited thermal cycling tests. The high density of the outer oxide layer results from the growth conditions in which the temperature and the partial pressure of oxygen are carefully controlled. The good adhesion is probably related to several factors. These include the very strong bond between the dipped metallic layer and the substrate (before the oxidation treatment) and the controlled growth conditions of the ZrO_2 that allow near-equilibrium conditions to be reached in the layers. Similarity of expansion coefficients between the layer and substrate and the presence of yttrium in the most successful substrate also contributes to the strong bond.

Samples of Co-10Cr-3Y coated with ZrO_2 by the dip process withstood 10 thermal cycles in air between room temperature and $1000^\circ C$. Further testing was limited by contract time and funds. However the test was entirely successful and there was no microstructural evidence for any degradation of the thermal barrier. Unlike the ZrO_2 -based coatings, the CeO_2 -based coatings exhibited poor resistance to oxidation and thermal cycling in similar tests. The inferior properties of CeO_2 barriers are associated with the incorporation of Ni and Co in the external oxide layer of the thermal barrier. These metallic elements oxidize during thermal cycling in air causing rupture of the coating. The ZrO_2 layers do not contain Ni and Co because the slower rate of growth of ZrO_2 compared to

CeO₂, allows sufficient time for the metallic elements to diffuse ahead of the growing oxide front. Efforts to reduce the growth rate of CeO₂ were unsuccessful.

The combined information from the work on the Ce-Ni and Zr-Ni-systems has given a reasonable understanding of the kinetics and method of formation of thermal barrier layers by selective oxidation of reactive metals. The dip process offers a better alternative to plasma sprayed ZrO₂ for the following reasons:

- (1) It produces an adherent duplex coating of an outer ZrO₂/Y₂O₃ dense layer over a composite ceramic/metal subscale. The latter layer should have a thermal expansion coefficient intermediate between the outer ceramic and the inner superalloy substrate.
- (2) The outer ZrO₂/Y₂O₃ layer has very low porosity. The low porosity is critically important in preventing the permeation of oxidants or molten salt contaminants (particularly sodium sulfate, present in gas turbine environments) through the coating. Therefore, these coatings can be expected to prevent catastrophic hot corrosion of the underlying metal components.
- (3) Hot dipping is not limited to line-of-sight and therefore offers the capability of coating reentrant shapes.

The information generated from this study forms the basis to develop this coating method into a practical commercial process.

RECOMMENDATIONS FOR FUTURE DEVELOPMENT

This program has established a new method of making thermal barrier coatings by selectively oxidizing a reactive metal contained in a thin layer on a superalloy. The process offers significant advantages over plasma spraying. The thrust of future work should be to develop the procedures for coating simulated components and to evaluate these components under realistic operating conditions. This development program would provide the technology for a future commercial process for coating gas turbine components.

Important tasks to be addressed include:

- (1) Define the conditions for producing dense stabilized zirconia coatings on selected superalloys.
- (2) Extend the thermal cycling tests to longer times and temperatures up to 1200°C.
- (3) Determine the effectiveness of the new thermal barriers in insulating cooled simulated components.
- (4) Evaluate coating durability in aggressive environments.
- (5) Investigate the parameters to scale up the dip process to apply stabilized zirconia thermal barriers to larger components.

REFERENCES

1. Metals and Ceramics Information Center, Engineering Property Data on Selected Ceramics, 3, Single Oxide, Rep. MCIC-HB-07, (July 1981).
2. F. J. Clauss, ed, Engineer's Guide to High-Temperature Materials, Series in Metallurgy and Materials Science, (Addison-Wesley, Reading, MA, 1969), p.221.
3. E. C. Subbarao, ed., Solid Electrolytes and Their Applications, (Plenum Press, New York, 1980), p. 270.
4. S. Stecura, Am. Ceram. Soc. Bull., 56 (12), 1081 (1977).
5. I. M. Allam, R. W. Bartlett, and G. N. Krishnan, "Dip Process Thermal-Barrier Coatings for Superalloys," SRI Final Report PYU 8658, AFOSR Contract No. F49620-79-C-0225 (1980).
6. I. M. Allam and D. J. Rowcliffe, "Dip Process Thermal Barrier Coating for Superalloys," SRI Report PYU 2509, AFOSR Contract No. F49620-81-K-0009 (1981).
7. I. M. Allam and D. J. Rowcliffe, Thin Solid Films, 100 (1), 25 (1983).
8. M. Hansen, Constitution of Binary Alloys, 2nd edition, (McGraw-Hill, New York, 1950).
9. R. A. Rapp, Corrosion, 21, 382 (1965).
10. I. M. Allam, D. P. Whittle, and J. Stringer, Oxidation of Metals 12 (1), 35 (1978).

PUBLICATIONS, PRESENTATIONS, AND PATENTS

1. I. M. Allam, "Dip Process Thermal Barrier Coating for Superalloys," paper presented at Bay Area High Temperature Corrosion meetings, organized by Professor D. P. Whittle at Lawrence Berkeley Laboratory, University of California, Berkeley (December 1, 1981).
2. I. M. Allam and D. J. Rowcliffe, "A Dip Process For Thermal Barrier Coating on Superalloys," presented at The International Conference on Metallurgical Coatings and Process Technology, held April 9, 1982, San Diego, California; Thin Solid Films, 100 (1), 25 (1983).
3. P. J. Jorgensen and R. W. Bartlett, "Process for Applying Thermal Barrier Coating to Metals and Resulting Products," U.S. Patent Application 325,504 (November 27, 1981).
4. I. M. Allam and D. J. Rowcliffe, "Development of Zirconia Thermal Barrier Coating from Zr-Ni Eutectics," Invention Disclosure, SRI-Docket No. P-1752.
5. I. M. Allam and D. J. Rowcliffe, "Zirconia Thermal Barriers Produced by Dip-Coating," to be presented at American Ceramic Society Meeting, Chicago, April 1983.
6. I. M. Allam and D. J. Rowcliffe, "Structure and Properties of Thermal Barriers Grown by Selective Oxidation," to be submitted to Journal of the American Ceramic Society, 1983.

DISTRIBUTION LIST Materials

AFOSR/NE
Dr A.H. Rosenstein
Bolling AFB Washington DC 20332

1 Copy Each:

AFWAL/MLLM
Attn: H. Graham
Wright-Patterson AFB OH 45433

AFWAL/MLLM
Attn: N. Geyer
Wright-Patterson AFB OH 45433

AFWAL/MLLN
Attn: Branch Chief
Wright-Patterson AFB OH 45433

AFWAL/MLB:1
Attn: Branch Chief
Wright-Patterson AFB OH 45433

AFWAL/MLPJ
Attn: Branch Chief
Wright-Patterson AFB OH 45433

DARPA
Attn: Lt Col Jacobson
1400 Wilson Blvd
Arlington VA 20339

Office of Naval Research
Attn: Dr R. Pohanka
800 N. Quincy St.
Arlington VA 22203

U.S. Naval Air Systems Command
Attn: Mr. I Machlin (AIR 52031B)
Washington DC 20360

NASA-Lewis
Attn: H.B. Probst (Stop 49-3)
21000 Brookpark Rd
Cleveland OH 44135

National Bureau of Standards
Attn: S.M. Wiederhorn
Washington DC 20234

Materials Research Lab(AMMRC)
Attn: Dr R.N. Katz
Watertown MA 02172

16 Annual Tech Reports
16 Final Tech Report (1 Draft)
6 Reprints of Each Publication

AFWAL/MLLS
Attn: Branch Chief
Wright-Patterson AFB OH 45433

AFWAL/MLLM
Attn: B. Ruh
Wright-Patterson AFB OH 45433

AFWAL/MLBP
Attn: Branch Chief
Wright-Patterson AFB OH 45433

AFWAL/MLLP
Attn: Branch Chief
Wright-Patterson AFB OH 45433

AFWAL/MLPO
Attn: Branch Chief
Wright-Patterson AFB OH 45433

D.O.E(Material Sciences)
Attn: R.J. Gottschall
Office of Energy Research
Washington DC 20545

U.S. Army Research Office
Metallurgy and Materials Sciences
P.O. Box 12211
Research Triangle Park NC 27709

U.S. Naval Research Laboratory
Attn: Dr. R.W. Rice, Chem Div (6360)
Washington DC 20375

J.A.Carpenter Jr
Oak Ridge National Lab
Oak Ridge TN 37830

N.S.F. (Materials Research)
Attn: B.A. Wilcox
1800 G Street, N.W.
Washington DC 20550

DOE Fossil Energy Div
Dr S.R. Skaggs
FE-3/C-156 Germantown
Washington DC 20544

Dr F.F. Lange
Rockwell International Science Center
Thousand Oaks CA 91360r)

Dr A.H. Heuer
Dept of Material Science
Case Western Reserve University
Cleveland OH 43201

Dr G.H. Meier
Dr F.S. Pettit
Metallurgical and Materials Engineering
University of Pittsburgh
Pittsburgh PA 15261

Dr L. Kaufman
Manlabs, Inc
21 Erie St
Cambridge MA 02139

Dr Roger R. Wills
Section Manager, Ceramics and
Materials Processing Section
Battelle Columbus Labs
Columbus OH 43201

LME

— 8