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Direct Carbon Replication
of Uranium Tetrafluoride Films
on Uranium Dioxide

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W. P. Ellis and Dana L. Douglass

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DIRECT CARBON REPLICATION OF URANIUM TETRAFLUORIDE FILMS ON URANIUM DIOXIDE

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ABSTRACT

Direct carbon replicas of bare UO_2 and of UF_4 films formed on UO_2 by reaction with $\text{HF}(\text{g})$ were examined by electron microscopy. In contrast with the collodion replication study reported in IA-3183, carbon replication provides a correlation between optical blemishes in fluoride interference layers and surface morphology of the film. Observations indicate a growth of microcrystallites within the fluoride layer at reaction temperatures above 300°C .

INTRODUCTION

In the interval 200° to 300°C , first- and second-order interference films of UF_4 produced on polished UO_2 by hydrofluorination are smooth, uniformly colored, and optically isotropic.¹ Kinetic data for this range of temperatures are reproducible.^{2,3} Above 300°C the films are characteristically blemished. Collodion replicas reveal no superficial microstructure to correlate with the blemishes below 450°C .¹ Collodion replicas are not always reliable however.^{4,5} With direct carbon replicas we have observed surface topography which correlates with the color blemishes seen in interference films. At temperatures above 300°C , crystalline growth of the UF_4 film occurs. This observation agrees with the results of differential thermal analysis of UF_4 hydrates by Dell and Wheeler⁶ who reported an exothermic recrystallization of powdered UF_4 at 320°C .

EXPERIMENTAL

Substrate preparation, hydrofluorination, and metallography are described in references 1, 2, and 3. Briefly, fused polycrystalline UO_2 was sectioned on a diamond saw, lapped through $1\text{-}\mu$ diamond paste (Struers, Copenhagen) on Buehler "Metcloth," and reacted twice for 90 min with 400-torr $\text{HF}(\text{g})$ at 285°C . Each fluoride film was removed by soaking

for 90 sec in 0.2 M HNO_3 followed by successive rinses in distilled water, acetone, and chloroform. The bare oxide surface was then ready for replication or for subsequent reaction with $\text{HF}(\text{g})$. All hydrofluorinations were conducted with 400-torr of $\text{HF}(\text{g})$. The only difference between the work reported here and that reported in IA-3183 is that in the present work the surfaces were replicated directly with carbon. The replicas were removed in dilute aqua regia, and the carbon side next to the replicated surface was shadowed with Pd.

RESULTS

A. Bare UO_2

With bare UO_2 , electron micrographs of direct carbon replicas show microcracks, pits, and grain boundaries (Fig. 1). At high magnification the surface is smooth and free of the Type II structure reported in IA-3183. The shallow, disc-shaped micropits, i.e., Type II structure, appear to be characteristic of the collodion process rather than representative of the true nature of the surface being replicated. The Type I structures of IA-3183 are pits in the UO_2 substrate which are also seen with carbon replicas (Fig. 1c).

B. 285°C Reaction

Hydrofluorination of UO_2 at 285°C produces uniformly colored interference films. As seen by

comparison of Fig. 1 with Fig. 2, the surface topography appears the same as for bare UO_2 . Microcracks, pits, and grain-boundaries are displayed. At high magnification the surface is smooth (Fig. 2d).

C. 326°C Reaction

Reaction at 326°C produces blemished films with striking interference effects (cf IA-3183). At this temperature the growth of blemishes is initiated at sites of surface roughness. As the reaction proceeds, the optical blemishes grow onto the metallographically smooth areas until the entire surface is covered with a birefringent mosaic microstructure (cf CP IVc and FM Va of IA-3183). Whereas the collodion technique did not reveal surface structure to correlate with the growth of blemishes, the carbon replicas reveal a corresponding microroughness. Figures 3a, b, and c are electron micrographs of a specimen reacted 5 1/2 min at 326°C. Two distinct areas are seen. Most of the surface is smooth, but there are islands on which the texture is more coarse. This coarser texture is not seen on bare UO_2 , or on fluoride films produced at 285°C. During a 50-min reaction the rough-textured area increased in size and surrounded the smoother areas (Figs. 4, 5). During a 5-hr reaction the entire surface became covered (Fig. 6). There are striated areas in Figs. 5a and 6a which suggest that localized stress relief may be a factor. At this temperature, distinctly resolvable crystallites are not formed but the structure is similar to that resulting from reaction at higher temperature where crystal faces are produced.

D. 361°C Reaction

Hydrofluorination at 361°C produces films which are very similar to the thicker, more coarse-textured 326°C layers. The rough-textured surfaces are less striated, however (Fig. 7).

E. 462°C Reaction

The topography of the fluoride layers formed at 462°C is rougher than that produced by reaction at 326°C or 361°C. The superficial topography bears little resemblance to the UO_2 substrate except for

gross features such as pits or microcracks (Fig. 8b). At high magnification, oriented microcrystallites and crystal faces are resolved (Fig. 8c,d). In a small area the crystallites are oriented parallel to each other with an average size of approximately 0.1 μ .

A fluoride film produced by reaction at 285°C undergoes a morphological change when heated 13 min at 463°C as shown in Fig. 9. Although the texture is approximately the same as with reaction at 462°C, crystalline faces are not so well developed. Evaporation of the UF_4 product is not significant at this higher temperature.

CONCLUSION

Electron microscopic examinations of direct carbon replicas have demonstrated the correspondence of optical blemishes in fluoride interference films on UO_2 with superficial microroughness. Hydrofluorination at 462°C produces resolvable microcrystallites. These observations are consistent with the results of differential thermal analysis of $\text{UF}_4 \cdot n\text{H}_2\text{O}$ by Dell and Wheeler⁶ who observed recrystallization of powdered UF_4 at 320°C. It thus appears that blemishes in fluoride interference films on UO_2 result from microscopic recrystallization of the UF_4 product.

ACKNOWLEDGMENT

The authors appreciate discussions with R. L. Schwoebel of Sandia Corporation who recommended direct carbon replication.

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Fig. 1. Bare UO_2 . a - 12,000X, b - 48,000X, c - 48,000X, d - 120,000X.

Fig. 2. 285°C, 90-min reaction. Film is approximately 0.2-μ thick.
a - 12,000X, b - 48,000X, c - 48,000X, d - 120,000X.

Fig. 3. 326°C, 5 1/2-min reaction. Surface is sparsely covered with microgranularity. a - 10,000X, b - 48,000X, c - 120,000X. Same area.

Fig. 4. 326°C, 50-min reaction. Surface is mostly coarse-textured except for smooth islands. Corresponds to Color Plate Id,e,f of IA-3183. 30,000X.

Fig. 5. Same specimen as Fig. 4. a - 24,000X, b - 48,000X, c - 48,000X, d - 120,000X.

Fig. 6. 326°C, 5-hr reaction. Entire surface is rough. a - 12,000X, b - 96,000X.

Fig. 7. 361°C, 30-min reaction. Surface is similar to that produced by 326°C reaction; film is ca. 0.2-μ thick. a - 48,000X, b - 48,000X.

Fig. 8. 462°C, 10-min reaction. Film is ca. 0.2- μ thick.
a - 19,000X, b - 22,000X, c - 48,000X, d - 120,000X.

Fig. 9. 285°C, 90-min reaction with HF(g) followed by 13 min at 463°C in Ar. a - 48,000X, b - 48,000X, c - 120,000X.