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PERFORMANCE OF COATED COLUMBIUM AND TANTALUM ALLOYS IN PLASMA ARC REENTRY SIMULATION TESTS

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16. Abstract

The evaluation of coated refractory metals screened in stagnation model plasma arc tests is reported. Columbium alloys FS-85, C-129Y, and Cb-752 coated with Si-20Cr-20Fe (R512E) were tested at 1390° C. Three silicide coatings on Ta-10W were tested at 1470° C. Half-hour cycles and a 6.5×10^2 N/m^2 stagnation pressure were used. The best R512E coated columbium alloy was FS-85 with first local coating breakdowns occurring in 12 to 50 cycles. At coating defects, low metal recession rates (0.005 mm/min) were generally observed on coated columbium alloys while high rates (0.15 mm/min) were observed on coated Ta-10W. Coated columbium suffered large emittance losses (to below 0.7) due to surface refractory metal pentoxide formation.

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SUMMARY

The evaluation of coated refractory metals screened in stagnation model plasma arc tests is reported. The purpose of these tests was to evaluate several potential radiative thermal protection system (TPS) materials. Thin sheet specimens of columbium alloys FS-85, Cb-752, and C-129Y coated with Si-20Cr-20Fe (R512E) and of tantalum alloy Ta-10W coated with Si-20Cr-10Ti-4Mo-4W-2V (SA-13), Si-2.5Mn-33Ti (TMS), or 50W-20Mo-15Ti-15V slurry plus silicon pack (NS-4) were tested. Half-hour square wave heating cycle exposures at a stagnation pressure of 6.5×10^2 newtons per square meter (4.9 torr) were used. As-coated and intentionally defected coated columbium specimens were scheduled for up to 50 and 5 exposures, respectively, at 1260° C. As-received and intentionally defected coated Ta-10W specimens were scheduled for up to 25 and 5 cycles of exposure, respectively, at 1425° C. Actual average exposure temperatures were about 1390° C for coated columbium alloys and about 1470° C for Ta-10W.

In these tests, local coating breakdowns began at specimen edges, intact coatings protected the alloys from mechanical property degradation, and natural coating cracks did not widen significantly.

The best R512E coated columbium alloy was FS-85 with times to first local coating breakdown of 12 to 50 cycles. Low metal recession rates (about 0.005 mm/min) were observed at intentional coating defects in columbium alloys. Large emittance losses (generally to below 0.7) occurred as a result of the formation of surface refractory metal pentoxides on coated columbium alloys.

The SA-13 and NS-4 coatings protected Ta-10W for five cycles. The TMS coating performed erratically with coating breakdowns occurring in as little as one exposure cycle. High Ta-10W recession rates (about 0.15 mm/min) were generally observed at coating breakdowns. Erratic self-healing occurred with the TMS coating. The rapid rate of metal recession at coating breakdowns makes the suitability of tantalum for TPS applications questionable.

INTRODUCTION

Refractory metals, when protected from oxidation by silicide coatings, have a use potential in selected areas of thermal protection systems (TPS) on reentry vehicles. Fused slurry silicide coatings for refractory metals are being developed (refs. 1 to 4) and evaluated (refs. 1 to 3 and 5) under laboratory simulated orbital and reentry flight conditions. In furnace reentry simulation tests, coated columbium alloys show a strength potential for a 100-mission reusable TPS operating at a maximum temperature of 1315^{o} C (2400^{o} F), while coated tantalum shows a potential for a 50-mission reusable TPS operating at a maximum temperature of 1425^{o} C (2600^{o} F). Both coated systems with intentional coating defects have the potential for surviving several reentries without structural failure.

To determine the potential for coated columbium and tantalum alloys under high mass flow conditions, the best substrate/coating systems developed under NASA contracts (refs. 1 to 3) were made part of a screening study conducted in the Aerotherm Division/Acurex Corporation 1-megawatt plasma arc facility under a contract with NASA-Ames (ref. 6). All TPS candidates at that time were included in the screening - ablators, ceramic rigidized surface insulation, carbon/carbon composites, coated refractory metals, and bare superalloys. This report covers the evaluation of coated columbium and tantalum specimens tested in this high mass flow stagnation mode screening study.

An examination was made of the changes which occurred in the silicide coatings after high mass flow exposures up to a maximum of 50 half-hour cycles. The planned test temperature was 1260^{o} C for R512E (Si-20Cr-20Fe) coated columbium alloys Cb-752, C-129Y, and FS-85 and 1425^{o} C for silicide coated Ta-10W. Actual test temperatures were somewhat higher than intended, as will be described later. The stagnation pressure was 6.5×10^{2} newtons per square meter (4.9 torr). The effects of exposures on coated specimens and intentionally defected specimens (holes, areas of coating removal, notches and impact impressions) were evaluated by visual examination during exposure and in the post-test condition by metallography. In addition, selected mechanical property tests and X-ray diffraction (XRD), electron microprobe (EMP), X-ray fluorescence (XRF), and scanning electron microscope (SEM) analyses were performed.

EXPERIMENTAL PROCEDURES

Materials

At the time of this screening study, three coated columbium alloys (FS-85, C-129Y, and Cb-752) were potential candidates for a metallic TPS. The coating for all three alloys was R512E (Si-20Cr-20Fe), a fused slurry silicide. The tantalum alloy Ta-10W

was tested in combination with three coatings: SA-13 (Si-20Cr-10Ti-4Mo-4W-2V) (ref. 2) and TMS (Si-2.5Mn-33Ti) (ref. 3), both fused slurry silicide coatings developed under NASA contract, and a limited number coated with NS-4 (50W-20Mo-15Ti-15V slurry plus silicon pack), a metallic sintered slurry plus pack silicide coating also developed under NASA contract (ref. 7). The alloy and coating compositions are given in table I.

The test specimens were 60° pie-shaped segments cut from a 5.3-centimeter circle with a 1.5-centimeter circle removed at the center as shown in figure 1. To hold the specimens in place during exposure, 90° tabs were used on the inside and outside circumference.

Pretest Sample Preparation

All twelve coated specimens from each major alloy/coating group were inspected, measured for total thickness, and weighed before nine were intentionally defected. The specimens were defected to simulate possible types of in-service coating damage such as impact by runway debris, meteorites, or handling abuse. Three specimens of each group were defected by a 0.45-centimeter-diameter pellet fired from an air rifle. The pellet struck the coated specimens at either 15 or 30 meters per second causing a 0.20 to 0.30-centimeter-diameter cupped impression in the surface with a depth of 0.30 to 0.50 centimeter. Pellet impact caused coating cracking in all cases, but the 30 meter per second impact also caused visual cracking and some loss of coating on the side opposite the impact. Figure 1 shows typical intentionally impact defected areas before test.

Four specimens of each group were defected by grit blasting with 50-micron alumina grit through a 0.079-centimeter hole in a soft copper mask until the coating was abraded away down to the substrate. The diameter of the abraded area was 0.092 ± 0.008 centimeter. Two of these specimens were then penetrated at the defect site by a number 64 drill to produce a 0.092-centimeter through-hole.

Two specimens of each group were defected midway along a radial edge by cutting through the coating with a jeweler's saw to produce a notch about 0.028 centimeter wide and from 0.04 to 0.05 centimeter deep. This damage was intended to simulate edge damage or premature coating edge failure.

Test Configuration and Conditions

Figure 2 shows the specimen and instrumentation arrangement of the test model. Six specimens per 12-centimeter-diameter flat face stagnation model were scheduled to

be tested in a 20-centimeter test stream. Test temperature was monitored with two optical pyrometers and spring loaded thermocouples. The primary optical pyrometer, measuring in the 1.7- to 2.6-micrometer wavelength range, was sensitive to specimen emittance. Thus, rather than supplying accurate test temperature information, it supplied emittance estimates when compared to temperature measurements obtained with the thermocouples. The secondary pyrometer, operating at 0.8 micrometer, was relatively insensitive to specimen emittance and thus gave reasonable temperature estimates. The specimen backwall temperature was measured by spring-loaded 0.075-millimeter wire platinum - platinum-13-percent-rhodium thermocouples. Further details of the 1-megawatt arc facility, as shown in figure 3, are described in reference 6. The as-coated specimens were scheduled for either 25 or 50 half-hour exposure cycles, while intentionally defected specimens were scheduled for either 1 or 5 exposure cycles.

Coated columbium and tantalum specimens were scheduled for exposure at nominal temperatures of 1260° and 1425° C, respectively, at 6.5×10^{2} newtons per square meter (4.9 torr) air. This was to be accomplished with nominal enthalpies of 1.5×10^{7} and 2.2×10^{7} joules per kilogram for coated columbium and tantalum, respectively. Free stream gas velocity was about Mach 6. The average exposure temperatures were about 1390° C for coated columbium alloys and about 1470° C for coated tantalum as calculated and discussed in the appendix.

At the end of scheduled one or five cycle exposures, or periodically during longer time exposures, the specimens were measured for surface recession, weighed to follow oxidation behavior, and photographed to follow general macroscopic behavior.

Visual Changes

Photographs taken after the exposures recorded the extent of visible coating/substrate degradation. The specimens were visually examined during their test schedule only to the extent necessary to determine when a specimen was near its useful limit. Such specimens were removed from the test.

Weight Changes

All the specimens were characterized as to their total weight, coating weight, average coating thickness before exposure, and, where warranted, after exposure.

Tensile Specimens

Subsize tensile specimens (fig. 4) were made from selected as-received and exposed specimens by electrode discharge machining. These were used to determine if there was a significant change in alloy room temperature strength and ductility as a result of exposure.

Surface Chemistry and Structure

Selected specimens were analyzed by surface X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and electron microprobe raster micrograph techniques. Phases in the coatings and oxides and qualitative changes in element distributions were determined.

Exposed specimens were sectioned through the defected area, the center of the specimen, or some other area of interest and then examined by optical metallographic and EMP raster micrographic techniques to determine the response of the coatings to the plasma arc environment. Coating-substrate interdiffusion zones were measured at a ×500 magnification with a filar micrometer. Growth of these zones was compared with their growth in as-received specimens which were annealed in a furnace at two selected temperatures and times. This was done to confirm the plasma arc test temperature and determine the magnitude of temperature variations over the test model.

RESULTS AND DISCUSSION

Coated Columbium

Visual changes. - Photographs of R512E coated FS-85, C-129Y, and Cb-752 specimens after plasma arc exposure are shown in figures 5 to 7. All FS-85 specimens and the defected C-129Y and Cb-752 specimens were exposed for the scheduled number of cycles. The nondefected Cb-752 and C-129Y specimens (fig. 5) all suffered local coating breakdowns at edges and were removed from the test earlier than the scheduled 25 or 50 cycles. Average temperatures at three radial positions are shown in figure 5.

Before exposure, the R512E coated columbium alloys (FS-85, Cb-752, and C-129Y) had a light gray matte appearance as can be seen from figures 1(a) to (c). After exposure there were four discernable trends in specimen appearance. The first trend was due to the substrate. At short times the substrates ranked according to oxide color as follows: C-129Y (darkest), Cb-752, and then FS-85 (lightest). A second trend was the variation in specimen color with radial position. Oxides formed nearer the hotter arc

center were lighter than those formed farther out. Third, from the appearance of the specimens exposed for more than 20 cycles (fig. 5), it is apparent that the radial edges were effected more by the exposures than the body of the specimen. This indicates that the edges reached higher temperatures than the central portion of the specimens. Finally, the back side of all specimens showed this edge effect as can be seen from figure 8. The oxide formed at the edges as a result of flow under the specimens was nearly white, whereas the bulk of the specimen is covered by a dull uniform brown to black oxide. This dark oxide is similar to the oxides formed on R512E coated columbium in low pressure, slow cycle air exposures in a furnace at about 1300° C (ref. 1).

Local coating breakdowns were initiated at specimen edges. Failures at edges are not surprising in this test since the edges were observed to run hotter than the surfaces. Also, the specimens were coated prior to development of the edge-striping technique for uniformly coating edges and alleviating the edge failure problem observed on thin coated refractory metals (ref. 1).

As is evident from figures 6 and 7, catastrophic growth of the defects in coated columbium does not occur under the temperature and flow conditions of this series of exposures. The impact and coating removal damaged specimens did not develop through holes as a result of oxidation. The through-hole and edge notch defects tended to seal as a result of oxidation of the substrate.

Weight changes. - The coated Cb-752 and C-129Y specimens generally showed large weight losses after 12 to 18 exposure cycles indicating coating failure and substrate metal recession at edges. The FS-85 specimens showed relatively stable weights after an initial rapid weight gain except when tabs were lost.

Tensile test results. - Results of tensile tests on as-coated and plasma arc tested coated columbium alloys are presented in figure 9. The short gage length of the tensile specimen and the friction gripping method did not permit instrumentation to determine an accurate yield strength. All exposed tensile specimens were cut so that there was no region of oxygen ingress at the gage sections as a result of coating breakdown or intentional defects.

All three columbium alloys with the R512E coating show excellent retention of tensile strength and ductility up to 25 cycles. In terms of time at peak temperature, 25 cycles correspond closely to a 100 reentry mission life. After 50 exposure cycles, the R512E coated FS-85 system shows a loss of strength and ductility. However, the 20-percent loss in tensile strength is due primarily to a 15-percent reduction in load bearing substrate thickness as a result of silicon diffusion.

Defect growth. - The four types of intentional coating damage (through-hole, coating removal from the upper surface, impact damage, and edge notching) did not produce serious columbium substrate degradation in up to five plasma arc exposure cycles. Only the growth of the through-hole defect was followed quantitatively. The increase in diameter of the defect as a result of substrate oxidation is plotted in figure 10 - the defect

diameter increased only 0.02 to 0.1 centimeter. This is comparable to the metal recession observed at through-hole defects in a static furnace environment (refs. 1 and unpublished information obtained from J. D. Culp, et al., McDonnell-Douglas Astronautics Co., under NASA contract NASA 3-15546). The through-hole defects tended to plug with substrate oxide. After five cycles, the defect in FS-85 was completely plugged with oxide as shown in the ×75 scanning electron micrograph (fig. 11). For the three alloys, the other three coating defect types underwent slight growth in up to five exposure cycles. Examples of oxidation at surface coating removal defects are illustrated in figure 12. Here, a through-hole was not developed in R512E coated FS-85 after five plasma arc exposures. Extensive cracking of the coating and interstitial oxygen contamination of the substrates occurred at the impact damage sites as illustrated by the microstructures of R512E coated FS-85 in figure 13. However, very little substrate oxidation occurred.

Surface chemistry. - In situ XRD analyses of the as-deposited R512E coating on FS-85, C-129Y, and Cb-752 detected hexagonal MSi_2 and M_5Si_3 phases similar to $CbSi_2$ and Cb_5Si_3 (table II). In all cases several weak unaccounted for lines were also detected. XRD analyses of the three systems after plasma arc exposure indicated that the primary oxide phase was highly modified Cb_2O_5 or $Cb_4Ta_2O_{15}$ with a monoclinic structure (table II).

In situ XRF analyses indicated a relatively stable surface chemistry with respect to the nonvolatile oxide formers: columbium and tantalum, table III. Although an analysis was not performed, the same is expected to be true for zirconium, hafnium, and yttrium. The volatile oxide formers (tungsten and chromium) generally showed decreasing surface concentration with increasing exposure time. The same is true for iron concentration. Thus, the modifier elements in Cb_2O_5 were primarily those found in the respective substrates.

Lines attributable to silica were detected in XRD and XRF analyses of all oxidized specimens. Their relative intensity increased with exposure time.

The R512E coated FS-85 system also formed a modified $MCbO_4$ phase. This phase was not detected on R512E coated Cb-752 and was not conclusively identified on R512E coated C-129Y. The $MCbO_4$ phase is generally found after furnace exposure of these coated systems (ref. 1). The ability of R512E coated FS-85 to form this phase in the plasma arc may be responsible, in part, for the superior performance of this system.

Oxide morphology. - Scanning electron micrographs of R512E coated FS-85 and C-129Y are presented in figure 14. Scanning electron micrographs of R512E coated Cb-752 were similar to R512E coated FS-85. The network of hairline cracks produced during the coating firing cycle is evident on both ×300 photographs. Their presence is not critical to overall coating performance although these cracks may play a significant role in premature failure at the edges of coated thin sheet.

The R512E coated C-129Y has a generally finer texture but less uniformity and more large pits than R512E coated FS-85. The surface structure of coated C-129Y can be broken down into two areas: fine textured areas covering most of the surface, and coarser textured areas as typified by the lower center of the ×300 photograph. The fine texture is attributed to acicular silicide crystals oriented normal to the surface, and the coarser texture is attributed to crystals oriented parallel to the surface. Less evidence of an acicular structure is apparent on R512E coated FS-85 and Cb-752.

Figure 15 shows the oxidized surfaces near the forward edge of R512E coated FS-85 after 1, 5, 25, and 50 plasma arc exposure cycles. After one cycle, the surface is 90 percent covered with needle-like oxide particles. After five cycles, the oxide needles agglomerate into bundles covering about 60 percent of the surface. The additional exposure also increases the coarseness of the needles. The 25 and 50 cycles of exposure result in further agglomeration of the needles. A lacy oxide is formed in the gaps between the bundles and over spalled areas.

The oxidation process is both time dependent, as just described, and temperature dependent. Comparison of forward and rear areas of any specimen generally revealed the following: the needle height and size, the extent of oxide agglomeration into bundles, and the extent of formation of lacy oxides between bundles is much less at the cooler rear of the sample than at the front.

A comparison of oxides formed after five plasma arc exposure cycles on the three coated columbium alloys is shown in figure 16. The oxides on FS-85 and Cb-752 are similar except for the degree of agglomeration of needles, while the oxide on C-129Y (fig. 16) still resembles the original coating structure. Evidence of either spalling or inhomogeneity of the coating is evident in the upper left corner of 16(c).

Figure 16(d) shows an example of spalling at the edge and on the surface of R512E coated C-129Y after five plasma arc exposure cycles. This was also found with the other substrates. Spalling at the edges may be partially responsible for premature coating failures.

A second cause for edge failures, as mentioned earlier, was the tendency for the edges to run hotter than the major surface at the same radial position. This is revealed by the coarser oxide needles found at the edge location (fig. 16(d)) compared to the surface location (fig. 16(c)).

Metallography and EMP analysis. - Cross section photomicrographs of the R512E coating as deposited on FS-85, Cb-752, and C-129Y are presented in figure 17. All three coatings are nominally 0.09 millimeter thick. For the convenience of discussion, the coating is divided into three major zones labeled 1, 2, 3 (outer, middle, diffusion). The mount, substrate, and oxide (where present) are labeled M, S, and O, respectively. The coarse surface features seen in the SEM micrographs are apparent in the coating cross sections. The R512E coating is smoother on C-129Y than on the other two substrates.

Zone 1 generally has a thin outer skin caused by depletion of volatile constituents during the 1-hour coating firing cycle at 1415° C. The major part of zone 1 consists of large, generally equiaxed grains of the MSi_2 and M_5Si_3 phases. With the exception of the outer skin, the darker etching material in zone 1 is rich in chromium and iron as revealed by X-ray raster micrography. The lighter etching major phase consists of disilicide rich in elements derived from the respective substrates. Zone 2 has a columnar structure and is rich in chromium and iron. Zone 1 is richer in chromium than iron, the opposite holds true for zone 2.

Zone 3 consists of two sublayers. The thicker outer layer is single phase in FS-85 and heavily loaded with second phase particles in C-129Y and Cb-752. The EMP line scans detected no silicon gradient across the outer band of zone 3 whereas the inner darker etching band exhibited a silicon concentration gradient. The growth of this layer was used to estimate the temperatures of specimens subjected to plasma arc exposure. The growth of this layer was characterized by exposing coated specimens in a furnace for temperatures and times spanning the plasma arc exposure conditions.

Figure 18 shows the microstructures of coated FS-85 after 1, 5, 25, and 50 cycles of plasma arc exposure. After one cycle, as shown in figure 18(a), the surface oxide consists primarily of small crystals of two oxide phases. An exposure for five cycles, figure 18(b), gives a coarsened oxide structure richer in dark oxide (SiO_2). The agglomerated light colored surface oxide is $Cb_4Ta_2O_{15}$ as revealed by EMP raster micrographs and XRD analysis. Appreciable tungsten and chromium were also present in this oxide. Except for some internal oxidation and a reduction in the thickness of zone 1, no great change in overall coating structure or composition occurs in up to five plasma arc exposure cycles.

After 25 plasma arc exposure cycles, as shown in figure 18(c), zone 1 of the R512E coating on FS-85 is further consumed while zone 3 and the surface oxide thickness increased considerably. The light $Cb_4Ta_2O_{15}$ phase is now present as coarse particles. The dark continuous oxide is now clearly the major oxide phase. This was observed as the lacy oxide between bundles of coarse sintered light oxide needles in the SEM micrographs. The EMP raster micrographs revealed depletion of iron and chromium from zone 1 of the coating. The oxide formed on the under side of the plasma arc exposed specimens was about one-third the thickness of that formed on top. It was essentially SiO_2 with some isolated particles of coarse refractory metal pentoxide still present. Less coating depletion occurred on the bottom surface than on the top surface.

An exposure for 50 cycles results in additional growth of zone 3, essentially no change in the thickness of zone 2, and continued depletion of zone 1 as shown in figure 18(d). Extensive porosity in zone 2 is now evident. The surface oxide thickness did not change appreciably from that at 25 cycles.

Photomicrographs of R512E on Cb-752 after 5 and 22 cycles and on C-129Y after 5 and 24 cycles are shown in figure 19. The rate of surface oxide formation on R512E in combination with these substrates, the amount of Cb_2O_5 formed or retained, and the degree of columbium oxide segregation in the surface oxide are greater than on FS-85. The Cb_2O_5 formed on R512E coated C-129Y showed a strong tendency to orient perpendicular to the surface whereas with the other systems orientation was parallel to the surface. The EMP raster micrographs detected the presence of hafnium in the Cb_2O_5 on C-129Y. The oxide coating interface in the R512E coated C-129Y system is more irregular than with the other substrates.

All three coated columbium systems show very little oxidation widening of natural coating cracks in contrast to the behavior commonly found in slow cycle furnace exposures. Whether this is caused by lower permeability of the oxides formed in the plasma arc as a result of exposure temperatures that were higher than projected use and furnace test temperatures or by the lack of significant time at intermediate temperatures as a result of the square wave heating cycle is indeterminate.

Coated Tantalum

Visual changes. - Photographs of coated Ta-10W specimens after plasma arc exposure at 1470° C are shown in figures 20 to 22. Average temperatures at several radial locations are indicated in figure 20. The SA-13 and NS-4 coatings changed from a uniform brown to a spectrum of colors (yellows, greens, browns) after exposure. In low pressure air/slow cycle furnace exposures, the color is a hue of browns depending on the length of exposure and air pressure. The TMS coating changed from a metallic light gray to much darker colors than the SA-13 and NS-4 coatings. With the TMS coating, low pressure/slow cycle furnace exposure causes the metallic light gray coating to change to a glossy dark gray depending on the length of exposure and air pressure.

Unlike the coated columbium specimens, there was not a clear trend in coating appearance after exposure. The combination of higher exposure temperatures, less developed coating systems, and the rapid rate of tantalum oxide formation once the coating failed all contributed to the inconsistencies in the visible coating changes that took place in the first few cycles. Figures 20 to 22 show this variability, especially where extensive substrate oxidation and oxide removal by the high mass flow occurred. Four specimens which were exposed at a lower temperature (1390° C) for 5 to 32 cycles prior to exposure at a higher temperature (1470° C) for 1 to 3 cycles are shown in figure 20. They appear different from those specimens exposed only at the higher temperature with the combined exposures producing a glassier surface oxide.

Weight change. - Eighteen of the twenty-four Ta-10W specimens were intentionally damaged before exposure. Of these, ten specimens were exposed for one cycle and the

weight change recorded. The weight gain for these ten specimens varied from 20 to 148 milligrams depending on the coating, the damage type, and the amount of substrate loss. Only two undamaged specimens were weighed after five exposure cycles. These specimens, coated with SA-13 and NS-4, had weight gains of 20 and 55 milligrams, respectively.

Tensile test results. - The room temperature ultimate tensile strengths and elongations after five plasma arc exposures for the SA-13 and NS-4 coated Ta-10W alloy (fig. 23) are typical of those found in laboratory low air pressure/slow cycle environments for SA-13 coated Ta-10W alloy after 20 cycles (ref. 2). The SA-13 specimens after one cycle at 1425° and 1540° C, in the laboratory environment, show an immediate 25-percent loss of ultimate tensile strength with the elongation going to 1 to 2 percent from 12 to 16 percent. However, after 20 cycles at these temperatures, the ultimate tensile strength returns to the as-coated strength of around 6.5×10^2 meganewtons per square meter with an elongation of 7 to 13 percent. The changes in ultimate tensile strength and elongation of TMS coated Ta-10W specimens are not as pronounced as with the other two coatings.

Defect growth. - In the plasma arc exposures, most defected tantalum specimens and those specimens which failed prematurely exhibited rapid substrate metal recession and exfoliation of tantalum oxide in a few cycles. This is illustrated by the growth of through-hole defects in SA-13 and TMS coated Ta-10W (fig. 24). In general, the glassy oxide forming TMS coating afforded more protection at coating defects than the SA-13 coating. The difference in behavior was most pronounced in the through-hole coating removal and edge notch damaged specimens and was less pronounced in impact damaged specimens. The growth of through-hole defects in TMS coated Ta-10W is compared with results for SA-13 in figure 24. In one instance the defect healed (as shown in fig. 25); in the other it grew at a rate comparable to defects in SA-13 coated Ta-10W. Comparison of defect growth in SA-13 coated Ta-10W at its test temperature with defect growth in columbium alloys at their test temperature (fig. 24) reveals the severity of the coating defect problem with coated Ta-10W. The intolerance of the substrate to coating defects makes the multimission usefulness of coated Ta-10W questionable.

Surface chemistry. - The as-received coatings on Ta-10W consisted of an MSi_2 phase and a lower silicide as listed in table IV. The NS-4 and SA-13 coatings had SiO_2 and tantalum containing oxide phases present on the surface as a result of preoxidation treatments at 1425° C for 1 hour in air. In the plasma arc tests, the three systems lost some of their volatile oxide formers (Si, Cr, Mo, and W) and high vapor pressure constituents (Cr, Mn, V) from the surface region as shown in table V. The surface chemistries of the NS-4 and TMS coatings which were designed to be relatively free of tantalum were less stable in the plasma arc tests than SA-13 with regard to the nonvolatile oxide formers (tantalum and titanium). The surface region of the TMS system which

started as an essentially $TiSi_2$ plus TiSi coating became richer in tantalum and leaner in titanium with plasma arc exposure time. The primary oxide phases formed were TiO_2 and SiO_2. The surface region of the NS-4 system became richer in tantalum and titanium and primarily formed SiO_2 and $TiTa_2O_7$. The SA-13 system still has SiO_2 and $CrTaO_4$ as primary oxide phases after one cycle. Both phases were depleted after exposure for five cycles and Ta_2O_5 and $TiTa_2O_7$ formed.

Oxide morphology. - The TMS coating had a rough texture and characteristic coating microcracks in the as-received condition (fig. 26(a)). After one exposure cycle (fig. 26(b)), silica containing pores and TiO_2 inclusions were formed in the hotter forward areas. After five cycles (fig. 26(c)), the relative amount of TiO_2 increased. Fusion of the oxide appears to have occurred. The fact that SiO_2 and TiO_2 form a eutectic liquid at about 1550° C (ref. 9) gives some indication of the actual exposure temperature. In cooler rear areas the oxidized surface bore a closer resemblance to the original coating. After one cycle the predominant silica phase was primarily located in depressions between coating particles. TiO_2 was the predominant phase after five cycles and the silica was extensively crazed.

The as-received NS-4 coating had a relatively smooth surface texture with characteristic coating microcracks (fig. 27(a)). After five cycles evidence of oxide fluidity is present (fig. 27(b)). The major oxide, $TiTa_2O_7$, melts congruently at about 1660° C, and TiO_2 can form a eutectic liquid with SiO_2 at 1550° C (ref. 8). At a higher magnification the light colored areas are revealed to have a coral-like microstructure.

The SA-13 had the roughest surface texture of the three coatings used to protect Ta-10W (fig. 28(a)). After one plasma arc exposure the texture was somewhat smoother. Some evidence of oxide fluidity is present after one and five cycles (figs. 29(b) and (c)), respectively).

Metallography and EMP analysis. - Photomicrographs of the TMS coating on Ta-10W in the as-received condition and after one and five cycle exposures are shown in figure 29. The mount, oxide, coating, and substrate are labeled M, O, C, and S, respectively. The initial nominal coating weight was 29 milligrams per square centimeter, and the initial nominal coating thickness was 0.08 millimeter. The large grained, heavily etched outer stratum of the as-received coating is rich in titanium, manganese, and silicon. The intermediate columnar region, which also etched heavily, is rich in titanium, tantalum, tungsten, and silicon. The inner columnar region is a tantalum and tungsten rich silicide. After one cycle a thick modified silica layer forms. Particles of the outer coating stratum and TiO_2 are included. After five cycles only a thin oxide scale rich in titanium, tantalum, and silicon and containing little manganese is retained. The residual coating also retains little manganese and has a relatively uniform titanium distribution.

The heavy NS-4 coating (60 to 80 mg/cm^2) is shown in figure 30 after five cycles of plasma arc exposure. The internally oxidized and intact coating layers remain relatively

thicker than the comparable layers on the TMS and SA-13 coatings (figs. 29(c) and 31(c), respectively).

The 0.1-millimeter-thick preoxidized SA-13 coating, as shown in figure 31(a), already exhibits appreciable internal oxidation. The sample exposed for one cycle (fig. 31(b)) has a very thick oxide consisting of modified silica as the continuous phase. The microstructure of the sample after five cycles of exposure (fig. 31(c)) does not appear to be derived from that of the sample exposed for one cycle. This is probably due to a significant difference in specimen exposure temperatures with the specimen exposed for one cycle seeing a higher average temperature. The thin surface oxide retained on the sample exposed for five cycles contains either Ta_2O_5 or $TiTa_2O_7$. The intermediate dark band is modified silica. The multiphase oxide adjacent to the coating contains all of the constituents initially present in the coating. Extensive internal oxidation of the coating is apparent.

Oxidation widening of natural coating microcracks was not observed in any of the three coated Ta-10W systems. All three systems appear to have significant residual coating life after five cycles of exposure. However, local coating breakdowns caused by overheating or imperfections in the coating and resultant rapid rates of metal recession made additional testing of these systems unwarranted under the test conditions used.

CONCLUDING REMARKS

The average test temperature for R512E coated columbium alloy specimens was about 1390° C. This average temperature was 130° C above the intended test temperature. Taking this into consideration, the coated columbium specimens, and in particular R512E coated FS-85, performed satisfactorily from the standpoint of times to first local coating breakdown and rate of metal recession at coating defects. The range of times to first local coating breakdown for R512E coated FS-85 (12 to 50 cycles) corresponds in time at peak temperature to about 35 to 150 atmospheric reentry exposures. However, the emittance of R512E coated columbium alloys was reported to be at low levels - 0.5 to 0.75 (ref. 6). These values are considerably below the range of 0.8 to 0.9 determined in static furnace exposures (ref. 1), but they are in good agreement with an emittance of about 0.65 to 0.70 reported for R512E coated FS-85 after 10 reentry simulation profile plasma arc exposures to a temperature of 1290° C (ref. 9) and an emittance of 0.58 reported for R512E coated Cb-752 exposed in a plasma arc for one 30-minute cycle at 1465° C (ref. 10). In view of the fact that the surface oxide layer formed in the plasma arc is Cb_2O_5 (or $Cb_4Ta_2O_{15}$ in the case of FS-85) with a reported emittance of 0.7 (ref. 11), the cited plasma arc emittance results (refs. 6, 9, and 10) are considered to be more indicative of the emittance behavior of R512E coated columbium

during reentry than the reported emittance behavior for furnace exposures (ref. 1). Formation of surface refractory metal pentoxides was due to rapid losses of chromium and iron from the oxide and coating. The severity of the loss of coating constituents in plasma arc exposure and the associated loss in emittance is probably exaggerated to some extent by testing at temperatures higher than the anticipated use temperature. Further characterization and alleviation of this problem should be a primary objective of any future tests of coated columbium alloys.

The average test temperature for coated Ta-10W specimens was about 1470° C. This was 45° C above the intended test and use temperature. The SA-13 and NS-4 coatings protected Ta-10W for five cycles. The TMS coating developed local coating breakdowns in as little as one cycle. Unacceptably high rates of metal recession at local coating breakdowns and intentional coating defects were observed for Ta-10W. This factor makes the viability of coated tantalum, even for limited heat shield applications, very questionable.

SUMMARY OF RESULTS

Thin sheet samples of columbium alloys FS-85, Cb-752, and C-129Y coated with R512E and of Ta-10W coated with TMS, SA-13, and NS-4 were screened using half-hour cycle stagnation model plasma arc tests at 6.5×10^2 newtons per square meter (4.9 torr) air pressure and free stream gas velocities of about Mach 6. As-coated and intentionally defected coated columbium alloy specimens were scheduled for up to 50 and 5 cycles of exposure respectively at 1260° C. As-received and intentionally defected coated Ta-10W specimens were scheduled for up to 25 and 5 cycles of exposure respectively at 1425° C. Actual average exposure temperatures were about 1390° C (130° C higher than the planned test temperature or the nominal intended use temperature for a coated columbium TPS) for coated columbium alloys and about 1470° C (45° C higher than planned) for the coated tantalum alloy. The following results were obtained for R512E coated columbium alloys:

1. The best R512E coated columbium alloy was FS-85 with times to first local coating breakdown of 12, 30, and greater than 50 cycles. First local coating breakdown occurred on R512E coated Cb-752 and C-129Y in 6 to 18 cycles at a temperature 130° C higher than the intended use temperature.

2. Metal recession rates of less than 0.005 millimeter per minute were observed at intentional defects in coated columbium alloys. This is comparable to the low rates of metal recession reported for static furnace tests.

3. The off-white oxide surface scales formed on R512E coated columbium were depleted in chromium and iron compared to the as-deposited coating. The principal oxides

formed were Cb_2O_5 or $Cb_4Ta_2O_{15}$ and SiO_2. The coating elements lost and the oxides formed account for the reported emittance (ref. 6) being generally less than 0.7.

The following results apply to both coated columbium alloys and coated Ta-10W:

1. All local coating breakdowns initiated at specimen edges.

2. Where the coatings remained intact, they protected the alloys from significant loss of strength and ductility.

The following results pertain to coated Ta-10W only:

1. The SA-13 and NS-4 coatings were protective for five cycles, whereas the TMS coating performed erratically with local coating breakdowns occurring in as little as one exposure cycle.

2. High metal recession rates (about 0.15 mm/min) were generally observed at intentional coating defects and local coating breakdowns. Erratic self-healing was observed with the TMS coating.

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U.S. Army Air Mobility R&D Laboratory,
Cleveland, Ohio, December 14, 1973,
501-01.

APPENDIX - ARC TUNNEL TEST TEMPERATURES

Average values of heat flux, measured backwall thermocouple temperature, and primary and secondary optical pyrometer temperature are presented in table VI for each coating/substrate combination. A more detailed breakdown of these data is given in reference 6. The backwall thermocouples indicated temperatures which were estimated to be 55° C too low for columbium specimens and 30° C too low for tantalum specimens because of heat sink effects, poor contact with the specimens, and contamination by silicon derived from the coatings (private communication with J. S. Schaefer of the Aerotherm Division/Acurex Corporation). The average corrected thermocouple temperature for the columbium specimens was 1390° C (with a range from 1365° to 1435° C). The average secondary pyrometer reading was 1325° C (with a range from 1260° to 1390° C). The emittance sensitive primary pyrometer indicated an average temperature of 1235° C (with a range from 1165° to 1275° C). Emittance values ranging from 0.5 to 0.75 were estimated from indicated temperatures (ref. 6).

Laboratory diffusion zone growth measurements were used to augment the temperature measurements made during the plasma arc screening tests. Untested specimens were cut into small segments and annealed in vacuum at NASA-Lewis Research Center for times and temperatures spanning the range of plasma arc exposures. For R512E on C-129Y, Cb-752, and FS-85, diffusion anneals were conducted at 1215° and 1425° C for 2 and 12 hours. The specimens were then prepared in the standard manner for metallography. Measured diffusion zone growth data were used to estimate parameters in equations of the form

$$X^2 - X_o^2 = At \exp\left(\frac{-Q}{RT}\right)$$

where X_o is the diffusion zone thickness after coating application, X the diffusion zone thickness after exposure, A a rate constant in micrometer squared per hour, t time in hours, Q activation energy in joules per mole, R gas constant in joules per $^{\circ}$K-mole, and T absolute temperature in $^{\circ}$K. The parameters estimated from the diffusion couples are as follows:

Alloy	Diffusion zone thickness after coating application, $X_{o,}^2$ μm^2	Rate constant, A, $\mu m^2/hr$	Activation energy, Q, J/mole
C-129Y	13.4	1.5×10^2	1.58×10^5
Cb-752	21.9	8.0×10^3	2.11
FS-85	18.5	5.53	2.03

Average diffusion zone thicknesses and computed temperatures for each level of exposure and each alloy are listed in table VI. The computed average columbium specimen temperature based on diffusion zone growth measured at all locations was 1380° C. The average peak specimen temperature based on diffusion zone growth at front and center locations was 1410° C (with a range from 1345° to 1485° C). These results are in good agreement with the estimated corrected plasma arc backwall thermocouple temperature of 1390° C (with a range from 1365° to 1435° C). Based on these results the coated columbium specimens were exposed to an average temperature of about 1390° C. The forward areas of the specimens were about 10° C hotter.

The average corrected backwall thermocouple temperature was 1470° C (with a range from 1440° to 1495° C), and the average secondary pyrometer temperature was 1450° C (with a range from 1410° to 1520° C) for coated Ta-10W specimens. The emittance sensitive primary pyrometer average temperature was 1390° C (with a range from 1325° to 1425° C). Evidence of oxide melting, as discussed earlier, indicates that local temperatures at least as high as 1550° C were reached.

Diffusion anneals of as-received SA-13 and TMS coated Ta-10W were run for 1 and 5 hours at either 1425° or 1540° C. The data were fit to the same equation as used for columbium. The following values of the parameters were obtained.

Coating	Diffusion zone thickness after coating application, X_{o}^2, μm^2	Rate constant, A, $\mu m^2/hr$	Activation energy, Q, J/mole
SMT	27.8	1.22×10^4	1.99×10^5
SA-13 (estimated values)	40.3	9.24×10^4	2.28×10^5

The parameters for the SA-13 system are considered unreliable since the diffusion couples were taken from a specimen that appeared to have a different preoxidation treatment than normal. Use of the equation with these parameters, however, was assumed to give reasonable estimates of relative temperatures on SA-13 and NS-4 specimens but inaccurate estimates of absolute temperatures. Using computed temperature estimates for TMS coated Ta-10W only, the average specimen temperature was 1460° C and the average peak temperature was 1475° C (with a range from 1365° to 1535° C). These values are in reasonable agreement with the estimated corrected backwall thermocouple temperature of 1465° C (with a range from 1435° to 1490° C) for SA-13 specimens (ref. 6). Based on these results the average test temperature for coated Ta-10W was about 1470° C. The forward areas of the specimens were about 10° C hotter.

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TABLE I. - ALLOY AND COATING COMPOSITIONS SCREENED

Alloy designation and composition	Coating designation and composition	Slurry coating - application method	Coating firing	Average fired coating weight and thickness
Columbium alloy: FS-85 (Cb-28Ta-10W-1Zr) Cb-752 (Cb-10W-2.5Zr) C-129Y (Cb-10W-10Hf-0.1Y)	R512E (Si-20Cr-20Fe)	Dip and spray edges	1-hr at 1415° C fusion-diffusion treatment in vacuum (10^{-4})	22 Mg/cm^2; 0.009 cm (~0.003 in.)
Tantalum alloy: Ta-10W	SA-13 (Si-20Cr-10Ti-4Mo-4W-2V)	Spray	5-min at 1525° C fusion-diffusion treatment in vacuum (10^{-5}); preoxidized in air for 1 hr at 1425° C	24 to 30 Mg/cm^2; 0.008 to 0.01 cm (~0.003 in.)
Tantalum alloy: Ta-10W	TMS (Si-2.5Mn-33Ti)	Spray	1-hr at 1400° C fusion-diffusion treatment in helium	28 to 30 Mg/cm^2; 0.008 cm (~0.003 in.)
Tantalum alloy: Ta-10W	NS-4 Modifier: 50W-20Mo-15Ti-15V Pack: Silicon	Spray modifier and sinter; pack silicide	Sintering cycle: 1510° to 1620° C for 15 hr vacuum (10^{-5} to 10^{-6}) Silicide cycle: 1175° C for 15 hr; preoxidized in air for 1 hr at 1425° C	60 to 80 Mg/cm^2; 0.010 to 0.013 cm (~0.004 to 0.005 in.)

TABLE II. - X-RAY DIFFRACTION ANALYSES OF R512E COATED COLUMBIUM ALLOYS - AS-COATED AND AFTER PLASMA ARC EXPOSURE AT 1390° C

Substrate	Exposure, cycles	Phases detected[a]				
		MSi_2	M_5Si_3	Cb_2O_5	$MCbO_4$	SiO_2
FS-85	0 1 5 25 50	↓	↓	↑[b]	↑	↑
Cb-752	0 1 5 22	↓	↓	↑		↑
C-129Y	0 1 5 24	↓	↓	↑	↑	↑

[a]Relative amount increases with exposure time, ↑; relative amount decreases with exposure time, ↓; uncertain identification, ¦.

[b]$Cb_4Ta_2O_{15}$ and Cb_2O_5.

TABLE III. - X-RAY FLUORESCENCE DATA[a] FOR COLUMBIUM ALLOYS - BARE, AS-COATED R512E, AND AFTER PLASMA ARC EXPOSURE AT 1390° C

Substrate	Condition	Elements							
		Columbium	Tungsten	Tantalum	Zirconium	Hafnium	Silicon	Chromium	Iron
FS-85	Bare	10 200	325	1821	160	NA[b]	16	9	31
	As-coated	9 309	443	1109	77	↓	1171	318	226
	After exposure, cycles:								
	1	9 791	143	1244	NA	↓	311	79	100
	5	9 621	143	1193	↓	↓	548	141	64
	25	9 631	125	1226	↓	↓	665	62	72
	50	9 817	114	1236	↓	↓	697	55	57
Cb-752	Bare	21 476	335	7	935	NA	NA	NA	24
	As-coated	17 282	239	NA	295	↓	1709	342	221
	After exposure, cycles:			↓					
	1	17 920	164	↓	NA	↓	519	117	98
	5	17 931	159	↓	NA	↓	729	178	73
	22	16 144	131	↓	NA	↓	803	115	71
C-129Y	Bare	16 604	316	NA	NA	788	NA	NA	NA
	As-coated	15 712	254	↓	↓	306	1444	313	271
	After exposure, cycles:								
	1	16 376	129	↓	↓	NA	316	81	172
	5	17 353	137	↓	↓	NA	188	69	54
	24	17 155	135	↓	↓	NA	355	79	49

[a]Total counts minus background.
[b]Element not analyzed, NA.

TABLE IV. - X-RAY DIFFRACTION ANALYSES FOR COATED Ta-10W - AS-RECEIVED AND AFTER PLASMA ARC EXPOSURE AT 1470° C

Coating	Exposure, cycles	Phases detected[a]							
		MSi_2	MSi	M_5Si_3	SiO_2	TiO_2	$TiTa_2O_7$	$CrTaO_4$	Ta_2O_5
TMS	0	↓	↓						
	1	↓	↓	↑	↓	↑			
	5	↓	↓	↑	↓	↑			
NS-4	0	↓		↑	↑		↑		↑
	5	↓		↑	↓		↑		↑
SA-13	0	↓		↑	↑		↑	↑	↑
	1	↓		↑	↓		↑	↑	↑
	5	↓		↑	↓		↑	↑	↑

[a]Relative amount increases with exposure time, ↑; relative amount decreases with exposure time, ↓; uncertain identification, ⇡.

TABLE V. - X-RAY FLUORESCENCE DATA[a] FOR Ta-10W - BARE, AS-RECEIVED AFTER COATING PROCESSING, AND AFTER PLASMA ARC EXPOSURE AT 1470° C

Coating	Condition	Elements							
		Tantalum	Tungsten	Silicon	Chromium	Titanium	Manganese	Vanadium	Molybdenum
None	Bare	3924	223	NA[b]	NA	NA	NA	NA	NA
TMS	As-coated	480	115	2024	NA	13 198	391	NA	NA
	After exposure, cycles:								
	1	580	42	3717	NA	11 517	21	NA	NA
	5	1354	20	1019	NA	9 021	10	NA	NA
NS-4	As-coated and preoxidized	102	986	4702	NA	505	NA	293	3575
	After exposure, cycles:								
	5	1472	534	1779	NA	867	NA	32	2401
SA-13	As-coated and preoxidized	1800	412	1075	1166	1 596	NA	71	317
	After exposure, cycles:								
	1	1763	165	2575	362	1 502	NA	48	605
	5	2287	97	1675	206	1 403	NA	5	328

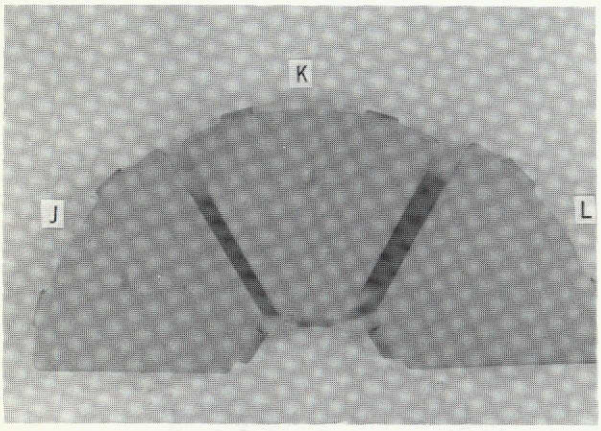
[a]Total counts minus background.
[b]Element not analyzed, NA.

TABLE VI. - PLASMA ARC TEST CONDITIONS

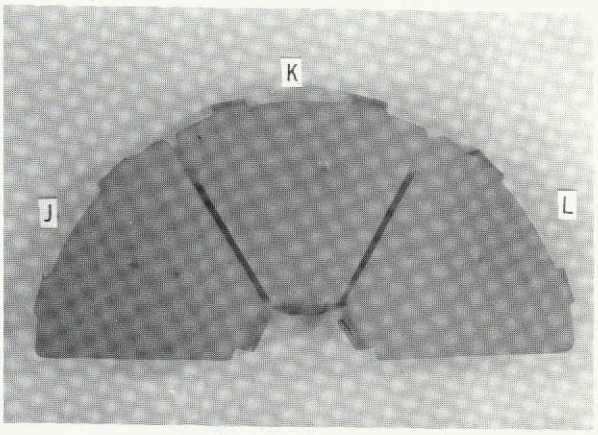
[All temperatures rounded to 5° C.]

Coating	Substrate	Average measured values					Exposure, cycles	Diffusion zone growth							
		Heat flux, J/m^2-sec	Back wall temperature, °C	Pyrometer temperature, °C		Total gas enthalpy, J/kg		Front of specimen		Center of specimen		Rear of specimen		Average 2σ, m	Total number of observations
				Primary	Secondary			Average diffusion zone, μm	Computed temperature, °C	Average diffusion zone, μm	Computed temperature, °C	Average diffusion zone, μm	Computed temperature, °C		
R512E	C-129Y	$(4.7\pm0.5)\times10^5$	1325±15	1255±20	1340±45	$(2.6\pm0.35)\times10^7$	1	4.2	1430	4.0	1360	4.0	1360	1.3	28
							5	5.4	1385	5.1	1355	4.2	1215	1.2	22
							18 to 24	----	1365	----	1345	----	----	1.2	8
							Average	----	1400	----	1355	----	1285	1.2	--
	Cb-752	$(4.7\pm0.5)\times10^5$	1325±45	1325±35	1325±65	$(2.6\pm0.35)\times10^7$	1	5.3	1440	5.1	1395	5.1	1395	1.2	28
							5	7.1	1430	6.8	1410	6.2	1370	1.3	22
							18 to 24	----	1410	----	1415	----	----	1.4	8
							Average	----	1425	----	1405	----	1385	1.3	--
	FS-85	$(4.7\pm0.6)\times10^5$	1350±35	1225±60	1315±55	$(2.6\pm0.45)\times10^7$	1	5.1	1445	4.8	1465	4.5	1285	1.2	28
							5	7.3	1435	7.1	1425	5.4	1305	1.4	22
							25	13.3	1425	14.0	1440	----	----	2.4	4
							50	15.0	1375	16.7	1485	----	----	1.0	6
							Average	----	1420	----	1455	----	1295	1.4	--
TMS	Ta-10W	[a]$(5.7\pm1)\times10^5$	-------	[a]1365±50	[a]1465±55	[a]$(6.9\pm0.2)\times10^7$	1	7.3	1520	7.6	1535	6.9	1500	3.9	40
							2	8.1	1465	7.9	1460	8.8	1495	1.6	6
							4	13.7	1530	13.5	1525	8.1	1350	1.6	6
							5	10.3	1410	9.0	1365	9.3	1375	2.9	10
							Average	----	1480	----	1470	----	1430	3.4	--
SA-13	Ta-10W	[a]$(5.7\pm1)\times10^5$	[a]1440±30	[a]1395±30	[a]1430±35	[a]$(6.9\pm0.2)\times10^7$	1	10.6	1580	10.5	1580	8.1	1460	2.4	28
							2	12.4	1550	12.6	1560	9.0	1435	1.2	6
							3	15.1	1565	14.9	1560	10.7	1455	4.8	14
							5	17.2	1540	17.3	1540	----	----	2.2	4
							Average	----	1560	----	1560	----	1450	3.1	--
NS-4	Ta-10W	[a]5.7×10^5	-------	[a]1405	--------	[a]7.0×10^7	5	16.8	1530	18.0	1550	----	----	1.4	4

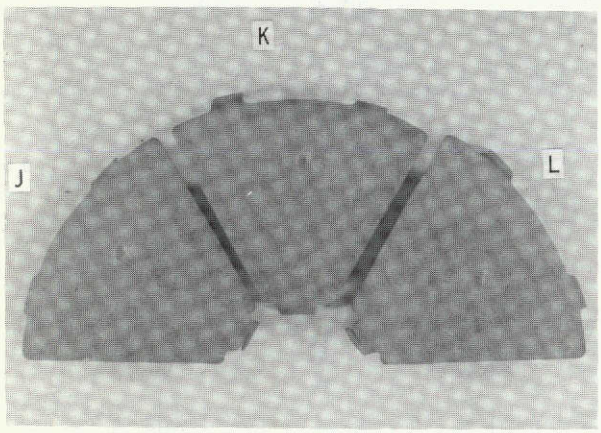
[a]Value questionable.



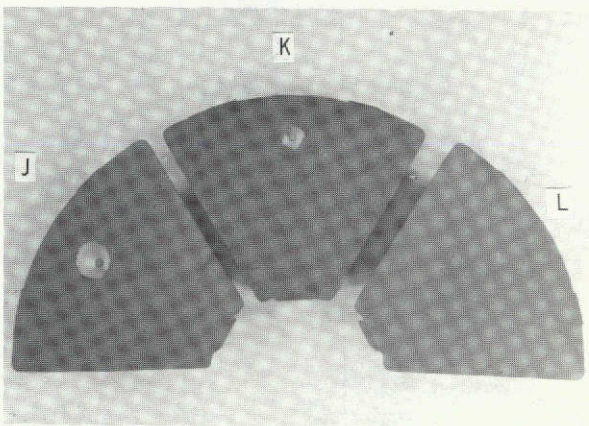
(a) R512E coated Cb-752.



(b) R512E coated FS-85.

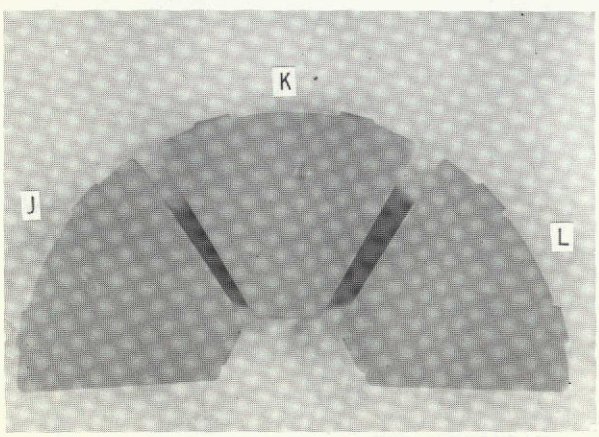


(c) R512E coated C-129Y.



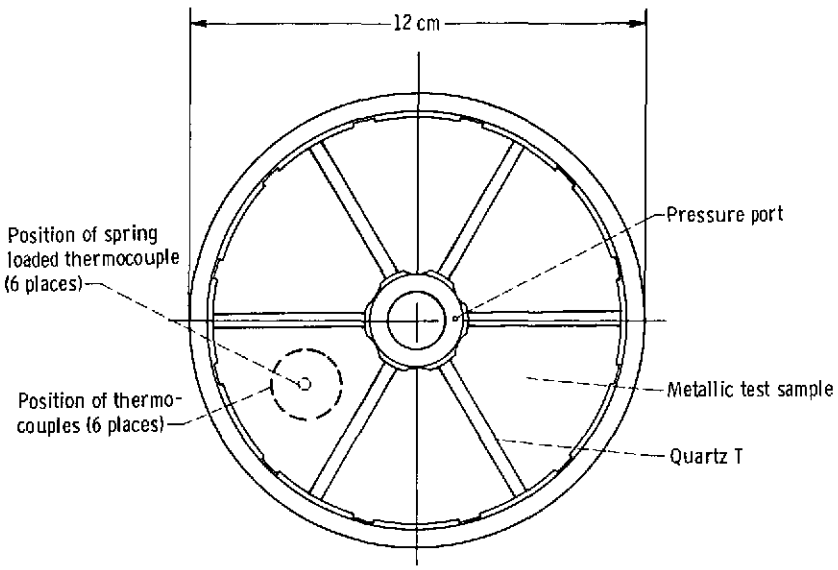
(d) SA-13 coated Ta-10W.

1 cm

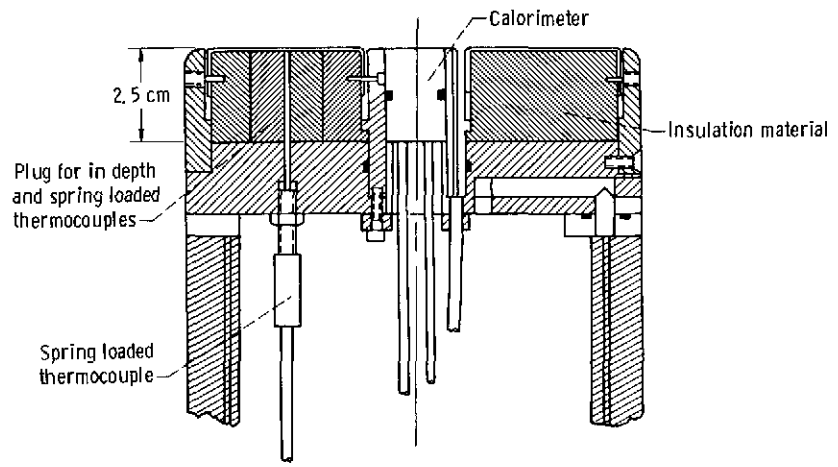


(e) TMS coated Ta-10W.

Figure 1. - Intentionally impact damaged specimens prior to test. Specimens J and K by 30 meter per second pellet; specimen L by 15 meter per second pellet.



(a) Front view.



(b) Cross section.

Figure 2. - Metallic test model (ref. 6).

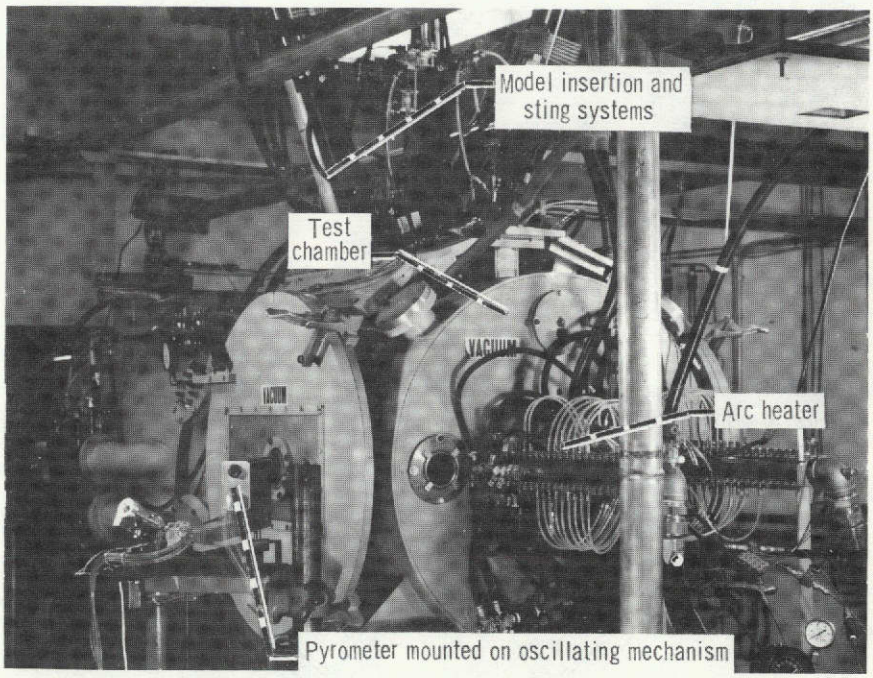
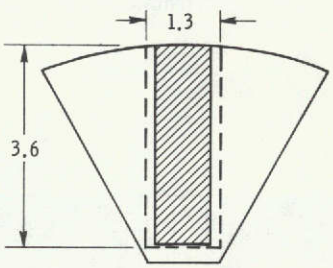
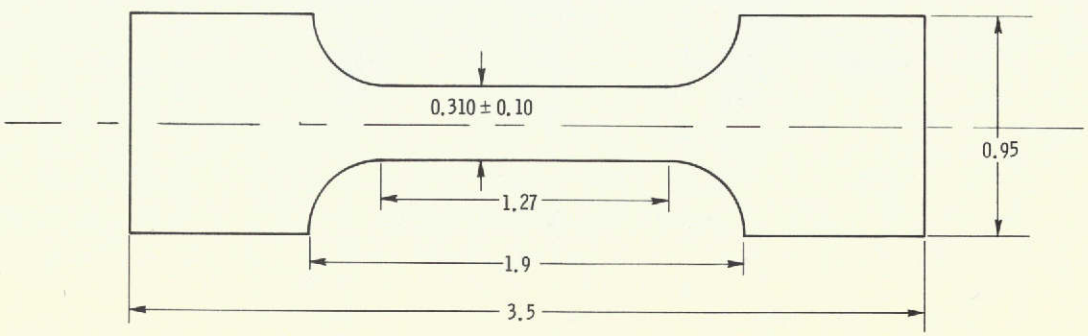


Figure 3. - 1.5-Megawatt plasma arc reentry simulation facility (ref. 6).



(a) Layout of tensile specimen on 60° plasma arc specimen.



(b) Tensile specimen.

Figure 4. - Tensile specimen configuration. Dimensions in centimeters.

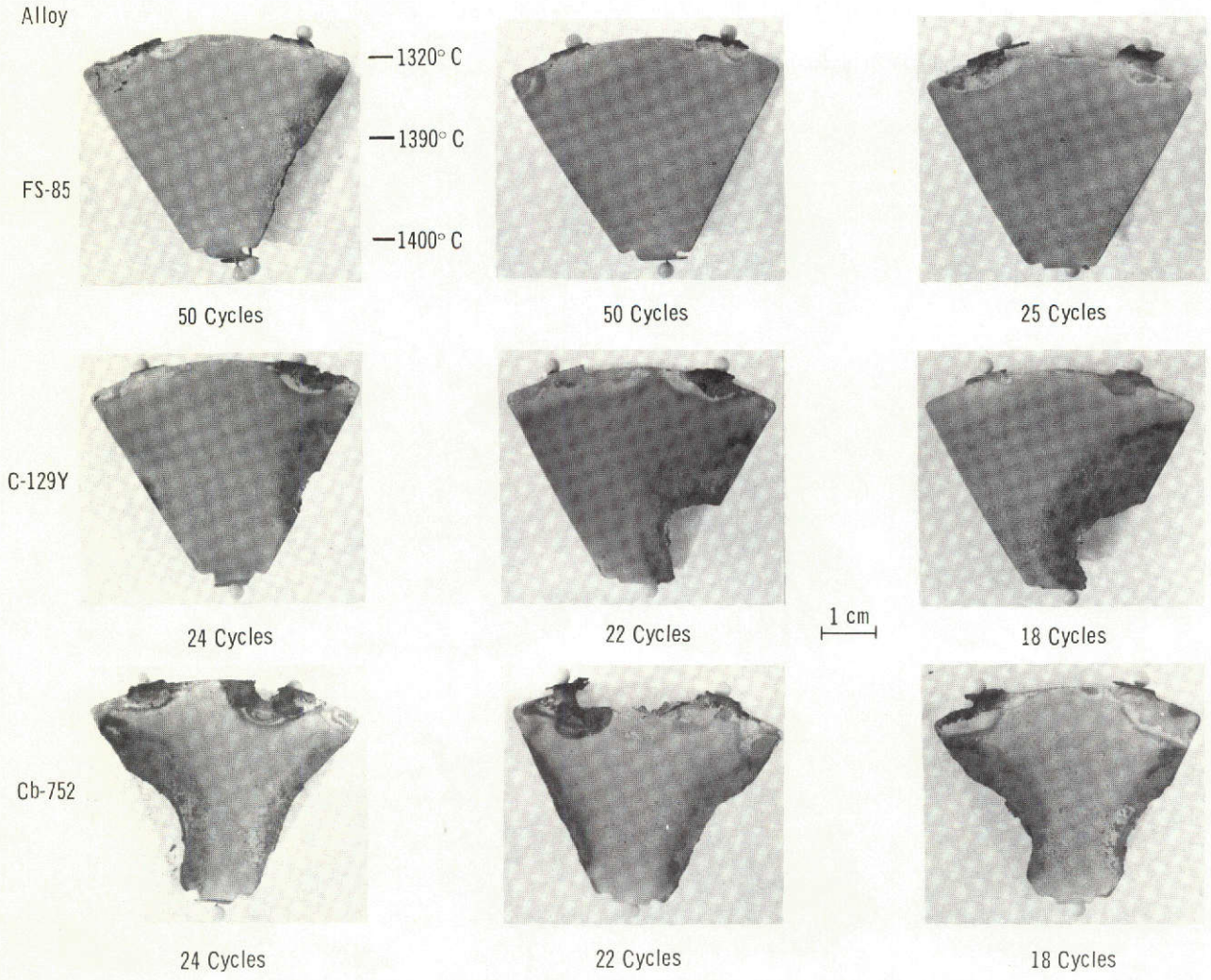
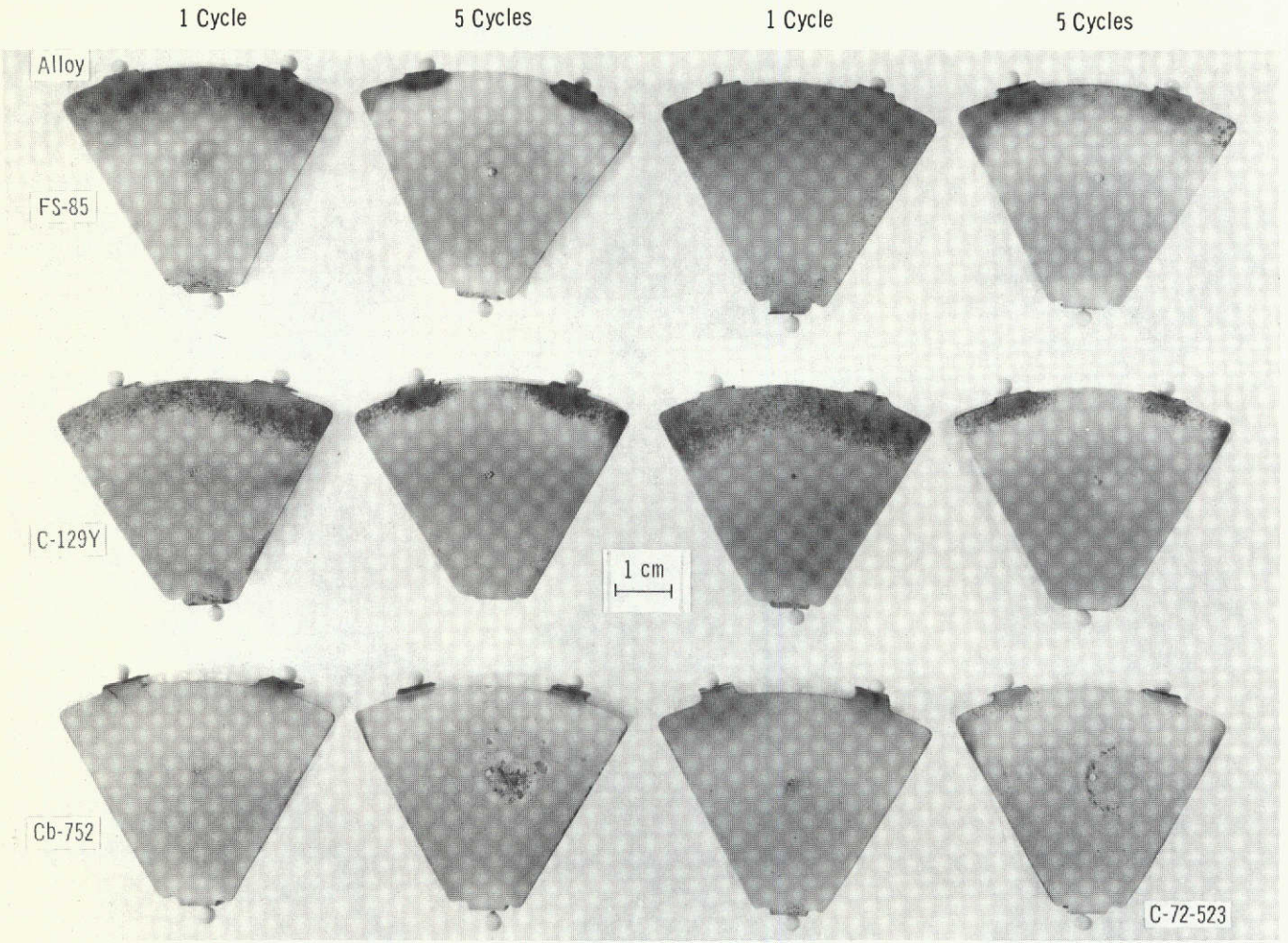
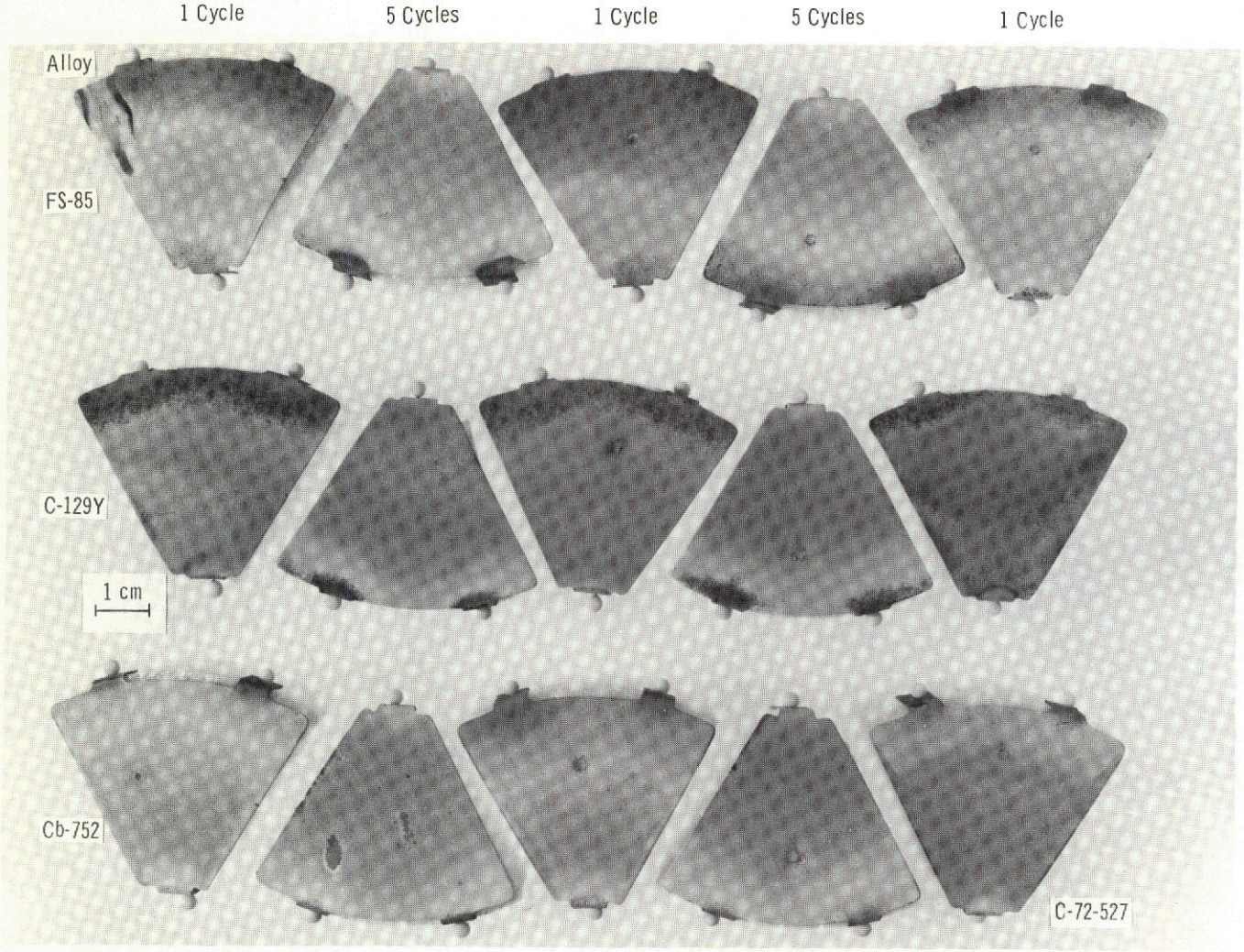


Figure 5. - R512E coated columbium alloys after 1390° C plasma arc exposure.



(a) Through-hole defect, 0.092 centimeter. (b) Coating removal defect, 0.092 centimeter.

Figure 6. - Intentionally defected R512E coated columbium alloys after 1390° C plasma arc exposure.



(a) Edge notch defect.

(b) Impact defect, 0.35 gram, 30 meters per second.

(c) Impact defect, 0.35 gram, 15 meters per second.

Figure 7. - Intentionally defected R512E coated columbium alloys after 1390° C plasma arc exposure.

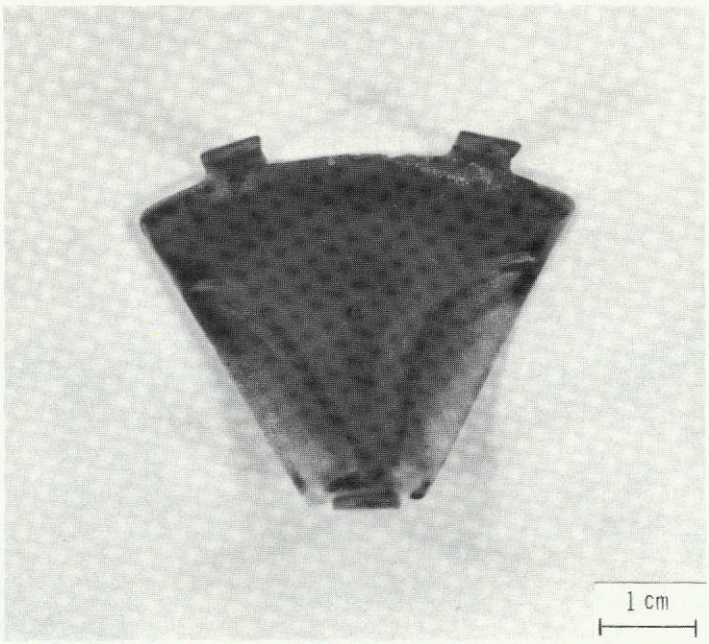


Figure 8. - Oxidation pattern on underside of R512E coated FS-85 after five plasma arc exposure cycles at 1390° C.

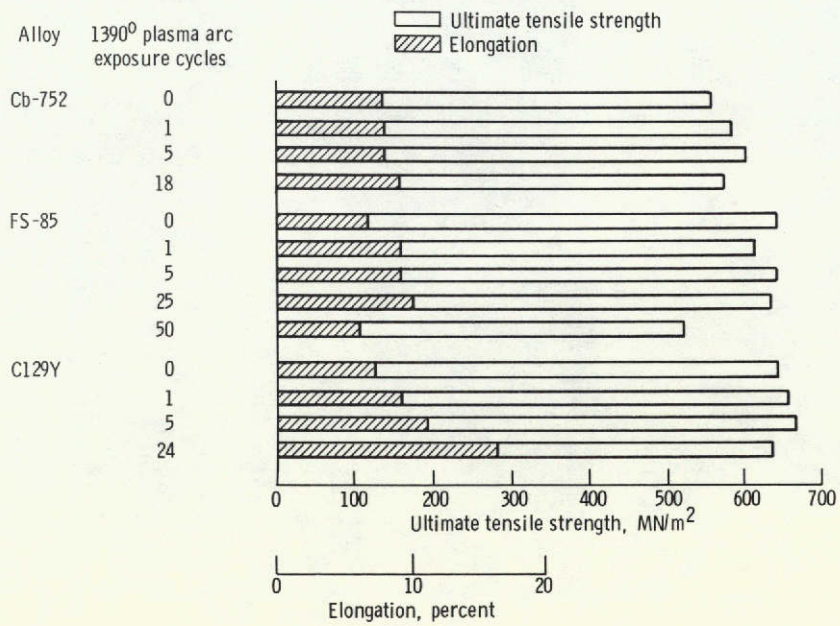


Figure 9. - Room temperature tensile test results for R512E coated columbium alloys. Ultimate tensile strength based on substrate remaining after coating application.

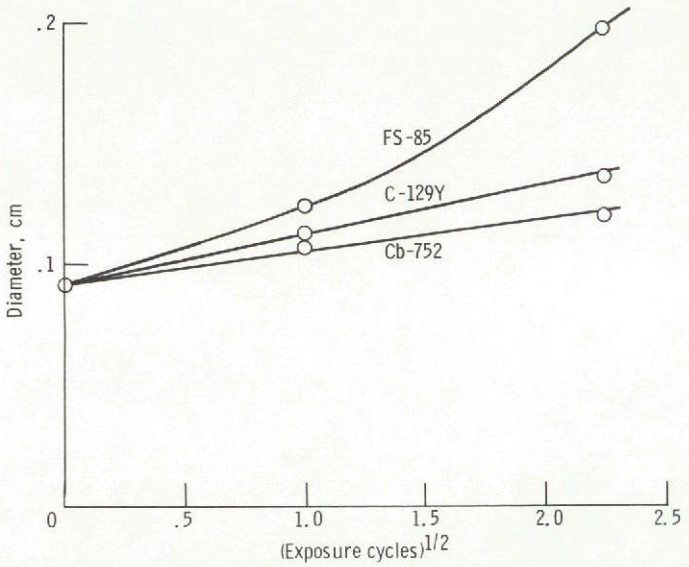


Figure 10. - Metal recession at 0.092-centimeter-diameter through-hole defects in R512E coated columbium alloys after plasma arc exposure at 1390° C.

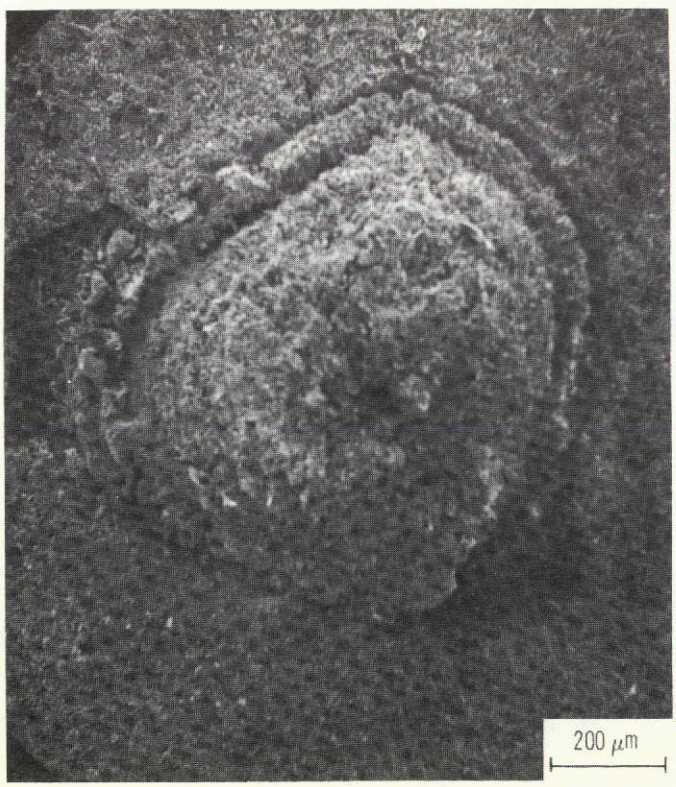
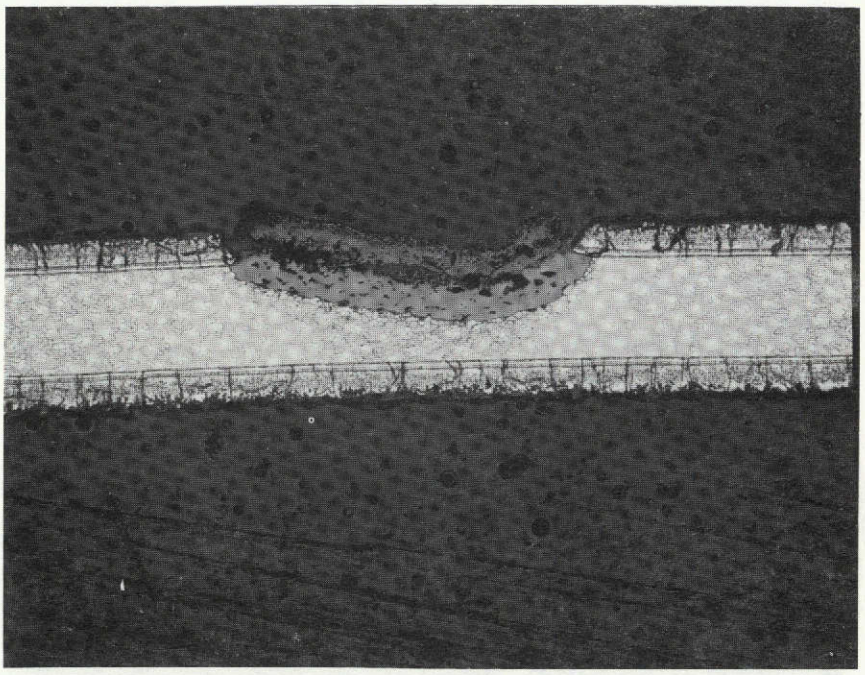
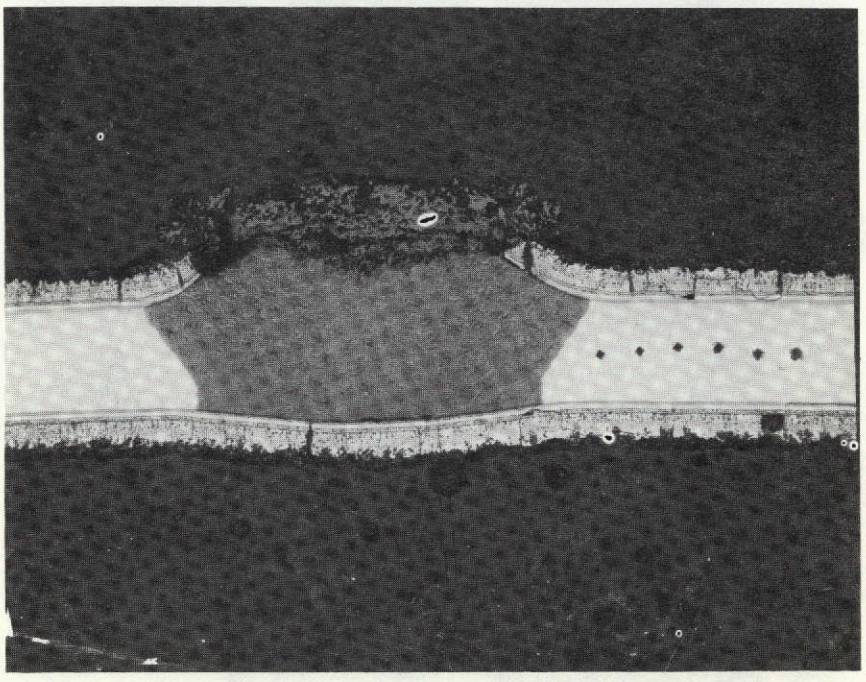


Figure 11. - Scanning electron micrograph showing plugging of 0.092-centimeter through-hole defect in R512E coated FS-85 with substrate oxide after five plasma arc exposure cycles at 1390° C. Scanning electron microscope conditions: 7 picoamperes, 25 kilovolts.

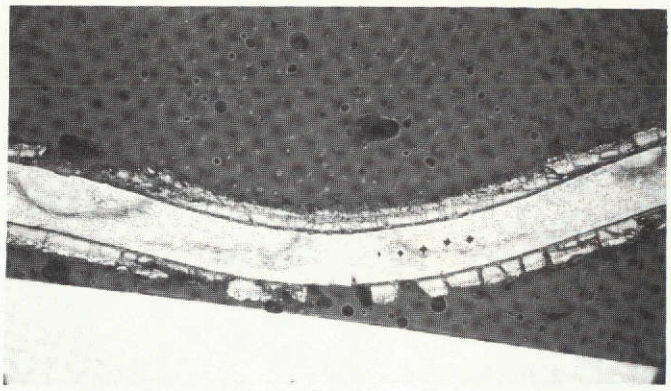


(a) One cycle.

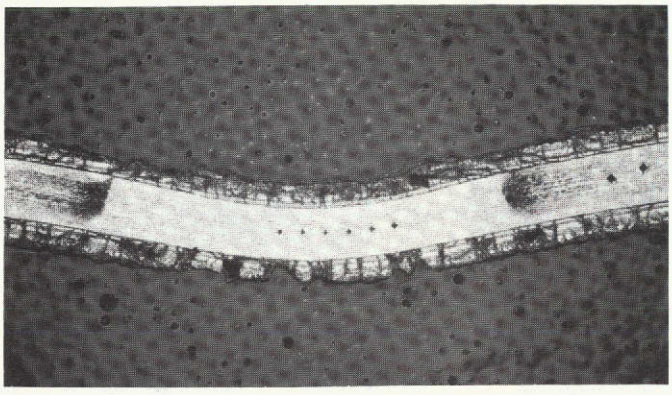


(b) Five cycles.

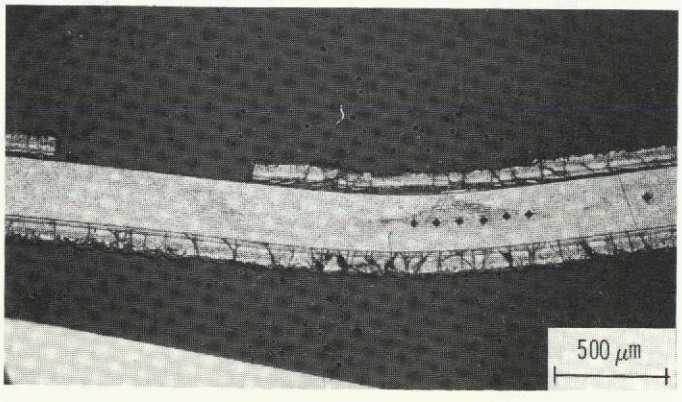
Figure 12. - Microstructures of R512E coated FS-85 at 0.092-centimeter-diameter intentional coating removal defects after plasma arc exposure at 1390° C.



(a) Exposed for one cycle after impact by 30 meter per second, 0.18-gram, 0.45-centimeter-diameter pellet.

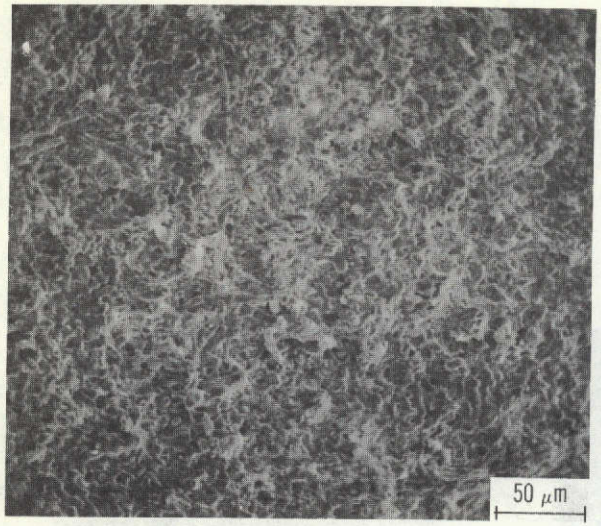


(b) Exposed five cycles after impact by 30 meter per second, 0.18-gram, 0.45-centimeter-diameter pellet.

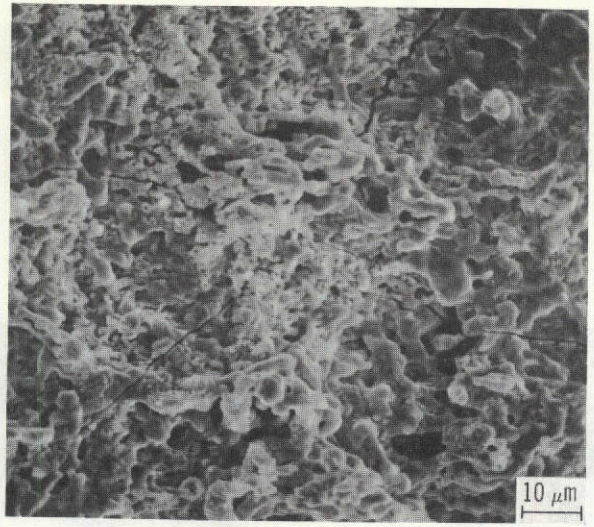


(c) Exposed for one cycle after impact by 15 meter per second, 0.18-gram, 0.45-centimeter pellet.

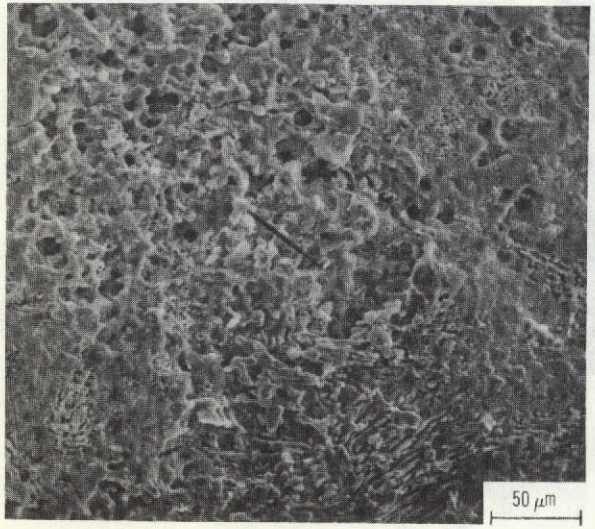
Figure 13. - Microstructures of R512E coated FS-85 at intentional impact damage sites after plasma arc exposure at 1390° C.



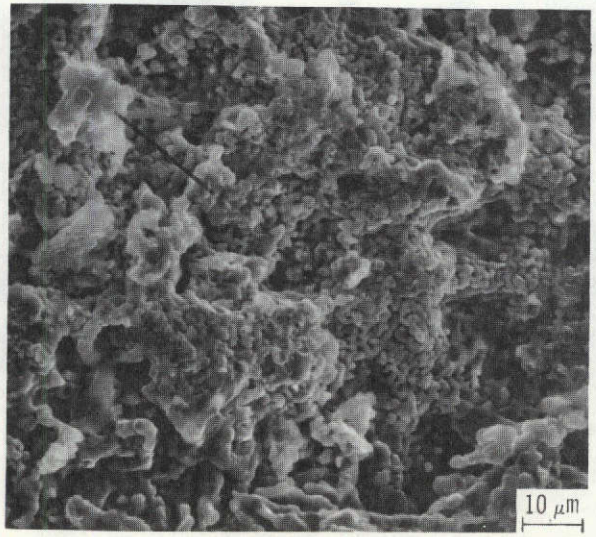
(a) R512E coated FS-85.



(b) R512E coated FS-85.

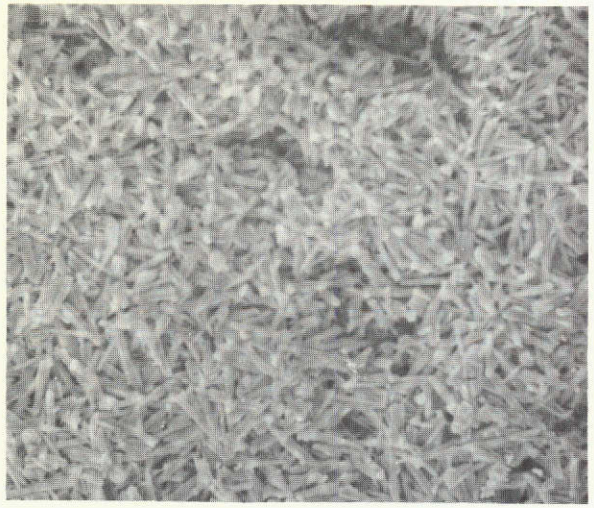


(c) R512E coated C-129Y.

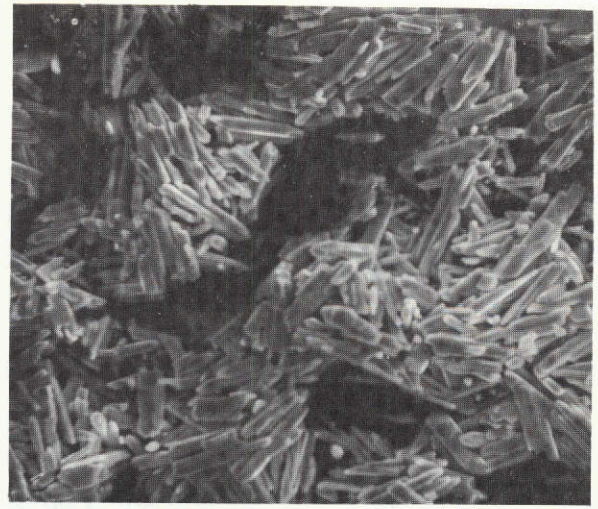


(d) R512E coated C-129Y

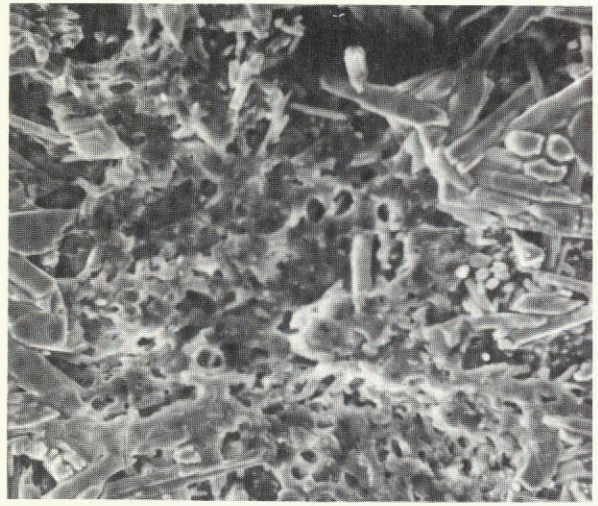
Figure 14. - Scanning electron micrographs of R512E on FS-85 and C-129Y, as-coated. Scanning electron microscope conditions: 20° tilt, 25 kilovolts.



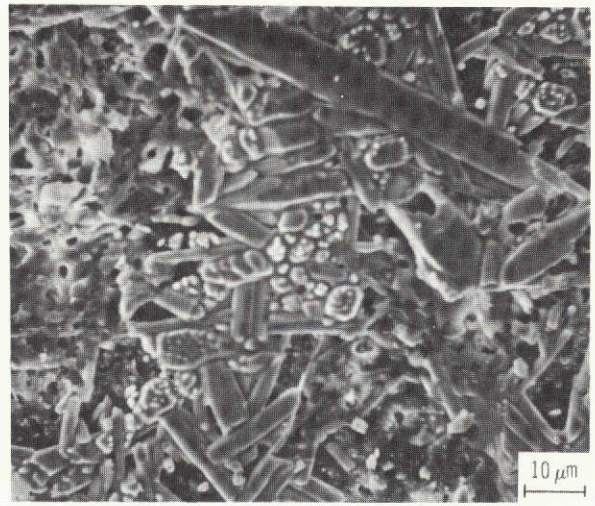
(a) After 1 cycle.



(b) After 5 cycles.

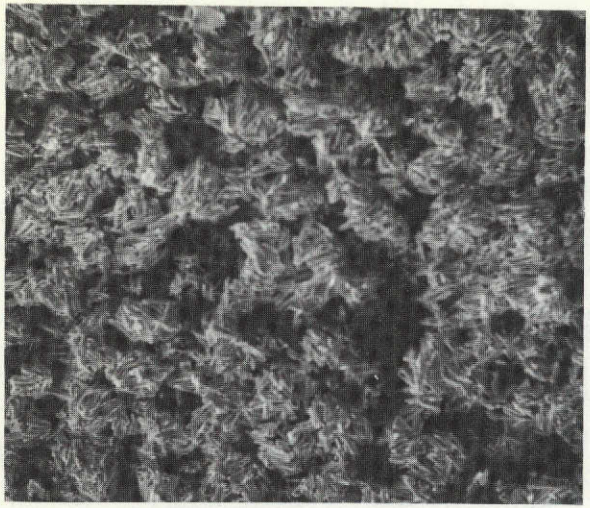


(c) After 25 cycles.

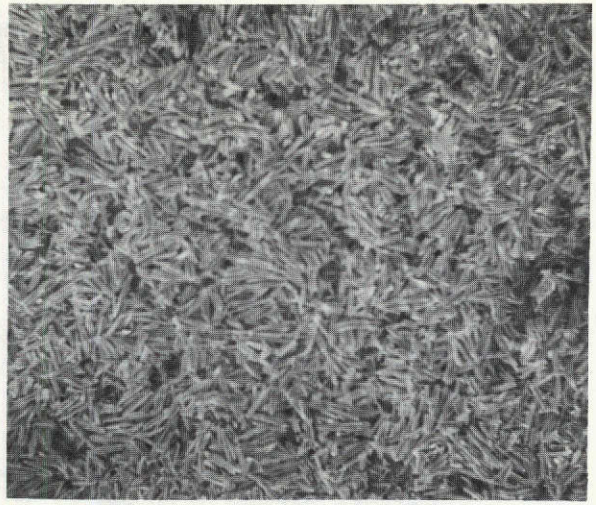


(d) After 50 cycles.

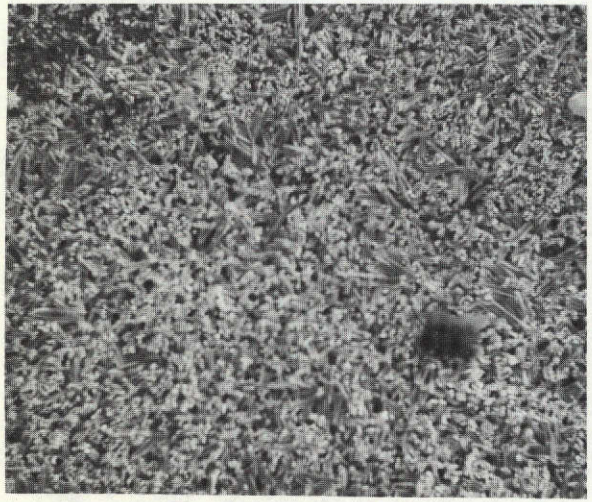
Figure 15. - Scanning electron micrographs of R512E coated FS-85 after plasma arc exposure at 1390° C. Locations, top surface at specimen centerline near forward edge. Scanning electron microscope conditions: 0° tilt, 25 kilovolts.



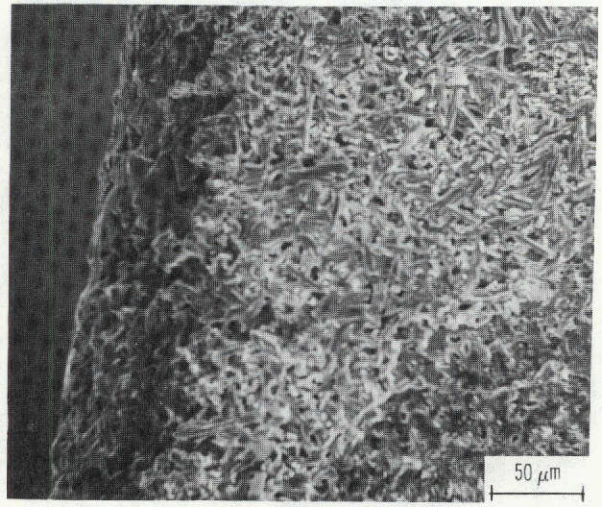
(a) R512E coated FS-85 at specimen centerline near forward edge.



(b) R512E coated Cb-752 at specimen centerline near forward edge.

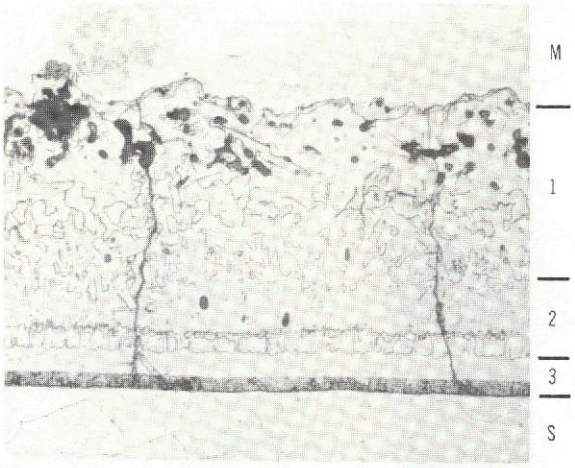


(c) R512E coated C-129Y at specimen centerline near forward edge.

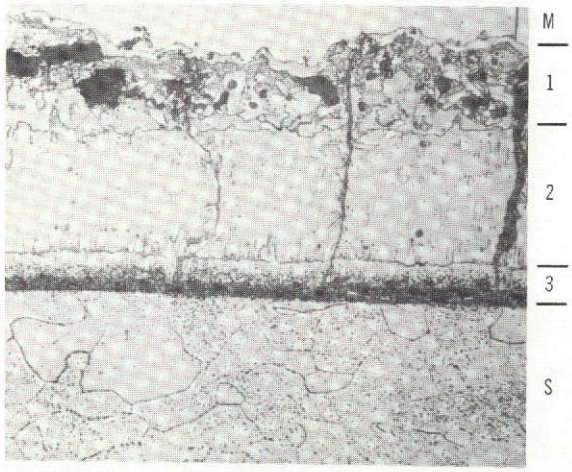


(d) R512E coated C-129Y at side edge near forward edge.

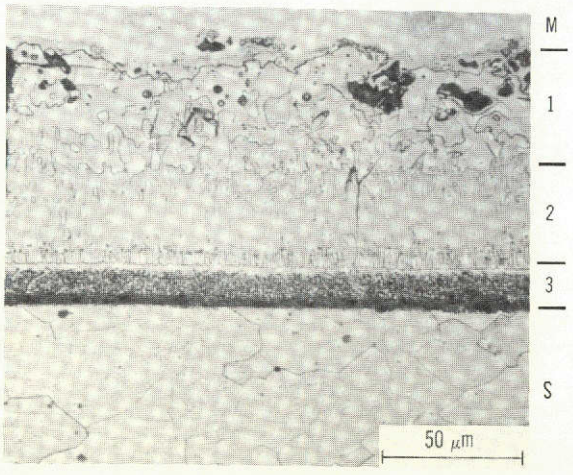
Figure 16. - Scanning electron micrographs of R512E on FS-85, Cb-752, and C-129Y after five cycles of plasma arc exposure at 1390° C. Scanning electron microscope conditions: 0° tilt, 25 kilovolts.



(a) R512E on FS-85.

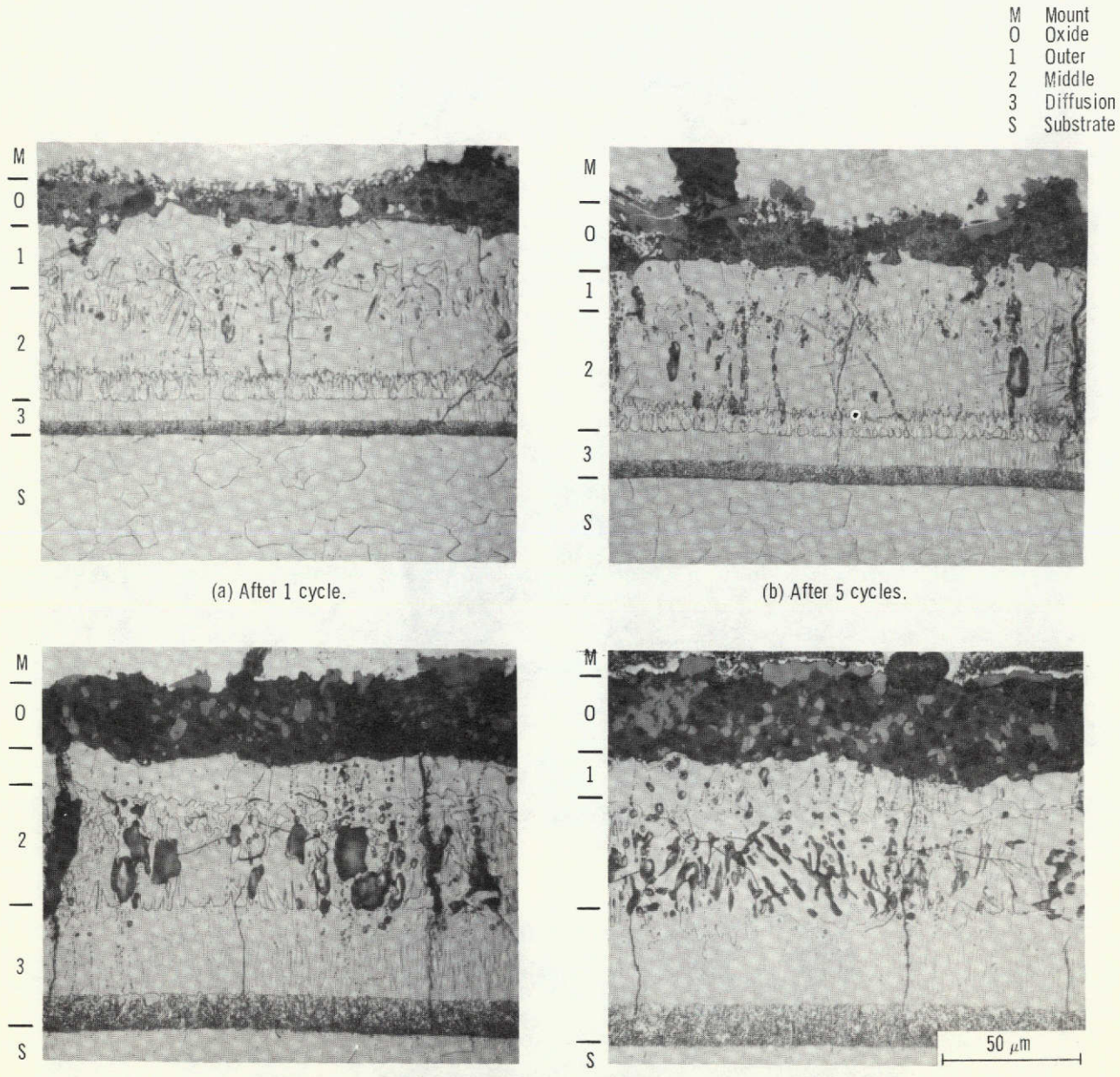


(b) R512E on Cb-752.



(c) R-512E on C-129Y.

Figure 17. - Photomicrographs of R512E coating as deposited on three columbium alloys.



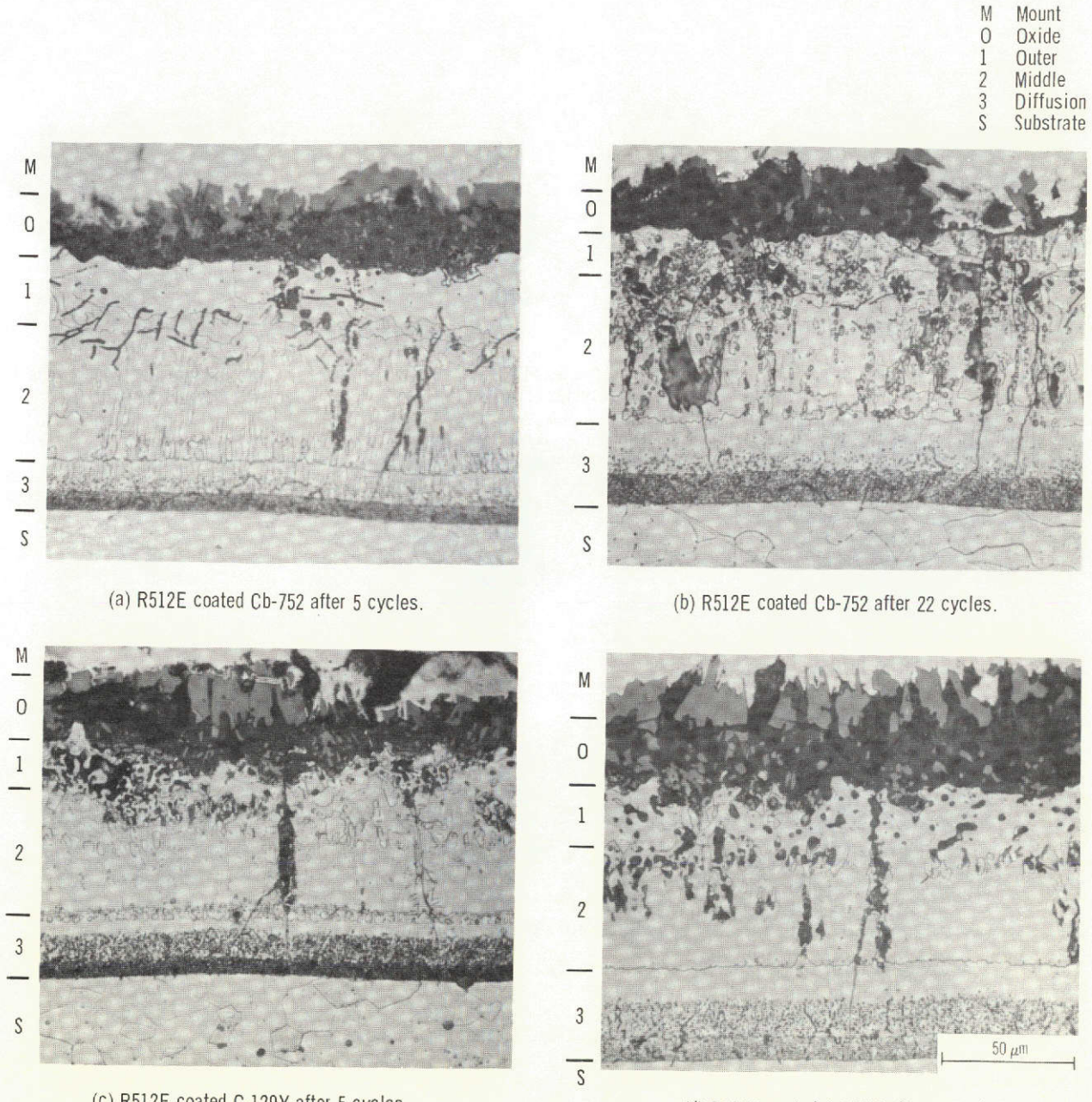
(a) After 1 cycle.

(b) After 5 cycles.

(c) After 25 cycles.

(d) After 50 cycles.

Figure 18. - Photomicrographs of R512E on FS-85 after plasma arc exposure at 1390° C. Locations, top surface near forward edge.



(a) R512E coated Cb-752 after 5 cycles.

(b) R512E coated Cb-752 after 22 cycles.

(c) R512E coated C-129Y after 5 cycles.

(d) R512E coated C-129Y after 24 cycles.

Figure 19. - Photomicrographs of R512E on Cb-752 and C-129Y after plasma arc exposure at 1390° C. Locations, top surface near forward edge.

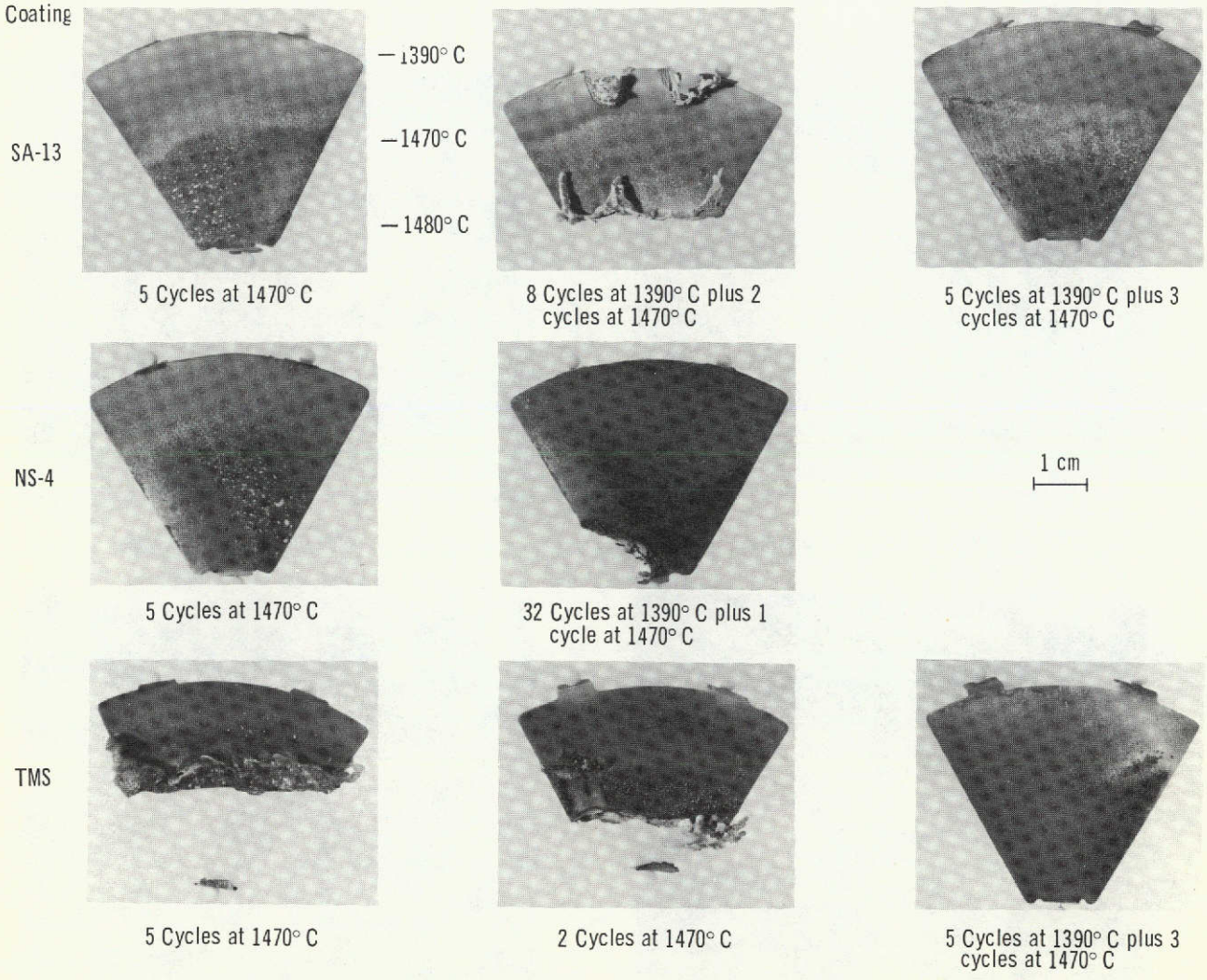
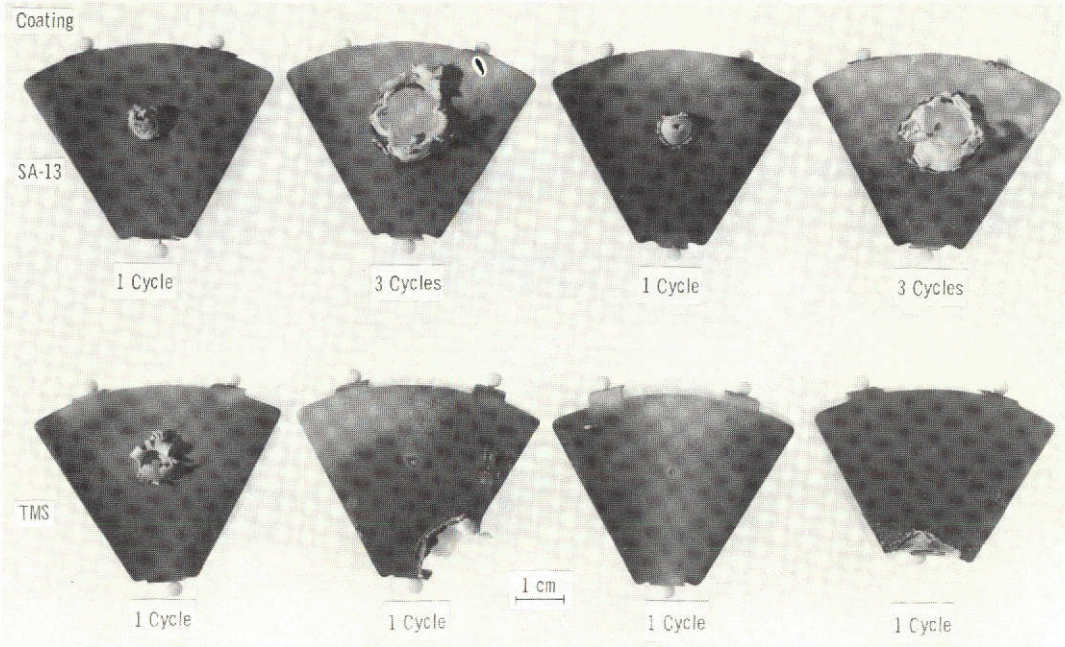


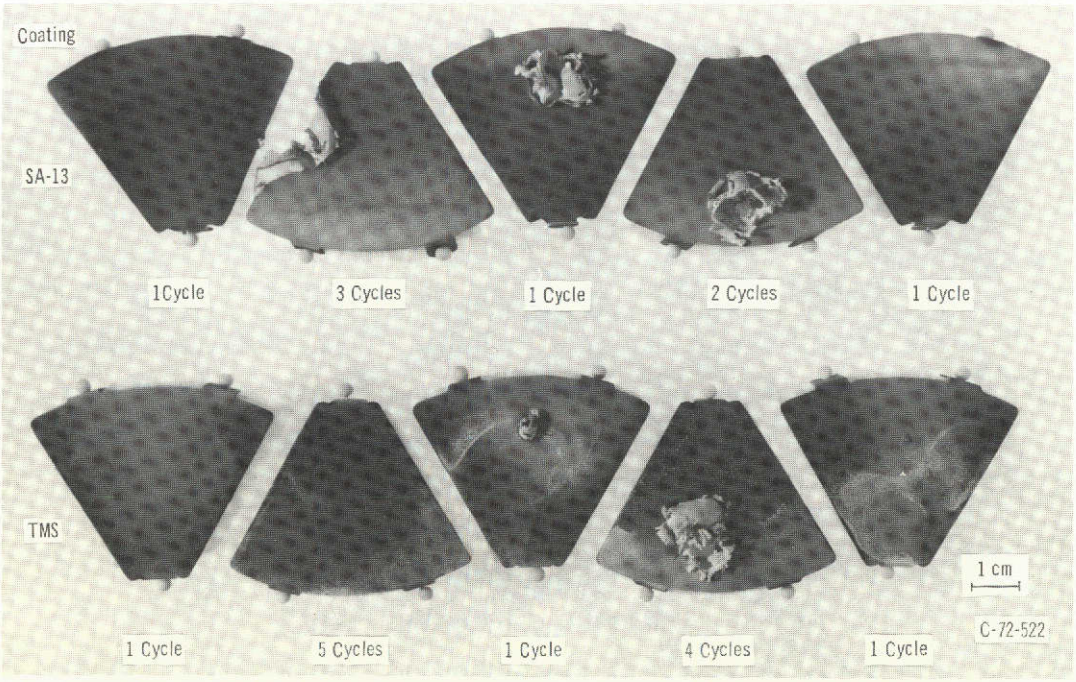
Figure 20. - Silicide coated Ta-10W after plasma arc exposure.



(a) 0.092-Centimeter through-hole defect.

(b) 0.092-Centimeter coating removal defect.

Figure 21. - Intentionally defected silicide coated Ta-10W after 1470° C plasma arc exposure.



(a) Edge notch defect.

(b) Impact defect, 0.35 gram, 30 meters per second.

(c) Impact defect, 0.35 gram, 30 meters per second.

Figure 22. - Intentionally defected silicide coated Ta-10W after 1470° C plasma arc exposure.

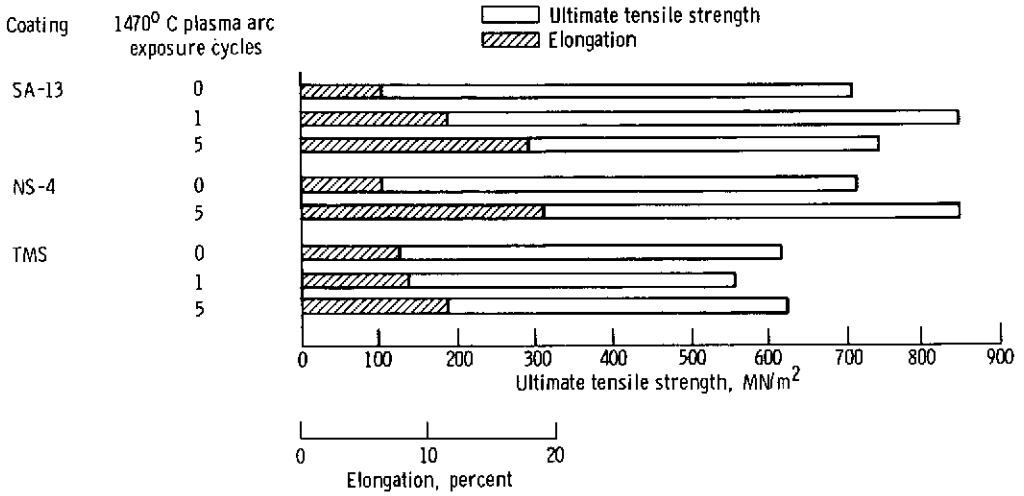


Figure 23. - Room temperature tensile test results for silicide coated Ta-10W. Ultimate tensile strength based on substrate remaining after coating application.

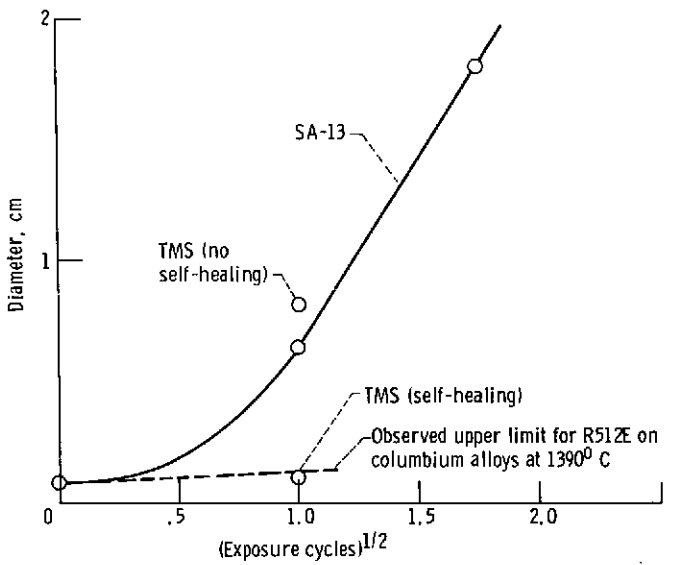


Figure 24. - Metal recession at 0.092-centimeter-diameter through-hole defects in SA-13 and TMS coated Ta-10W after plasma arc-exposure at 1470° C.

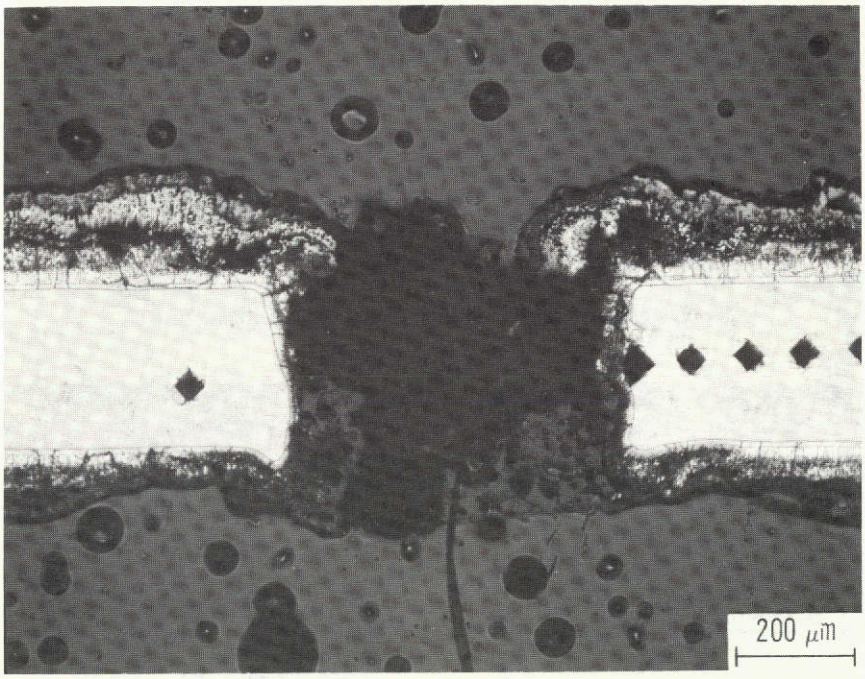
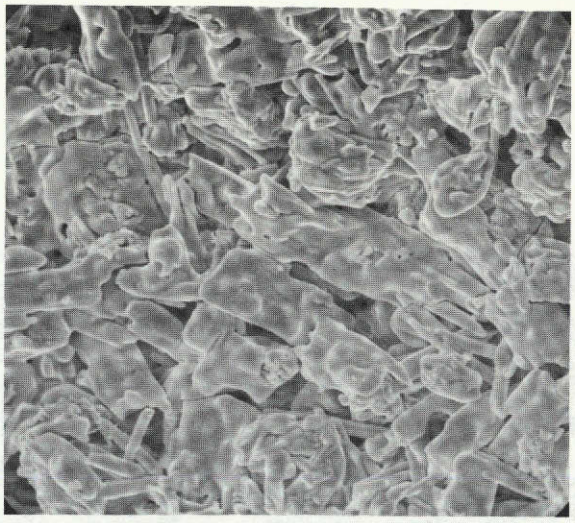
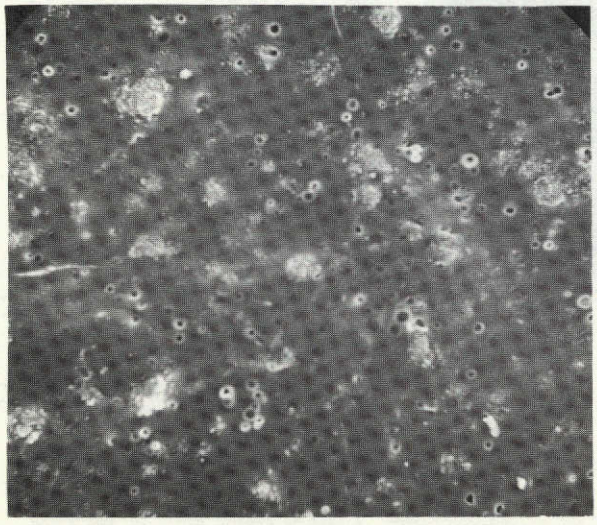


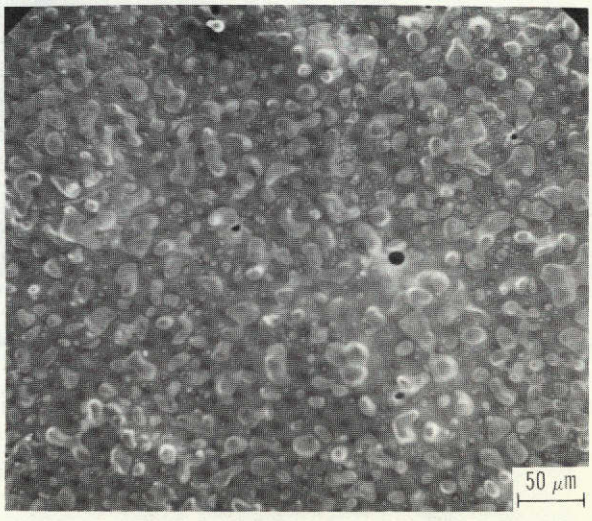
Figure 25. - Healed 0.092-centimeter through-hole defect in TMS coated Ta-10W after one 1470° C plasma arc exposure cycle.



(a) As-coated. Scanning electron microscope conditions: 20° tilt, 11 picoamperes, 25 kilovolts.

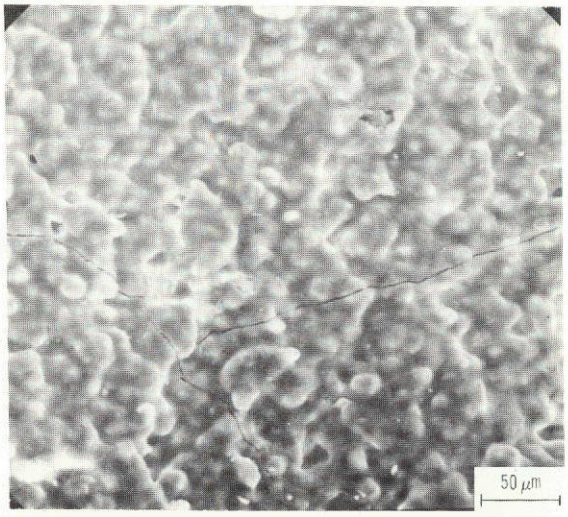


(b) After one plasma arc exposure at 1470° C. Location, close to forward edge. Scanning electron microscope conditions: 0° tilt, 13 picoamperes, 25 kilovolts.

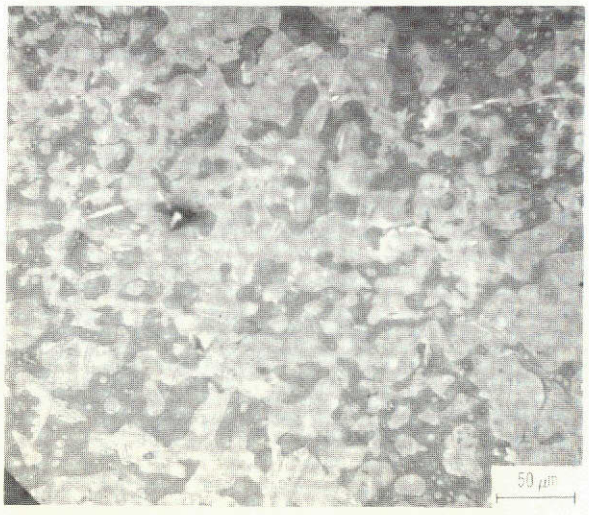


(c) After five plasma arc exposures at 1470° C. Location, close to forward edge. Scanning electron microscope conditions: 0° tilt, 13 picoamperes, 25 kilovolts.

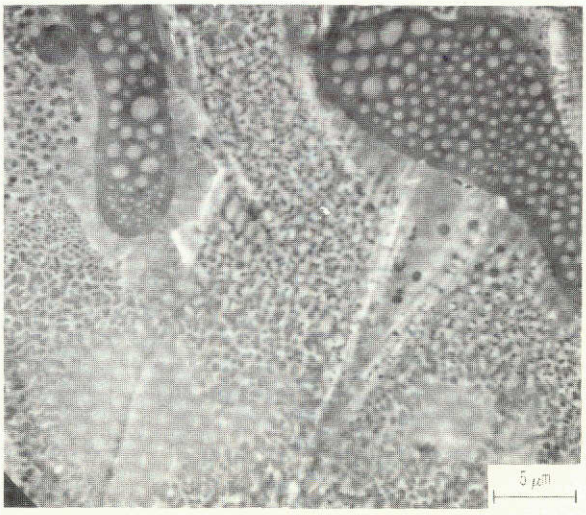
Figure 26. - Scanning electron micrographs of TMS coated Ta-10W.



(a) As-received. Scanning electron microscope conditions: 20° tilt, 12 picoamperes, 25 kilovolts.

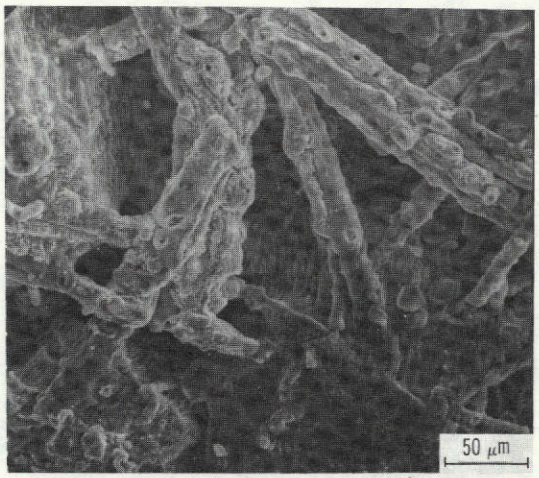


(b) After five plasma arc exposures at 1470° C. Location close to forward edge. Scanning electron microscope conditions: 0° tilt, 9 picoamperes, 25 kilovolts.

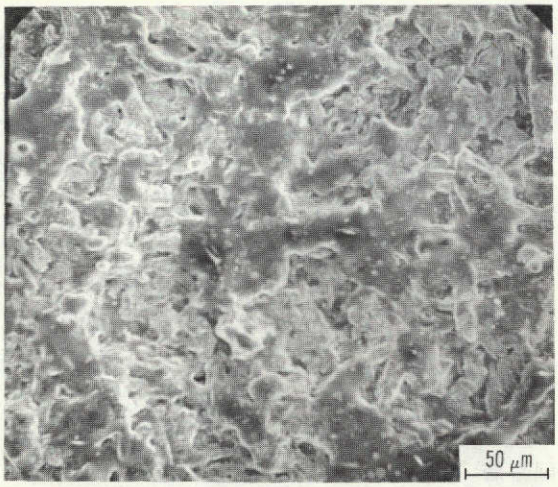


(c) After five plasma arc exposures at 1470° C. Location, close to forward edge. Scanning electron microscope conditions: 0° tilt, 9 picoamperes, 25 kilovolts.

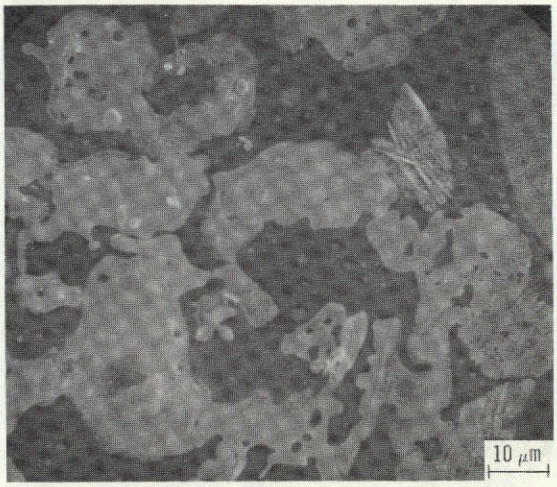
Figure 27. - Scanning electron micrographs of NS-4 on Ta-10W.



(a) As-received. Scanning electron microscope conditions: 20° tilt, 12 picoamperes, 25 kilovolts.

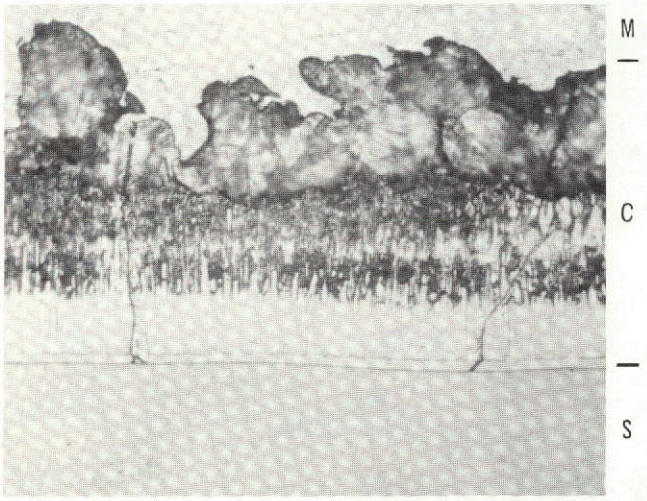


(b) After one plasma arc exposure at 1470° C. Location, close to forward edge. Scanning electron microscope conditions: 0° tilt, 10 picoamperes, 25 kilovolts.

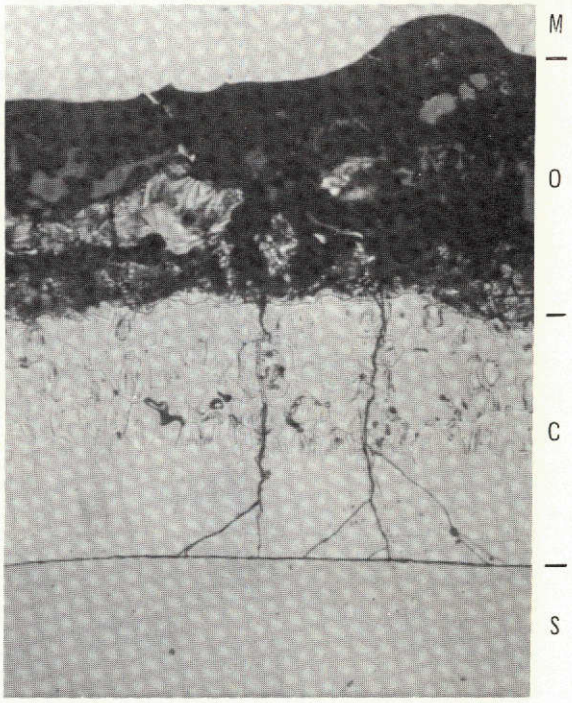


(c) After five plasma arc exposures at 1470° C. Location, close to forward edge. Scanning electron microscope conditions: 0° tilt, 9 picoamperes, 25 kilovolts.

Figure 28. - Scanning electron micrographs of SA-13 on Ta-10W.



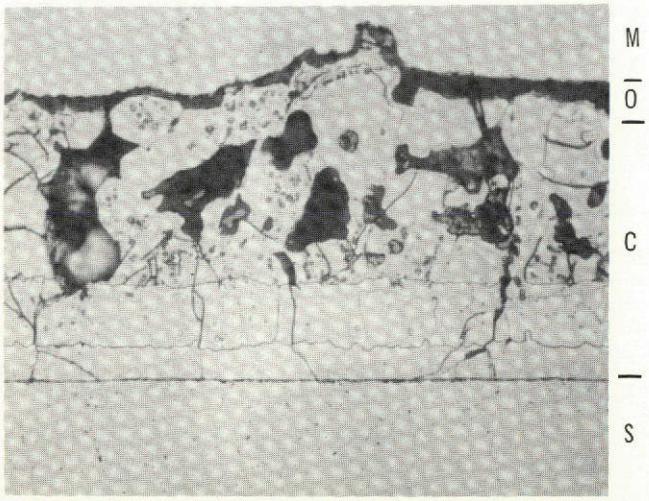
(a) As-coated.



(b) After one cycle at 1470° C.

M Mount
O Oxide
C Coating
S Substrate

50 μm



(c) After five cycles at 1470° C.

Figure 29. - Photomicrographs of TMS coated Ta-10W. Location on exposed specimens, top surface near forward edge.

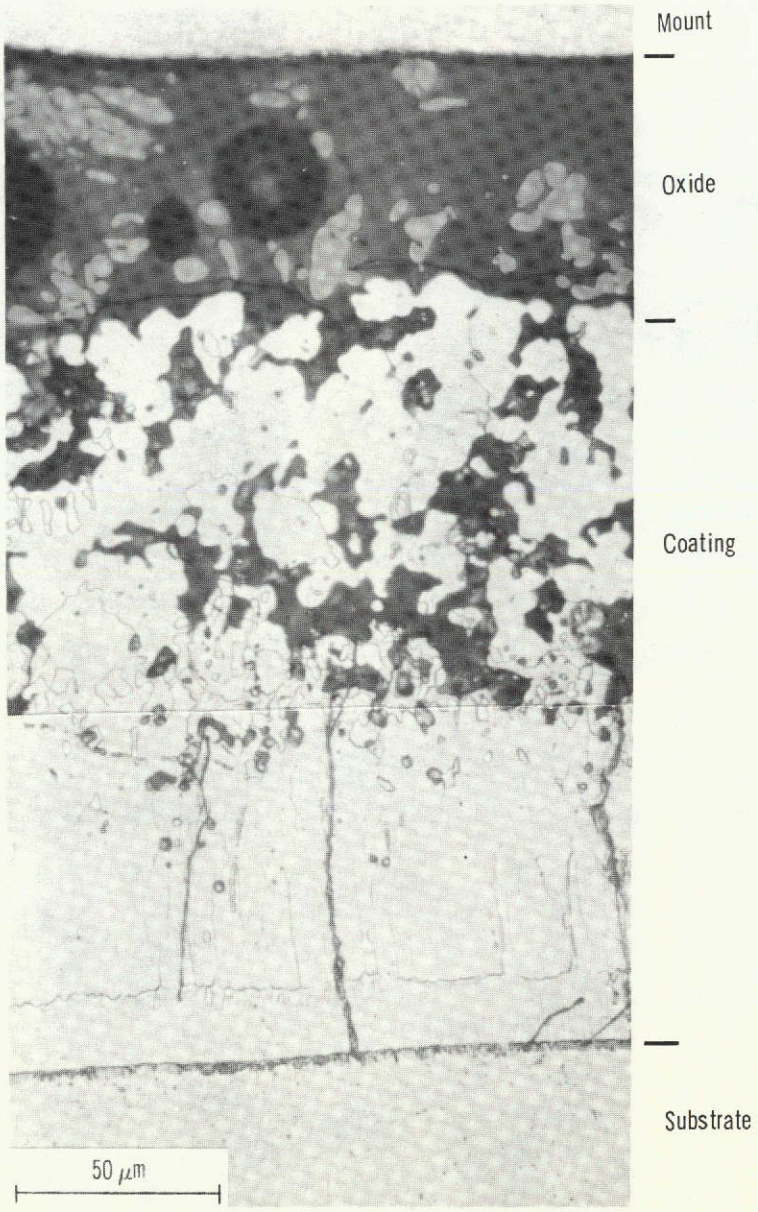
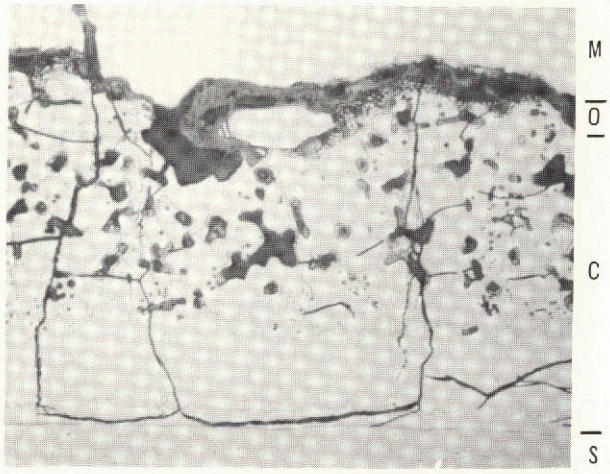
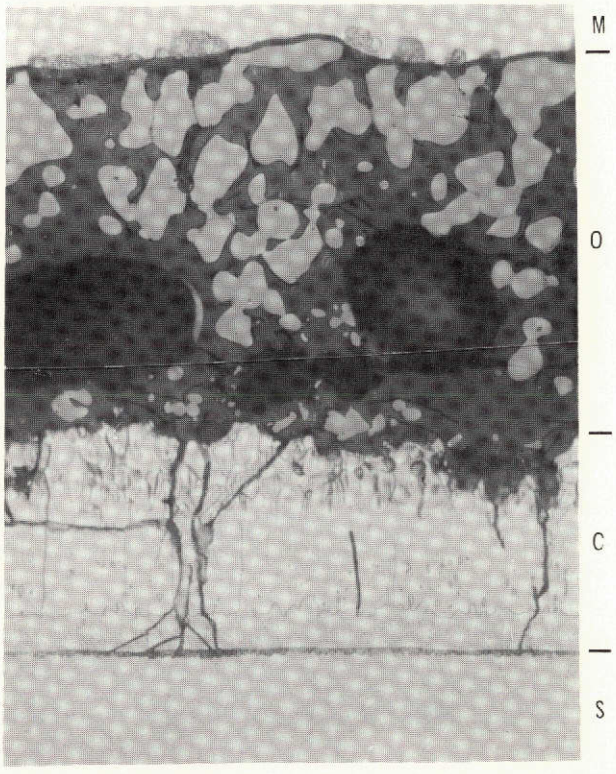


Figure 30. - Photomicrograph of NS-4 coated Ta-10W after five plasma arc exposures at 1470° C. Location, top surface near forward edge.



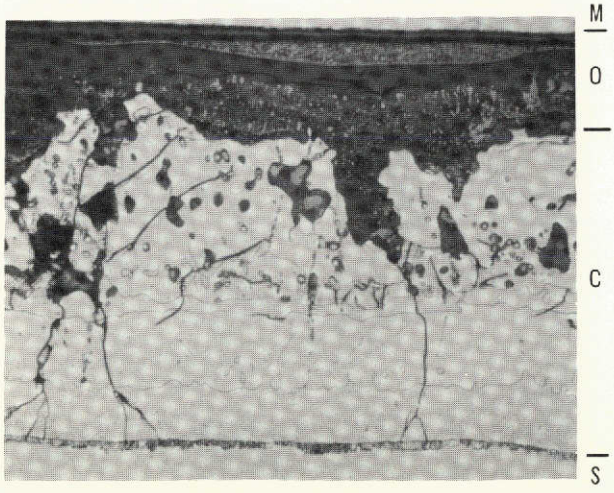
(a) As-received (coated and preoxidized).



(b) After one cycle at 1470° C.

M Mount
O Oxide
C Coating
S Substrate

50 μm



(c) After five cycles at 1470° C.

Figure 31. - Photomicrographs of SA-13 coated Ta-10W. Location on exposed specimens, top surface near forward edge.