



Second United Nations  
International Conference  
on the Peaceful Uses  
of Atomic Energy

A/CONF.15/P/27  
Abstract (UNITED KINGDOM)  
18 March 1958

ORIGINAL: ENGLISH

Confidential until official release during Conference

THE TRANSFORMATION BEHAVIOUR OF SOME DILUTE URANIUM ALLOYS

by

\* M. D. Jepson  
R. D. Kehoe  
R. W. Nichol/s  
G. F. Slattery

Abstract

1. Metallographic and dilatometric studies of the heat treatment behaviour of technical uranium and certain alloys of interest for use in natural-uranium fuelled reactors are described.
2. The micro-structure and secondary phases present in high purity and technical purity uranium are first discussed and the time-temperature-transformation data presented. Results on binary alloys comprising U/Al, U/Cr, U/Fe, U/Mo, U/Nb, U/Ti, U/V and U/Zr, containing up to about 2 atomic per cent of the alloying element, are described. Cr, Fe and Zr were found to be the most effective grain refining agents. Al and V were satisfactory under some conditions whereas Mo, Nb and Ti were ineffective.
3. The grain-size results together with the time-temperature-transformation curves indicated that grain refinement is associated with depression of the temperature of transformation on heat treatment, the extent of this depression for a given cooling rate being dependent on the alloy content. In practice it was found that alloys such as U/Zr and U/Fe responded to water quenching treatments, and optimum refinement of others (e.g. U/Cr) resulted from isothermal treatment at 500 to 600°C.

\* U.K. Atomic Energy Authority, Industrial Group.

*Springfields*

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**



Second United Nations  
International Conference  
on the Peaceful Uses  
of Atomic Energy

A/CONF.15/P/27  
UNITED KINGDOM  
15 May 1958

ORIGINAL: ENGLISH

Confidential until official release during Conference

TRANSFORMATION BEHAVIOUR OF SOME DILUTE URANIUM ALLOYS

M. D. Jepson +  
R. B. Kehoe +  
R. W. Nichols +  
G. F. Slattery +

1. INTRODUCTION

The behaviour of uranium metal fuel under irradiation is discussed in detail in a number of papers(1). These show that three effects are important:-

- (1) Anisotropic growth or wrinkling
- (2) Irradiation and thermal creep leading to bowing in stacked elements.
- (3) Inert gas diffusion and swelling.

All these effects are structure sensitive, though to varying degrees, but attempts to minimise them may lead to conflicting requirements as regards the structure of the fuel.

Grain size has a marked effect on wrinkling, fuel distortion being minimised by a fine random structure; on the other hand creep resistance is favoured by a coarse grain structure. The measurement and control of grain size has therefore been a major consideration and has necessitated study of the transformation characteristics and kinetics of possible fuel alloys.

Creep properties and swelling can be significantly affected by the form and distribution of particulate phases. The stability of these phases and of grain size must also be assured if properties are to be maintained over the long periods required for economic reactor service.

---

+ U.K. Atomic Energy Authority, Industrial Group

Over a number of years, partly in conjunction with the development of more creep resistant alloys(2), structure and heat treatment data have been accumulated on a range of binary and more complex alloys based on technical purity uranium. All these alloys have been suitable, because of their restricted alloy content of materials of high capture cross-section, for use in natural uranium fuelled reactors. At these low levels of alloy addition, normally below 1 at. % total, equilibrium data was not available in any detail and has had to be established. Many of the phases produced, or present in the base metal, had to be identified or techniques developed to distinguish them in the presence of impurity phases of markedly similar distribution.

This paper presents a summary of the metallographic and dilatometric information obtained on dilute uranium alloys containing one or more of:- Aluminium, Chromium, Iron, Molybdenum, Niobium, Silicon, Titanium, Vanadium and Zirconium.

## 2. TECHNICAL PURITY URANIUM

### 2.1 IDENTIFICATION OF SECOND PHASES

The technical purity uranium used in the present studies is produced by the thermal reduction of uranium tetrafluoride by magnesium and subsequent remelting of the reactor billet and casting into approximately 1 inch rods. A typical composition (p.p.m.) would be:-

C	O	N	H	Fe	Al	Si	Cr	Mn
700	15	20	2	100	40	20	5	15

The inclusions normally present in uranium are: uranium carbide, oxides and nitrides and various intermetallic compounds often in the form of a network. These features can be observed metallographically after preparation with emery papers followed by polishing with alumina or diamond paste on a "Selvyt" pad and an electrolytic polish in a bath consisting of 1 volume H<sub>2</sub>SO<sub>4</sub>, 1 volume H<sub>3</sub>PO<sub>4</sub>, 2 volumes CH<sub>3</sub>COOH and 1 volume of water.

Uranium carbide inclusions are present in discrete angular shapes conveniently described as cuboids, Fig. 1. Etching in 50% HNO<sub>3</sub> stains these cuboids black. The identity of the cuboids has been confirmed by X-ray examination but this does not exclude the possibility of some UO and UN in solution. The amount of carbon present is much greater than the solubility limit in solid uranium and thus the cuboids are unaffected by solid state heat treatments.

Complex cuboids containing uranium carbide, oxide and possibly nitride, which are all isomorphous, are also observed in uranium, Fig. 2.

Uranium monoxide is a light polishing globular phase which suffers edge attack but is not stained in nitric acid, Fig. 1. Uranium mononitride is only occasionally observed as a light grey constituent in the vicinity of slag inclusions and it is neither attacked nor stained by nitric acid. However a slight edge attack can be obtained with an electrolytic etch with 10% aqueous chromic acid.

Uranium dioxide is seldom observed as an inclusion, Fig. 3, and usually occurs as a surface contaminant. As polished, it shows a purplish tinge and when observed under polarised light it displays a reddish interference colour.

Occasionally "flake" type inclusions are observed. These may be associated with the presence of uranium hydride, consisting of a spine of dark particles surrounded by a brown stain, Fig. 4.

The presence of network type structure, Fig. 5, is due to aluminium, iron and silicon impurities. In chill cast material they are semicontinuous and intergranular but on annealing give a more eutectoidal appearance. The "network" can be observed in the polished condition but is better defined by etching. The  $UAl_2$  phase is detected by an electrolytic etch (2% citric acid,  $\frac{1}{2}$ % nitric acid; 40 seconds with an e.m.f. of 6 volts).  $U_6Fe$  is made more readily visible by an immersion etch in equal parts of nitric and acetic acids for 10-15 minutes.

## 2.2 GRAIN STRUCTURE

The grain structure of uranium is best studied using polarised illumination after anodising in a solution consisting of 12 g  $CrO_3$ , 200 ml  $H_3PO_4$  and 50 ml  $H_2O$  to increase the grain contrast. The grain structure of cast uranium is variable and contains grains of up to several millimetres diameter. X-ray microbeam studies(11) of technical purity uranium have indicated that the macro-grain structure as normally observed by microscope is generally broken down into subgrains with a characteristic size of 1-10 microns, and differing from one another in orientation by only a few degrees. This sub-structure is unaffected by annealing and can be observed under the microscope, Figs. 6 a and b. Higher purity uranium (produced by an electrolytic route and melted in an electron bombardment furnace, and having total impurities of less than 100 parts per million) does not show this fine sub-structure when annealed, but has a characteristic macro-grain size (i.e. between grains differing widely in orientation) of about 50 microns.

The characteristic coarse macro-grain structure of the technical purity uranium requires refinement. Experience has shown that wrinkling is virtually eliminated by a reduction in grain size down to 0.3 mm or less, i.e. by a factor of 10 or more from the normal grain size. In the following paragraphs, such a reduction in grain size is implied by the term "adequate refinement".

Heat treatment, by quenching from the beta or gamma phases, does not refine the grain structure of this uranium except for a thin surface skin or through very thin sections.

### 2.3 TRANSFORMATION CHARACTERISTICS

Time-temperature-transformation curves have been determined dilatometrically on samples of 1 inch length and  $\frac{1}{8}$  inch diameter. In all cases an initial soak for 30 minutes at 720°C was given followed by quenching into a lead bath for the isothermal transformation. The specimen reached the bath temperature within about five seconds.

The T.T.T. curve for the high purity uranium consisted of a single loop, see Fig. 7. That of the technical purity uranium showed two loops, Fig. 8, the upper being small in size and apparently being the effect of the introduction of additional impurities. This upper loop, with its nose at 640°C, extends down to the break at 610°C. The nose of the lower curve is below 570°C. This curve is typical of technical purity uranium and the changes induced by alloying additions will be described relative to this standard curve.

## 3. BINARY ALLOYS

### 3.1 URANIUM-ALUMINIUM

In technical purity uranium, aluminium impurities are present in the semi-continuous network which is not related to the alpha-phase grain boundaries. A gamma-phase anneal and furnace cool is required to precipitate the  $UAl_2$  phase completely; more rapid treatments such as chill casting result in incomplete precipitation. In gamma-phase annealed specimens, a reasonable correlation between the amount of network and aluminium content can be obtained, Figs. 9a, b and c.

The general form of the equilibrium diagram has been published<sup>(3)</sup>. More detailed information concerning the uranium-rich end of the diagram up to 1.5 at. % has been obtained for alloys based on technical purity uranium (Fig. 10). The eutectoid (gamma uranium to beta uranium +  $UAl_2$ ) reaction occurs at a composition of 1.4 at. % aluminium. The maximum solubility of aluminium in beta-uranium is approximately 1.0 at. % at 750°C. There was no evidence for a eutectoid decomposition in the beta phase, the solubility of aluminium in alpha-uranium being less than 0.08 at. %. Gamma-annealing followed by water-quenching will retain the aluminium in solution. On subsequent alpha-annealing at 550°C the aluminium is precipitated in a finely-dispersed form which is quite different from the cast network structure. It occurs within and around the alpha macro-grains and also delineates the sub-structure within the alpha grain.

Gamma-quenching gives more consistent refinement than beta-quenching and it is only limited in practice by the tendency to cracking at higher aluminium levels. After quenching, the lattice is strained as evidenced by X-ray back reflection photographs, and an alpha-anneal of 15 hours at 550°C is required to complete the precipitation process. The fine grain structure obtained by quenching is stable on annealing at temperatures up to 550°C; grain boundary precipitation is known to restrict grain growth and this may be a contributory factor.

The T.T.T. diagram for the addition of  $\frac{1}{2}$  at. % aluminium (Fig. 11) shows the two loops of technical purity uranium but the temperature range of the upper loop is extended, the shear type of transformation starts at lower temperatures and the induction period is increased.

### 3.2 URANIUM-CHROMIUM

Uranium -  $\frac{1}{2}$  at. % chromium can be grain refined to a uniform equiaxed structure with a grain size not exceeding 0.15 to 0.2 mm by heating into the beta range followed by isothermal transformation at 550°C., see Figs. 12a and b. Lowering of the transformation temperature decreases the grain size but the grain boundaries become irregular, Fig. 13a, and below 500°C an acicular structure is produced, Fig. 13b.

Uranium -  $\frac{1}{2}$  at. % chromium appears single phase after isothermal transformation at temperatures between 500°C and 550°C, but this is not an equilibrium structure, as is evidenced by the fact that reheating for 12 hours at 550°C precipitated an unidentified second phase at the grain boundaries, Fig. 14.

The T.T.T. curve for the  $\frac{1}{2}$  at. % chromium alloy, Fig. 15, consists of two loops with a well defined break between them. The nose of the upper loop is at 575°C and is just above the optimum isothermal transformation temperature for refinement.

Compared with technical purity uranium a considerable degree of beta stabilisation is obtained. This is such that water quenching leads to transformation at a low temperature at which the beta phase is brittle, and this in turn leads to severe cracking.

### 3.3 URANIUM-IRON

The uranium rich end of the uranium-iron equilibrium system (4)(5) has been re-examined in detail up to 1 at. % using technical purity uranium (Fig. 16). The maximum solubility of iron in beta uranium was found to be 0.5 at. %, the solid solution decomposing eutectoidally into alpha uranium and  $U_6Fe$  at 0.2 at. % iron. The solubility in the alpha phase was too low to be determined.

Good grain refinement was produced by water quenching from 750°C but excess of iron resulted in retention of the beta phase and quench cracking



together with the formation of massive  $U_6Fe$  at the grain boundaries. At lower iron contents the iron was retained in solution but precipitated in a finely dispersed form on a subsequent anneal.

Transformation studies (Fig. 17) indicate that the effect of  $\frac{1}{4}$  at. % iron is to increase the induction period preceding transformation, transformation by shear thus being retarded. The temperature range of the upper loop is similar to that of technical purity metal.

### 3.4 URANIUM-MOLYBDENUM

The addition of  $\frac{1}{2}$  at. % molybdenum does not facilitate grain refinement on heat treatment and refinement by beta - quenching can only be obtained in the thin sections. The molybdenum rich phase is soluble in beta uranium and can be completely retained in solution by water quenching, Fig. 18a. Subsequent alpha-annealing causes the phase to be precipitated in a finely dispersed form, Fig. 18b.

Where the beta-alpha transformation occurs isothermally above  $550^{\circ}C$  a well defined lamellar structure is obtained (see Fig. 19a) simultaneously with the decomposition of the beta phase into polygonal grains of alpha uranium by nucleation and diffusion. This lamellar eutectoid becomes finer as the temperature of transformation is lowered, Fig. 19b. At lower temperatures, where a shear mechanism of transformation is operative, the secondary phases are precipitated from supersaturated alpha solid solution subsequently to the beta - alpha transformation.

The beta-stabilising effect of the  $\frac{1}{2}$  at. % molybdenum alloy is only slight, and water quenching an alloy from the beta phase produced only a shallow area of beta phase on the rim of the specimen. Transformation of this retained phase occurs at room temperature by a shear mechanism, the alpha phase growing as plates and needles along several directions within a beta-grain to give smaller units of ultimate alpha phase structure, Figs. 20a, b and c.

A preliminary survey of the uranium end of the uranium-molybdenum constitutional diagram has been made. A series of alloys were made by arc melting technical purity uranium and molybdenum and the structures after heat treatment were examined metallographically. The results indicate that the solubility of molybdenum in beta uranium is between 1000 and 2000 p.p.m. at  $750^{\circ}C$  and between 2000 and 3000 p.p.m. at  $700^{\circ}C$ . The solubility in alpha uranium is less than 1000 p.p.m. at  $625^{\circ}C$  and  $600^{\circ}C$ . Of the equilibrium diagrams previously published (6)(7) the present results appear to be more in accordance with that given by Saller, Rough and Vaughan (7).

Dilatometric work on the  $\frac{1}{2}$  at. % alloy (see Fig. 21) shows that the upper nucleation and diffusion loop is displaced to very much lower temperatures than in uranium, extending down to  $450^{\circ}C$ , and at the upper end being asymptotic to about  $620^{\circ}C$ . This is in agreement with the metallographic evidence. Again the tendency to beta stabilisation is only slight.

### 3.5 URANIUM-NIOBIUM

Alloys containing less than 1 atomic percent of niobium do not refine on heat treatment. With 1 at. % niobium gamma quenching gives some refinement but causes surface cracking. Isothermal transformations in the range 450°C-550°C do not refine the cast grain size, but may be made effective by the addition of chromium.

### 3.6 URANIUM-SILICON

The addition of small amounts of silicon promotes refinement by water quenching from the beta range. Increasing the silicon content to 0.8 at. % gives a high degree of beta stabilisation which is greater than the equivalent for iron. Quenching from the gamma phase causes cracking of the specimens due to the high stabilisation. When silicon and iron are present together the stabilising effects are roughly additive.

### 3.7 URANIUM-TITANIUM

The uranium-titanium alloys up to 1 atomic percent titanium were even less responsive than the uranium-niobium series to the heat treatment, since the U + 1 at. % Ti did not even refine on gamma quenching. Titanium reacts with the carbon present in the uranium, altering the composition and form of the carbide without significantly affecting its distribution. The T.T.T. diagram of the  $\frac{1}{2}$  at. % alloy shows a broad upper loop extending from about 670°C (Fig. 22) down to the onset of the lower loop at 500°C with very little variation in induction period over this temperature range.

Uranium-titanium alloys are not susceptible to refinement by isothermal transformation but, as with uranium-niobium alloys, may be rendered refinable by the addition of chromium.

### 3.8 URANIUM-VANADIUM

The uranium-vanadium equilibrium diagram is reported (8) to be a simple eutectic system with no intermediate phases. Gamma and beta uranium solid solutions both decompose by eutectoid reactions to the appropriate uranium phase and a vanadium-rich solid solution. The maximum solubility of vanadium in gamma-uranium has previously been quoted as 10 at. %, in beta-uranium as 2 at. %, and in alpha uranium as 1 at. %. The present metallographic study on alloys based on technical purity uranium would however suggest that the solubilities quoted above for the beta phase and alpha phase are too high, and it is now proposed that the solubility in beta uranium at 730°C is less than 0.54 at. % vanadium and in the alpha uranium it is very much less than this value.

There is a strong indication that uranium-vanadium alloys based on technical purity uranium are refinable by standard heat treatments. A 1 at. % vanadium alloy was refined on gamma-quenching but not beta-quenching; some

alloys were susceptible to beta-retention on gamma-quenching. This resulted in transformation at or near room temperature to an irregular acicular structure (Fig. 23); this transformed structure is often produced during the metallographic preparation. The uranium  $\frac{1}{2}$  at. % vanadium alloy is best refined by isothermal transformation at about 500°C if cracking is to be avoided. A form of rapid induction heating and spray quenching is more effective in promoting refinement from either the gamma or beta phase fields than the normal anneal and tank quench. This may be due to reduced grain growth of the high temperature phase as a result of the shorter anneal. An interesting effect was produced in a 1 at. % vanadium alloy: slow cooling from the gamma-phase range to that of the beta phase produced a heavy eutectoid structure with another phase in the form of needles, (Fig. 24). Repeat heat treatment failed to reproduce this needle type structure. A similar structure has been observed in the 2 at. % vanadium alloy. Attempts to identify it using X-ray glancing angle and powder techniques were not successful. It is believed that these needles are a vanadium-rich solid solution and if so, their occurrence must depend on the achievement of some very specific cooling conditions over the gamma-beta transformation range. These conditions were presumably satisfied in the first heat treatment but not subsequently. The 2 at. % vanadium alloy is unusual in that it can be obtained in a fine grain condition by chill casting.

The upper loop of the T.T.T. curve of the 2% vanadium alloy (Fig. 25), is depressed by about 70°C relative to that of the base uranium, with the onset of the lower loop at about 540°C. The lower loop is remarkable in showing below 500°C an induction period of about 23 seconds which does not vary with temperature.

### 3.9 URANIUM-ZIRCONIUM

Alloy additions up to 2 atomic per cent zirconium gave good refinement on both beta and gamma quenching. Zirconium, like titanium, tends to form carbides in the uranium, even in these low addition alloys. Normal casting and beta phase heat treatments do not disperse the carbide but it is possible that treatment high in the gamma-phase range may result in a finer dispersion.

## 4. COMPLEX ALLOYS

### 4.1 URANIUM-MOLYBDENUM-CHROMIUM

Additions of molybdenum enhance the creep strength of technical purity uranium but the binary alloy cannot be refined by heat treatment. Since chromium is a good beta-stabilising element it can be used as an addition to promote refinement. The ternary alloy requires an isothermal heat treatment since water quenching causes cracking of the material. Polygonal grains of alpha-uranium are formed above 500°C whilst acicular type structures are produced by transformation between 500°C and 450°C. In the more highly stabilised alloys, e.g.  $\frac{3}{8}$  at. % Mo +  $\frac{3}{8}$  at. % Cr refinement is obtained after

continuous cooling at 3°C/min. from both the beta phase and gamma phase temperature ranges. There is no observable grain growth on alpha-annealing at 600°C for 24 hours.

The secondary phases were completely soluble in the beta phase. The structure of the binary  $\frac{3}{8}$  at. % Mo alloy was completely eutectoid after transformation above 500°C and this eutectoid structure remained unaffected by the addition of chromium up to  $\frac{3}{8}$  at. %.

The T.T.T. curves of three of these ternary alloys have been determined:  $\frac{1}{8}$  Mo +  $\frac{1}{8}$  Cr,  $\frac{1}{4}$  Mo +  $\frac{3}{8}$  Cr and  $\frac{1}{2}$  Mo +  $\frac{1}{2}$  Cr, and progressive changes appear through the series. The temperature of the nose of upper loop remains unchanged but the induction period increases from 25 seconds to 250 seconds. Increasing alloy content widens the break between the loops and markedly increases the induction periods at the relevant temperatures. This is shown in the curves given in Figs. 26a, b and c.

It is interesting that the induction times for the commencement of transformation in the richest alloy are much greater than the sum of the times in the binary  $\frac{1}{2}$  at. % chromium and  $\frac{1}{2}$  at. % molybdenum alloys.

#### 4.2 URANIUM-CHROMIUM-IRON

The presence of iron as impurity causes an increase in the grain size of the uranium +  $\frac{1}{2}$  at. % chromium alloy for a given isothermal transformation and depresses the temperature at which an acicular type structure is formed. The grain size increases with iron content up to 0.34 at. % but additions up to 0.86 at. % appear to have little further effect. Iron additions produce a phase not present in the binary U +  $\frac{1}{2}$  at. % chromium alloy after isothermal transformation at 500°C, Fig. 27.

The effect of a 0.2 at. % iron addition to the uranium -  $\frac{1}{2}$  at. % chromium alloy is to produce an overall reduction of induction times by a factor of about five. The temperature of the nose and the break are lowered by 50°C, see Fig. 28.

#### 4.3 URANIUM-CHROMIUM-ALUMINIUM

Aluminium has little effect on the grain size of U +  $\frac{1}{2}$  at. % chromium; alloys up to 2000 p.p.m. aluminium have substantially the same grain size after heat treatment as the binary alloy.

#### 4.4 URANIUM-MOLYBDENUM-IRON

The presence of iron is to increase the slight beta stabilising effect of the molybdenum and the combined effect is more than additive. Small additions of iron do not affect the structure of the uranium -  $\frac{1}{2}$  at. % molybdenum after transformation and the structure still appeared to be of eutectoid composition. The secondary phase of the  $\frac{1}{2}$  at. % Mo +  $\frac{7}{8}$  at. %

Fe alloy was completely soluble in beta uranium and could be retained in solution by quenching.

#### 4.5 URANIUM-SILICON-IRON

An alloy containing small additions of iron and silicon has been observed to transform at 280°C after beta treatment apparently by a shear mechanism; in some grains shear took place along only one major direction. The resulting alpha grain size was of similar shape and size to the parent beta grain, Figs. 29a, b and c. The transformation temperature appears to govern whether shear is possible along a single or multiple directions. In single direction shear, restriction of the beta phase grain size by alloying or shorter heat treatments at temperatures low in the beta phase range should help to limit the ultimate alpha grain size.

### 5. DISCUSSION

In discussing the data summarised in the preceding sections of this paper it is not proposed to consider their application to the design of improved fuel elements or their effect on properties. Rather it is proposed to consider the grain-refinement results as a whole to try to establish general trends in the structural effects produced by alloying uranium.

It has been shown fairly convincingly (9) that the mechanism of transformation in pure uranium is a shear type. The expression 'shear type' is taken to mean that a daughter alpha grain is nucleated by a shear process involving the co-operative movement of lattice planes, an orientation relation thus being formed between parent and daughter grains. The resulting nucleus may then grow either by a continuation of the shear process, or by diffusion or both combined; at low temperatures the process would be expected to be one of shear alone.

The ease with which a co-operative shear movement can occur is well known to be markedly decreased by the presence of impurity atoms, thus it is not unexpected that, in the present work, the shear mechanism is retarded greatly by relatively small additions. The diffusion rate however will be largely unaffected by the presence of foreign atoms at these low concentrations and transformation by diffusion can be expected to play an increasingly large part, at the expense of the shear mechanism, as the alloy content increases.

The work of White (10) on the series of chromium alloys and the present TTT work, indicate that the lower loop of a double loop TTT diagram may be identified with the single loop of pure uranium, i.e. to correspond to transformation by shear. The upper loop is of the form well known to correspond to a nucleation and diffusion process and the equiaxed nature of the grain structure produced by transformation at upper loop temperatures confirms this. The loop arises from the product of two factors, a nucleation term which

increases as temperature decreases and a diffusion term which increases as temperature increases. In the lowest part of the loop, a mixed acicular/equiaxed structure obtains which can be taken to confirm the view that nucleation, now proceeding beyond the sub-microscopic stage, is a shear process. At slightly higher temperatures, the high nucleation rate and slow diffusion growth results in the development of numerous small equiaxed grains.

All the alloying additions studied tend to depress the transformation temperature at any specific cooling rate and to reduce the rate of transformation, but their efficiency in these respects varies widely. Chromium has a very marked effect while molybdenum is largely ineffective when added in similar proportions. Some generalisation is possible from a consideration of the equilibrium diagrams: those elements which exhibit a marked change in solubility across a phase change, Fe, Si, Cr, for example, have a much greater effect than those still partially soluble in the lower temperature phase such as Mo and Nb. No quantitative relationship on this basis has yet been established.

If the effects of the impurity on the uranium lattice are such as not to interfere very greatly with the shear mechanism, the shear is not clearly separated from the nucleation and diffusion loop. It is then impossible to obtain in an equiaxed condition the fine grain structure which forms below the upper nose, since the shear process takes part in the grain growth.

The conclusion to be drawn, therefore, is that if the TTT curve has reasonable separation between the two loops, then an isothermal transformation at a temperature just below the nose of the upper loop will produce equiaxed refinement as discussed above.

Suitable refinement by quenching from a higher phase clearly cannot result from a diffusion-controlled growth of the nuclei. This is reflected in the fact that the structures obtained have an irregularity not present in diffusion-refined alloys. This can be seen by comparing the micro-structure of the gamma quenched U-1 at. % V alloy (Fig. 23) with that of the isothermally treated U- $\frac{1}{2}$  at. % Cr alloy (Fig. 12b). The reason for refinement seems to be that a large number of nuclei form, and each can therefore grow only a small amount. The structure is highly stressed and an anneal, in addition to relaxing stresses, allows a small amount of diffusion to occur which 'rounds off' the grains. In high purity uranium, annealing results in recrystallisation and produces an equiaxed structure. When transformation is by shear and diffusion simultaneously the system proceeds directly to a stress-free condition, and no 'rounding off' then occurs. For beta quenching to give adequate refinement it is essential to have some depression of the transformation temperature; transformation at a higher temperature even within the shear loop will not suffice. The TTT curves and the quenching results support this view, although transformation times considerably shorter than those determined are more relevant to beta-quenching conditions; where the diagram shows no start of transformation in 10 seconds at about 400°C beta quenching can be expected to be effective. If however transformation is so delayed that it occurs at temperatures near to atmospheric, larger grain sizes may be obtained and quench cracking commonly occurs (e.g. U +  $\frac{1}{2}$  at. % Mo +  $\frac{1}{2}$  at. % Cr, Fig. 26 (c)). Cracking results from the stresses which are

produced by volume changes in the transformation occurring at a temperature where both beta and alpha uranium are relatively brittle. With alloys showing appreciable delay in start of transformation to relatively low temperatures there is the possibility of grain refinement in the intermediate cooling rates associated with chill casting. This was the case for U-2 at. % V (see Fig. 25).

In complex alloys a major item of interest is whether the effects of individual elements can be more than additive. That there is interaction is very clear, as is shown by the fact that the deleterious effect of iron in the chromium  $\frac{1}{2}$  at. % alloys is counteracted by aluminium and by the markedly cumulative effect of chromium and molybdenum. The latter is particularly striking in view of the very small effect produced by Mo alone and the similarity to the effect of these elements in combination in steel treatment. The variation in behaviour from one addition to another, together with the too limited data, make it impossible to establish a general rule on which to predict behaviour.

For certain purposes there may be little to choose between different alloys on a basis of, say, physical and mechanical properties, and the choice is then one based on convenience in production. Where the choice is between an alloy responding to direct quenching against one requiring isothermal treatment, the latter has a number of advantages:-

- (1) The final product achieved is under close control.
- (2) The heat treatment is little affected by fairly large amounts of other impurities; this may be particularly useful in handling enriched or recycled metal,
- (3) The product is usually in a stable condition, and precipitation is complete or can be completed in the same process by extending the transformation time allowed.

Against this, the process is slow and requires more complex equipment than a direct quenching treatment.

REFERENCES

- 1.(a) Eldred, V. W., Greenough, G. B. and Leach, P., Fuel element behaviour under irradiation.
- (b) Hardy, H. K., and Lawton, H., Assessment and testing of fuel elements.
- (c) Barnes, R. S., and others, Swelling and inert gas diffusion in irradiated uranium. Second United Nations International Conference on the Peaceful uses of Atomic Energy (1958) (to be published).
2. Heal, T. J., and McIntosh, A. B., High temperature mechanical properties of uranium and its alloys. Second United Nations International Conference on the Peaceful uses of Atomic Energy (1958) (to be published).
3. Slowman, H. A. "The Uranium - Aluminium system" A.E.R.E. X/R 137 (1947)
4. Grogan, J. D. "The Uranium - Iron system" J. Inst. Metals 77, 571-580 (1950).
5. Gordon, P. and Kaufman, A. R. "The alloy system Uranium-Aluminium and Uranium-Iron" J. Metals, 2 (1), 182 (1950)
6. Pfeil, P. C. L., "The constitution of the Uranium-Molybdenum alloys" J. Inst. Metals 77, 553 (1950)
7. Saller, H. A., Rough, F. A. and Vaughan, B. A. "The constitutional diagram of uranium-rich uranium-molybdenum alloys" B.M.I. 72 (1951).
8. Saller, H. A. and Rough, F. A. "Vanadium-uranium constitution diagram". J. Metals, 15, 545-548 (1953).
9. Butcher, B. R. "The beta to alpha phase change in pure uranium". A.E.R.E. M/R 1944 (1956).
10. White, D. W. "The transformation kinetics in uranium-chromium alloys". K.A.P.L. 595 (1951).
11. Hill, C.R., and Lewis, D., "Optical and X-ray micro-beam examination of cast uranium" I.G.R.-IM/C-0123 (1957)

Acknowledgements

The authors gratefully acknowledge the contributions made by many colleagues at the Springfields and Culcheth laboratories of U.K.A.E.A. (I.G.), especially Mr. W. A. Pollock who was responsible for most of the metallographic work.



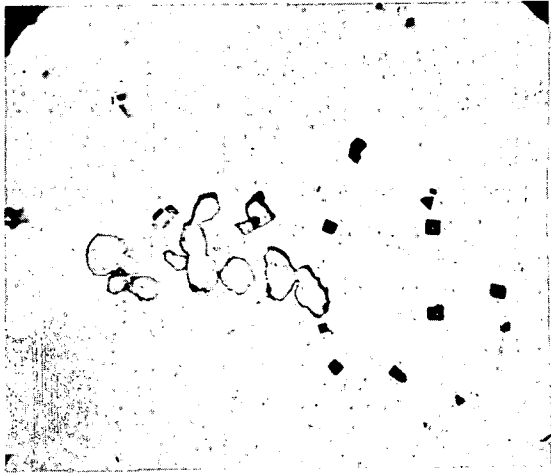


Fig. 1.  
Globular UO (light) and cubic UC  
inclusions (black). Etched 50% HNO<sub>3</sub>.  
(X550)

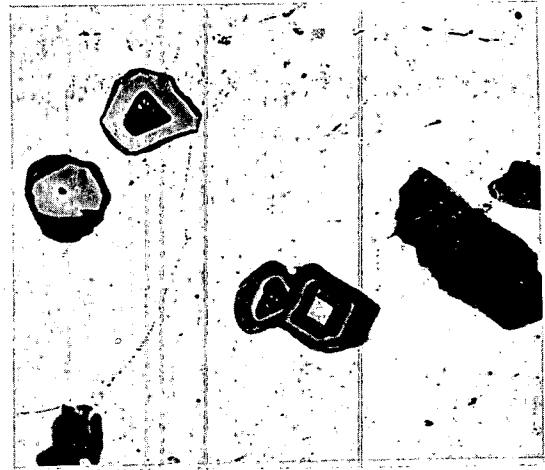


Fig. 2.  
Complex cuboids, UC with subsidiary  
oxide and nitride. Etched 50% HNO<sub>3</sub>.  
(X550)

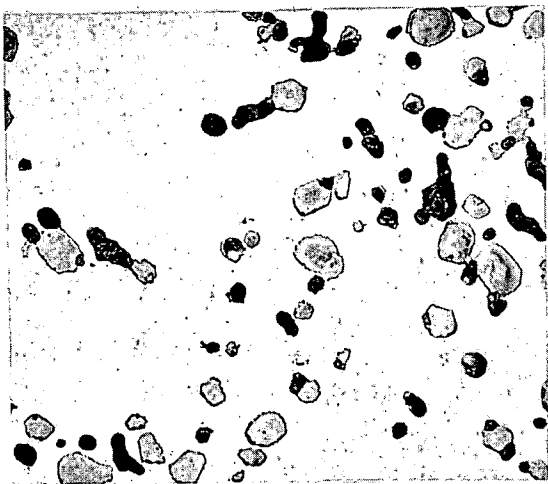


Fig. 3.  
UO<sub>2</sub> inclusions (dark) and UO  
inclusions (light). (X550)

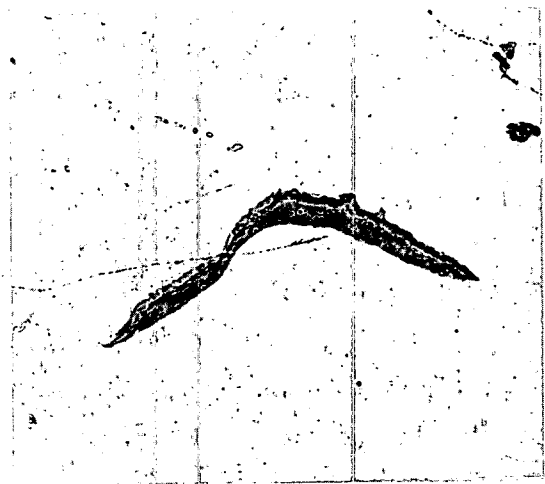


Fig. 4.  
"Flake" type inclusions, probably  
uranium hydride. (X500)

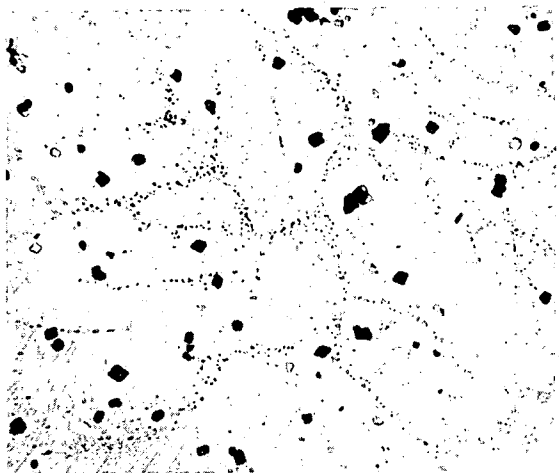


Fig. 5.  
Typical network structure in  
uranium. Electrolytically etched  
in nitric-citric acid mixture.  
(X550)

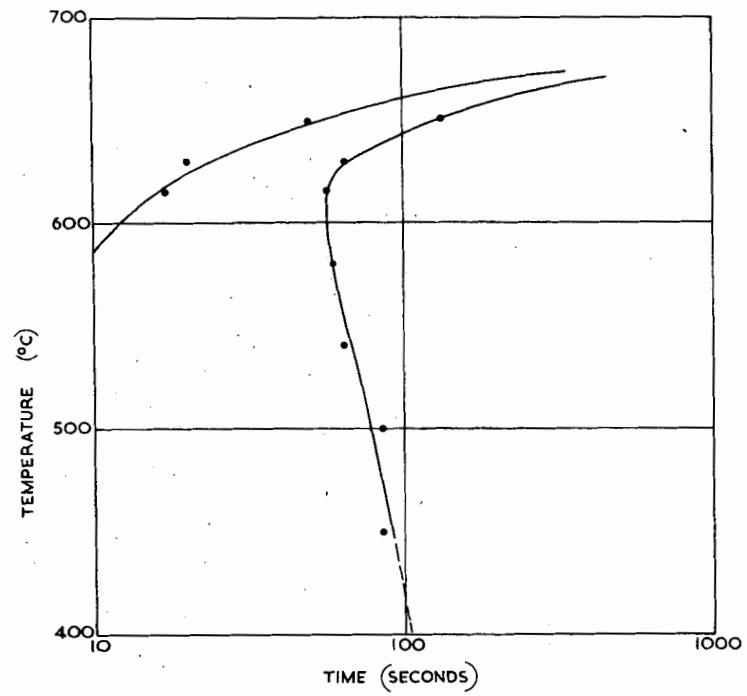


FIG. 7 T.T.T. DIAGRAM OF HIGH PURITY URANIUM.

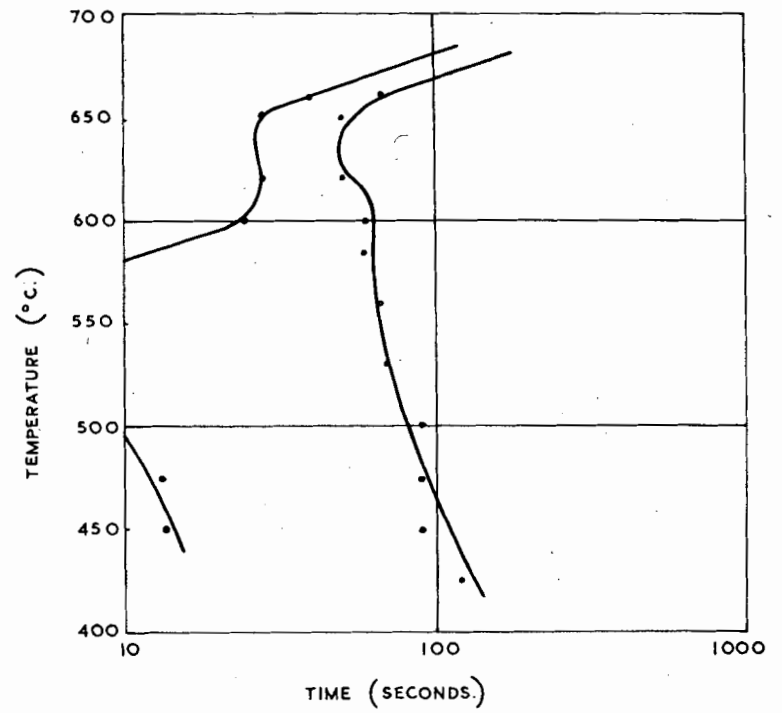


FIG.8 T.T.T. DIAGRAM OF TECHNICAL PURITY URANIUM.

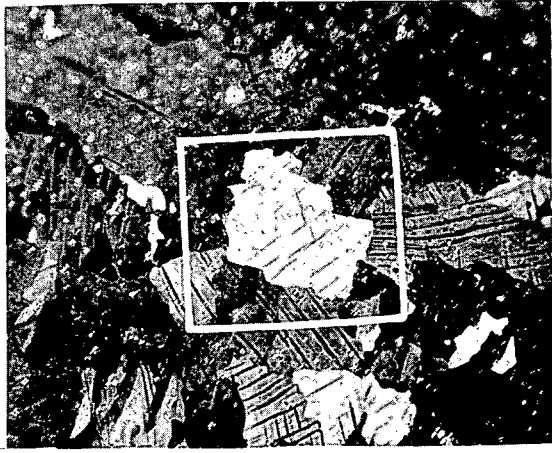


Fig. 6a

Typical macrograin in uranium



Fig. 6b.

The same grain displaying sub-structure, revealed by rotating the specimen. (Polarised light). (X300)

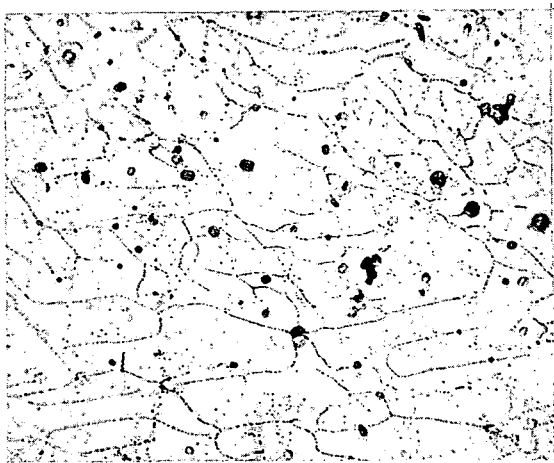


Fig. 9a.

Uranium + 0.65 at.% Al, gamma-annealed and furnace cooled. (X250)

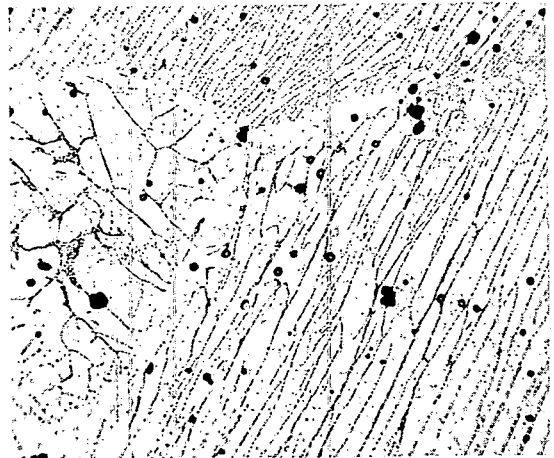


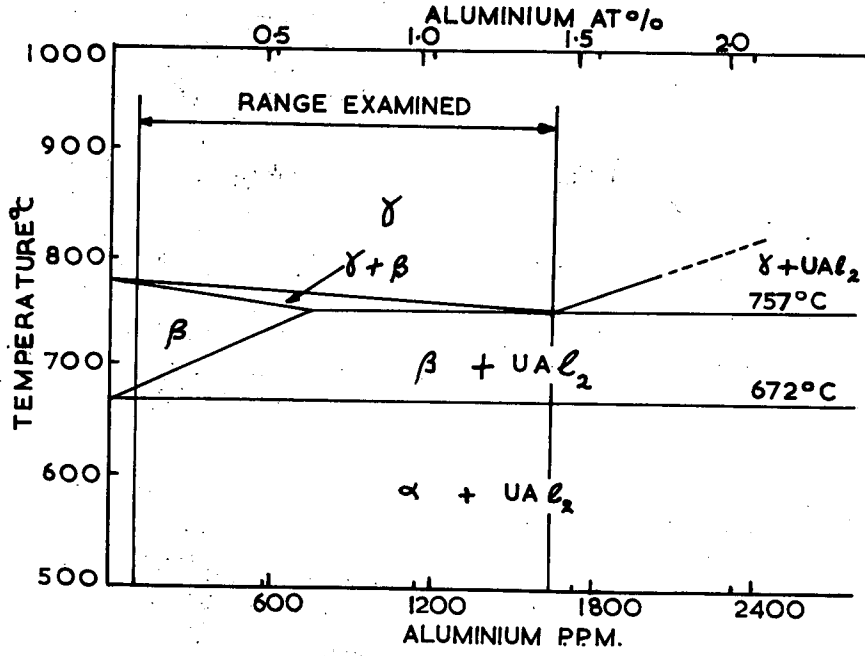
Fig. 9b.

Uranium + 0.83 at.% Al, same treatment. (X250)



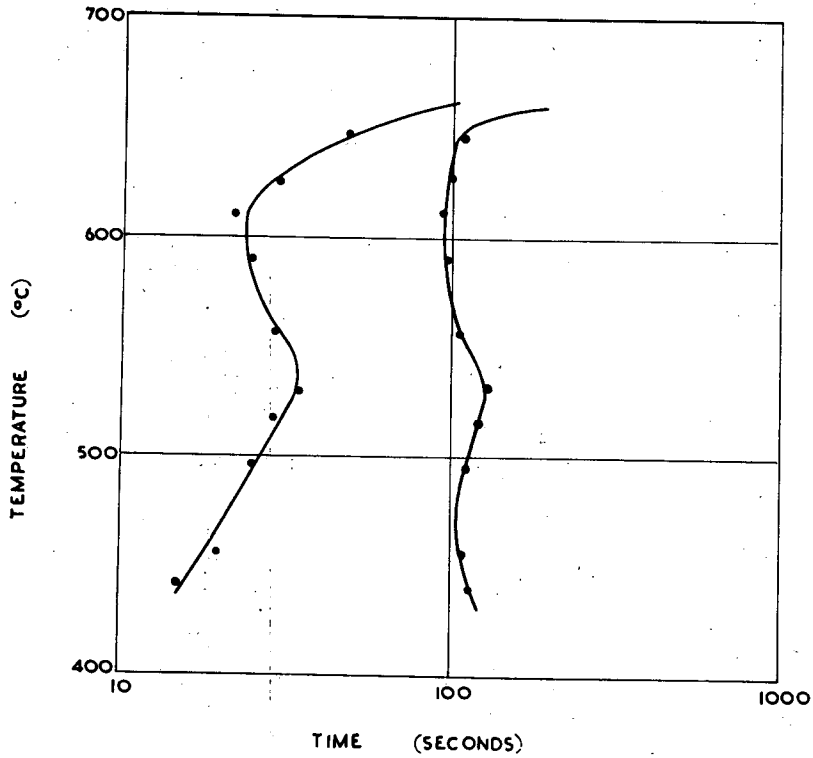
Fig. 9c.

Uranium + 1.00 at.% Al, same treatment. (X250)



TENTATIVE URANIUM-ALUMINIUM  
DIAGRAM UP TO 1600 P.P.M. ALUMINIUM

FIG. 10.



T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % ALUMINIUM. FIG. 11

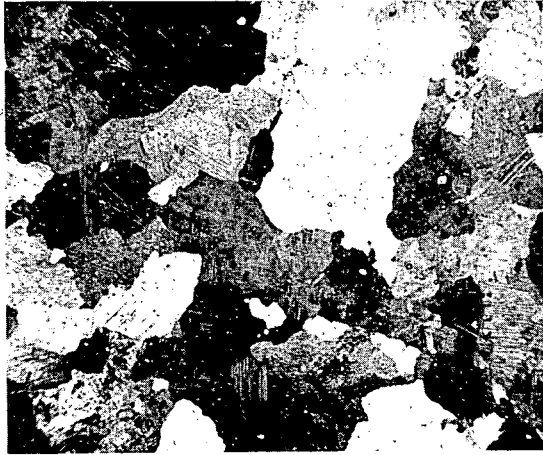


Fig. 12a.  
Uranium +  $\frac{1}{2}$  at. % Cr, as cast. (X 35)

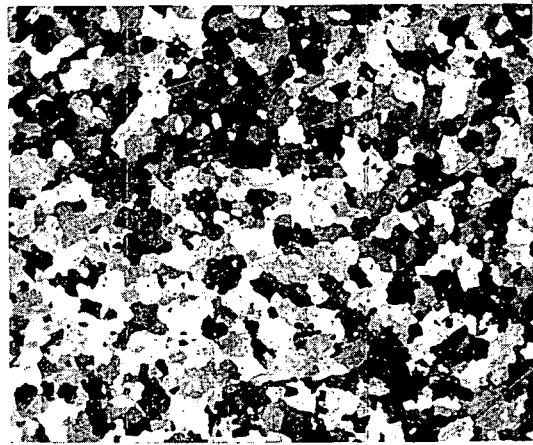


Fig. 12b.  
Alloy as above, isothermally transformed at 550 C. Equiaxed structure. (X35)

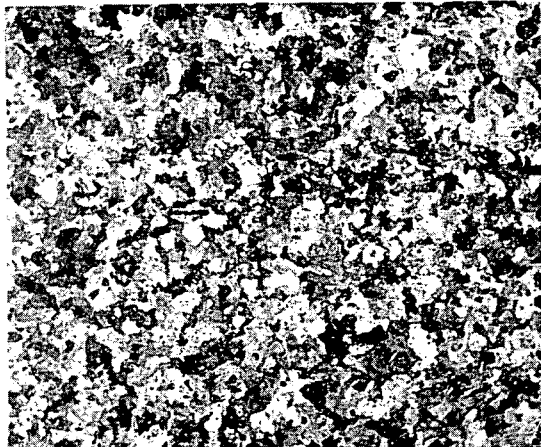


Fig. 13a.  
Uranium +  $\frac{1}{2}$  at. % Cr, Acicular structure (X100)



Fig. 13b.  
Uranium +  $\frac{1}{2}$  at. % Cr, Transformed at 550 C and reheated to 500 C for 12 hours. Etched in nitric-citric acid. (X500)

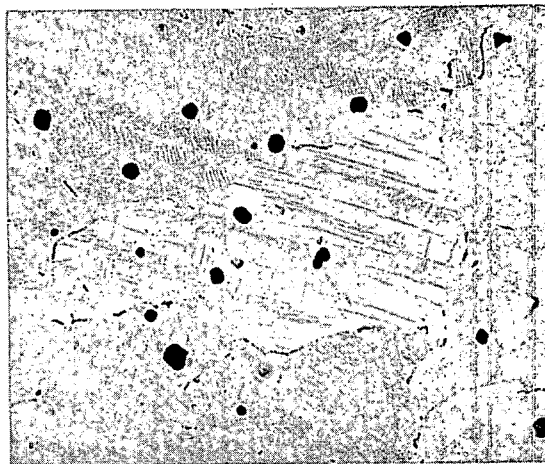


Fig. 14.  
Uranium +  $\frac{1}{2}$  at. % Cr, transformed at 500 C. Irregular structure.

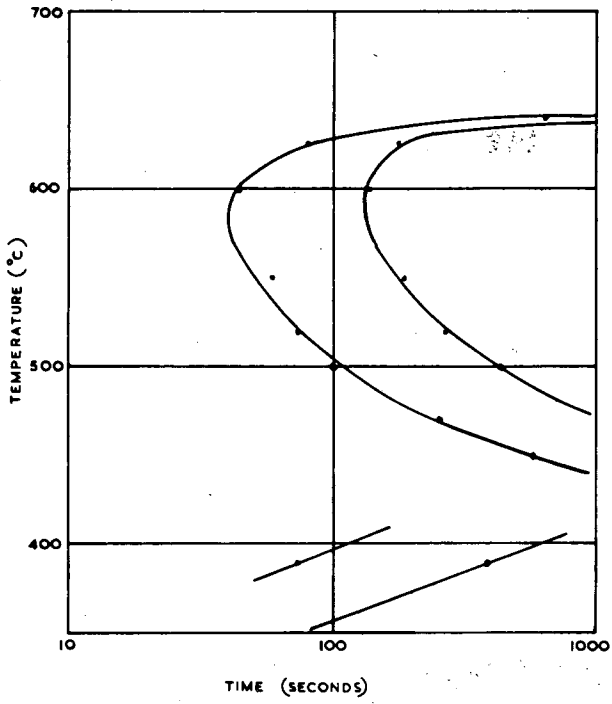


FIG.15 T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % CHROMIUM

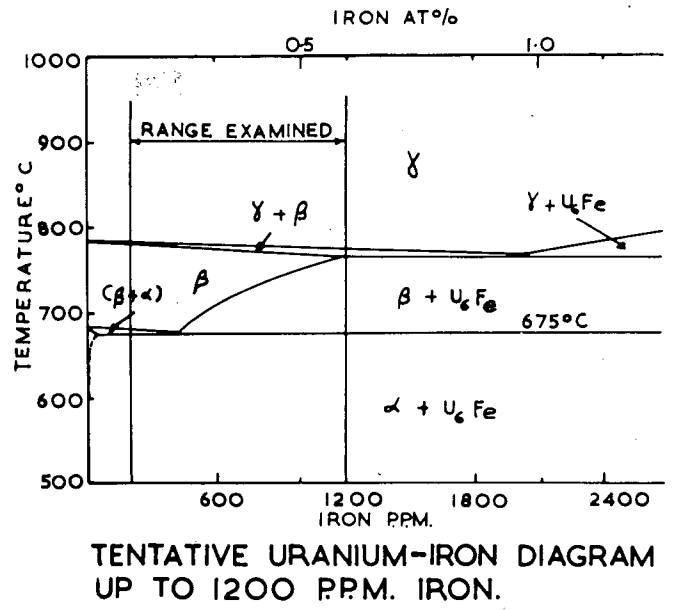


FIG. 16.

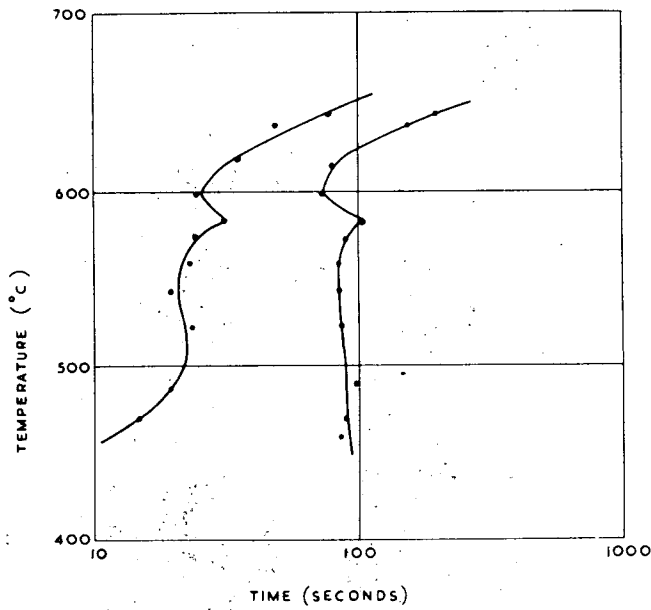


FIG.17 T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{4}$  AT. % IRON.

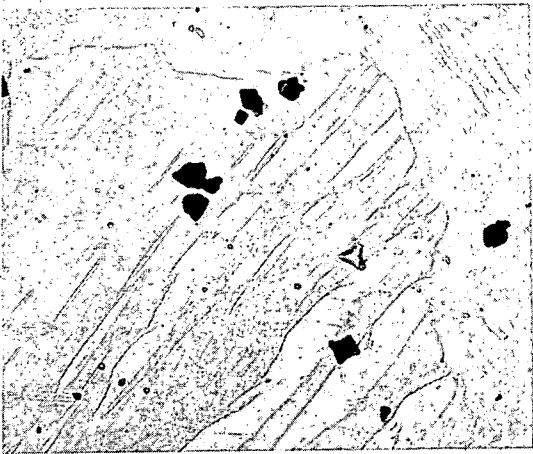


Fig. 18a.  
Uranium + 1/2 at.% Mo. Water-  
quenched from 720°C. Etched. (X550)

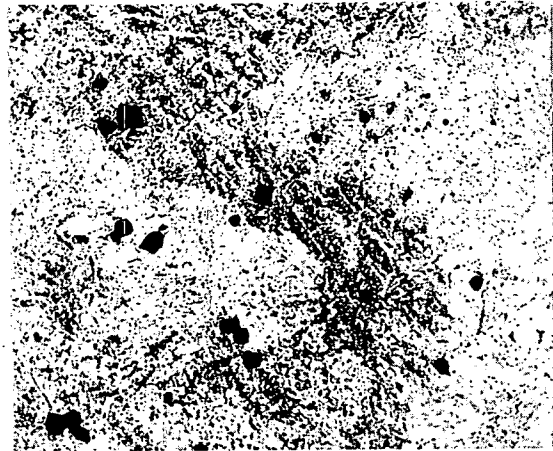


Fig. 18b.  
As above, annealed at 550°C  
for 1 hour. Etched. (X550)

Room temperature transformation of the beta phase of a  
U-Mo alloy:

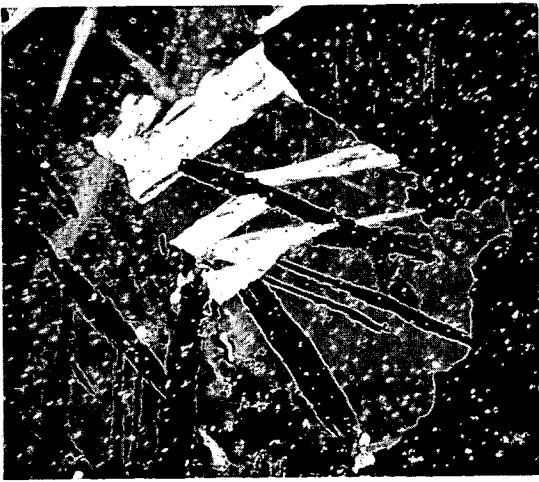


Fig. 20a.  
Transformation to alpha phase pro-  
ceeding along several directions  
in the beta grain. 20 hours after  
quenching. (X150)

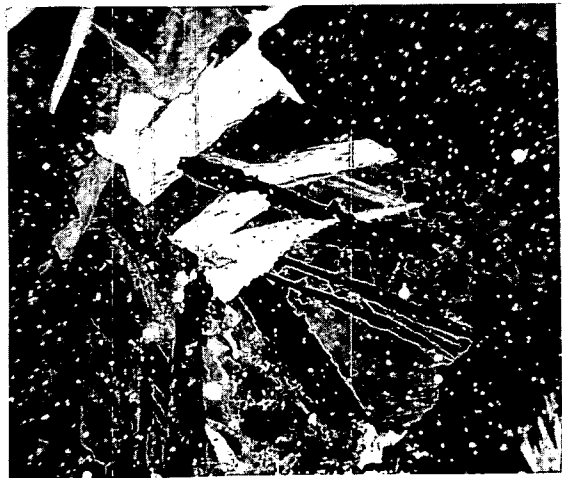


Fig. 20b.  
24 hours after quenching. (X150)

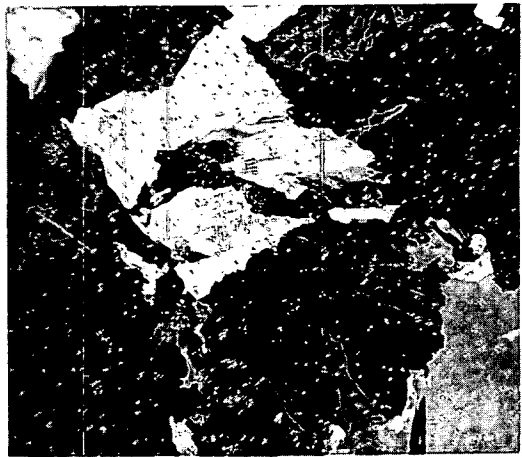


Fig. 20c.  
Complete transformation of the beta  
grain. (X150)

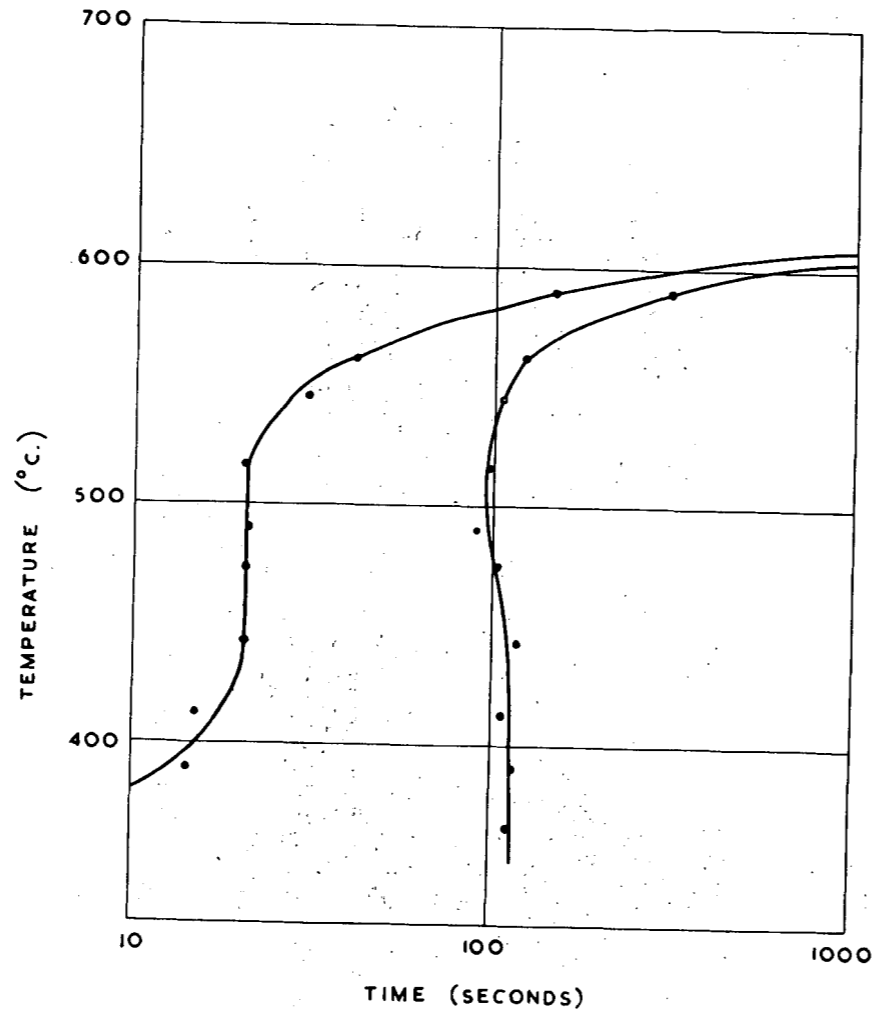


FIG. 21  
 THE T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % MOLYBDENUM.

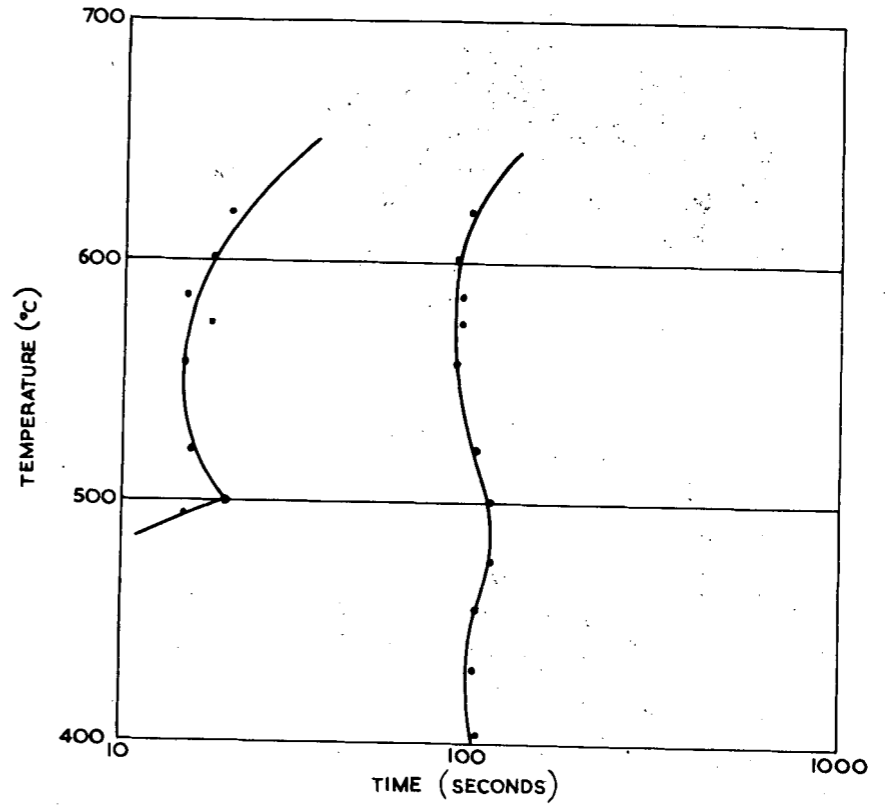


FIG. 22  
 THE T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % TITANIUM.





Fig. 19a.

Uranium + 1/2 at.% Mo. Isothermally transformed at 600°C. Etched. (X550)



Fig. 19b.

Same alloy. Isothermally transformed at 550°C. Etched. (X550)

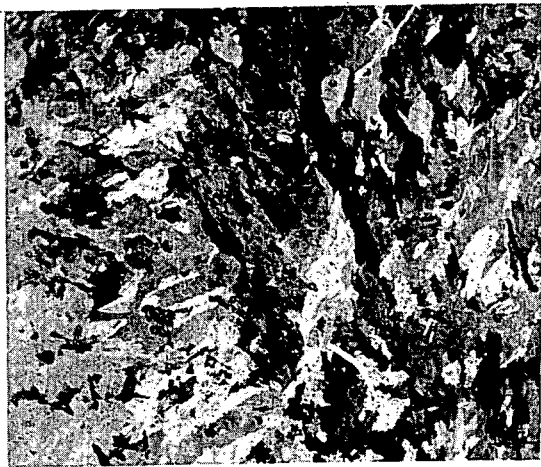


Fig. 23.

Uranium + 1 at.% V, gamma-quenched. Etched electrolytically. (X 35)



Fig. 24.

Uranium + 1 at.% V, slowly cooled from 900°C. Etched electrolytically. (X300)

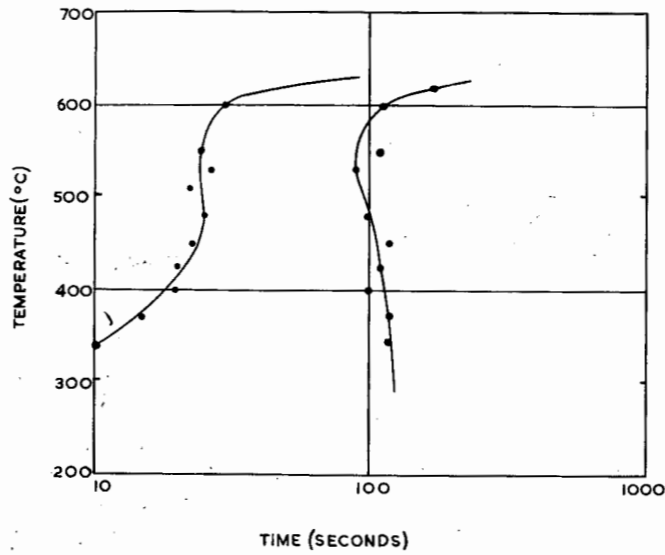


FIG. 26(a)

T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{8}$  AT. % MOLYBDENUM  
+  $\frac{1}{8}$  AT. % CHROMIUM

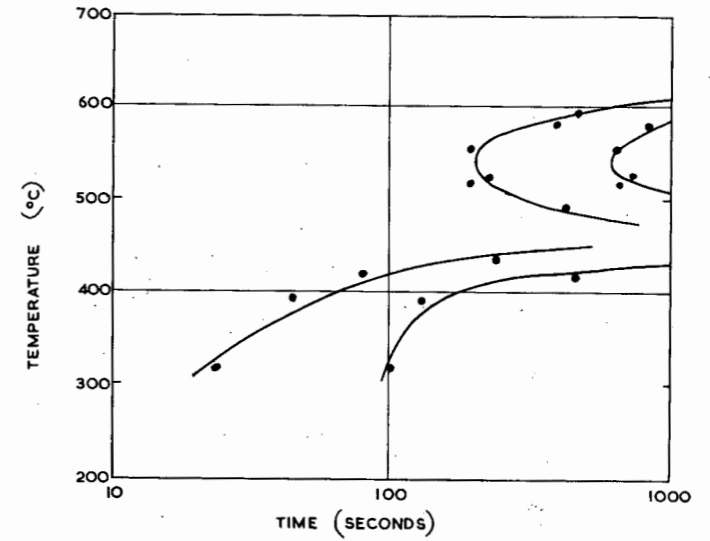


FIG. 26(b)

THE T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{4}$  AT. % MOLYBDENUM  
+  $\frac{3}{8}$  AT. % CHROMIUM.

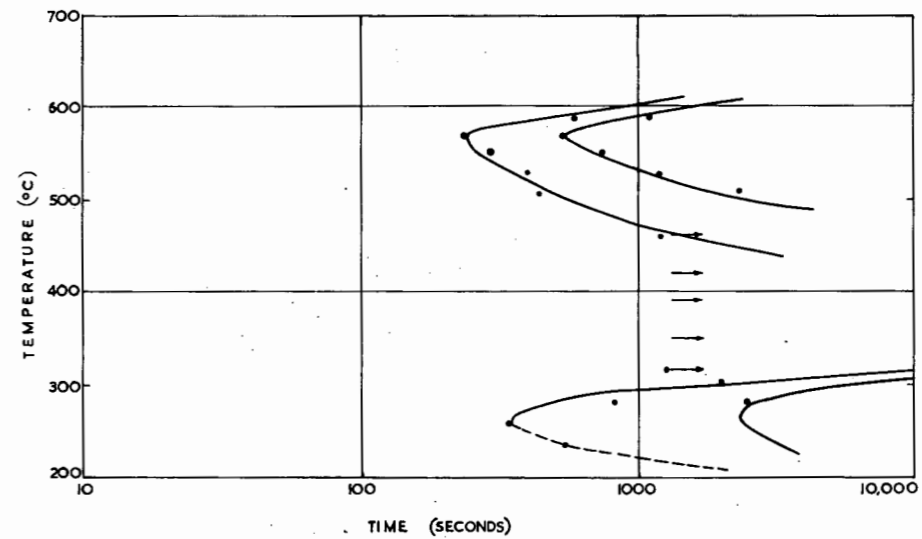


FIG. 26(c) T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % MOLYBDENUM  
+  $\frac{1}{2}$  AT. % CHROMIUM.

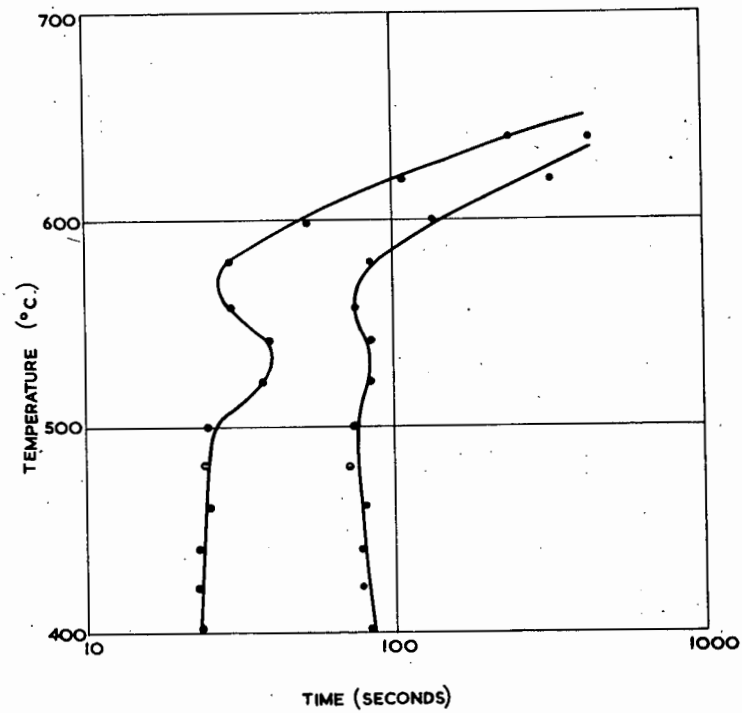


FIG. 25 THE T.T.T. DIAGRAM OF URANIUM + 2 AT. % VANADIUM

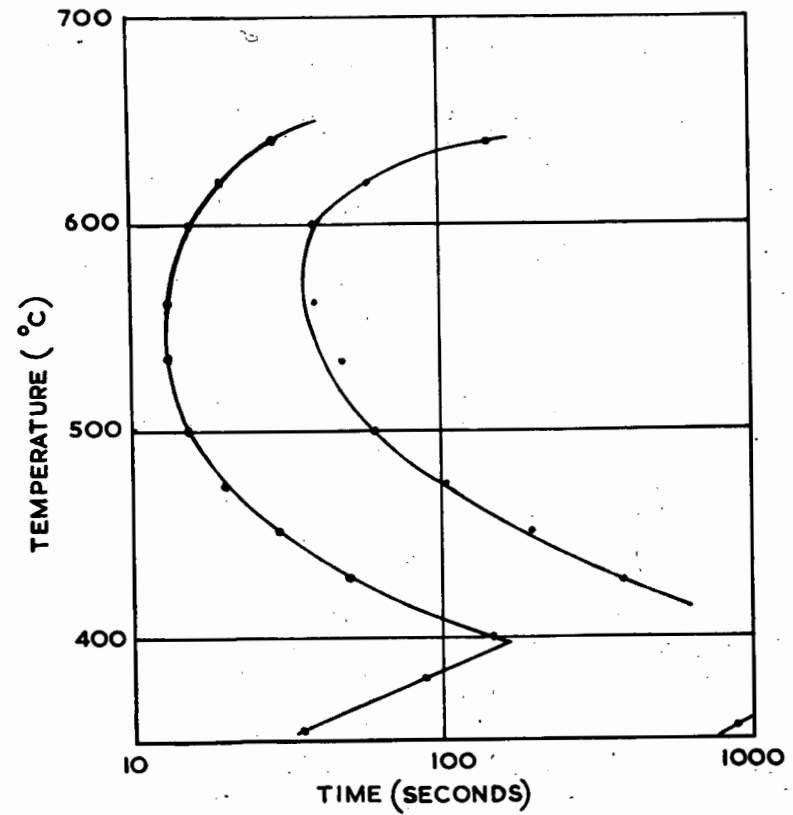


FIG. 28 T.T.T. DIAGRAM OF URANIUM +  $\frac{1}{2}$  AT. % CHROMIUM + 0.2 AT. % IRON.

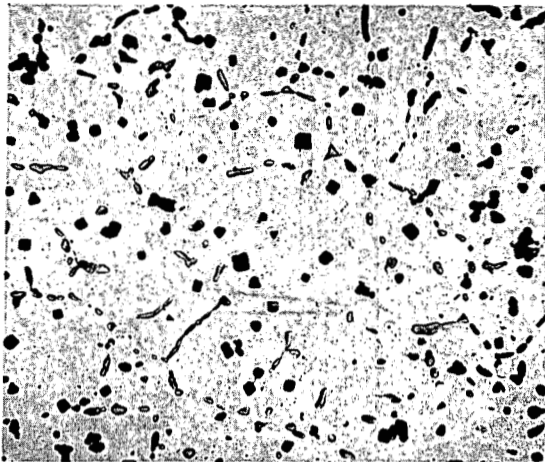


Fig. 27.

Uranium + 1/2 at. % Cr + 0.85 at. % Fe, transformed at 500°C. Etched in nitric-citric acid. (X400)

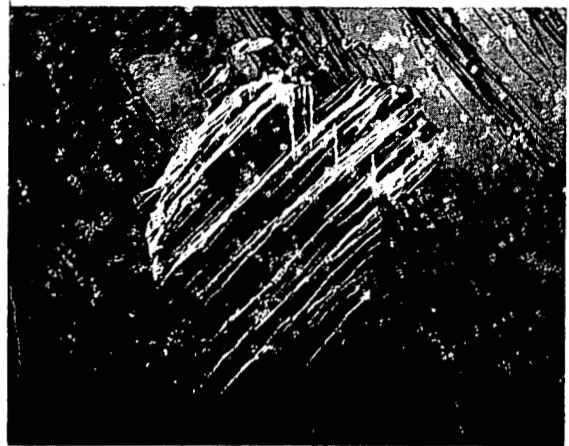


Fig. 29a.

Incomplete transformation after 5 minutes at 280°C. Alpha phase forming along one major direction. (X250)

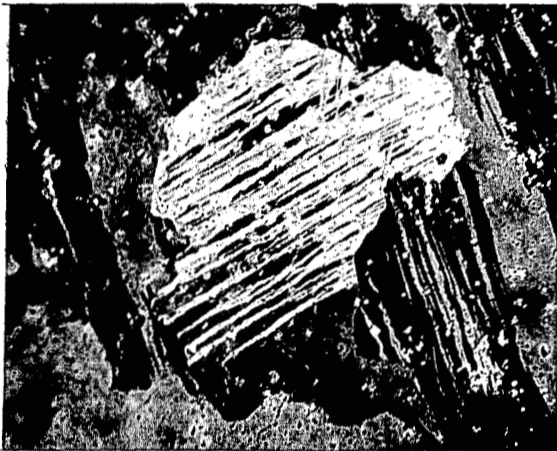


Fig. 29b.

After 10 minutes at 280°C. Transformation almost complete.

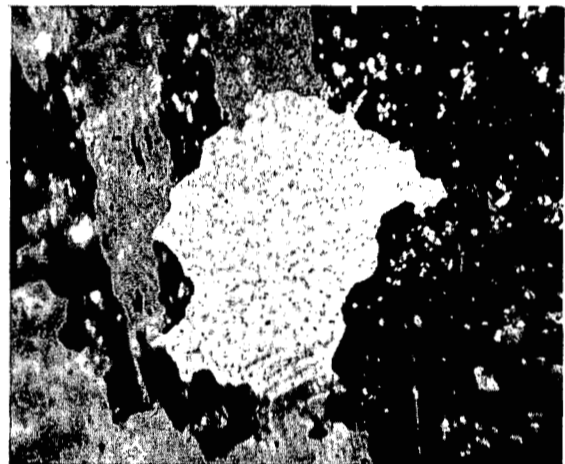


Fig. 29c.

After 25 minutes at 280°C. Transformation complete.