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METALLOGRAPHIC PREPARATION OF ARC-CAST THORIUM CARBIDES AND CORRELATION OF THEIR MICROSTRUCTURES WITH COMPOSITION

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Price: Printed Copy $3.00; Microfiche $0.65

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ORNL-4354

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

METALLOGRAPHIC PREPARATION OF ARC-CAST THORIUM CARBIDES AND CORRELATION OF THEIR MICROSTRUCTURES WITH COMPOSITION

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MARCH 1969

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ABSTRACT

Arc-cast thorium carbide specimens with C/Th atom ratios varying from 0.8 to 2.1 (4.0 to 10.0 wt % carbon) were prepared for metallographic examination, and their microstructures were correlated with the chemical analyses, the X-ray diffraction analyses, and the products of hydrolysis. The thorium monocarbide phase was found to exist over a range of composition from about $ThC_{0.94}$ (4.6% carbon) to at least as low as $ThC_{0.81}$ (4.0% carbon). Specimens with compositions from $ThC_{0.99}$ to $ThC_{1.88}$ (4.8 to 8.8% carbon) were two-phase mixtures of the mono- and dicarbides at room temperature. The maximum combined-C/Th atom ratio obtained by arc-melting with graphite electrodes was 1.96 (9.2% carbon). There was no evidence for any significant range of composition for the dicarbide at room temperature.

A new metallographic procedure contributed significantly to the study. A solution containing equal parts (by volume) of nitric acid (70 wt %) and water was used to passivate and etch thorium dicarbide and two-phase thorium dicarbide-monocarbide specimens. Advantages of this technique over air-etching are: (1) the microstructures are more clearly defined; (2) specimens can be observed directly in air (no protective oil film is necessary); and (3) specimens can be examined more leisurely than air-etched specimens, which continue to react rapidly with moisture even under an oil film. Single-phase thorium monocarbide specimens were prepared for metallographic examination by an attack-polish procedure, using dilute nitric acid and 0.3-μ alumina; etching was done in a solution containing 50 parts (by volume) of 70 wt % HNO_3, 50 parts of water, and 2 parts of concentrated HCl.

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1. INTRODUCTION

The properties of the thorium carbides are of interest to the nuclear energy program because these compounds, like the uranium carbides, exhibit stability at

high temperatures and have good heat-transfer characteristics. Metallography serves as one means of determining the phases present in thorium carbide specimens. It is probably the most effective technique available for analyzing coated-particle fuels in which quantitative chemical or mechanical separation of the coating from the kernel is virtually impossible.

Previous investigators of the thorium-carbon system have generally used "air-etching" (exposure of the polished surface to the moisture in ambient air) to reveal the microstructures.[1-5] While air-etching does reveal some microstructural features, the results are not as distinctive as in the chemical etching of metals. In addition, the specimen must be examined hurriedly after metallographic preparation since the moisture from the air reacts continually with the specimen. A new procedure using nitric acid to passivate and etch thorium dicarbide gives microstructures that are much more clearly defined than those developed by air-etching.[6,7]

This report describes the application of this new nitric acid procedure to the metallography of arc-cast specimens with total-C/Th atom ratios varying from 1.0 to 2.1 (4.8 to 10.0 wt % carbon). An attack-polish procedure and a HNO_3-H_2O-HCl etchant were developed for single-phase thorium monocarbide specimens with compositions of $ThC_{0.8}$ and $ThC_{0.9}$ (4.0 and 4.6% carbon). Samples of these same carbide specimens were used in extensive chemical studies of their hydrolytic properties.[8,9] The specimens were also carefully characterized by chemical and X-ray diffraction analyses.

Acknowledgment. — The authors gratefully acknowledge the advice and support of R. J. Gray, ORNL Metals and Ceramics Division, during the course of this work. In addition, we wish to thank other members of that Division for their aid in this study: R. E. McDonald and L. Queener for arc-melting the carbides, and J. P. Hammond and C. Hamby for heat-treating specimen ThC-3H. Assistance was also provided by the ORNL Analytical Chemistry Division as follows: X-ray analyses by R. L. Sherman, and most of the chemical analyses by the group of W. R. Laing. We are indebted to J. F. Land, ORNL Chemical Technology Division, for the thermogravimetric analyses of the carbides for thorium.

2. THORIUM CARBIDE SPECIMENS

2.1 Preparation

The thorium carbides were prepared in the form of 100-g buttons by arc-melting high-purity thorium metal and spectroscopic-grade carbon in a 50 vol % argon--50 vol % helium atmosphere. Graphite electrodes were used in order to avoid tungsten contamination* except in the case of specimen 16, which was arc-melted with a tungsten electrode in an argon atmosphere. The buttons were melted until visual examination showed that all the carbon had dissolved in the melt; then they were melted an additional four times (2-min melts) to ensure complete reaction. Specimens containing 7.8% carbon or less shattered when struck by the arc; thus, after each melt the scattered fragments had to be collected and returned to the button mold before remelting could be accomplished. Mixtures initially containing less than 8.5 wt % carbon acquired an average of about 0.1 wt % carbon from the graphite electrodes during melting, while those initially containing 9.0% carbon or more lost carbon (Table 1). Specimen 8 was heat-treated in a graphite crucible for 65 hr at 1600°C, using a Brew High Vacuum Furnace, No. 424B.

2.2 Elemental Chemical Analyses, and Phases Identified by X-ray Diffraction Analysis

Table 2 summarizes the analyses of the thorium carbide specimens for thorium, total carbon, free carbon, oxygen (< 0.07 wt %), and nitrogen (40 to 172 ppm), and lists the major carbide constituents as identified by X-ray diffraction analysis. The maximum combined-C/Th atom ratio was 1.96, rather than the stoichiometric 2.00. Specimen 16 contained 6.1% tungsten as an impurity from the tungsten electrode. The other specimens, which were prepared with graphite electrodes, contained only 10 to 90 ppm of tungsten. Spectrographic analyses showed that specimens contained

*Attempts to prepare thorium dicarbide with tungsten electrodes resulted in specimens containing about 6 wt % tungsten.

Table 1. Composition Control in Arc-Melting Thorium Carbides with Graphite Electrodes

Specimen Code	Carbon (wt %) Synthetic[a] Th + C Mixture	Carbon (wt %) Product Carbide
ThC-4A	3.98	4.00
ThC-10A	4.50	4.61
ThC-7A	4.90	4.86
ThC-2A	4.90	5.00
ThC-8D	4.92	5.21
ThC-5A	5.85	6.15
ThC-3A	6.76	6.88
ThC-6A	7.65	7.88
ThC_2-5B	8.52	8.40
ThC_2-4	8.76	8.78
ThC_2-3	8.96	8.91
ThC_2-6	9.38	9.23
ThC_2-8B	9.38	9.28
ThC_2-7	10.22	9.98

[a]Calculated from weights of carbon and thorium used.

Table 2. Composition of Thorium Carbide Specimens

Specimen No.	Specimen Code	Fig. No.	Elemental Analysis (wt %) Th	Total C	Free C	O	W	(ppm) N	Total-C/Th Atom Ratio	Combined-C/Th[a] Atom Ratio	X-Ray Powder Pattern[b] ThC	ThC_2	For Hydrolysis Studies See Reference
1	ThC-4A	3	95.74	4.00	0.01	0.06	0.003	125	0.81	0.81	S[c]		8
2	ThC-10A	4	95.14	4.61	0.07	0.01	e	172	0.94	0.92	S[d]		9
3	ThC-7A	5	94.90	4.86	0.02	0.01	e	126	0.99	0.99	S[f]		9
4	ThC-2A	6	94.80	5.00	0.03	0.06	0.001	118	1.02	1.02	S[f]		8
5	ThC-8D	7	94.67	5.21	0.02	0.01	e	172	1.06	1.06	S	W	Appendix
6	ThC-5A	8	93.67	6.15	0.02	0.03	0.002	85	1.27	1.27	S	M	8
7	ThC-3A	9	93.06	6.88	0.02	0.03	0.003	92	1.43	1.43	S	S	8
8	ThC-3H[g]	10	93.07	6.92	0.03	0.02	e	92	1.44	1.44	S	S	
9	ThC-6A	11	92.10	7.88	0.06	0.01	0.008	50	1.65	1.65	M	S	8
10	ThC_2-5B	12	91.60	8.40	0.02	0.07	<0.001	57	1.77	1.78	M	S	8
11	ThC_2-4	13	91.26	8.78	0.10	0.02	0.009	42	1.86	1.84	W	S	8
12	ThC_2-3	14	91.02	8.91	0.09	0.01	0.004	40	1.89	1.88	T	S	8
13	ThC_2-6	15	90.76	9.23	0.06	0.03	0.001	51	1.97	1.96	-	S	8
14	ThC_2-8B	16	90.66	9.28	0.33	0.01	e	116	1.98	1.91	-	S	
15	ThC_2-7	17	89.97	9.98	0 90	0.02	0.006	44	2.14	1.95	-	S	8
16	ThC_2-1A	18	86.0	9.07	0.90[h]	0.05	6.1	45	h	~1.8[h]	-	S[i]	8

[a]Corrected for oxygen, assuming that oxygen is present as ThO_2. Note that combined-C/Th atom ratios for these specimens, as given in refs. 8 and 9, were not corrected for oxygen and, in a few cases, may be slightly different.
[b]S, strong; M, moderate; I, weak; and T, trace.
[c]Lattice parameter, 5.340 A.
[d]Lattice parameter, 5.345 A.
[e]Not analyzed.
[f]Lattice parameter, 5.346 A.
[g]Specimen ThC-3A after heat-treatment for 65 hr at 1600°C.
[h]Amount of carbon combined with the tungsten is not precisely known.
[i]Plus a few, faint, unidentified, extra lines.

about 6 ppm of calcium, 3 ppm of iron, 2 ppm of aluminum, 2 ppm of magnesium, and 1 ppm of copper. All other metallic impurities were less than 1 ppm. The analytical procedures used are described in the Appendix.

The monocarbide ($ThC_{1.0}$) and dicarbide ($ThC_{1.96}$) X-ray powder patterns were the same as those reported by Kempter and Krikorian.[10] In the X-ray diffraction analysis of mixtures, there were no detectable shifts in the spacings of the monocarbide lines as the total-C/Th atom ratio increased from 0.99 to 1.44, or in the dicarbide lines as the ratio increased from 1.65 to 2.14. Based on calculations by means of a weighted Nelson and Riley extrapolation,[11] the lattice parameter of thorium monocarbide was found to be 5.346 A in the specimen with a combined-C/Th atom ratio of 1.02, 5.345 A in $ThC_{0.92}$, and 5.340 A in $ThC_{0.81}$.[12] No thorium metal was detected by X-ray diffraction analysis of the $ThC_{0.81}$ or the $ThC_{0.92}$ specimens. Thorium monocarbide was detected in the $ThC_{1.88}$ specimen, but not in specimens with combined-C/Th atom ratios of 1.91 or higher. The 6 wt % tungsten impurity in specimen 16 could not be detected by X-ray diffraction analysis of the original specimen; however, after the specimen had been hydrolyzed and all the thorium had been dissolved in 6 M HCl, half of the tungsten was recovered as unreacted W_2C (X-ray diffraction analysis). One diffraction line that could have been attributed to WC was also observed in the X-ray powder pattern of this residue. The combined-C/W atom ratio in the residue could not be determined by elemental analysis since the tungsten compound(s) could not be separated from the graphite. It is not known what chemical species of tungsten [e.g., W, W_2C, WC, or possibly a $(W_xTh_y)C$] hydrolyzed.

2.3 Hydrolysis

The two thorium carbides yielded distinctly different gaseous products on reaction with water at 25 to 99°C.[8,9] Thorium monocarbide produced mostly methane, and also two moles of hydrogen for each mole of thorium which was in excess of the 1:1 Th/C atom ratio. Thorium dicarbide produced C_2- to C_8-hydrocarbons, wax, and hydrogen. The preponderance of hydrocarbons with an even number of carbon atoms in the gas from the hydrolysis of the dicarbide is to be expected because of the

presence of discrete C_2 units in the dicarbide crystal lattice.[13] Carbon spacing in the thorium monocarbide lattice has not been studied; however, the carbon is probably present in the form of single-C units as in uranium monocarbide,[14] which also yields methane when hydrolyzed.[15] The total volume of evolved gas decreased from 110 ml/g to 49 ml/g as the combined-C/Th atom ratio increased from 0.81 to 1.96 (Fig. 1). Specimens with compositions between $ThC_{1.0}$ and $ThC_{1.96}$ gave the expected products for binary mixtures, showing a regular decrease in the amount of methane and a corresponding increase in the amount of C_2- to C_8-hydrocarbons as the C/Th atom ratio increased (Fig. 2).[8] Fifteen percent of the carbon in $ThC_{1.02}$ (specimen 4) and 14% in the $ThC_{0.99}$ (specimen 3) was found to be present as C_2- to C_8-hydrocarbons (which are dicarbide products), as compared with only 5% from $ThC_{0.81}$ (specimen 1), 7% from $ThC_{0.92}$ (specimen 2), and 8% from $UC_{0.97}$.[16] This indicates that the $ThC_{0.99}$ and $ThC_{1.02}$ specimens probably contained a small amount of thorium dicarbide, even though none was detected by X-ray diffraction analysis. A more complete discussion of the hydrolytic properties of the specimens used in this study is given in ref. 8.

3. METALLOGRAPHIC PROCEDURES

Specialized procedures were required for the metallographic preparation of thorium carbides because of their rapid reaction with moisture.

3.1 Preparation of Thorium Dicarbide and Two-Phase Monocarbide-Dicarbide Specimens

The procedures used in the metallographic preparation of thorium dicarbide and monocarbide-dicarbide mixtures were similar to those previously developed for $(Th,U)C_2$.[6,7] Fragments of the arc-melted specimens were mounted in epoxy resin and then rough-ground on 320-, 400-, and 600-grit silicon carbide papers, using either absolute ethyl alcohol or silicone oil as the lubricant. The specimens were then either vibratorily polished 6 to 12 hr within a "dry" box, using a silicone oil – 0.3-μ alumina slurry on a nylon cloth, or were mechanically polished 3 min outside the dry box, using an absolute ethyl alcohol – 0.3-μ alumina suspension on a wheel that was covered with

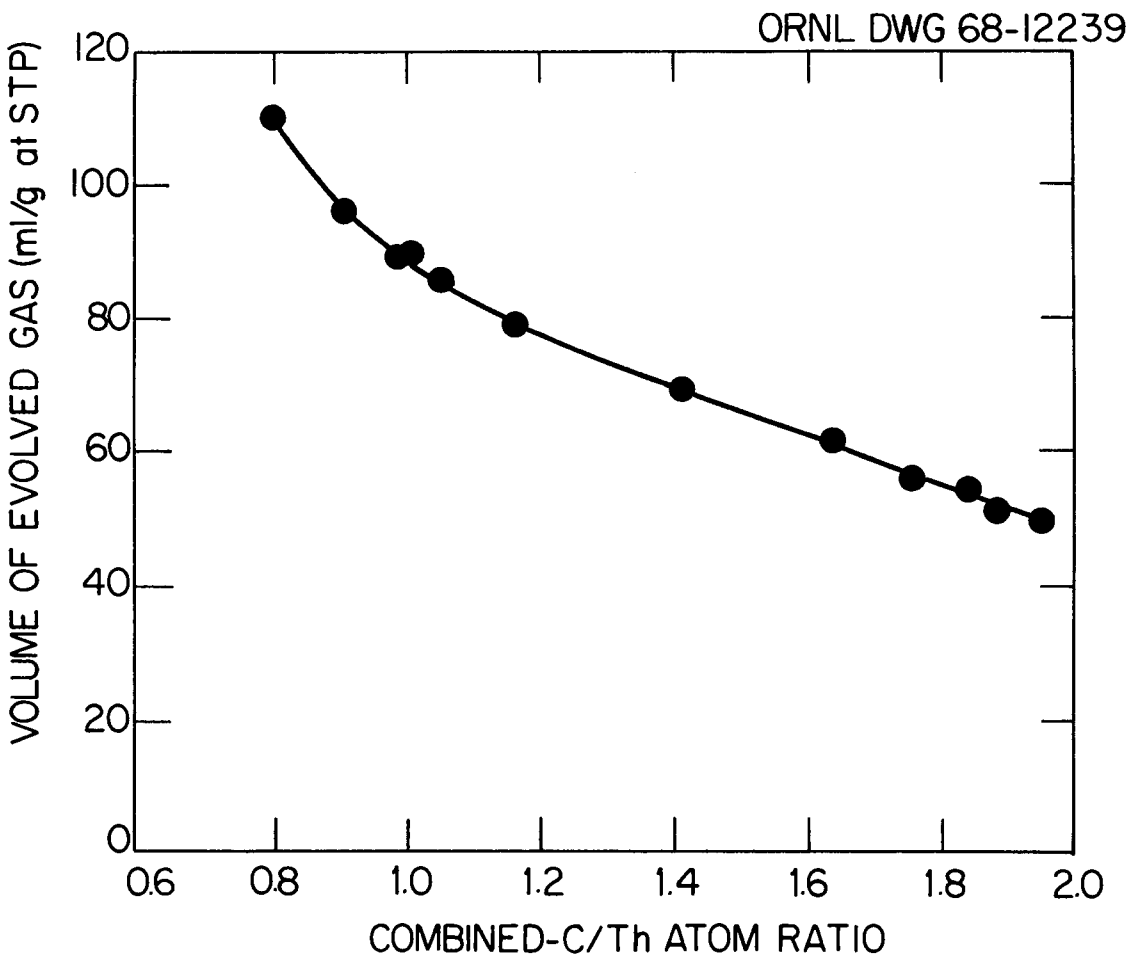


Fig. 1. Volume of Gas Evolved in the Hydrolysis, at 80°C, of As-Cast Thorium Carbides.

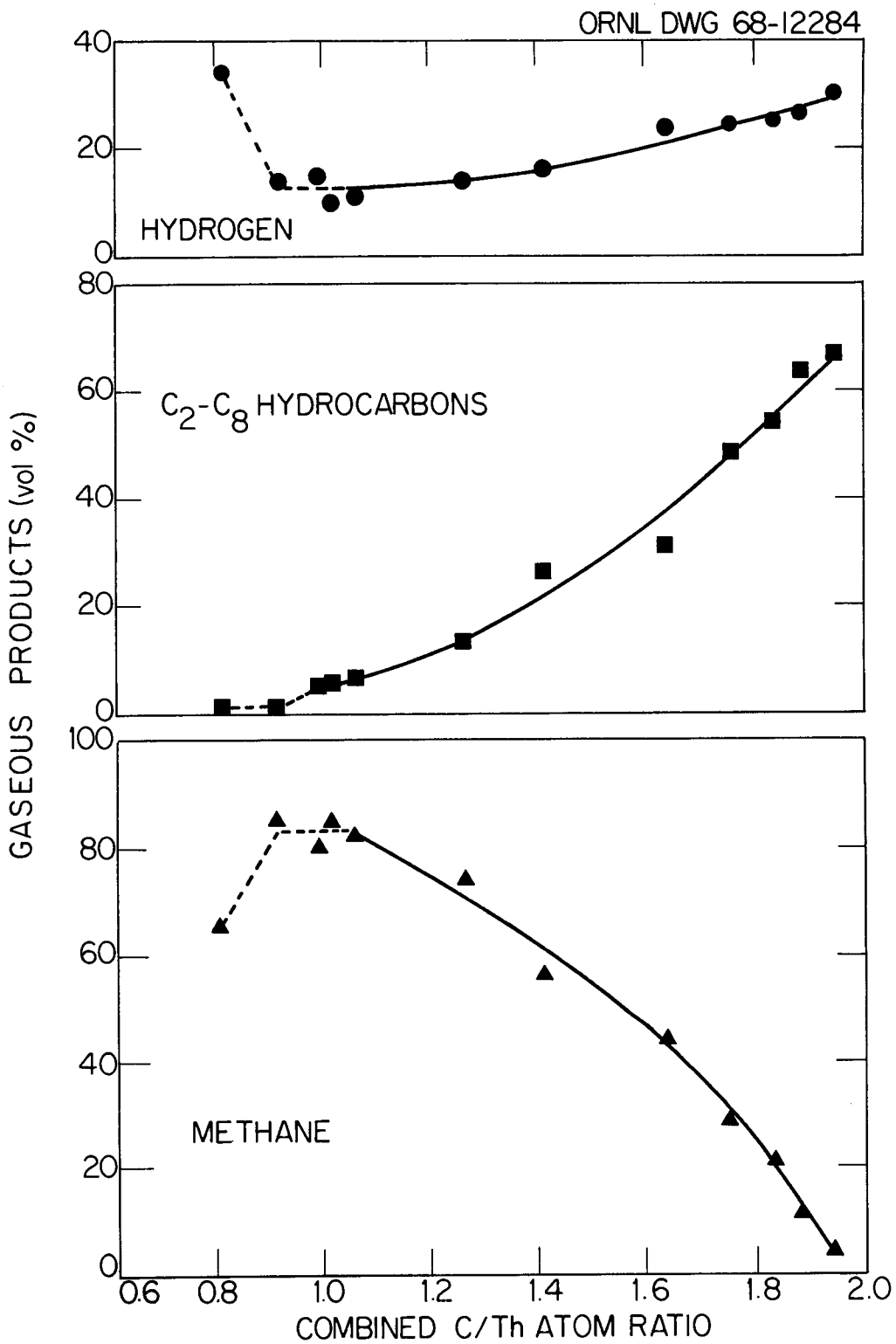


Fig. 2. Gaseous Products From the Hydrolysis, at 80°C, of As-Cast Thorium Carbides.

a nylon cloth and was operated at 100 to 200 rpm. Direct exposure of the active polished surface to the moisture contained in room air was avoided by immediately washing the surface with absolute ethyl alcohol and then immersing it in a solution of equal parts (by volume) of nitric acid (70 wt %) and water without allowing the alcohol to evaporate completely. After immersion in the nitric acid solution for 1 min, specimens were washed with ethyl alcohol and dried with an air dryer.

Immersion in the nitric acid solution produced a passive film on the thorium carbides which retarded reaction with moisture. While this treatment gave only limited protection, it did protect the surface from moisture for about 1 hr, which was sufficient time to complete the microscopic observation.

The nitric acid solution also served as an etchant for specimens consisting of mixtures of thorium mono- and dicarbides. Although the dicarbide did not appear to be appreciably etched by the nitric acid solution when viewed under bright field illumination, its microstructure was satisfactorily revealed under polarized light. Single-phase thorium monocarbide was not etched by the nitric acid.

The nitric acid technique just described has several advantages over the air-etching technique:[1-5] (1) more clearly defined microstructures were obtained; (2) specimens could be observed directly in air without immersing them in oil to minimize the reaction with moisture; and (3) specimens could be examined more leisurely than air-etched specimens, which, even under an oil film, continue to react rapidly with the moisture in the air.

3.2 Preparation of Single-Phase Thorium Monocarbide Specimens

Thorium monocarbide was more difficult to prepare for metallographic examination than either the dicarbide or monocarbide-dicarbide mixtures. During polishing, thorium monocarbide behaved rather toughly, and it was necessary to use an attack-polish procedure to remove grinding scratches. Specimens were: (1) mounted in epoxy resin; (2) ground on 320-, 400-, and 600-grit silicon carbide papers, using ethyl alcohol as the lubricant; (3) rough-polished 3 to 5 min, using a 0.5-μ diamond compound and fairly heavy pressure on a Metcloth wheel; and (4) attack-polished

for 3 min, using 0.3-μ alumina and dilute nitric acid (9 parts by volume of water to 1 part 70 wt % HNO_3) on a Microcloth wheel operated at 100 to 200 rpm. Each specimen was then etched by immersion, for 5 min, in a solution containing 50 parts (by volume) of HNO_3 (70 wt %), 50 parts of water, and 2 parts of concentrated HCl. Since this etchant attacks thorium monocarbide along the edges and at pits and crevices, it can only be used for specimens whose polished surfaces are fairly free of pits and crevices. During the etching, a dark blue film forms and must be removed by rubbing the specimen with a cotton swab in running distilled water. After washing, the specimen was dried with an air dryer.

This attack-polish procedure yielded a polished surface that appeared to be free of scratches. Yet, etching this surface with most etchants always uncovered polishing scratches that could not be removed even by repeated cycles of polishing and etching. These scratches were quite fine, and were undoubtedly produced in the last polishing stage. The HNO_3-H_2O-HCl etchant, which acted somewhat as a chemical polish, removed most of the polishing scratches and also satisfactorily delineated the grain boundaries. Therefore, this etchant was employed even though it presented considerable difficulty because of its gross attack at cracks and crevices, which were always present in the single-phase thorium monocarbide.

4. MICROSTRUCTURES OF THE THORIUM CARBIDES

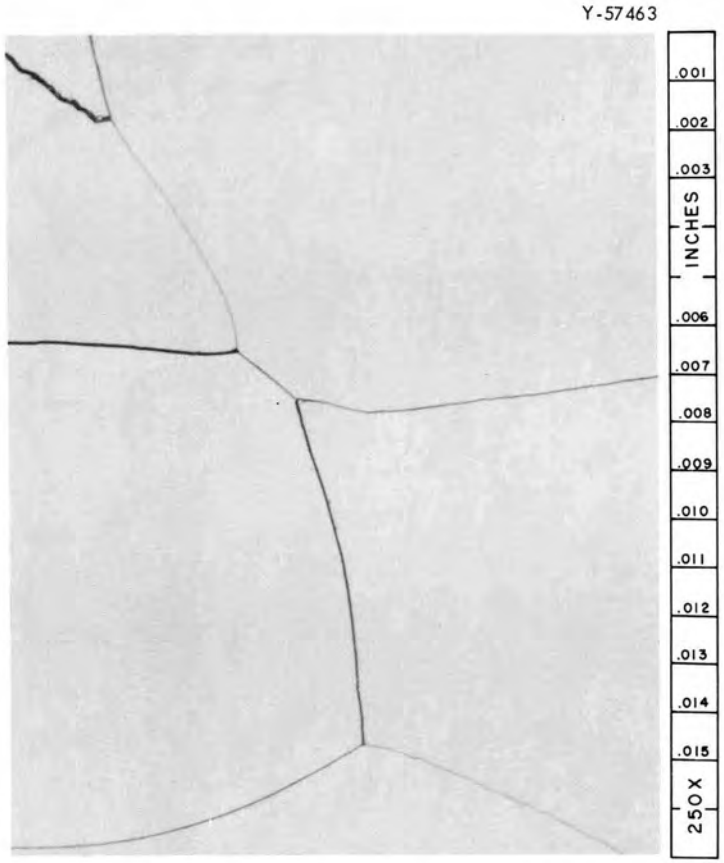
Photomicrographs (at 250X and 1000X) of arc-cast thorium carbides with total-C/Th atom ratios varying from 0.8 to 2.1 (4.0 to 10.0 wt % carbon) are shown in Figs. 3 to 18. Specimens with compositions of $ThC_{0.81}$ and $ThC_{0.92}$* were single-phase, carbon-deficient thorium monocarbide (Figs. 3 and 4). These specimens were difficult to prepare for metallographic examination because they scratched easily during polishing. The $ThC_{0.99}$ and $ThC_{1.02}$ specimens (4.9 and 5.0% carbon) contained

*The compositions given in the figure titles refer to the amount of combined carbon, except in Figs. 16-18, where free carbon is observed in the microstructures and both the total- and the combined-carbon are indicated.

significant amounts of thorium dicarbide (which was not detected by X-ray diffraction analysis) in addition to the thorium monocarbide matrix (Figs. 5 and 6). Specimens with compositions from $ThC_{0.99}$ to $ThC_{1.88}$ (4.9 to 8.9% carbon) were two-phase mixtures of the mono- and dicarbides (Figs. 5 to 14). Bright field illumination was slightly more effective for detecting small amounts of thorium dicarbide in the monocarbide matrix, while, near the dicarbide end of the range, small amounts of monocarbide could be detected only under polarized light as a general cloudiness of the microstructure. Specimen 13 (total-C/Th atom ratio, 1.97; combined-C/Th atom ratio, 1.96) was single-phase, high-purity thorium dicarbide (Fig. 15), while specimen 14 (total-C/Th atom ratio, 1.98; combined-C/Th atom ratio, 1.91), which had a similar total-carbon content, was a mixture of dicarbide with a trace of graphite (Fig. 16). Large amounts of graphite as a thorium dicarbide-graphite eutectic were observed in specimen 15, which had a total-C/Th atom ratio of 2.14 (9.98% C; combined-C/Th atom ratio, 1.95) (Fig. 17). Bright field illumination revealed the graphite in thorium dicarbide more effectively than polarized light.

A characteristic feature of the microstructure of the as-cast thorium dicarbide matrix was the banded substructure within the grains, as revealed under polarized light. This substructure consisted of main bands, which were apparent in each specimen having a dicarbide matrix (Figs. 11-18), and subbands, which are most obvious in specimen 13. Cook[18] attributes the main bands and the subbands to a double-shear mechanism as the carbide transforms from the high-temperature face-centered cubic structure to the body-centered tetragonal structure at 1500 ± 25°C. Cook[18] believes that the second polymorphic transformation from the body-centered tetragonal to the monoclinic form at 1430 ± 10°C does not change the microstructure significantly, since he was able to anneal out most of the banded structure by heat-treating at 1350, 1400, and 1455°C.

Specimen 16, which contained 6% tungsten, consisted of grains of relatively high-purity thorium dicarbide, with a eutectic structure at the grain boundaries. This eutectic precipitated into graphite and a tungsten-containing phase as the specimen cooled from the melt (Fig. 18).



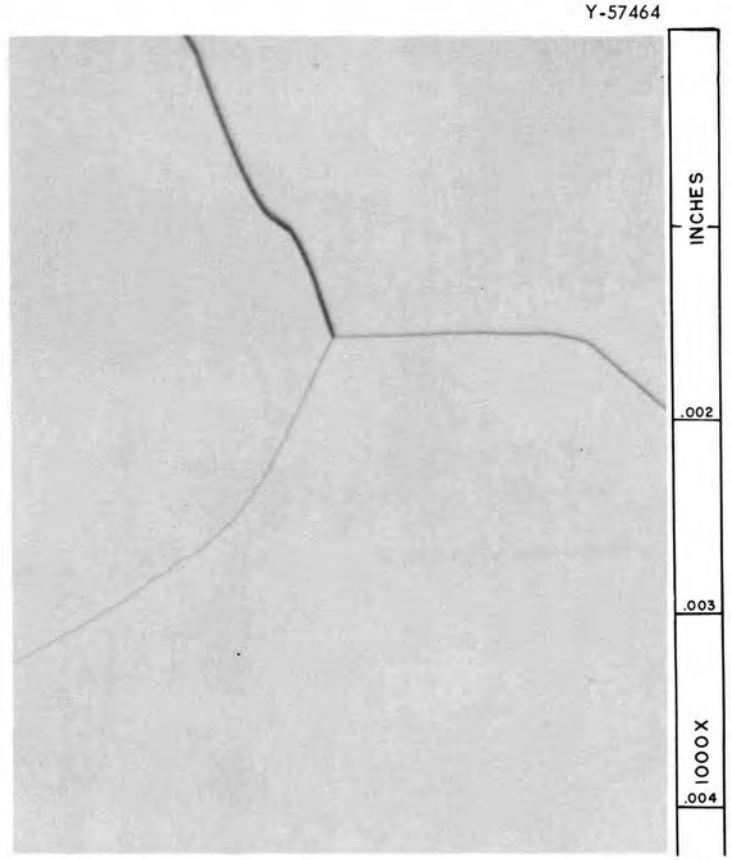
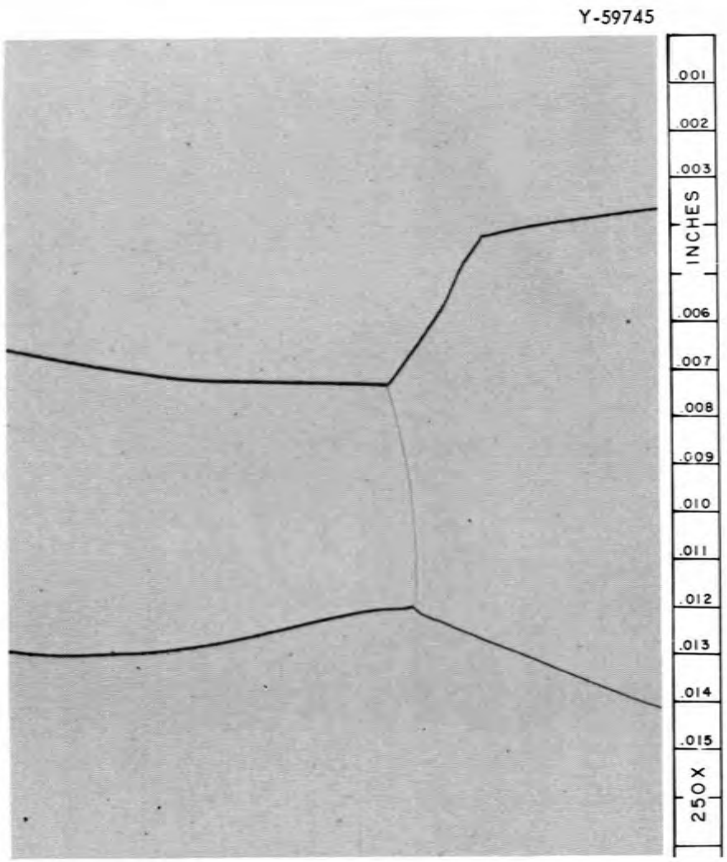


Fig. 3. As-Cast $ThC_{0.81}$ (3.99% C; Specimen 1), Showing Single-Phase Thorium Monocarbide. Free metal was not observed. The single-phase thorium monocarbide specimens were difficult to prepare because grinding and polishing scratches were not easily removed and the HNO_3-H_2O-HCl etchant grossly attacked the specimens at cracks and crevices. Bright field illumination.



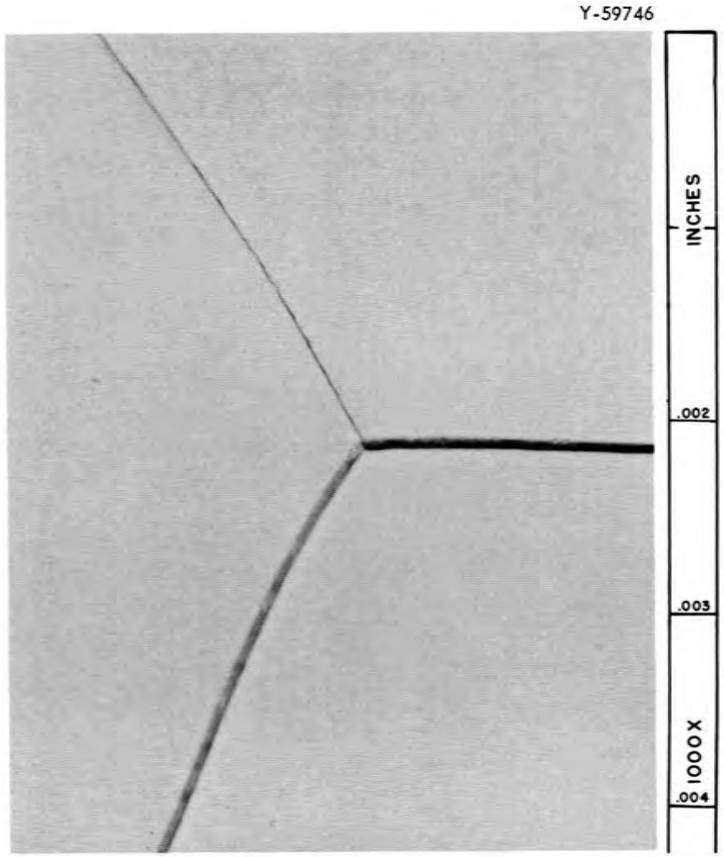


Fig. 4. As-Cast $ThC_{0.92}$ (4.54% C; Specimen 2), Showing Single-Phase Thorium Monocarbide. Free metal was not observed. This specimen was also difficult to prepare. Bright field illumination; nitric-hydrochloric acid etch.

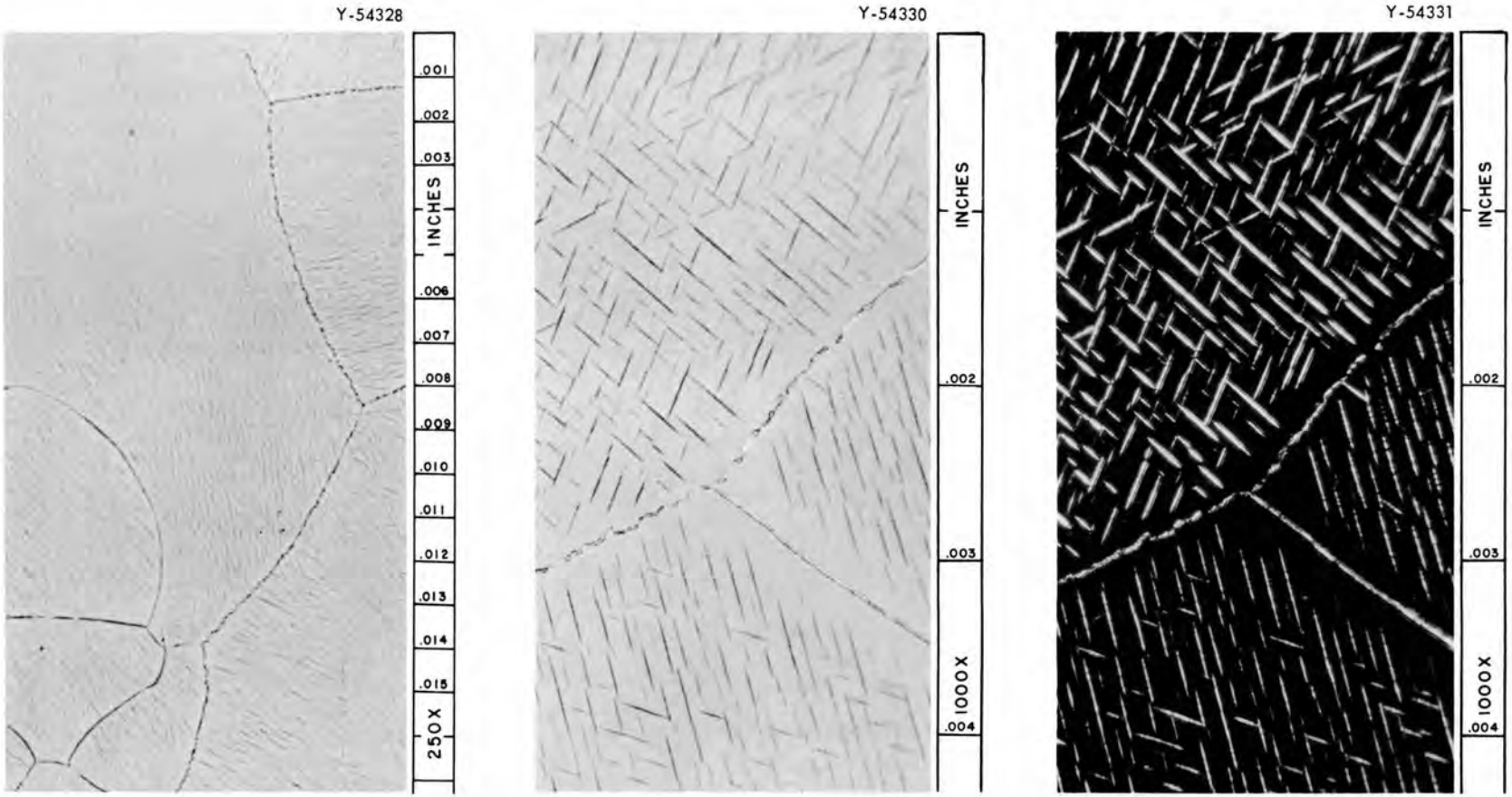


Fig. 5. As-Cast $ThC_{0.99}$ (4.84% C; Specimen 3), Showing Thorium Monocarbide Matrix with Dicarbide Platelets Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). The specimen contains a significant amount of thorium dicarbide impurity, which was not detected by X-ray diffraction analysis. Nitric acid etch.

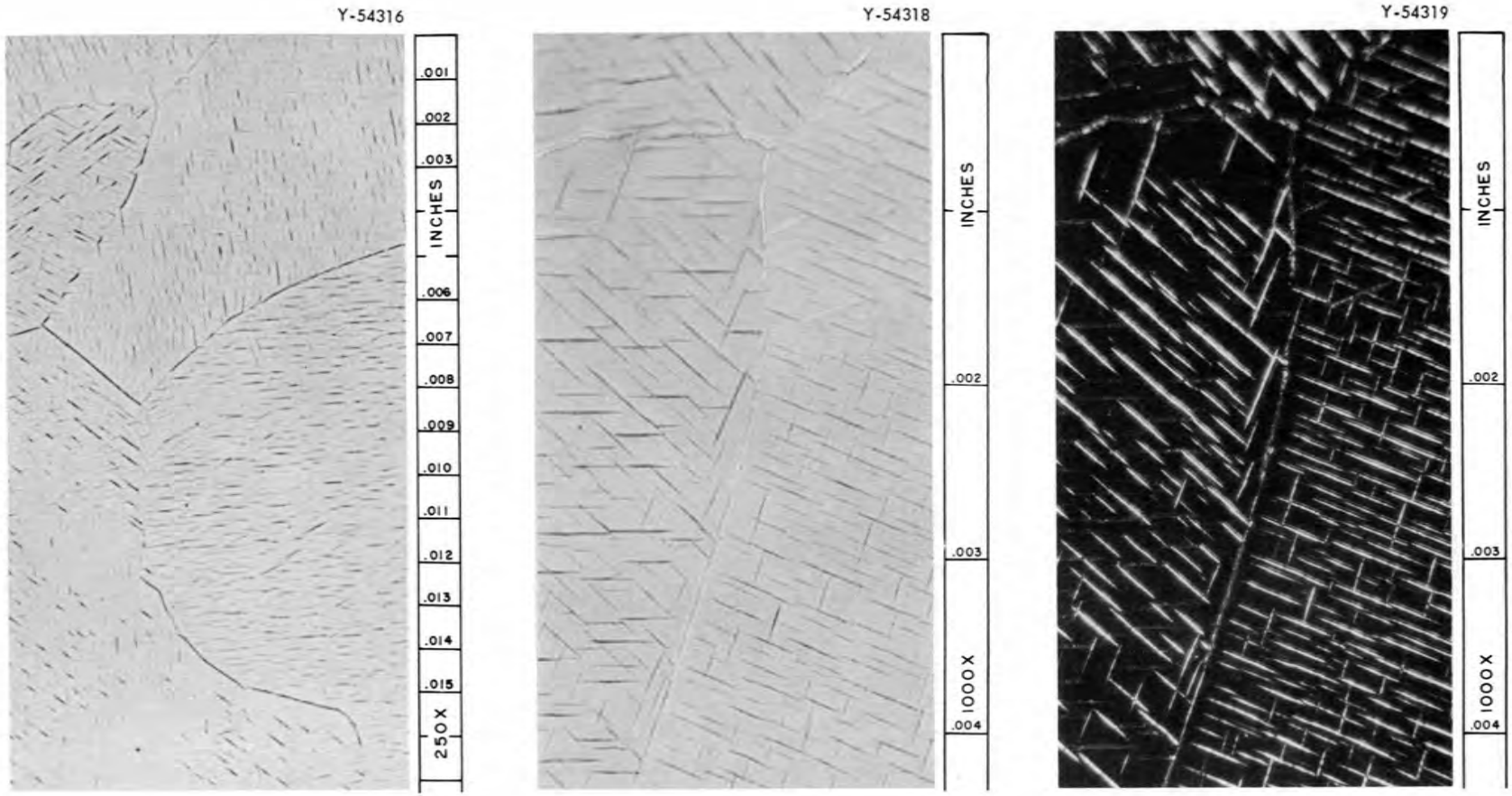


Fig. 6. As-Cast $ThC_{1.02}$ (4.97% C; Specimen 4), Showing Thorium Monocarbide Matrix with Dicarbide Platelets Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). The specimen contains a significant amount of thorium dicarbide impurity, which was not detected by X-ray diffraction analysis. Nitric acid etch.

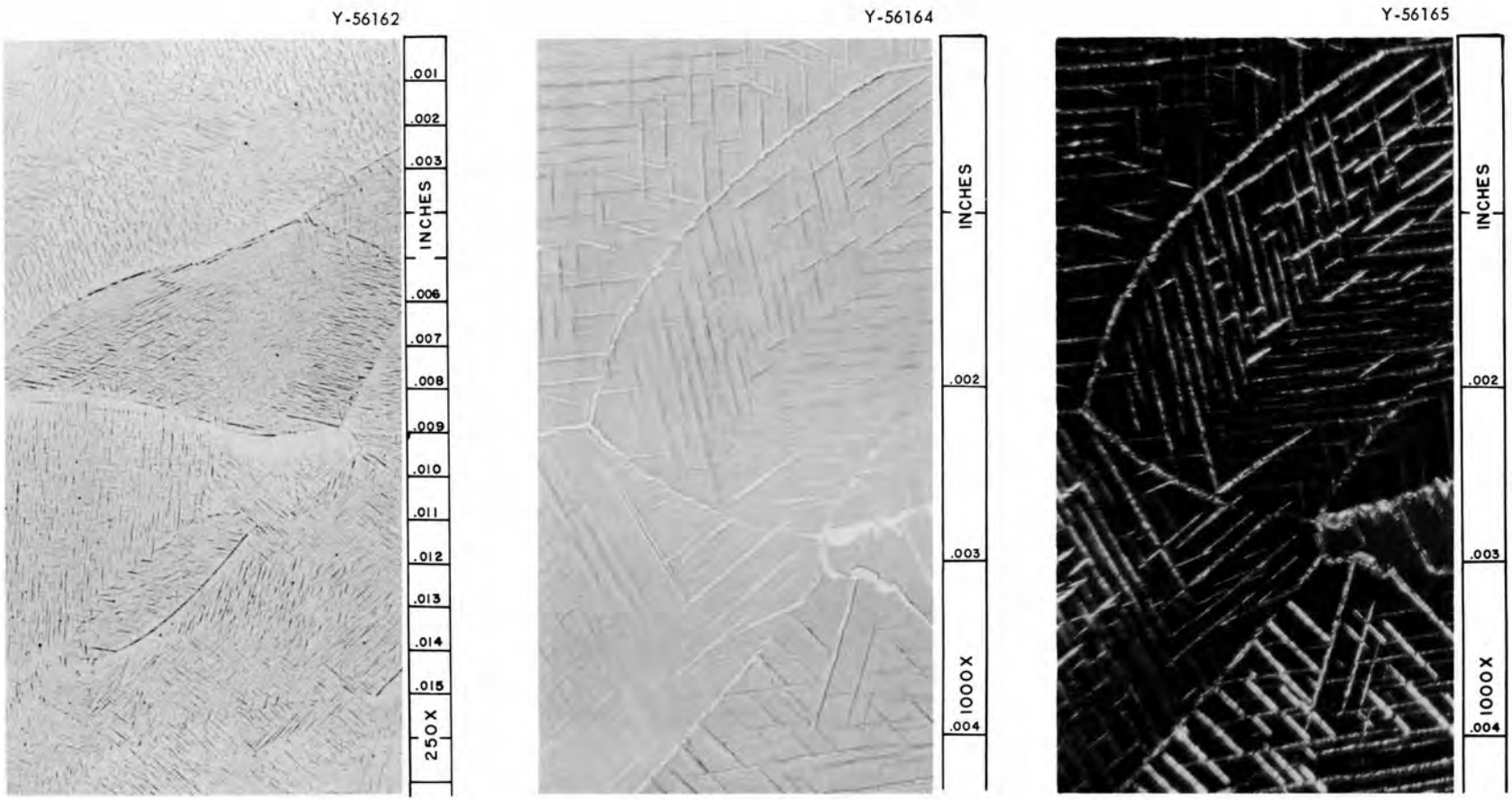


Fig. 7. As-Cast $ThC_{1.06}$ (5.19% C; Specimen 5), Showing Thorium Monocarbide Matrix with Dicarbide Platelets Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). Thorium dicarbide was detected by X-ray diffraction analysis of this specimen. Note the dicarbide-rich, intergranular structure, which could be caused by nonequilibrium freezing (since there is a minimum in the liquidus at ~ 6% carbon).[1] Nitric acid etch.

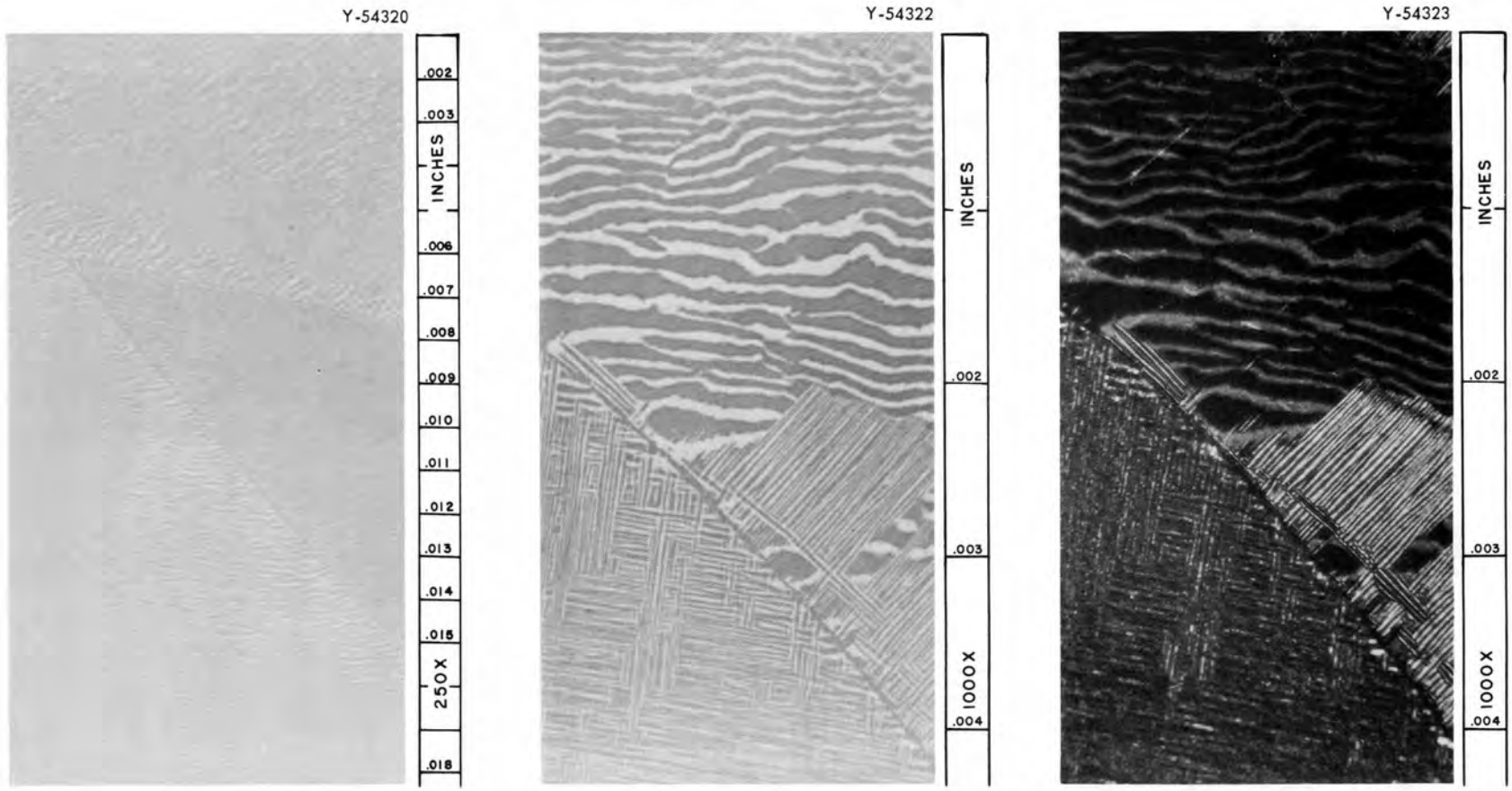


Fig. 8. As-Cast $ThC_{1.27}$ (6.13% C; Specimen 6), Showing Thorium Monocarbide (Dark) and Dicarbide (Light) Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). This composition is close to the minimum in the liquidus,[1] and the specimen has almost no intergranular structure. Nitric acid etch.

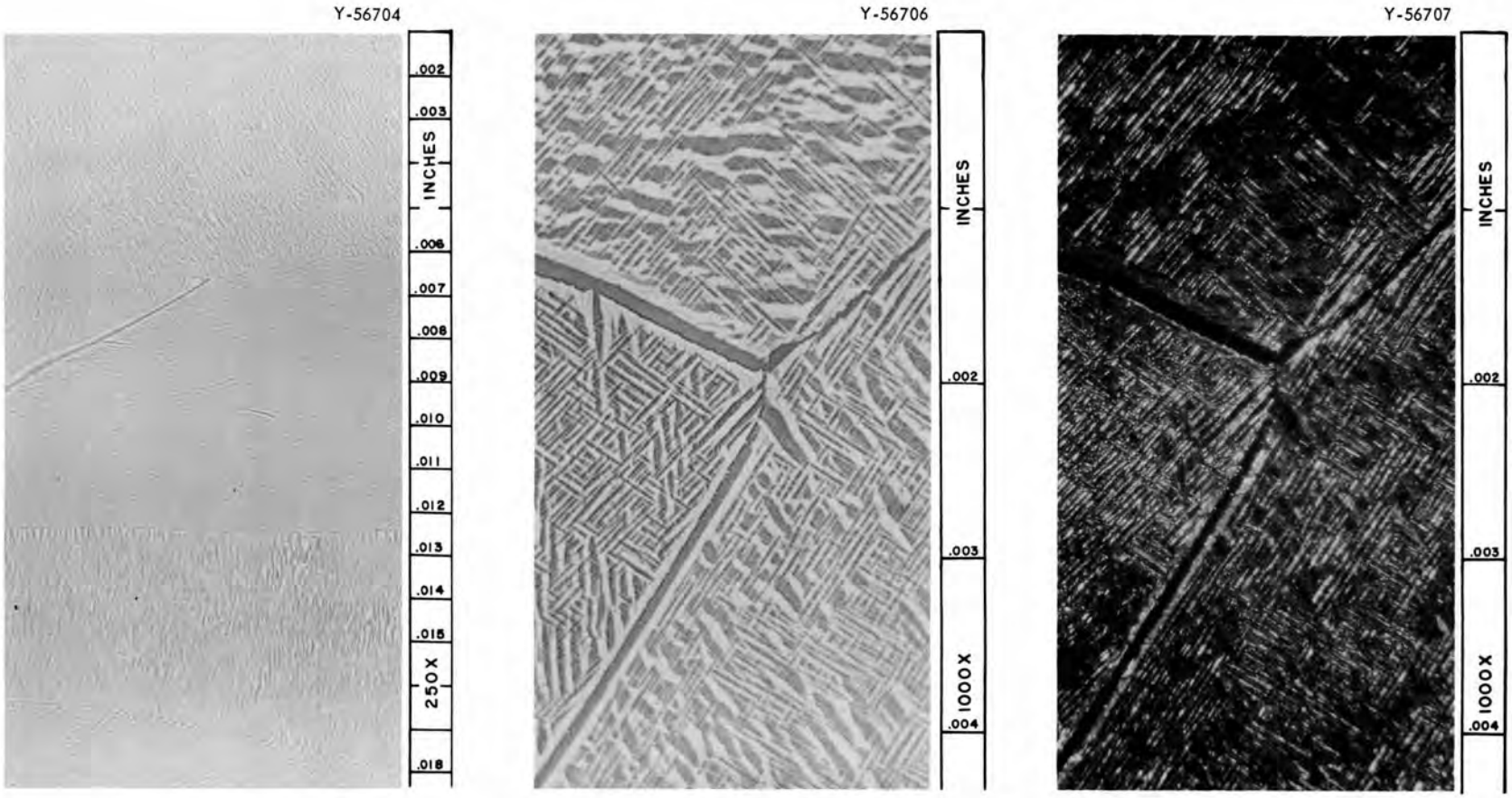


Fig. 9. As-Cast $ThC_{1.43}$ (6.86% C; Specimen 7), Showing Thorium Monocarbide (Dark) and Dicarbide (Light) Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). Note the monocarbide-rich intergranular structure, which could be caused by nonequilibrium freezing (since there is a minimum in the liquidus at ~ 6% carbon).[1] Nitric acid etch.

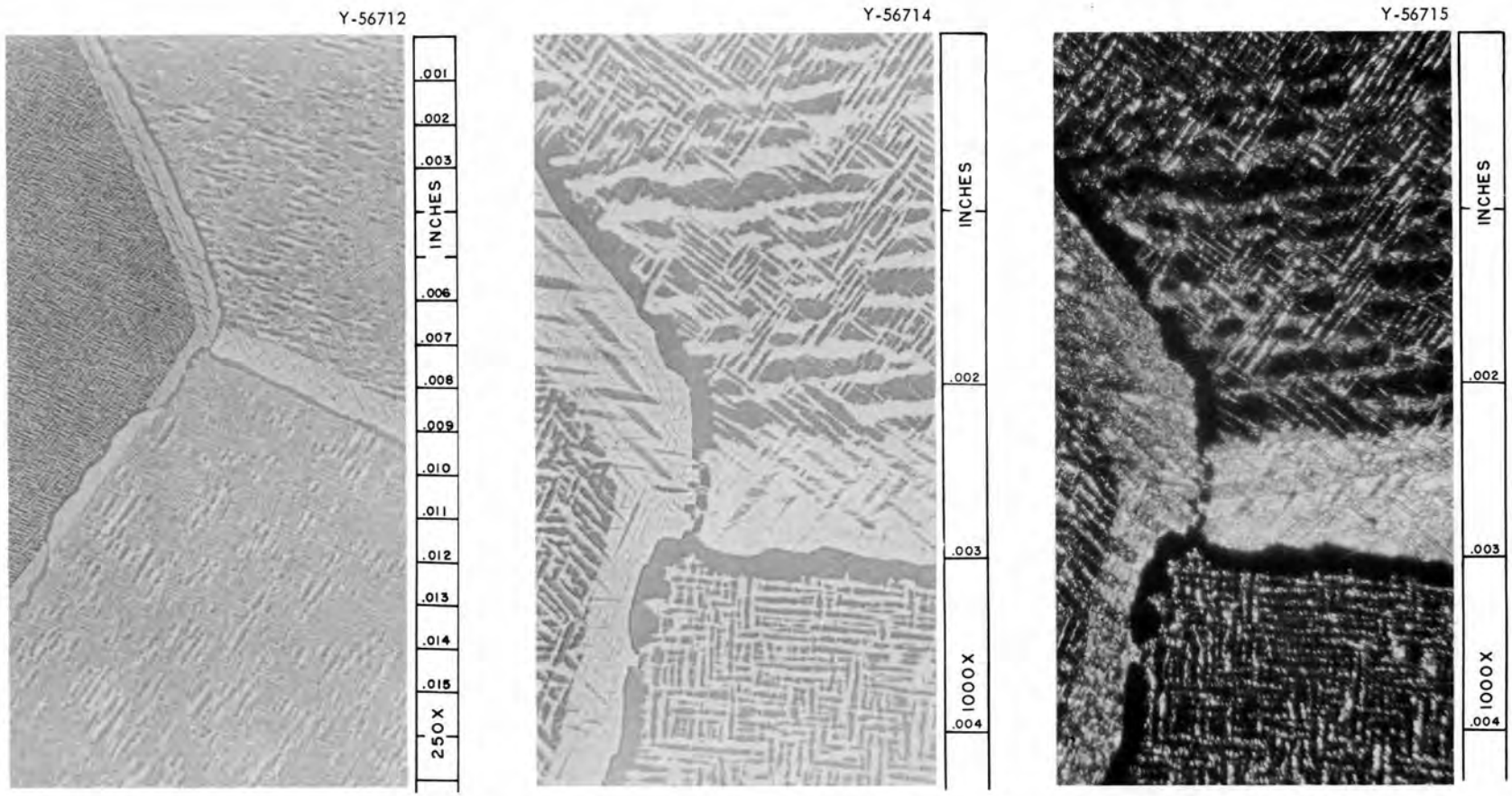


Fig. 10. $ThC_{1.44}$ Heat-Treated for 65 hr at 1600°C and Rapidly Furnace-Cooled (6.89% C; Specimen 8), Showing Thorium Monocarbide (Dark) and Dicarbide (Light) Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). The specimen appears to have been heated in a single-phase region. There is no indication of sesquicarbide formation, as occurs in the uranium-carbon system under these conditions.[17] Nitric acid etch.

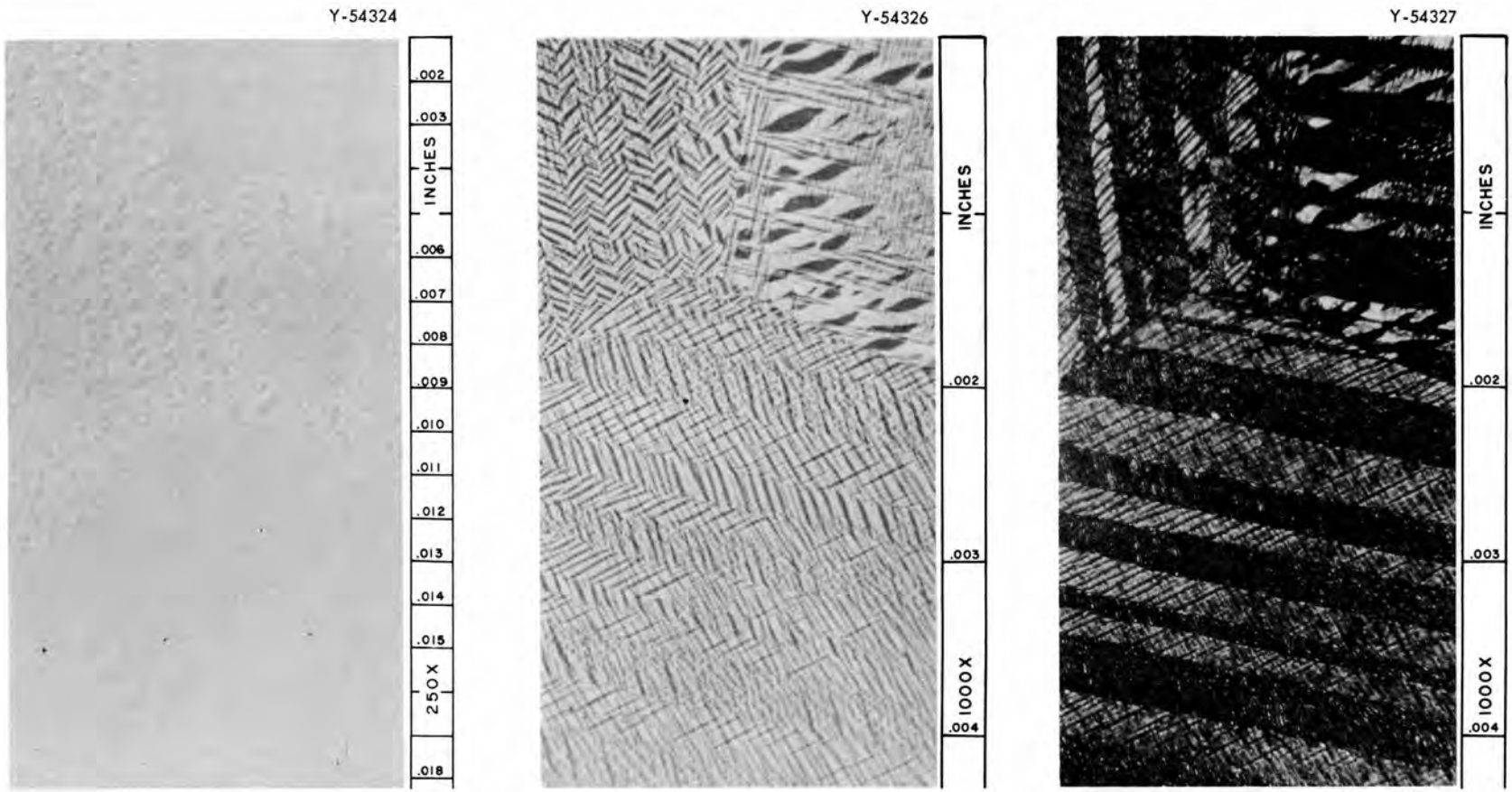


Fig. 11. As-Cast $ThC_{1.65}$ (7.82% C; Specimen 9), Showing Thorium Dicarbide (Light) and Monocarbide (Dark) Under Bright Field Illumination (Left and Center) and Polarized Light (Right). Note that the thorium monocarbide platelets do not cross the boundary of the dicarbide bands within the grains; this indicates that they did not precipitate from solid solution until after the dicarbide transformation from the high-temperature face-centered-cubic to the body-centered-tetragonal structure had occurred. Nitric acid etch.

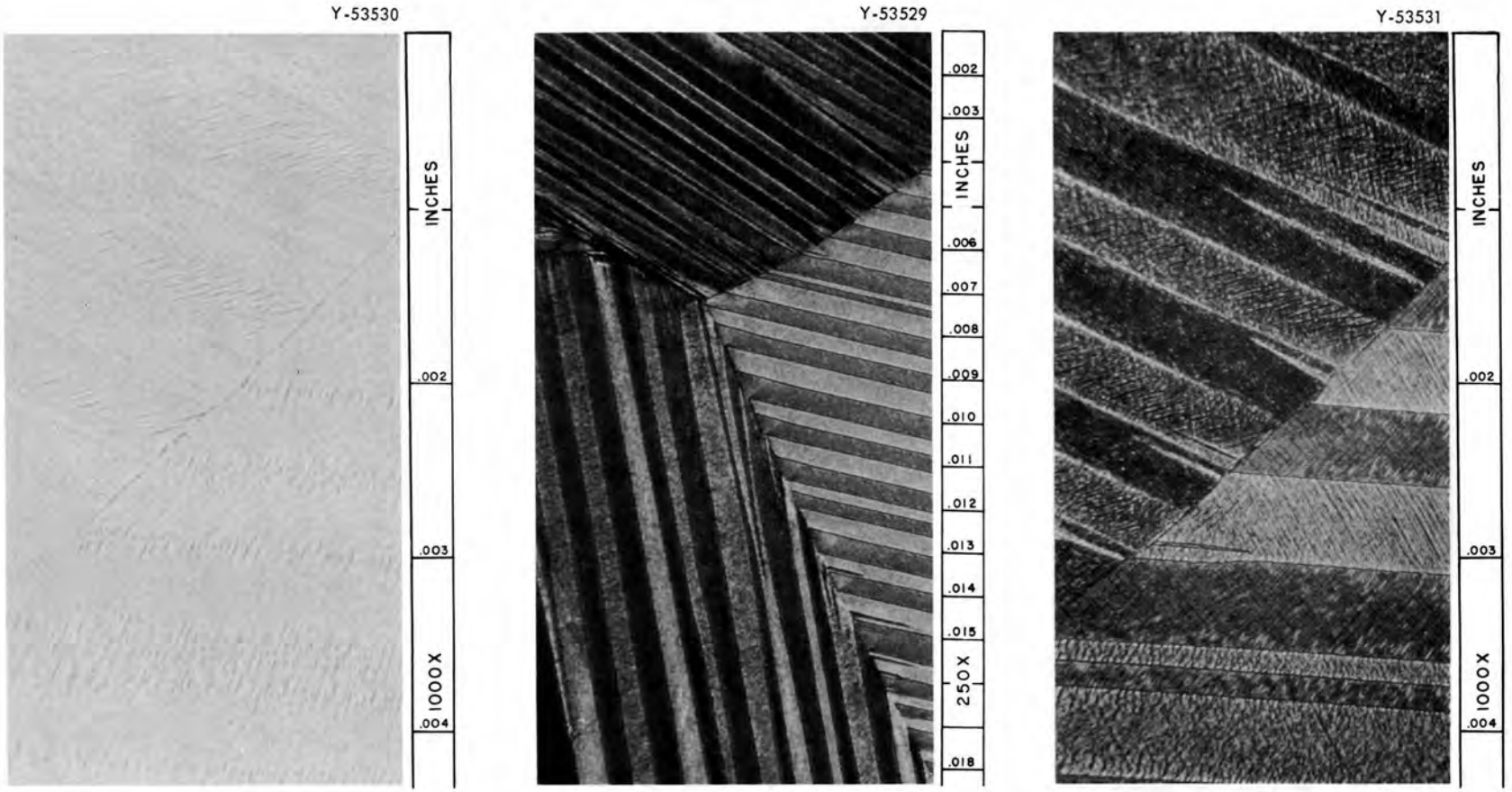


Fig. 12. As-Cast $ThC_{1.78}$ (8.38% C; Specimen 10), Showing Thorium Dicarbide Matrix with Monocarbide Under Bright Field Illumination (Left) and Polarized Light (Center and Right). The monocarbide is dark under bright field illumination. Nitric acid etch.

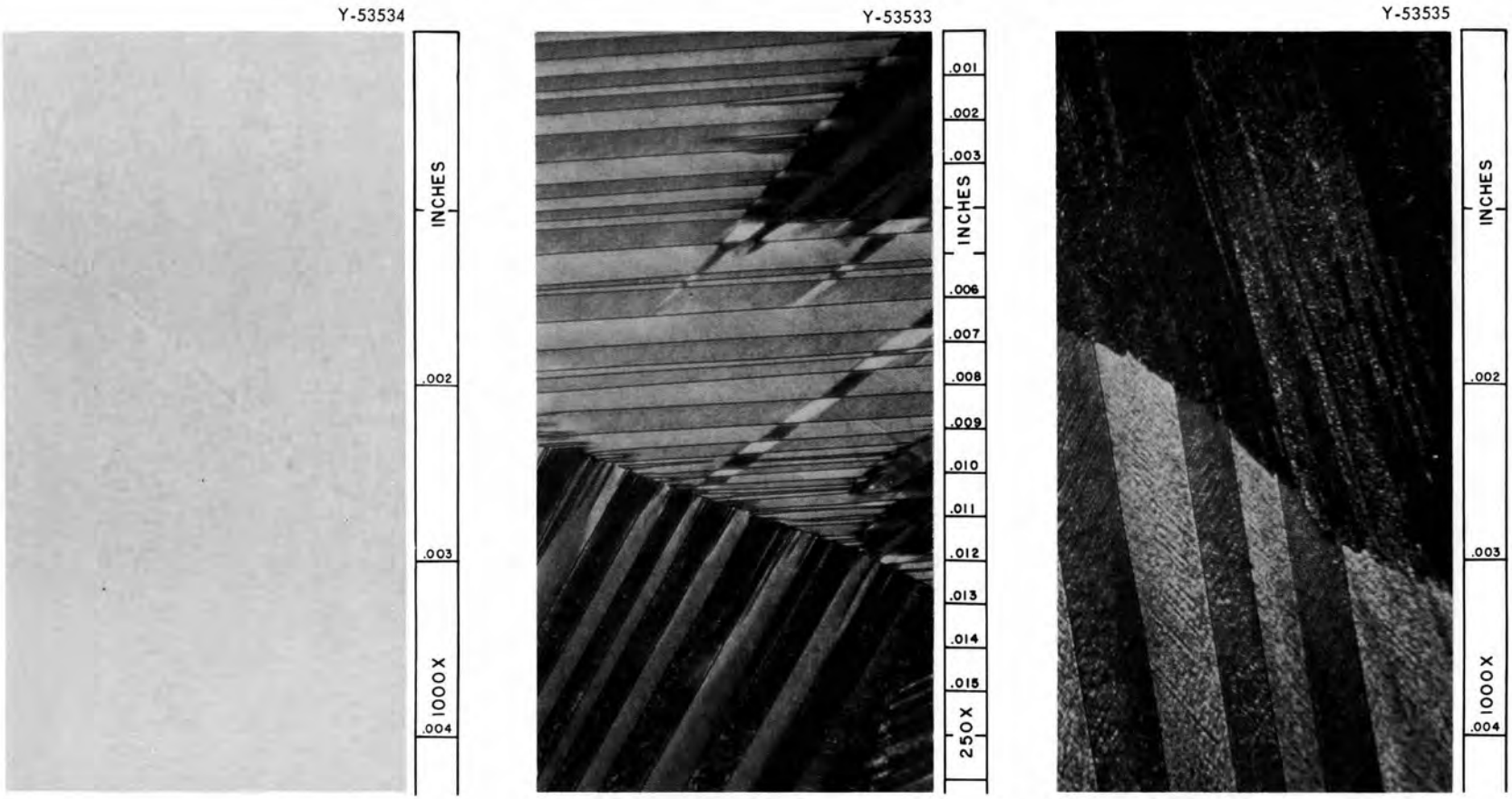


Fig. 13. As-Cast $ThC_{1.84}$ (8.68% C; Specimen 11), Showing Thorium Dicarbide Matrix with Monocarbide. The monocarbide is only faintly visible under bright field illumination (left), but shows up as a cloudiness under polarized light (center and right) at 1000X when compared with Fig. 15. Nitric acid etch.

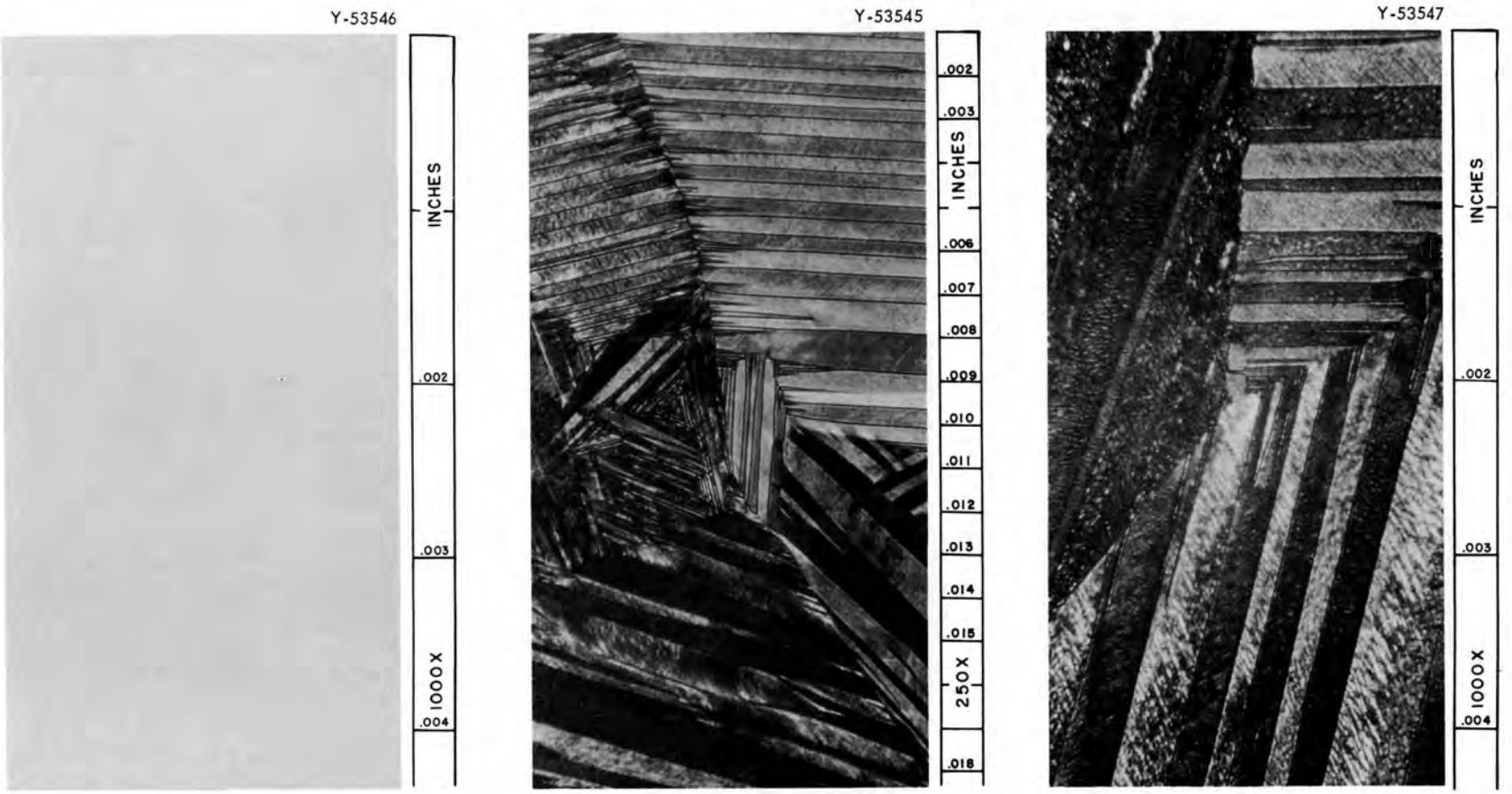


Fig. 14. As-Cast $ThC_{1.88}$ (8.82% C; Specimen 12), Showing Thorium Dicarbide Matrix with a Trace of Monocarbide. The monocarbide is not visible under bright field illumination (left), but shows up as a cloudiness under polarized light (center and right) at 1000X when compared with Fig. 15. Thorium monocarbide was detected by X-ray diffraction analysis of this specimen. Nitric acid etch.

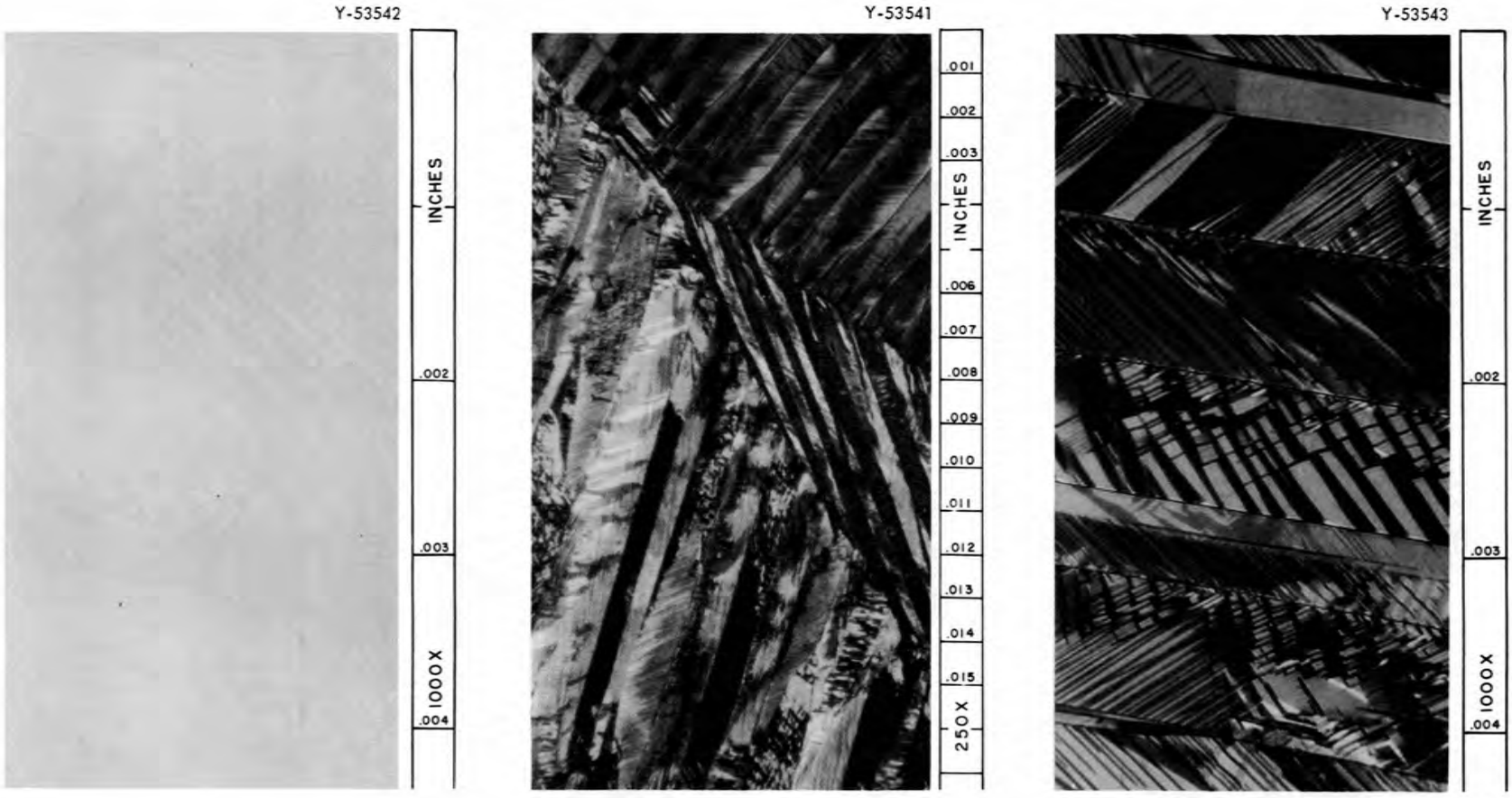


Fig. 15. As-Cast $ThC_{1.96}$ (9.17% C; Specimen 13), Showing High-Purity, Single-Phase Thorium Dicarbide Under Bright Field Illumination (Left) and Polarized Light (Center and Right). No thorium monocarbide was detected by X-ray diffraction analysis. Nitric acid etch.

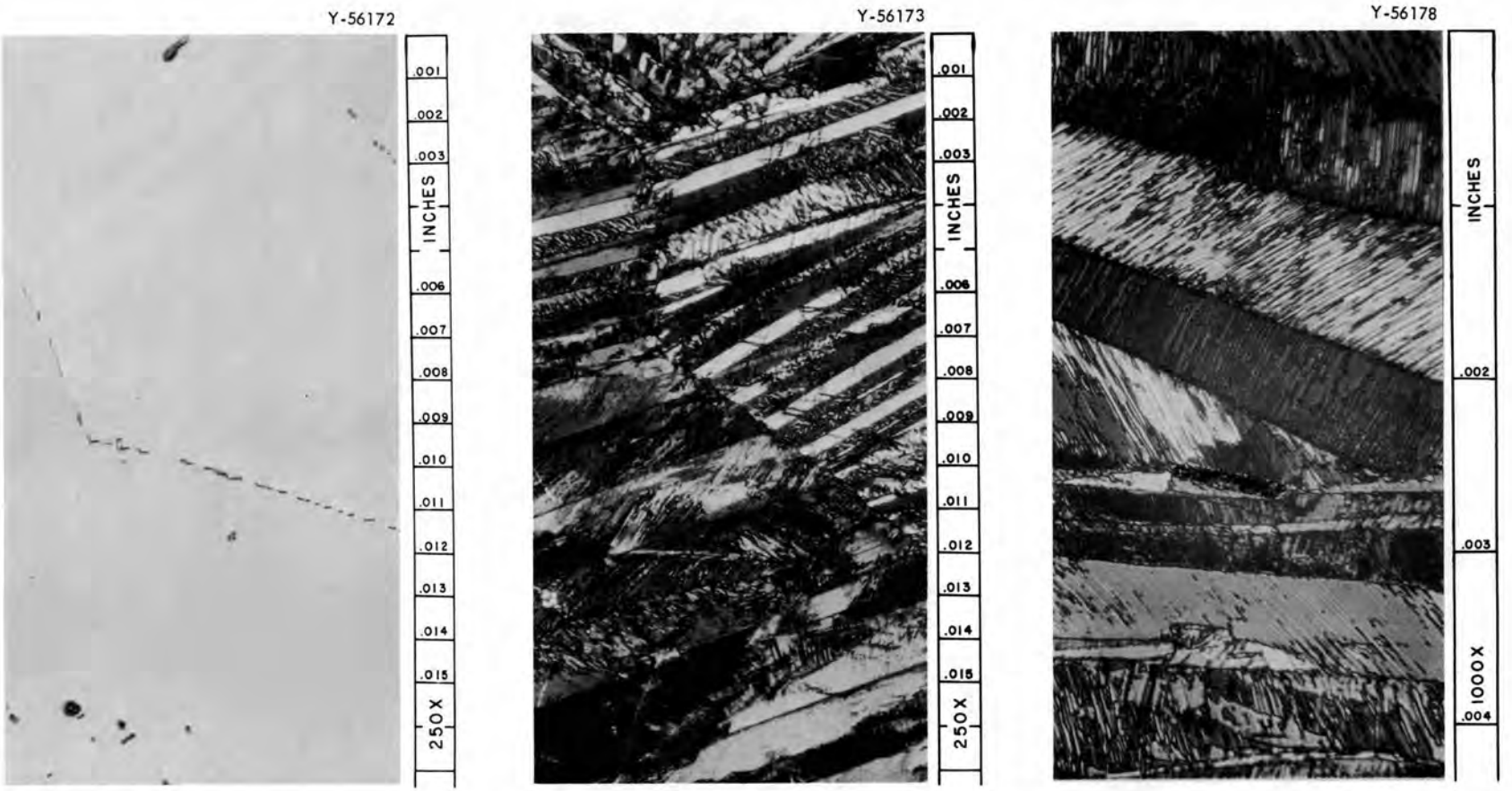


Fig. 16. As-Cast $ThC_{1.98}$ (9.28% C; Specimen 14), Showing Thorium Dicarbide with a Combined-C/Th Atom Ratio of 1.91 and a Trace of Graphite Under Bright Field Illumination (Left) and Under Polarized Light (Center and Right). The graphite shows up more clearly under bright field illumination. No thorium monocarbide was detected by X-ray diffraction analysis. Nitric acid etch.

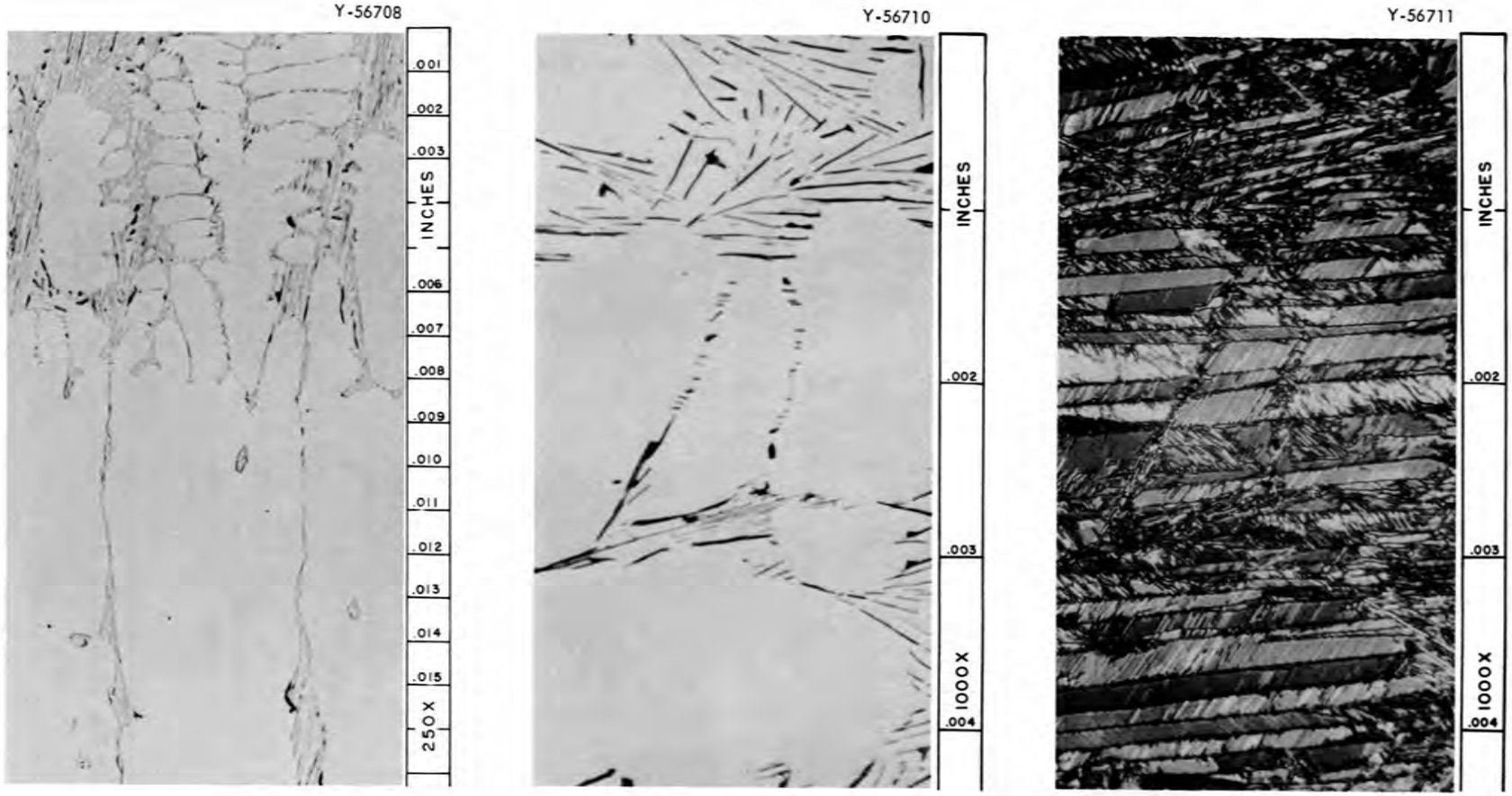


Fig. 17. As-Cast $ThC_{2.14}$ (9.98% C; Specimen 15), Showing Primary Thorium Dicarbide with a Combined-C/Th Atom Ratio of 1.95 and a Thorium Dicarbide-Graphite Eutectic Under Bright Field Illumination (Left and Center) and Under Polarized Light (Right). Nitric acid etch.

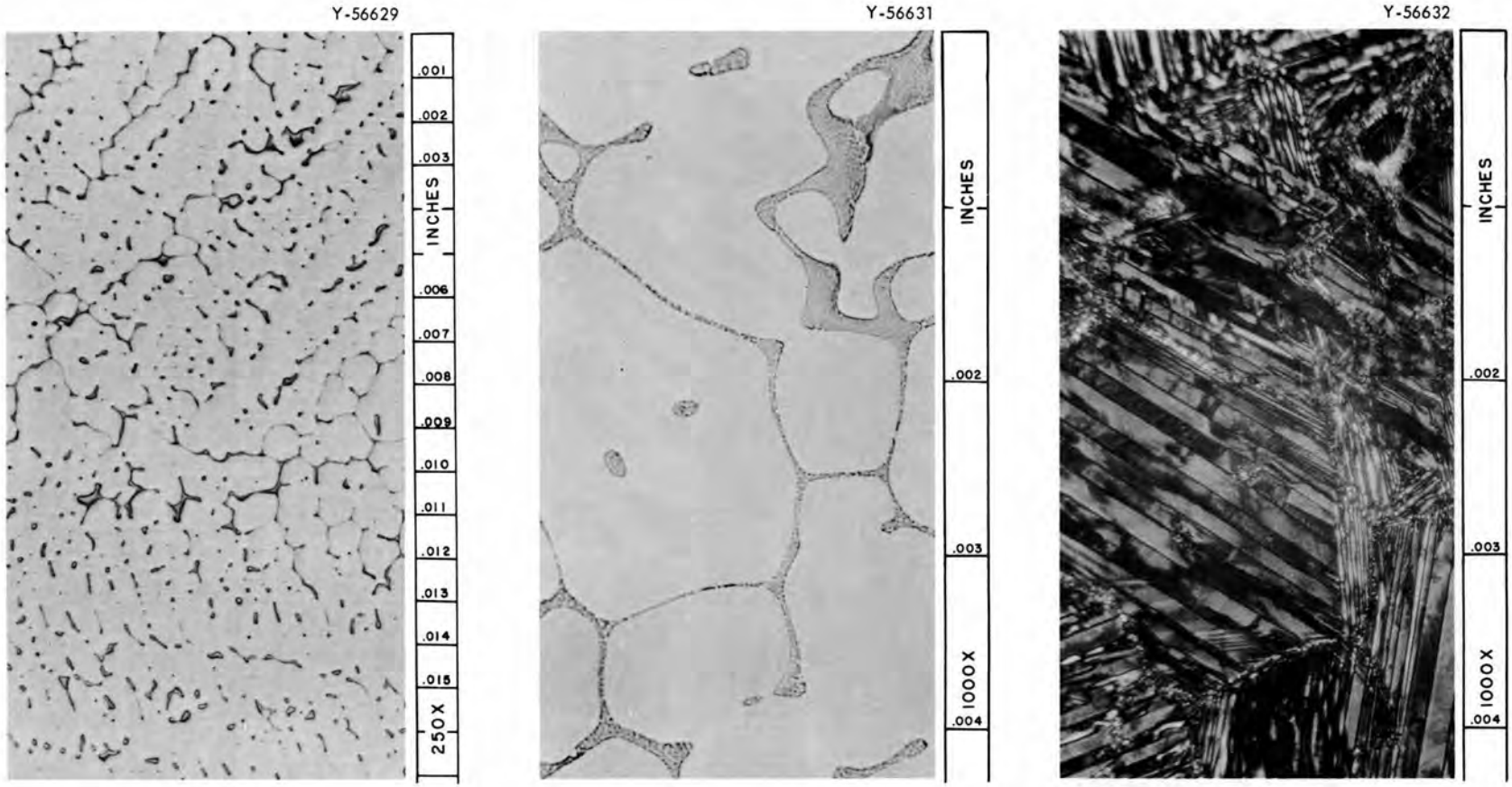


Fig. 18. As-Cast $Th_{1.00}W_{0.09}C_{2.04}$ (9.1% C, 6.1% W; Specimen 16), Showing Grains of Thorium Dicarbide, with a Lower-Melting Eutectic Structure at the Grain Boundaries. The eutectic precipitated into graphite and a tungsten-containing phase as the specimen cooled from the melt. Chemical and X-ray diffraction analyses indicated that at least half of the tungsten was present as W_2C. Left and center, bright field illumination; right, polarized light. Nitric acid etch.

5. PHASES PRESENT IN ARC-CAST THORIUM CARBIDES

Our metallographic and X-ray diffraction studies showed that the thorium monocarbide phase existed over a range of composition from about $ThC_{0.94}$ to at least as low as $ThC_{0.81}$. Specimens with C/Th atom ratios lower than 0.81 were not examined in this study; however, other investigators have reported that the monocarbide phase extends to even lower carbon concentrations.[19-24] The break in the lattice-parameter-vs-composition curve places the upper limit for the monocarbide phase at about $ThC_{0.94}$ (Fig. 19), rather than the stoichiometric 1.00. This value agrees well with results of metallographic studies, which showed that specimens with the $ThC_{0.99}$ and $ThC_{1.02}$ compositions contained 5 to 8% thorium dicarbide impurity. Thorium dicarbide was not detected by X-ray diffraction analysis (16-hr exposures) of these specimens; however, after hydrolysis, 14 to 15% of the carbon in these specimens was found to be present as C_2- to C_8-hydrocarbons (which are dicarbide products), as compared with only 5% from $ThC_{0.81}$ and 7% from $ThC_{0.92}$.[16]*

The thorium monocarbide lattice parameter, as determined in this study for as-cast $ThC_{0.99}$ and $ThC_{1.02}$ specimens, was 5.346 A, which is exactly the value reported by Kempter and Krikorian[2] and Nevitt and Rosen.[19] Other values that have been reported are: 5.344 (Henny, Jones, and Hill,[24] after annealing for 47 hr at 1600°C), 5.3438 (Huber, Holley, and Krikorian[24a] for an as-cast specimen containing 0.16 wt % oxygen), 5.342 (Chiotti and White[23]), 5.34 (Wilhelm and Chiotti[1] and Benesovsky and Rudy[25]), 5.335 (Street and Waters[22]), and 5.327 (Laube and Nowotny[26]). Most of the lower values were obtained for specimens that were prepared by sintering thorium metal and graphite powders and were more likely to contain dissolved oxygen (which lowers the lattice parameter[24]) than arc-cast specimens.

The lattice parameter of 5.340 A for as-cast $ThC_{0.81}$, as determined in this work, is considerably larger than the values reported by others for specimens of similar

*In the hydrolysis of uranium carbide mixtures, a few of the single-C units from the monocarbide reacted with other carbon units to form C_2- to C_8-hydrocarbons.[15] Therefore, one cannot conclude that $ThC_{0.81}$ contains 2% dicarbide because it yields 5% C_2- to C_8-hydrocarbons; however, one can conclude that the $ThC_{1.02}$ specimen contained more dicarbide than the $ThC_{0.81}$ specimen because it yielded more C_2- to C_8-hydrocarbons.

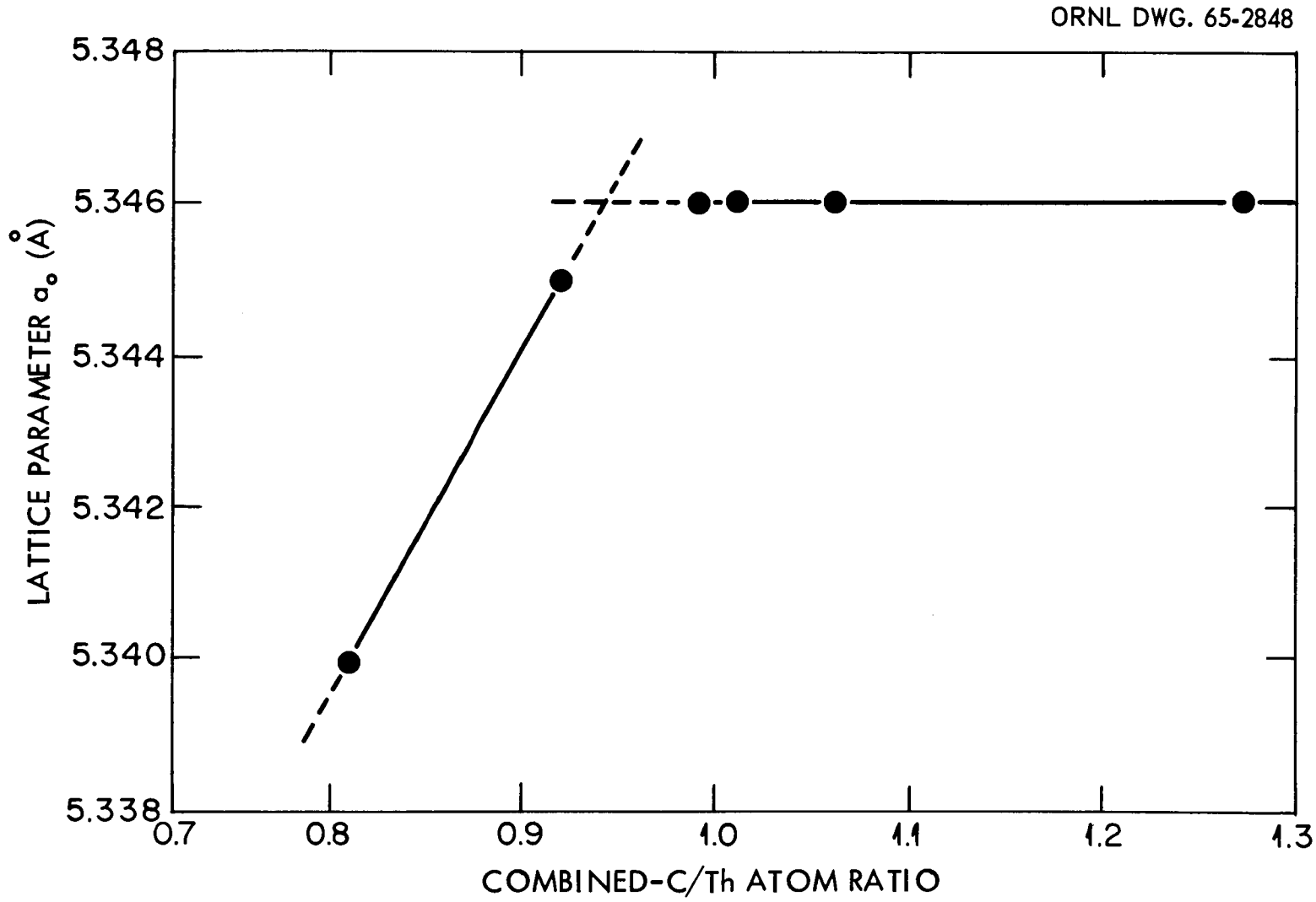


Fig. 19. Variation of the Lattice Parameter of Arc-Cast Thorium Monocarbide with Composition.

carbon composition (Fig. 20). Some of the differences may be due to dissolved oxygen in the specimens prepared by sintering; some may be due to errors in the compositions since only our data and those of Aronson and Sadofsky[21] and Huber, Holley, and Krikorian[24a] are based on actual chemical analyses of the carbide specimens for carbon and thorium (and even Aronson and Sadofsky did not analyze their specimens for oxygen). Since all of the other studies except for Huber et al.[24a] were made with annealed specimens, there is also the possibility that in arc-casting thorium monocarbide a larger lattice can be quenched than is stable at lower temperatures. Obviously, additional studies of the variation of the thorium monocarbide lattice parameter with composition, particularly the oxygen content, and heat-treatment are needed to clarify this region of the phase diagram.

The maximum combined-C/Th atom ratio obtained by arc-melting with graphite electrodes was 1.96. Material of this composition was prepared and was shown to be single phase by both metallographic and X-ray diffraction examination; this indicates that thorium dicarbide can be slightly carbon deficient. Specimens with total-C/Th atom ratios greater than 1.96 always contained free carbon, according to metallographic and chemical analyses. Scaife and Wylie[27] reported a maximum combined-C/Th atom ratio of 1.95 for specimens prepared by heating thorium oxide and sugar charcoal at 2170°C. Using Kempter and Krikorian's[10] analytical data, the composition of their thorium dicarbide specimen can be calculated to be $ThC_{1.95}$ if it is assumed that the missing 0.37 wt % in their analytical summation was due to oxygen present as ThO_2, $ThC_{1.89}O_{0.06}$ if it is assumed to be due to dissolved oxygen, or $ThC_{1.88}$ if there was an error in the thorium analysis. In some studies with thorium dicarbide, the specimens contained so much free carbon[4,28,29] that it is doubtful if the analyses were sufficiently accurate to differentiate between combined-C/Th atom ratios of 1.96 and 2.00, since the amount of combined carbon was determined by the difference between the total carbon and the free carbon.

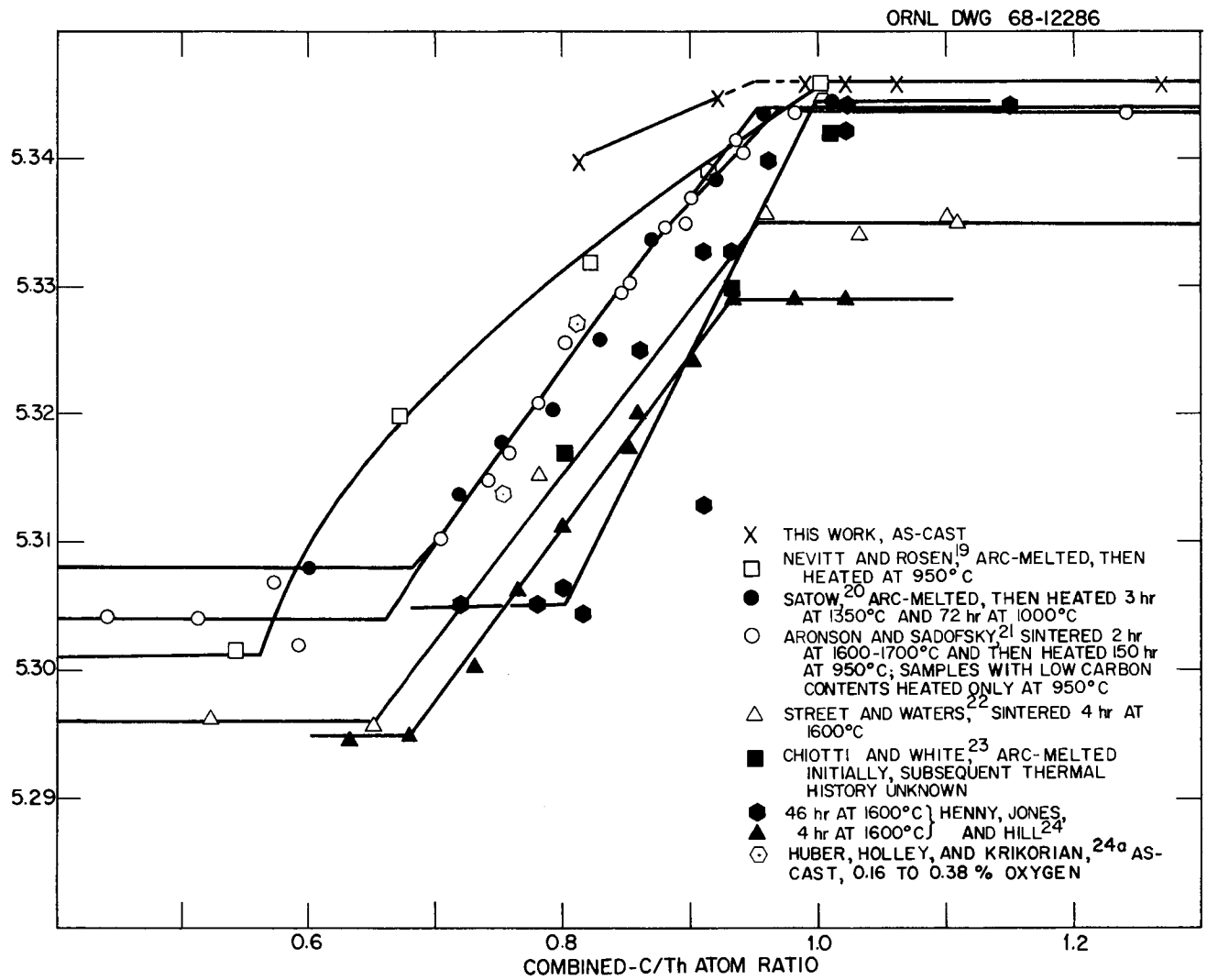


Fig. 20. Experimental Values for Lattice Parameter, at Room Temperature, of Thorium Monocarbide as a Function of Composition.

Specimens with compositions from $ThC_{1.06}$ through $ThC_{1.88}$ were shown to be two-phase mixtures of thorium monocarbide and thorium dicarbide by metallographic and X-ray diffraction analyses at room temperature. There was no detectable shift in the spacings of any of the X-ray diffraction lines in the dicarbide powder pattern as the carbon content varied. We found no evidence to support the belief of Langer et al.[4] or Satow[30] that thorium dicarbide has a wide range of composition at room temperature. The presence of finely dispersed platelets throughout the specimens indicates that, at elevated temperatures, there is complete solid solution formation between monocarbide and dicarbide across the entire range of composition from $ThC_{1.0}$ to $ThC_{1.96}$. Note that, in Fig. 11, the thorium monocarbide platelets do not cross the boundary of the dicarbide bands within the grains; this indicates that they did not precipitate from solid solution until after the transformation of the dicarbide from the face-centered-cubic structure to the body-centered-tetragonal structure had occurred. In addition, note that in Fig. 10, the specimen appears to have been heat-treated at 1600°C in a single-phase region. These observations appear to be at odds with the phase diagrams given in refs. 1, 31, and 32 which show a miscibility gap between thorium monocarbide and face-centered-cubic dicarbide. The high-temperature X-ray diffraction results of Jones and Henney[31] indicate that monocarbide was present with face-centered-cubic dicarbide before the transformation to the body-centered-tetragonal occurred. It may be that, while some thorium monocarbide precipitates before the transformation, an even greater amount of monocarbide precipitates on cooling either at or after the dicarbide transformation.

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7. APPENDIX

7.1 Analytical Procedures

X-ray Analyses. – X-ray powder patterns were determined with a Debye-Scherrer 114.59-cm-diam powder camera, using Cu K-α radiation.

Thorium. – Thorium was determined by burning 1 g (ThC) to 2 g (ThC_2) of carbide, which had been crushed to -10 +50 mesh particles, and determining the weight of ThO_2 at 950°C on a thermobalance. The weight of ThO_2 had to be measured at high temperatures since the finely divided powder, even after heating at 1250°C, gained weight upon cooling (due to surface sorption) and resulted in a significant error (~ 2%) in the thorium analysis. The $ThC_{0.8}$ specimen had to be crushed to -50 mesh particles before quantitative oxidation to ThO_2 could be achieved.

Specimen 16, which contained 6% tungsten, was treated as follows: the specimen was hydrolyzed, the resulting thorium dioxide was dissolved in 6 N HCl, the residue was removed by filtration, and the filtrate was analyzed gravimetrically for thorium by precipitation as the oxalate.

Total Carbon. – Total carbon in all samples was determined by burning 0.7 g (ThC_2) to 1 g (ThC) of carbide, which had been crushed to -10 +50 mesh particles, in pure oxygen at 1000°C for 2 hr.[33] The effluent gases were passed first through copper oxide (650°C) to ensure complete combustion to CO_2, then through an Anhydrone trap to remove the water, and finally through an Ascarite and Anhydrone trap to sorb the CO_2. Carbon was determined by weighing as CO_2. Complete combustion was not achieved with larger particles because the ThO_2 product formed a protective layer over the carbide. Since the thorium carbides ignite in oxygen at about 550°C, the combustion tube was cooled below 450°C before the sample was introduced.

Free Carbon. – Free carbon was determined after dissolving 1.5 to 3.0 g of carbide, as -10+100 mesh particles, in refluxing 6 M HCl and filtering through a Leco disposable filtering crucible (No. 528-30, Laboratory Equipment Corp., St.

Joseph, Michigan).[33] The residue was washed with acetone and ether (to dissolve any wax) and dried; then the carbon was determined as CO_2 in the Leco apparatus.

Oxygen. – A fluorination procedure was used for the oxygen analysis.[34]

Nitrogen. – In the analysis of thorium carbides for nitrogen, 200 to 250 mg of crushed carbide was dissolved in 9 M H_3PO_4--2.5 M H_2SO_4.[33] The solution was then made basic, and the resulting ammonia was steam-distilled into a receiver containing dilute sulfuric acid. The ammonia was determined spectrophotometrically with sodium phenate.[35]

Tungsten. – In the work reported here, tungsten was determined by neutron activation analysis after the carbide was dissolved in nitric acid containing a trace of hydrofluoric acid.[36] However, for future analyses of specimens containing more than 3% tungsten, we recommend the gravimetric procedure previously used for uranium-tungsten-carbide.[37] Neutron activation is still the best method for specimens having low concentrations of tungsten. Colorimetric determination gave less-reproducible results than neutron activation. This may have been caused, in part, by the difficulty in destroying the colored organic species that are formed when thorium dicarbide or its hydrolysis products are dissolved in nitric acid.

7.2 Hydrolysis Procedure

The procedure used for hydrolyzing the thorium carbides is described in detail on pp. 107-9 of ref. 17.

7.3 Gaseous Products from Hydrolysis of Specimen 5

The hydrolytic properties of most of the thorium carbides have been discussed previously.[8,9] Data for specimen 5 are given in Table 3.

Table 3. Hydrolysis Data for Specimen 5

Gaseous Products[a]	vol %	Product	% of Combined Carbon
Hydrogen	11	Methane	73
Methane	82	C_2-C_8 hydrocarbons	17
Ethane	4	Wax	2
Propane	0.4	Unaccounted for	8
Butanes	0.5		
C_5-C_8 alkanes	0.2		
Alkenes	0.8		
Alkynes	1.0		
Unidentified	0.3		

[a]Volume of gas evolved = 86 ml (STP) per gram of carbide.

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