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SLURRY APPLIED DUPLEX COATINGS
FOR TANTALUM AND COLUMBIUM ALLOYS

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ABSTRACT

A duplex silicide coating process is described in which a modifier alloy is slurry applied and vacuum sintered onto the substrate preparatory to pack siliciding. Data are presented on the ability of the coatings to protect tantalum and columbium alloys from oxidation in the temperature range of 1600 to 3600 F. The data indicate protective lives of the coatings on the T222 tantalum alloy in excess of 600 hours at 1600 and 2400 F, in excess of 20 hours at 3100 F, up to 8.5 hours at 3500 F and up to 1.75 hours at 3600 F. Columbium alloys are afforded in excess of 570 hours of protection at 1600 F and in excess of 220 hours at 2400 F under a variety of test conditions. After both ballistic and falling ball impacting at R.T. and 2200 F, the coatings are protective for 1 to more than 16 hours in the temperature range of 1600 to 2400 F. Basically, the compositions are W and/or Mo silicide modified with titanium and/or vanadium. The three most promising compositions are $(35Mo\text{-}35W\text{-}15Ti\text{-}15V)Si_2$, $(95W\text{-}5Ti)Si_2$, and $(95Mo\text{-}5Ti)Si_2$.

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INTRODUCTION

For well over ten years coating technologists have recognized that silicide coatings afford the greatest potential for reliably protecting the refractory metals from oxidation at temperatures as high as 3100 F. Weaknesses have been recognized, e.g., brittleness, "pest" behavior, low-pressure deterioration, active oxidation and craze cracking due to differential expansion. Competitive systems including aluminides, beryllides, superalloys, hafnium-tantalum alloys and noble metal cladding have received some consideration, but weaknesses in these systems, particularly regarding oxygen diffusion, poor cyclic performance, rapid interdiffusion, short life, and very poor pest and low pressure performance (beryllides and aluminides) have severely limited their usage.

After the ten years of intensive study of coatings systems, silicides still have retained their pre-eminence and appear to offer the greatest potential for development, particularly for long-term protection at intermediate temperatures of 2500 F and below.

We should begin to ask ourselves, "Why, after all of these years of development and millions of dollars of investment in research, haven't we optimized the silicide coating system?" There is no simple answer to this query. Coating objectives have changed from very short life at very high temperatures to multiple hundred hours of protection at 2500 F and down. Consideration for application to aircraft gas turbines or to multiple use heat shields for hypersonic airplanes and re-entry gliders is responsible for the change in emphasis. One stigma, more than any other, can probably be blamed for the slow progress in the development of silicide coatings. This has been the emphasis placed on the development of pack cementation techniques for the deposition of the coating constituents rather than directing efforts toward obtaining inherently protective compositions.

Early success in the protection of molybdenum alloys by pack cementation provided the coating technologists with the optimistic view that perhaps this deposition technique was the panacea for the formation of silicide coatings on all refractory metals. Coating program after coating program studied this technique for development of "modified" silicide coatings by codeposition or multiple-cycle deposition. Careful analyses revealed that many of the "modified" coatings were not chemically modified at all, or were only slightly modified, or lacked reproducibility with batch size. For example,

- the "Cb" modified Si coating for molybdenum alloys contained no columbium in the coating;
- the W-Si coating for tungsten when applied to molybdenum showed no tungsten in the coating;
- the duplex (90 a/o Ti-10 a/o W)-Si coating for tantalum alloys showed only traces of tungsten in the coating, although the pack contained approximately 31 percent by weight tungsten;
- the (Ti-Cr)-Si coating, although effecting significant surface modification in columbium alloys, has had severe problems of reproducibility.

For the deposition of silicon alone, the pack technique remains as a useful technique; but for the deposition of other elements in controlled quantities, the process is severely lacking. Kinetic and thermodynamic factors impede transferring relatively slowly diffusing elements. To obtain significant mass transport, the process has been limited to the elements Ti, Cr, V, Al, B and Si, thus limiting the coatings to elements forming only moderately oxidation resistant silicides having coefficients of thermal expansion as much as 60 to 100 percent greater than those of the refractory metals. Restricting comments to columbium and tantalum alloys, the coatings obtained by codeposition with silicon are primarily $CbSi_2$ or $TaSi_2$ which have no temperature range in which they exhibit good oxidation resistance. Using these silicides as bases for oxidation resistant coatings is inherently unsound and with only a few exceptions has produced coatings with only marginal performance.

After the limitations of the pack cementation technique were recognized, other application techniques were considered having the potential for producing a specific coating composition rather than the results of exposure to a given set of process conditions. A partial list of these newer processes are shown below.

1. Electrophoretic deposition of disilicides followed by isostatic pressing and sintering.
2. Chemical vapor deposition.
3. Fused salt deposition.
4. Slurry application followed by fusion.
5. Slurry application of a modifier alloy followed by (1) sintering in vacuum, and (2) application of silicon by pack cementation.

All of these processes have considerably more control of final coating composition than do the pack-cementation modification processes. Based on the current stage of development of each process, the latter two (Nos. 4 and 5) show the greatest potential for effective protection of columbium and tantalum alloys. The difference in the end product for the two processes is quite marked. With the fusion process, considerable dissolution of the substrate occurs leaving large amounts of tantalum or columbium in the protective silicide. With the sintered coating, the substrate is not introduced into the coating, and, consequently, the coating tends to retain the nature of the applied slurry.

This paper summarizes both the development and evaluation of the sintered slurry coatings; the data were obtained at Solar and at other companies. The principal emphasis has been on tantalum alloys (Ref. 1), but to a limited extent, coatings for the columbium alloys were also studied (Ref. 2).

COATING COMPOSITION

The known oxidation resistance and thermal expansion characteristics of various silicides in bulk form were reviewed to determine which metals should be used in the surface alloying process. The modifier alloy compositions listed in Table I were selected to produce, upon siliciding, oxidation-resistant coatings. Of the disilicides having melting points exceeding 2400 F, tungsten disilicide has the lowest coefficient of expansion, with the possible exception of costly rhenium disilicide. Even the low coefficient of expansion of WSi_2 is 13 percent greater than that of the T222 alloy at 1800 F and is 45 percent greater at 400 F. Thus, cooling coated substrates below the application temperature would be expected to place the coatings in a state of tension with a resultant potential for crack formation. Although matching coefficients of thermal expansion of the coating and a tantalum substrate appeared to be impossible, minimization of the extent of the mismatch seemed desirable. With columbium alloys the expansion match can be very close for compositions high in $MoSi_2$ and WSi_2. The expansion characteristics of tungsten disilicide coupled with respectable oxidation resistance, particularly at higher temperatures, suggested that tungsten was a logical candidate for inclusion in the surface-modifier alloys.

The excellent oxidation resistance of molybdenum disilicides is well known and is superior to that of the tungsten disilicide at lower temperatures. Although the thermal expansion coefficient for molybdenum disilicide is slightly greater than that of tungsten disilicide, molybdenum was also considered to be a logical modifier alloying element.

Titanium, vanadium and chromium were used as sintering aids and to improve the low-temperature oxidation resistance of the substrate and silicide layer. The 2535 F minimum in the solidus curve of the chromium-titanium system (Ref. 3) allows liquid-phase sintering to be accomplished where these metals are present.

EXPERIMENTAL STUDY

TANTALUM ALLOYS

In brief, the coating process involved:

- Spraying a slurry of the powdered modifier metals onto the tantalum alloy substrate.
- Vacuum sintering.
- Siliciding in a pack.

A flow chart for the process is shown in Figure 1. Elemental powders were mixed in the desired proportions by ball milling in an organic vehicle. The corners and edges of the 1-inch by 2-inch by 1/16-inch T222 tantalum alloy samples (Ta-9.6W-2.4Hf-0.01C) were rounded by tumbling in a ball mill charged with arrowhead-shaped deburring media. Sandblasting and acid etching the substrate preceded application of the slurry using a conventional paint spray gun. After drying, the sprayed coatings were sintered at 2435 to 2760 F for either 30 minutes or 15 hours in a vacuum of 10^{-5} Torr. The coatings containing chromium experienced liquid-phase sintering and were sintered for 30 minutes, while the balance of the compositions involved solid-state (and vaporization-condensation) sintering and were sintered for 15 hours. The resultant 0.003 to 0.006-inch thick sintered coatings were silicided by packing the samples in minus 200 mesh silicon without activator, and heating to 2150 to 2250 F in gettered argon (800 Torr) for a period of 7 to 8 hours (although no activator was added to the silicon, trace amounts of halide impurities may have been present and promoted silicon transfer). Siliciding resulted in weight gains in the range of 20 to 48 mg/cm^2 for the different coatings.

The as-sintered microstructure of Coating B (95.3Mo-4.7Ti) and Coating J (35W-35Mo-15Ti-15V) are shown in Figure 2. Coating B had the most coherent microstructure of the molybdenum-rich and tungsten-rich coatings, while Coating J had about the least coherent microstructure. The noticeable porosity (exaggerated by pullout during sample polishing) did not prove to be deleterious to the oxidation resistance; rather, the pores appeared to be beneficial in allowing incorporation of comparatively large quantities of silicon into the coating without disruptive effects. Figure 3 contains the as-silicided microstructure of the same two coatings. The crack in the outer layer of Coating B does not traverse the light-colored porous zone adjacent to the substrate while cracks traversed completely through Coating J. The fully dense layer of high hardness beneath Coating J is indicative of the diffusion of silicon completely through the coating and into the substrate, a phenomenon not manifest with Coating B. During siliciding, the thickness of nearly all the coatings increased approximately 0.003 inch.

OXIDATION TESTING - SOLAR

The coated samples were placed on Dyna-Quartz (99 percent SiO_2 fiber) pads resting on Carbofrax silicon-carbide soap bricks. Oxidation at 1600 F and 2400 F was conducted in static air in electrically heated furnaces. The cyclic oxidation process corresponded to eight overnight cycles (15 to 17 hours) and one weekend (63 to 64 hours) cycle in an initial test period, which was extended by oxidizing the samples each night and over weekends until a total of 600 hours had been accumulated, at which point testing was normally discontinued. A number of samples were withdrawn from testing, particularly for metallographic examination, at the conclusion of the initial 200-hour test period.

The oxidation lives of the better coatings are shown in Figure 4. The open bars depict oxidation at 1600 F, while the shaded bars represent results obtained at 2400 F. The vertical lines on the bars correspond to specimen failures; an arrow through a vertical line indicates that testing was discontinued without specimen failure. A number of coatings yielded samples having oxidation lives in excess of 600 hours; however, early failures were also common.

Coatings B and J were the only compositions for which samples exceeded the 600-hour goal at both 1600 F and 2400 F. Samples from any single coating experiment involving Coating B were not good at both temperatures. The results did indicate that the inherent chemical nature of Coating B is such that 600 hours of protection at 1600 and 2400 F can be provided, but improvement of the reliability of the coating by way of elimination of early failures was needed.

The results obtained with Coating J were very interesting. In addition to achievement of the 600-hour goal at both oxidation temperatures, it was noted that no specimen having Coating J failed with less than 200 hours of exposure at either temperature. None of the second set of J-Coated specimens (5 oxidized at each temperature) or the third set of specimens (3 oxidized at each temperature) failed in 600 hours of testing at either temperature. One sample was continued in oxidation at 2400 F and experienced failure at 1084 hours only as a result of the slow cooling associated with a furnace power failure.

The oxidation resistance of Coating I (40W-30Ti-30V) was quite interesting and different from most of the other coatings in that the low-temperature performance was better than the high-temperature performance. The absence of early failures (less than 100 hours) coupled with good low-temperature oxidation resistance was considered to be an indication of a potential for becoming an excellent coating with further development.

All three of the chrome-containing coatings demonstrated poor oxidation resistance; none survived 16 hours at 1600 F, and at 2400 F the results were inconsistent (however, one L-Coated specimen survived 600 hours).

As a group, the results indicated the usefulness of the addition of titanium and vanadium to molybdenum and tungsten to yield effective modifier alloys, which when silicided, provide considerable protection for the tantalum alloy substrate. Chromium additions provided no benefit.

The microstructures of Coating B oxidized in excess of 600 hours at the two temperatures are shown in Figure 5. Examination of the photomicrographs revealed that elimination of pores is not a requisite to good oxidation resistance (many samples having coatings much less continuous than Coating B survived 600 hours of oxidation without failure). The microstructure of the coating which survived 612 hours at 2400 F has some similarity to the as-silicided microstructure with the exception that the long exposure resulted in the formation of a light-colored zone of high hardness beneath the porous coating. This light-colored hard sublayer does not have the ability to stop coating cracks from penetrating to the substrate and was shown (by electron-microprobe analysis) to result from diffusion of silicon into the substrate. The microstructure of Coating B oxidized for 659 hours at 1600 F retained more of the character of the as-silicided microstructure. Silicon did not completely penetrate the porous sintered modifier layer. The porous light-colored zone adjacent to the substrate appeared to have retained its crack-stopping ability as evidenced by the photomicrograph. The softness of the substrate of the specimens oxidized at either temperature suggested that the contamination of the substrate by oxygen or nitrogen did not take place to any appreciable extent. Bend ductility (as measured by a simple 90-degree bend test) was not lost as a result of oxidation, even though the average oxygen content of the substrate rose to 850 ppm during 612 hours of oxidation testing at 2400 F. Good room-temperature impact resistance was demonstrated in that the coating remained intact in the areas struck by the hammer used in the bend test.

The microstructures of Coating J oxidized in excess of 600 hours at the two temperatures are shown in Figure 6. Once again, most of the character of the as-silicided coatings was retained. Silicon, which diffused completely through the sintered alloy layer during the siliciding operation, continued to diffuse into the substrate during oxidation. Diffusion was faster at the higher oxidation temperature as would be expected. Although cracks completely traversed the coating, they did not interfere with the long-term oxidation protection. As the samples were heated to temperature at the outset of each oxidation cycle, the cracks undoubtedly closed, at least partially, as a result of the greater thermal expansivity of the coating relative to the substrate. Completion of crack closure (particularly for oxidation at temperatures below the pack siliciding temperature) was probably accomplished by the formation of a very small quantity of oxides in the form of a mixture of glass and crystalline material. Thermal expansion matching of coating and substrate appeared to be much less important than the makeup and rate of formation of the crack-healing oxides.

Room-temperature X-ray diffraction patterns for the in situ coatings indicated that Coating B consisted primarily of $MoSi_2$. Oxidation at 1600 F resulted in the formation of alpha-cristobalite SiO_2 on Coating B while oxidation at 2400 F produced rutile TiO_2 in addition to the cristobalite. The most readily detected phase in the as-silicided Coating J was the $(Ti_{0.8}Mo_{0.2})Si_2$ material characterized on ASTM card 7-331; however, $MoSi_2$, WSi_2(or a possible solid solution of the two), and VSi_2 appeared to be present. Although rutile was readily detected as a product of oxidation of Coating J at either test temperature, determination of additional phases was quite uncertain; beta-cristobalite and low-tridymite appeared to result from oxidation at 2400 F while oxidation at 1600 F appeared to have yielded the distorted quartz structure represented by ASTM card 12-708. The rutile formed by oxidation of either Coating B or Coating J at 2400 F was observed to show a preferred orientation of the (110) plane parallel to the surface.

The microstructure and the results of electron microprobe analysis of the J Coating "as-glassed" and after 1080 hours of exposure at 2400 F are shown in Figures 7 and 8. The somewhat porous structure of the coating and the use of mechanically mixed powders gives the traverse a major saw-tooth appearance. The principal difference in the traverses is in the formation of the oxide on the 2400 F specimens and the formation of the M_5Si_3 layer within the substrate. As would be predicted thermodynamically, the oxide is free of Mo and W and V and contains primarily Si and Ti. The subsilicide thickness is only 0.003-inch after this extended exposure.

Figure 9 contains representative plots of the weight gain during oxidation at 2400 F. The curves tend to have a general parabolic shape; frequently, steps in the curves were noted and attributed to crack formation and healing. Usually the curves for different specimens of a single coating composition were reasonably closely grouped; however, some rather widespread dispersions were observed, as indicated for Coating C. Although adherence of small quantities of the Dyna-quartz support medium to the oxidation samples tends to diminish somewhat the usefulness of the weight change data, some observations should be noted. There appears to be no correlation between oxidation resistance and weight gain. The specimen having the L Coating that survived 610 hours showed a much larger weight gain than the specimens having the B Coating. Of the samples having the B Coating, the short-lived samples displayed weight-gain versus time curves nearly coincidental with the curve for the sample which survived 612 hours.

Conversion of 20 milligrams of silicon/square centimeter to silica would yield to a weight gain of 22.8 milligrams/square centimeter. Thus, only a fraction of the silicon was consumed by oxidation as it was introduced into the coatings to the extent of 20 to 48 milligrams/square centimeter. In the case of the B-alloy-coated and also the J-alloy-coated samples oxidized in excess of 600 hours at 2400 F, less than 15 percent of the silicon was oxidized. Generally speaking, silicon consumption by oxidation was lower with the molybdenum-rich and the tungsten-rich coatings in comparison with the other compositions.

During long-term oxidation, loss of silicon by diffusion from the coating into the substrate may be more important than consumption by oxidation (Ref. 4). Diffusion of silicon across the interface between a disilicide layer and its metallic substrate results in the formation of M_5Si_3-type silicides on both sides of the original interface. Because these subsilicides are generally less oxidation resistant than the corresponding disilicides, diffusion of silicon from the disilicide coatings into their substrates is deleterious. Electron-microprobe analysis revealed that about 600 hours at 2400 F were required to convert the 0.001-inch thick disilicide sublayer within the substrate beneath Coating J to the M_5Si_3-type subsilicides. Thus, about 600 hours passed before silicon depletion of the silicided modifier alloy layer commenced.

PROCESS MODIFICATION

In an effort to eliminate the early oxidation failures, a study was made of the impregnation of the as-silicided coatings with a finely milled slip of glass frit. Silicided coatings of composition C were impregnated with a glass and were air fired at 1800 F for 10 to 14 minutes prior to initiation of the standard oxidation tests. Impregnation resulted in increasing the time of the earliest failure of a typical set of three samples at 1600 F from 16 hours to 111 hours in one experiment, and to 347 hours in another experiment. Glass impregnation of Coating J was investigated, but the absence of failures of the impregnated and unimpregnated control samples precluded determination of any effects of the impregnation. In Figure 4, five of the seven specimens that survived 600 hours at 1600 F and five of the eight specimens that survived 600 hours at 2400 F were actually impregnated.

To assess the statistical performance of the coatings, a series of forty T222 alloy specimens (0.060-inch x 1-inch x 2-inches) was processed with each of the Coatings C and J using glass impregnation as the final test step. The specimens were divided into two groups for 600-hour cyclic furnace testing at 1600 and 2400 F (20 specimens of each coating at each temperature). The test cycles were two hours for the first 40 hours and 20 hours for each cycle thereafter. A specimen was removed, as a contractual requirement, after every 40 hours of testing. (If no failures occurred, only six specimens would remain at the end of testing.) With the J Coating no specimens failed in 600 hours at 1600 or 2400 F. The failure times for the C Coating are shown in the Weibull plot, Figure 10. For this coating the minimum 1600 F life was 40 hours and the maximum was 160 hours; at 2400 F, the minimum life was 380 hours and the maximum was 440 hours.

OXIDATION TESTING - OTHER ORGANIZATIONS AND SPECIAL TESTS

Although the sintered slurry coatings were developed primarily for use at 2400 F and down, there is interest in the more refractory coatings for use at temperatures up to 3600 F. McDonnell-Douglas, Inc., in their Tantalum System Evaluation (Ref. 5), and TRW, Inc., in a coating development program (Ref. 6), are considering tungsten silicide as a candidate protective system for tantalum alloys. The C Coating in the glass impregnated condition has been evaluated by both organizations. A summary of their test results is presented in Table II, and a comparison with pack or slurry silicided tungsten applied by chemical vapor deposition is presented in Figure 11. The results at McDonnell indicate a more consistent performance of the slurry-sinter process at 3500 F and below and a slightly longer life for the other coatings at 3600 F.

Although the furnace test at McDonnell-Douglas or the torch tests at TRW may indicate a useful life for the W-Si type of coatings at 3500 F, such usage must be preceeded by more sophisticated testing, particularly for re-entry applications. In a recent single test on a four-inch diameter, simulated nose cap provided with the Coating C (substrate 90Ta-10W), the coating failed in a low pressure hypersonic plasma arc test in seconds at an initial uncorrected optical setting of 3150 F. The conditions for this test, performed by Space General, are shown in Table III.

Immediately after insertion of the cap in the arc, a red glow was noted which was probably the vaporization of the glass used in impregnation and the surface silica. Within 10 to 15 seconds the optical temperature increased to 3800 F (approximately the melting point of WSi_2), and then rapidly increased to 4000 F. The test was terminated after 15 to 20 seconds when failure was apparent.

The inside and outside of the cap are shown in Figures 12 and 13. Fusion of the silicide was readily apparent on the inside of the cap. Based on these results, it appears that the emittance of the coating under the condition of the test must have dropped from perhaps 0.8 initially to 0.4 or lower. The temperature at constant heat flux thus increased producing the rapid coating failure. At this juncture in the application of the coating to aerospace structures, it appears that the use of the coating should be restricted to below a heat flux of 75 btu/ft^2 sec under low pressure, high velocity conditions. This conclusion is based on the appearance of the nose cap in the area exposed to this heat flux.

Although most of the test results above 2500 F have been obtained for the C modification, a series of diffusion bonded T222 alloy box beams (0.6-inch x 0.6-inch x 5.0-inch x 0.030-inch wall) for compression tests were provided with Coating J (Fig. 14). At the time of writing of this paper only one had been tested. The specimen shown in Figure 15 was inductively heated in air to 2800 F twice for five minute periods. On the second heating a compressive load of 865 pounds was applied to the beam, through dense Al_2O_3 cylinders and J coated 1/8-inch T222 pressure plates, at a strain rate of 0.003 in/in minute. The test was terminated when the beam bent 0.040-inch instead of bulging, and when one of the Al_2O_3 cylinders cracks. Total compressive stress in the beam was 12,300 psi. The appearance, as can be noted in Figure 15, is excellent after the test. The coating had a generally vitreous appearance without craze cracks. The pressure plates were tenaciously bonded to the beam at the conclusion of the test.

COATINGS FOR COLUMBIUM-BASE ALLOYS

In separate research programs (Ref. 2 and 7), two of the more promising coating compositions (B and J) were evaluated (with and without modification) on the columbium base alloys Cb752 (Cb-10W-2.5Zr), D43 (Cb-10W-1Zr-0.1C) and Cb132M (Cb-20Ta-15W-5Mo-1 to 2Zr-0.1 to 0.2C). These coatings were also evaluated by the Pratt and Whitney Division of the United Aircraft Corporation (Ref. 8).

The coatings on columbium alloys were applied by procedures similar to those described for tantalum alloys. Compositionsl studies were concentrated on Coating B, (95Mo-5Ti)-Si, with the goal of improving the inconsistency of the protection at 1600 F. Iron, manganese and boron were added to increase glass formation at this low temperature. Titanium was increased in several compositions, and glass slip impregnation, as described for the coatings on tantalum alloys, was investigated.

The furnace cyclic oxidation life of the experimental coatings on 0.030-inch x 1-inch x 2-inch Cb752 alloy specimens and their compositions are shown in Table IV (MAB-201M test cycles were used, i.e., 24-hour cycles at 1600 F and 1-hour cycles at 2400 F). Using the standard B coating as a reference, increasing titanium content had an adverse effect on coating life at 2400 F and slightly improved the 1600 F life; boron was deleterious to 2400 F and highly beneficial to the 1600 F life; manganese had no effect at either temperature; and iron additions or glass impregnation retained the excellent 2400 F performance and also markedly increased 1600 F oxidation life.

Test data are far more limited on the coated columbium alloys than on tantalum alloys; however, Pratt and Whitney, on an Air Force contract (Ref. 8), evaluated the glass impregnated B Coating for impact and erosion resistance. The latter test was performed under both thermal fatigue and isothermal erosion conditions. Solar, on two Air Force contracts (Ref. 2 and 7), investigated the thermal fatigue performance of the B and J Coatings in two types of rigs and also the performance of the coating after impact.

The erosion rig-thermal fatigue data and test conditions are summarized in Table V. The data illustrate that both the J and B Coatings routinely exhibit lives in excess of 100 hours at 2400 F in erosion rig testing. Perhaps an even more significant point is the resistance of the coated alloys to thermal fatigue. The coating within the test duration (1000 to 2400 cycles to T_{max} as high as 2500 F) have exhibited no failure in either large erosion rigs or the miniature erosion rig (Ref. 7). In the latter rig in which T_{max} is reached in 12 seconds and held for 30 seconds, a superalloy (WI-52) heated to T_{max} of 2000 F (calibrated using TD-Nickel) cracked in 15 cycles. Since the coated columbium alloy withstands the up-shock considerably better than a commonly used superalloy, thermal fatigue definitely will not limit the utilization of coated columbium alloys.

The impact resistance of coated alloys was evaluated by Pratt and Whitney (Ref. 8) and Solar (Ref. 2). P&W used a ballistic impact test (0.75 gm pellet) at two velocities (200 and 500 ft/sec) and two impact temperatures (R.T. and 2200 F). Oxidation testing after impact was performed at 2200 F. Solar used a one-inch diameter, 12 ft-lb falling ball test at room temperature. The specimens were impacted both on an edge and in the center, and were tested at 1600 F and 2400 F. The test results are summarized in Table VI.

Neither Coating B nor Coating J exhibited catastrophic attack in one hour under any of the test conditions. A combination of edge impact testing and 1600 F subsequent exposure produced the most consistent early failures (two hours). Many of the specimens impacted at the center, either at R.T. or 2200 F, and subsequently oxidation tested at 2200 to 2400 F showed no failure in 5 to 16 hours. Typical falling ball impact test specimens with Coating J are illustrated in Figure 16 (center impact) and Figure 17 (edge impact).

SUMMARY AND CONCLUSIONS

The application of modifier alloys by slurry techniques followed by vacuum sintering allowed the application of tungsten-rich and molybdenum-rich alloys, in addition to other alloys. These modifiers yielded silicide coatings capable of protecting the T222 tantalum alloy for more than 600 hours at 1600 and 2400 F and the columbium alloys (D43, Cb752 and Cb132M) for more than 570 hours at 1600 F and 220 hours at 2400 F. Short-time, high-temperature performance indicated that the C Coating, (95W-5Ti)Si, may be protective for up to 1.75 hours at 3600 F and for longer periods of time throughout the entire lower temperature range.

Titanium and vanadium were observed to be beneficial components in the molybdenum-base and tungsten-base modifier alloys, while additions of chromium were not helpful. The porosity of the coatings after sintering was also observed to be beneficial (1) in allowing the deposition of up to 45 mg/cm^2 of silicon without edge damage, and (2) in acting as a crack terminus minimizing the number of cracks extending to the substrate-coating interface.

The coating providing the most consistent performance on the T222 alloy was J (35Mo-35W-15Ti-15V)Si. This coating exhibited no failures in less than 200 hours at either 1600 or 2400 F with a total of 62 specimens tested (31 at each temperature). This coating also exhibited the longest life time -- 1080 hours at 2400 F. Data on coated columbium alloys is too limited to select a specific coating composition with the best performance. In erosion rig testing the B composition, (95Mo-5Ti)-Si, after impregnation with a glass may be slightly superior to the other coatings; the coating has withstood more than 1500 cycles to 2500 F and up to 240 hours of erosion testing at temperatures Of 2200 to 2500 F. Ballistic impact and falling ball tests on coated columbium alloys at R.T. and 2200 F indicate that the J and B coatings are protective for 1 to more than 16 hours at 1600 to 2400 F after severe deformation.

Preliminary data indicates that impregnation with a barium boro-silicate glass of those coatings exhibiting early failure at 1600 F, i.e., B and C, exhibit markedly improved performance. Weight added is only 0.5 to 1.5 mg/cm^2 or less than 0.5 to 1.5 percent of the total coating weight. Oxidation resistance at 2400 F is unaffected or improved.

Coatings were applied in which silicon was driven partially or completely through the modifier. The J Coating appeared to require complete penetration to afford maximum protection; whereas, the C Coating exhibited satisfactory perform- with or without complete penetration by the silicon.

PATENT APPLICATIONS

Appropriate patent disclosures have been filed on the coating chemistries and deposition procedures described in this paper(1).

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TABLE I

SELECTED MODIFIER ALLOYS*

COATING DESIGNATION	COMPOSITION (wt %)				
	W	Mo	Ti	V	Cr
A	97.5	-	2.5	-	-
B	-	95.3	4.7	-	-
C	95	-	5	-	-
D	10	-	90	-	-
E	40	-	60	-	-
F	70	-	30	-	-
G	-	40	60	-	-
H	35	35	30	-	-
I	40	-	30	30	-
J	35	35	15	15	-
K	35	-	30	-	35
L	-	35	30	-	35
M	-	-	30	30	40

* All modifier alloys silicided after application to the substrate before oxidation testing.

TABLE II

SUMMARY OF VERY HIGH TEMPERATURE TESTING ON COATING C$^{(1)}$

Testing Organization	Ref.	Substrate Alloy	Test Technique	Test Cycle	Life-Hours				
					1600 F	2000 F	3100 F	3500 F	3600 F
McDonnell-Douglas	5	T111	Furnace	60 min.	20+, 20+, 20+	---	20+, 7, 10+		
				30 min.				5.5, 5.5, 2.5	
				15 min.					1.75, 0.5, 0.25
							2400 F	3000 F	3500 F
TRW	6	T222	Furnace or induction	0.8 to 3 hrs	---	39.5	86.0$^{(2)}$	0.5	0.08$^{(3)}$
					---	39.5	86.0$^{(2)}$	2.0	0.08$^{(3)}$
					---	14.5	93.0$^{(2)}$	8.5	0.08$^{(3)}$
			Torch (localized heating)	0.5 to 1.0	---	---		2.0	1.16$^{(4)}$
				"	---	---		2.25	1.88$^{(4)}$
			Plasma arc	"	---	---		3.0	
			O_2-C_2H_2	0.5 to 1.0	---	---	6.5		
				"	---	---	12.0		
				"	---	---	13.0		

(1) (95W-5Ti)-Si (2) Support failure (3) Optical temperature, uncorrected

(4) Uncorrected optical reading of 3150 F, melted at optical reading of 3300 F.

TABLE III

TESTING OF C-COATED 4-INCH DIAMETER Ta-10W NOSE CAP MODEL

(Data for Space General testing of Solar Model)

Cold Wall Heat Flux*	Stagnation Point 95.2 btu/ft^2 sec 15° 98.3 btu/ft^2 sec 30° 76.4 btu/ft^2 sec
Gas Enthalpy	3010 but/lb
Model Stagnation Pressure	0.003527 atm (2.68 Torr)
Nozzle Stagnation Pressure	0.008553 atm (6.50 Torr)
Gas Flow	0.02405 lbs/sec

*Fusible copper calorimeter used.

TABLE IV

OXIDATION PERFORMANCE OF THE (Mo-Ti)-Si AND (Mo-Ti-X)-Si COATING SYSTEMS ON 0.030-INCH Cb752 ALLOY

Coating Composition	Oxidation Performance Hours to Failure for Each Specimen	
	1600 F	2400 F
(70Mo-30Ti)-Si	<96, <144, <264	11, 14, 35
(90Mo-10Ti)-Si	<24, <24, <24	104, 166, 166
(95Mo-5Ti)-Si	<24, <24, <24	130, 171(1), 281
(80Mo-5Ti-6B)-Si	>576, >576, >576	24, 31, 36
(86Mo-4Ti-10Fe)-Si	<24, >576, >576	202, 210, 220
(86Mo-4Ti-10Mn)-Si	<24, <24, <24	166, 166, 166
(95Mo-5Ti)-Si-impregnated	<240, >552, >552	222, 229, 255

1. Specimen dropped and damaged.

TABLE V

EROSION RIG TEST DATA

Erosion Rig Test Organization	Coating	Ref.	Alloy	Cycle (rotation)	Fuel	Life Hours or Cycles	Comments
P&W(1)	B (95Mo-5Ti)-Si	8	Cb132M	20 hrs (1750 rpm)	JP-5	100 hrs 2200 F + 100 hrs 2400 F +40 hrs 2500 F	No substrate loss. Evidence of substrate oxidation (2 specimens).
Solar(1)	B	2	D43	6 to 8 hrs (1750 rpm)	JP-5	+100 hrs, +100 hrs, +63 hrs, 17 (all 2400 F)	
Solar(1)	J (35W-35Mo-15Ti-15V)-Si	2	D43	6 to 8 hrs (1750 rpm)	JP-5	+100 hrs, 77-1/2 (100) hrs (all 2400 F)	Both specimens satisfactory at 100 hrs, but one showed pinhole defect at 77-1/2 hrs.
Thermal Fatigue Test Organization							
P&W(3)	B	8	Cb132M	1 min. hot 1/2 min. air blast (1850 rpm)	JP-5	600 cycle 2200 F +400 cycles 2400 F +1200 cycles 2500 F	No failure. Test continued.
Solar(1)	B	2	D43	3 min.hot 2 min. cool (1750 rpm) Mach 0.85	JP-5	1000 cycles 2400 F	No failure. Test stopped. Some glass flow (3 specimens).
Solar(1)	J	2	D43	"	JP-5	"	"
Solar(2)	J	7	D43	12 sec. to 2400 F 30 sec.hot air cool	Propane-oxygen	"	No failure, no fatigue cracking (2 specimens).

(1) Large erosion rig, 1/2" chamfered bar specimens, 3 inches long. (3) Standard paddle
(2) Miniature erosion rig .030 radius, 15° angle specimens, 1-1/2 inch long.

TABLE VI

IMPACT TEST RESULTS - COATED COLUMBIUM ALLOYS

Coating	Alloy	Test Organization	Ref.	Type of Test	Test Conditions	Post Impact Test Type	Hours to Failure	Comments
B (95Mo-5Ti)-Si	Cb132M Paddle	P&W	8	Ballistic (0.75 gm projectile)	200 ft/sec 70°F	Erosion rig 2200°F	1	Oxide surrounding impact depression
B	Cb132M Paddle	P&W	8	Ballistic (0.75 gm projectile)	200 ft/sec 2200°F	Erosion rig 2200°F	16+	No failure, stopped test.
B	Cb132M Paddle	P&W		Ballistic (0.75 gm projectile)	500 ft/sec 70°F	Erosion rig 2200°F	16+	No failure, stopped test.
B	Cb132M Paddle	P&W	8	Ballistic (0.75 gm projectile)	500 ft/sec 2200°F	Erosion rig 2200°F	1	Slight oxide surrounding impact depression.
B	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) center	12 ft-lbs R.T.	Furnace 2400°F	5	Oxide tension side only.
J (35Mo-35W-15Ti-15V)-Si	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) center	12 ft-lbs R.T.	Furnace 2400°F	5+	No failure, stopped test.
B	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) edge	12 ft-lbs R.T.	Furnace 2400°F	5	Slight oxidation.
B	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) center	12 ft-lbs R.T.	Furnace 1600°F	5	Slight oxidation.
J	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) center	12 ft-lbs R.T.	Furnace 1600°F	5	No oxidation.
B	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) edge	12 ft-lbs R.T.	Furnace 1600°F	2	Severe oxidation.
J	D43 0.030" x 1" x 2"	Solar	2	Falling ball (1" dia) edge	12 ft-lbs R.T.	Furnace 1600°F	2	Severe oxidation.

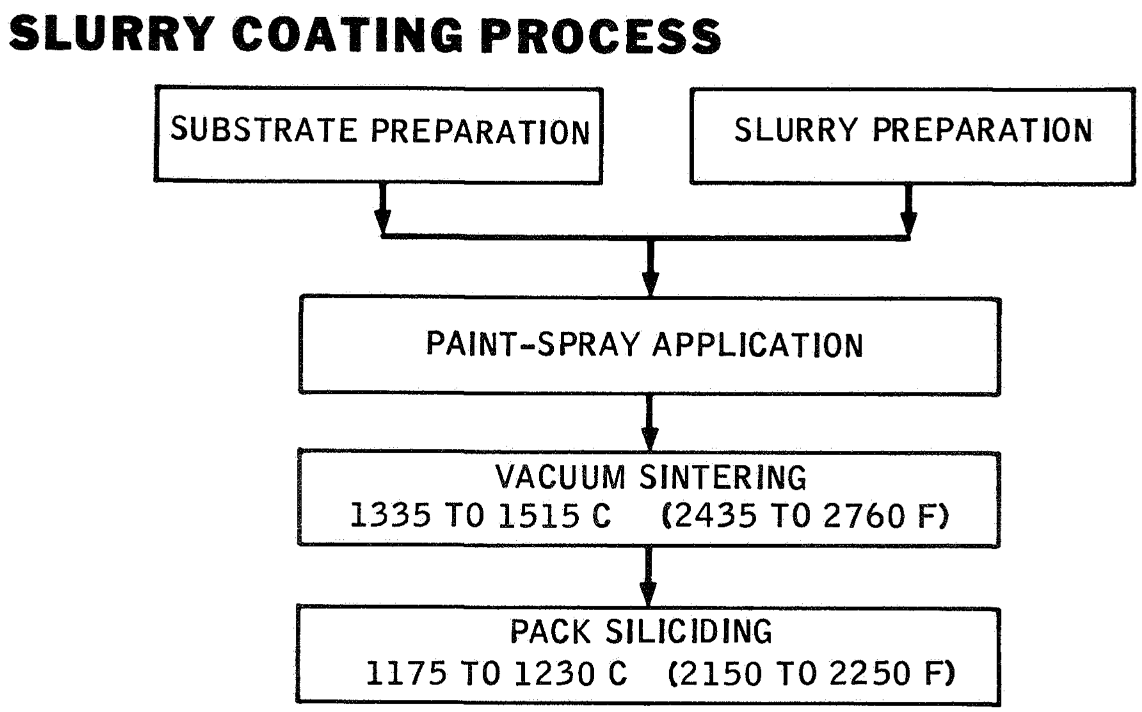
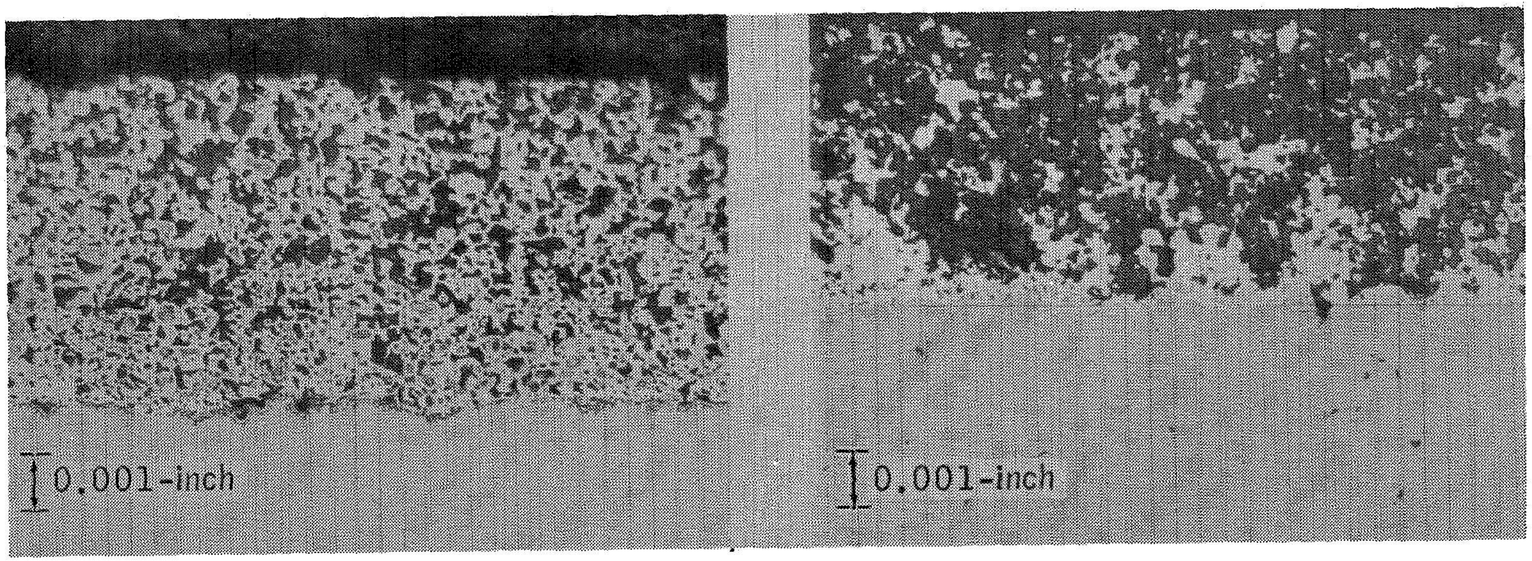

SLURRY COATING PROCESS

FIGURE 1.

AS-SINTERED SLURRY COATINGS

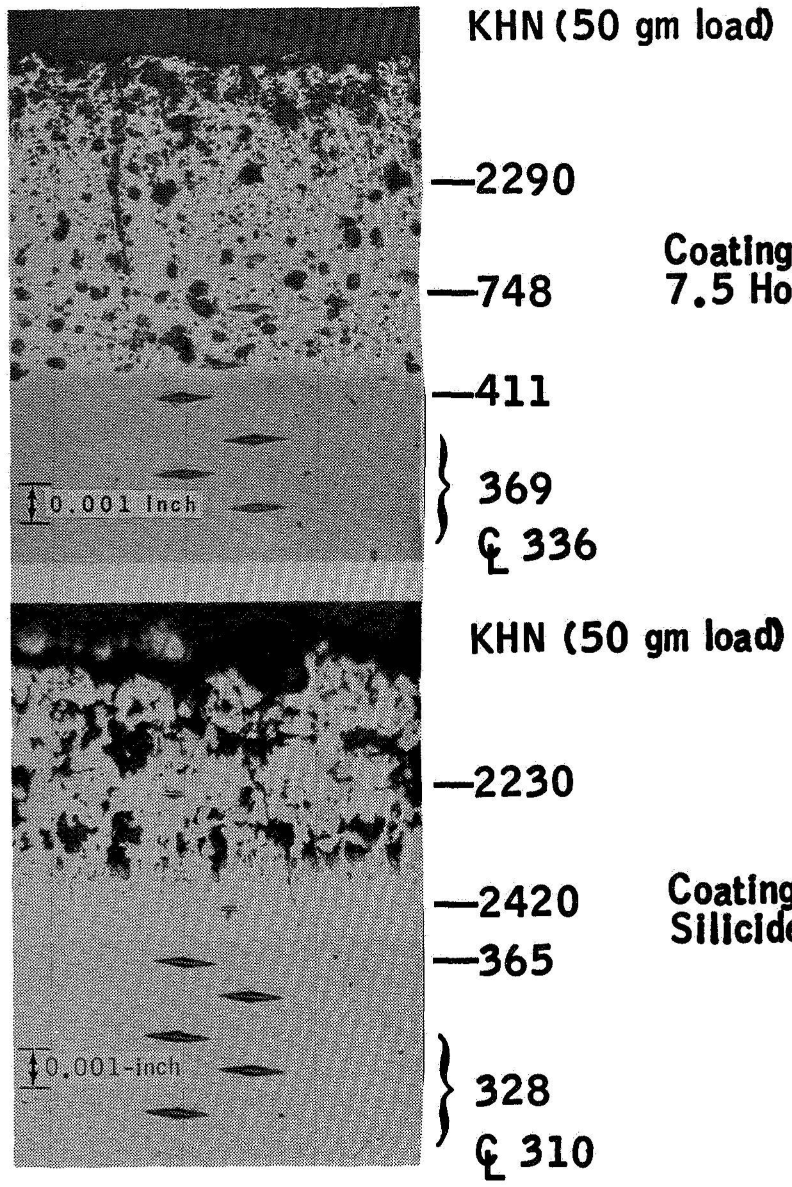


Coating B (95.3Mo-4.7Ti) Sintered
15 Hours at 1515 C (2760 F)

Coating J (35W-35Mo-15Ti-15V)
Sintered 15 Hours at 1515 C (2760 F)

FIGURE 2.

AS-SILICIDED SLURRY COATINGS



Coating B (95.3Mo-4.7Ti) Silicided
7.5 Hours at 1175 C (2150 F)

Coating J (35W-35Mo-15Ti-15V)
Silicided 7.5 Hours at 1175 C (2150 F)

FIGURE 3.

SOLAR A DIVISION OF INTERNATIONAL HARVESTER COMPANY

OXIDATION TEST RESULTS

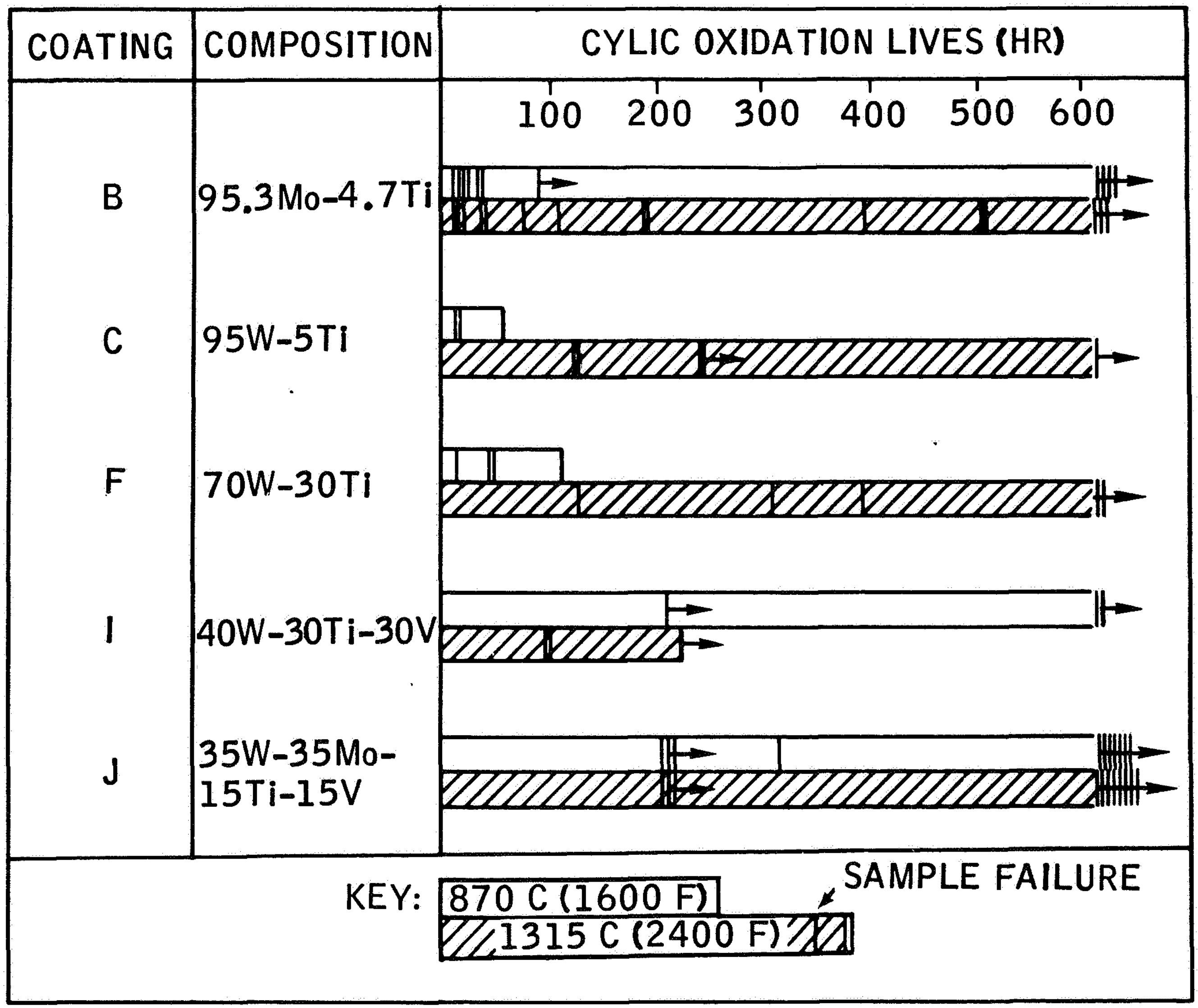
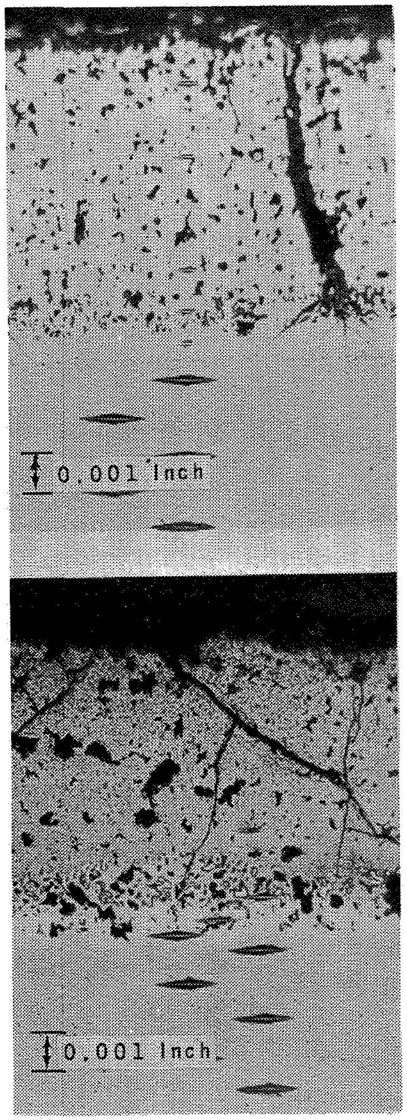


FIGURE 4.

COATING B AFTER OXIDATION



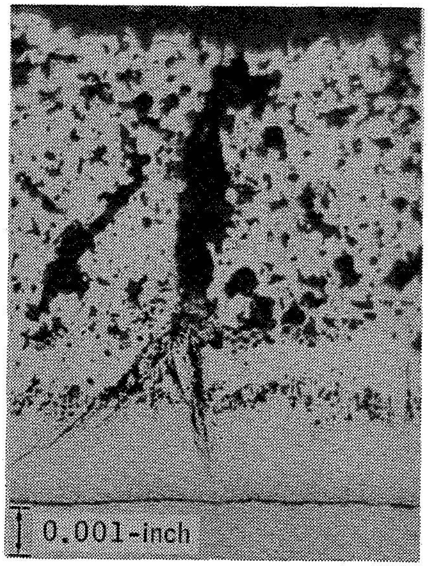
Oxidation Temperature: 1315 C (2400 F)
Oxidation Time: 612 Hours

Modifier Alloy B : 95.3Mo-4.7Ti

Oxidation Temperature: 870 C (1600 F)
Oxidation Time: 659 Hours

FIGURE 5.

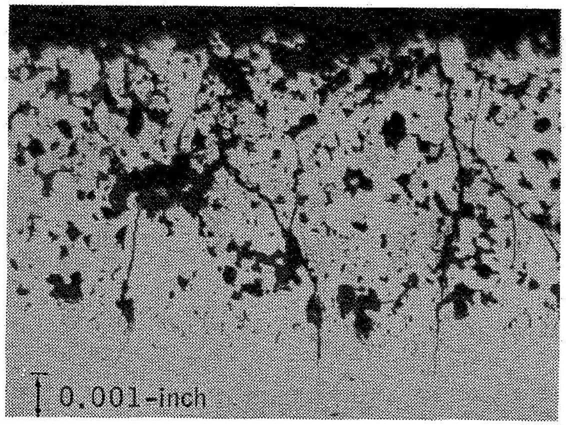
COATING J AFTER OXIDATION



Oxidation Temperature: 1315 C (2400 F)

Oxidation Time: 622 Hours

Modifier Alloy J : 35W-35Mo-15Ti-15V



Oxidation Temperature: 870 C (1600 F)

Oxidation Time: 630 Hours

FIGURE 6.

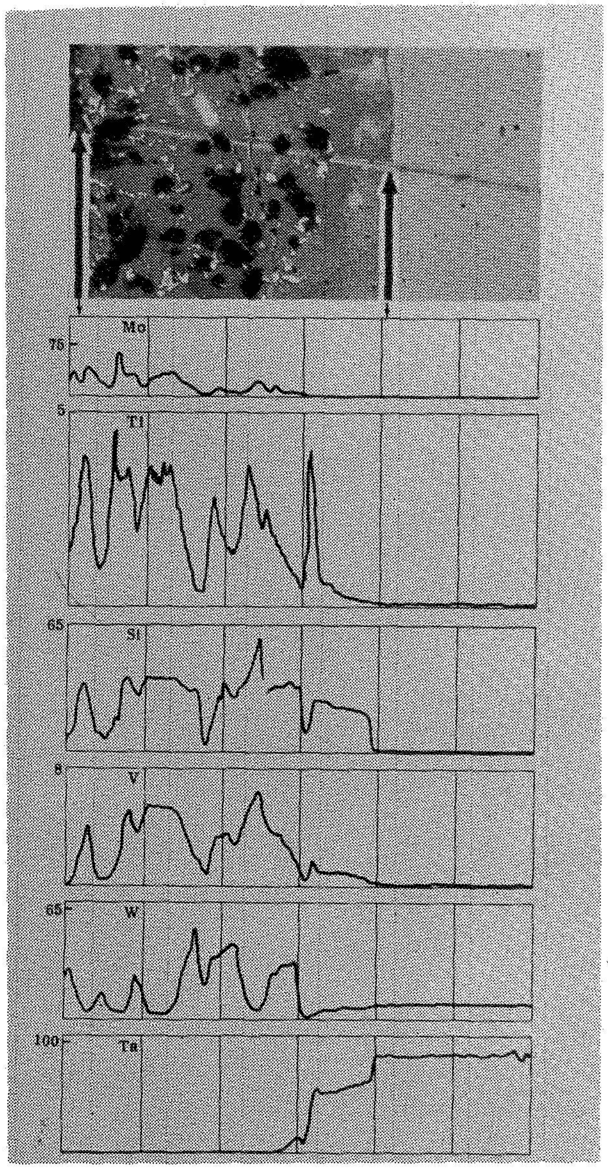


FIGURE 7. AS-GLASSED COATING J.

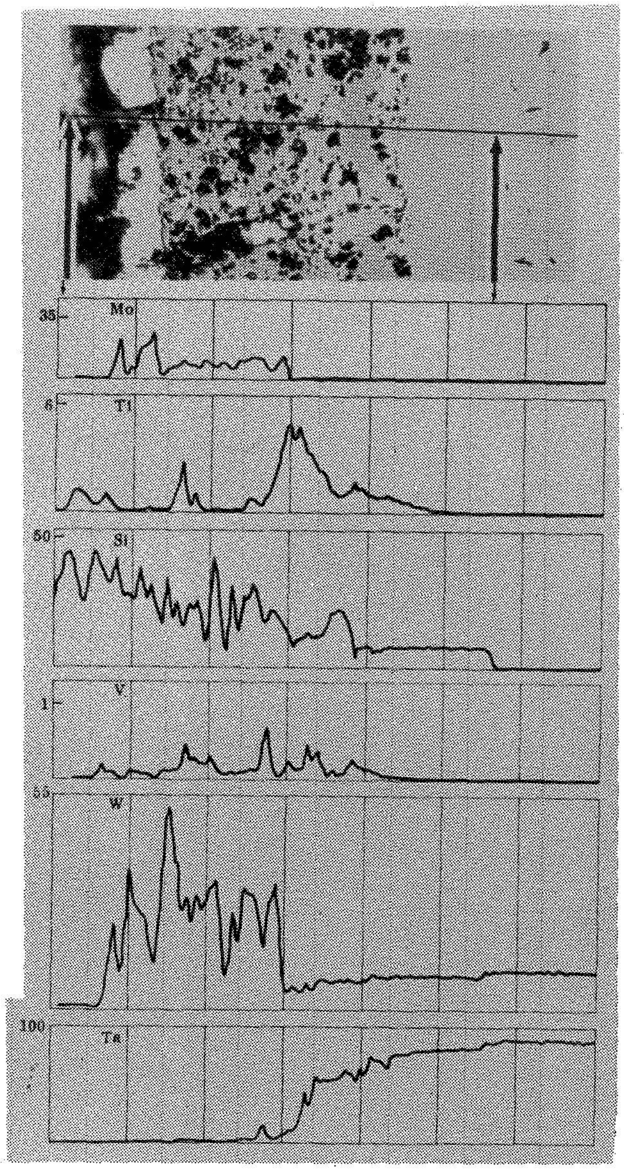


FIGURE 8. COATING J OXIDIZED 1080 HOURS AT 2400 F.

WEIGHT GAIN DATA

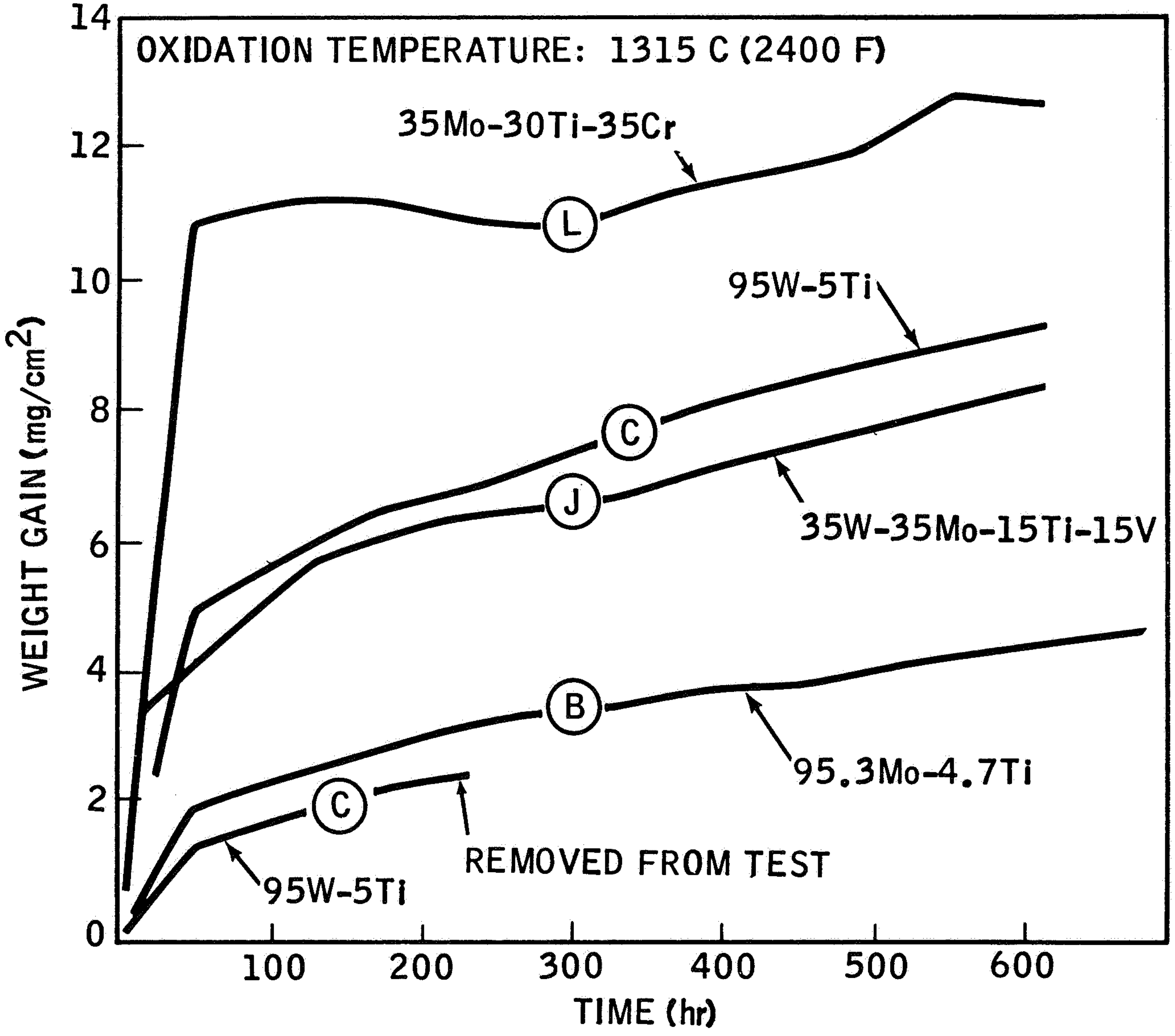


FIGURE 9.

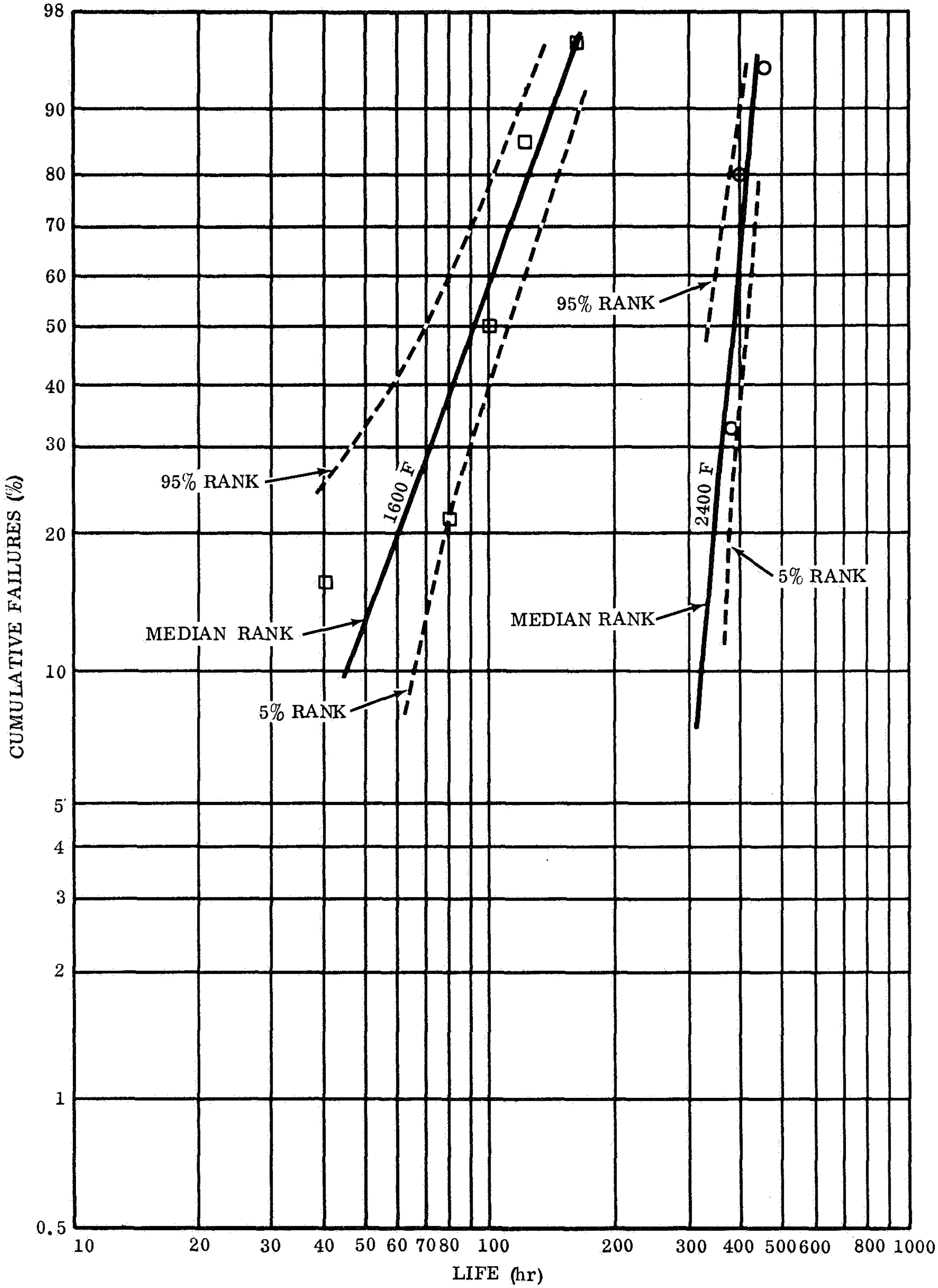


FIGURE 10. WEIBULL ANALYSIS OF TEST RESULTS FOR COATING C.

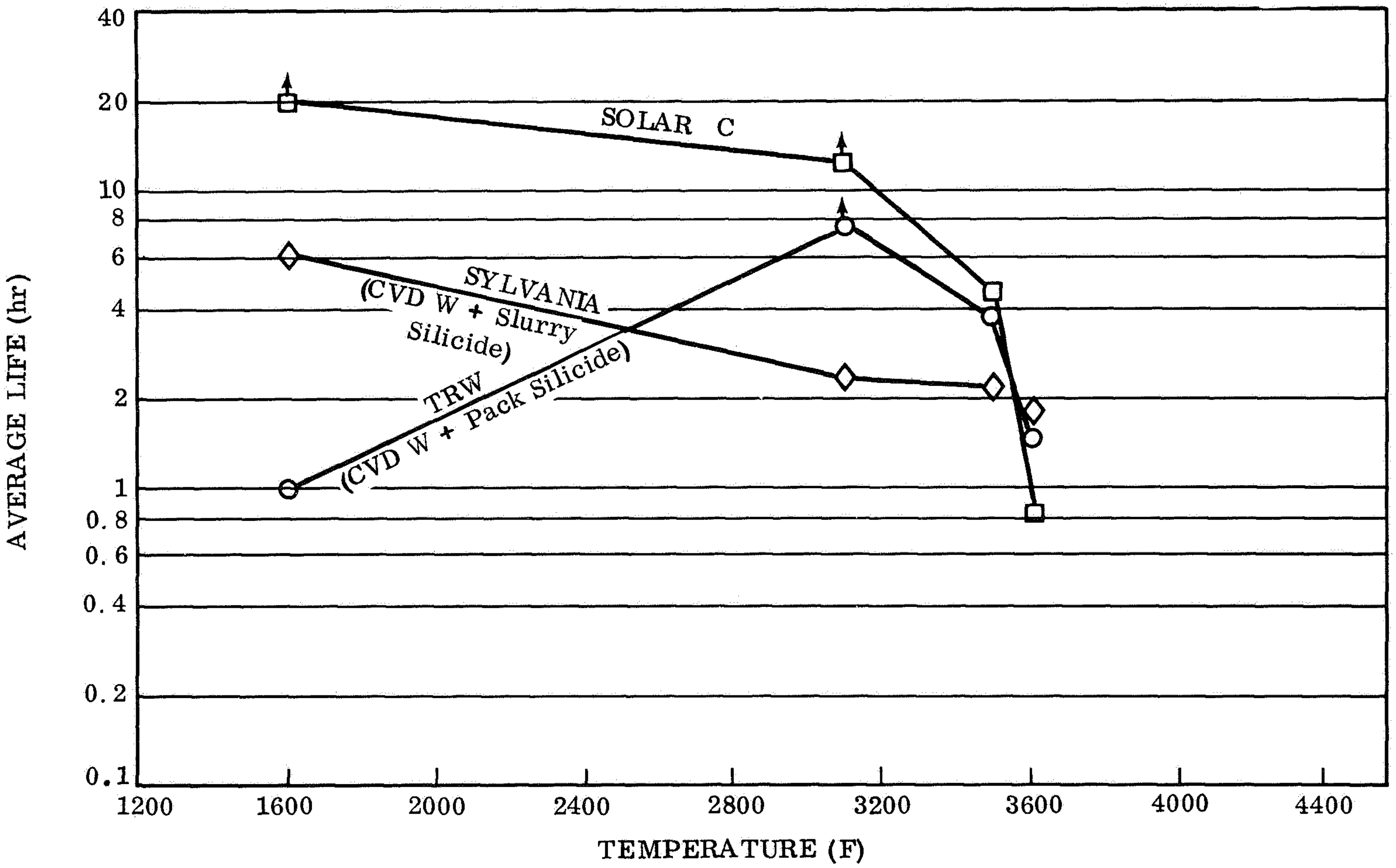


FIGURE 11. CYCLIC TEST RESULTS OF W-Si COATINGS ON T111.
(McDonnell, Ref. 5)

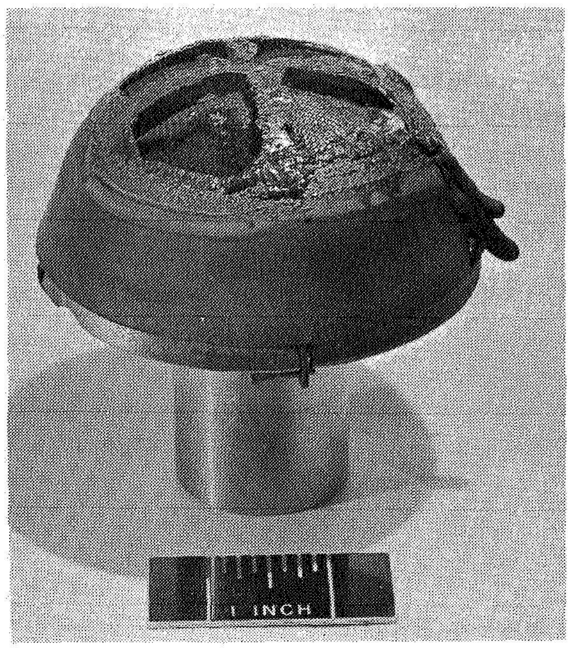


FIGURE 12. TESTED 4 INCH DIAMETER 90Ta-10W CAP COATED WITH C. EXTERNAL VIEW (See Table III for Test Conditions.)

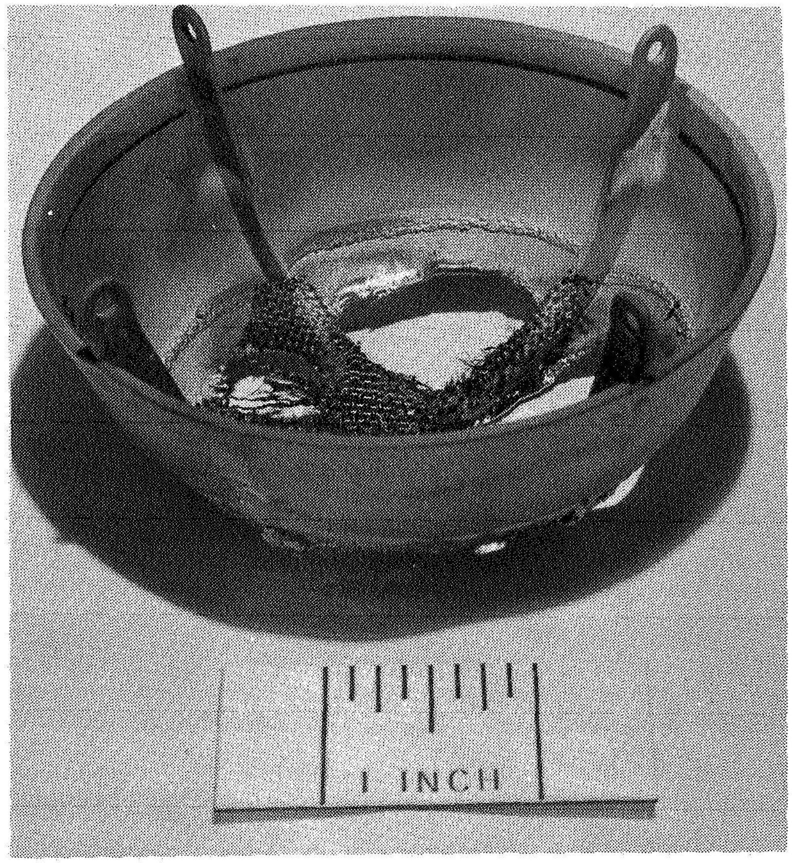


FIGURE 13. TESTED 4 INCH DIAMETER 90Ta-10W CAP COATED WITH C. (Inside of Cap with Mounting Hardware and Graphite Cloth Insulation Removed.) (See Table III for Test Conditions.)

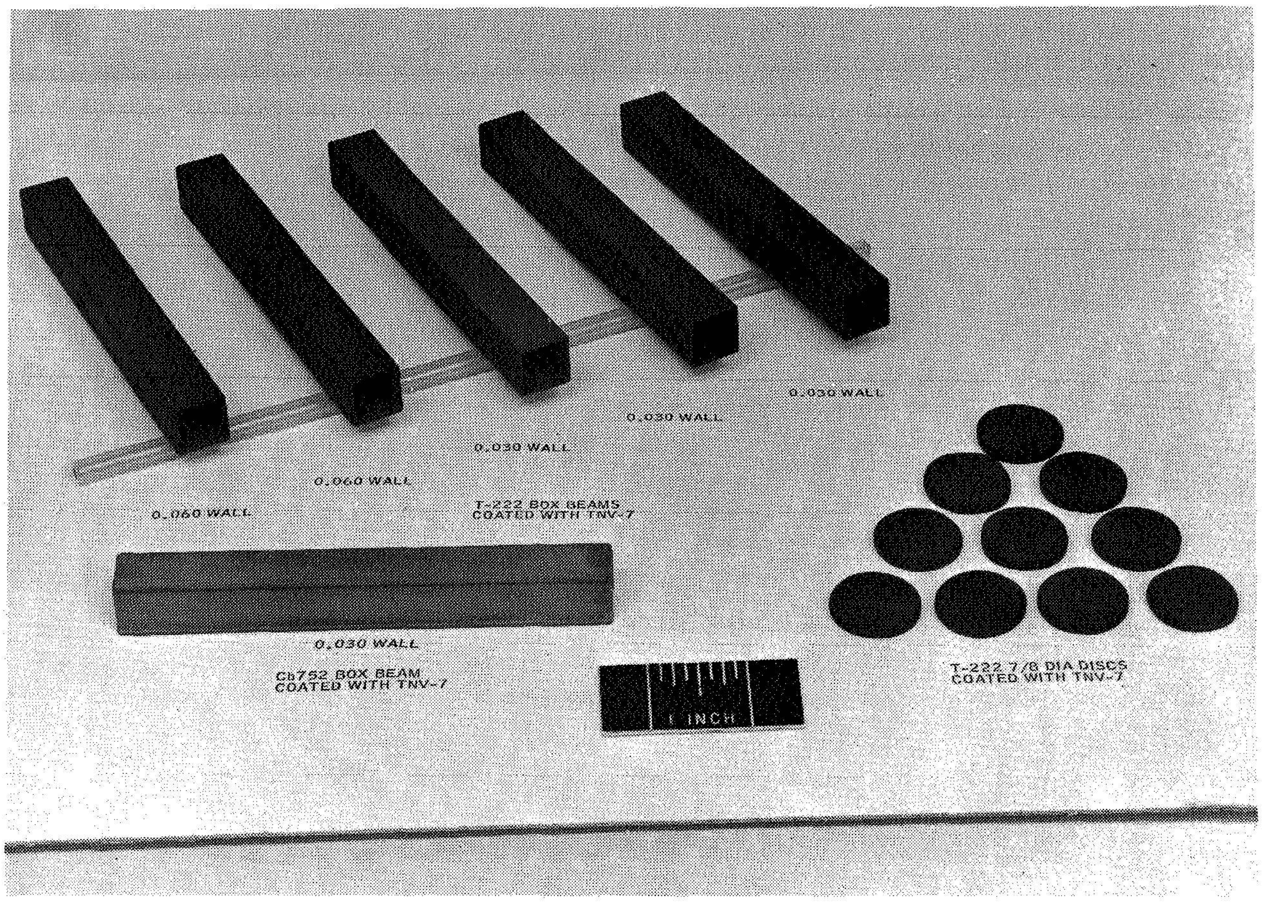


FIGURE 14. T222 BOXED BEAM WITH THE J COATING.

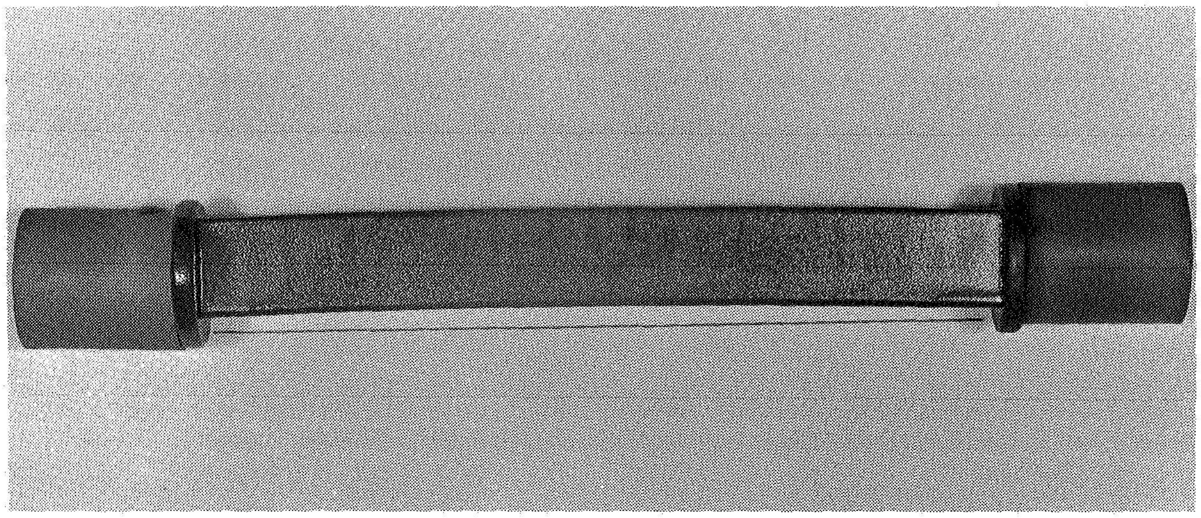
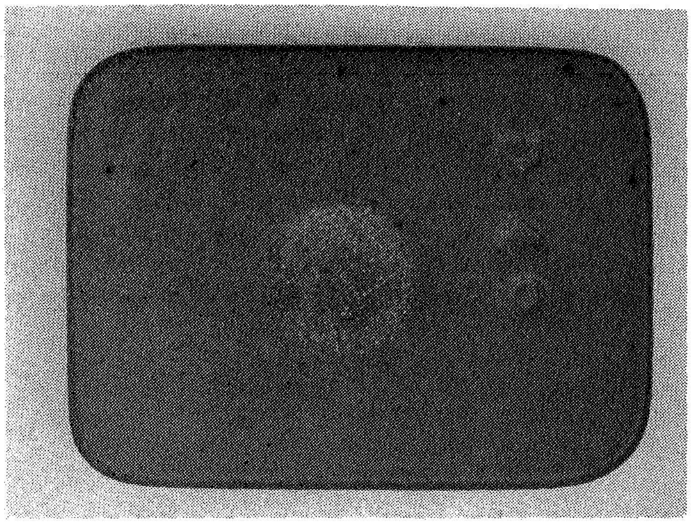
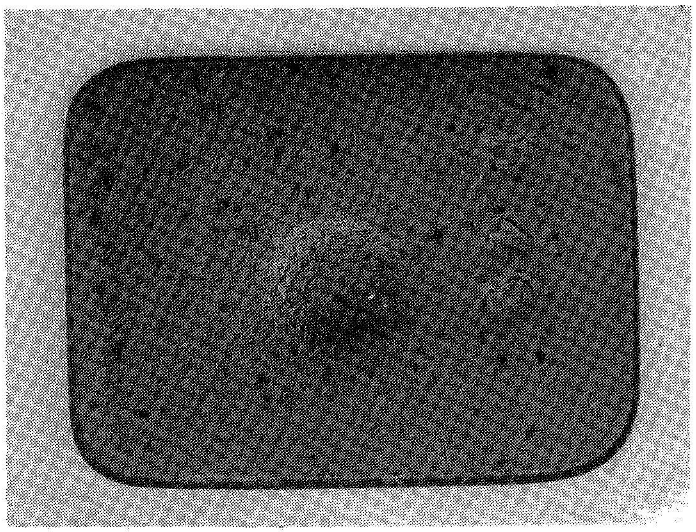


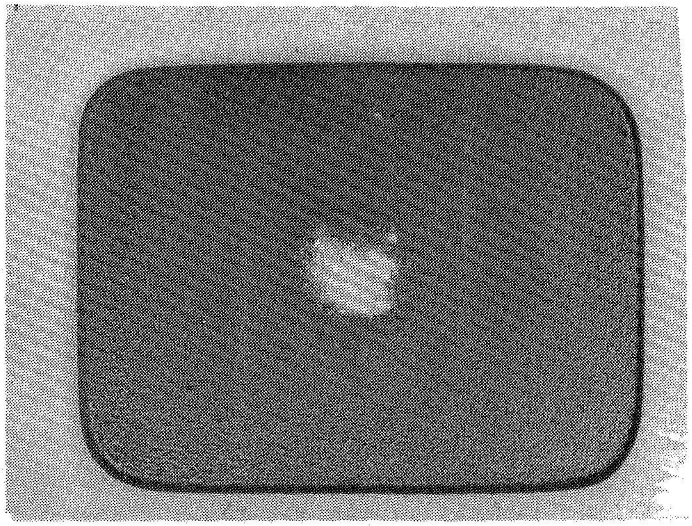
FIGURE 15. T222 BOXED BEAM COMPRESSION TESTED AT 2800 F IN AIR.



Specimen After Impact at 12 ft-lbs.

Compression Side After
5 Hours at 2400 F.

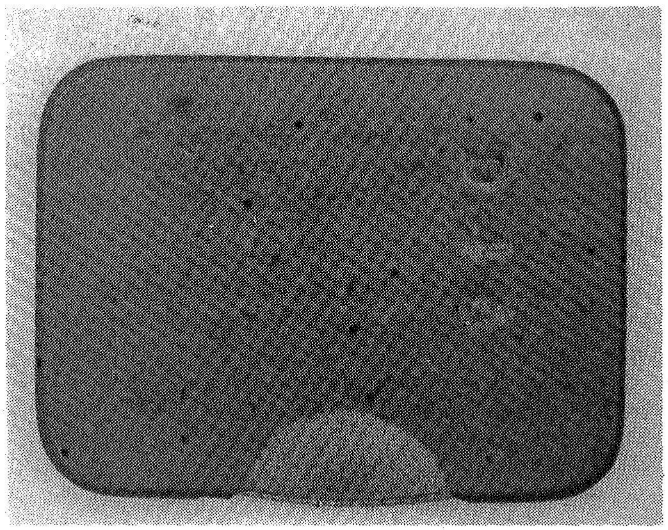




Magnification 3X

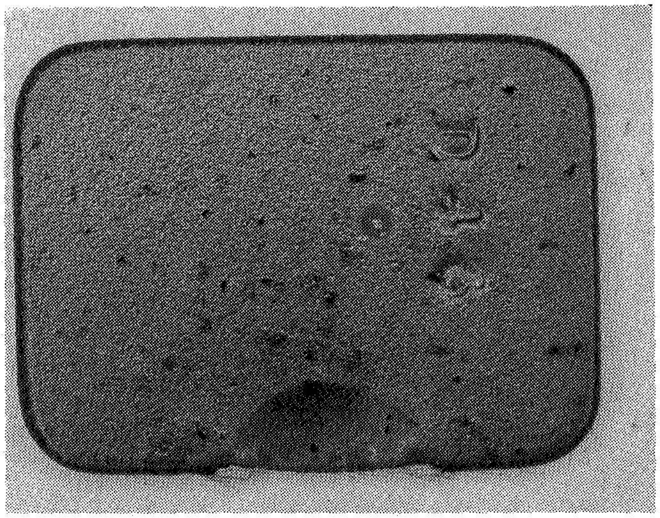
Tension Side After 5 Hours at 2400 F.
(White Area is Adhered Dyna-Quartz)

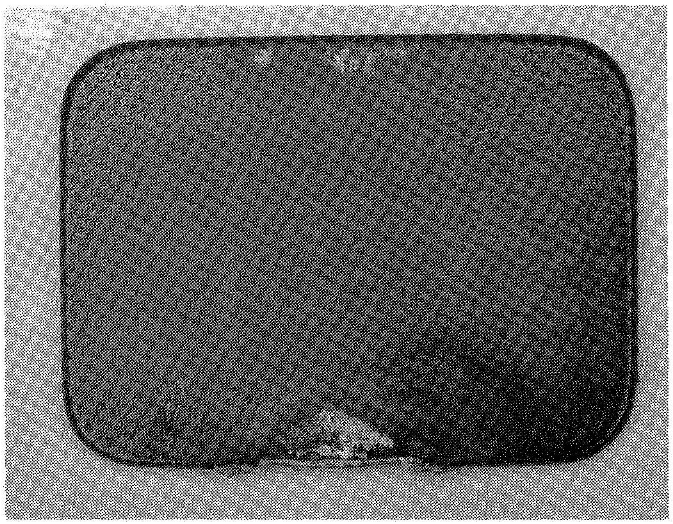
FIGURE 16. SPECIMENS AFTER CENTER BALL IMPACT; J Coating on 0.030-Inch D43 Alloy.



Specimen After Impact at 12 ft-lbs.

Compression Side After
5 Hours at 2400 F.





Magnification 3X

Tension Side After 5 Hours at 2400 F.

FIGURE 17. SPECIMENS AFTER EDGE BALL IMPACT TEST; J Coating on 0.030-Inch D43 Alloy.