CEA 1750 - ACCARY A., CAILLAT R.

SINTERING WITH A CHEMICAL REACTION AS APPLIED TO URANIUM
MONOCARBIDE (1960)

Summary. - The present paper provides a survey of different inves-
tigations whose aim was the preparation and fabrication of uranium
monocarbide for nuclear use.
       If a chemical reaction takes place in the sample during the
sintering operation, it may be expected that the atom rearrangements
involved in this reaction should favour the sintering process and
thereby lower the temperature needed to yield a body of a given density
With this hypothesis in mind, the following methods have been studied :
       - Sintering of U-C mixtures
       - Sintering of UO_2-C mixtures
       - Hot pressing of U-C mixtures
       - Extrusion of U-C mixtures.
       To generalize our result, it could be said that a chemical
reaction does not lead to high densification, if one depends on a
simple contact between discrete particles.
       On the contrary, a chemical reaction can help sintering
if, as our hot pressing experiments show, the densification can be
achieved prior to the reaction.

CEA 1750 - ACCARY A , CAILLAT R.

FRITTAGE-REACTION DANS LE CAS DU MONOCARBURE D'URANIUM (1960).

Sommaire. - Le présent article résume les études faites pour le compte
du Commissariat à l'Energie Atomique dans le but de préparer du mono-
carbure d'uranium pour usage nucléaire.
       Si, en même temps que l'on fritte une poudre, celle-ci est le
siège d'une réaction chimique, on peut s'attendre à ce que le réarran-
gement atomique d'une réaction chimique favorise le frittage et, ainsi
abaisse la température de travail nécessaire pour obtenir une densité
donnée.
       Nous avons étudié les méthodes suivantes :
       - frittage des mélanges U-C
       - frittage des mélanges UO_2-C
       - frittage sous charge des mélanges U-C
       - filage des mélanges U-C.
       Nos résultats montrent qu'une réaction chimique en cours de
frittage ne conduit pas à un produit de haute densité si on opère sur
un mélange de poudres. Par centre, elle permet d'atteindre de hautes
densités si la densification peut être obtenue avant la réaction
chimique.

SINTERING WITH A CHEMICAL REACTION

AS APPLIED TO URANIUM MONOCARBIDE

par

A. ACCARY et R. CAILLAT

Rapport C E A N° **1750**

Service de Chimie des Solides
Section des Combustibles Céramiques

SINTERING WITH A CHEMICAL REACTION

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A. ACCARY, R. CAILLAT

— 1960 —

SINTERING WITH A CHEMICAL REACTION

AS APPLIED TO URANIUM MONOCARBIDE-

By :

- A. ACCARY
- R. CAILLAT

after experimental studies conducted at :

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  Département de Métallurgie,
  Service de Chimie des Solides,
  by =

  - J. DUBUISSON
  - H. HOUYVET
  - E. LE BOULBIN
  - R. LUCAS
  - C. MORANVILLE

- The Société d'Electro-Chimie, d'Electro-
  Métallurgie et des Aciéries Electriques
  d'Ugine,
  by =

  - E. DIOT
  - R. MAYER
  - P. POTET

- The Tréfileries et Laminoirs du Havre,
  under the direction of J. HERENGUEL,
  by =

  - J. BOGHEN
  - D. WHITWHAM.

SINTERING WITH A CHEMICAL REACTION

AS APPLIED TO URANIUM MONOCARBIDE.

The present paper provides a survey of different investigations carried out for the Commissariat à l'Energie Atomique (Département de Métallurgie, Service de Chimie des Solides).

Their aim was the preparation and fabrication of uranium monocarbide for nuclear use.

The required properties for the product were :

- a high density approaching the theoretical value ;
- a chemical composition as close as possible to the stoechiometric UC ;
- a good mechanical and chemical stability ;
- a cost as low as possible.

Two different types of methods have been considered for such a production :

   - Melting and casting :
   - Sintering.

The first method presents the great technical difficulty of handling the molten carbide at very high temperatures. In practice, graphite may be used but presents a difficult problem for control of the carbon pick up from the mold.

The investigations conducted so far at the C.E.A., as well as else where, do not seem to have [1] [2] completly solved this problem ; micrographs of the product always disclose traces of either free uranium or dicarbide in the mass of monocarbide (fig. 1).

However, carbon pick up can be avoided if sintering is employed.

Sintered products in UC may be obtained by starting from UC powder. This powder is made by carburizing reduction of an uranium oxide and leads to a clinker which is then ground. The powder is then compacted and sintered.

Unfortunately, this method leads to low-density products (generally less than 80 pour cent [3] of the theoretical density). It also requires a high working temperature and the many technical difficulties result in a high cost.

Because of these difficulties, inherent in melting-casting and carbide sintering, it was decided to investigate low temperature sintering methods.

If a chemical reaction takes place in the sample during the sintering operation, it may be expected that the atom rearrangements involved in this reaction should favour the sintering process and thereby lower the temperature needed to yield a body of a given density. The following methods have been studied :

- Sintering of U-C mixtures
- Sintering of UO_2-C mixtures
- Hot pressing of U-C mixtures
- Extrusion of U-C mixtures

I - SINTERING OF URANIUM CARBON MIXTURES - [1]

In a first set of experiments, the most conventional method was used. It consisted in cold pressing a mixture of powders of uranium and carbon. The pressed pellets were then sintered at a temperature lower than the melting point of uranium (1130 °C).

Different uranium and carbon powders were used and the influence of the cold compacting pressure, sintering temperature and sintering time were investigated.

A - Influence of cold compacting pressure -

Figure II shows the variation of "green density" (curve A) and of the sinter density (curve B) as a fonction of the cold compacting pressure.

It may be noted that the curves A and B intersect. Therefore sintering results in a densification of the green pellets for cold compacting pressures lower than the critical value corresponding to this intersection, and in a volume increase for higher pressures. This important fact has been exploited in the "thermal" sintering described later.

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[1] This experimental work was carried out by R. MEYER, P. POTET and E. DIOT.

It should also be noted that the points corresponding to durations from 2 hours to 13 1/2 hours fall on very much the same curve.

Likewise sintering temperatures ranging from 1.000 °C to 1.125 °C lead practically to the same density for a given compacting pressure.

The curves of figure II were determined using an uranium powder prepared by decomposition of uranium hydride. This powder was caracterized by a very small particle size an a flake-like particle shape.

Figure III presents the same curves for two other powders :

1° A different batch of hydride decomposition powder. The curve C shows the variation of green density, whilst curve D shows the variation of sinter density.

2° A powder prepared by calcium reduction of uranium dioxide. This powder has a spherical particle shape with an average grain size of about 10 μ. Curve E reveals the variation of green density and curve F the sinter density.

Comparison of curves A and C on the one hand, and B and D on the other, demonstrates that the density of the green or of the sintered pellets does not depend only on the compacting pressure, even for a given type of powder.

Comparison of E an F with the other curves of figure III shows that for spherical particles, the green density is not as dependant on compacting pressure as it is in the case of flakelike particles, as might be expected from the general behaviour of powders.

A last fact which should be pointed out is the expansion taking place during sintering. This phenomenons is the very reverse of that usually occurring in single phase sintering. It is obviously connected with the chemical reaction between carbon and uranium.

B - Influence of sintering temperature -

For temperatures ranging from 900 °C to 1.125 °C, the density of the sintered pellets depends very little on the sintering temperature.

Nevertheless, as pictured by figure IV, the reaction is more complete at higher temperatures for a given reaction time.

C - Influence of sintering time -

Figures II and III showed that the sintering time has little effect on the final density. But, the sintering time is not without effect on the uranium-carbon reaction.

Figure V shows that, as the sintering time is prolonged, the reaction uranium-carbon approaches completion for all the experimental conditions studied ; dispersion in the fraction of combined carbon is thereby reduced. At the same time, the maximum value of combined carbon increases slightly.

D - Chemical composition -

X ray analysis revealed the formation of the compound UC only, with no UC_2 nor $U_2 \cdot C_3$.

On the other hand, the impurities, mainly UO_2 and UN, present in the uranium powder although apparent as inclusions in the

structure of sintered pure uranium, do not appear in the sintered monocarbide. Since the reaction temperature is not high enough to bring about their reduction to metal, it seems reasonable to assume the formation of a solid solution of UX in which X can be C, N or O.

E - Purely thermal sintering -

The main drawback of sintering, as described above, arises from the difficulties involved in pressing bodies the diameter of which is small compared to their length : the preparation of slugs or rods then becomes impossible.

Meanwhile figure II shows that, although the green density is greatly improved by increased compacting pressure, the sinter density does not improve to the same extend.

These facts suggest that it should nevertheless be possible, under suitable conditions, to prepare slugs with a density of the order of 10 g/cm3, using purely thermal sintering.

Such a result has been achieved [2] by using a vertical cylindrical die. The bottom end is closed and the die is filled with a mixture of uranium and graphite powders. The filling was carried out layer by layer with gentle tamping. The top end is closed and the die is then placed in a vacuum furnace in which the temperature is slowby raised to 1.200 °C.

The rate of heating has a critical effect on the density of the sintered slug produced. If the heating rate is too high, the reaction between the uranium and the carbon becomes too rapid and the final density is low (at even higher rates of heating the compacted powder can even desintegrate without any sintering).

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[2]
   Study conducted by M. Dubuisson, C.E.A. - Département de Métallurgie
   Service de Chimie des Solides - .

This method yield slugs with a density of about 7-13 g/cm3 depending on the uranium powder employed and the percentage of graphite. Since, practically no pressure has been applied for compacting, the volume change accompanying the reaction is a contraction and, in particular, an uniform contraction which maintains a perfectly cylindrical slug. This method could probably be extended to bodies of any shape.

II - SINTERING OF UO_2 - GRAPHITE MIXTURES.-

In this method, a compacted mixture of UO_2 and graphite is heated. The reaction.

$$UO_2 + 3\ C \longrightarrow UC + 2\ CO$$
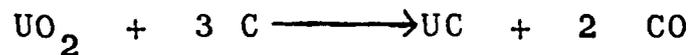
takes places and the final product is UC.

In our experiments, a vacuum induction furnace was used. The powders, after mixing, were cold pressed, using a binder, and the resultant pellets placed in the furnace where the reduction was carried out.

The reduction temperatures used ranged from 1.500 °C to 1.800 °C and the heating time from 1 to 3 hours.

The densities of the sintered bodies obtained those ranged from 7 g/cm3 to 10 g/cm3 : this compares with 7 to 13 g/cm3 for the sintering of uranium-graphite mixtures.

Over 1.500 °C, the completness of the reduction did not depend very much upon either the temperature or the time of heating.

The percentage of reacted oxygen taken as a measure of this completness ranged from about 93 pour cent at 1.500 °C to about 98 pour cent at 1.800 °C, and was practically the same for times from 1/4 to 2 hours.

The purity of the carbide product was not always as good as that prepared from uranium and graphite ; some UC_2 appeared in the sintered pellets, due probably to the higher temperature employed.

III - HOT PRESSING OF URANIUM GRAPHITE MIXTURES -

The hot pressing method was applied to mixtures of uranium and graphite powders mixed in the stoechiometric ratio corresponding to UC [3] [4] .

The pressing was performed in a double punch floating die : the inner diameter of the die being 30 mm. and the height 100 mm. The die proper was contained in a molybdenum cylinder, the role of which . was to withstand the lateral pressure. The pressure used was 250-300 Kg/cm^2, corresponding to the strengh limit of the graphite used for the punches.

The working temperatures ranged from 770 °C to 1.000 °C. For temperatures lower than 850 °C, the pellets after sintering had no mechanical strength and desintegrated after a few hours exposure to the atmosphere. This indicates that practically no sintering had occured at these low temperatures.

The mechanism of sintering can be more thoroughly followed by studying the volume change of the pellet during sintering,

3) Experimental work by J. DUBUISSON, A. HOUYVET, E. LE.BOULBIN, R. LUCAS, C. MORANVILLE - C.E.A. Département de Métallurgie, Service de Chimie des Solides -.

4) GENEVA Cont- (1958) - A/Conf./15/P/1162 -

the volume change being measured as a function of the temperature (figure VI A). Alternativly, the volume change per degree (°C) can be studied (figure VII A).

The volume change per degree (°C) increases with temperature up to a temperature very close to the α/β transformation of uranium, then falls rapidly to a much lower but steady value until a temperature very close to the β/γ transformation is reached. At this temperature, the volume change per degree (°C) increases brusquely, but thereafter falls towards zero as the maximum density is approached.

The forgoing changes in the rate of volume change per degree (°C) can be explained if it is assumed that they correspond to a plastic deformation of the uranium, since, for a given applied pressure, it is known that α uranium is more plastic than β uranium and γ uranium more plastic than α and β uranium.

This point of view is confirmed if the curves VI A and VII are compared with the curves VI B and VII B corresponding to the same experiment made on pure uranium. The curves for pure uranium have the same shape as the curves for uranium graphite mixtures : this demonstrates that the basic mechanism involved in these volume changes is the plastic deformation of the uranium. The differences between the two sets of curves can be explained as follows.

In the α phase region where the volume change for mixturesis faster than for pure uranium, the difference is attributed to the lubricant action of graphite.

In the γ phase region where the volume change is faster for pure uranium, the difference can be ascribed to the start of

reaction in the uranium-carbon mixtures producing a framework of UC particles or "bridges" which must be broken down in order to continued the plastic deformation.

The comparison of curves for mixtures and for pure uranium gives a rough estimate of the temperature at which the reaction begins. This temperature is taken as that at which the rate of volume change starts to fall as a result of carbide formation (i.e approximately the temperature for which the velocity is the same for pure uranium and mixtures). From figure VII it can be estimated at 440-450 °C.

Roughly speaking the hot pressing of uranium involves two stages :

A first stage corresponds to compaction of the uranium, in which the unreacted or partially reacted graphite is embedded. At the end of this stage, the density of the body is very neare to the calculated density of the uranium + graphite mixture.

Then in a second stage the uranium and the graphite react to form the monocarbide. Since, the theoretical volume change due to the reaction is a very slight increase and since no porosity formation occurs during the diffusion of carbon in uranium or mono-carbide, the reaction brings about a complementary densification. The final density reaches about 98 pour cent of the theoretical one.

The product obtained by this process is UC free of UC_2. If there is any excess of carbon, it remains as free graphite.

It should also be noted that the oxygen and nitrogen initially present in the uranium powder and which give rise in sintered pure uranium to a grain boundary precipitate do not appear in the UC structure.

As the temperature is not high enough to provoke the reduction of UO_2 and UN to UC, it is suggested that these impurities pass into solution in the U.C.

IV - EXTRUSION OF URANIUM GRAPHITE [5] -

A few runs have been made, using sinter-extrusion of a mixture of uranium and graphite powders contained in a copper sheath, pre-heated to 800 °C. The densification achieved was only partial, but the degree of reaction was greater than might be expected from the very short time at temperature.

This effect is obviously connected with the high pressure applied and the important deformation of the compact during the extrusion process.

Such a deformation should favor the reaction in various ways.

- First, by assuring a very close contact between metal and graphite, the oxide film on the uranium being away by friction.

- Secondly, by continual renewing of the reacting surfaces during the plastic deformation of the body.

Finally, the heat produced by the plastic deformation may well increase the velocity of the carburization reaction.

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[5]

These experiments have been conducted at the T.L.H. under the direction of J. HERENGUEL, by J. BOGHEN and D. WHITWHAM.

V - DISCUSSION -

Examination of our results shows that if a mixture of uranium and graphite is reacted, the volume change may be :

- A densification, in the case of purely thermal sintering ;
- An expansion, in the case of cold pressing and sintering ;
- Practically no volume change, in the case of hot pressing, if, in this case, it is assumed that the densifiaction is due to plastic deformation of uranium.

In the case of carburizing reduction, the volume change is also an expansion.

To generalize our result, it could be said that a chemical reaction does not lead to high densification, if one depends on a simple contact between discrete particles.

Our experiments agree with the results published by Rhines and Meussner 5 , and their theory of reaction at "Strategic points". When the reaction takes place between discrete particles, it does so in a limited number of points, producing a framework of carbide which owing to its very high melting temperature does not permit any appreciable sintering at the temperatures used in our experiments and thus "cripples" the densification.

On the contrary, a chemical reaction can help sintering
if, as our hot pressing experiments show, the densification can
be achieved prior to the reaction.

This method offers considerable promise for many other
cases, such as a carbide, boride, nitride, fabrication, etc...
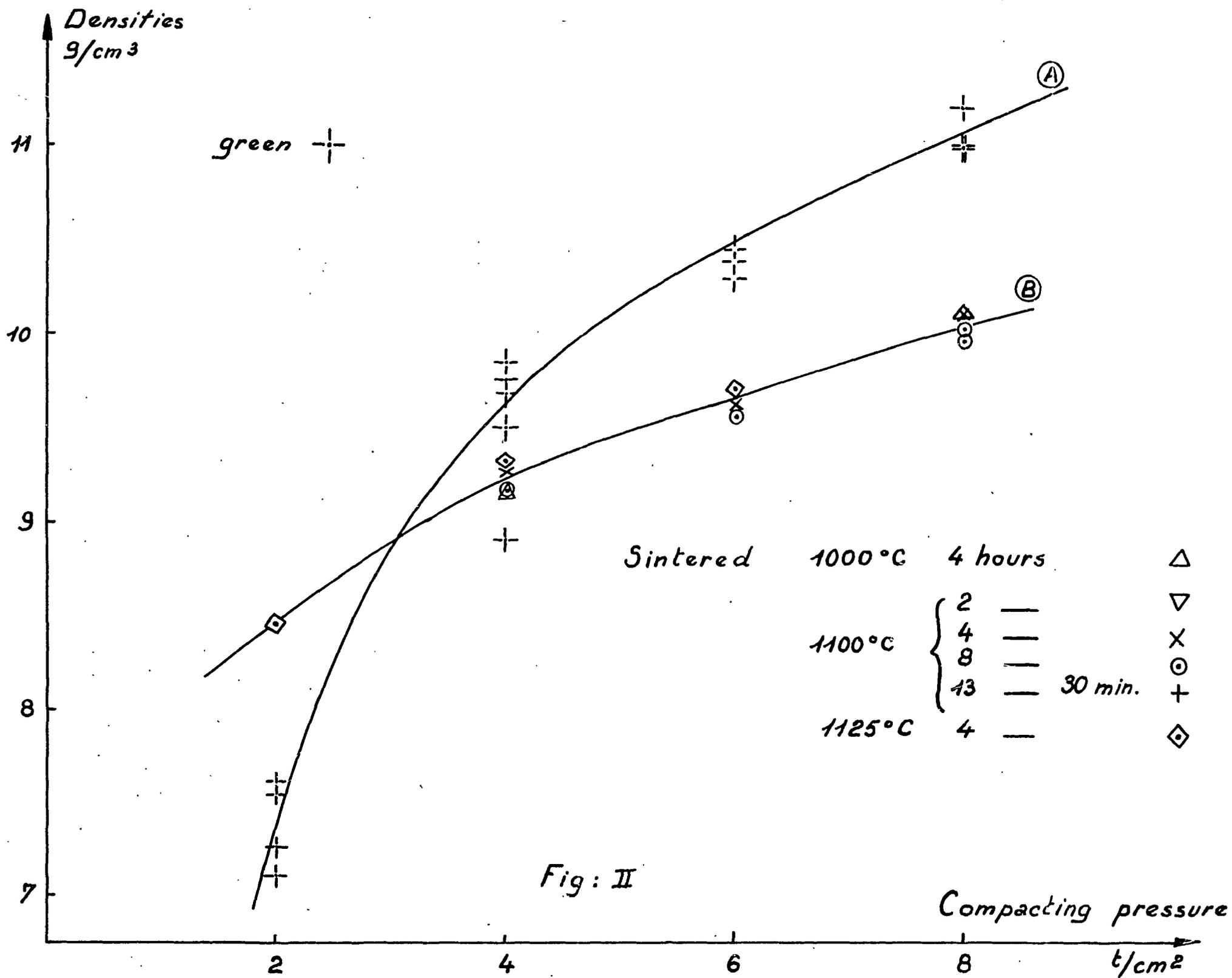starting from the metal + metalloïd mixture.
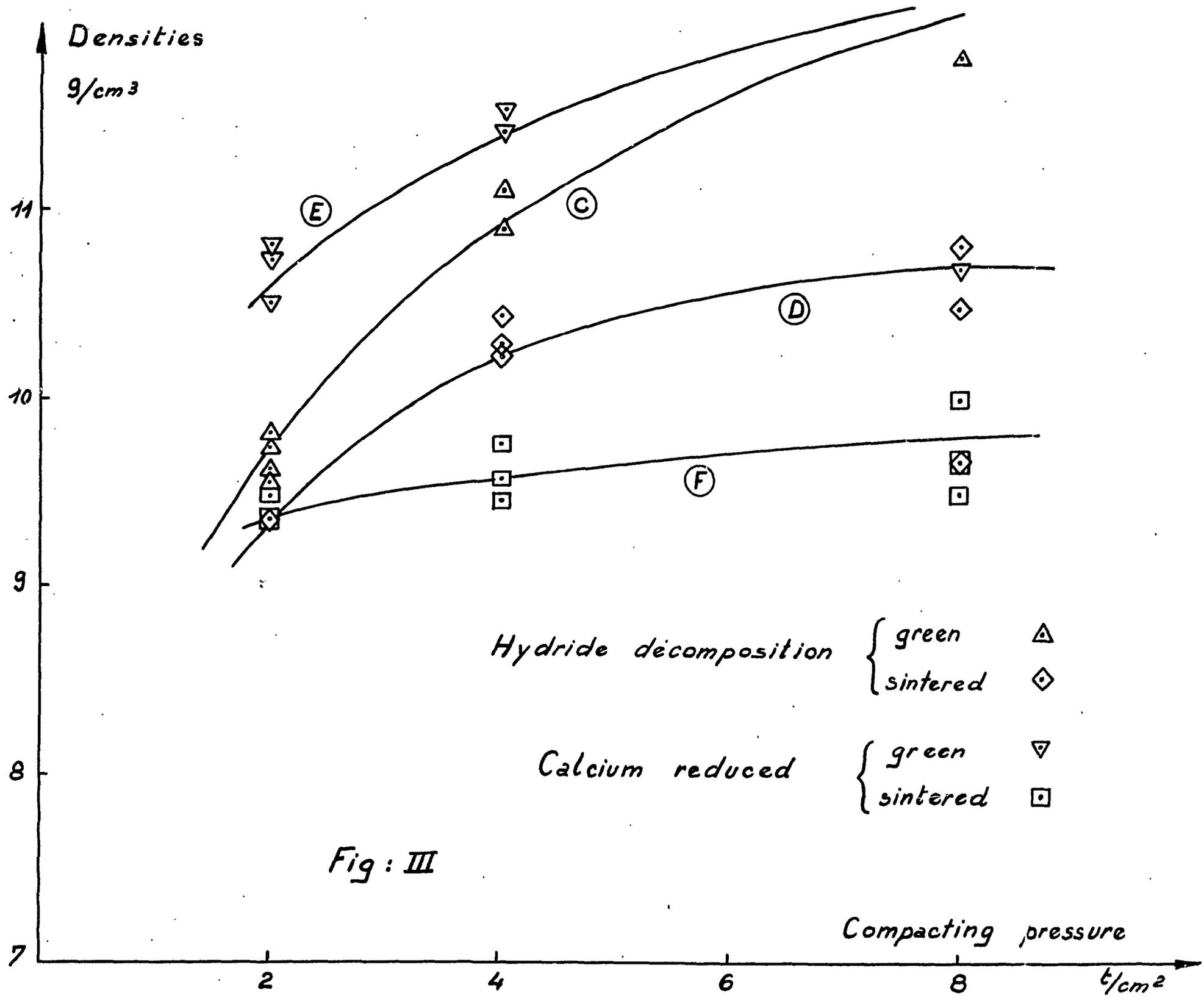
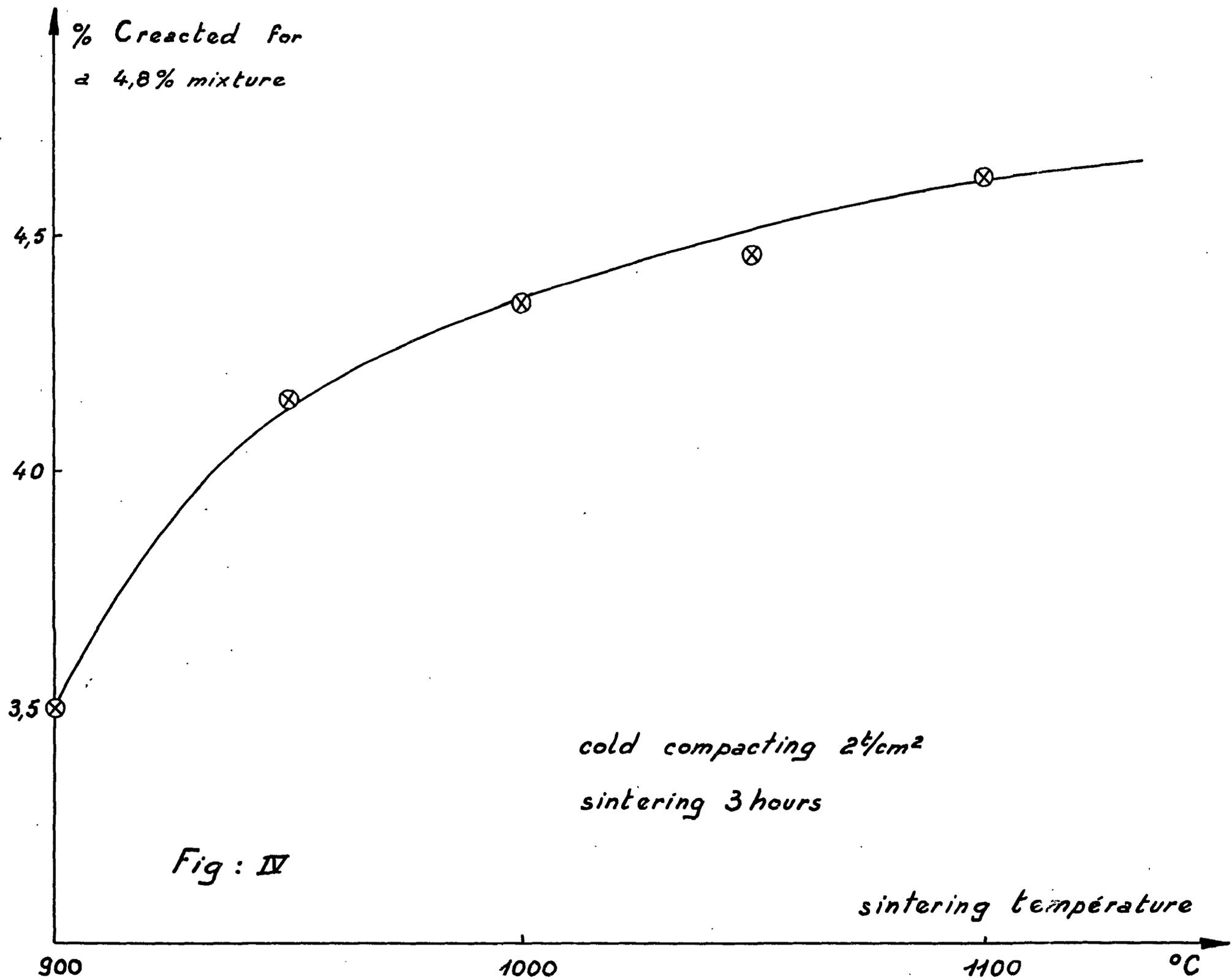Manuscrit reçu le 30.9.60.

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Fig. I - Micrograph of uranium monocarbide   X 300 -
disclosing traces of dicarbide
(Wiedmannstäten structure)
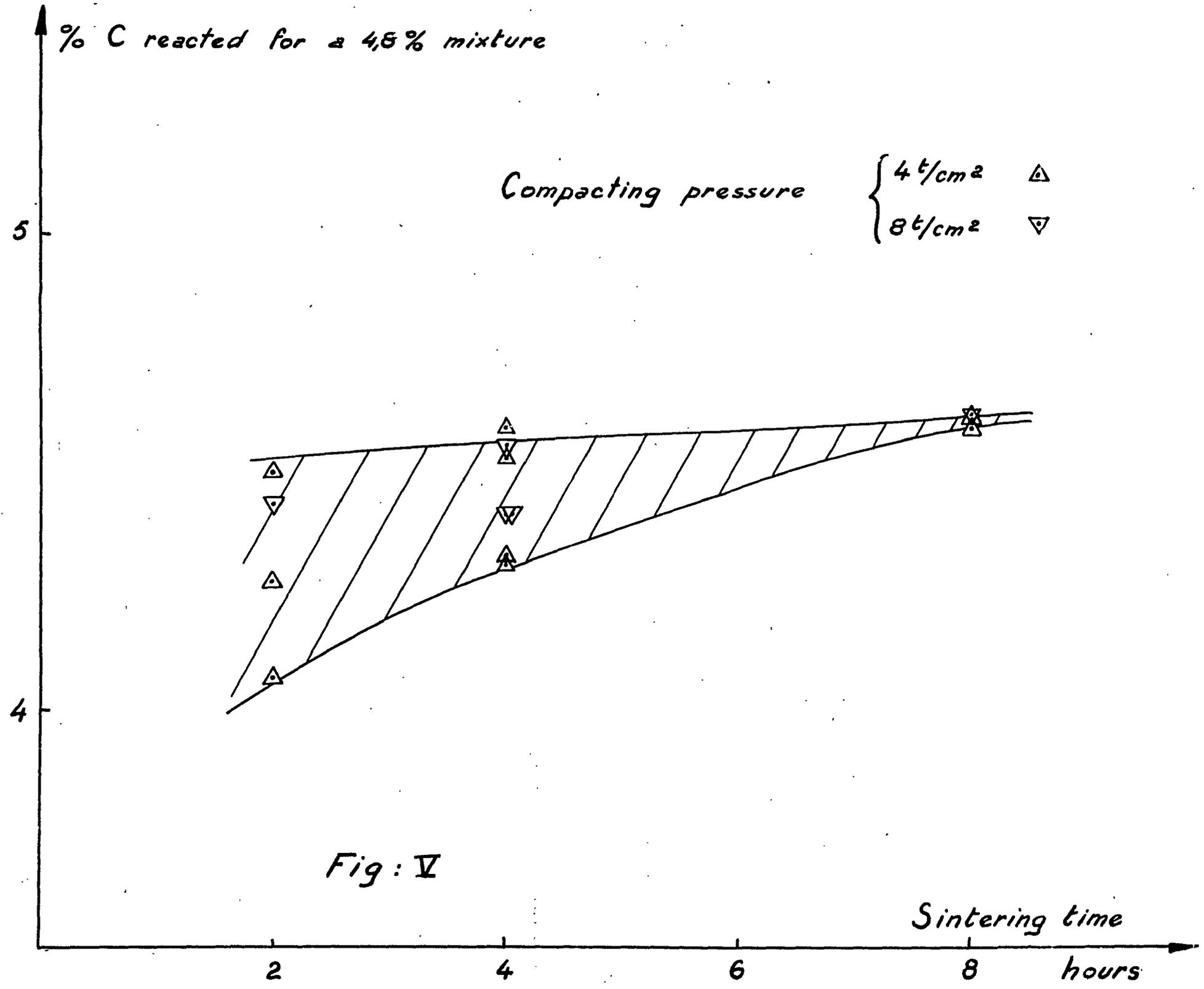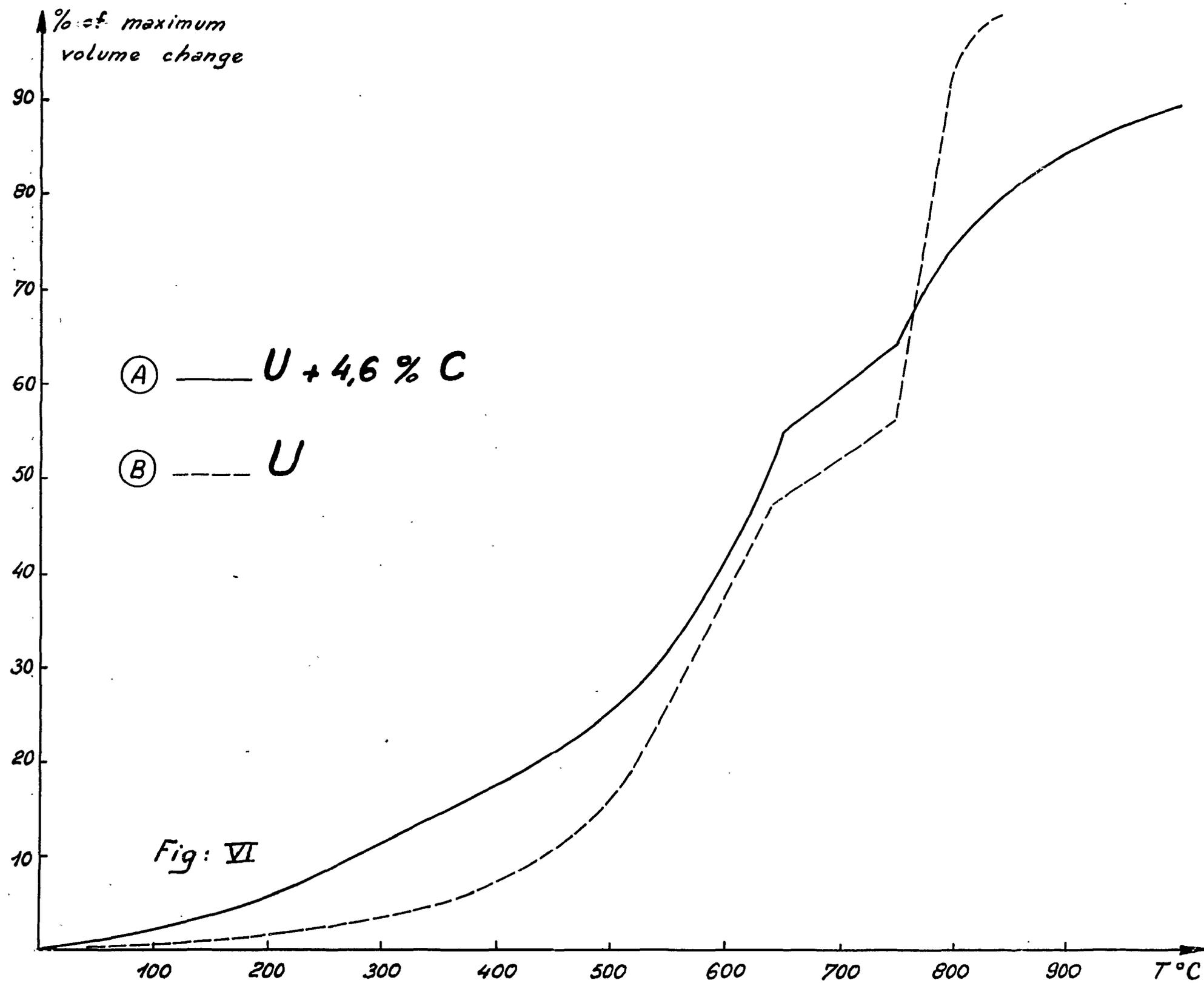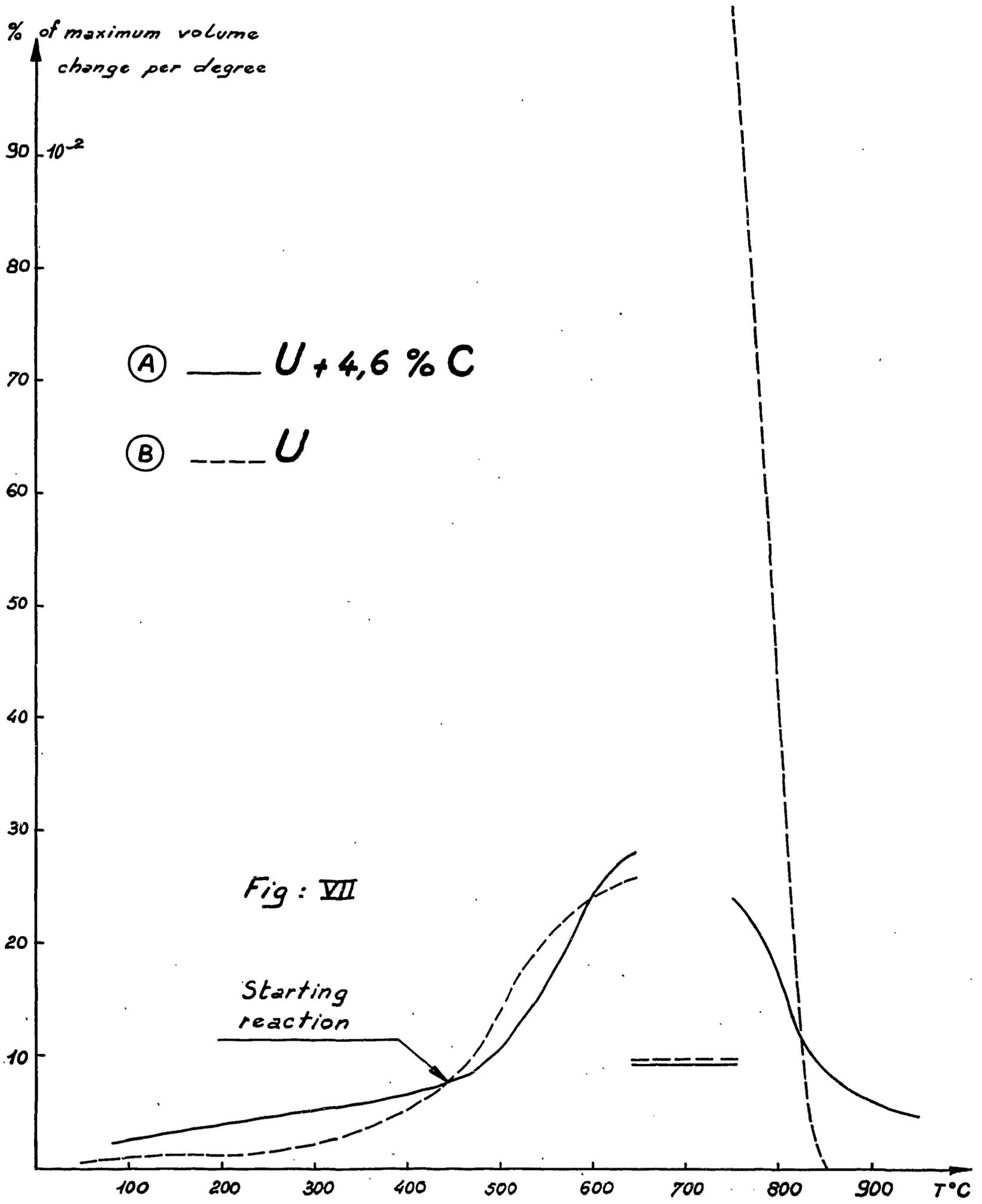
Fig: II

Fig : III

Densities g/cm³ — Compacting pressure (t/cm²)

Hydride decomposition { green △, sintered ◇ }

Calcium reduced { green ▽, sintered ⊡ }

Fig : IV

% Creacted for a 4,8% mixture

cold compacting 2t/cm²
sintering 3 hours

sintering température

Fig : V

Fig: VI

% of maximum volume change per degree

90 ⎯ 10^{-2}

Ⓐ ⎯⎯ $U + 4,6\ \%\ C$

Ⓑ ⎯⎯⎯ U

Fig : VII

Starting reaction

$T°C$

FIN