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DIFFUSION STUDIES OF SEVERAL OXIDATION RESISTANT COATINGS ON Mo-0.5Ti MOLYBDENUM ALLOY AT 2,500° F

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

Results of a study on the diffusion effects of several silicide-base coatings on Mo-0.5Ti molybdenum-alloy sheet are presented. The magnitude of substrate thickness loss due to solid-state diffusion at 2,500° F is presented; this indicates the possible need for diffusion barriers between coating and substrate in some applications. The phase changes in the coatings during exposure at 2,500° F in air were studied to obtain an understanding of coating behavior. The phases which formed were identified by X-ray diffraction techniques. From these identifications an explanation is given for the superior oxidation protection of one of the coatings.

INTRODUCTION

Refractory metals are frequently considered for the external surfaces of heat shields in the thermal protection systems of aerospace vehicles. These applications may involve repeated flights which subject the heat shields to temperatures from 2,000° F to 3,000° F for time periods of 15 minutes or longer during each flight. Since all alloys of columbium, tantalum, molybdenum, and tungsten considered for these applications oxidize rapidly in air in this temperature range, their use in such an application requires that they be coated. The high density of these alloys makes it mandatory to utilize them in very thin gages, as thin as 0.001 inch in extreme cases.

A number of considerations are important to the coating used on refractory metals in an application such as that previously mentioned. Although the most important consideration for the thin-gage refractory metal application is reliable protection of the substrate from oxidation, other detrimental effects caused by diffusion must be considered. The substrate must retain sufficient strength and ductility over the intended range of usefulness. The coating, therefore, must not embrittle the refractory metal substrate during its application or in subsequent service. In addition, the coating must provide a barrier to diffusion of gases such as nitrogen, hydrogen, and oxygen, small concentrations of which may embrittle refractory metals at high temperatures. Since it is generally recognized that the oxidation resistant coatings have negligible load-carrying capacity, solid-state diffusion between the coating and the substrate must be limited because any decrease in substrate thickness results in corresponding loss of strength in the structural component.

There are several coating systems in various stages of development for the refractory metals. Among these, the silicide-base coatings have shown the most promise to date for the protection of molybdenum alloys. Coating studies found in the literature generally report on the coating life under given environments, mechanical properties of coated specimens, and so forth. One such study is reported in reference 1 for various silicide-base coatings on Mo-0.5Ti molybdenum alloy. However, there is little information on the diffusion problem encountered. The study reported herein was initiated to determine the magnitude of the solid-state diffusion effects for several silicide-base coatings on Mo-0.5Ti molybdenum alloy and to identify some of the mechanisms involved. The objectives for this investigation were:

(1) To determine whether the coatings had embrittled the molybdenum-alloy substrate beyond the range of usefulness in the coating application.

(2) To determine the magnitude of substrate loss due to solid-state diffusion during various exposures in air at 2,500° F.

(3) To obtain some insight into the mechanisms involved in the oxidation protection and solid-state diffusion processes by identification of the several phases present in the silicide-base coating after exposures in air at 2,500° F.

SPECIMENS AND PROCEDURES

Specimens

The specimens used in this investigation were small coupons, $1\frac{5}{8}$ inch by 3/4 inch by 0.012 inch (nominal before coating), machined to size by the National Aeronautics and Space Administration from arc cast Mo-0.5Ti molybdenum-alloy sheet. The sheet was obtained in the cold rolled and stress-relieved condition. The specimens utilized in the present study were obtained from the same lot procured for the study reported in reference 1. The thickness of each coupon was determined by micrometer measurement and the weight of each was tabulated before shipment to the coating supplier. The coated specimens were supplied to NASA during the period from July to December 1961. Upon receipt of the coated specimens, the weight of each specimen was again determined. Coated specimens with the smallest deviation from the average weight were selected for the present study. All the coatings investigated were silicide-base coatings with various other elements added as coating modifiers in some of the coatings. The coatings, methods of application, and coating constituents are given in table I along with references to additional information. Relative amounts of constituents and temperature time histories used in the application of the coatings on the Mo-0.5Ti molybdenum-alloy sheet were generally withheld as proprietary information by the coating suppliers.

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Procedures

High-temperature exposure.- The specimens were heated at ambient pressure in slowly moving air at 2,500° F in an electric furnace and continuously weighed. The weighing apparatus is described in reference 1. For each coating, one specimen was sectioned as coated, another after 1 hour continuous exposure, another after 8 hours continuous exposure, and another after coating failure as evidenced by a weight loss of at least 10 percent due to the formation of volatile MoO_3. For these specimens which failed, enough unoxidized areas remained to permit satisfactory thickness determinations.

Metallography.- The specimens were sheared warm (300° F to 500° F) into four sections and embedded, edges down, in lucite. They were then ground successively on No. 240, 320, 400, and 600 grit metallographic wet emery and polished in three stages on a vibratory polisher as follows:

(1) 14 micron diamond paste on nylon

(2) 0.3 micron levigated gamma alumina on nylon

(3) 0.1 micron levigated gamma alumina on microcloth

Etch-polish-etch procedures with the Murakami etch

$$\left[10 \text{ g } K_4Fe(CN)_6 \cdot 3H_2O, \quad 10 \text{ g KOH}, \quad 100 \text{ ml } H_2O \right]$$
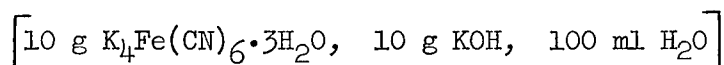
were used.

Thickness measurements were made by using a filar micrometer eyepiece on a bench microscope at approximately X150 magnification. The micrometer eyepiece was calibrated against a ruled grating. Each measurement reported represents an average of at least 12 readings on each specimen.

Microhardness measurements.- Microhardness measurements were made on a microhardness tester, using the Knoop indenter with a 100-gram load. Figure 1(a) indicates the pattern in which the hardness indentations were made on each specimen. Two cross-sectional traverses of 6 to 8 indentations were made in the substrate, and 9 to 12 indentations were made along the center line of each specimen beginning at the edge. In addition, hardness indentations were made in each of the various layers of the coating where possible.

A typical pattern of Knoop indentations is shown in figure 1(b). The substrate indentations indicate uniform properties throughout the cross section. The difference in hardness between the substrate and the coating is evident. Since the hardness of the substrate was uniform for each specimen tested, each Knoop hardness number reported for the substrate indicates an average of at least 21 indentations. Each Knoop hardness number reported for a coating phase indicates an average of at least 8 indentations.

Coating phase identifications.- Phase identifications in the coatings were made by combining metallographic examination and X-ray analysis. Specimens of each coating were mounted in lucite on edge and face down for metallographic and X-ray analysis. The procedure for the X-ray analysis consisted of obtaining a diffraction record by exposing the specimen to CuK_α radiation on a diffractometer. After exposure the specimen was ground by using metallographic wet silicon carbide papers until 0.0002 to 0.0005 inch of surface was removed as determined by micrometer measurements. The specimen was again exposed, and another diffraction record was obtained. Successive grindings and exposures were made until the base metal substrate was reached. Comparisons between the analyzed X-ray records and photomicrographs of the same specimen on edge made possible the identification of the coating phases present.

RESULTS AND DISCUSSION

Metallography and Microhardness

In this section results are presented for uncoated molybdenum-alloy sheet and for tests on the material with six different coatings. Although the purpose of the present study was not concerned with either coating life or mechanical property data, these results are of basic interest and are presented in figures 2 and 3 for completeness. These data are summarized from reference 1 and apply to the coatings in the present study. Figure 2 presents the oxidation test results under continuous and cyclic temperature exposure. In general, the life of the coated specimens was greatly decreased under cyclic temperature exposure. In figure 3, a summary of the tensile test results is presented. Microhardness results, thickness results, and photomicrographs obtained in the present investigation for each coating after various exposures are presented in figures 5 to 18.

General characteristics.- The arc-cast Mo-0.5Ti sheet used in this investigation was supplied in the stress-relieved condition. Typical photomicrographs of the Mo-0.5Ti sheet before coating and in the as-coated condition are shown in figure 4. The cross section of the uncoated material, which has a room-temperature ultimate strength of 133.4 ksi and an elongation of 11 percent in 2 inches, has a Knoop hardness of 398. The coating shown in figures 4(c) and (d) is a typical silicide-base coating and is designated as coating D in table I. The coating appears uniform and regular along the surface of the sheet but irregular at the edges indicating the susceptibility to edge failures which are often found with silicide-base coatings on refractory metals of thin gage. A discussion of edge failures for the coatings investigated herein is found in reference 1. In figures 4(c) and (d) the molybdenum-alloy substrate has been partially recrystallized by the temperature and time required in the coating process. The 1 hour recrystallization temperature of the 0.012-inch-thick Mo-0.5Ti sheet used in this investigation is approximately 2,400° F (ref. 2).

Coatings A and A(G).- Coatings A and A(G) were applied by a pack cementation process. This process consists of packing the specimen in a powder mixture in a

retort which is then heated and stabilized at a specific temperature for a sufficient length of time to produce a chemical reaction between the reactive elements in the pack and the surface of the specimen. This process produces an oxidation resistant layer on the surface of the specimen. Although this coating was applied to all specimens supplied by the contractor, approximately one-half were supplied to NASA in the as-coated condition, and one-half were subjected by the contractor to a "preglassing" treatment consisting of an exposure at 2,800° F for 1 hour in an oxidizing atmosphere. For the purpose of this study, these coatings were treated as two different coatings - that is, coating A, which was not preglassed, and coating A(G), which was subjected to the preglassing treatment.

[THESE ARE PROBABLY SILICIDE COATINGS]

Figure 5 presents photomicrographs of typical areas and hardness values for specimens of coating A. The coating procedure recrystallized approximately 65 percent of the Mo-0.5Ti substrate of the oxidation coupons. Average thickness values are given in table II and are shown graphically in figure 6 along with substrate hardness and percent recrystallization as functions of process and exposure time at 2,500° F. After full recrystallization, the substrate hardness did not change substantially with 8 hours exposure time at 2,500° F. There was a small increase in substrate Knoop hardness at 260 hours. The reduction in substrate thickness and increase in coating thickness with exposure time and the trends of decrease in total thickness in 1 hour followed by an increase for longer exposure times are shown in figure 6.

Similar data are presented in table II and figures 7 and 8 for coating A(G). The preglassing procedure completely recrystallized the Mo-0.5Ti substrate. The as-coated preglassed substrate, which had a tensile strength of 60 ksi at room temperature and an elongation of 3 percent (fig. 3), had a Knoop hardness of 252. These properties are substantially the same as those obtained for the uncoated Mo-0.5Ti sheet exposed for 1 hour at 2,800° F in vacuum. These results indicate that any embrittlement due to the coating or preglassing procedures was slight. The same trends are evident for the preglassed specimens subjected to high-temperature exposure that were discussed previously for the not preglassed specimens.

Coating B.- Coating B is reported to be a pure silicide coating with no additives (ref. 3). It is applied in a fluidized bed with a time-temperature combination sufficiently low so that the coating process resulted in less than 5-percent recrystallization of the substrate. Photomicrographs of typical areas and hardness values for specimens of coating B are presented in figure 9. The as-coated substrate, which had a tensile strength of 115 ksi at room temperature and an elongation of 8 percent (fig. 3), had a Knoop hardness of 361. The general trend of decrease in substrate thickness with time at 2,500° F as given in table II and figure 10 is evident. *[THIS IS PROBABLY BOEING'S DISIL]*

Coating C.- Coating C contained aluminum and chromium in the pack in addition to silicon. The coating procedure recrystallized approximately 25 percent of the substrate. In cross section this coating appears irregular in thickness in contrast to the other coatings studied which were generally uniform along the surface of the sheet. In figure 11(a) the thickness of coating C varies from

[PROBABLY THE VOUGHT COATING]

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0.0005 inch to 0.0017 inch in the typical cross section shown for the as-coated condition. Thickness values, tabulated in table II and shown graphically in figure 12, therefore tend to be less meaningful for this coating than for the others investigated. The as-coated substrate, which had a tensile strength of 120 ksi at room temperature and an elongation of 7 percent (fig. 3), had a Knoop hardness of 375. Substrate hardness change with exposure time was negligible after full recrystallization.

Coating D. - Coating D contained chromium in the pack in addition to silicon. (See ref. 4.) Figure 13 presents photomicrographs of typical areas and hardness values for specimens of coating D. The coating procedure recrystallized approximately 5 percent of the Mo-0.5Ti substrate. The as-coated substrate, which had a tensile strength of 120 ksi at room temperature and an elongation of 7 percent (fig. 3), had a Knoop hardness of 366. Average thickness values are presented in table II and figure 14. [PROBABLY THE CHROMALLOY W-2 COATING]

Coating E. Coating E was applied in a double pack cementation process - first a chromized coating, then a silicide coating. (See ref. 5.) Photomicrographs of typical areas of specimens of coating E are shown in figure 15. The coating procedure recrystallized approximately 40 percent of the substrate in the midplane of the sheet. The average hardness of the as-coated substrate is taken in this case as a weighted average of uniformly higher readings in the unrecrystallized zones and uniformly lower readings in the recrystallized band. The as-coated substrate, which had a tensile strength of 96 ksi at room temperature and an elongation of 8 percent (fig. 3), had a Knoop hardness of 347. Thickness values, given in table II and shown graphically in figure 16, indicate the reduction in substrate thickness and increase in coating thickness with 2,500° F exposure. The total specimen thickness decreased in the first hour at 2,500° F exposure and then increased with increasing time. Substrate hardness change with exposure time was negligible. [PFAUDLER PFR-5 COATING]

Coating F. Coating F contained columbium in the pack in addition to silicon. (See ref. 5.) Figure 17 presents photomicrographs of typical areas on specimens of coating F and hardness results. The coating procedure recrystallized approximately 40 percent of the substrate in the midplane of the sheet. As indicated for coating E, the as-coated substrate Knoop hardness of 317 is a weighted average. The as-coated substrate had a tensile strength of 97 ksi at room temperature and an elongation of 8 percent. The variations in thicknesses and substrate hardness with exposure time are shown in figure 18. Substrate hardness change with exposure time was negligible. [PFAUDLER PFR-6 COATING]

Comparison of Results for Various Coatings

Microhardness data.- It was noted previously for each coating in the as-coated condition that the hardness of the substrate was either uniform through the thickness or uniform for the recrystallized and unrecrystallized areas of the specimens of coatings E and F. These data indicate that the application of the coatings investigated did not embrittle the substrate beyond its range of usefulness. This effect was confirmed by the tensile test results. The substrate properties were significantly affected only by the magnitude of the temperature

utilized in the coating application and not by the presence of the coating. Hardness values for the specimens after the various exposures in air at 2,500° F were also uniform through the substrate thickness. It has been shown (ref. 4) that substrate Knoop hardness can be severely affected just below a large crack in the coating presumably because of penetration of atmospheric gases into the substrate. Those data (ref. 4) indicated that the difference in hardness between the center line and the outer edge of the Mo-0.5Ti substrate was as large as 200 Knoop numbers. The absence of this effect in the present investigation indicates that all the coatings had provided a diffusion barrier at 2,500° F to significant amounts of atmospheric gases until failure of the coatings. Knoop hardness numbers for the substrates of each of the coatings investigated are plotted in figure 19. The substrate hardnesses vary considerably in the as-coated condition due to the different amounts of recrystallization of the substrate produced by the coating applications. After various exposures at 2,500° F, the substrate has been fully recrystallized and substrate hardness values are approximately the same for all coatings.

Solid-state diffusion relationships.- The magnitude of the decrease in substrate thickness with exposure time in air is indicated in figure 20 by the test points for all the coatings investigated. An empirical relationship (eq. (1)) was found to describe the substrate thickness decrease with time satisfactorily for all the coatings investigated.

$$S = S_0 - \alpha t^\beta \tag{1}$$

where

S substrate thickness at time t

S_0 as-coated substrate thickness

t exposure time at 2,500° F in air

α, β constants

The difficulty of measurements of change in substrate thickness for coating C, noted previously, makes these results less reliable than for the other coatings and also suggests the possibility that the low diffusion rate indicated may be in error. The constants α and β for equation (1) were calculated on the basis of a least-squares analysis and are presented in table III for all coatings. The correlation between the empirical curves computed from equation (1) and the experimental points is shown in figure 20. The magnitude of the substrate thickness decrease for the silicide-base coatings on Mo-0.5Ti molybdenum alloy with time at 2,500° F is on the order of 0.001 to 0.003 inch in the first 10 hours. This indicates that solid-state diffusion barriers may be required when coated refractory metals of thin gage are utilized for high-temperature service in aerospace vehicles.

In order to provide a more thorough description and understanding of the diffusion phenomena which occur in the commercial silicide coatings and the Mo-0.5Ti substrate, a detailed X-ray diffraction investigation was undertaken to identify the various phases which form by a diffusion mechanism after extended lengths of time at 2,500° F.

Two silicide coatings were chosen for this investigation. Coating B was chosen because it is a pure silicide with no additives. Only silicon is used as the reactive element in the fluidized bed to produce a pure $MoSi_2$ coating. Coatings A and A(G) were chosen because of their long lives at high temperatures as shown in figure 2. If the effect of the additions to the silicon in the coating pack for coatings A and A(G) were understood, an explanation for the long 2,500° F oxidation life could be postulated.

Coating B.- Photomicrographs of coating B showing the growth and phase changes which occur during exposure are presented in figure 9. In the as-coated condition, the coating is essentially a single-phase layer of $MoSi_2$ as determined by X-ray diffraction. Figures 21(a) and 21(b) show highly magnified views of a typical specimen after 20.7 hours at 2,500° F with the various phases identified. In figure 21(a), the remainder of the original coating ($MoSi_2$) can be seen as a very thin layer in the outer boundary after diffusion has occurred. Figure 21(b) illustrates the optical activity of the $MoSi_2$ phase under polarized light. Included in this layer is an appreciable concentration of Mo_5Si_3. The Mo_5Si_3 formation has occurred at the expense of the $MoSi_2$ with the liberated silicon participating in the formation of an outer glassy layer on the specimen. It is this extremely thin layer of glass that has been postulated to provide oxidation protection and self-healing characteristics (ref. 3). This layer is not visible on the photomicrographs but is evident on inspection of the specimens after high-temperature tests. Further discussion of this phenomenon can be found in reference 1.

Adjacent to the layer of $MoSi_2$ and Mo_5Si_3, there is a relatively wide band of Mo_5Si_3. This layer was not immediately identifiable from X-ray diffraction patterns because of its strong preferential orientation. This preferred orientation resulted in X-ray patterns which did not readily correspond to data in the ASTM card catalog. Because of this, arc melted buttons of the synthesized compounds $MoSi_2$, Mo_5Si_3, and Mo_3Si were obtained to further pursue the identification of this phase. X-ray diffraction patterns of the Mo_5Si_3 button in the arc melted condition were the same as those of the coating phase in question. The Mo_5Si_3 button was then ground up, and a diffraction pattern of the powdered sample was obtained. This pattern resulted in the normal diffraction pattern for Mo_5Si_3. This indicates that the Mo_5Si_3 formed by the oxidation of $MoSi_2$ was randomly oriented, and the Mo_5Si_3 formed by diffusion of silicon toward the substrate was formed with a strong preferred orientation.

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Adjacent to the Mo_5Si_3 there is a very thin band next to the substrate material. This band was too thin to be identified by X-ray diffraction but could be expected to be Mo_3Si from stoichiometric considerations.

Coatings A and A(G).- Photomicrographs of coatings A and A(G) showing the growth and phase changes which occur during exposure are shown in figure 5 for specimens of coating A and in figure 7 for specimens of coating A(G). Before preglassing, the coating is essentially a single-phase layer of $MoSi_2$ but it can be seen that the preglassing treatment itself has caused phase changes. Figure 22 shows highly magnified views of coating A(G) after 120 hours exposure at 2,500° F with the various phases identified. In figure 22, at the outer surface the first intermetallic phase is a thin continuous band of Mo_5Si_3 which has formed upon decomposition of the original $MoSi_2$ with the liberated silicon reacting with oxygen to increase the glassy layer thickness. Next to the Mo_5Si_3 is a continuous layer of $MoSi_2$. Adjacent to this phase is a relatively thick layer of Mo_5Si_3, preferentially oriented as explained for coating B. Adjacent to the layer of Mo_5Si_3 there is a thin band identified as molybdenum boride silicide, $Mo_5(B,Si)_3$. Although this band appears to provide no protection against oxidation or diffusion, it does serve as an indication of the direction of mass flow. It has been shown (ref. 6) that inert marker movement is in a direction opposite to the predominating mass flow. It can be seen from figures 22 to 24, that this phase is moving in a direction towards the outer glassy layer indicating that diffusion of silicon inward is the predominating mass flow.

The phase adjacent to the $Mo_5(B,Si)_3$ is also Mo_5Si_3 formed when silicon diffusion penetrates the $Mo_5(B,Si)_3$. The thin phase adjacent to the substrate is assumed to be Mo_3Si.

An X-ray and metallographic examination of coatings A and A(G) after 260 and 1,000 hours exposure at 2,500° F indicates that, after approximately 200 hours exposure at 2,500° F, the Mo_3Si layer begins to grow appreciably in size. Figures 23 and 24 show sections of coated specimens after 260 and 1,000 hours, respectively. Growth of the Mo_3Si is evident.

There is also evidence that the Mo_5Si_3 layer adjacent to the glassy layer also decomposes as did the $MoSi_2$, forming Mo_3Si with random orientation and free silicon to react with oxygen and form more glass on the surface of the specimen.

The evidence of a boron compound in the coating itself indicates that boron might also be found in the outer glassy layer producing borosilicate glass in addition to the silica produced by oxidation of the silicon. The glassy layer of the coating A and coating A(G) specimens may therefore be expected to be a viscous liquid over a temperature range from below 2,000° F to over 3,000° F. The boron and traces of other additives, particularly aluminum, in the pack could also act to retard recrystallization of the outer glassy layer thereby retaining oxidation protection and self-healing characteristics in these coatings for long periods of time. A qualitative discussion of these phenomena in the formation and transitions in glass is found in reference 7.

CONCLUSIONS

An investigation was made to determine the diffusion effects of several silicide-base coatings on Mo-0.5Ti molybdenum-alloy sheet and to obtain a better understanding of coating behavior. The following conclusions are made for the data presented herein:

1. Solid-state diffusion barriers may be required when using silicide-base coatings on thin-gage refractory metals at high temperatures in aerospace vehicles.

2. The addition of detectable amounts of boron to one of the coatings appears to have provided a significant increase in oxidation protection over the other coatings investigated for Mo-0.5Ti molybdenum-alloy sheet.

3. The application of the coatings investigated did not severely embrittle the Mo-0.5Ti sheet. The changes which did occur in the mechanical properties of the substrate were attributed to the high-temperature exposure in the coating process. All coatings appear to have provided a diffusion barrier for the substrate against atmospheric gases at 2,500° F until failure.

4. The change in substrate thickness with exposure time at 2,500° F was satisfactorily described by an empirical relationship for the coatings investigated.

5. The X-ray diffraction techniques appear well suited for identification of coating phases as thin as 0.0001 inch and thus provide a means for identification of phase changes in coatings.

Langley Research Center,
    National Aeronautics and Space Administration,
        Langley Station, Hampton, Va., September 5, 1963.

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TABLE I.- PERTINENT INFORMATION FOR SEVERAL OXIDATION RESISTANT COATINGS

FOR Mo-0.5Ti MOLYBDENUM ALLOY

Coating	Method of application	Constituent elements in pack or bed	Source of information
A *Anature*	2-cycle pack cementation	Si, B, Cr, Cb, Al, C	Ref. 3, p. 111
A(G) *VICKOTE*	2-cycle pack cementation plus 1 hour preglassing treatment at 2,800° F	Si, B, Cr, Cb, Al, C	Ref. 3, p. 111
B *Boeing Crsil*	Fluidized bed	Si	Ref. 3, p. 95
C *VOUGHT*	2-cycle pack cementation	Si, Al, Cr	Ref. 3, p. 103
D *CHROMALLOY W-2*	2-cycle pack cementation	Si, Cr	Ref. 4
E *PFAUDLER*	2-cycle pack cementation	Si, Cr	Ref. 5
F *PFAUDLER (PFR-5)*	1-cycle pack cementation	Si, Cb	Ref. 5

TABLE II.- EFFECTS OF EXPOSURE TIME IN AIR AT 2,500° F ON SPECIMEN, COATING,

AND SUBSTRATE THICKNESSES FOR COATED Mo-0.5Ti MOLYBDENUM-ALLOY SHEET

Coating	Length of exposure, hr	Total thickness, in.	Substrate thickness, in.	Coating thickness, in.
A	Before coating As coated 1 8 260	0.0122 .0133 .0128 .0131 .0143	0.0099 .0096 .0099 .0051	0.0017 .0016 .0016 .0046
A(G)	Before coating As coated 1 8 1,000	0.0122 .0126 .0126 .0130 .0152	0.0092 .0075 .0072 .0055	0.0017 .0025 .0029 .0049
B	Before coating As coated 1 8 29.1	0.0108 .0111 .0120 .0112 .0121	0.0081 .0095 .0072 .0067	0.0015 .0016 .0020 .0027
C	Before coating As coated 1 8 22.1	0.0120 .0134 .0115 .0137 .0125	0.0106 .0095 .0093 .0097	0.0014 .0010 .0022 .0014
D	Before coating As coated 1 8 25.1	0.0121 .0133 .0132 .0130 .0134	0.0109 .0102 .0090 .0072	0.0012 .0015 .0020 .0031
E	Before coating As coated 1 8 70.1	0.0118 .0137 .0119 .0133 .0146	0.0091 .0071 .0059 .0056	0.0023 .0024 .0037 .0045
F	Before coating As coated 1 8 47.4	0.0116 .0135 .0132 .0130 .0148	0.0097 .0080 .0074 .0068	0.0019 .0026 .0028 .0040

TABLE III.- CONSTANTS FOR THE FORMULA $S = S_O - \alpha t^\beta$ DESCRIBING

Mo-0.5Ti SUBSTRATE THICKNESS DECREASE WITH

EXPOSURE TIME IN AIR AT 2,500° F

Coating	S_O, in.	α	β
A	0.0099	0.00030	0.248
A(G)	.0092	.00165	.1153
B	.0081	.00033	.4510
C	.0106	.00110	.0762
D	.0109	.00073	.5090
E	.0091	.00207	.1323
F	.0097	.00171	.1355
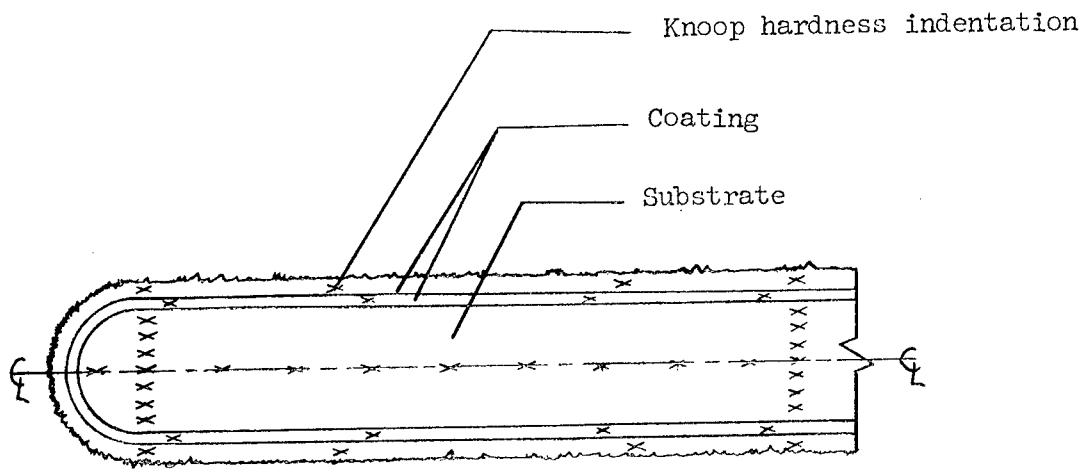
(a) Pattern used to obtain hardness data.

(b) Photomicrograph showing typical Knoop indentations. X160.   L-63-4768

Figure 1.- Procedures for hardness investigations on cross sections of coated Mo-0.5Ti specimens.
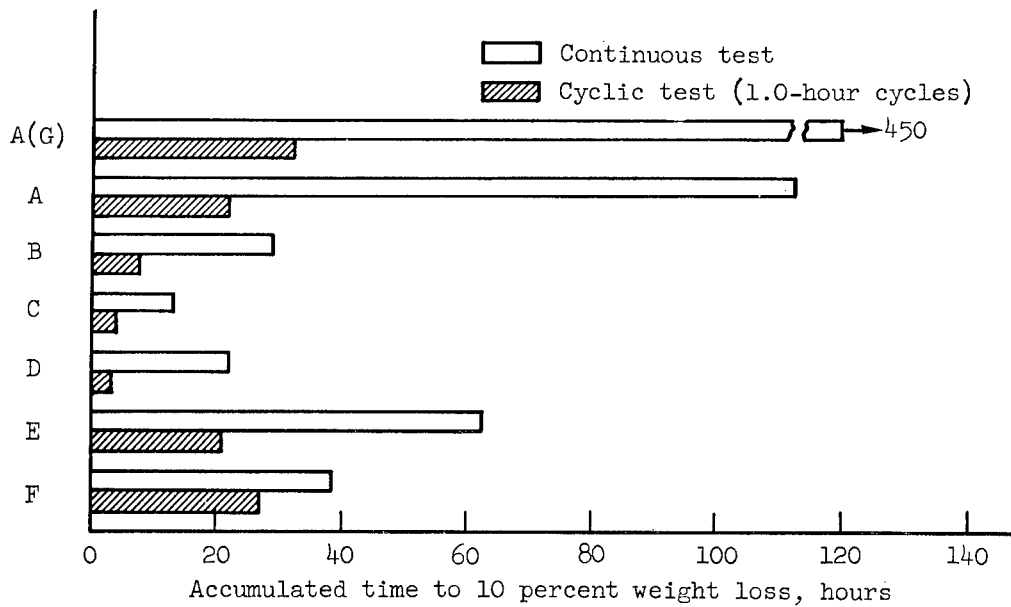
Figure 2.- Continuous and cyclic exposure coating life for various coatings on
Mo-0.5Ti molybdenum-alloy sheet (ref. 1).
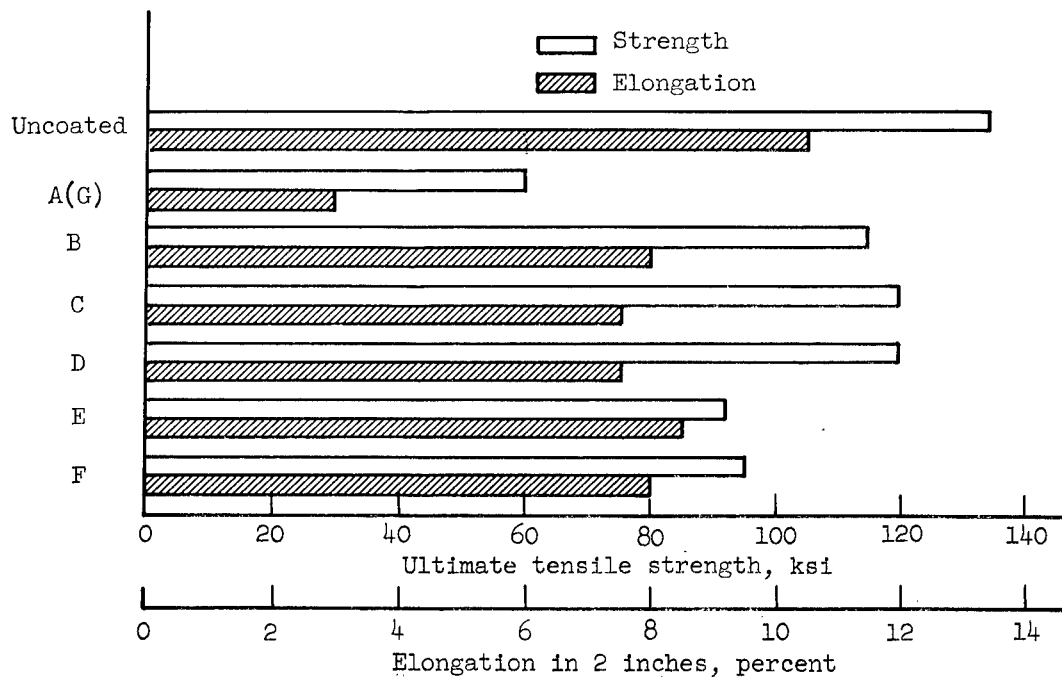
Figure 3.- Results of tensile tests at room temperature of uncoated and coated
Mo-0.5Ti molybdenum-alloy sheet specimens from reference 1. Strength is
based on cross-sectional area before coating.
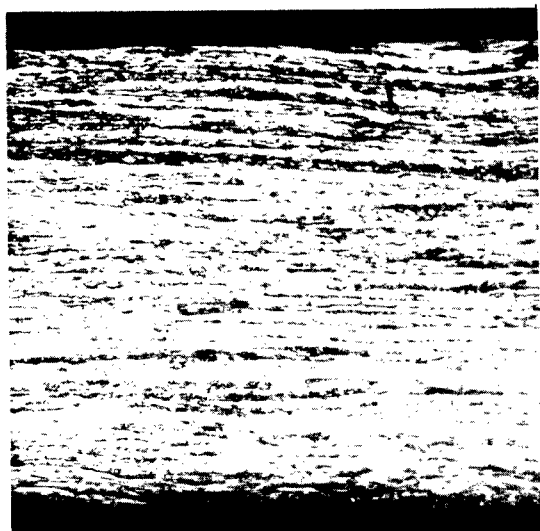
(a) Before coating.
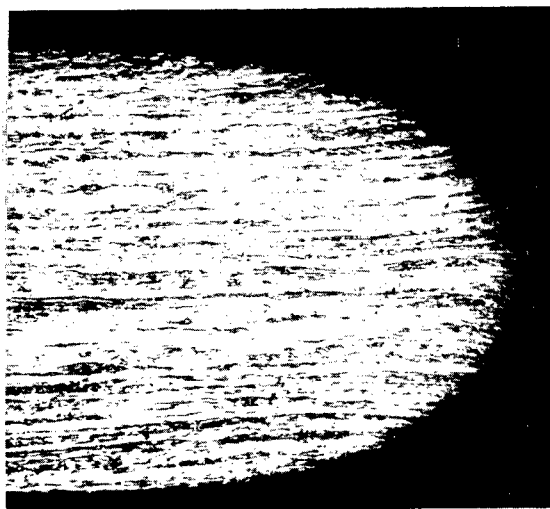
(b) Before coating at tumbled edge.
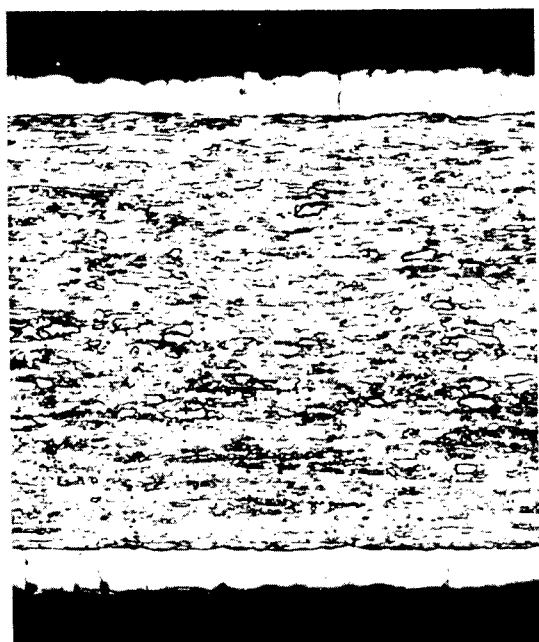
(c) As coated.

(d) As coated at tumbled edge.

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Figure 4.- Typical cross-sectional views of Mo-0.5Ti sheet before and after coating. X200.

1315 Kn
1453 Kn
274 Kn

1129 Kn
1182 Kn
247 Kn

1531 Kn

250 Kn

1364 Kn

323 Kn

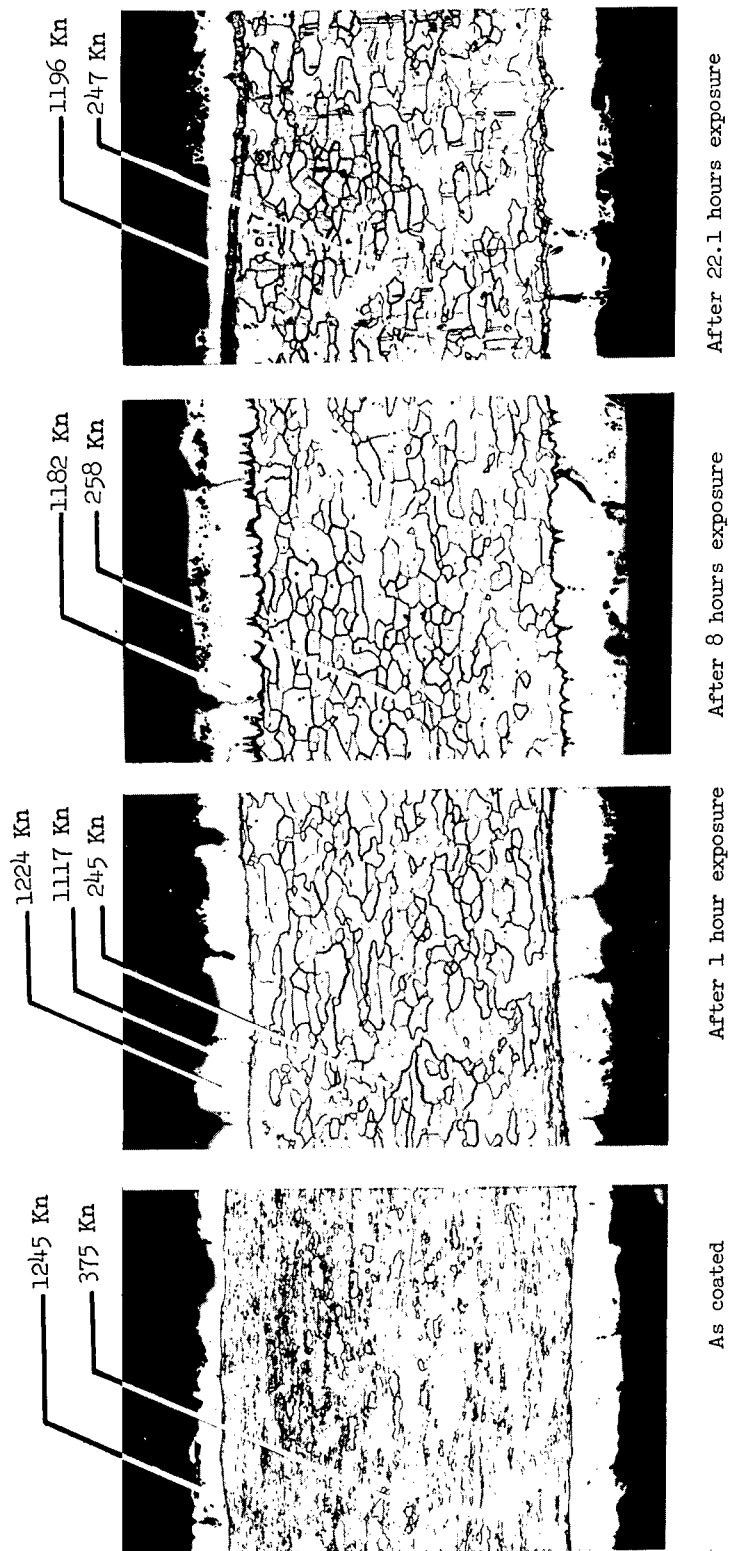As coated, not preglassed   After 1 hour exposure   After 8 hours exposure   After 260 hours exposure
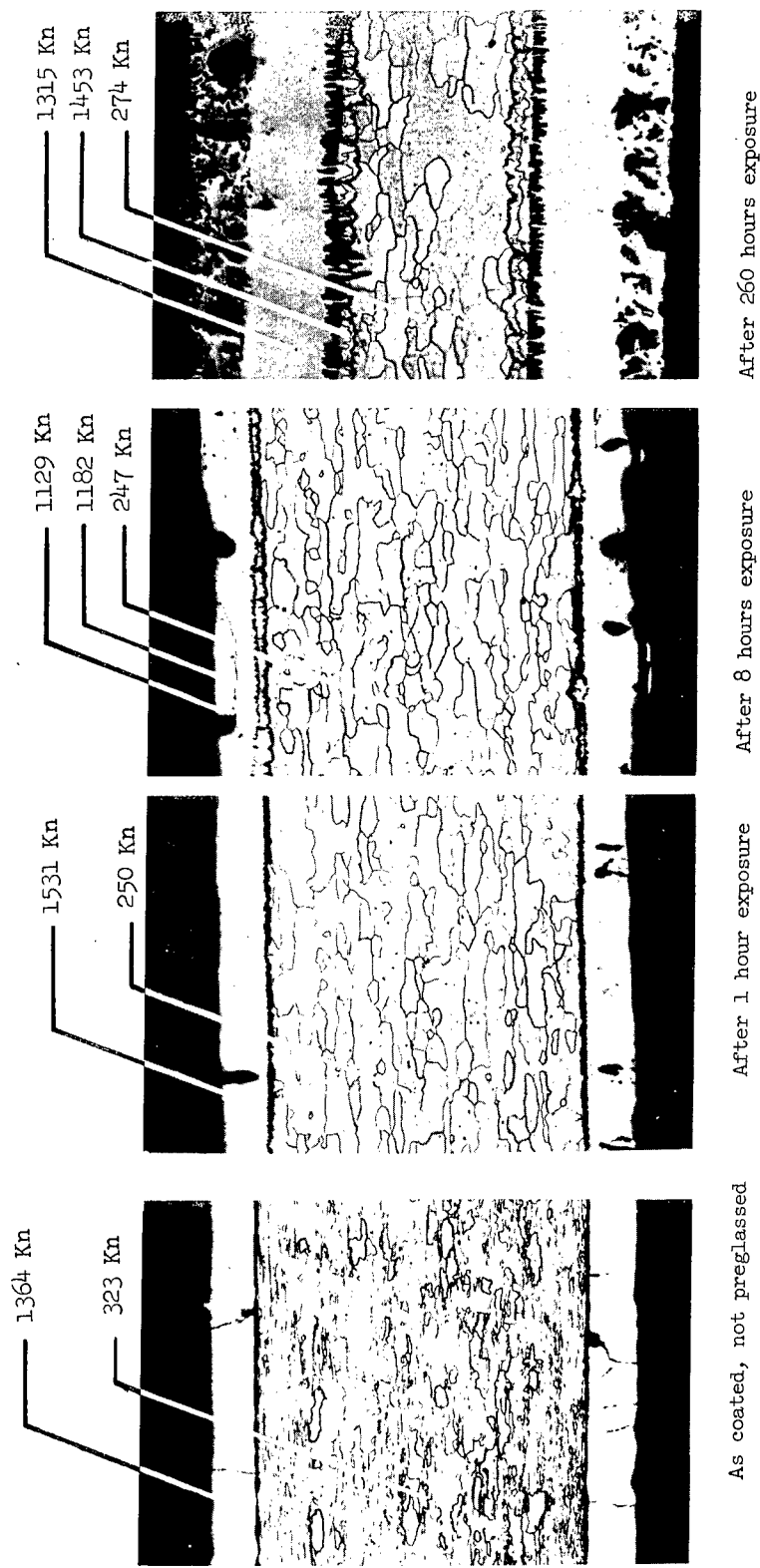
Figure 5.- Cross-sectional views of coating A on Mo-0.5Ti after various exposures in air at 2,500° F. X200.
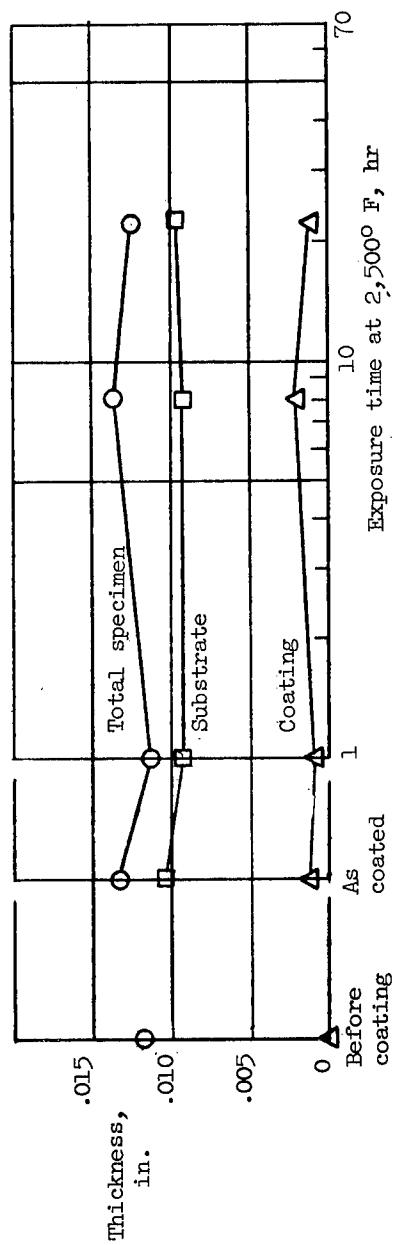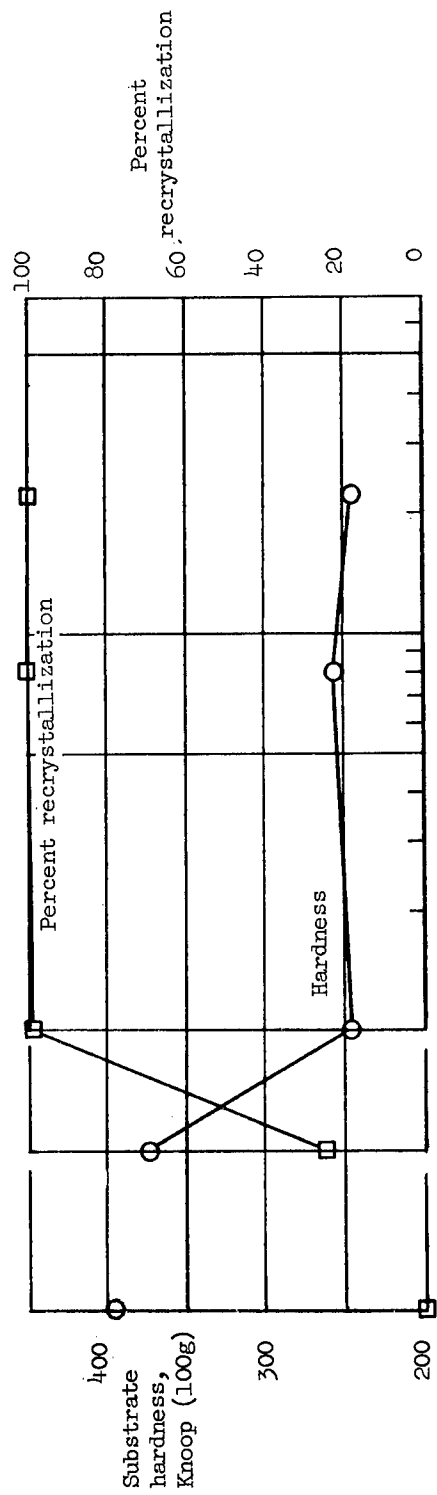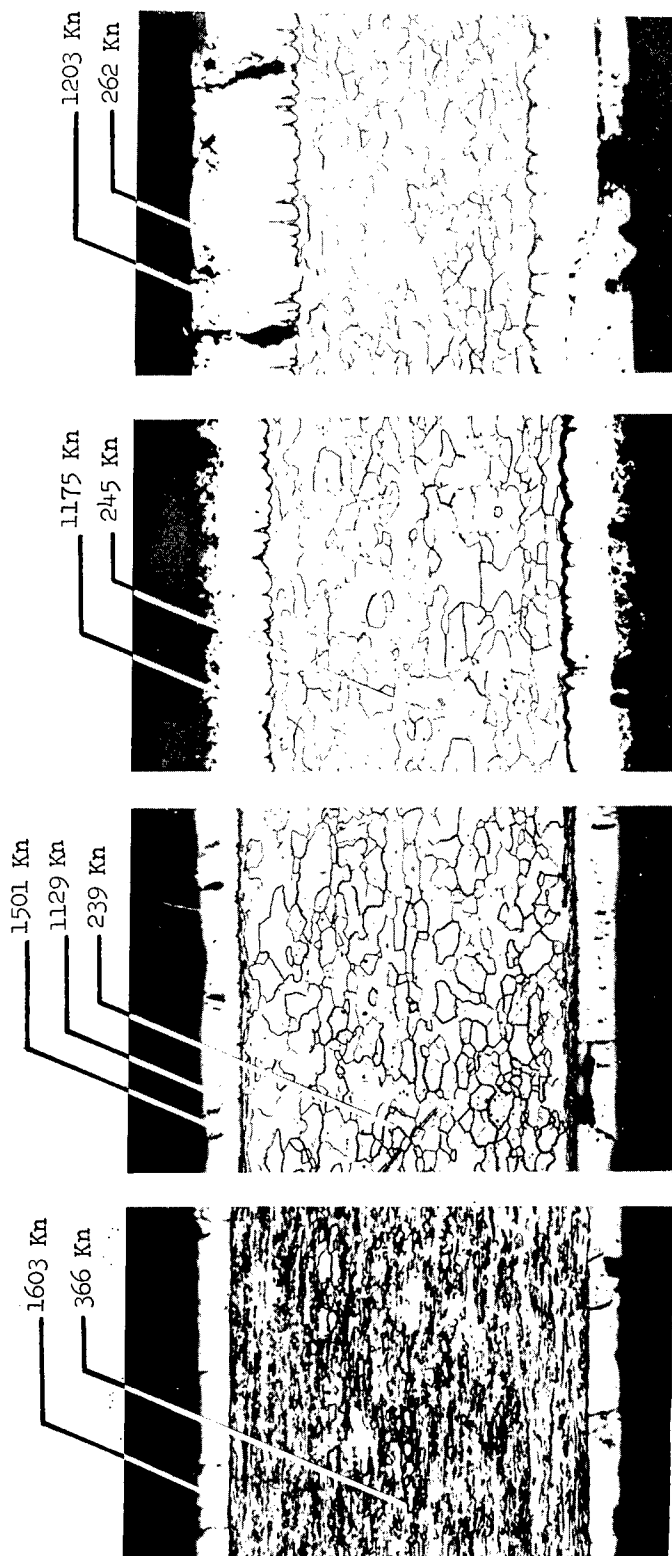
L-63-4770
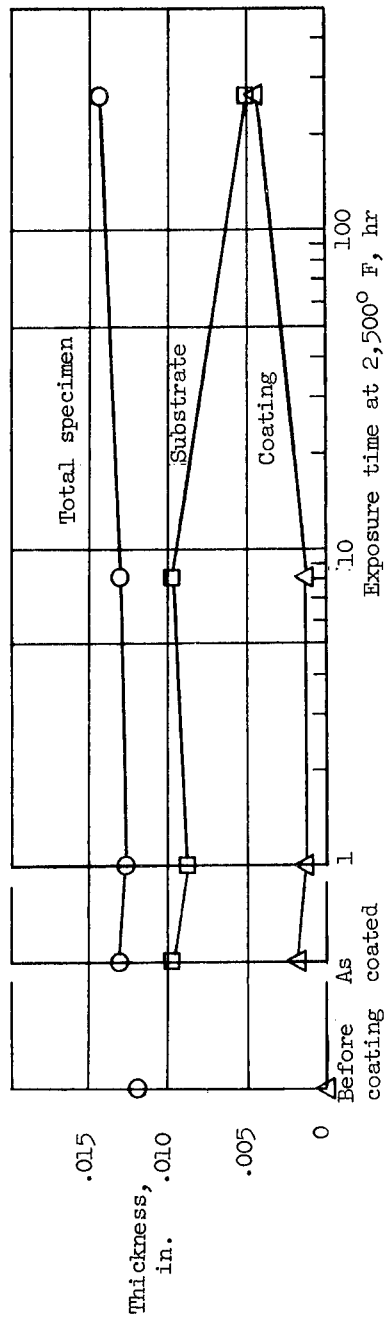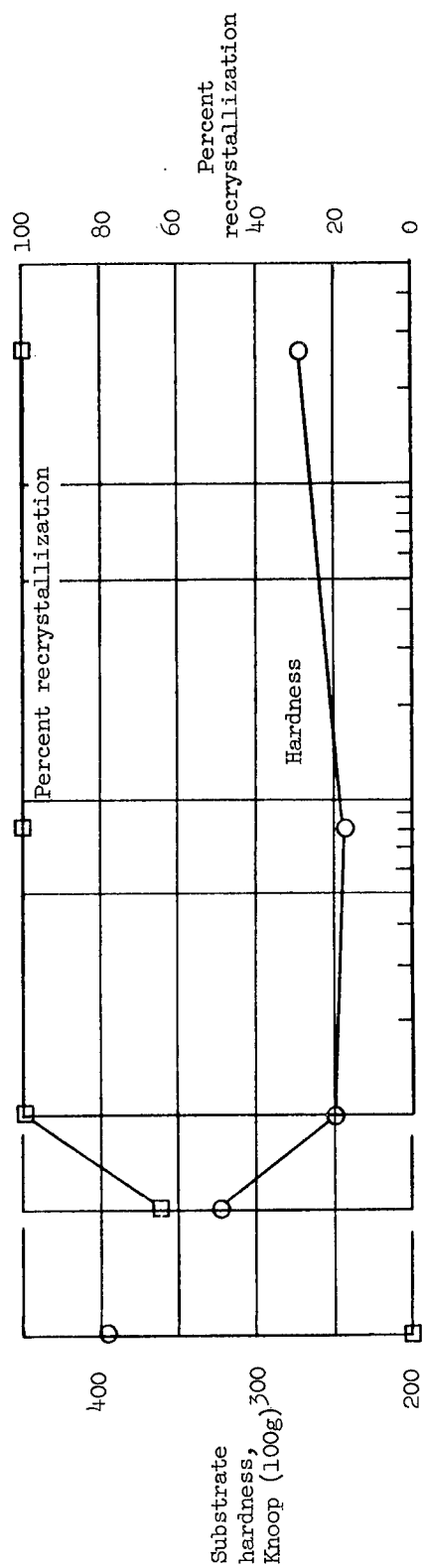
Figure 6.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating A on Mo-0.5Ti alloy.

19

Figure 7.- Cross-sectional views of coating A(G) on Mo-0.5Ti alloy after various exposures in air at 2,500° F. X200.
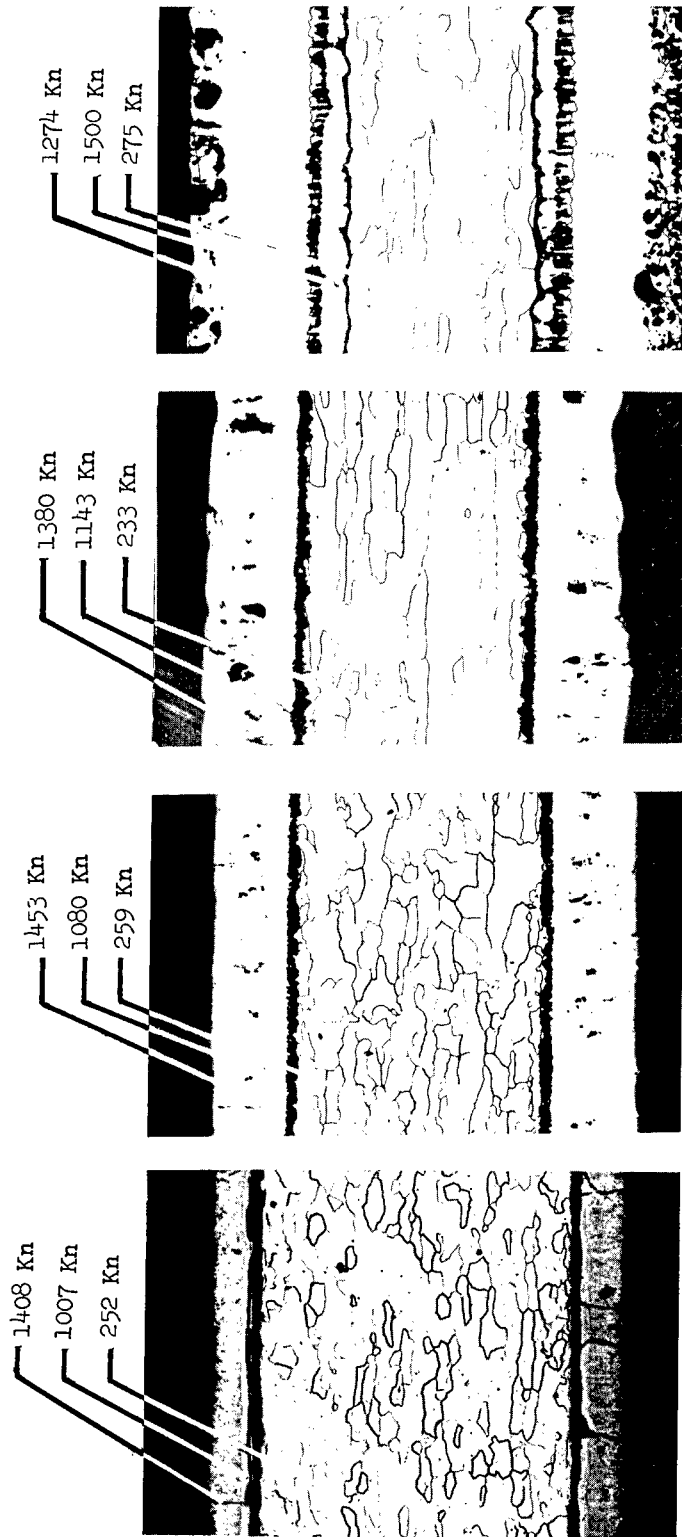
I-63-4771

As coated, preglassed   After 1 hour exposure   After 8 hours exposure   After 1,000 hours exposure

1408 Kn
1007 Kn
252 Kn

1453 Kn
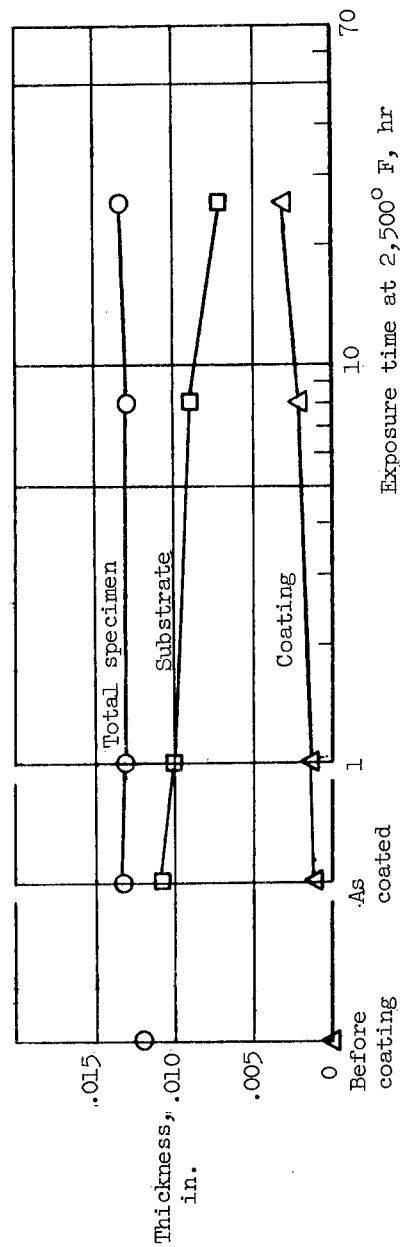1080 Kn
259 Kn

1380 Kn
1143 Kn
233 Kn

1274 Kn
1500 Kn
275 Kn
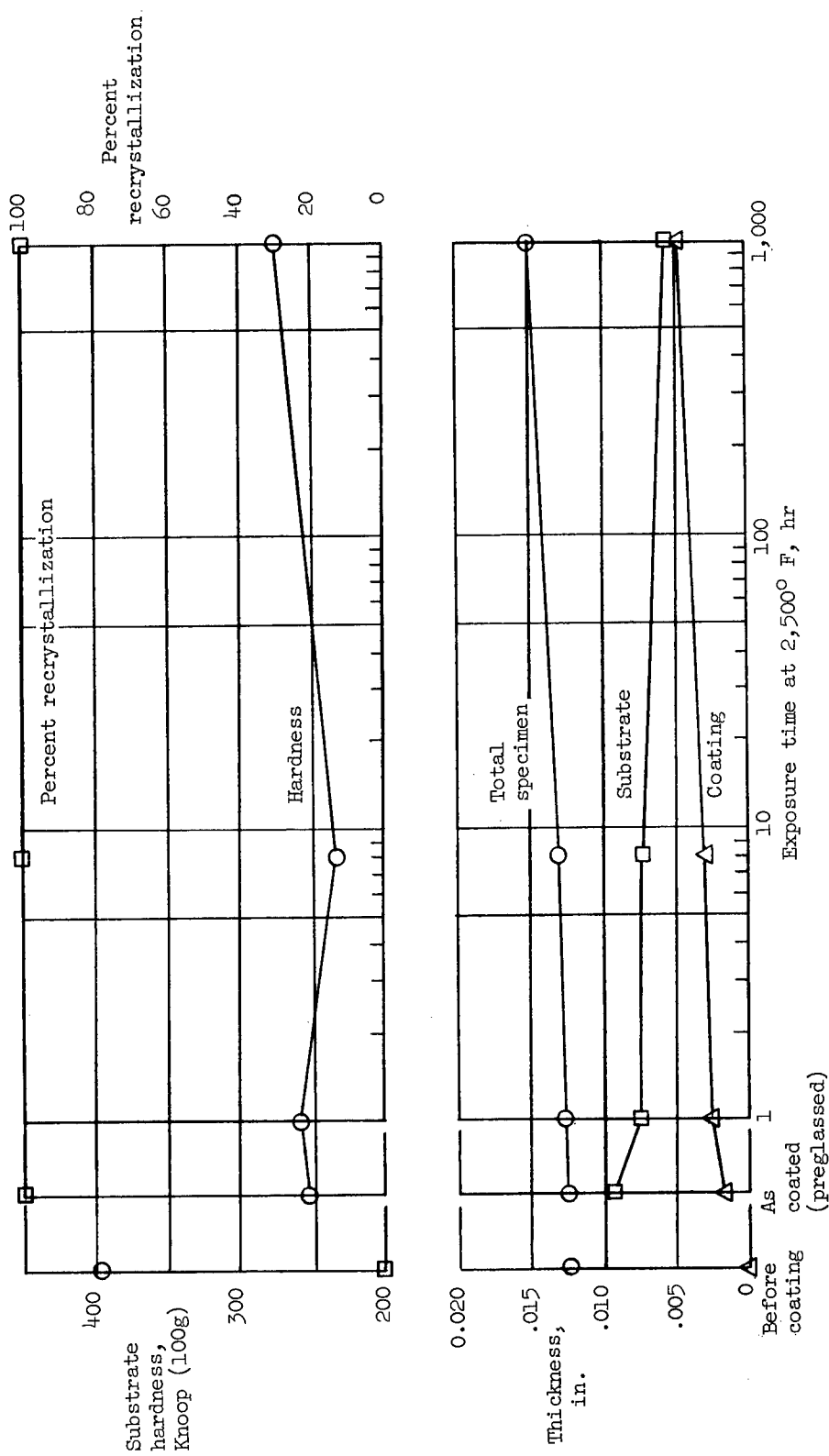
Figure 8.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F in air for coating A(G) on Mo-0.5Ti sheet.

21
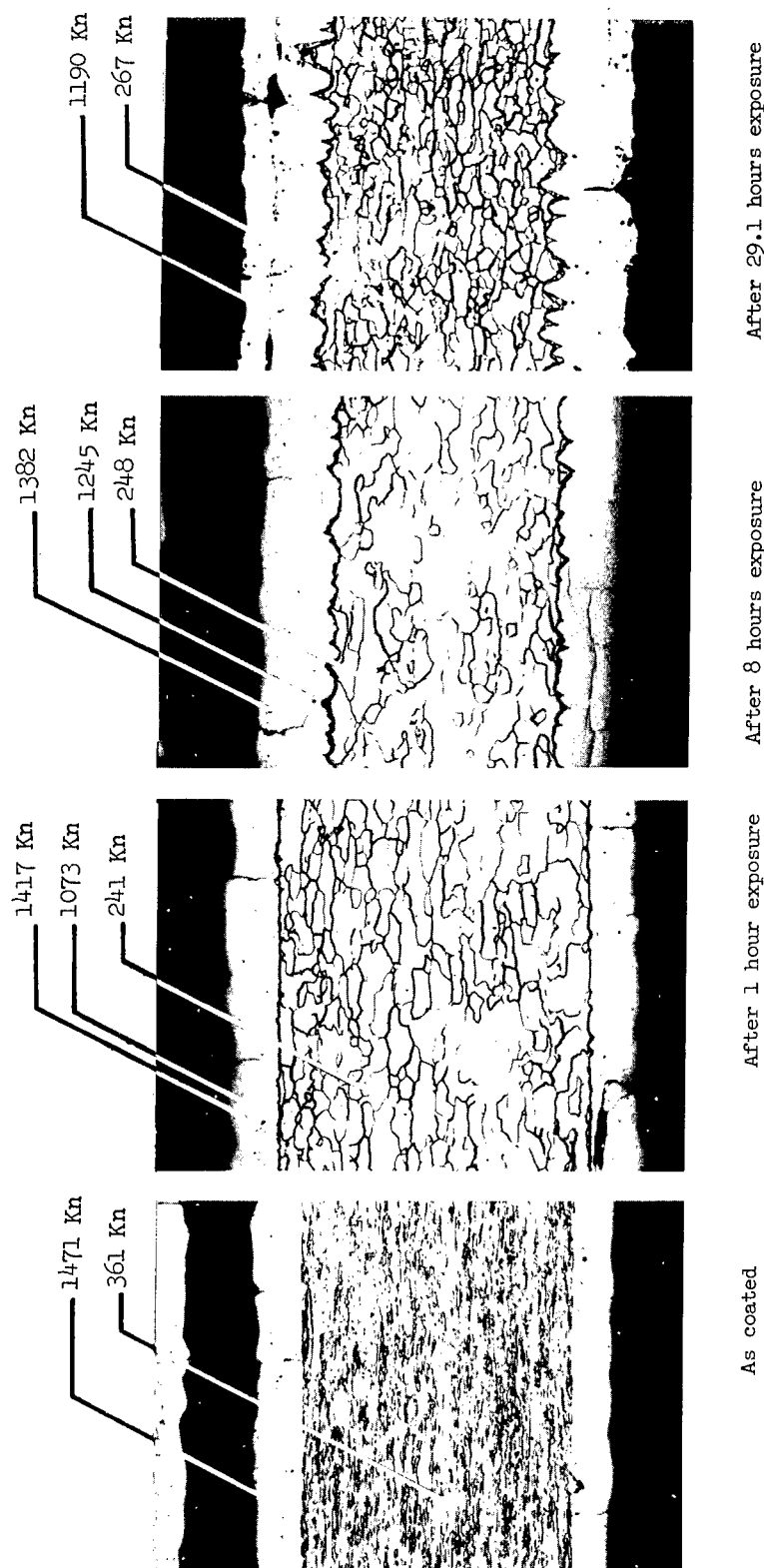
Figure 9.- Cross-sectional views of coating B on Mo-0.5Ti alloy after various exposures in air at 2,500° F.   X200.

As coated   After 1 hour exposure   After 8 hours exposure   After 29.1 hours exposure

1471 Kn
361 Kn

1417 Kn
1073 Kn
241 Kn

1382 Kn
1245 Kn
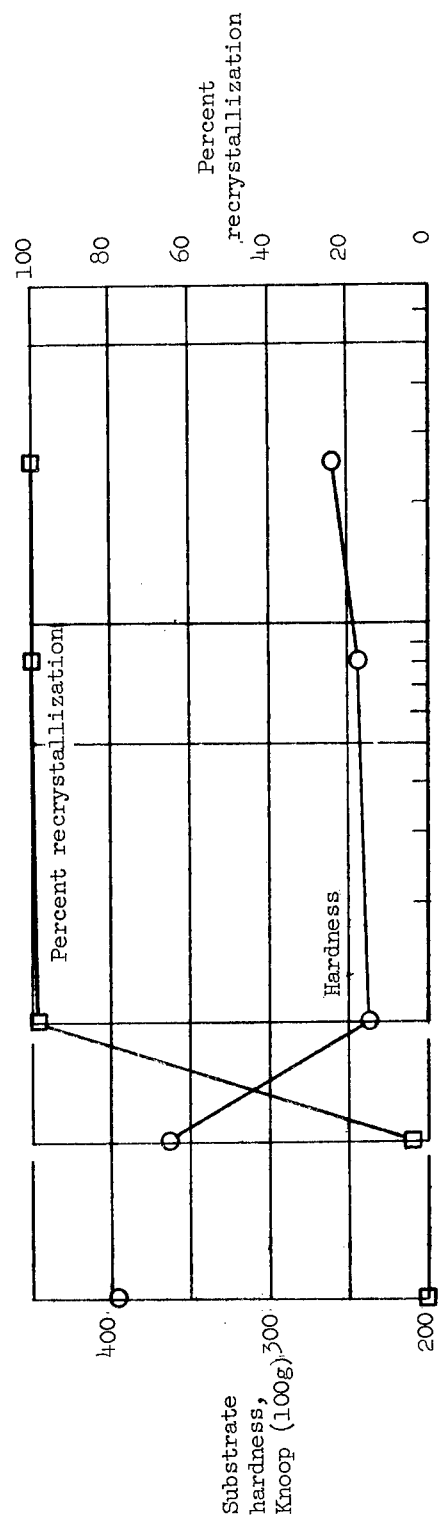248 Kn

1190 Kn
267 Kn

L-63-4772
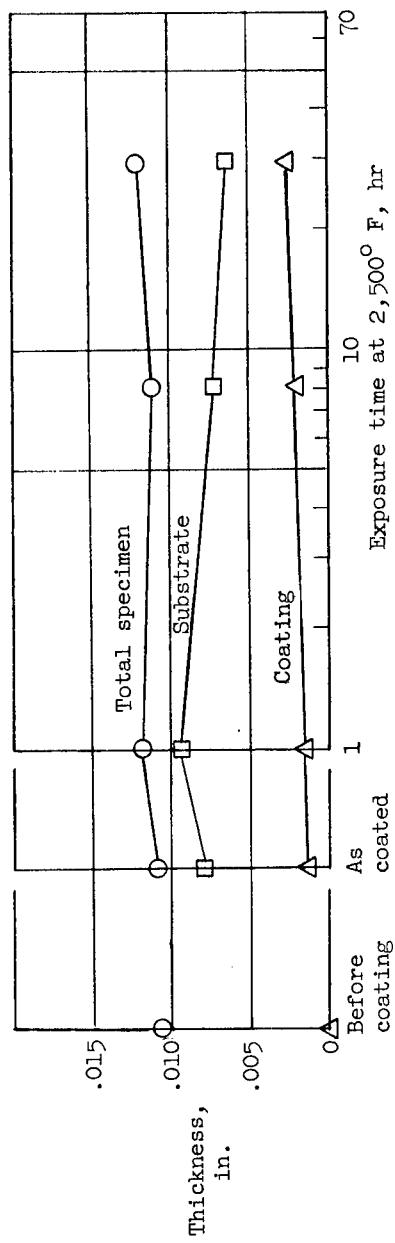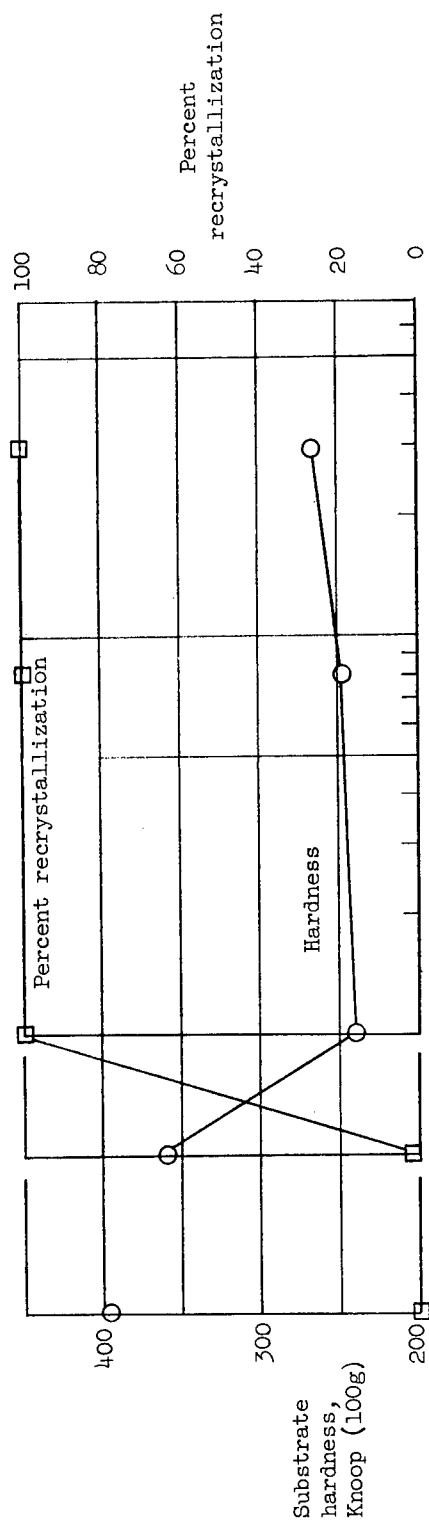
Figure 10.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating B on Mo-0.5Ti alloy.
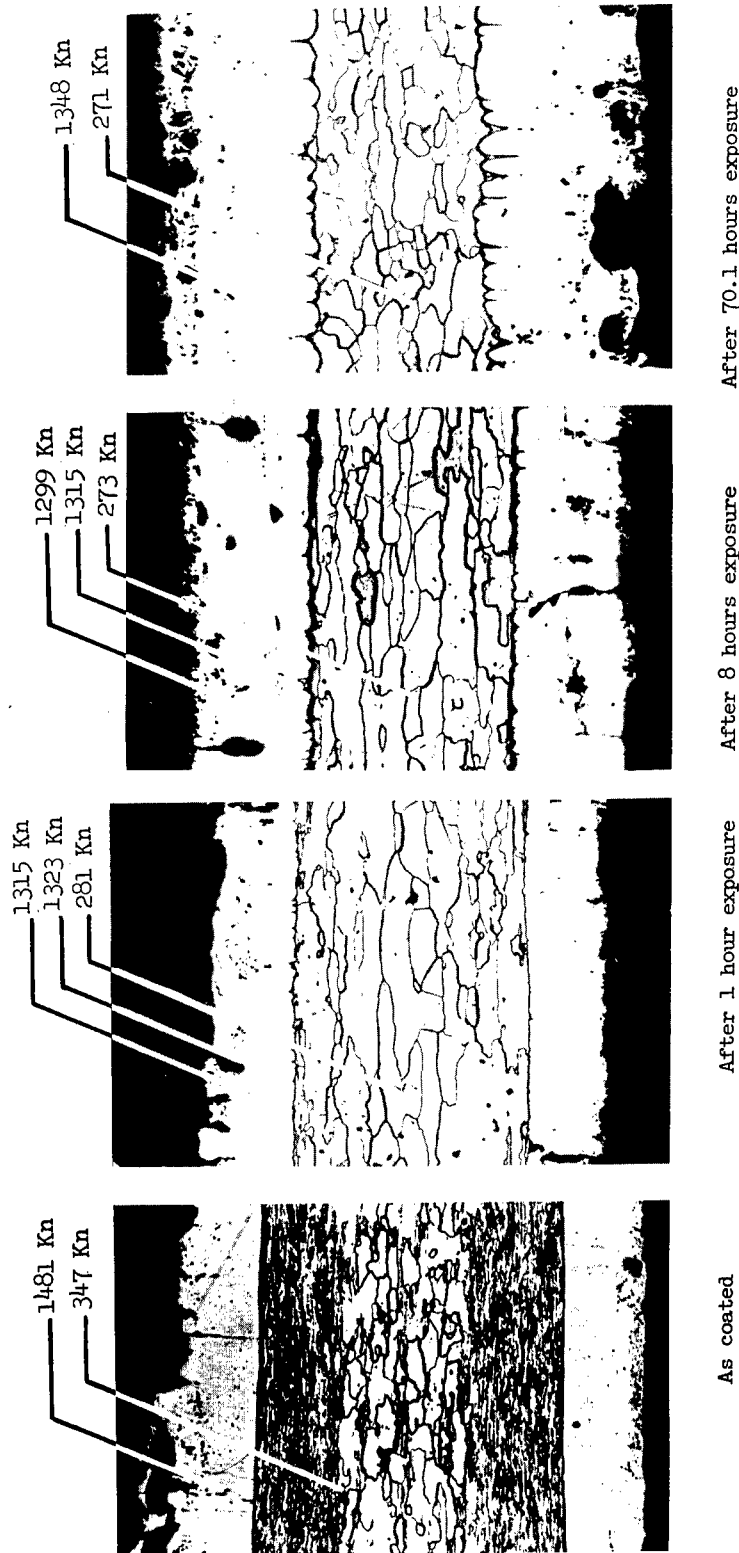
23

1245 Kn
375 Kn

As coated

1224 Kn
1117 Kn
245 Kn

After 1 hour exposure

1182 Kn
258 Kn

After 8 hours exposure

1196 Kn
247 Kn

After 22.1 hours exposure

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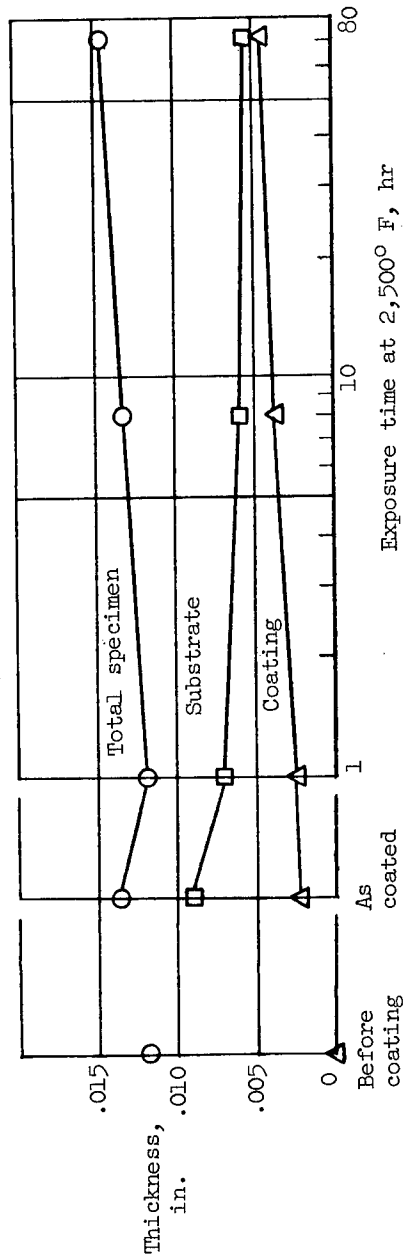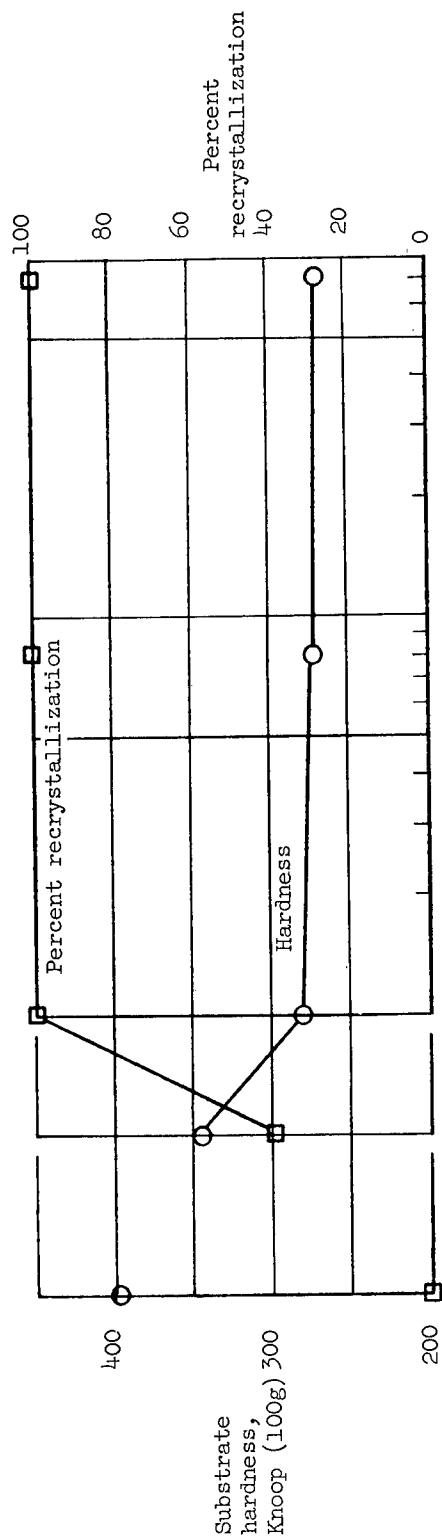Figure 11.- Cross-sectional views of coating C on Mo-0.5Ti alloy after various exposures in air at 2,500° F. X200.

Figure 12.- Variation of substrate hardness, percent recrystallization, and coating substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating C on Mo-0.5Ti alloy.

25

1603 Kn
366 Kn

1501 Kn
1129 Kn
239 Kn

1175 Kn
245 Kn

1203 Kn
262 Kn

As coated　　　　　　After 1 hour exposure　　　　　After 8 hours exposure　　　　　After 25.1 hours exposure

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Figure 13.- Cross-sectional views of coating D on Mo-0.5Ti alloy after various exposures in air at 2,500° F. X200.

Figure 14.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating D on Mo-0.5Ti alloy.
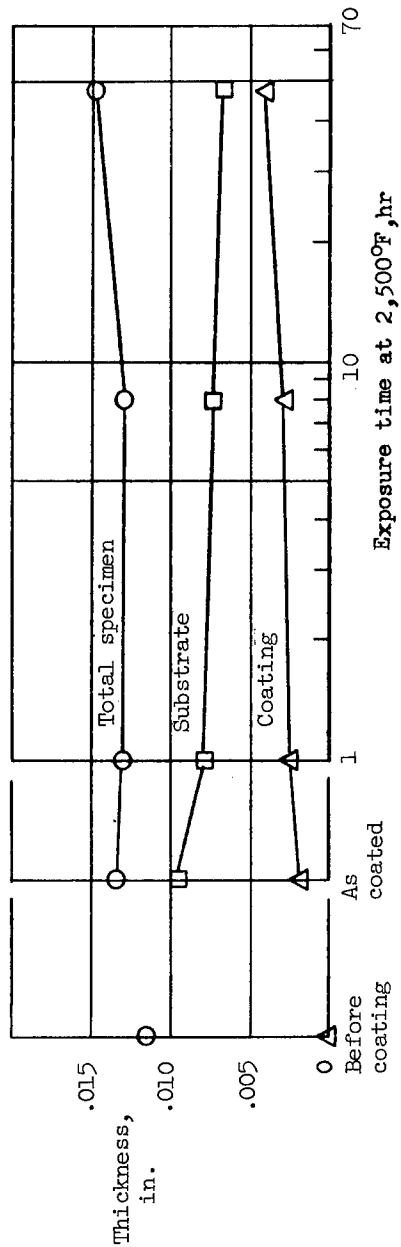
27

1481 Kn
347 Kn

As coated

1315 Kn
1323 Kn
281 Kn

After 1 hour exposure

1299 Kn
1315 Kn
273 Kn

After 8 hours exposure

1348 Kn
271 Kn

After 70.1 hours exposure

Figure 15.- Cross-sectional views of coating E on Mo-0.5Ti alloy after various exposures in air at 2,500° F. X200.

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Figure 16.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating E on Mo-0.5Ti alloy.
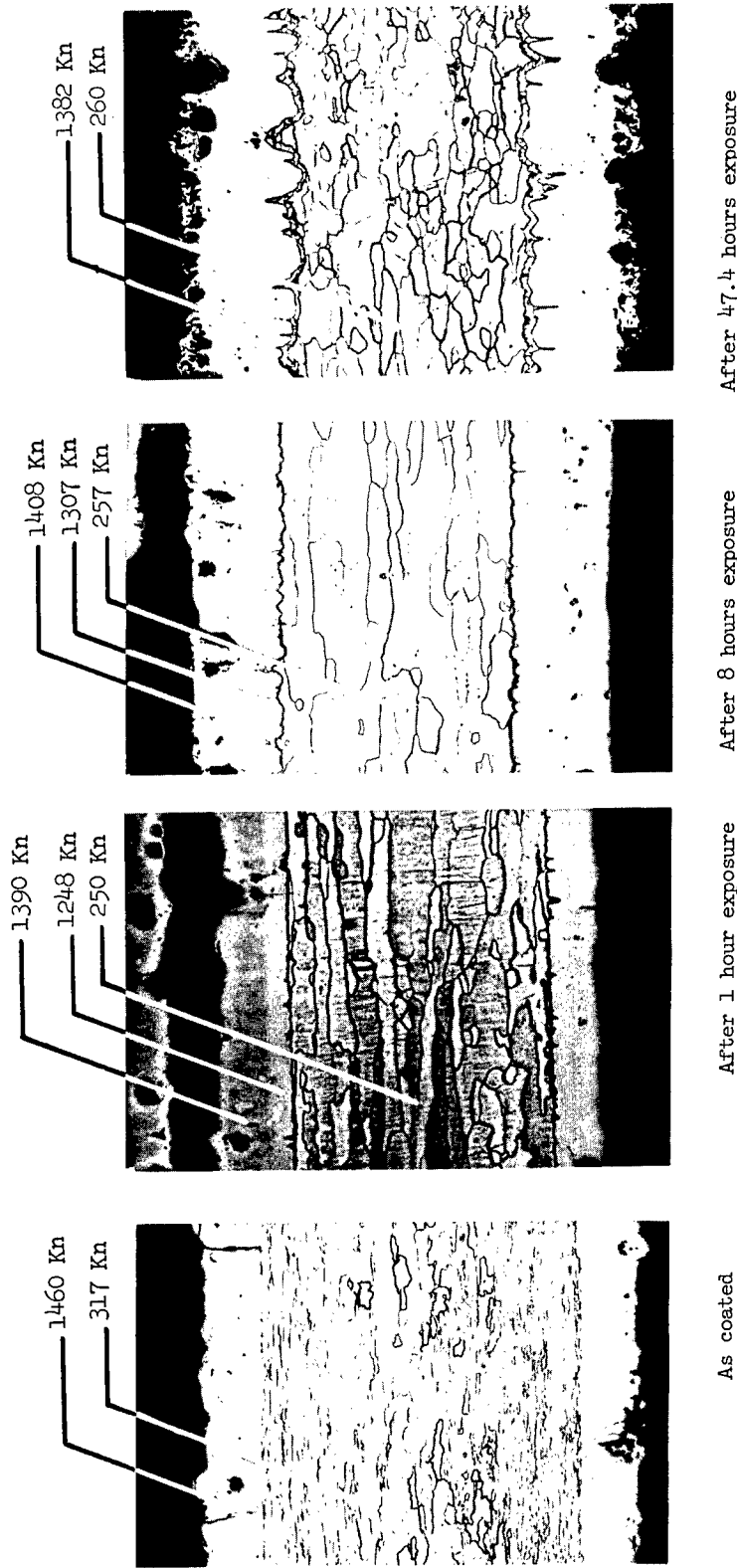
Figure 17.- Cross-sectional views of coating F on Mo-0.5Ti alloy after various exposures in air at 2,500° F. X200.
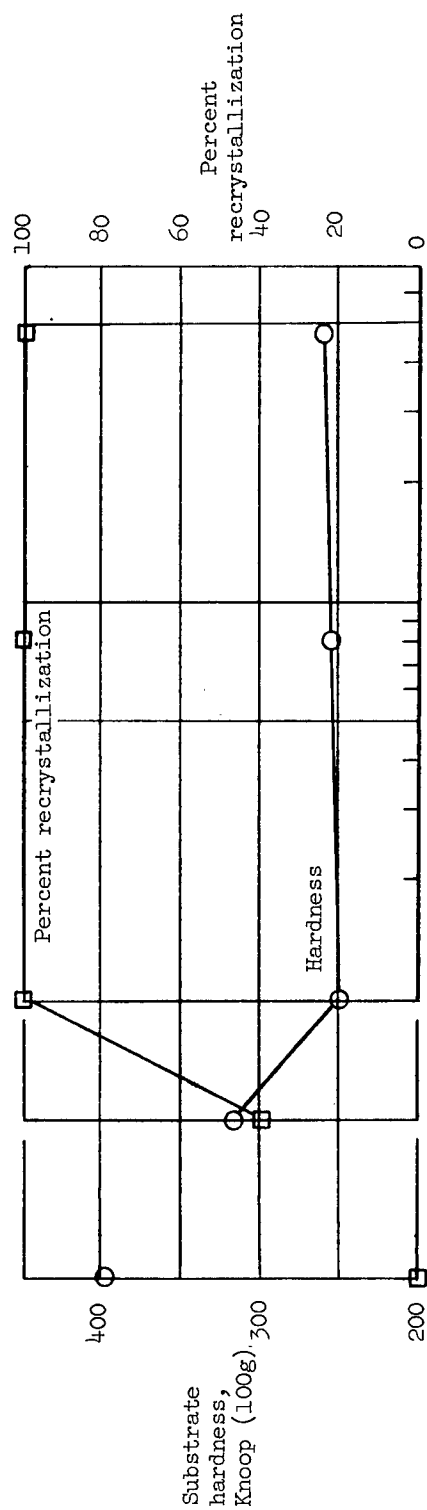
L-63-4776

As coated   After 1 hour exposure   After 8 hours exposure   After 47.4 hours exposure

1460 Kn
317 Kn

1390 Kn
1248 Kn
250 Kn

1408 Kn
1307 Kn
257 Kn

1382 Kn
260 Kn

Figure 18.- Variation of substrate hardness, percent recrystallization, and coating, substrate, and total-specimen thickness with coating application and exposure time at 2,500° F for coating F on Mo-0.5Ti alloy.

31
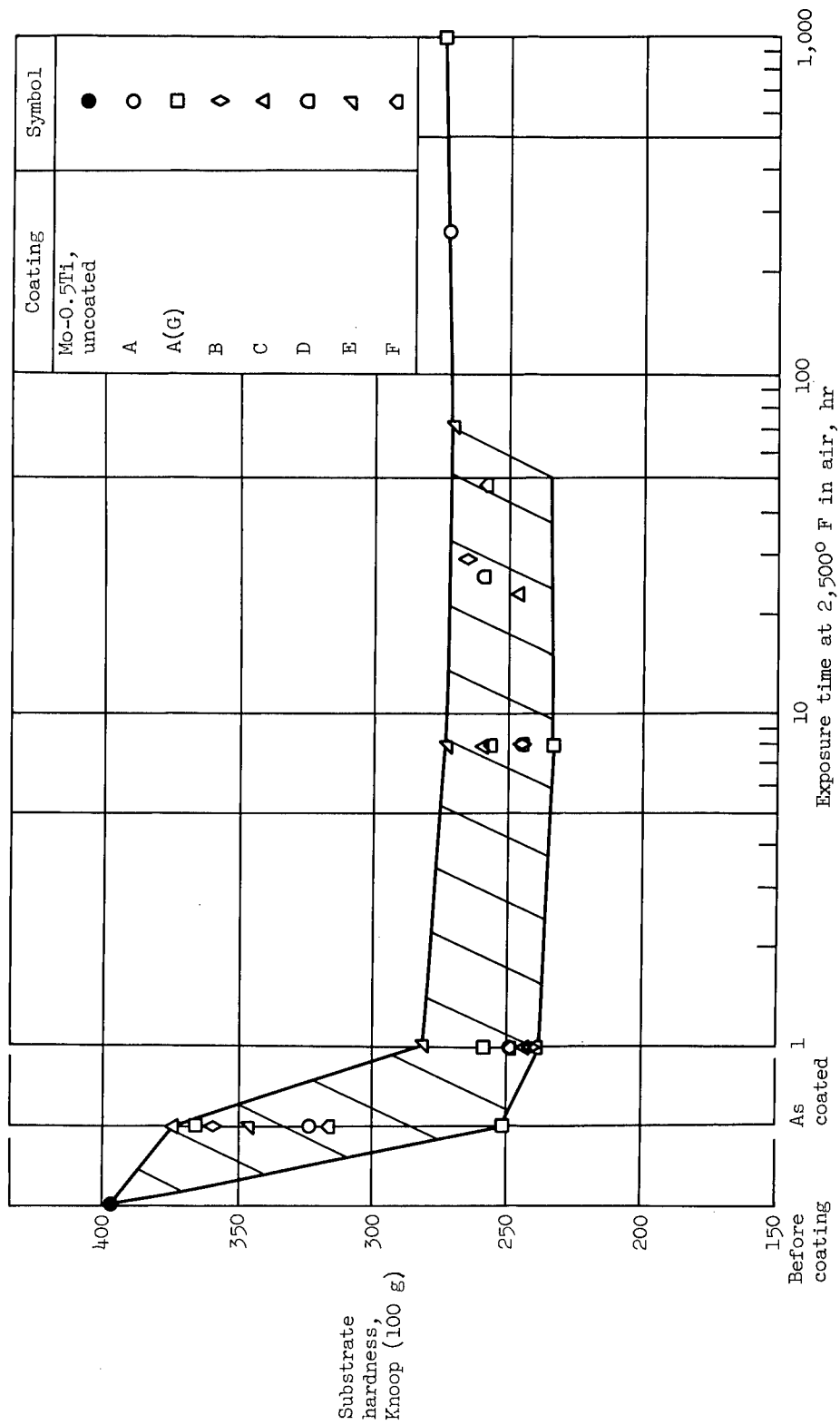
Figure 19.- Comparison of substrate-hardness results for several silicide-base coatings on Mo-0.5Ti sheet.
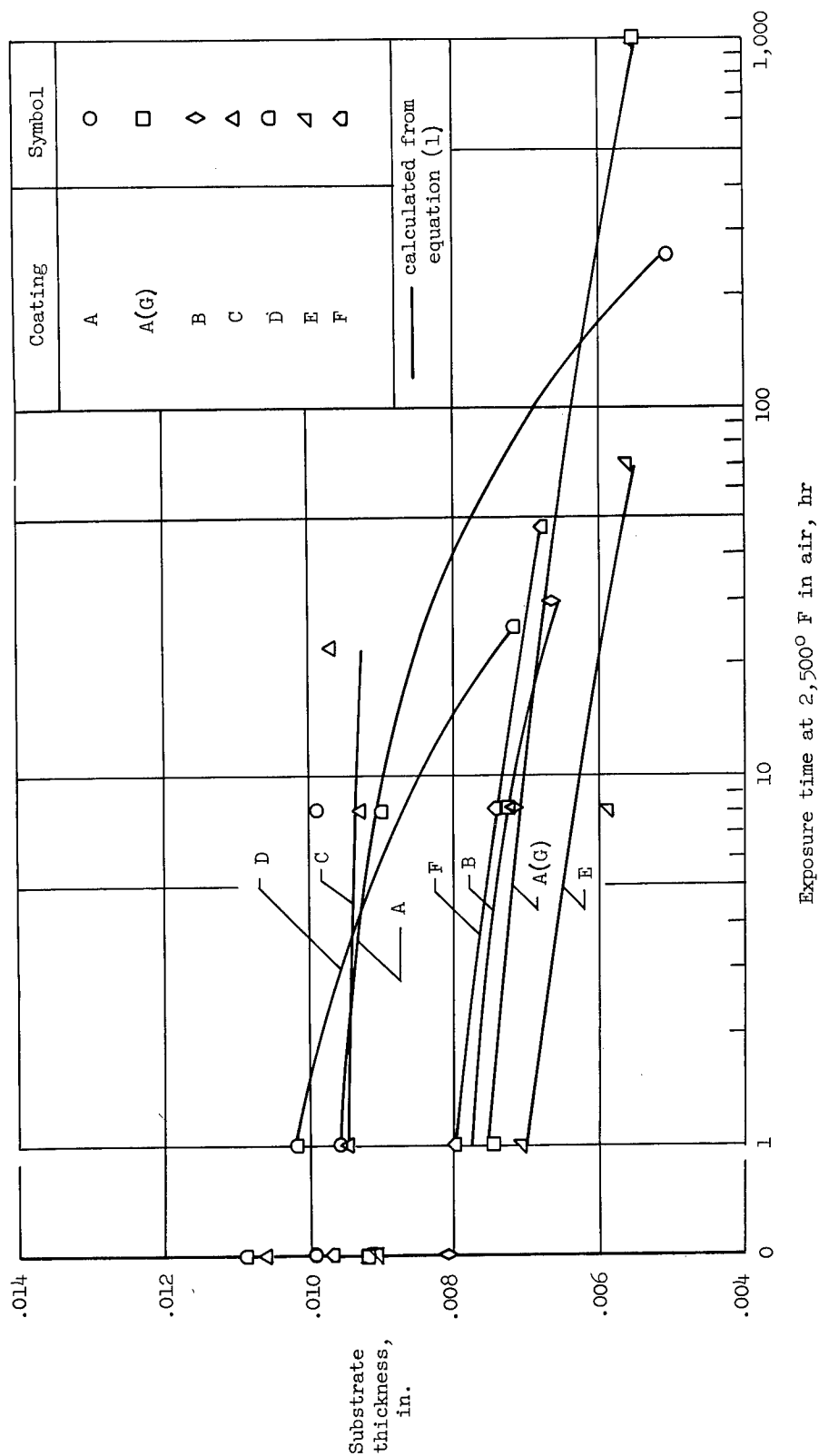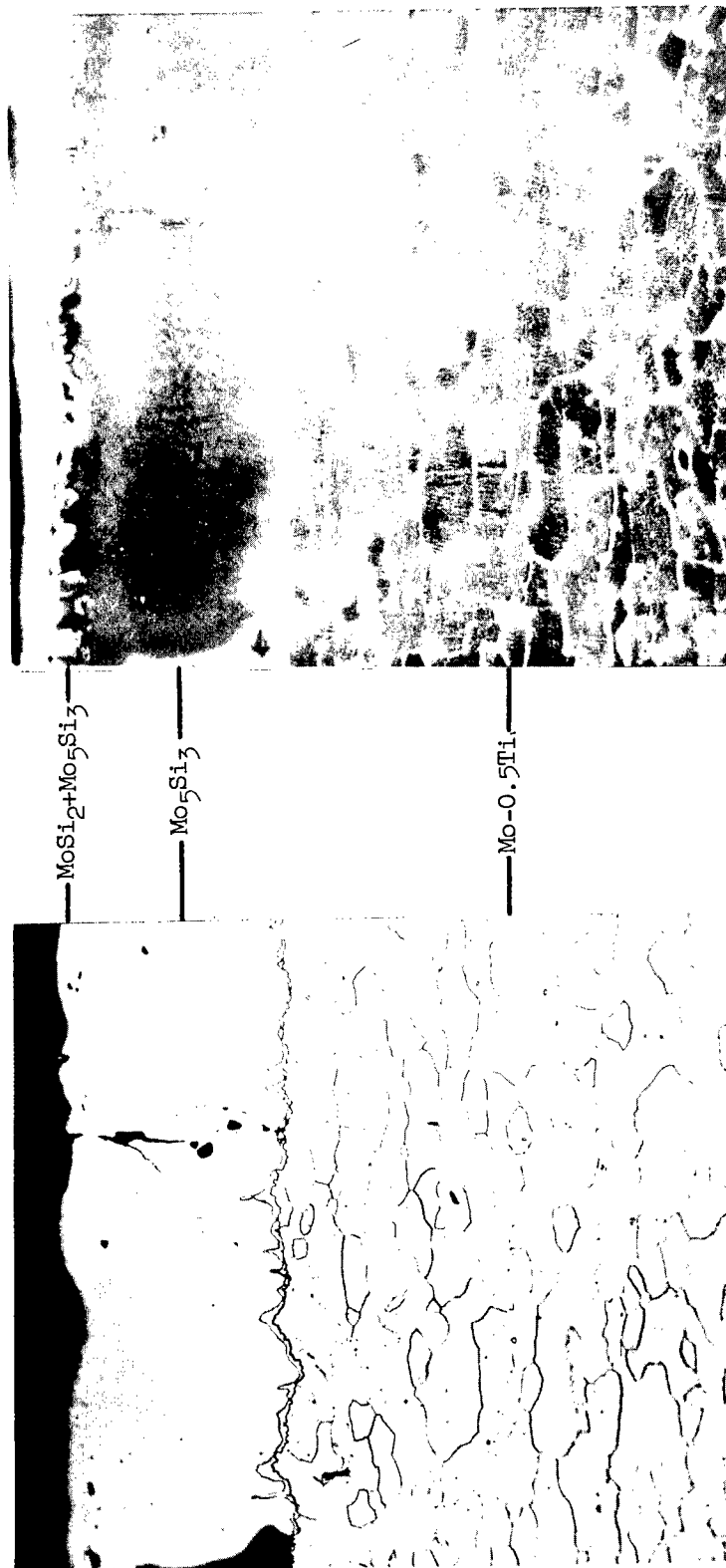
Figure 20.- Comparison of experimentally determined substrate-thickness decrease due to solid-state diffusion (symbols) with empirical approximations calculated from equation (1) (curves) for the various coatings investigated on Mo-0.5Ti sheet.

MoSi$_2$+Mo$_5$Si$_3$

Mo$_5$Si$_3$

Mo-0.5Ti

(a) Bright field illumination.

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(b) Polarized light.

Figure 21.- Cross-sectional views of coating B on Mo-0.5Ti sheet after 20.7 hours at 2,500° F in air. X500.
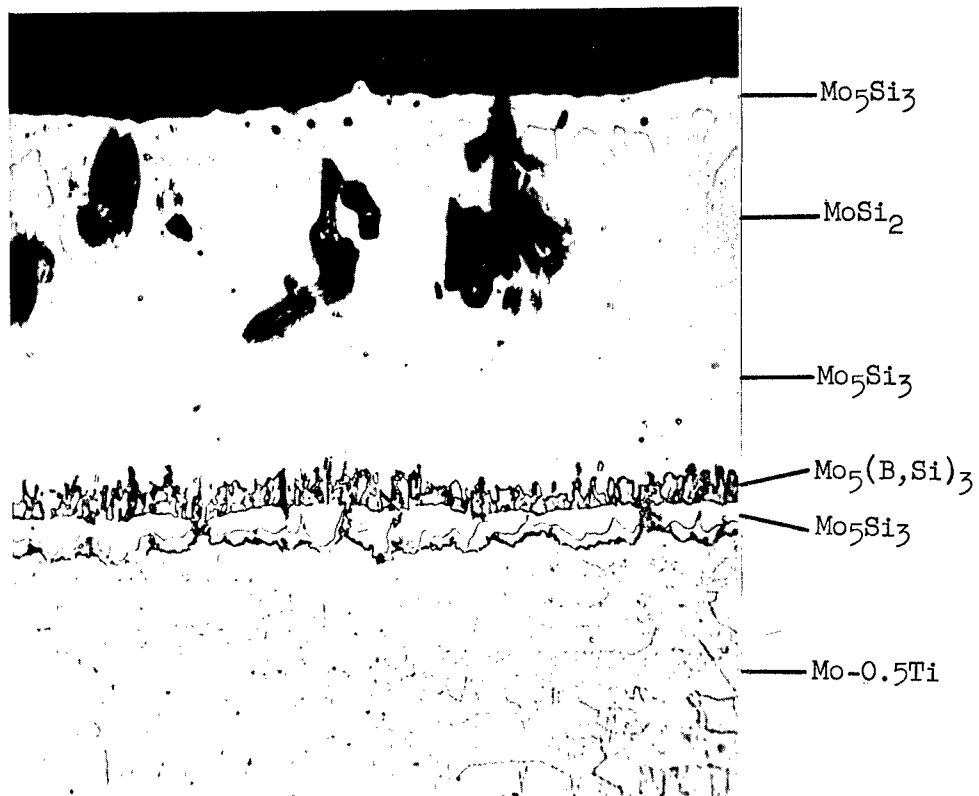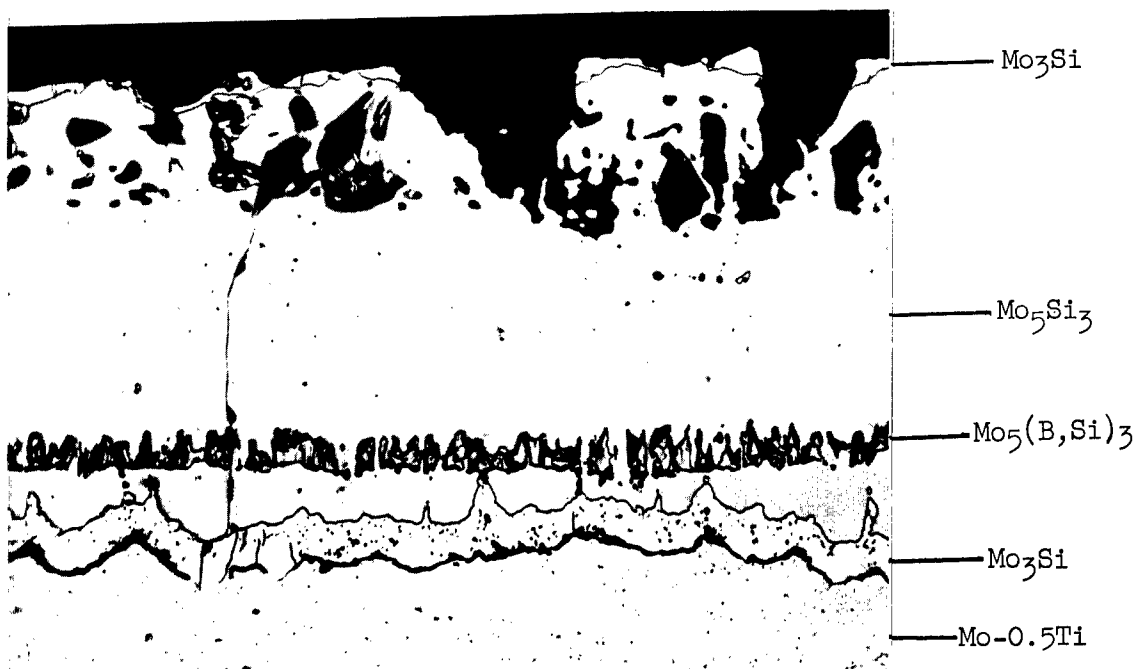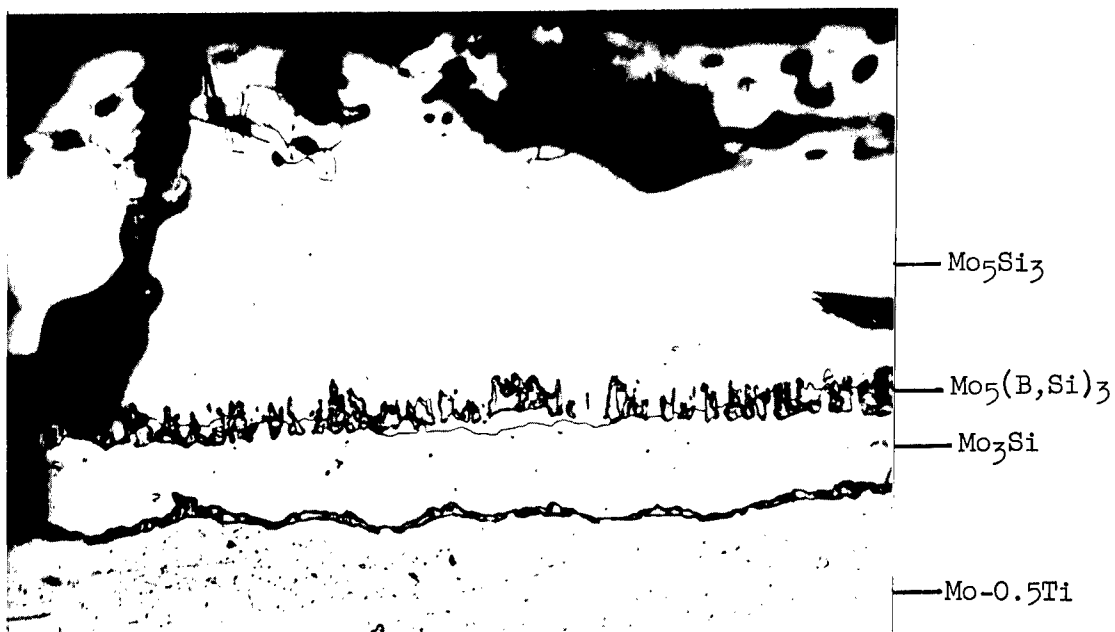
Figure 22.- Cross-sectional view of coating A(G) after 120 hours exposure at 2,500° F in air. X500.

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35

Figure 23.- Cross-sectional view of coating A after 260 hours exposure at 2,500° F in air. X500.

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Figure 24.- Cross-sectional view of coating A(G) after 1,000 hours exposure at 2,500° F in air. X500.

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W. Barry Lisagor.   August 1964.   36p.   OTS price,
$1.00.   (NASA TECHNICAL NOTE D-2039)

Results of a study on the diffusion effects of several
silicide-base coatings on Mo-0.5Ti molybdenum-
alloy sheet are presented.   The magnitude of sub-
strate thickness loss due to solid-state diffusion at
2,500° F is presented; this indicates the possible
need for diffusion barriers between coating and sub-
strate in some applications.   The phase changes in
the coatings during exposure at 2,500° F in air were
studied to obtain an understanding of coating behavior.
The phases which formed were identified by X-ray
diffraction techniques.   From these identifications
an explanation is given for the superior oxidation
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