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Institut für Material- und Festkörperforschung
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# Metallography of Uranium Carbides and Uranium-Plutonium Mixed Carbides

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## KURZFASSUNG

Dieser Bericht gibt einen Überblick über den Literaturstand der Metallographie von Uran-Karbiden und Uran-Plutonium-Mischkarbiden. Die in dieser Arbeit beschriebenen eigenen Arbeiten befassen sich vorwiegend mit dem Problem der Identifizierung der verschiedenen Phasen in diesen Karbiden. Zusätzlich wird eine Arbeitsanleitung gegeben, nach der man bei der metallographischen Präparation von karbidischen Kernbrennstoffen vorgehen sollte.

## ABSTRACT

### Metallography of Uranium Carbides and Uranium-Plutonium-Mixed Carbides

This report gives a survey on the status of the literature on the metallography of uranium-carbides and uranium-plutonium-carbides. Our own work, which is described in this paper deals on the problem of phase identification in different carbide fuels. In addition some hints for the metallographic preparation of carbide fuel are given.

Content:

## 1. Introduction

Metallographic examination forms an important part in the characterisation of fuel materials along with X-Ray diffraction, electron microprobe analysis and chemical analysis. A thorough characterisation is a prerequisite for any fuel irradiation work. After the phases have been identified, the evaluation of compatibility of the fuel with the probable cladding material can be made with the help of metallography. Metallography is often a very accurate tool in determining whether a particular batch of material is acceptable for test-irradiation and can thus be used as an effective means of quality control, once the detailed structural specification of the fuel is available.

The information normally available from a metallographic observation of a pellet includes the degree of homogeneity, the porosity attributes of size, distribution and type, the identification of phases , their volume and distribution, apart from revealation of macro-defects like capping and laminations in the pellet.

Uranium carbides and uranium-plutonium mixed carbides have attracted the attention of metallographers for quite some time. Many workers have tried to develop special metallographic techniques which can positively identify the different phases in the (U,Pu)C system. The present work was carried out to study metallographically a series of specimens both of uranium carbides and uranium-plutonium mixed carbides, prepared through the sintering route.

## 2. Background Information

A systematic collection of photo-micrographs of different arc-cast and heat treated uranium carbide specimens with compositions ranging from $UC_{0.4}$ to $UC_{2.4}$ (2 to 11 wt % carbon) has been presented by Sears et al. [1]. This serves as a good reference album at standard magnifications of 250 x and 1000 x. The phases were identified by X-ray diffraction. But in these micrographs in specimens that are predominantly dicarbide, uranium mono-carbide phase can not be differentiated from sesqui-carbide and graphite platelets.

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An interesting observation by Takahashi et al. [2] was the variation in the degree of resistance to chemical etchants offered by the different phases in the U-C-system as revealed by electron microscopic observation of the surfaces. Optical microscopy revealed that the etching treatment stained the UC areas more rapidly than it did the $U_2C_3$ or $UC_2$ areas, and that $U_2C_3$ darkened faster than did $UC_2$. On the other hand, electron microscopy clearly indicated by a significant difference between the surface levels that $UC_2$ was chemically dissolved to a greater extent than was UC or $U_2C_3$. No distinct difference was observed between the surface levels of UC and $U_2C_3$ areas. The explanation offered by the authors is, that when immersed in the etchant, the UC possibly develops a protective film of low reflectivity which retards the etching reaction and thus shows the rate of dissolution.

For earlier investigators in the field of uranium-plutonium mixed carbides, the first problem was one of identifying the phases by purely metallographic means. This meant that specific etchants were to be developed for preferentially etching different phases. The dicarbide has a specific mode of appearance in a mixed carbide specimen and they are distinguished by a characteristic "Widmannstätten" pattern produced by the needles. In the hypo-stoichiometric specimens, the free metal phase appears in the grain boundaries. The sesqui carbide phase in hyper-stoichiometric specimens appears also in the same areas and have the same general appearance as the metallic phase. The microstructure of sintered mixed carbide pellets is further complicated by the presence of dioxide particles.

The first attempt to distinguish between the free metal and the sesquicarbide phase was by Chamberlaine and Paige [3]. They suggested a 2 minute immersion of the specimens in a solution containing 10 Vol.-% bromine in industrial methylated spirit after they have been electro-polished in a solution of lactic acid, sulpheric acid and acetic acid. The bromine attacked the free metal phases but left MC, $M_2C_3$ and $MC_2$ phases unaffected. The above treatment holds for UC specimens also. The authors observed that prolonged immersion of some hyper-stoichiometric (U,Pu) carbides in the bromine solution produced a deterioration of the surface after about five minutes.

Another procedure for differentiating between hypo and hyper-stoichiometric carbides in a manner similar to the above technique has been reported by French et al. [4]. It consists of swabbing the specimen with a solution of $HF:HNO_3:H_2O$ (1:39:60). The etchant attacks only the metal rich areas turning them black but does not attack $(U,Pu)_2C_3$ which remains light coloured. Etching times of only 10 seconds are required as opposed to the 2 - 10 minutes necessary for the bromine-methanol etch.

An interesting feature observed by the same authors in the metallography of hypo-stoichiometric material was gross pull-out at the pellet periphery implying a loss of intergranular metal phase by volatilisation during sintering. This would leave the grains in the region loosely held, resulting in pull-out during the grinding operation.

A metallographic technique that distinguishes between the metallic, dicarbide and sesqui-carbide phases and precipitates of plutonium silicide in sintered (U,Pu) carbides was suggested by Bender [5]. The prepared specimens were first etched electrolytically in (1:1:1) lactic acid, nitric acid, acetic acid (2.5 VD.C., 9 sec., touch probe). Diamond point micro-hardness testing of the precipitates and the surrounding matrix grains proved valid in detecting the metallic phases, i.e. the metallic phase had lower hardness than the matrix. Precipitates with higher hardness numbers than the matrix were found to be sesqui carbides, plutonium silicides or agglomerates of the metallic phase and plutonium silicides, on analysis. A preferential etch for plutonium silicide, a solution of $HF/HNO_3/$ Methanol (1:1:3) swab applied after the usual electrolytic etch colours the Pu-Si precipitate green, red or orange, removes all colouration from the matrix grains and leaves the metallic or sesqui-carbide precipitates white.

Bender [6] observes that the time for chemical etching with a solution of acetic acid, nitric acid and water (1:1:1) varied with the sample composition. Prolonged chemical etching for stoichiometric specimens never defined grain boundaries suitably for photo-micrography. The chromic acid, acetic acid electrolyte etched all compositions but the micrographs exhibited lack of contrast. According to him, lactic acid, nitric acid, acetic acid electrolyte at a potential of 2.5 V D.C. for 10 seconds (touch probe) etches all $(U,Pu)C_x$ specimens evenly and gives good contrast in optical micrography.

# 3. Metallographic Preparation of Specimens

## 3.1 Sectioning

The fuel pellets were sectioned by a diamond cut-off wheel with a silicone oil lubricant. For arc-melted buttons, it is easier to break a piece by hammering rather than trying to cut it as they are very brittle and chips fall off during cutting. A slow speed of cutting is prefered. If possible both longitudinal and cross-sections should be taken.

## 3.2 Mounting

For the present work specimens were mounted in transparent lucite by hot mounting. Consistently good results were obtained with this technique. For some very porous specimens, a coating of araldite was applied over the sample surface after mounting, before grinding and this was found to improve the quality of the surface preparation. The specimens were left overnight for curing after the application of araldite.

## 3.3 Grinding and Polishing

The specimens were ground on adhesive-backed silicon-carbide abrasive paper discs over a wheel. Normally a paper of 400 mesh and 600 mesh was used depending on the surface condition of the pellet. The lubricant chosen was a water-free, low viscosity oil. The time for grinding was normally 3 to 5 minutes in each stage. For intermittant cleaning between the different stages of grinding, ultra sonic cleaning was used with carbon-tetra-chloride as the cleaing agent. The specimens were dried with tissue papers and transfered to the polishing box.

Polishing was carried out on wheels with automatic specimen holders. Diamond paste abrasive (Elektroschmelzwerk Kempten GmbH., München) was used in 6 micron and 1 micron particle size ranges for the rough and final polishing respectively. A nap-less cloth (Struers) was used for the rough polishing and a short napped cloth for the final polishing. The paste was smeared over the wheel after saturating the cloth with the lubricant.

The lubricant used for this stage was a solution of isopropyl alcohol and glycerin (10:1). During the course of polishing a slow drip feed of the lubricant was maintained. The polishing time in each stage was normally 10 to 15 minutes.

### 3.4 Etching

For the present work, the most-widely accepted chemical etchant of a solution of acetic acid, nitric acid and water (1:1:1) at room temperature was adopted for most of the specimens. Special etchants with application notes have been mentioned at the end of this report (Table 1).

## 4. Observations

Mainly three types of uranium carbide specimens and two types of mixed uranium-plutonium carbides were studied during the course of this work.

The uranium carbides were:

- i) pre-dominantly mono-carbide,
- ii) pre-dominantly di-carbide,
- iii) pre-dominantly sesqui-carbide.

The mixed carbide specimens were found to be pre-dominantly mono-carbide with some sesqui-carbide and a little dicarbide. Excepting the arc-melted uranium mono-carbide specimens, all the others were sintered pellets prepared by the oxide-reduction route. The atmosphere in the metallography glove-box train was air and the specimens showed tendency for oxidation in varying degrees. The arc-cast mono-carbide (UC) specimen was the worst affected. It permitted a relatively short time for examination before it would bloat up and make any further observation impossible. The dicarbide and the sesqui-carbide specimens developed thin films on prolonged stay.

Examination at lower magnifications gave a good idea about the homogeneity of the specimens but it was often necessary to observe the structure at higher magnifications to locate small areas of second phase. When viewed under the microscope, the uranium mono-carbide and dicarbide had varying colour-tones where as the sesqui-carbide specimens appeard in general blue or purple.

Micro-hardness measurements were attempted on all the specimens but with little success as the **surfaces** were very brittle and did not permit a clear indentation in most of the cases. The specimens were analysed by X-Ray diffraction to identify the phases present in them.

The uranium mono-carbide specimen had an inhomogeneous structure. It showed big isolated grains of angular shape with some "Widmanstätten" precipitates of dicarbide in a few grains (Fig. 1). No difference was observed in the appearance of the mono-carbide specimen in bright field illumination and under polarised light. The matrix grains were in general dark with varying colour tones and the dicarbide etched bright. At higher magnifications (Fig.2) the "Widmanstätten" pattern of the needles was clearly visible. Attempts were made to quantitatively estimate the volume of the second phase but it was not successful as some of the mono-carbide grains had a lustre almost comparable to that of the second phase. The matrix grains showed a micro-hardness of 763 kp/mm$^2$ with a test load of 10 ponds.

The dicarbide specimens had a very fine needle-like precipitate inside the grains (Fig. 3). The needles responded to polarised light (Fig. 4) and it was possible to have a quantitative estimate of the needle phase volume which was about 12 %. X-Ray studies indicated the **presence** of both mono-carbide and sesqui-carbide phases in a dicarbide matrix. It may be possible that the neddles are composed of both of these phases and it was not possible to identify them separately. The presence of pores complicated the structure further as the etchants had a tendency to come out from the pores and stain parts of the surface even when the etching had been stopped. Twins were observed in large number inside the grains. The matrix showed a micro-hardness of 676 kp/mm$^2$ with a test load of 10 ponds.

The sesqui-carbide specimens were extremely porous. These contained some mono-carbide phase which was quite inhomogeneously distributed, appearing only in one segment of the pellet. Fine needles were observed inside the mono-carbide grains and probably these are dicarbide, as the X-Ray studies indicate the presence of a very small amount of dicarbide (Fig. 5). The grain stucture of the sesqui-carbide phase was faintly visible and no improvement was observed even by the application of polarised light. The microhardness of the matrix was found to be 1250 kp/mm$^2$ with a test load of 10 ponds.

In both of the mixed carbide specimens the matrix was mono-carbide (U,Pu)C which etched dark. The predominant second phase was sesqui-carbide $(U,Pu)_2C_3$ which etched bright. With the normal acetic acid, nitric acid, water chemical etch, only a few dicarbide needles were observed (Fig. 6) but needles were observed in larger number when the specimens where etched in $HF/HNO_3/H_2O$. The needles displayed a "Widmanstätten" pattern which was distinct at higher magnification (Fig. 7, 8 ). An attempt to quantitatively estimate the volume of the sesqui-carbide phase yielded a value of 11 % Vol. In this specimen the sesqui-carbide phase decorated the grain-boundaries and was also present inside the grains in the form of cuboids.

In the other type of mixed carbide (Fig. 9, 1C) specimen the sesqui-carbide phase appeared mostly around the pores and sometimes in grain boundaries. There appeared to be some non-homogeneity in the plutonium distribution in the specimen as evidenced from the variation of colour tone of the oxide etchant film from place to place. A needle phase was observed inside the matrix grains. The needles did not respond to polarised light. Some of the needles appeared as fine black lines and the other were thicker platelets. The micro-hardness value obtained on the sesqui-carbide phase was similar in both types of mixed carbide specimens and was about 1495 kp/mm$^2$ with a test load of 10 ponds. The hardness of the **matrix** grains in one sample was found to be 638 kp/mm$^2$. But in the other type of specimen, the matrix hardness varied from 540 kp/mm$^2$ to 813 kp/mm$^2$ in the regions which etched blue and light brown respectively.

## 5. Discussion

The sequence of specimen preparation reported here works quite satisfactorily. It has been felt that for the more porous specimens, vacuum impregnation with a cold-setting resin would have produced better results. Inert atmosphere inside the preparation boxes would certainly be advantageous. It seems to be difficult to distinguish between mono-carbide and sesqui-carbide phases in a dicarbide matrix in the U-C-system, by metallographic means. Quantitative estimation of the different phases is often difficult because of the complex texture of sintered specimens complicated further by the presence of pores and the resulting etch stains around them. The mixed carbide specimens displayed two types of needle phases which has been earlier observed by French et al. [4], who believed the fine needles to be dicarbide and the thicker platelets to be any of the following:

- Formation of $(U,Pu)_2C_3$ from the reaction between existing $(U,Pu)C_2$ needles and the (U,Pu)C matrix, thus retaining this type of crystallographically oriented structure,
  i.e. $(U,Pu)C + (U,Pu)C_2 \rightarrow (U,Pu)_2C_3$.

- Co-precipitation of $(U,Pu)C_2$ and $(U,Pu)O_2$. The reaction proceeds by dissolution of oxygen followed by simultaneous precipitation of $(U,Pu)C_2$ and $(U,Pu)O_2$.

- "Ghost" areas of (U,Pu)C and graphite resulting from the decomposition of $(U,Pu)C_2$.

Determination of micro hardness serves as a means of identification of the phases only when the sample is not brittle and allows clear indentation on the different phases present. The thickness of the oxide film formed after etching is often a handicap towards the exact measurement of the indentation diagonal.

## Acknowledgement

The authors are grateful to Mr. Kaiser for his valuable technical assistance.

References:

[1] Mildred Bradley Sears, Robert J. Gray, Leslie M. Ferris, B.C. Leslie: Correlation of composition and heat-treatment with the microstructures of uranium carbides, ORNL-3515 (1968)

[2] S. Takahashi, B. Ishii, K. Yamamoto, H. Uchikoshi, J. Akimoto: Microstructures of U-C alloys in compounds of interest in nuclear reactor technology, Vol. X of Nuclear Metallurgy ed. by J.T. Waber, P. Chiotti and W.N. Miner, IMD Special Rep. No. 13. The metallurgical Society of the AIME, 1964, p. 621 - 640.

[3] H.E. Chamberlain and E.L. Paige:
A metallographic technique for distinguishing between metal and sesqui-carbide phases in the U-C and (U,Pu)C system, AERE-R 4334.

[4] P.M. French, M.H. Hodge, W.R. Jacobi, P.D. Shalek:
The role of metallography in the characterisation of modified and unmodified (U,Pu)C potential fast reactor fuels,
Conf. 690 920, Proc. of the 2-nd Annual Techn. Meeting of the Int. Metallographic Society 1969

[5] J.H. Bender:
Qualitative metallography of uranium-plutonium mixed carbide fuels, Proc. of the 22-nd Metallography Group Meeting 1968, Conf. 680 614

[6] J.H. Bender:
Metallography of hypo, hyper and stoichiometric sintered (U,Pu)C, Proc. of the 21st Metallography Group Meeting 1967, Conf. 670 533

Table 1: Some etchants for uranium carbide and uranium-plutonium mixed carbides

| Etch | Application | Used for | Response |
|---|---|---|---|
| (1) Nitric acid/ Acetic acid/Water ( 1:1:1 ) | Swab 5-30 sec. | U-C (U,Pu)C | Phase contrast, grain boundaries |
| (2) Nitric acid/ Hydrochloric acid ( 3: 1 ) | Swab | U-C | Similar to No. 1 |
| (3) 85 % Orthophosphoric acid | a) Swab | (U,Pu)C | Emphasizes impurity phases like $(U,Pu)O_2$ or $(U,Pu)NC_2$ |
| | b) Electrolytic etch 5 V, 15 sec. | $Cr_{23}C_6$ modified (U,Pu)C | Grain boundaries and second phase |
| (4) Hydrofluoric acid/ Nitric acid/Water ( 1:39:60 ) | a) Swab | (U,Pu)C | Emphasizes needle phase |
| | b) Swab after electrolytic etch in (5) | (U,Pu)C | Attacks free metal and distinguishes between hypo and hyper stoichiometric specimens |
| (5) Lactic acid/Sulphuric acid/Acetic acid | Electrolytic<br>a) 7 sec. at 7 V<br>b) 10 sec. at 10 V | U-C<br>(U,Pu)C | Grain boundaries |
| (6) Lactic acid/Nitric acid/Acetic acid | Electrolytic<br>2.5 V<br>9-10 sec.<br>(touch probe) | (U,Pu)C | Grain boundaries and precipitates |
| (7) Hydrofluoric acid/ Nitric acid/Methanol | Swab after etch with (5) | (U,Pu)C | Designates Pu-Si grains as green, orange or red. |
| (8) Cathodic vacuum etching | 1.5 kV<br>150 micron Argon<br>4 min.cycle of 30 sec. power on and 30 sec.power off. | All types of (U,Pu)C | Grain boundaries and precipitates |

Table 2: Observed micro-hardness values (with test load of 10 ponds)

| U - C System | $kp/mm^2$ |
|---|---|
| a) Mono-carbide matrix | 763 |
| b) Di-carbide matrix | 676 |
| c) Sesqui-carbide matrix | 1250 |
| **(U,Pu)C System** | $kp/mm^2$ |
| Specimen Type I | |
| a) Mono-carbide matrix | 638 |
| b) Sesqui-carbide area | 1495 |
| Specimen Type II | |
| a) Mono-carbide matrix | 540 - 810 |
| b) Sesqui-carbide area | 1495 |

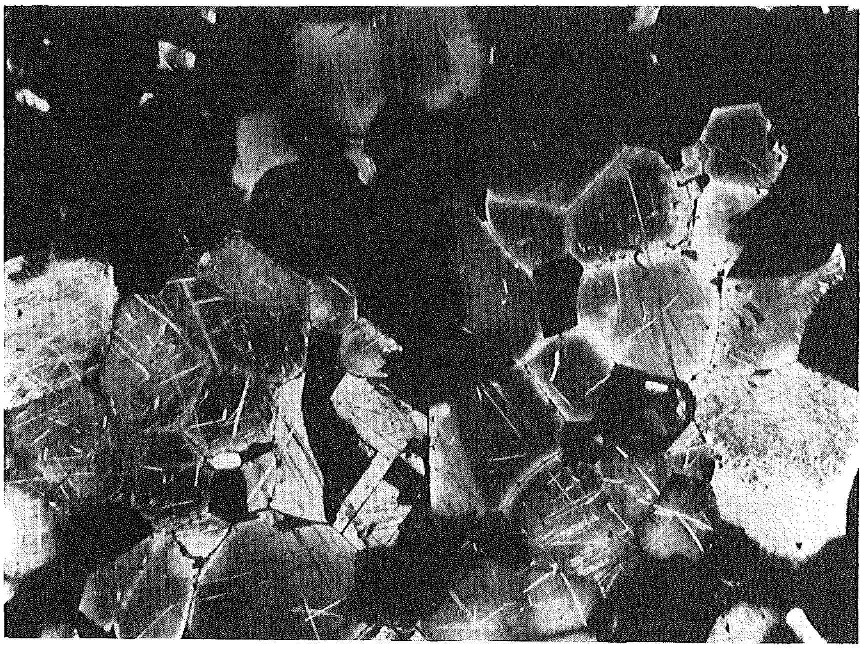

Fig. 1 Uranium monocarbide with dicarbide needles, mag. 30 x, Etchant 1

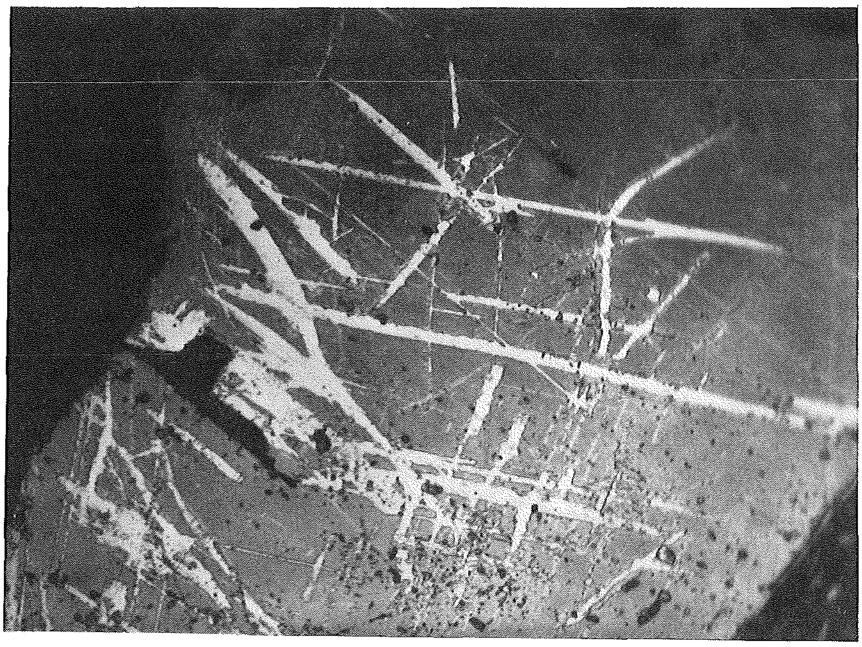

Fig. 2 Same sample as in Fig. 1, mag. 300 x, Etchant 1

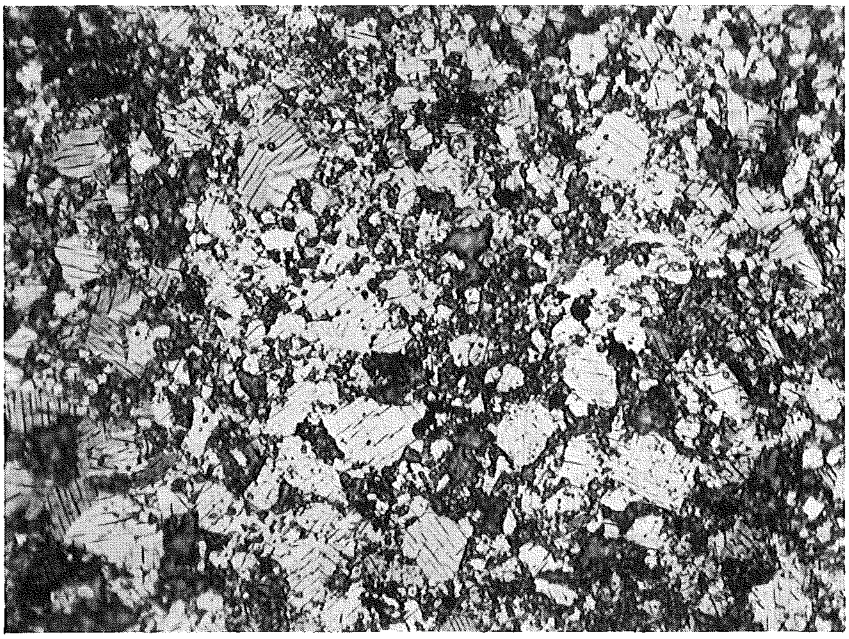

Fig. 3 Uranium dicarbide,
mag. 600 x, Etchant 1

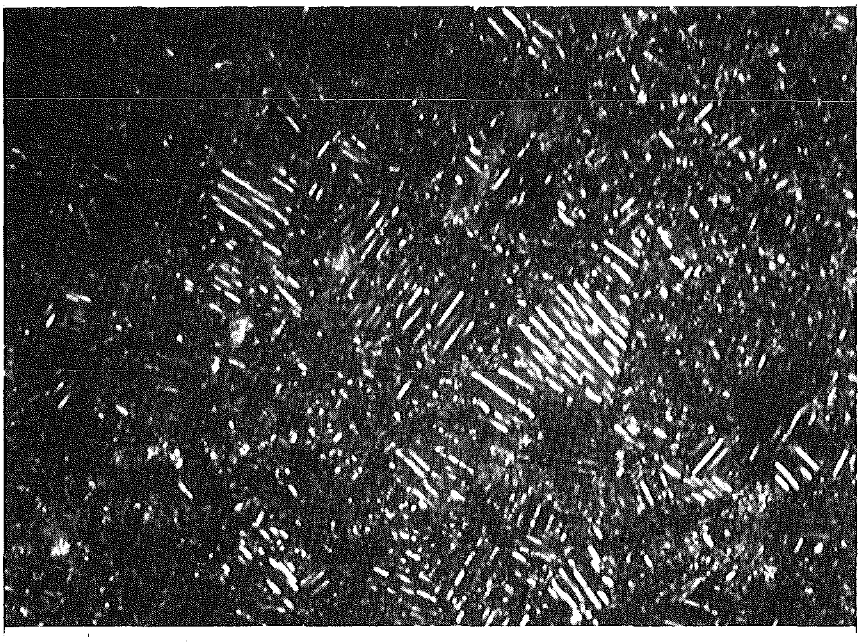

Fig. 4 Uranium dicarbide polarised light,
mag. 800 x, Etchant 1

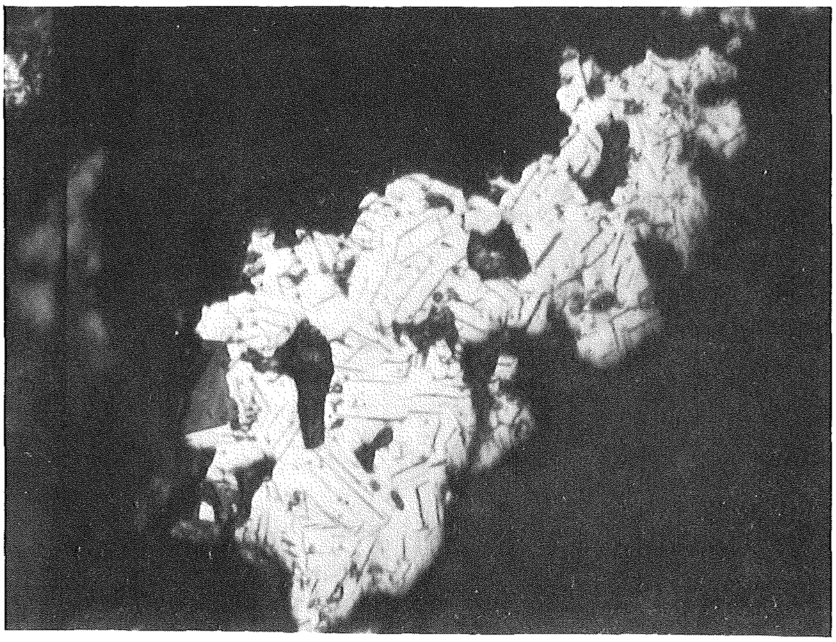

Fig. 5 Monocarbide area in sesquicarbide sample, mag. 750 x, Etchant 1

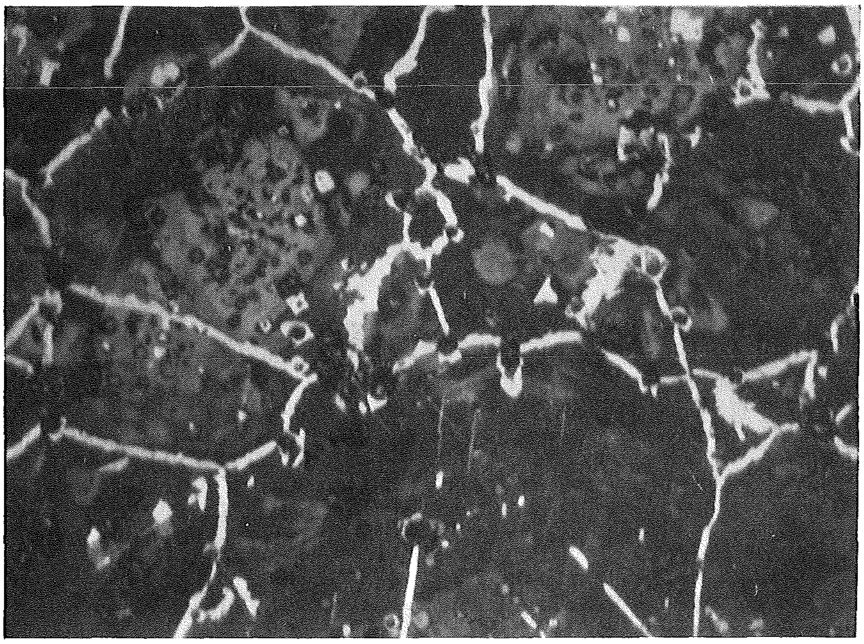

Fig. 6 (U,Pu)C sample A, mag. 200 x, Etchant 1

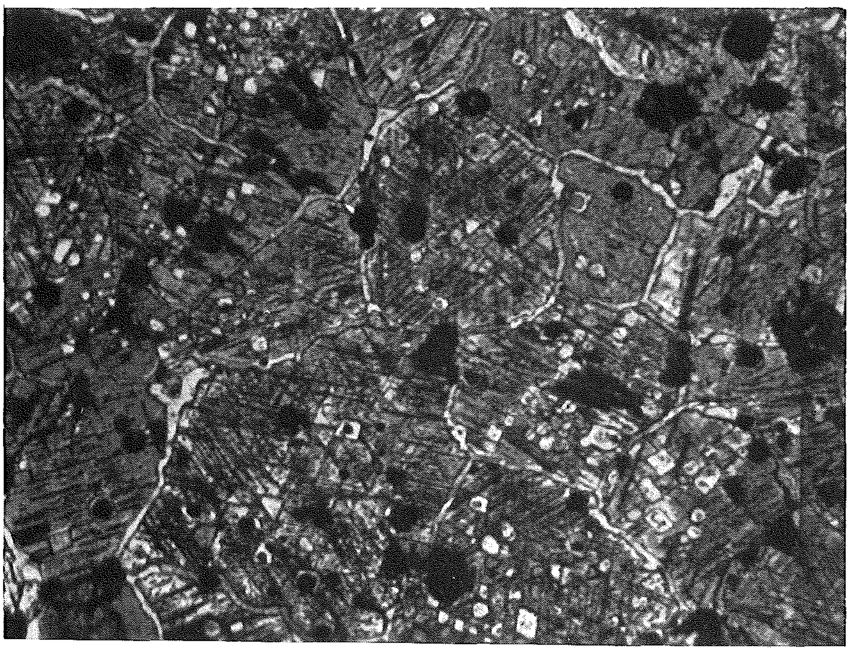

Fig. 7 (U,Pu)C sample A,
mag. 200 x, Etchant 4

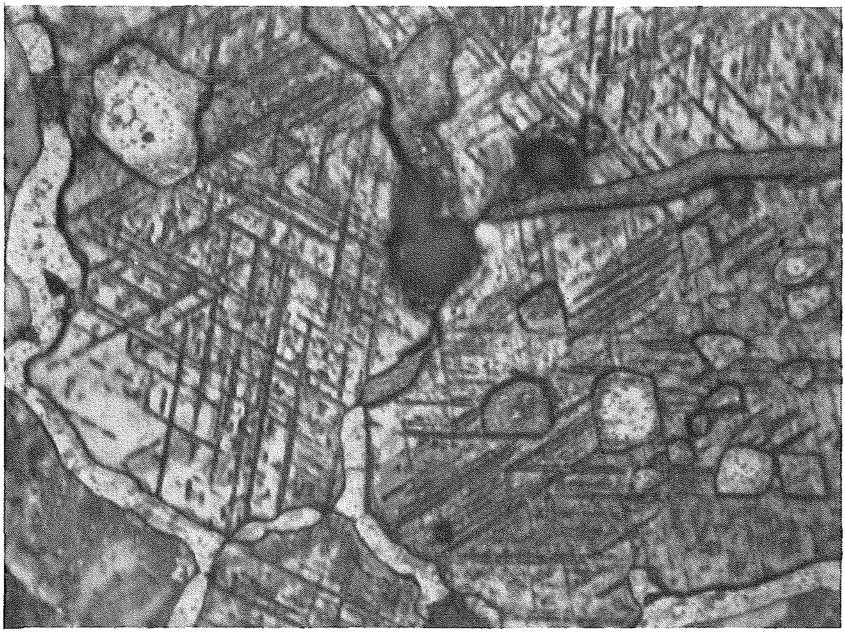

Fig. 8 Same sample as in Fig. 7,
mag. 750 x, Etchant 4

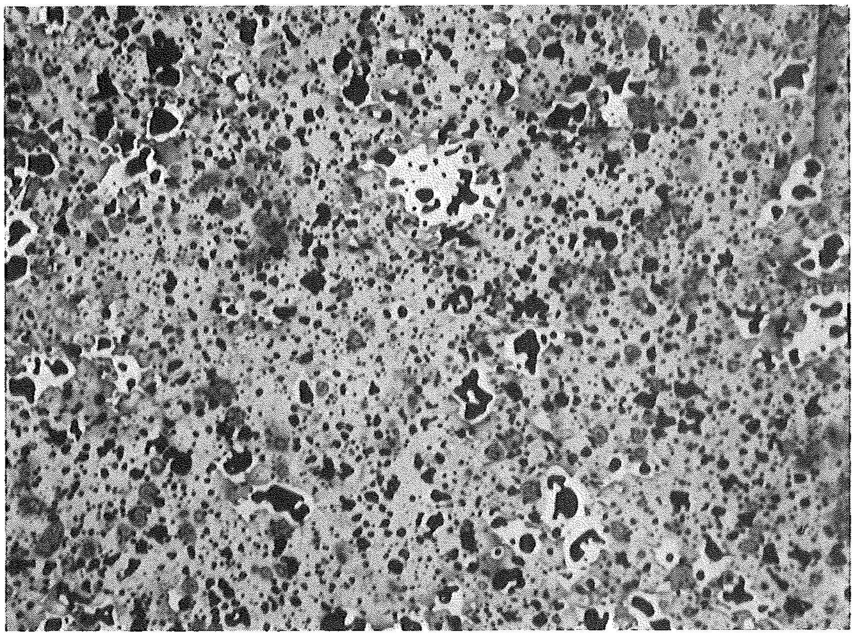

Fig. 9 (U,Pu)C sample B,
mag. 100 x, Etchant 1

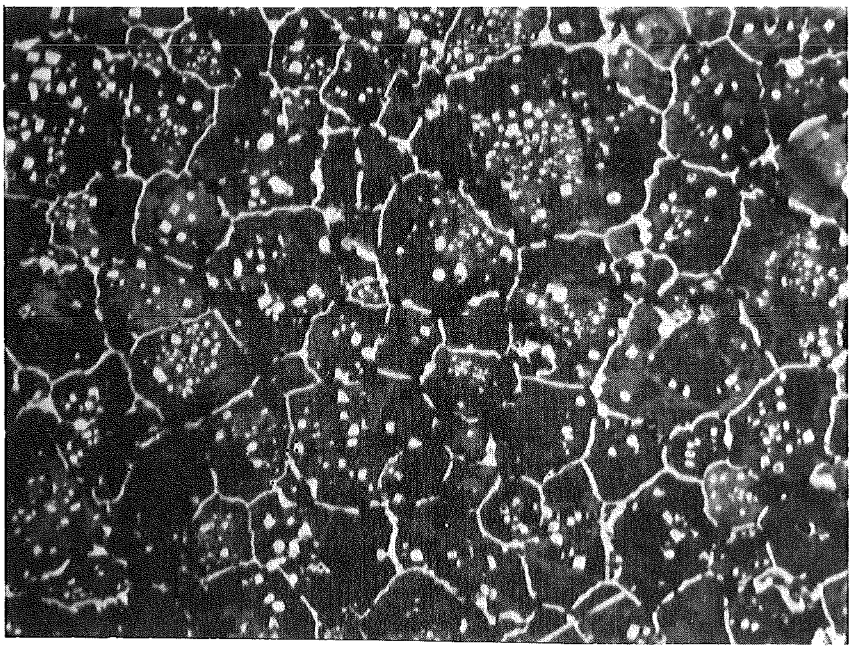

Fig. 10 (U,Pu)C sample A,
mag. 100 x, Etchant 1