S 65. *The Carbides of Uranium and Thorium.**

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Uranium carbides corresponding to UC (C, 4·8%) and UC_2 (C, 9·16%) are shown to exist. There is no evidence of solubility of uranium in the monocarbide. The monocarbide is stable at room temperature, and the dicarbide is stable at high temperatures but partly decomposes into monocarbide and carbon at lower temperatures. There is evidence of solubility of carbon in the dicarbide at high temperature. At high temperatures and at compositions in the neighbourhood of 7% of carbon there is a possibility either that a compound, U_2C_3, exists, which dissolves UC and UC_2, or that the last two carbides form a continuous solid solution. Although the Widmanstätten type microstructure indicates that " U_2C_3 " consists of one phase at high temperature, all attempts to retain this one-phase structure by quenching have been unsuccessful.

Metallographic and *X*-ray investigations indicate that no compounds other than those listed above occur between uranium and carbon.

Thorium carbides, ThC and ThC_2, are shown to exist. From a study of thorium–carbon alloys containing up to 14% of carbon no definite evidence is found either by microscopic observation, *X*-ray analysis, or melting-point data for the existence of other compounds. The monocarbide has a face-centred cubic sodium chloride type structure with a lattice constant $a_0 = 5{\cdot}325$ A., and the dicarbide has a pseudo-tetragonal lattice. The melting points of ThC and ThC_2 are found to be 2625° ± 25° and 2655° ± 25°, respectively. The dicarbide forms a eutectic with graphite melting at 2500° ± 35°.

(I) *Uranium Carbides.*

Perhaps the earliest attempt to make uranium carbides was that of Moissan (*Compt. rend.*, 1896, **122**, 247), who reported the preparation of a metallic, crystalline material by reaction between U_3O_8 and carbon in an electric furnace to give a compound which he supposed to be U_2C_3. Although his analyses showed a carbon content slightly higher than the theoretical value, he thought that U_2C_3 was a definite compound and also that it was the highest carbon compound possible in this system.

In 1911 Lebeau (*Compt. rend.*, **152**, 955) reported the preparation of UC_2, which he assumed to be the same material as Moissan's U_2C_3. He explained the difference in formula by supposed errors existing in the analytical method used by Moissan. Also in 1911, Ruff and Heinzelmann (*Z. anorg. Chem.*, **72**, 72) reported the preparation of a compound giving an analysis closely corresponding to the theoretical composition of UC_2. They reported the melting point to be 2425°. Polushkin (Iron Steel Inst., London, Carnegie Schol. Mem., 1920, **10**, 137), while investigating iron–uranium alloys, heated U_3O_8 mixed with petroleum, coke and steel turnings and found that uranium carbides were present in the iron. These carbides were assumed to be UC and U_2C_3. Hägg (*Z. physikal. Chem.*, 1931, **12**, 42) made *X*-ray diffraction studies of a UC_2 sample prepared by Arnfeld and gave its crystalline structure.

With the exception of Hägg, none of these investigators had any definite proof of the existence of their " compounds." In each case the composition was deduced from chemical analysis with slight additional evidence that such a compound actually existed.

EXPERIMENTAL.

Finely divided uranium metal and uranium oxides of high purity were used in this investigation, and the carbon used was in most cases high-purity powdered graphite. The uranium powder was prepared by thermal decomposition of uranium hydride.

Samples made by powder techniques were mixed and then pressed in a steel die by means of a hydraulic press. A high-frequency induction furnace was used for heating in the preparation and subsequent heat-treatment of most of the samples. The furnace heater, consisting of a graphite crucible with a tight-fitting cover and a long central chimney, was well insulated by a layer of lamp-black retained in a fused silica sleeve. Temperatures estimated to be as high as 3000° were attainable with this set-up.

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Often a special uranium carbide base was used to support the sample and to reduce the reaction with the graphite crucible. For samples in which no change in carbon content on heating was desired, beryllia crucibles were sometimes used inside the graphite heater. The beryllia was found to be satisfactory because of its unusual resistance to cracking from thermal shock and the fact that it does not react with carbon appreciably below 2000°.

Temperature measurements were made by means of an optical pyrometer. The long chimneys used on the heater crucibles insured reasonably good black-body conditions for the optical pyrometer readings.

The carbide structures could be satisfactorily etched by a short dip in aqueous 50% nitric acid solution which gave high contrast. Finer detail was brought out by a 10% oxalic acid electrolytic etch.

Monocarbide.—A sample containing C, 4·8% (composition for UC) was carefully prepared by briquetting a mixture of powdered uranium and carbon and heating it on a carbide support to 2000° in an inert atmosphere. Owing to the extremely pyrophoric nature of powdered uranium, the briquetting was also done in an inert atmosphere. However, after such mixtures were pressed the briquettes could be handled for a short time in air without serious oxidation. The microstructure of the monocarbide sample showed one phase (Fig. 1). Chemical analyses showed that practically no change in composition had taken place during the sintering process. *X*-Ray diffraction studies on this sample confirmed the existence of uranium monocarbide and showed no other phases present at this composition. Samples prepared in the same manner but with less carbon gave no evidence of a lower carbide when examined at room temperature.

The lattice spacings of the purest samples of uranium monocarbide (prepared from uranium and carbon in an atmosphere free from nitrogen and oxygen) were determined by using a symmetrical, self-focussing, back-reflection camera of 5 cm. radius and copper-*K* radiation (Rundle, Baenziger, Wilson, and McDonald, *J. Amer. Chem. Soc.*, 1948, **70**, 99). Spacings varying from 4·951 A. to 4·948 A. were obtained in various samples.

Uranium monocarbide contains four uranium atoms in face-centred positions. The probable structure is consequently either the sodium chloride or the zinc blende structure. A comparison of the intensity of the diffraction maxima (420) and (331) showed that the more probable structure is that of sodium chloride.

Uranium monoxide and mononitride have also been reported to exist (Rundle *et al.*, *loc. cit.*). Both of these compounds are said to be isomorphous with the monocarbide, with all three having nearly equal lattice spacings (UN = 4·88 A., UO = 4·91 A., UC = 4·95 A.). Conditions are therefore ideal for mutual replacement of carbon, nitrogen, and oxygen in a mono-uranium compound.

In all preparations where there was not a careful exclusion of nitrogen and oxygen the spacing of the monocarbide was lower than when prepared in an inert atmosphere. In order to confirm this point, equimolar amounts of monocarbide and mononitride were heated together at 1950° for 15 minutes. Analysis of the resulting product showed that the spacings of each compound were changed toward a common average, indicating that continued heating probably would have caused a complete conversion into one phase. Similar experiments have not yet been carried out with uranium monoxide owing to the difficulty of preparing this compound. However, there is good evidence that replacement of carbon by oxygen is possible. It is believed that the most reliable value for the lattice parameter of the monocarbide is the highest that has been obtained, namely, a = 4·951 A., giving a theoretical density of 13·63 g./c.c.

Dicarbide.—Uranium dicarbide, UC_2, is readily prepared by heating a near-stoicheiometric mixture of finely divided UO_2 and graphite in a graphite crucible to a temperature above 2400°. The product is molten and reacts only slowly with air at this high temperature. At room temperature the dicarbide (C, 9·16%) is quite hard and crystalline.

As reported in 1931 (Hägg, *loc. cit.*) and confirmed in this laboratory, uranium dicarbide is body-centred tetragonal and its structure is isomorphous with that of calcium carbide. Pure dicarbide lattice constants are a = 3·517 A. and c = 5·987 A. The *X*-ray density is 11·68 g./c.c.

The *X*-ray diffraction pattern and the microstructure (Fig. 2) show that, when uranium dicarbide is slowly cooled from high temperatures or when quenched samples are annealed, the dicarbide contains a second phase in appreciable quantities. *X*-Ray analysis indicates that this additional phase is the monocarbide. Even when a considerable excess of free carbon is present the monocarbide structure is noted. On the other hand, if the dicarbide is quenched from temperatures above 2400° no monocarbide phase is present (Fig. 3). On annealing such a quenched sample the typical striated microstructure of furnace-cooled samples is restored (Fig. 4). The possibility that UN or UO is the second phase appearing in the UC_2 matrix has been considered, but samples of UC_2 prepared at low pressures give the same microstructures as those prepared at atmospheric pressure. Consideration of chemical analyses, *X*-ray spacings, and microstructures indicate that, at some temperature below 2400°, uranium dicarbide is unstable and decomposes partly into monocarbide and carbon.

In order to determine whether or not a higher carbide than the dicarbide exists, samples containing up to 13% of carbon were prepared by heating uranium–carbon mixtures to 2800°. The microstructure of these samples, furnace-cooled, consists of precipitated carbon in a dicarbide structure (Figs. 5 and 6), indicating that molten dicarbide dissolves carbon and that this carbon is precipitated on cooling. *X*-Ray study showed no carbide higher than the dicarbide to be present. When the 13% carbon samples were dissolved and the insoluble residue examined, it was found to be graphite. A sample of uranium dicarbide saturated with carbon (C, 11·9%) and quenched from 2700° showed the characteristic UC_2 maxima in the *X*-ray diffraction pattern but with slight reductions in lattice constants. Annealing this sample restored the dicarbide lattice constants to their normal values. The solubility of carbon in the dicarbide is very small at temperatures below 1000°.

" *Sesquicarbide.*"—Samples of composition corresponding to uranium sesquicarbide (U_2C_3) were prepared by heating mixtures of the dioxide and carbon in graphite crucibles to above 2400°, and also by heating briquetted uranium–carbon mixtures on carbide supports. In order to produce the assumed U_2C_3 it was necessary to add excess of the dioxide to the melt while the reaction between carbon and the dioxide was occurring. When this procedure was not followed, the carbon pick-up from the crucible was sufficient to carry the carbon content far above that required for the sesquicarbide. If a melt of composition corresponding to U_2C_3 is allowed to cool slowly to room temperature, very large cubic crystals up to 1 cm. or more on a side can be obtained from the very crystalline mass. At 7·03% of carbon, the formula value for U_2C_3, these macrocrystals appear to be perfect cubes, but when the carbon composition is just a little higher or lower than this value, the cubes are distorted although the microstructure is practically unchanged.

The microstructure at this composition appears as two phases arranged in a striking Widmanstätten pattern (Figs. 7 and 8). When *X*-ray diffraction studies are made the phases are shown to be UC and UC_2. " Single-crystal " *X*-ray diffraction patterns showed further that the mono- and the di-carbide phase had crystallised with their axes parallel.

Because of the Widmanstätten structure appearing at this range of composition, it seems probable that this carbide consists of one solid phase at some high temperature. The data therefore suggest the existence of a solid solution of UC and UC_2 at high temperatures or possibly an unstable compound U_2C_3 in which the other two carbides are soluble at high temperatures. A series of experiments was carried out in which compositions corresponding to U_2C_3 were quenched from various temperatures in an effort to obtain a one-phase microstructure, but in each case the typical Widmanstätten pattern resulted. Even quenching from the molten state in liquid lead did not change the micro-structure. From the form of the macrocrystals, uranium sesquicarbide, if it does exist, can be assumed to be cubic.

(II) *Thorium Carbides.*

The preparation of the dicarbide of thorium in an electric-arc furnace was reported by Troost (*Compt. rend.*, 1893, **116**, 1229) and later by Moissan and Étard (*ibid.*, 1896, **122**, 573). Stackelberg (*Z. physikal. Chem.*, 1930, *B*, **9**, 437) reported the dicarbide as having a face-centred tetragonal lattice with four molecules per unit cell with a_0 = 5·85 A. and c_0 = 5·28 A. More recent *X*-ray studies at Battelle Memorial Institute (Progress Reports, Feb. 1, 1945, CT-2700; Mar. 1, 1945, CT-2778) on alloys formed in the process of determining the oxygen content of thorium by the vacuum-fusion method gave evidence of a dicarbide with a body-centred tetragonal lattice with a_0 = 4·14 A. and c_0 = 5·28 A., a monocarbide with a face-centred cubic lattice with a_0 = 5·29 A., and rather slight evidence of a carbide with a face-centred cubic structure, believed to be of the CaF_2 type, with a_0 = 5·85 A. *X*-Ray investigations by Baenziger (Ames Laboratory, June 1945, unpublished data) showed the dicarbide to have a pseudo-tetragonal structure, and he proposed an orthorhombic lattice with a_0 = 8·26 A., b_0 = 10·52 A., and c_0 = 4·22 A.

EXPERIMENTAL.

All samples studied in these investigations were prepared by powder metallurgy methods. Mixtures of thorium metal powder and graphite powder were pressed in steel dies at approximately 50,000 lb./sq. in. to give relatively dense compacts, which were then heated to the desired temperature under vacuum or a helium atmosphere. *X*-Ray analysis, m. p. data, and microscopic examination of samples prepared in this manner were used to establish the existence of the two compounds, the mono- and the di-carbide.

The thorium metal used was in the form of minus 30 mesh powder prepared from massive thorium metal by the hydride process, which consists essentially of heating the metal in a hydrogen atmosphere at approximately 600°, forming the dihydride, followed by further reaction with hydrogen at 325—200°, thus forming a rather finely divided product which is decomposed to the metal powder by reheating to 500° and finally at 700° under vacuum. Spectrographically pure graphite powder of approximately the same particle size was used in preparing the compounds and alloys studied.

The m. p.s of alloys containing up to 14% of carbon were determined by Pirani and Alterthum's method (*Z. Electrochem.*, 1923, **29**, 5), which consists of heating a pressed compact by passing an electric current through it and observing the melting temperature by means of an optical pyrometer focussed on a small hole drilled into the compact. In these experiments, mixtures of the metal and graphite powders were pressed into ¼″ × ¼″ × 4″ bars at 50,000 lb./sq. in. in a suitable steel die. A small hole, 0·039″ in diameter and 0·150″ deep, drilled with a long-tapered point drill in the centre of the bars normal to the long axis, was found to give suitable black-body conditions. These compacts were pre-sintered in a molybdenum tube furnace at or above 1400° for approximately 10 minutes to render them sufficiently conductive at 8 volts or less to be heated electrically. The sintered bars were then mounted between water-cooled copper electrodes and heated under vacuum or a helium atmosphere. An 8 KVA step-down transformer operating on a 230-volt single-phase input to give, 2, 4, or 8 volts at 4,000, 2,000, or 1,000 amp., respectively, was used as a high-current source. The output could be varied continuously from zero to the maximum rated value by means of a variable autotransformer in the input circuit.

A disappearing-filament type optical pyrometer was used in taking temperature readings. The pyrometer was calibrated by observing the m. p.s of pressed molybdenum and nickel bars by the above procedure. Two bars of molybdenum were observed to melt at 2590° and 2580°. The readings were taken through a Pyrex-glass window and were then corrected for absorption by the glass window using the relation, $1/T - 1/T_a = -0{\cdot}0000046$, developed by Foote, Fairchild, and Harrison (" Pyrometric Practice," Nat. Bur. Standards, Tech. Paper 170, 1921, p. 117), where T is the true absolute temperature and T_a is the apparent or observed absolute temperature. The corrected temperatures are therefore 2628° and 2618°, respectively, which are in good agreement with the literature value of 2620° ± 10° for molybdenum (Worthing, *Physical Rev.*, 1925, **25**, 846). The m. p. of nickel determined in the same manner was found to be 1448°, which is in fair agreement with the accepted value of 1452°.

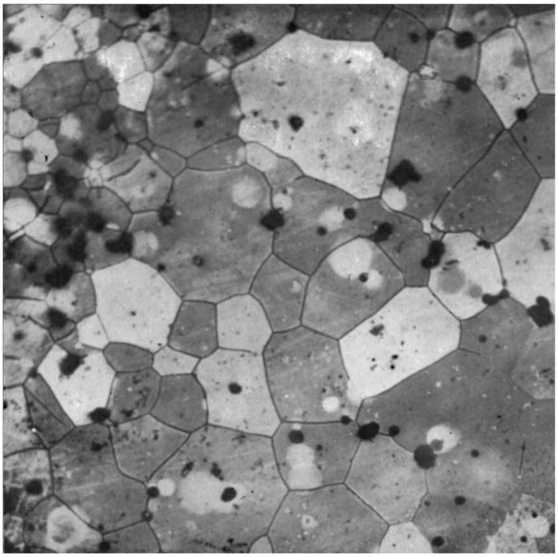

FIG. 1.

(× 250) C, 4·8%. *Uranium monocarbide, etched by dilute nitric acid* (1 : 1).

FIG. 2.

(× 500) C, 9·16% (*approx.*). *Uranium dicarbide, furnace-cooled. Etched by dilute nitric acid* (1 : 1).

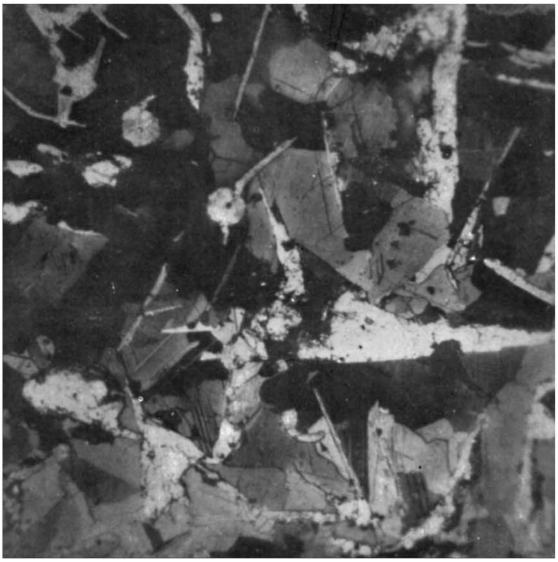

FIG. 3.

(× 500) C, 10·66%. *Carbide sample oil quenched from* 2700°. *No laminations due to decomposed* UC_2 *are visible in this sample even at* × 1000. *Etched by dilute nitric acid* (1 : 1).

FIG. 4.

(× 250) C, 10·66%. *Quenched sample shown in Fig.* 3. *Annealed at* 2200–2300° *for* 20 *mins.* 10% *Oxalic acid electrolytic etch.*

FIG. 5.

(×500) C, 11·0%. *Decomposed* UC_2 *and graphite; white areas are graphite inclusions; sample originally heated to* 2700°. 10% *Oxalic acid electrolytic etch.*

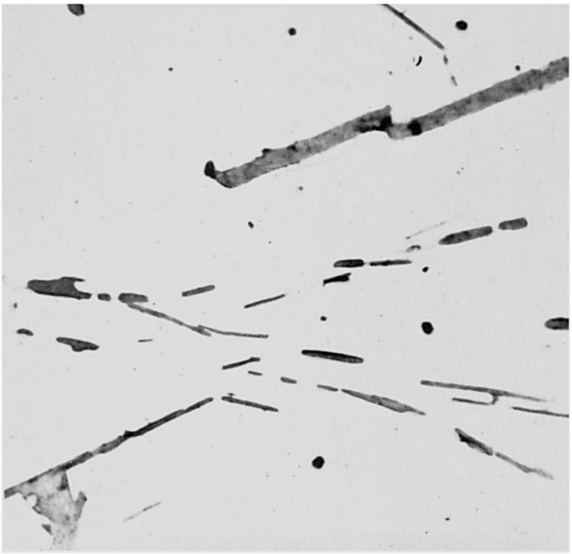

FIG. 6.

(×250) C, 9·5%. *Decomposed* UC_2 *plus carbon; dark inclusions are free graphite. Note the regularity of the precipitated graphite. Sample originally heated to* 2500° *and furnace-cooled. Unetched.*

FIG. 7.

(×100) C, 7% (*approx.*). *Sample showing Widmanstätten structure; at* 7·03% *of carbon macrocrystals are perfect cubes.* 10% *Oxalic acid electrolytic etch.*

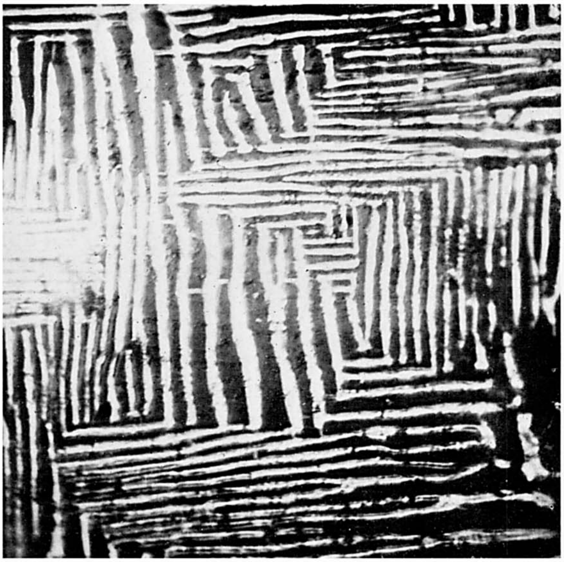

FIG. 8.

(×500) C, 6·5%. *Decomposed solid solution. Bands are* UC *and* UC_2. *Etched by dilute nitric acid* (1:1).

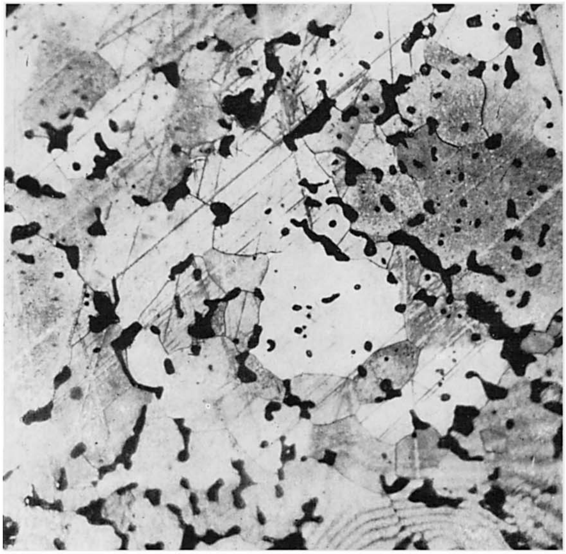

FIG. 9.

(×250). *Sintered compact,* C, 4·1%. *Heated at* 2100° *for* 10 *minutes.*

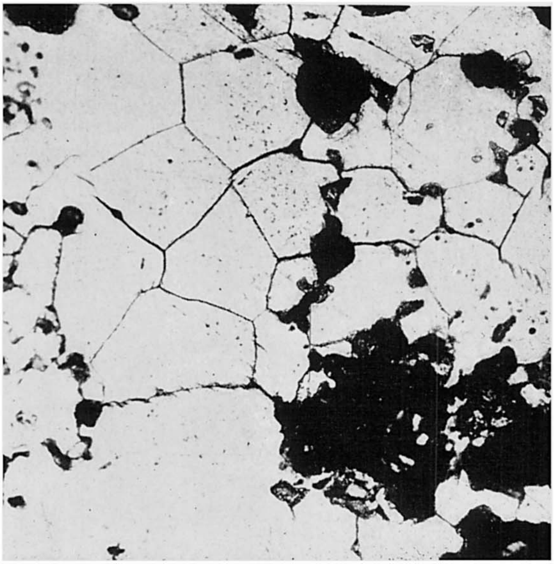

FIG. 10.

(×250). *Sintered compact,* C, 4·92%. (ThC) *heated at* 2400° *for* 10 *minutes.*

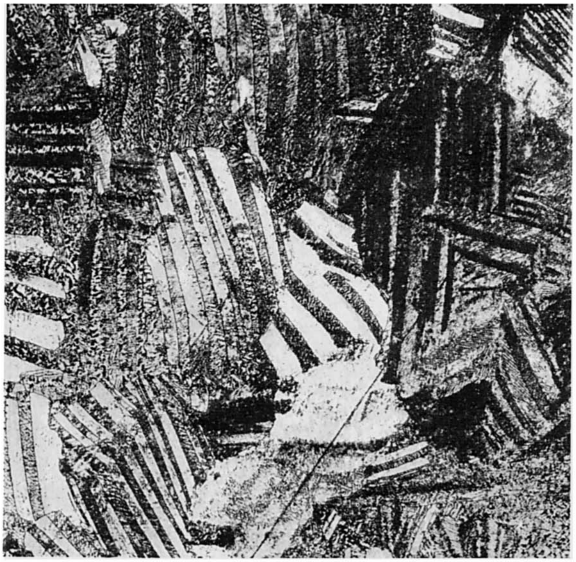

FIG. 11.

(×100). *Thorium dicarbide.*

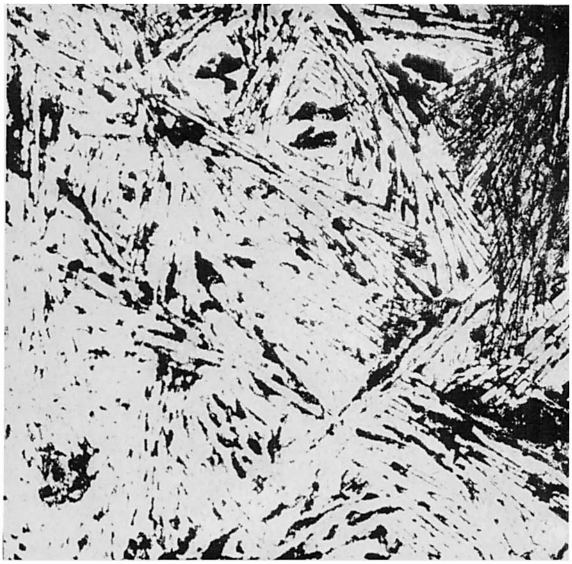

FIG. 12.

(×100). *Fused sample* ThC_2–C *eutectic, m.p.* 2500°±35°.

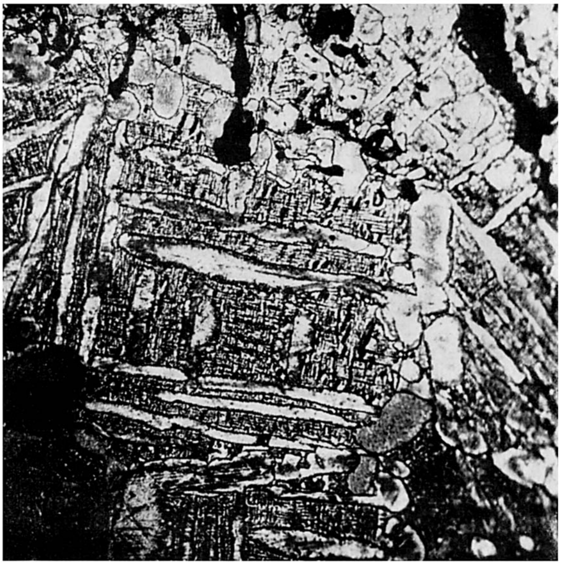

FIG. 13.

(×250). *Sintered compact,* C, 7·2%, *heated at* 2400° *for* 21 *minutes.*

FIG. 14.

(×250). *Sintered compact,* C, 8·0%, *quenched in helium from* 2655°.

Samples were also prepared by heating pressed compacts in a graphite crucible under vacuum in a high-frequency induction furnace. The graphite crucible was well insulated with finely divided graphite, and a slow cooling rate was attained. This was desirable in experiments in which the equilibrium state of samples at room temperature was studied. With this furnace the temperature dropped from 2100° to 1400° in approximately ½ hour, from 1400° to 1000° in approximately 1 hour, and then to near room temperature in about 10 hours.

All alloys containing more than 4·0% of carbon decompose rapidly on exposure to atmospheric moisture and cannot be prepared for microscopic examination by the usual polishing procedure. Well-sintered ¼″ × ¼″ bars are completely disintegrated on 8 hours' exposure to the atmosphere. These alloys are further characterised by extreme brittleness and friability. Furthermore, sintered alloys of the above composition range are very porous and this adds to the difficulty of obtaining a good polished microstructure.

The best results in polishing these samples were obtained by using fine-grit emery paper impregnated with paraffin wax. Polishing on a cloth wheel using a carborundum suspension in a carbon tetrachloride–wax solution proved fairly satisfactory.

Alloys containing less than 3·5% of carbon could be wet-polished by the usual procedure.

Samples for *X*-ray powder-diagram studies were prepared in a dry box and sealed in small glass capillaries.

Monocarbide.—A m. p. maximum of 2625° ± 25° was obtained at 4·92% of carbon, the composition of the monocarbide, indicating compound formation. This was confirmed by *X*-ray analysis and by microscopic observations. The structure of the monocarbide was observed to be face-centred cubic of the sodium chloride type with $a_0 = 5{\cdot}325$ A.

The solubility of thorium in the monocarbide is appreciable at room temperature. The lattice constant varies from 5·28 A. at approximately 3·9% of carbon to 5·325 A. at 4·92%. At elevated temperatures the solid solubility range increases considerably and has an apparent limit of about 2% of carbon at 1950°. At room temperature all alloys containing approximately 3·9% of carbon to near 0·2% are two-phase alloys, the two phases corresponding to that of the monocarbide and the metal. In this range of compositions, samples quenched from near their m. p.s also give no evidence for the formation of any compound with a carbon content less than that of the monocarbide.

The microstructures of samples containing 4·1% and 4·92% of carbon are shown in Figs. 9 and 10, respectively. The black areas shown are principally voids.

Dicarbide.—Another m. p. maximum of 2655° ± 25° was obtained at 9·38% of carbon, corresponding to the composition of the compound ThC_2. *X*-Ray analysis of samples of this composition gave a diffraction pattern corresponding to a pseudo-tetragonal lattice, as had been observed by Baenziger. Further work on the structure of this compound is being carried out by Mr. E. Hunt of this laboratory.

A characteristic microstructure of the dicarbide is shown in Fig. 11. Since *X*-ray analysis shows only one phase present, the large number of bands and lines are believed to be due to twinning.

The possibility of a transformation at some elevated temperature was also considered; however, samples of dicarbide quenched in helium from the melting temperature gave the same pseudo-tetragonal structure and the same microstructure as samples slowly cooled to room temperature. A sample prepared by heating thorium metal to approximately 2700° in a graphite crucible and then quenched from the molten state in oil also gave an *X*-ray diffraction pattern corresponding to a pseudo-tetragonal lattice. A slight change in lattice spacing was observed and this is believed to be due to the solubility of a small amount of graphite in the dicarbide. A few weak lines corresponding to maxima for free graphite were also observed but no evidence for any other phase. The dicarbide forms a eutectic with graphite melting at 2500° ± 35°. This eutectic has been established by m. p. data and from a study of the microstructures of alloys containing more than 9·38% of carbon. A pressed compact corresponding to the composition of ThC_2 heated in a graphite crucible melted at between 2500° and 2535°. By use of the method of Pirani and Alterthum, the m. p. of a sample containing 14·1% of carbon was determined to be 2500°, and that of a sample containing 11·1% of carbon to be 2545°. Evidently the m. p. of this eutectic was also observed to be approximately 2500° by Prescott and Hincke (*J. Amer. Chem. Soc.*, 1927, **49**, 2744), although it was mistaken by them as the m. p. of the dicarbide. A photomicrograph of the eutectic is shown in Fig. 12.

In view of the above evidence it seems reasonable to conclude that no compounds of a higher carbon content than that of the dicarbide exist.

Thorium does not form a sesquicarbide. Samples corresponding approximately to the composition of Th_2C_3, sintered at 2400° and slowly cooled to room temperature, were found to be two-phase alloys consisting of mono- and di-carbide. The lattice spacings of these two carbide phases were approximately the same as those for the pure compounds, showing little if any mutual solubility at room temperature. However, all samples of composition intermediate to that of the monocarbide and dicarbide when rapidly cooled in helium from their m. p.s gave microstructures indicating the formation of a complete series of solid solutions at elevated temperatures. Fig. 13 shows the microstructure of a sample containing 7·2% of carbon slowly cooled to room temperature from 2400°, and Fig. 14 the structure of a sample containing 8·0% of carbon rapidly cooled in helium from its m. p. As the carbon content is increased beyond that of the monocarbide, the m. p.s decrease slightly and then gradually increase to that of the dicarbide.

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