NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report No. 32-1014

Evaluation of Oxidation-Resistant Coatings for Inert-Atmosphere Applications

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GPO PRICE $ ____________

CFSTI PRICE(S) $ ____________

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

N67-15683 (ACCESSION NUMBER)	(THRU)
24 (PAGES)	1 (CODE)
CR-81191 (NASA CR OR TMX OR AD NUMBER)	17 (CATEGORY)

FACILITY FORM 602

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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Evaluation of Oxidation-Resistant Coatings for Inert-Atmosphere Applications

W. M. Phillips

Approved by:

D R Bartz

D. R. Bartz, Manager
Research and Advanced Concepts Section

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Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

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ABSTRACT

A series of oxidation-resistant coatings were tested in argon containing traces of oxygen and water vapor at 2000°F for 500 hr. Coatings tested were tin-aluminum and modified silicides applied to a substrate of Cb–1 Zr and an unmodified silicide applied to a subcoating of molybdenum on Cb–1 Zr. Evaluation of the samples was done by metallography, microhardness testing, bend testing, and microprobe analysis. The chromium-modified silicides offered little oxidation protection under these conditions and resulted in chromium diffusion into the substrate. The tin-aluminum coating produced adequate oxidation resistance despite spalling. The use of the unmodified silicide over a diffusion barrier of molybdenum appeared to be the most effective technique of protection.

I. INTRODUCTION

Work currently in progress on high-temperature power systems using refractory metals makes the use of an inert cover gas for test systems desirable for purposes of heat rejection. A major portion of these test systems can be protected from trace impurities in the cover gas by foil wrapping. The heat-rejection portion of these systems, however, must remain exposed. Protection of this portion of the system with an oxidation-resistant coating becomes desirable, if not necessary.

The selection of a protective coating requires a knowledge not only of the effectiveness of the coating in preventing oxidation, but also of the effect of the coating on the substrate.

Oxidation-resistant coatings have been developed by several suppliers, primarily for application on reentry vehicles and rocket nozzles. Testing of these coatings has in general been by furnace tests at atmospheric pressure or by oxyacetylene-torch impingement. The results of these tests cannot necessarily be extrapolated to reduced partial pressures of oxygen.

Investigations of reduced-pressure effects have been undertaken by Bartlett and Gage (Ref. 1) and by Moore and Stetson (Ref. 2) on higher strength columbium- and tantalum-base alloys.

Studies reported in Ref. 1, which were conducted under vacuum or partial vacuum conditions, were directed toward the definition of the temperatures and pressures at which pure silicide coatings are protective on molybdenum and tungsten. Results of studies on $MoSi_2$ from Ref. 1 are summarized in Fig. 1. This plot is for pure $MoSi_2$. An argon atmosphere might be expected to contain oxygen in the range of 1 ppm or 10^{-6} atm. Based on these test results, the protectiveness of this coating in the 1800 to 2000°F range becomes questionable.

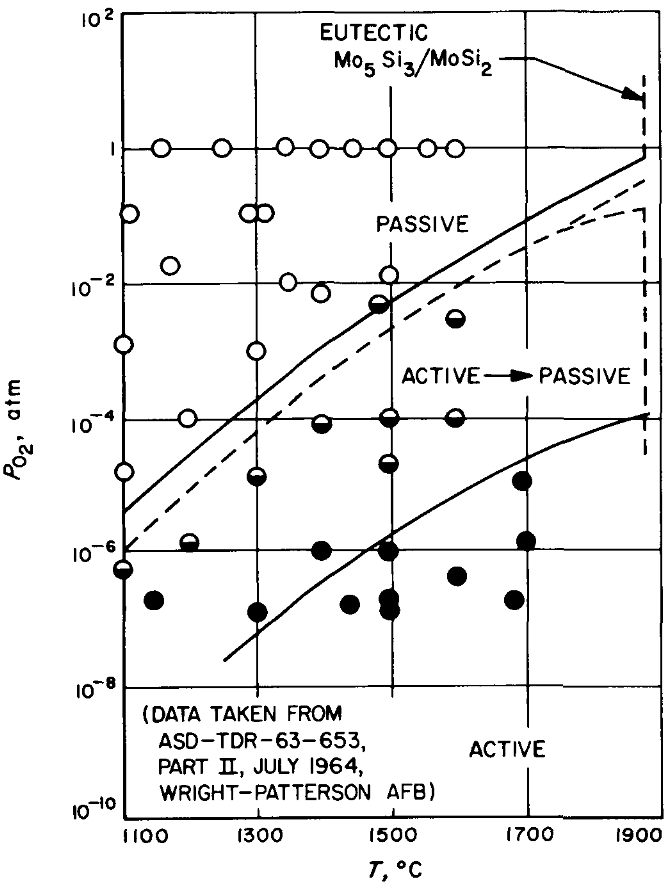


Fig. 1. Oxidation behavior of $MoSi_2$ samples compared with theoretical boundaries separating types of behavior (Ref. 1)

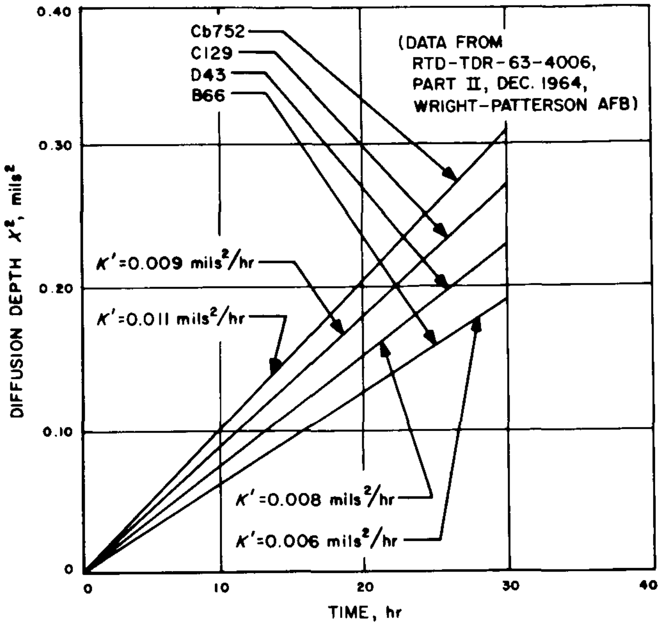


Fig. 2. Diffusion-rate plots of silicide coating into four columbium alloys at 2500°F (Ref. 2)

Work described in Ref. 2 indicated that the diffusion of coatings into columbium-alloy substrates is an important consideration. The research work emphasized advanced columbium-base alloys combined with the TRW Cr–Ti–Si coating and unmodified silicides. Results of these tests are shown in Fig. 2. The diffusion depth x is plotted in terms of x^2 to obtain a linear plot as a function of time. While these tests were run in high-purity argon, the test temperature was in excess of that expected in the heat-rejection portion of a refractory-metal test system. The duration of these tests was also markedly less than that normally required for a power-system test.

The tests conducted in the study reported herein were undertaken to determine if a suitable oxidation-resistant coating could be applied to a condensing coil of Cb–1 Zr alloy. The condensing coil is part of a Rankine-cycle space power experiment that is being run in an argon atmosphere containing approximately 1 ppm impurities.

II. COATINGS TESTED

The coatings used in this study were obtained from four commercial suppliers: Pfaudler Div., Pfaudler Permutit Inc.; Sylvania Electric Products, Inc.; Chromizing Corporation; and Vitro Laboratories. Samples on which these coatings were applied were 1/8-in.-thick sheet stock of Cb–1 Zr. Test tabs were sheared to 1/2 in. by 2 in. All sharp corners and edges were rounded. A 1/16-in. wire was welded to one end of each tab for support during testing. The tabs were then submitted to the vendors for coating.

Pfaudler Div. applied a single-cycle-process coating to two samples, which were designated PCA and PCB. A double-cycle coating was applied to two samples, PCC and PCD.

Sylcor tin-aluminum coating was applied to three samples by Sylvania Electric Products, Inc.

A series of four samples were coated by the Chromizing Corporation with their Durak KA coating.

Vitro Laboratories applied 0.003 in. of modified chromium-molybdenum disilicide to three samples. They felt that they could obtain a higher quality coating if the tabs were more rounded. Thus, on these samples the wire hanger was removed and the corners and edges were given increased radii. A fourth sample was precoated with a nominal 0.005 in. of molybdenum by halide decomposition. On this sample the wire was removed, but no additional rounding of edges was done. The protective coating applied was an unmodified molybdenum disilicide.

III. TEST PROCEDURE

The specimens that had attached wires were suspended in a tube furnace for the test. The balance of the samples were set on high-purity alumina pedestals. Argon flow rate was maintained at 4 SCFH. Prior to heating

Table 1. Microhardness measurements of Cb—1 Zr substrate after 500 hr at 2000°F

Coating	Diamond pyramid hardness numbers		
	At surface	1/32 in. under surface	Substrate core
Pfaudler samples:			
Single-cycle PCA	119	108	109
Single-cycle PCB	114	102	98
Double-cycle PCC	109	107	103
Double-cycle PCD	115	110	107
Sylvania samples:			
Sylcor 1	103	104	104
Sylcor 2	107	107	104
Sylcor 3	113	112	114
Chromizing samples:			
Durak KA-1	117	113	112
Durak KA-2	124	121	114
Durak KA-3	122	118	119
Durak KA-4	114	110	109
Vitro samples:			
Chromium-molybdenum disilicide VCA	112	115	107
Chromium-molybdenum disilicide VCB	105	109	107
Chromium-molybdenum disilicide VCM	129	111	106
Molybdenum disilicide on molybdenum VCM 5	103	105	102

and during the test, both the exhaust and inlet argon were monitored for oxygen and water vapor. Oxygen content varied from 1 to 3 ppm during the test. Water-vapor content was less than 10 ppm at the start of the test and decreased to 1 to 3 ppm within 24 hours, where it remained during the rest of the test.

Temperature was maintained at 2000°F ± 25°F for 500 hr. The samples were then thermally cycled to room temperature five times. Each cooling cycle required approximately 12 hr, while reheat was achieved in approximately 6 hr.

Depth of diffusion or contamination into the substrate of Cb–1 Zr was evaluated by metallography, microhardness testing, and microprobe analysis. Microhardness testing was done with a diamond pyramid indenter and a 25-gram load on a Tukon microhardness tester. The values quoted in Table 1 are averages of eight readings.

IV. RESULTS AND DISCUSSION

A. Pfaudler Div. Coating Samples

The Pfaudler coating samples after removal from test are shown in Fig. 3. It is apparent that cracking and spalling of the coating has taken place. Figure 4 is a photomicrograph typical of the single-cycle-process coating. The reaction layer is thin (Table 2) and cracked and the coating is porous, apparently due to volatilization of

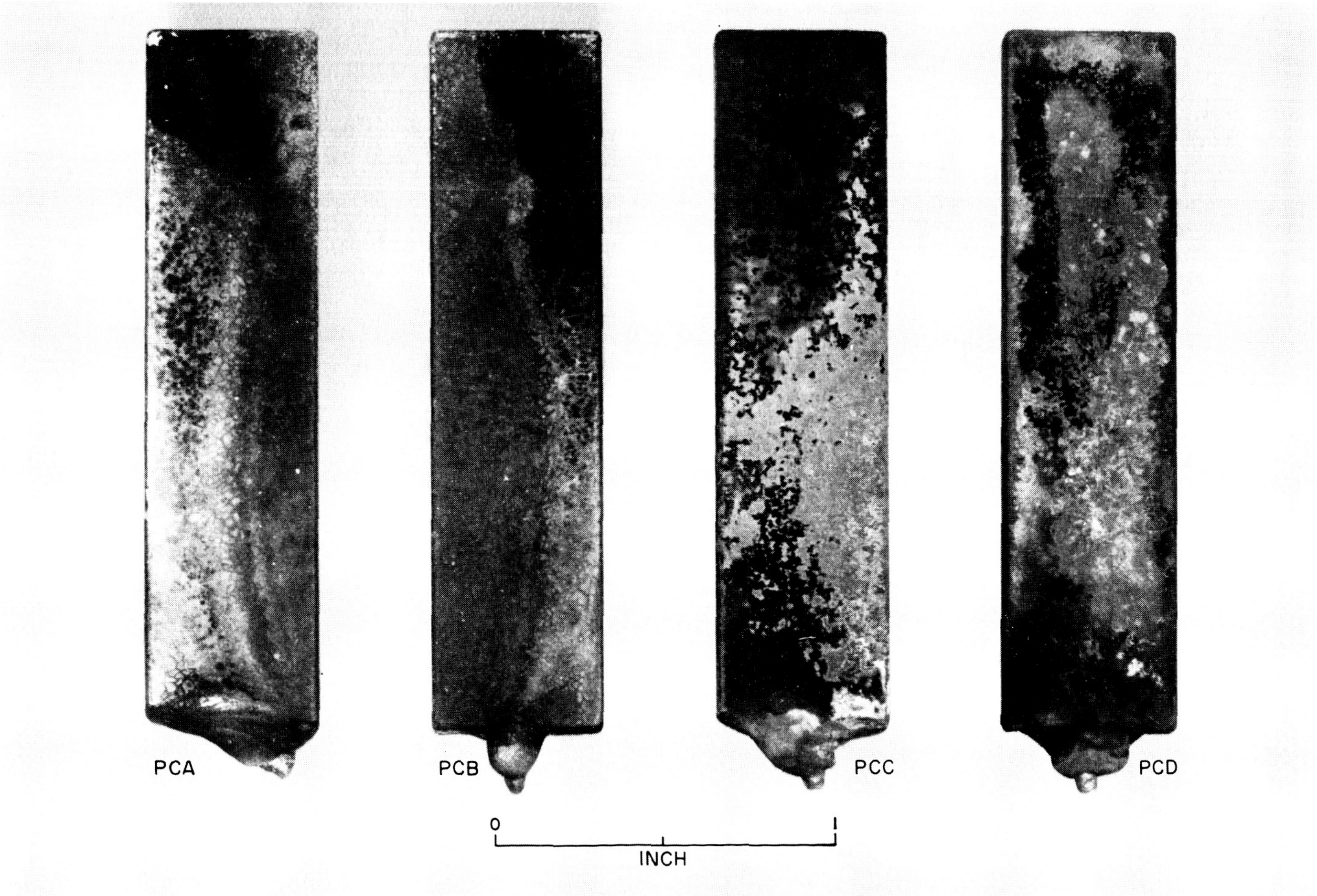


Fig. 3. Pfaudler coating after 500-hr test in flowing argon at 2000°F

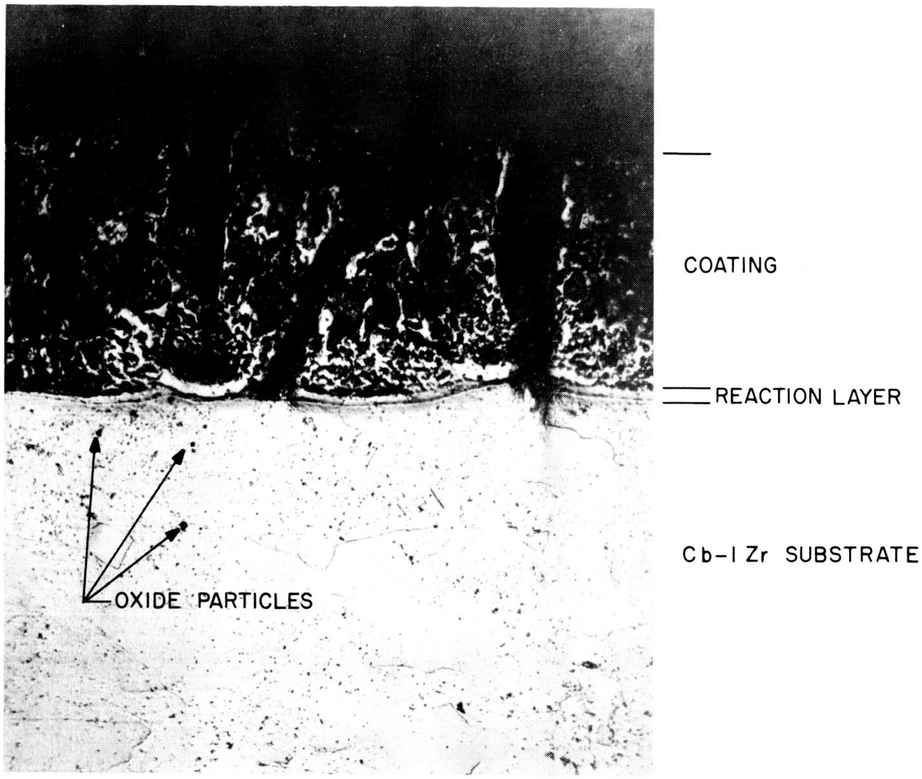


Fig. 4. Photomicrograph of Pfaudler single-cycle-process coating after test (magnified 250 times)

Table 2. Reaction layer thicknesses of coatings on Cb—1 Zr substrate after 500 hr at 2000°F

Coating	Reaction layer thickness, μ
Pfaudler single-cycle	8
Pfaudler double-cycle	50
Sylcor tin-aluminum	30
Chromizing Durak KA	5
Vitro chromium-molybdenum disilicide	20
Vitro unmodified molybdenum disilicide on molybdenum subcoating	15

constituents in the coating. The Cb–1 Zr substrate shows a marked increase in oxide precipitate particles near the surface of the substrate. Microhardness measurements (Table 1) indicated hardening of the substrate near the surface. The bend-test results (Table 3) indicated no change in ductility and no abnormally high yield strengths.

A photomicrograph of the double-cycle-process coating is shown in Fig. 5. The reaction layer is considerably thicker in these samples. This may be due to heating during application of the second-cycle coating. Cracking and volatilization are also apparent in these samples. Oxide particles are not as numerous; however, the bend-test and microhardness results indicated some strengthening and hardening of the substrate.

Microprobe analysis of the substrate indicated no diffusion of coating constituents into the base alloy to a depth beyond the reaction layer (Fig. 6 and 7).

B. *Sylvania Electric Products Coating Samples*

The Sylcor tin-aluminum coating samples after test are shown in Fig. 8. Heavy spalling of this coating is apparent. A photomicrograph typical of these samples is shown in Fig. 9. The reaction layer shows only occasional breaks. Microhardness measurements indicated some hardening of one of the samples; however, bend-test and metallographic examination did not show any differences in these samples.

Table 3. Yield strengths of test specimens in three-point bending after 500 hr at 2000°F

Coating	Yield strength, psi
Pfaudler samples:	
Single-cycle PCA	49,000
Single-cycle PCB	53,000
Double-cycle PCC	59,000
Double-cycle PCD	63,000
Sylvania samples:	
Sylcor 1	59,000
Sylcor 2	59,000
Sylcor 3	60,000
Chromizing samples:	
Durak KA-1	52,000
Durak KA-2	51,000
Durak KA-3	52,000
Durak KA-4	54,000
Vitro samples:	
Chromium-molybdenum disilicide VCA	72,000
Chromium-molybdenum disilicide VCB	67,000
Chromium-molybdenum disilicide VCM	81,000
Molybdenum disilicide on molybdenum VCM 5	89,000

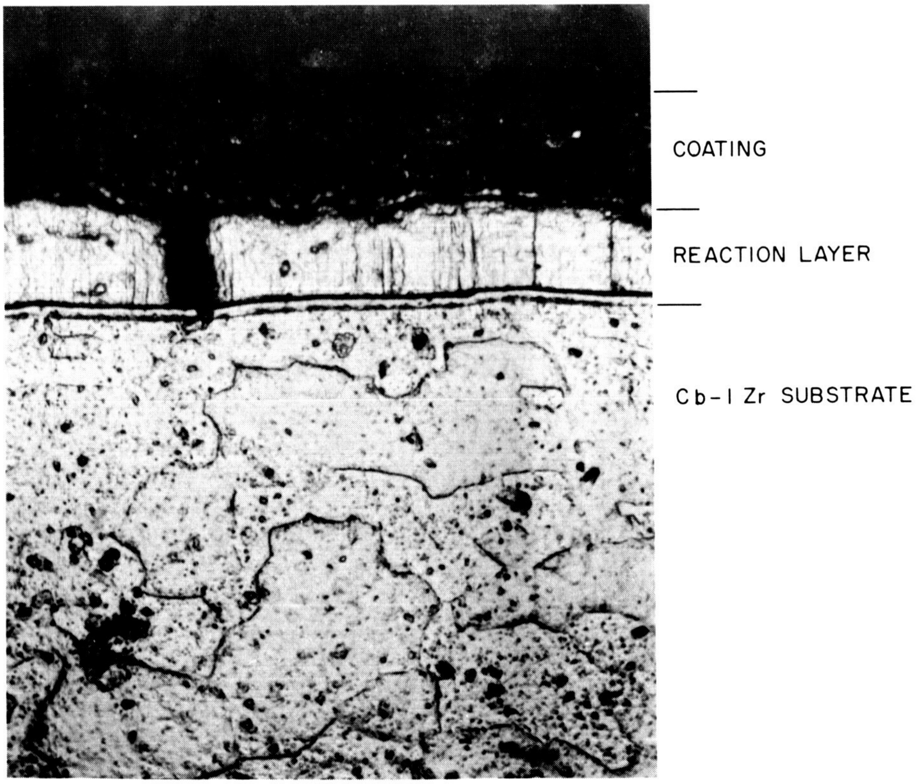


Fig. 5. Photomicrograph of Pfaudler double-cycle-process coating after test (magnified 250 times)

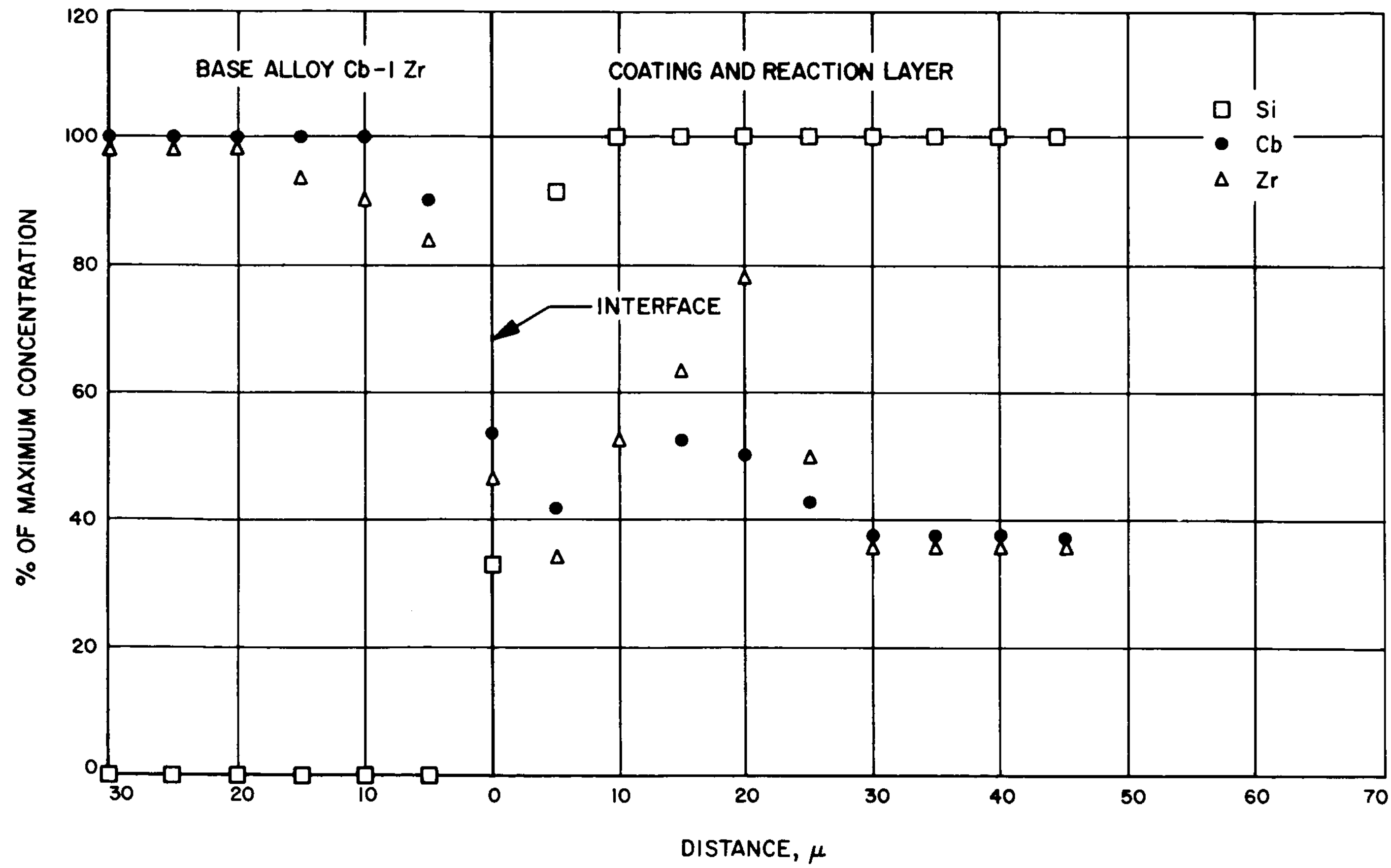


Fig. 6. Results of microprobe analysis on Pfaudler single-cycle-process coating

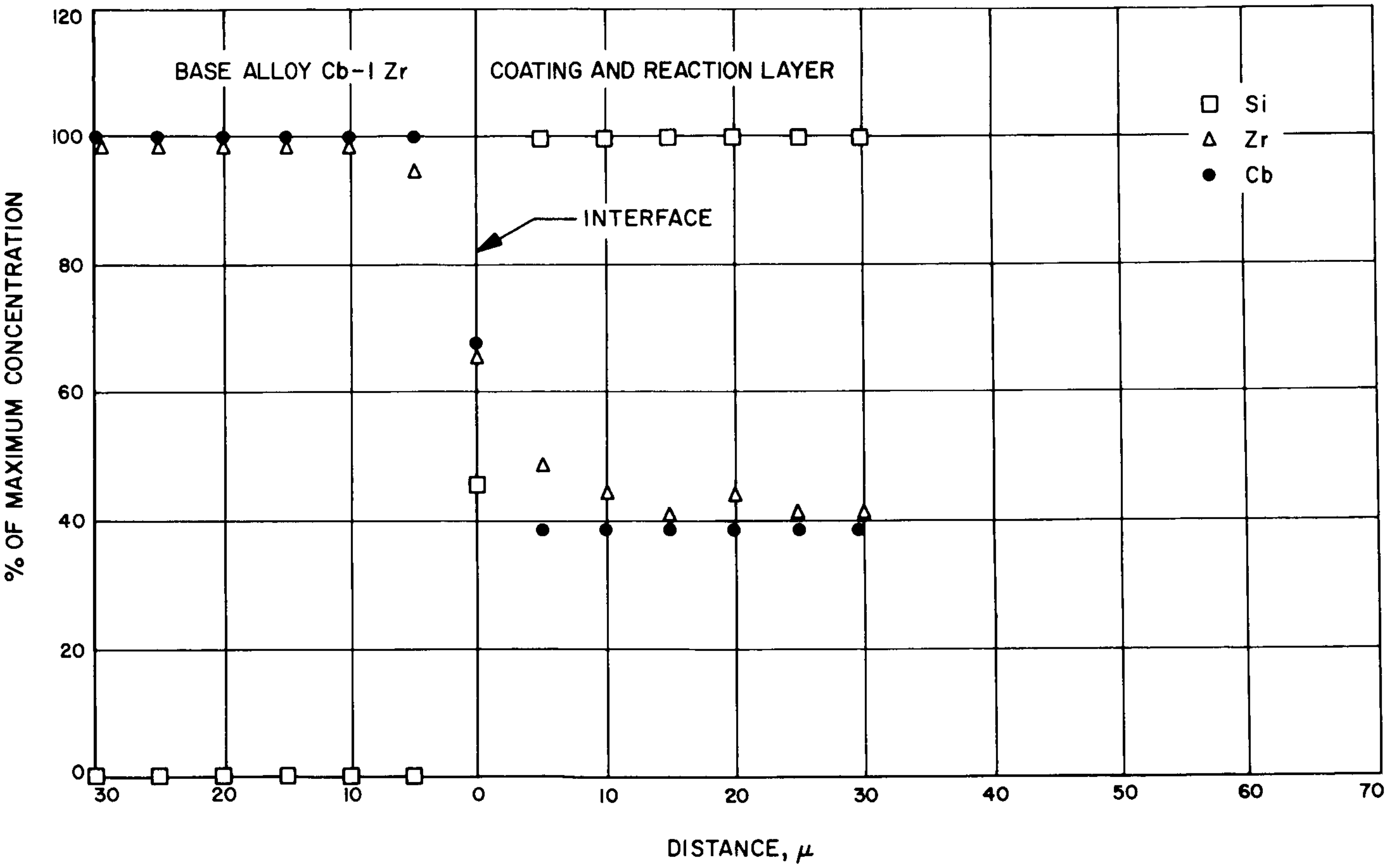


Fig. 7. Results of microprobe analysis on Pfaudler double-cycle-process coating

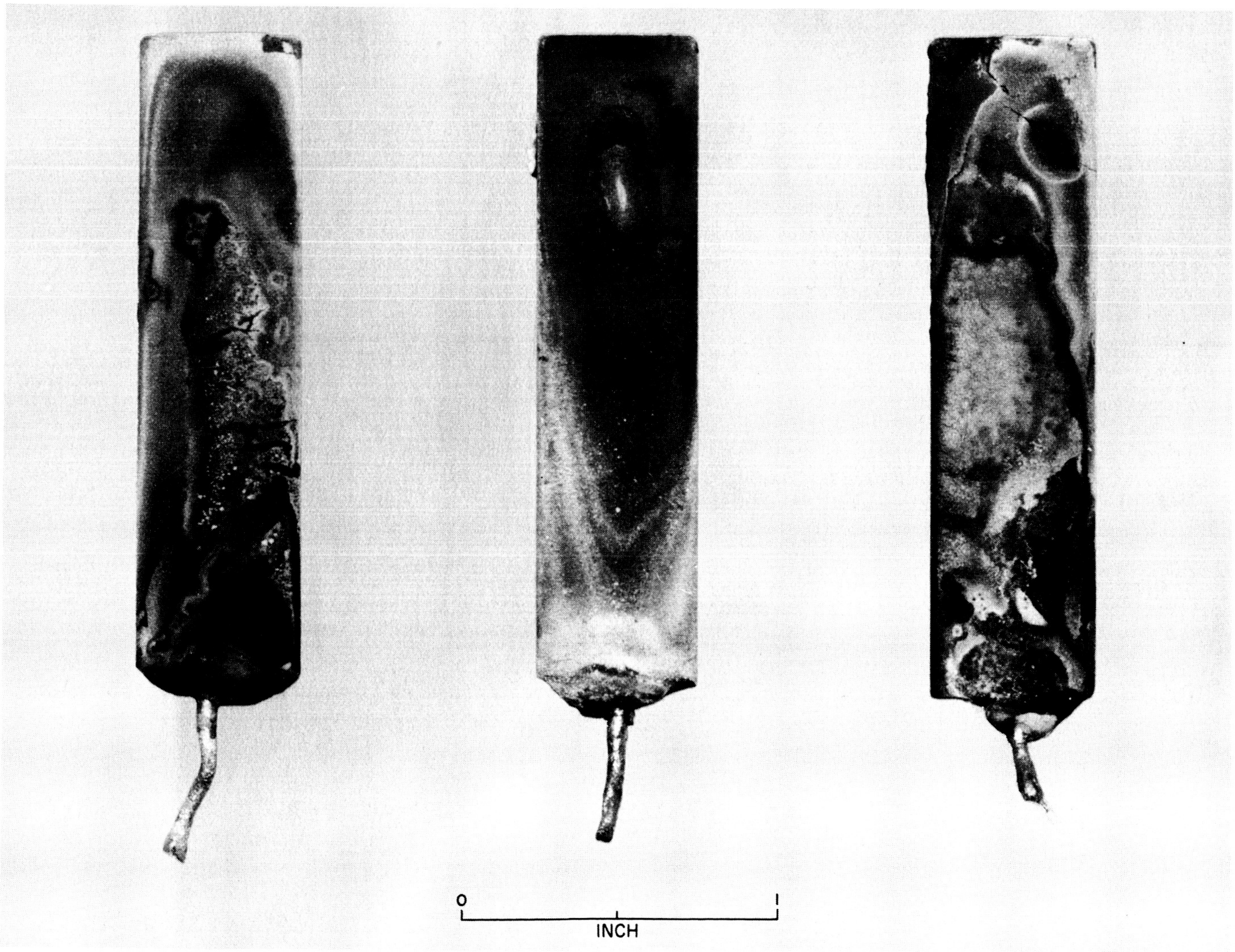


Fig. 8. Sylvania Sylcor tin-aluminum coating after 500-hr test in flowing argon at 2000°F

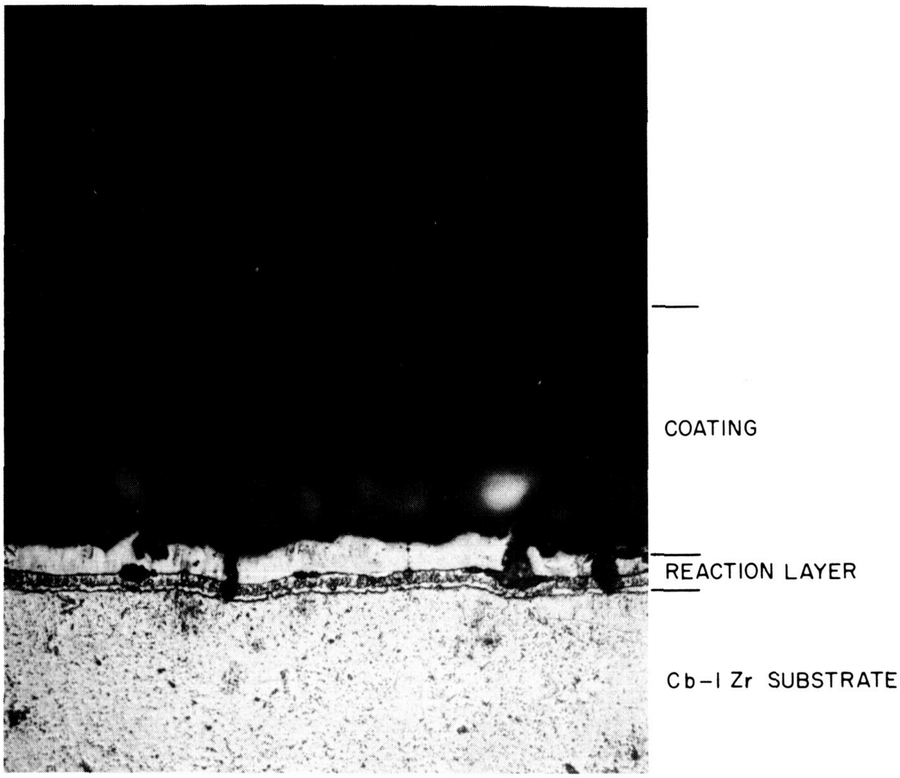


Fig. 9. Photomicrograph of Sylvania Sylcor tin-aluminum coating after test (magnified 250 times)

Microprobe analysis displayed slight depletion of the zirconium near the interface, but no diffusion of the coating constituents into the substrate beyond the reaction layer (Fig. 10).

C. Chromizing Corporation Coating Samples

The Durak KA samples from Chromizing Corporation are shown in Fig. 11 after test. Cracking of this coating is apparent; however, there are no indications of spalling. A photomicrograph of a typical area is shown in Fig. 12. A thin reaction layer is present, with numerous breaks allowing the formation of oxide in the substrate.

Microhardness measurements indicated hardening, although the bend-test results indicated neither loss of ductility nor strength increases. Microprobe analysis (Fig. 13) indicated some depletion of zirconium, but no diffusion of coating constituents into the substrate beyond the reaction layer.

D. Vitro Laboratories Coating Samples

The modified chromium-molybdenum disilicide samples (VCA, VCB, VCM) prepared by Vitro and the unmodified molybdenum silicide applied to a subcoating of molybdenum (specimen VCM 5) are shown in Fig. 14. Surface checking of these samples resulted from testing.

A photomicrograph of the modified coating after test is shown in Fig. 15. The coating does not display the effects of volatilization as greatly as the other Vitro samples. The reaction layer is porous and discontinuous. Large oxide particles are present near the interface and are almost continuous in the surface grain boundaries.

Microhardness measurements indicated some hardening of one of the samples. Marked strengthening of the samples in bending was observed.

Microprobe analysis indicated little diffusion of columbium into the coating and some zirconium diffusion into the coating (Fig. 16). No diffusion of molybdenum nor silicon into the substrate was observed. Chromium diffusion into the Cb–1 Zr substrate did occur.

The use of molybdenum as a diffusion barrier appeared successful. The reaction layer between the molybdenum and the silicide appeared continuous (Fig. 17). Bonding between the columbium and the molybdenum appeared sound. No hardening of the substrate was observed by microhardness measurements. Strengthening of this sample in bending was observed. This may be due to the added strength of the molybdenum coating rather than to an increase in the substrate strength. Microprobe analysis results (Fig. 18) indicated some zirconium present in both the molybdenum and the coating. No other interdiffusion was observed in the system.

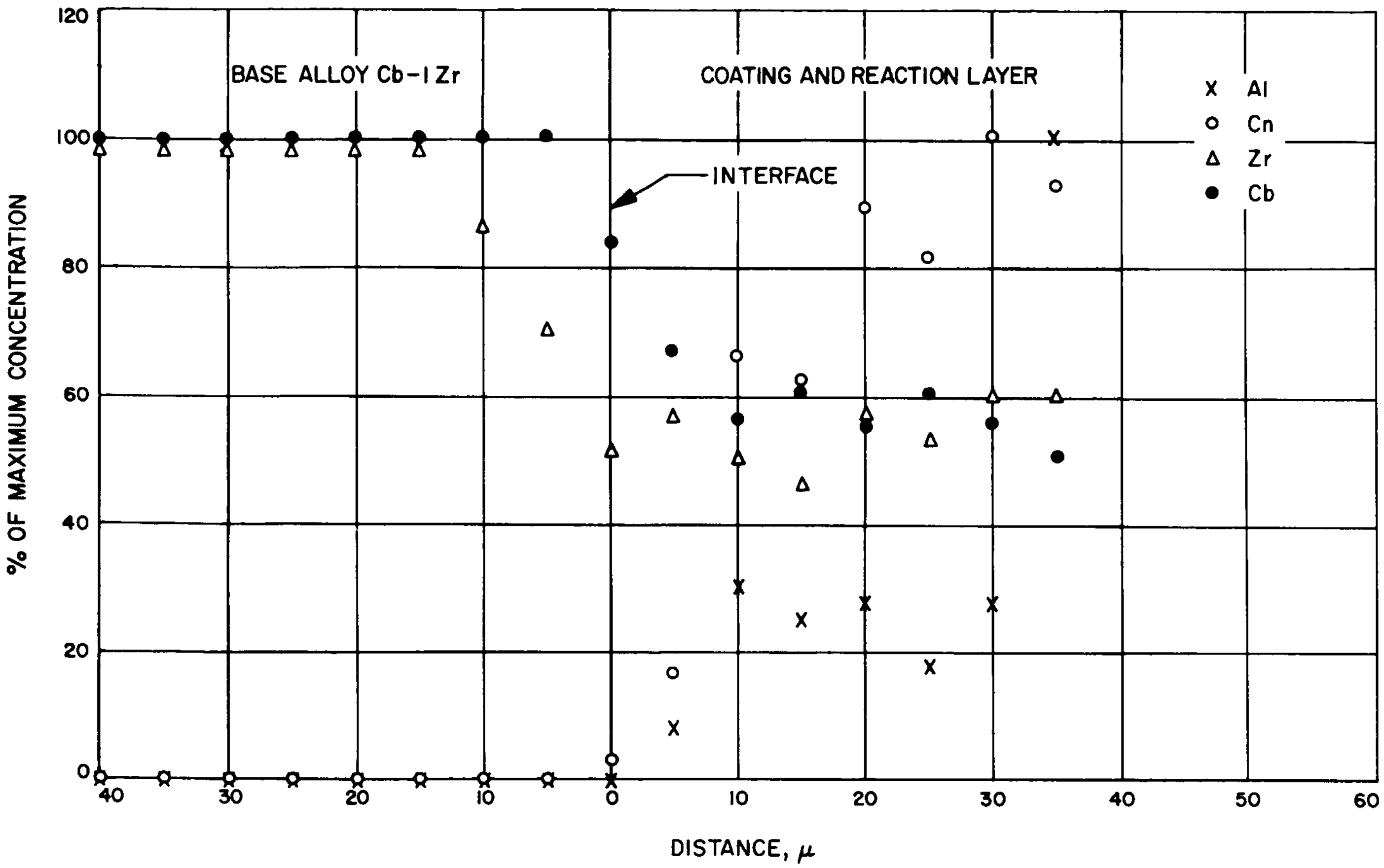


Fig. 10. Results of microprobe analysis on Sylvania Sylcor tin-aluminum coating

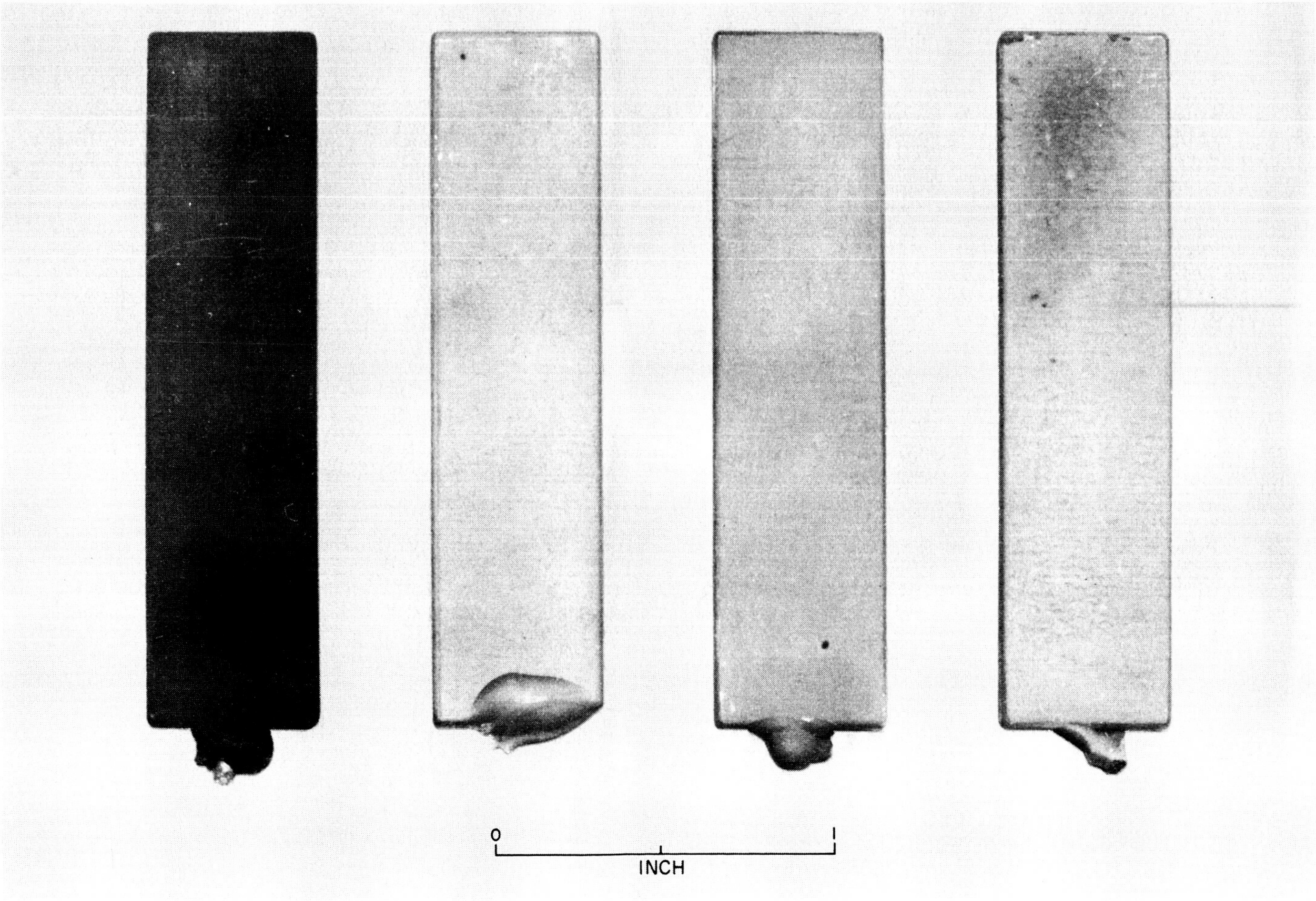


Fig. 11. Chromizing Corporation Durak KA coating after 500-hr test in flowing argon at 2000°F

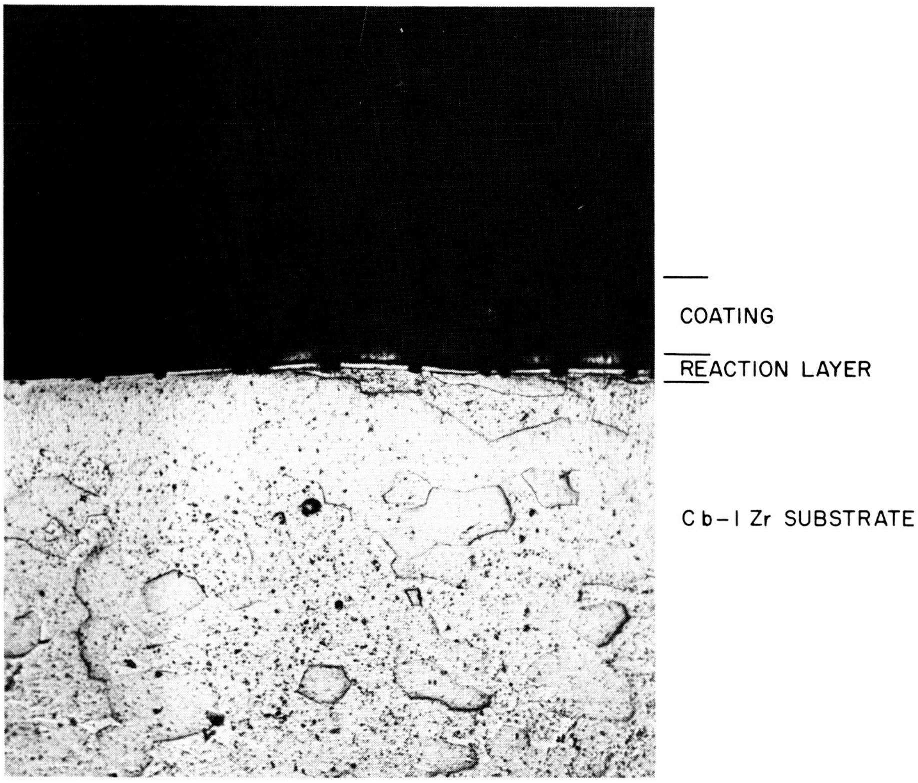


Fig. 12. Photomicrograph of Chromizing Corporation Durak KA coating after test (magnified 250 times)

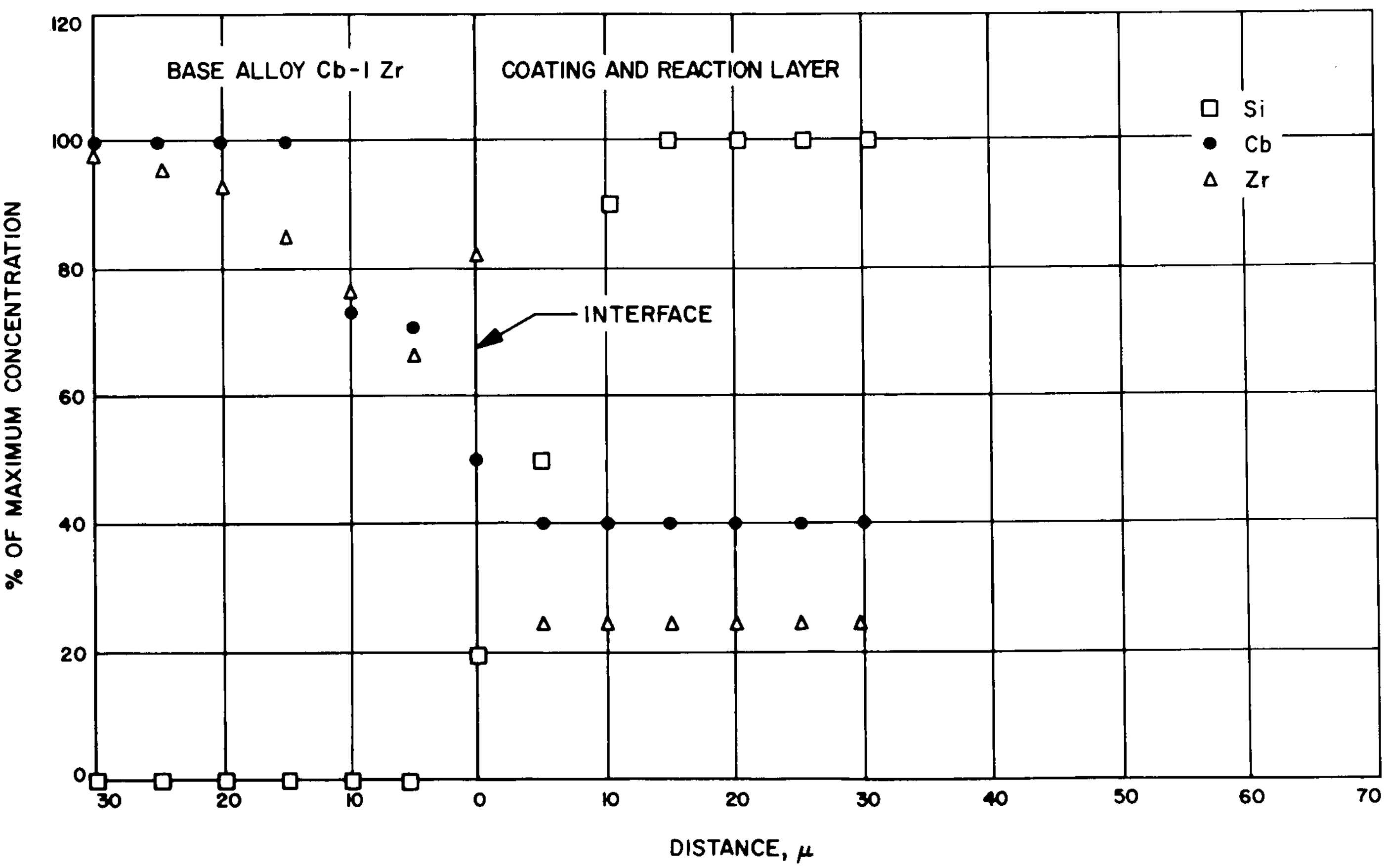


Fig. 13. Results of microprobe analysis on Chromizing Corporation Durak KA coating

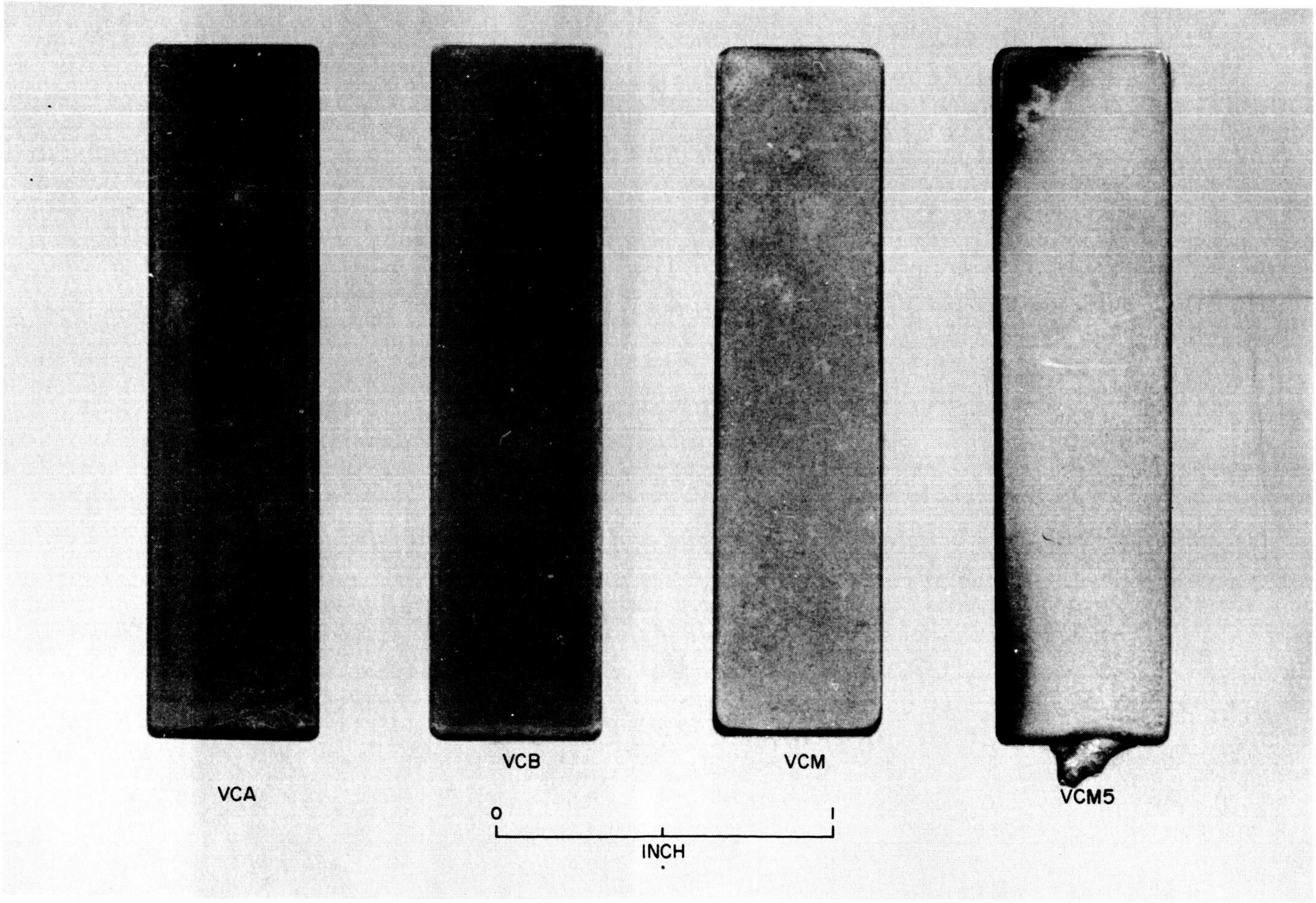


Fig. 14. Vitro coatings after 500-hr test in flowing argon at 2000°F

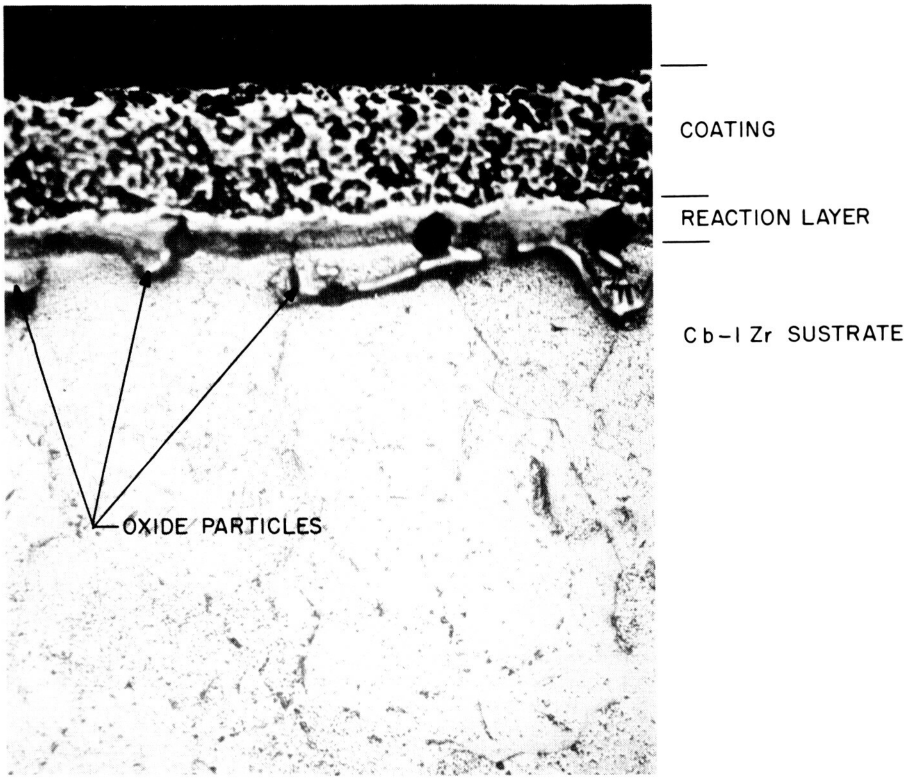


Fig. 15. Photomicrograph of Vitro chromium-molybdenum disilicide coating after test (magnified 250 times)

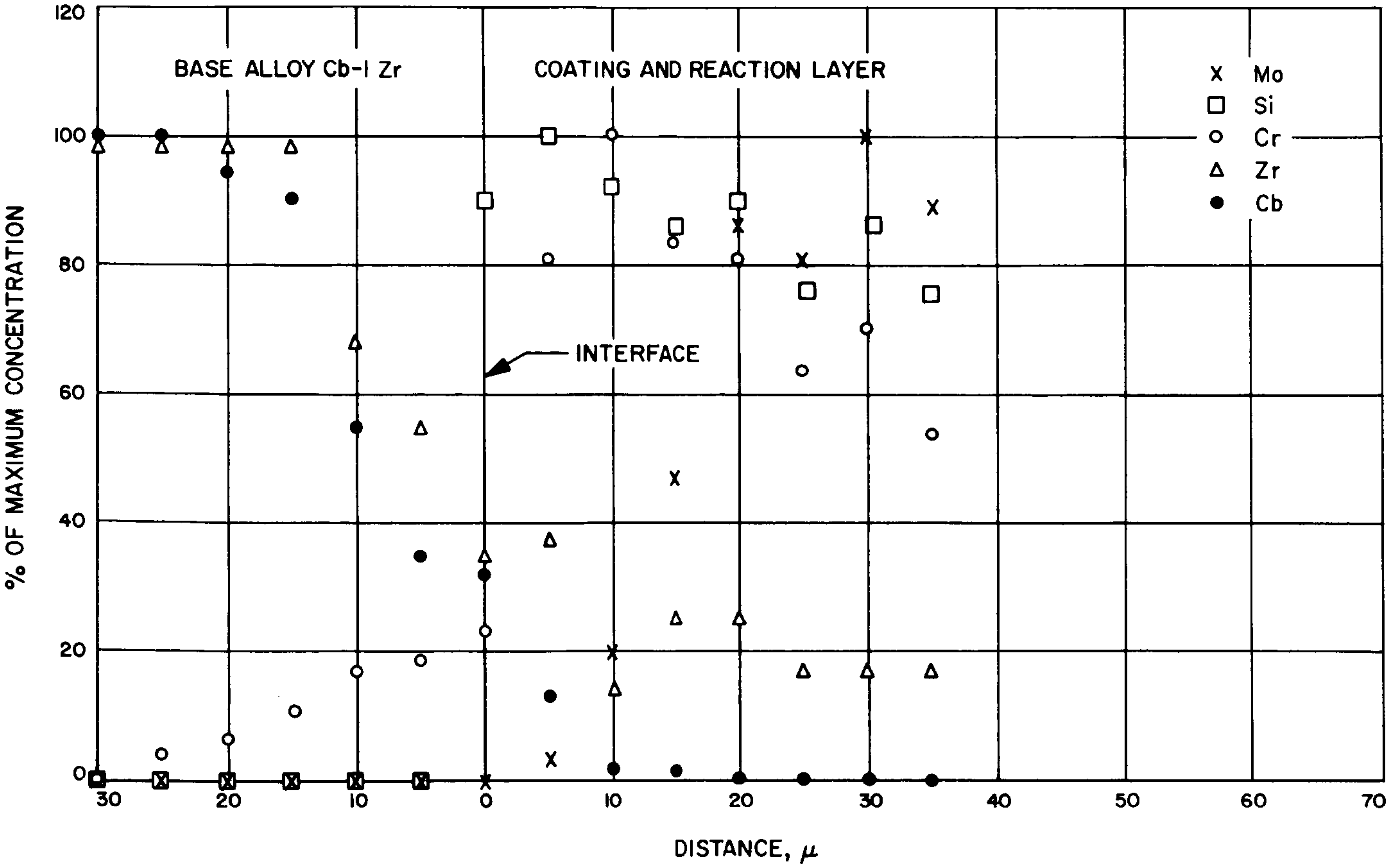
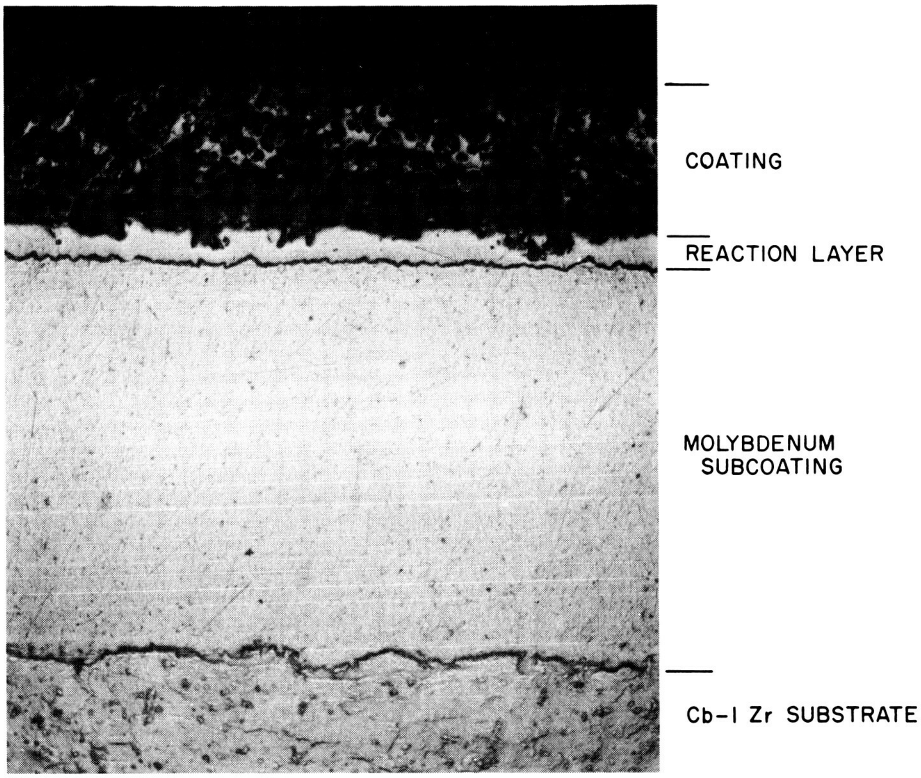


Fig. 16. Results of microprobe analysis on chromium-molybdenum disilicide coating

Fig. 17. Photomicrograph after test of Vitro unmodified molybdenum disilicide coating applied over a molybdenum subcoating (magnified 250 times)



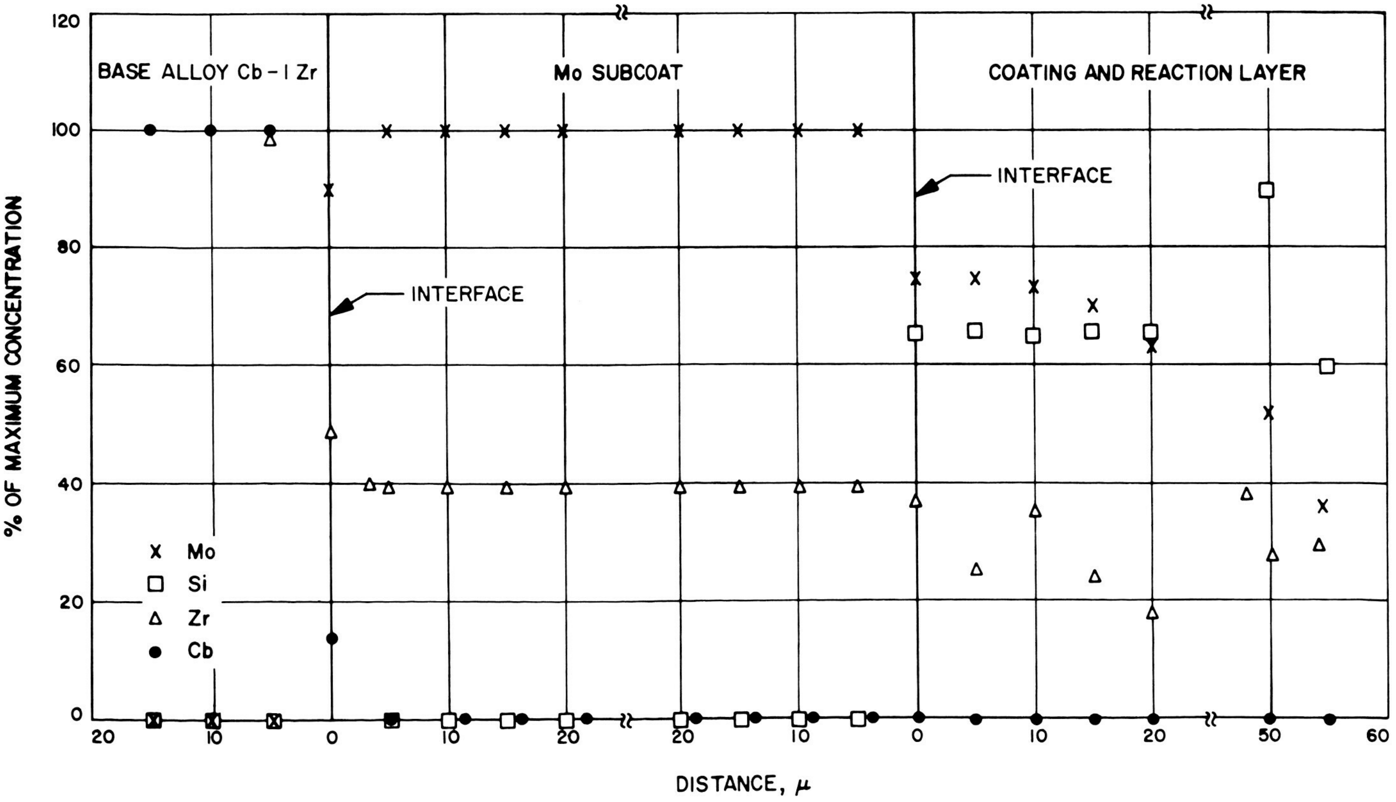


Fig. 18. Results of microprobe analysis on Vitro unmodified molybdenum disilicide coating applied over molybdenum subcoating

V. CONCLUSIONS

Of the coatings tested, the molybdenum disilicide applied to a molybdenum subcoating appeared to be the most effective. The chromium-molybdenum silicides were not protective and resulted in diffusion of chromium into the substrate. Both the Pfaudler coatings and the Chromizing Corporation Durak coatings allowed some oxidation of the substrate.

The tin-aluminum coating appeared to adequately inhibit oxidation in two of three samples, with little evidence of contamination in the third. This coating therefore is also believed to offer protection in inert-atmosphere applications.

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