PNL-SA-7888
CONF-790749--3

MASTER

DEVELOPMENT OF GRADED COMPOSITION CoCrAlY (+ Pt) SPUTTERED COATINGS*

J.W. Patten, R.W. Moss, D.D. Hays
Pacific Northwest Laboratory**
Richland, Washington 99352

and

J.W. Fairbanks
US Department of Energy
Division of Fossil Fuel Utilization
Washington, DC 20545

Progress is reported in the development of sputter deposited CoCrAlY-type coatings with Cr and Al concentration gradients through the coating thickness. The objective is to investigate the potential of high Cr coating surface compositions, gradients in Cr and Al composition, and Pt underlayers or graded Pt additions for significantly enhancing lifetimes of gas turbine engines operating on coal-derived liquid (and other alternative) fuels. Sputter coated burner rig test pins representing 15 different combinations of processing variables (including preoxidation heat treatment) sputter coated gas turbine first-stage blades with three different heat treatments, and several sputter coated fluidized bed turbine vanes are discussed along with testing status of these components.

*This research is supported by US Department of Energy, under Contract EY-76-C-06-1830.
**Operated by Battelle Memorial Institute.

DISCLAIMER

INTRODUCTION

Gas turbine hot-section vanes and blades operating with current light distillate fuels are often life-limited by hot corrosion effects (oxidation/sulfidation), particularly in the presence of fuel or air contaminants such as sulfur and vanadium.[1] The severity of these effects is multiplied by the use of more plentiful residual fuels and may be drastically increased by the use of minimally processed coal-derived liquid fuels. The plentiful supply of coal in the continental United States balanced against decreasing reliability and increasing expense of petroleum fuel sources further emphasizes the need to develop coating systems capable of withstanding long-term use of minimally processed coal-derived fuels and other potentially dirty fuels. Currently it is not technically feasible to use ceramic materials for airfoils,[2-4] and although ceramic coatings for airfoils hold great potential,[5-18] development of these coatings to the production stage is a long-term effort. Because of this, it is necessary to aggressively pursue improvements in existing protective coatings in order to permit expanded near-term use of residual fuel. Presently, the state-of-the-art production coatings for protection of gas turbine hot section vanes and blades from hot corrosion are variations of MCrAlY (frequently CoCrAlY) compositions, with extensive research efforts historically being concentrated on electron beam physical vapor deposited (PVD) coatings.[1,19-22] Therefore it is important to ensure that metallic coating development parallels the development of coal-derived liquid fuels to provide acceptable engine life.

For the past four years the compositions developed with the PVD process have been deposited by high-rate sputtering at the Pacific Northwest Laboratory (PNL). The coatings were well bonded to the substrates (burner rig pins and gas turbine airfoils) and were very fine grained with uniform thickness and very uniform microscopic composition distribution.[23-25] Engine testing and burner rig testing of these coatings has shown them to be superior in performance to all but one or two of the most advanced PVD coatings, and quite comparable to these other one or two "best" coatings. Significantly, this performance has been obtained on the first test specimens with PNL sputtered coatings, with no effort being devoted towards optimization of composition or coating design from the standpoint of the unique advantages of PNL sputter-deposition equipment and techniques.

Recent experimental evidence indicates that the following effects may influence MCrAlY coating performance and, therefore, component durability:

1) Chromium content and Cr/Al proportion at the coating surface -- A chrome oxide scale may provide early protection with an aluminum oxide scale gradually replacing the chrome oxide with increasing time. This effect may be more pronounced at lower service temperatures. If so, then optimum Cr content and Cr/Al proportion at the coating surface would be expected to depend on temperature, hot corrosion environment, erosion, distribution of Cr and Al in the coating (graded through thickness or degree of local segregation), and grain size of coatings (grain boundary area available for diffusion).

2) Aluminum gradient to coating surface -- The supply of Al available for oxide scale formation at the coating-flame surface could be influenced by an Al concentration gradient through the coating thickness with increasing Al concentration towards the substrate. In this manner, an initially low Al-high Cr surface could be provided that would increase in Al content with service time.

3) Aluminum content at the coating substrate interface -- This could influence both Al diffusion towards the coating surface, as above, and Al diffusion into the substrate, which would reduce Al available for oxide-scale formation and might also produce diffusion voids (Kirkendall effect) in some alloys. Further, Al content would be expected to influence coating ductility and thermal expansion compatibility (possible spalling) at the coating-substrate interface.

4) Platinum content -- Pt additions at the coating-substrate interface have been shown to be effective in increasing coating durability, possibly by restricting loss of Al in the coating (diffusion into substrate) through formation of platinum aluminides. However, data have also been obtained to indicate that the presence of Pt at the coating surface may decrease coating durability. Therefore, the optimum Pt content and distribution (concentration gradient through coating thickness) would be expected to depend on composition of the MCrAlY coating (Cr and Al distributions), coating microstructure and thickness, service temperature, hot corrosion environment, erosion, substrate chemistry, effect on coating ductility and thermal expansion compatability at the coating-substrate interface, etc.

High-rate triode sputter deposition techniques developed at PNL in earlier Navy-funded marine gas turbine component coating research are being used to produce defect-free, fine-grained, uniform composition (free of segregation) sputtered coatings for evaluation of these chemistry-related effects independent of interference from effects of segregation, leaders, etc.

MATERIALS AND PROCEDURES

The sputter deposition equipment and procedures used for the current research have been described elsewhere.[23] In general, CoCrAlY compositions and composition gradients were produced with independent opposed flat plate CoCrAlY and Cr targets. Pt deposits were produced between two concentric cylindrical Pt targets.

RESULTS AND DISCUSSION

A summary of sputter deposition experiments is included in Tables I and II. From these experiments, a total of 150 specimens are currently available for burner rig, engine or miscellaneous testing, overcoating with additional CoCrAlY layers, and metallographic evaluation. Of these, 39 are either ready for burner rig or engine testing or are currently being tested. Nine more were delivered to another contractor for additional coating.

The specimens available are discussed in four categories below:

1. IN-792 Pins (1/8" dia. x 1-1/2" long), sputter coating completed for burner rig testing.

   Thirty-two of these pins coated by PNL are available for burner rig testing. These pins represent 15 different combinations of composition and processing variables (i.e. Cr content and gradient in CoCrAlY, Pt underlayer or not and whether or not a "preoxidation" heat treatment was used). A total of 17 metallographic samples that represent most of the process variable combinations were evaluated at PNL. Figure 1 shows a graded CoCrAlY coating deposited over a sputtered Pt layer. Cr varies from 24.1% at the Pt layer to 32.6% at the surface. Al varies from 9.8% at the Pt layer to 8.4% at the surface. Figure 1 compares structure of the as-sputtered material to that heat treated for four hours at 1080°C in a vacuum and heat treated first for four hours at 1080°C in a vacuum, then for one hour at 1080°C in still air. Figure 2 shows a CoCrAlY coating (with no Pt underlayer) with a uniform composition of approximately 32.6% Cr and 9.38% Al.

2. Pins (1/8" dia. x 1-1/2" long), additional coating required.

   A total of 68 MAR-M509, IN-792, and X-40 pins were coated either with 0.0002 in. or 0.0005 in. of Pt at PNL in preparation for CoCrAlY overcoating. In addition three Pt-coated pins and two bare pins were sent to Airco Temescal for PVD CoCrAlY overcoating to provide control specimens for burner rig testing. Metallography representative of these coatings has been published elsewhere.[23,26]

3. Rolls Royce Blades, delivered for engine test

   Six Rolls Royce blades were coated with 0.0002 in. of Pt at PNL. Four of these were then overcoated with CoCrAlY with a high Cr content and a small Cr gradient and are scheduled for engine test using home heating fuel. Three different heat treatments were given to these blades. Two metallographic specimens were taken to characterize composition and structure of the deposit on these blades. Figure 3 shows the sputtered coating on a typical tip shield (used to mask a mounting surface from coating) after heat treatment for four hours at 1080°C in vacuum.

4. General Electric Vanes, disposition pending

Seventeen General Electric vanes were coated with Pt at PNL. Six of these vanes were shipped to Airco Temescal for PVD coating with CoCrAlY. Another four vanes were sputter coated with CoCrAlY at PNL. During metallographic examination of one of these samples extensive contamination (nonmetallic casting debris) was found on the surface of the vane. General Electric was provided with metallographic and chemical analysis of the surface contamination as well as composition and structure of the CoCrAlY deposit. Three metallographic samples representing three different heat treatments were used to characterize this material. Figure 4 illustrates typical coating structure and nonmetallic contamination (casting debris) at the airfoil-coating interface.

The pins listed in Table III were set aside for burner rig testing with conventional petroleum distillate fuels at Annapolis, NSRDC. Most of the other pins will be burner rig tested at the Cranfield Institute with coal-derived liquid fuel. Results of both series of tests are expected to be complete in approximately six months. Because duplicate coatings will be tested in petroleum and coal-derived fuels and because a wide variety of coatings including conventional PVD coatings will be examined, data will be obtained on the effects of coal-derived fuels relative to petroleum fuels and the relative durability of several advanced coating designs (composition and composition gradient effects) with both types of fuels.

CONCLUSIONS

Sputtered CoCrAlY coatings with various Cr and Al contents and Cr/Al proportions at the coating surface, concentration gradients through the coating thickness, and Pt additions have been produced on burner rig test pins and gas turbine airfoils. All coatings are free of growth defects, fine-grained, free of segregation, and well bonded to their substrates. Testing scheduled and in progress on these coatings with both coal-derived liquid fuels and petroleum fuels is expected to identify coating designs with promise for increasing durability of engine hot sections operated on aggressive fuels.

Special thanks are due to R.F. Stratton for sputter deposition. R.H. Beauchamp for optical metallography, and H.E. Kjarmo for x-ray fluorescence analysis.

TABLE I. CoCrAlY Sputter Deposition Experiments

Run No.	Substrate Alloy/ Substrate Type	Voltage on CR Target	Samples w/ Pt Underlayer	Pt Thickness (mils)	Samples w/o Pt Underlayer	CoCrAlY Thickness (mils)	Thermal Treatment of Pins	Metallography Samples	Deposit Composition(1)
4	IN738/GE Vanes	50' @ 500, 600, 700 V 70' 800V	3	0.2	--	3	Vac Ht 4 hrs @ 1080 + 1 hr air @ 1050°C	3	Cr: 23.8-25% Al: 12.8-13.5%
5	IN792/Pins	50' @ 500, 600, 700V 5' @ 800 V	2	0.2	2	~ 4.6	Vac Ht 4 hrs @ 1080°C	None	Cr: 25-30% (estimated)
6	IN792/Pins	55' @ 500, 600, 700, 800 V	2	0.2	2	~ 5.5	Vac Ht 4 hrs @ 1080°C	None	Cr: 25-30% (estimated)
7	IN792/Pins	60' @ 600, 700, 800V 10' @ 900	1	0.2	1 1	4.2 4.2	Vac Ht 4 hrs @ 1080°C, Vac Ht 4 hrs @ 1080°C + 1 hr @ 1080°C Air	3	Cr: 24.1-32.6 Al: 9.8- 8.4
8	IN792/Pins	60' @ 600, 700, 800, 900, 1000V	1 1	0.2 0.2	1	7.0 7.0	Vac Ht 4 hrs @ 1080°C Vac Ht 4 hrs @ 1080°C + 1 hr @ 1080°C Air	3	Cr: 25.3-31.0%
9	MAR-M-509/Pins X-40/Pins	60' @ 600, 700, 800 900, 1000V	--	--	4	~ 7.0	None	None	Cr: 25-35% (estimated)
13	IN792/Pins	1000V	--	--	3	6.5	Vac Ht 4 hrs @ 1080°C	2	Cr: 32.6% Al: 9.4%
14	IN792/Pins	800V	--	--	3	6	Vac Ht 4 hrs @ 1080°C	2	Cr: 30.0% Al: 9.5%
17	IN792/Pins	60' @ 600V 5' @ 700V	3	0.2	4	1.4	Sputter etched after ni- triding @ 900°C during HT	3	Cr: 22.5% (estimated)
18	IN792/Pins	60' @ 600, 700, 800, 900, 1000V	3 1	0.2 0.2	-- --	7 7	Sputter etched after ni- triding @ 900°C during HT As nitrided	4	Cr: 32-33.5% Al: 9.3- 9.2%
19	IN738C/RR Blades	60' @ 600, 700, 800, 900V; 30' @ 1000V	2	0.2	--	~ 5.7	Sputter etched after ni- triding @ 900°C + 1 hr @ 1080°C in air	1	Cr: 43-48 (estimated) Al: 8- 7 (estimated)
21	IN738C/RR Blades	60' @ 600, 700, 800 900V; 30' @ 1000V	1 1	0.2 0.2	-- --	~ 5.7 ~ 5.7	Vac Ht 4 hrs @ 1080°C Vac Ht 4 hrs @ 1080°C + 1 hr @ 1080°C	1	Cr: 43-48 Al: 8- 7

(1) CoCrAlY composition from substrate to outer surface.

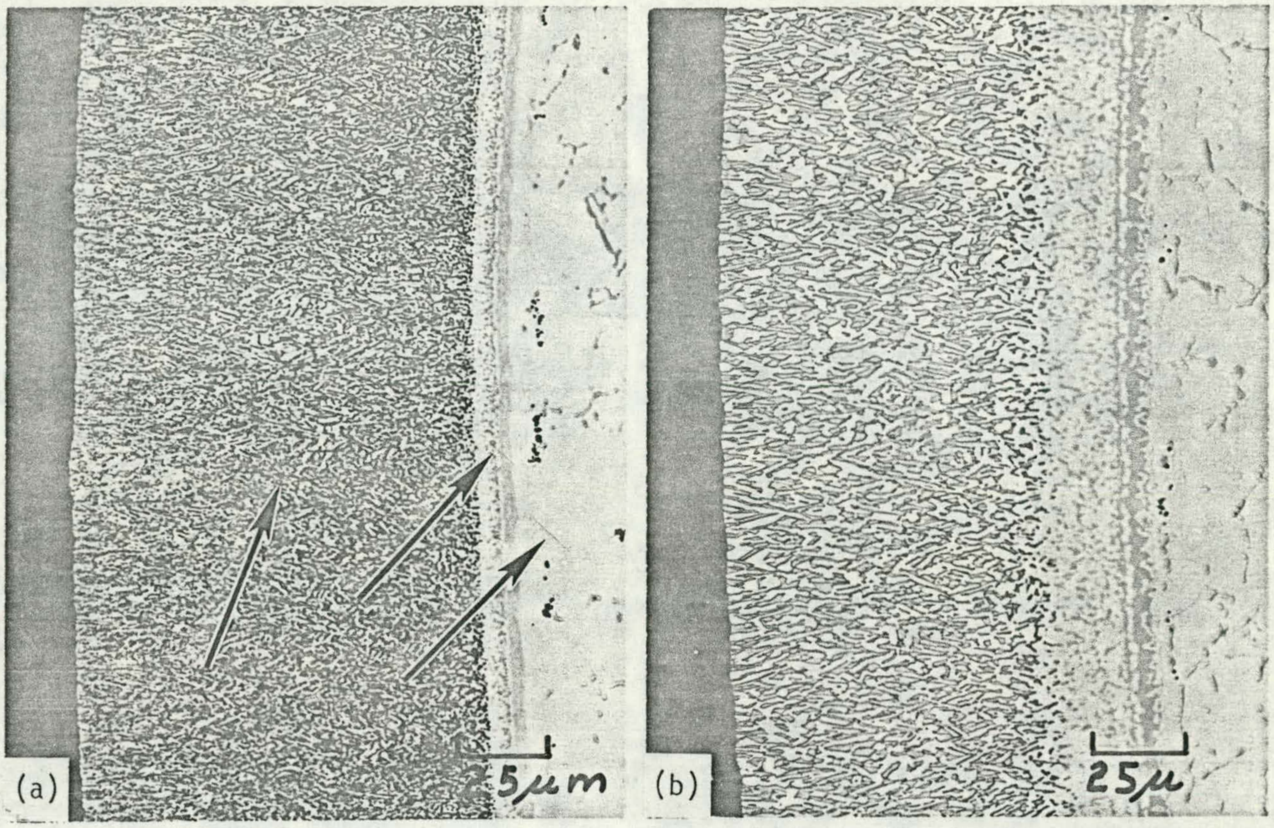
TABLE II. Platinum Sputter Deposition Experiments

Run No.	Samples Coated	Pt Thickness (mils)
1	18 GE Vanes	0.2
2	8 IN792 Pins 8 MAR-M-509 Pins 1 Nickel Pin	0.2
3	8 IN792 Pins 8 MAR-M-509 Pins 1 Nickel Pin	0.2
10	18 X-40 Pins	0.2
11	18 X-40 Pins	0.5
12	9 MAR-M-509 Pins 9 IN792 Pins	0.2 0.2
16	6 Rolls Royce Blades	0.2

TABLE III. 1/8" Diameter Pins for Burner Rig Testing at the Naval Ship R&D Center, Annapolis, MD

Run No.	Sample No.	Pin Alloy	Cr Target Voltage Ramp	Pt Underlayer Thickness (mils)	CoCrAlY Thickness (mils)	Thermal Treatment of Pins	Metallography Sample(1)	Deposit Composition(2)
5	2001	IN 792	50' @ 500, 600, 700 V, 5' @ 800 V	0.2	~ 4.6	Vac HT 4 hrs @ 1080°C	None	Cr: 25-30% (est)
	2018	"	" " " " " " " " " "	0	"	" " " " " "	"	" " "
6	2003	IN 792	55' @ 500, 600, 700, 800 V	0.2	~ 5.5	Vac HT 4 hrs @ 1080°C	None	Cr: 25-30% (est)
	2020	"	" " " " " " " "	0	"	" " " " " "	"	" " "
9	1037	X-40	60' @ 600, 700, 800, 900, 1000 V	0	~ 7.0	None (as-deposited)	None	Cr: 25-35% (est)
	5027	Mar-M-509	" " " " " " " "	"	"	" "	"	" " "
13	2027	IN 792	1000V	0	6.5	Vac HT 4 hrs @ 1080°C	2026B	Cr: 32.6% Al: 9.4%
14	2031	IN 792	800 V	0	6	Vac HT 4 hrs @ 1080°C	2030B	Cr: 30% Al: 9.5%
17	2051	IN 792	60' @ 600 V, 5' @ 700 V	0.2	1.4	Sputter etched after nitriding @ 900°C during HT	2034NE	Cr: 22.5% (est)
	2035	"	" " " " " " " "	0	"	Ditto	"	" " "
18	2054	IN 792	60' @ 600, 700, 800, 900, 1000 V	0.2	7	Sputter etched after nitriding @ 900°C during HT	2055NE	Cr: 32-33.5% Al: 9.3-9.2%
-	2038(3)	IN 792	--	0			--	
-	2058(3)	"	--	0.2			--	

(1) Metallography sample has same thermal history as pins.
(2) CoCrAlY composition from substrate to outer surface.
(3) PVD coated with CoCrAlY by Airco-Temescal, Berkeley, CA.



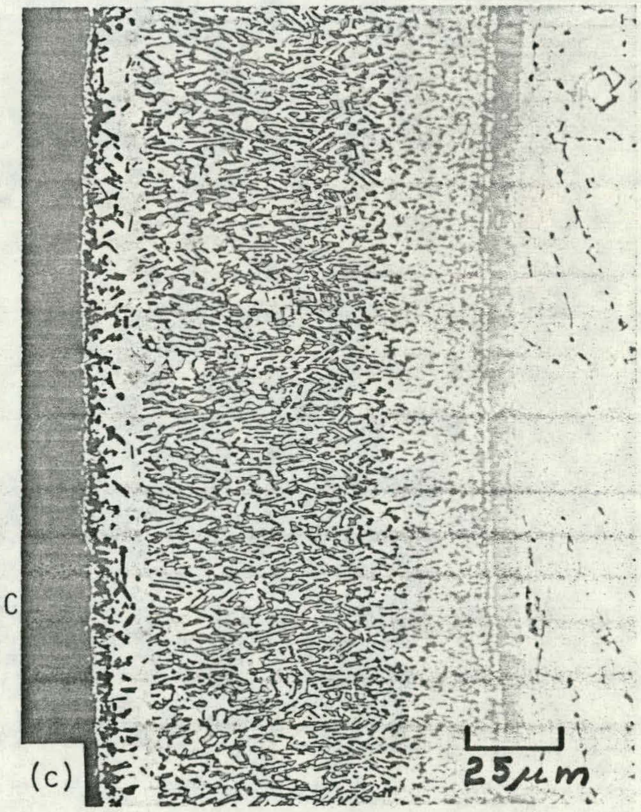


FIGURE 1
Graded CoCrAlY coating sputter deposited over sputter deposited Pt coating. (a) as-sputtered CoCrAlY (left arrow), Pt (center arrow), IN-792 pin substrate (right arrow); (b) heat treated four hours at 1080°C in vacuum; (c) heat treated four hours at 1080°C in vacuum then one hour at 1080°C in air, etched, 500x.

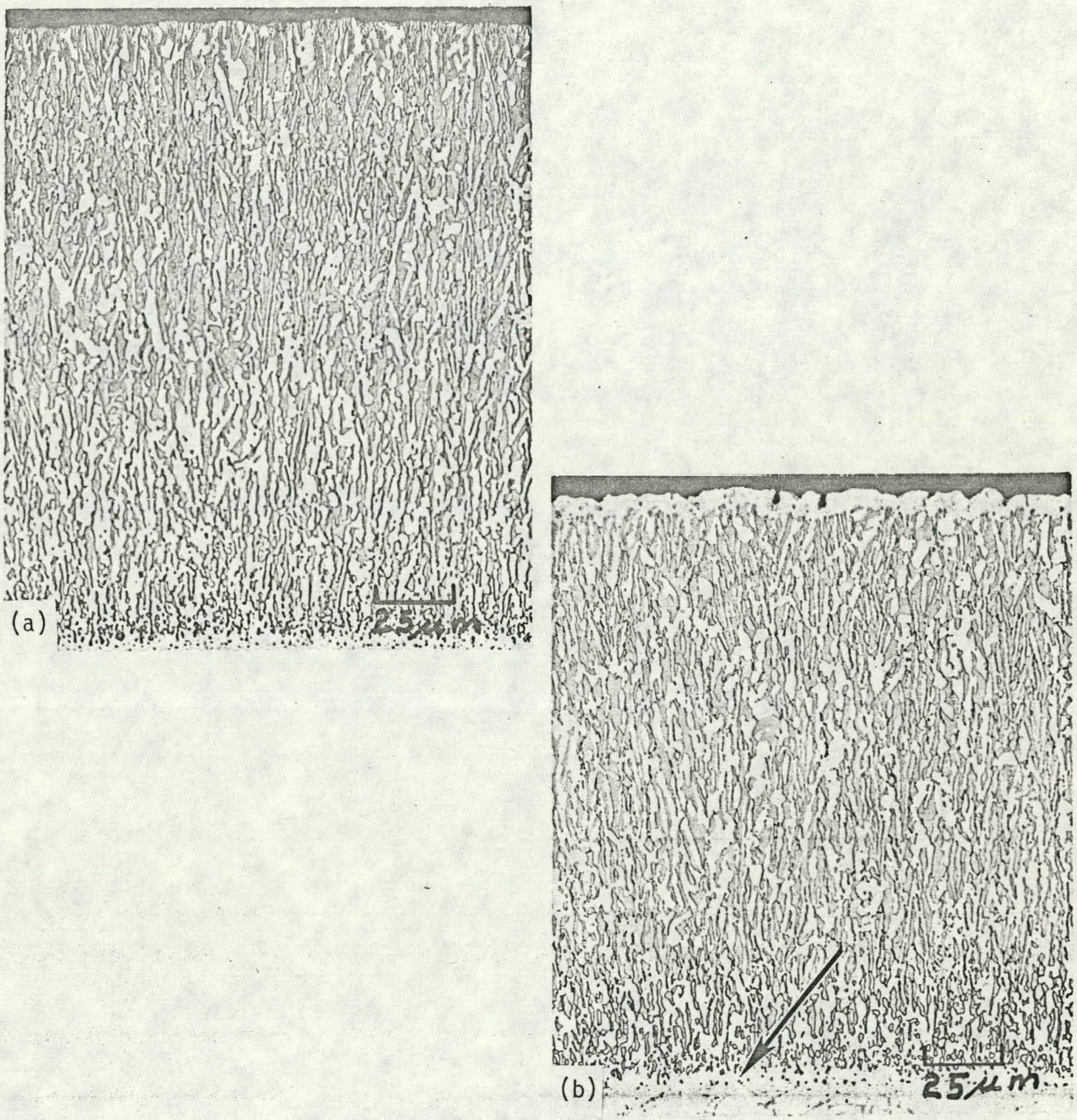


FIGURE 2

Constant composition (32.6% Cr) CoCrAlY sputter deposited coating on IN-792 pin substrate - (a) Heat treated four hours at 1080°C in vacuum; (b) heat treated four hours at 1080°C in vacuum then one hour at 1080°C in air, arrow indicates coating-pin interface, etched, 500x.

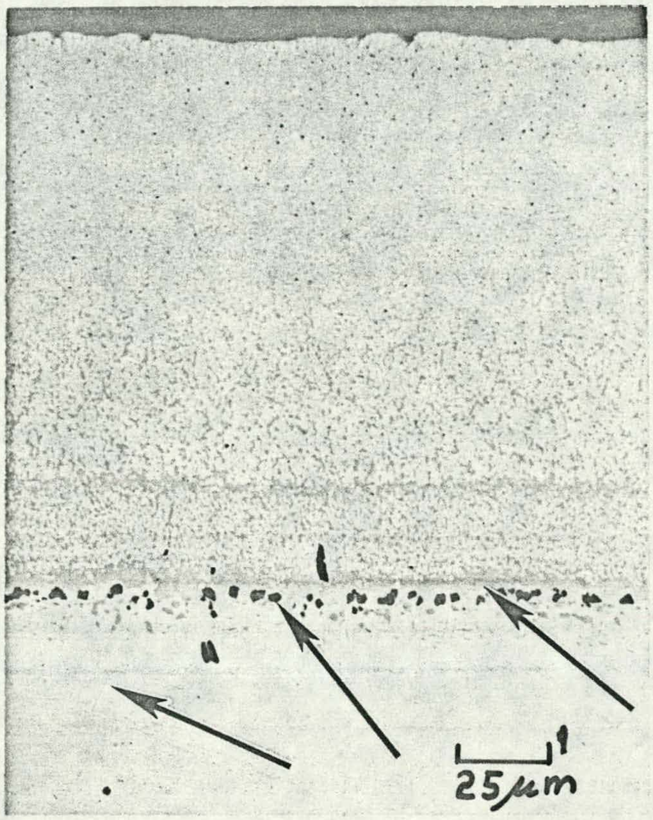


FIGURE 3
Sputtered graded composition CoCrAlY + Pt coating (right arrow) on tip shield of a Rolly Royce turbine blade (bottom arrow). Note non-metallic residue at the coating-blade interface (center arrow), as-polished, 500x.

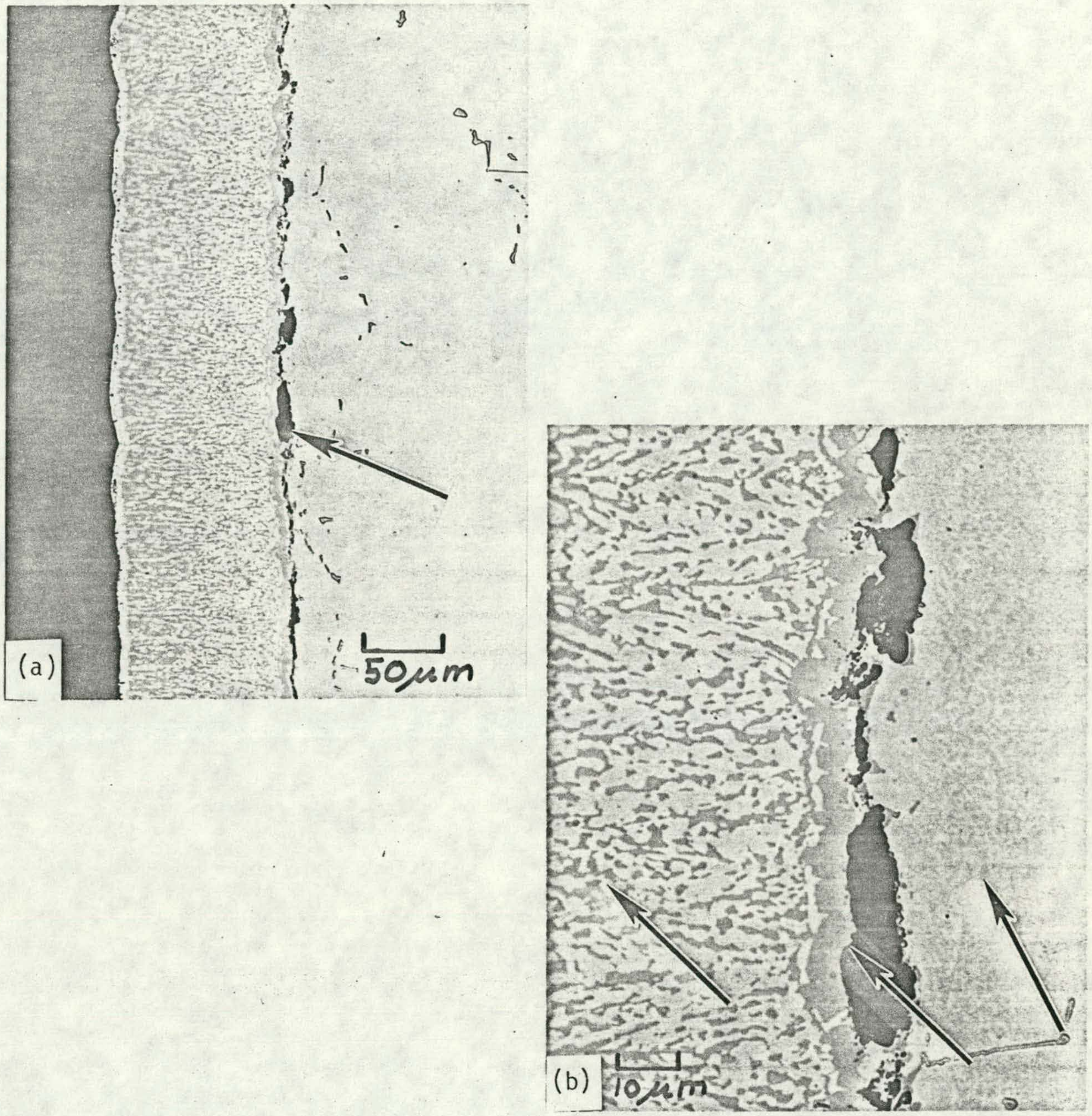


FIGURE 4
CoCrAlY + Pt sputtered coating on GE vanes. (a) Note non-metallic contamination at coating-vane interface (arrow) as-polished, 250x; (b) CoCrAlY coating (left arrow), Pt layer (center arrow), vane (right arrow), as-polished, 1000x.

REFERENCES

1. Goward, G.W., Thin Solid Films, 53 (1978) 223-224.

2. Walzer, P., and Förster, S., Proceedings of the 1977 Tokyo Joint Gas Turbine Congress, Gas Turbine Society of Japan, October 1977, 550-558.

3. Komeya, K., et al, Proceedings of the 1977 Tokyo Joint Gas Turbine Congress, Gas Turbine Society of Japan, October 1977, 538-543.

4. deBiasi, V., Gas Turbine World, (July 1977) 12-18.

5. Busch, R., Develop Sputter Deposited, Graded Metal-ZrO_2 Coating Technology for Application to Turbine Hot Section Components. Prepared for The Naval Sea Systems Command by Battelle, Pacific Northwest Laboratories, Richland, Washington. October 11, 1976. NAVSEA SYSCOM Contract N00024-75-C-4333.

6. Kvernes, I. and Fartum, P., Thin Solid Films, 53 (1978) 259-269.

7. Liebert, C.H., and Stepka, F.S., Potential Use of Ceramic Coating as a Thermal Insulation on Cooled Turbine Hardware. 1976. NASA TM X-3352.

8. Liebert, C.H., et al, Durability of Zirconia Thermal-Barrier Ceramic Coatings on Air-Cooled Turbine Blades in Cyclic Jet Engine Operation. 1976. NASA TM X-3410.

9. Stecura, S., Two-Layer Thermal Barrier Coating for Turbine Airfoils - Furnace and Burner Rig Test Results. 1976. NASA TM X-3425.

10. Butze, H.F., and Liebert, C.H., Effect of Ceramic Coating of JT8D Combustor Liner on Maximum Liner Temperatures and Other Combustor Performance Parameters. January 1977. NASA TM X-73581.

11. Stoner, B., Study of Thermal Barrier Coatings for High Temperature Gas Turbine Engines. Contract NAS3-20067, United Technologies, Power Systems Division. February 1977. NASA CR-135147.

12. Levine, S.R., and Clark, J.S., Thermal Barrier Coatings - A Near-Term, High Payoff Technology. ERDA Workshop on Ceramics for Advanced Heat Engines, Orlando, Florida. January 24-26, 1977. CONF-770110.

13. Muszar, K.E., Development and Evaluation of A Graded Metal-Ceramic Thermal Barrier for Gas Turbine Components. Detroit Diesel Allison Division, General Motors Corporation, Indianapolis, Indiana. July 31, 1975. Final report for Naval Air Systems Command, Department of the Navy Contract N62269-73-C-0357.

14. Dapkunas, S.J. and Clarke, R.L., Evaluation of the Hot-Corrosion Behavior of Thermal Barrier Coatings. Naval Ship Research and Development Center. November 1974. NSRDC-4428.

15. Clarke, R.C., and Dapkunas, S.J., Behavior of Stabilized Zirconia in Molten Sodium Sulphate, Naval Ship Research and Development Center. November 1974. NSRDC-4406.

16. Palko, J.E., Luthra, K.L., and McKee, D.W., Evaluation of Performance of Thermal Barrier Coatings Under Simulated Industrial/Utility Gas Turbine Conditions, Final Report, May 1978, DOE Contract EC-77-C-05-5402.

17. Becher, P.F., et al, Thin Solid Films, 53 (1978) 225-232.

18. Patten, J.W., et al, "Sputter Deposited Multilayered Ceramic/Metal Coatings," presented at International Conference on Metallurgical Coatings, AVS, San Diego, CA, April 23-27, 1979, to be published in Thin Solid Films.

19. Shen, S., Lee, D., and Boone, D., Thin Solid Films, 53 (1978) 233.

20. Boon, D.H., Strangman, L.W., Wilson, L.W., "Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys," J. Vac. Sci. Technol., 11(4) (July/August 1974).

21. Grossklaus, W., Ulion, N.E. and Beale, H.A., "Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys," presented at International Conference on Metallurgical Coatings, April 5-7, 1976.

22. Weiss, R. and Katz, G., "FT4-C Engines in GTV Asia Freighter, a Test of Gas Turbine Materials," presented at conference Gas Turbine Materials in a Marine Enviornment, US Naval Ship Engineering Center and UK Ship Dept. at Bath University, Bath, England, September 20-23, 1976.

23. Patten, J.W., Hays, D.D., Moss, R.W., and Fairbanks, J.W., Proceedings of the 1977 Tokyo Joint Gas Turbine Congress, Gas Turbine Society of Japan, October 1977, 527-537.

24. Fairbanks, J.W., Patten, J.W., Busch, R., and McClanahan, E.D., "High-Rate Sputter Deposition of Protective Coatings on Marine Gas Turbine Hot-Section Superalloys," Proceedings of the 1974 Gas Turbine Materials in the Marine Environment Conference, Battelle Metals and Ceramics Information Center MCIC 75-27, Castine, Maine, July 1974.

25. Patten, J.W. and Hays, D.D., "Application of High-Rate Sputtering Technology to the Formation of Hot Corrosion-Resistant Metallic Coatings on Marine Gas Turbine First-Stage Vanes and Blades," presented at conference Gas Turbine Materials in a Marine Environment, US Naval Ship Engineering Center and UK Ship Dept. at Bath University, Bath, England, September 20-23, 1976.

26. Patten, J.W., et al, "Preliminary Report on the Sputter Deposition of Platinum Coatings on Superalloy Pins," January 25, 1974, NAVSEA Contract N00600-73-C-0583.