



STUDIECENTRUM VOOR KERNENERGIE

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## CEN/SCK ACTIVITIES ON CERAMICS

A.J. FLIPOT

October 1984

A.J. FLIPOT  
BLG 572 (Oct. 1984)

#### CEN/SCK ACTIVITIES ON CERAMICS

Summary. - This report describes the technical experience CEN/SCK has developed in close collaboration with the Belgian nuclear industry, the recent developments carried out in the framework of a study on ceramic breeder materials for fusion reactors and the research on fabrication and characterization of advanced technical ceramics such as, for instance, silicon nitride or ceramics for heat exchangers.

The experience in the field of nuclear fuels covers oxides and carbides, pelleted and vibrocompacted fuels. Some important aspects such as homogeneity of the mixed fuel and diametral tolerances of the pellets are discussed.

An original method for preparing sinterable lithium metasilicate is described. It is essentially based on the formation of an intermediate phase the existence of which has been discovered during this study. This phase which is formed around 430°C is easily transformed into metasilicate by calcining it under wet air. The resulting metasilicate is high sinterable and suits perfectly to the fabrication of high-density pellets by cold compaction and sintering.

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Résumé. - Ce rapport décrit l'expérience technique que le CEN/SCK a acquise en étroite collaboration avec l'industrie nucléaire belge, les récents développements effectués dans le cadre d'une étude sur les céramiques tritigènes pour les réacteurs à fusion et les recherches de fabrication et de caractérisation de céramiques techniques avancées comme, par exemple, le nitrure de silicium ou des céramiques pour échangeurs de chaleur.

L'expérience acquise dans le domaine des combustibles nucléaires couvre les oxydes et les carbures, les combustibles à pastilles et les vibrés. Quelques aspects importants tels que l'homogénéité du combustible mixte et les tolérances diamétrales des pastilles sont discutés.

Une méthode originale de fabrication de métasilicate de lithium fritttable est décrite. Elle est essentiellement basée sur la formation d'une phase intermédiaire dont l'existence a été découverte à l'occasion de cette étude. Cette phase qui se forme vers 430°C se transforme facilement en métasilicate par calcination sous air humide. Ce métasilicate de lithium est très fritttable et convient parfaitement pour la fabrication de pastilles denses par pastillage à froid et frittage.

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#### SCK/CEN ACTIVITIES ON CERAMICS

Samenvatting. - Dit rapport beschrijft de technische ervaring die het SCK/CEN verworven heeft in nauwe samenwerking met de Belgische kernindustrie, de recente ontwikkelingen in het raam van een studie over keramische materialen voor het kweken van tritium in fusiereactoren en het onderzoek over fabricage en karakterisering van gevorderde technische keramieken zoals siliciumnitride of keramische materialen voor warmtewisselaars.

De ervaring op het gebied van kernspijlstoffen betreft oxyden en kribden, tabletten en vibro-gecompacteerde spijlstoffen. Enkele belangrijke aspecten zoals de homogeniteit van mengspijlstoffen en de tolerantie op de diameter worden besproken.

Een originele metode voor de bereiding van sinterbaar lithiummetasilikaat wordt beschreven. De metode is in essentie gebaseerd op de vorming van een overgangsfaze, waarvan het bestaan in de loop van het onderzoek is ontdekt. Deze faze wordt gevormd rond 430°C en is gemakkelijk om te zetten tot metasilikaat door calcinatie onder vochtige lucht. Het bekomen metasilikaat is zeer goed sinterbaar en leent zich uitstekend voor de fabricage van tabletten met hoge dichtheid via koudpersen en sinteren.

The silicon nitride study covers the following shape forming techniques: slip casting, injection molding, extrusion and hipping. The bodies are prepared from silicon nitride powders (SSN) or from silicon powders which are nitrated later on (RBSN). This study is performed in a computerized thermobalance, which makes, for instance, possible to pilot the furnace in such a way that the weight of the compact increases linearly with time.

L'étude du nitrure de silicium couvre les méthodes de mise en forme suivantes: moulage en barbotine, moulage par injection, extrusion et compression isostatique à chaud. Ces pièces sont réalisées à partir de poudres de nitrure de silicium (SSN) ou à partir de poudres de silicium puis nitrurées (RBSN). Cette étude est réalisée à l'aide d'une thermobalance couplée à un ordinateur, ce qui permet, par exemple, de nitrurer à vitesse constante.

De studie op siliciumnitride omvat de volgende vormgevingstechnieken: slibgieten, spuitgieten, extrusie en HIPpen. Deze stukken worden gevormd uitgaande van siliciumnitridepoeder (SSN) of van siliciumpoeder dat genitreerd wordt (RBSN). Dit onderzoek wordt uitgevoerd met een computergestuurde termobalans waardoor onder meer met konstante snelheid kan genitreerd worden.

# **CEN/SCK ACTIVITIES ON CERAMICS**

**A.J. FLIPOT**

**Seminar on  
CERAMICS FOR THE FUTURE  
Mol, SCK/CEN - 17/10/1984  
and on  
NEAR NET SHAPE FORMING  
TECHNIQUES OF METALLIC COMPONENTS  
Leuven, K.U.L. 18/10/1984**

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As you probably already know, we have been studied, for more than twenty years, the fabrication and characterization of nuclear fuels for thermal, fast and high-temperature reactors.

This has led us

- to study the fabrication processes of uranium and uranium-plutonium oxide and carbide pellets [1] ;
- to develop fuel rod fabrication techniques [2] and a resistance welding process [3].

These developments gave us the opportunity to collaborate with the Belgian nuclear industry.

The first uranium oxide pellets doped with dysprosium oxide [4] have already been studied in co-operation with M.M.N. (Métallurgie et Mécanique Nucléaires) in the sixties. The industrial finality of our activities increased with time. Our research in the field of mixed uranium and plutonium oxides is a striking example : these developments have been carried out in real symbiosis with Belgonucléaire. Thanks to the common efforts of CEN/SCK and Belgonucléaire, a plutonium industry has been set up in Belgium. Our common knowledge indeed allowed Belgonucléaire to construct on our site a semi-pilot plant for the fabrication of thermal reactor fuels. Later on a plutonium fuel fabrication plant was built at Dessel for thermal and fast reactor

fuels. Moreover, this close co-operation was put in a concrete form by the creation of a common research group constituted by both CEN/SCK and Belgonucléaire personnel. This group developed a fabrication process for mixed uranium-plutonium oxide pellets, used successfully by Belgonucléaire for the fabrication of fuel pins for the first SNR-300 reactor core, constructed at Kalkar in the Federal Republic of Germany. This industrial result represents more or less the issue of our research and co-operation with Belgonucléaire.

Presently, the prospects of the market for fast reactors, the knowledge acquired during the two last decades and the existing international agreements, do not justify the development of a new improved process in Belgium. For this reason, CEN/SCK has taken this opportunity to valorize its experience with nuclear ceramics and with the nuclear industry and to extend this knowledge to the broader field of high technology industrial ceramics, to be able to serve better a larger number of Belgian industries which are interested in this promising field.

This being said, I would like to comment on our activities by treating briefly four subjects :

1. nuclear fuel ;
2. lithium silicate ;
3. silicon nitride ;
4. ceramic heat exchangers.

#### Nuclear fuel

Through the twenty year study of nuclear ceramics, we have been familiarized to respect the four following criteria :

- chemical purity ;
- homogeneity ;
- dimensional precision ;
- control of the final density.

Chemical purity is required either for neutronic considerations or to avoid inner corrosion of the fuel cladding. Certain contaminations are limited to the fraction of a ppm, others to some tens of ppm ; this is for instance the case for the residual water content, which

is usually limited to 5 or 10 ppm ; this is also the case for the chlorine and fluorine contents, each being limited to 25 ppm.

Homogeneity of the fuel pellets is an other criterion to be met in view of avoiding any perturbation during reactor operation. A striking example is given by the fabrication of fuels with homogeneous burnable poisons. We had for instance to fabricate uranium oxide pellets containing 0.6 % homogeneously distributed dysprosium oxide. Macroscopic dysprosium variations, higher than 2 % relative, i.e. absolute deviations of 0.012 %, and the presence of any dysprosium rich particle [5] were unacceptable.

As shown in fig. 1, the problem could not be solved by simply mixing fine uranium oxide and dysprosium oxide powders, followed by high-temperature sintering. The diffusion rates are very low and microheterogeneities subsist. The dark areas are uranium oxide while the light ones represent dysprosium-rich particles measuring 20 to 25  $\mu\text{m}$ . To solve this problem we have consequently used diffusion promoters [4]. Fig. 2 shows that small additions of titanium oxide are very efficient : 300 ppm titanium oxide already yields a relatively very homogeneous fuel. The effect of titanium oxide and of alumina being cumulative, the effect of both additions allows to obtain a quasi uniform solid solution.

Dimensional precision of the sintered pellets has been one of our permanent concerns in order to be able to avoid grinding. We have developed a fabrication process for mixed uranium-plutonium oxide pellets for fast reactors which meets a tolerance of 50  $\mu\text{m}$  over a diameter of 6 mm. This process has been successfully industrialized by Belgonucléaire (Fig. 3).

When sintering of pellets to dimensions is required, it should be tried :

- to reduce the friction forces during pelletizing ;
- to use the most appropriate powders ;
- to sinter the pellets under very reproducible conditions by using a continuous sintering furnace.

We have been able to reduce the friction forces by :

- a judicious choice of the composition and the structure of the pelletizing dies based on friction coefficient measurements [6] ;
- an optimization of the lubrication of the pelletizing tools [7, 8].

We have established the importance of the good choice of the solid lubricant which will be used and of its physical characteristics. Zinc stearate is a good lubricant but all qualities of zinc stearate are not equivalent [9].

The granulometry of a lubricant constitutes a property which has to be taken into account when this lubricant has to be mixed with the powder to be compacted. We have also attempted direct lubrication of the compression tools in view of avoiding incorporation of a lubricant which has to be eliminated afterwards by dewaxing. This way, an original process [7] has been developed on a double-sided rotary-press [10], namely a high-capacity pelletizing press built up by two completely independent parts having each a filling shoe, compaction and injection stations (Fig. 4). Half of the machine is used for pelletizing a solid lubricant while the other half serves as production unit. Lubrication is realized by pelletizing cork granules mixed with lubricating powder. During compaction, a lubricant film deposits on the inner wall of the die and on the heads of the punches; at ejection, the lubricating pellet disaggregates again into granules as a result of the elasticity of the cork. These granules may be re-utilized and re-feed the filling shoe of the pelletizing press.

This process offers many advantages :

1. it is more efficient than the incorporation of the lubricant into the uranium oxide powder ;
2. it may be applied whatever be the shape and the dimensions of the pellets ;
3. its efficiency is not influenced by the powder granulometry.

As I just said, the powder characteristics [11] may influence the geometrical characteristics of the resulting pellets. For instance, the shape of the sinterability curve (i.e. the relation between green



densities and the sintered densities), controls the deformation and consequently the shape of the sintered pellets :

- when the part of the sinterability curve, which is actually used, is a straight line passing through the origin, the shrinkage due to sintering is independent of the density. In that case, any cylindrical green pellet will yield a cylindrical sintered pellet, i.e. theoretically without diabolos.
- the diabolos or barrel like shapes of the sintered pellets will be more pronounced if the sinterability curve deviates more from a straight line passing through the origin.

Control of the final density constitutes another problem to be resolved by the nuclear ceramist, because each reactor type has its specifications on the fuel density, the raw materials being what they are. Here also we have developed several processes in view of being able to fabricate low-density pellets starting from sinterable powders.

These processes are based on one of the following methods :

- the admixture of products decomposing at high temperature and leaving porosities [9];
- the use of de-activated granules [12, 13] ;
- the use of sintering inhibitors such as e.g. barium salts [9, 14] ;
- the addition of a certain quantity of finely milled rejected pellets. This allows to recycle the rejected pellets and to increase the fabrication output.

As you can see, ceramic nuclear fuel fabrication is an excellent school for the ceramist being confronted with the problems associated with the development of various fuels for various reactors.

Very recently we have worked on a wet process for fabricating high density mixed oxide pellets (> 95 % D.T.) with a nearly perfect homogeneity : it is based on the co-conversion of (U, Pu) nitrates by external gelation followed by pelletizing of the resulting kernels [15]. Sinterable kernels of about 300  $\mu\text{m}$  in diameter have been obtained by a gel precipitation method. The drops are produced by a horizontal vibrating nozzle. It should be possible to use this

technique in the non nuclear field. Possible applications should be searched when spherical particles of the same granulometry are needed or when the product is a mixture of different constituents that have to be intimately and uniformly distributed in each microsphere.

## 2. Lithium silicate

Through our experience acquired in the field of nuclear ceramics, we were particularly prepared to carry out successfully a study on the fabrication of ceramic breeder materials for future fusion reactors. It is consequently quite naturally that, since June 1983, we participate in a large programme co-ordinated by the European Communities in the scope of Fusion. We were more particularly asked to study the aspects of fabrication and behaviour of lithium metasilicate.

While our earlier studies on  $UO_2$  and  $UO_2-PuO_2$  were very often based on the use of commercial powders, this study has confronted us from the beginning with the problem of the supply of a lithium metasilicate powder, having an acceptable quality, i.e. sinterable and stoichiometric.

According to the literature, lithium metasilicate may be obtained from lithium carbonate and silica intimately mixed in the appropriate proportions and calcined near the melting point of the carbonate ( $718 \pm 3^\circ C$ ). Unfortunately the obtained metasilicate is little sinterable and is not suitable at all to the fabrication of high density pellets by cold pelletizing and sintering.

Finely milling the raw materials in view of making them more reactive makes no sense, because the resulting metasilicate is even less sinterable.

One should thus either re-activate the calcined materials by milling them or calcine the dried powder at a considerably lower temperature. Unfortunately,  $680^\circ C$  seems to be a minimum for obtaining a more or less complete reaction. Powders calcined at a lower temperature contain an appreciable quantity of ortho- and disilicate, the concentration of which increases as the calcination temperature decreases. Ortho- and disilicate transform into metasilicate at high

temperature but this seriously deforms the pellets and introduces many defects, leading to a poor density.

Dry milling has not been investigated because it presents some drawbacks such as an extra fabrication step and contamination risks and moreover because an original method has been found for producing very sinterable silicates.

This is based on the formation of an X-phase resulting from a reaction in a very narrow temperature range. Fig. 5 shows, indeed, that our fabrication method gives a product reacting at 400°C already. The maximum reaction is obtained at about 430°C for a 15 h heat treatment. When examining a sample treated under these conditions by X-ray diffraction, one can see some metasilicate, non reacted carbonate, and amorphous phase which is probably silica and a compound which we call X-phase because it has not been identified until now.

As shown by Fig. 6, the temperature plays an important rôle in the X-phase formation. It is worthwhile mentioning that the maximum X-phase concentration corresponds to the minimum concentration of non-reacted carbonate. The formation of this X-phase does not consume much silica. At a slightly higher temperature, X-phase reacts with silica to form metasilicate.

So it is possible to make pure metasilicate by treating the mixture first at about 430°C for 15 h and then at 550°C - 600°C for a few hours or by heating it very slowly from 410°C to 460°C.

The basic condition of the process is that the formation of metasilicate proceeds through the X-phase, which is not possible by direct calcination.

The method gives a very sinterable product which is perfectly suited for fabricating high density pellets by cold compaction and sintering. Densities exceeding 95 % T.D. have been reached [16]. It is, of course, also possible to use the process for producing pellets with lower density, e.g. 80 % T.D. : in this case, the process offers the additional advantage of producing a very fine structure : grain sizes smaller than 1 micron have been obtained.

So, the method, covering a large range of densities and grain sizes,

using commercially available raw materials and based on industrially applied technology is potentially attractive and justifies carrying on the study with confidence and optimism [17].

### 3. Silicon nitride

Within the framework of the diversification of our activities, we are also studying some fabrication and characterization techniques of advanced structural ceramics such as silicon nitride, silicon carbide and partially-stabilized zirconia.

The present basic programme covers different shape forming techniques such as slip casting, injection molding, extrusion and HIPping as well as characterization methods for powders and finished products.

Our short-term objective is to be able to make simple shape bodies in silicon nitride and to study, for different commercial powder qualities, the influence of the processing parameters on the mechanical properties of the finished products.

Fig. 7 summarizes the different techniques used to prepare silicon nitride bodies.

Reaction bonded silicon nitride consists of nitriding silicon bodies into silicon nitride. During the process, the compact gains simultaneously density and strength without any appreciable dimensional change. Most of the commercially available silicon nitride parts are made by this process.

To obtain high density and consequently high mechanical strength materials, the hot pressing or hot isostatic pressing techniques may be applied.

Hot pressing consists of applying simultaneously uniaxial pressure and heat on a powder in a graphite die : it is therefore limited to the obtention of simple shapes and is not suitable to mass production. This is the reason why hot pressing is nowadays overshadowed by the more attractive hot isostatic pressing. This process is usually applied on already dense materials as a method to reach a density approaching theoretical density. It is an area of first growing interest to produce high-quality silicon nitride components.

The sintered silicon nitride is another area of growing interest. This method implies that sintering aids are admixed to the silicon nitride powders because pure silicon nitride does not sinter to a high density.

Fig. 8 gives an idea of the bend strength of silicon nitride samples as a function of the densification method used. The point where the strength curves drop, depends somewhat on the types of the sintering aids but the trend of the curves remains basically correct.

If the reaction-bonded quality has a rather low bend strength because of its low density, it is interesting to note that its resistance does not decrease with temperature. This quality is therefore suitable for high-temperature applications. The other qualities have a higher bend strength up to a certain temperature. This is the consequence of the admixture of the sintering aids : they form a second phase with a lower melting temperature, which is deleterious to the high-temperature properties. This effectively limits the maximum working temperature to below 1200°C.

Reaction bonding and sintering of silicon nitride are, in fact, the two densification techniques we are presently studying, HIPping will also be applied very soon. We do not intend to investigate the possibilities of uniaxial hot pressing.

#### Reaction-bonded silicon nitride

The fact that reaction bonding is a near net shape process (dimensional changes smaller than 0.1 %) of moderate cost, is attractive. A low-density material is already produced on a small scale by commercial companies though all fabrication problems are not solved yet.

It is no secret to say, for instance, that the present current quality is sometimes inferior to the quality which has been achieved in the laboratory. The reproducibility of both microstructure and residual silicon can be a problem because the obtained quality is not always consistent. There is, in fact, a need for high-grade RBSN bodies : according to Dr F.L. Riley [18], there will be a growing market for such a silicon nitride quality. This need asks for a new

scientific research in order to obtain products of higher, more uniform or more reproducible quality than the present one.

One of the items requiring further attention is certainly the reaction rate control. Close control of the reaction rate is known to be of vital importance if homogeneous and reproducible microstructures are to be obtained but is not easy because of the exothermic character of the reaction. The necessary degree of control can only be achieved through linking the reaction zone temperature with the extent of nitridation. Important development work has been done by Mangels [19] who followed the degree of nitridation by the nitrogen consumption ("nitrogen demand" nitriding).

We have a different approach and monitor the nitridation rate by measuring the weight change during the process, using a thermobalance, equipped with a computer control unit. With this unit, it is possible to programme the furnace temperature as a function of the rate of the weight change. As shown in fig. 9 it is possible, for instance, to pilot the thermobalance in such a way that the weight of the compact increases linearly with time. The equipment is used to study the influence of the chemical composition and the granulometry of the silicon powders, on the one hand, and the effect of composition, flow-rate and pressure of the nitriding gas, on the other hand, on the microstructure of samples treated under known and reproducible process conditions.

Much information can be retained from such diagrams. As can be seen, for a given powder, there is a minimum temperature below which no nitridation takes place. As soon as the reaction starts there is an excess of heat due to the exothermic nature of the reaction. Even for small samples it is clear that immediately after the reaction starts the furnace temperature has to be lowered in order to protect the sample to react too vigorously. With heating cycles derived from such diagrams we were able to prepare RBSN samples with densities of about  $2.5 \text{ g/cm}^3$  and a degree of nitridation, as determined by X-ray diffraction, of more than 99.8 %. Experiments are now under way to scale up these results to larger samples.

### Sintered silicon nitride

Conventional sintering knows a rapidly growing interest since the availability of so-called "sinterable" powders. The basic difficulty is that silicon nitride shows practically no volume diffusion : it is therefore hardly feasible to densify silicon nitride compacts by the only effect of temperature. Sintering aids have to be added in order to obtain a liquid phase during sintering (this is also valid for HPSN and HIPSN). A further complication is that silicon nitride dissociates at high temperature : fig. 10 gives the stability diagram established by Greskovich and Prochazka. It is clear that an overpressure of nitrogen is necessary to avoid dissociation at the sintering temperatures involved. In this regard, a high-temperature high-pressure dilatometer is being installed in order to be able to follow sintering up to 2000°C and 100 atm.

Meanwhile, experiments have been carried out in a graphite resistance furnace, using the "powder bed" technique, a process which consists of embedding the samples to be sintered in a powder bed of silicon nitride. This is a means of counteracting the decomposition of silicon nitride and the evaporation of the sintering aids.

The first experiments have been performed on cold-pressed pellets. This is now completed with bodies obtained by slip casting and in a near future, by injection molding and hopefully also by extrusion. The sintering aids which have been investigated are magnesium oxide, alumina and yttrium oxide. Though MgO can be introduced by diffusion from the powder bed, this technique does not seem to be reliable and applicable to the fabrication of large bodies. A concentration gradient produces a heterogeneous microstructure and superficial failures. Wet milling could be the best technique to introduce the sintering aids because it gives homogeneous and intimate mixtures.

Fig. 11 shows the effect of some additives on the densities of silicon nitride pellets sintered 1 h at 1700°C under normal nitrogen pressure. The results are arbitrarily ranked.

This graph shows that

1. the obtained densities are higher when the "powder bed" technique is used ;
2. a "powder bed" in pure  $\text{Si}_3\text{N}_4$  i.e. without additives is already

- effective ;
3. the use of impure  $\text{Si}_3\text{N}_4$  powders to protect the pieces to be sintered is favourable ; it is supposed that some impurities of the powder migrate to the bodies to be sintered ;
  4. the heating rate also affects final density ;
  5. each additive has its own effectiveness :
    - alumina is no effective sintering aid ;
    - yttrium oxide increases final density but a combination of yttrium oxide and alumina has a real impact on the sintered densities.

Fig. 12 illustrates the influence of the method used for admixing MgO into silicon nitride powders. MgO is a very efficient sintering aid and its effectiveness increases after a 2 h milling operation in  $\text{Al}_2\text{O}_3$ . This is probably not only due to the change in granulometry and improvement in homogeneity but also to the  $\text{Al}_2\text{O}_3$  contamination. As shown by fig. 13, the MgO quantity in the  $\text{Si}_3\text{N}_4$  pellets and therefore the volume of the liquid phase formed has a marked effect on the final density. This graph confirms the favourable effect of a fast heating rate while fig. 14 also shows the influence of the sintering temperature on the final density.

#### 4. High temperature ceramic heat exchanger in corrosive environment

Finally I am very pleased to add that SCK/CEN has just started a study of a heat exchanger working in a corrosive environment.

The incentive for this study is found in the large amount of wasted energy in the off-gases of the iron and steel industry, the non-ferro industry and in glass and ceramic manufacturing.

Two main reasons can be indicated for the low percentage of recuperated heat energy :

- high temperature, over  $850^\circ\text{C}$  (20...40% of gas) ;
- the aggressive nature of the off-gases.

The aim of this project consists in testing high temperature ceramic and metallic materials, in selected industrial processes producing high-temperature corrosive off-gases, and in designing and demonstrating adapted heat exchanger concepts.



Ceramic materials such as SiC e.g. have good high temperature (1300°C - 1400°C) properties and, could be candidate materials.

In the near future a materials test station will be built in the off-gases ducts of an aluminium reverber furnace in order to perform in situ corrosion tests. The whole process and its off-gases will be characterized. Ceramic test pieces from various suppliers and from SCK/CEN will be characterized and corroded.

The results from these material tests must lead to the selection of the best suited candidate material for constructing a heat exchanger. Interested manufacturers of metallic and/or ceramic heat exchangers are invited for collaboration. This collaboration should result in the development and manufacturing of a ceramic or metallic heat exchanger, giving a yield of over 80% of the heat accumulated in the exhaust gases.

This project is now being financed by the Flemish Executive [21].

#### CONCLUSION

This was a short review of the experience we acquired with nuclear ceramics and of our present activities on non nuclear ceramics. Moreover, SCK/CEN envisages to have, in the future, some fabrication developments on ceramic membranes or ceramic sensors.

SCK/CEN hopes to be useful to the industry, particularly to the Belgian one. It can already render services and is searching a close collaboration with industrial partners having interest in high technological ceramics.

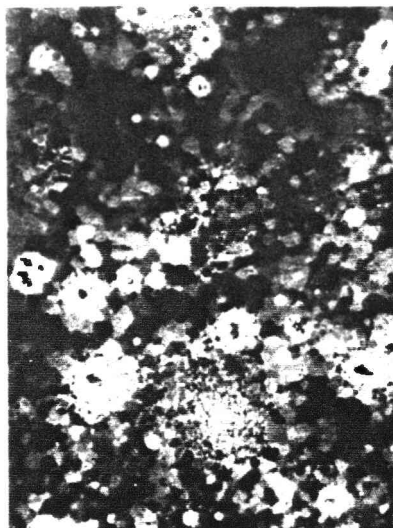
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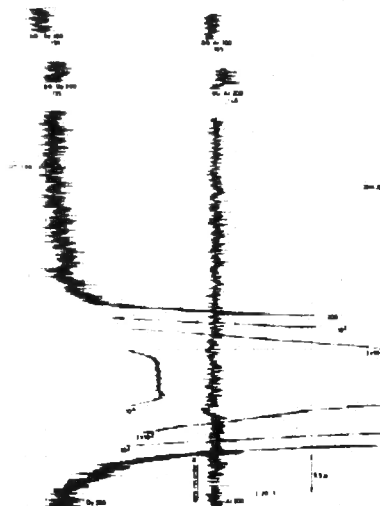
UO<sub>2</sub> - 0.6 wt% Dy<sub>2</sub>O<sub>3</sub>

Sintering: 4 h - 1650°C - H<sub>2</sub>



H<sub>2</sub>O<sub>2</sub> etched

20 μm



Microprobe diagram

Fig. 1 : UO<sub>2</sub>-0.6 % Dy<sub>2</sub>O<sub>3</sub> pellet sintered 4 h at 1650°C under hydrogen.

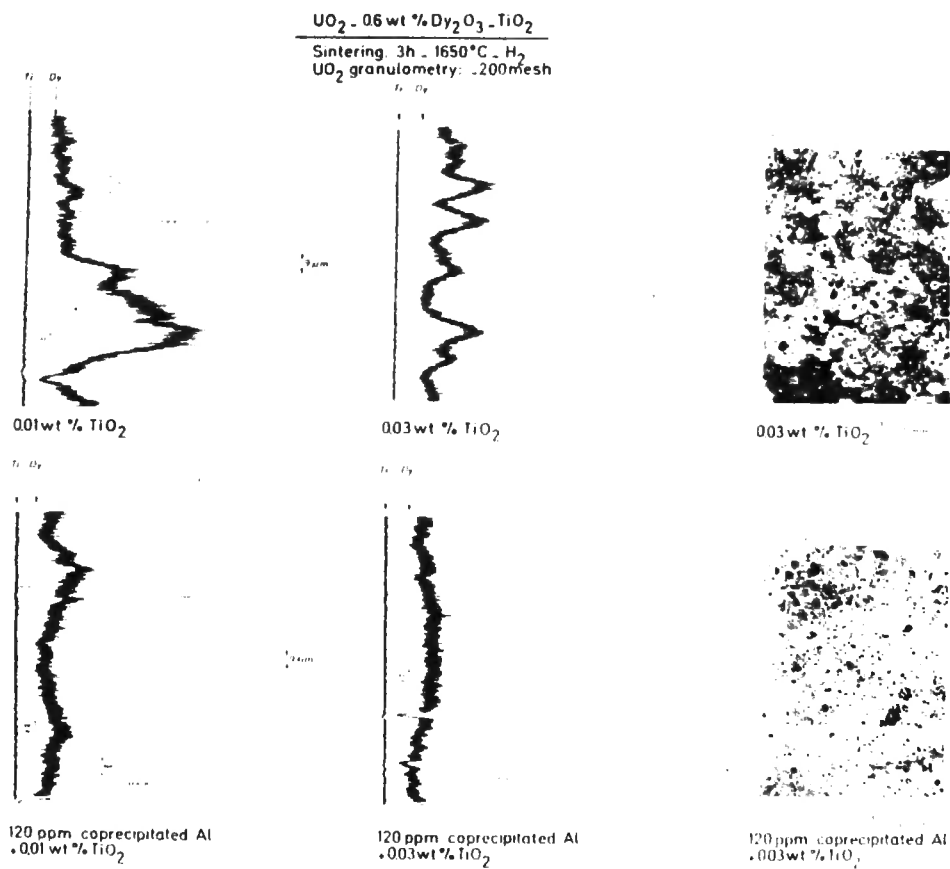
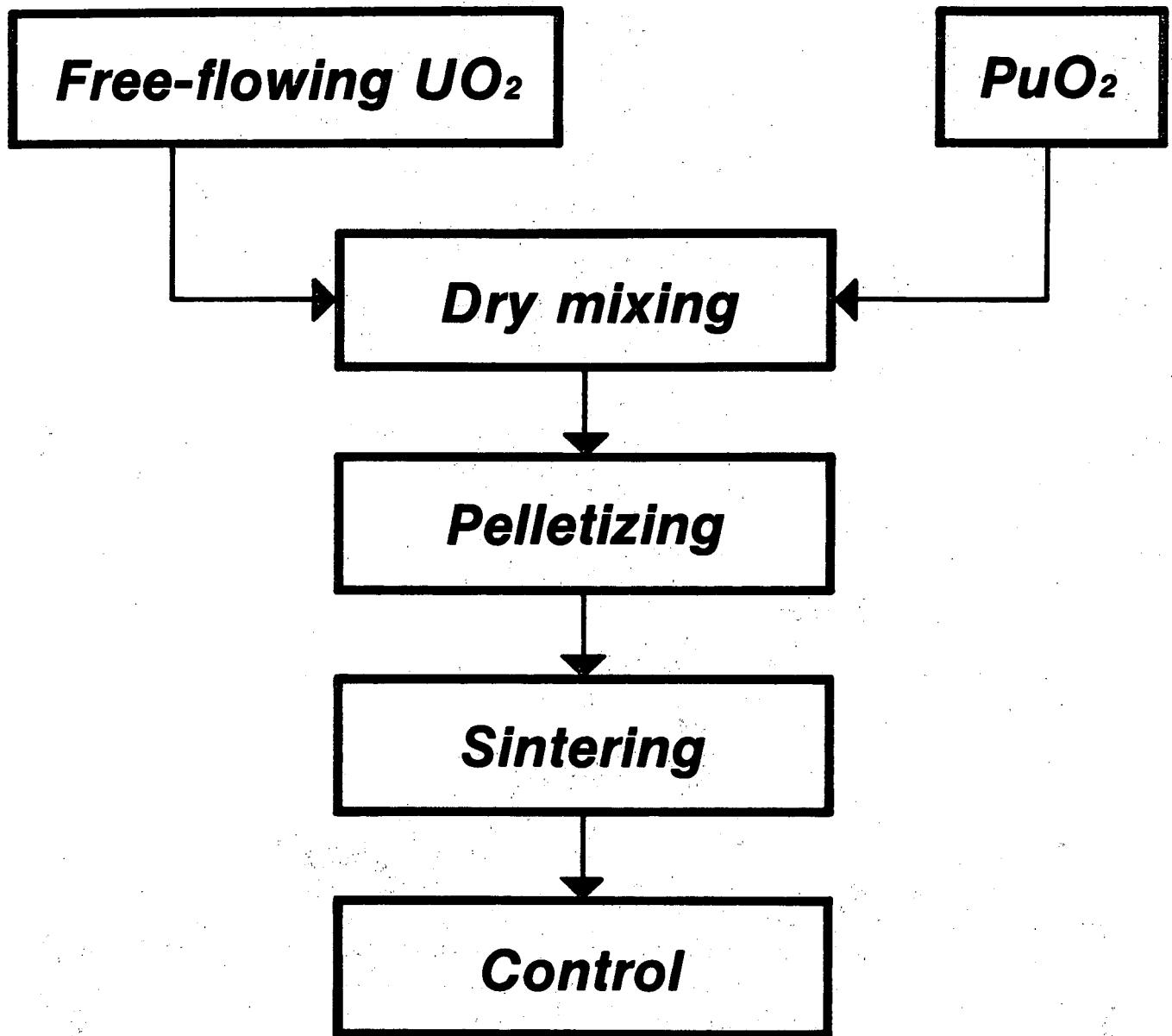
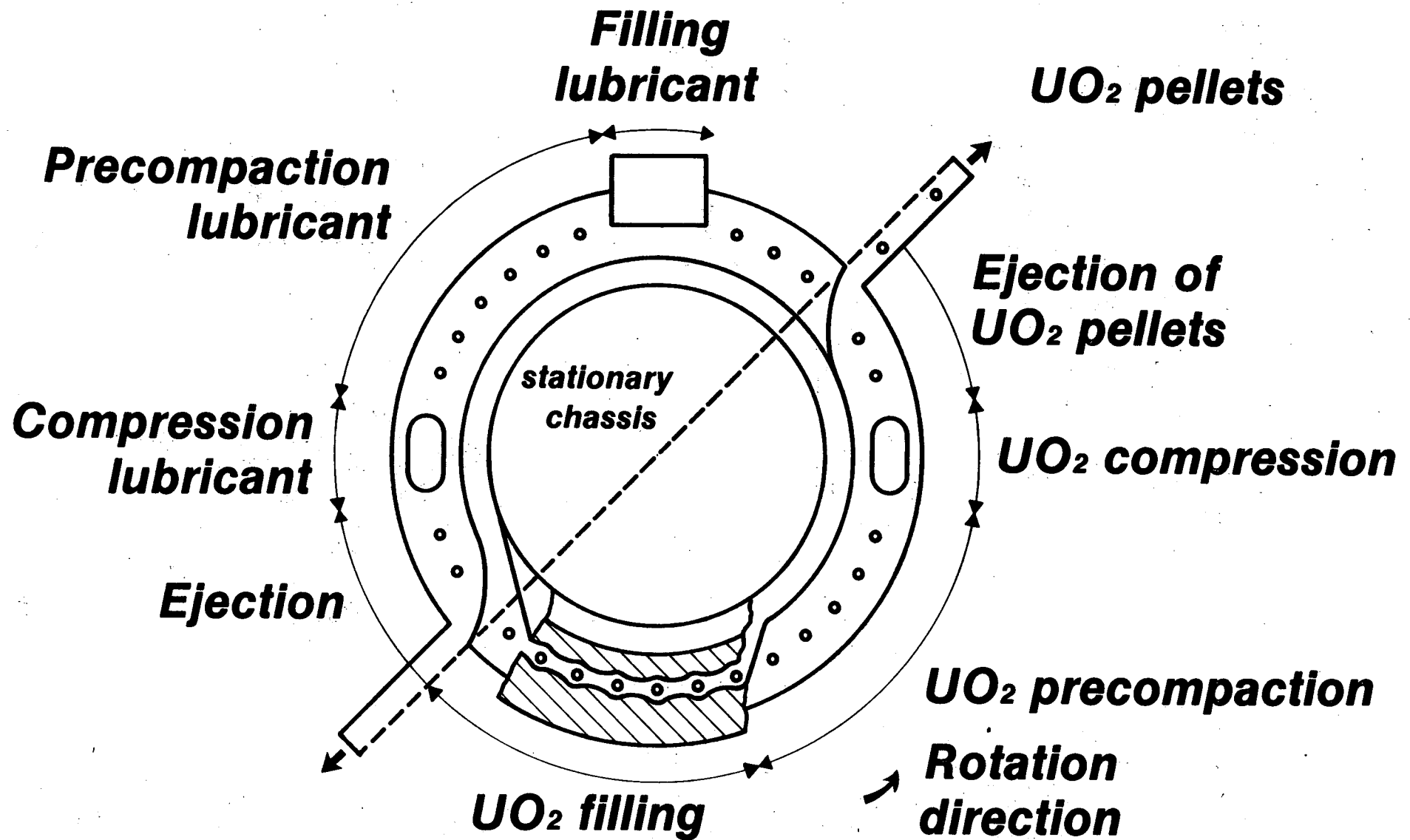


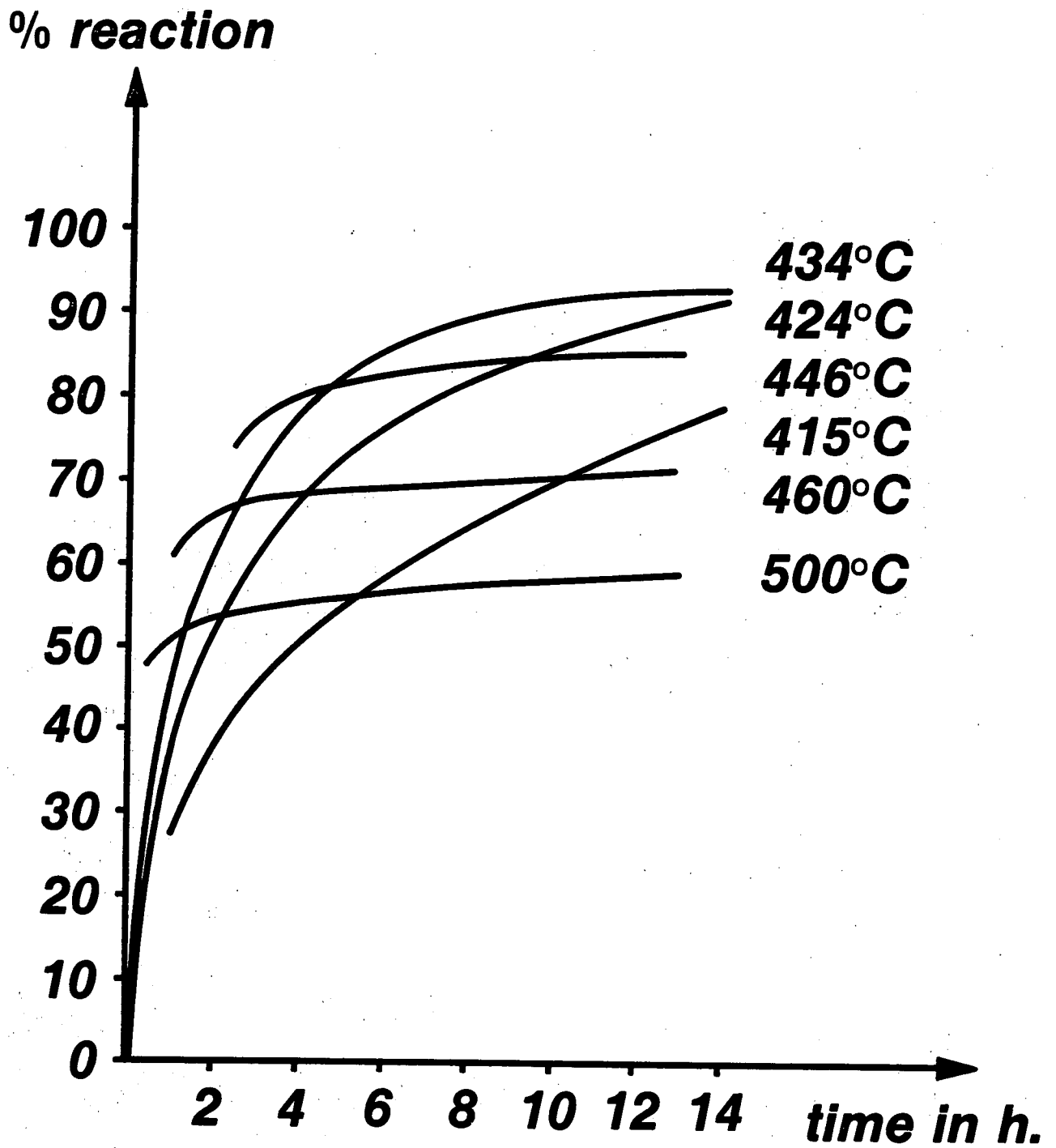
Fig. 2 : Influence of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> additions on the diffusion of dysprosium into uranium dioxide.



**Fig. 3** *Fabrication route of  $\text{UO}_2\text{-PuO}_2$  pellets for the SNR reactor*

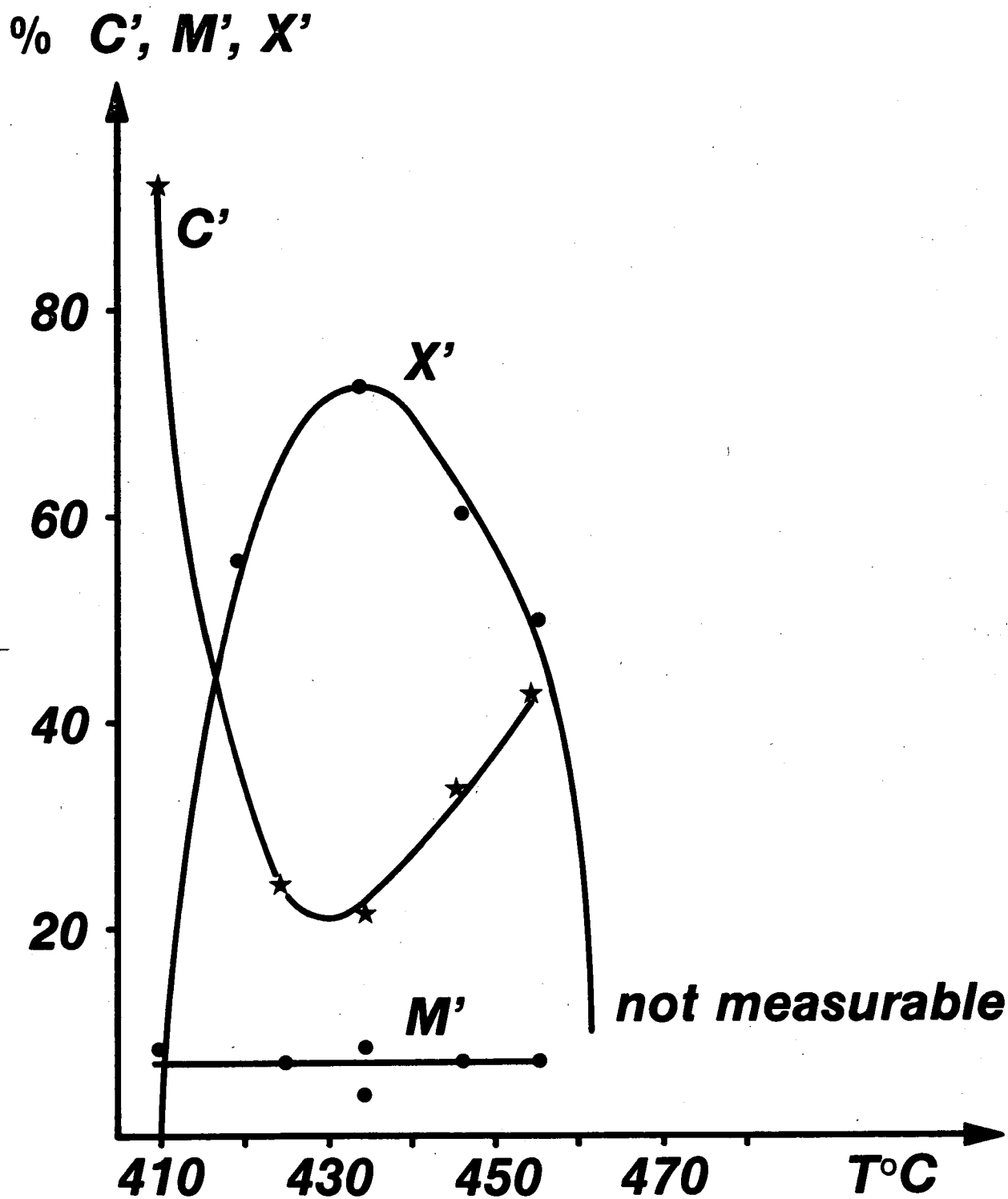


**Fig. 4** *Double-sided rotary press with direct lubrication of the dies*



**Fig. 5 Influence of temperature and time on the reaction degree between lithium carbonate and silica**



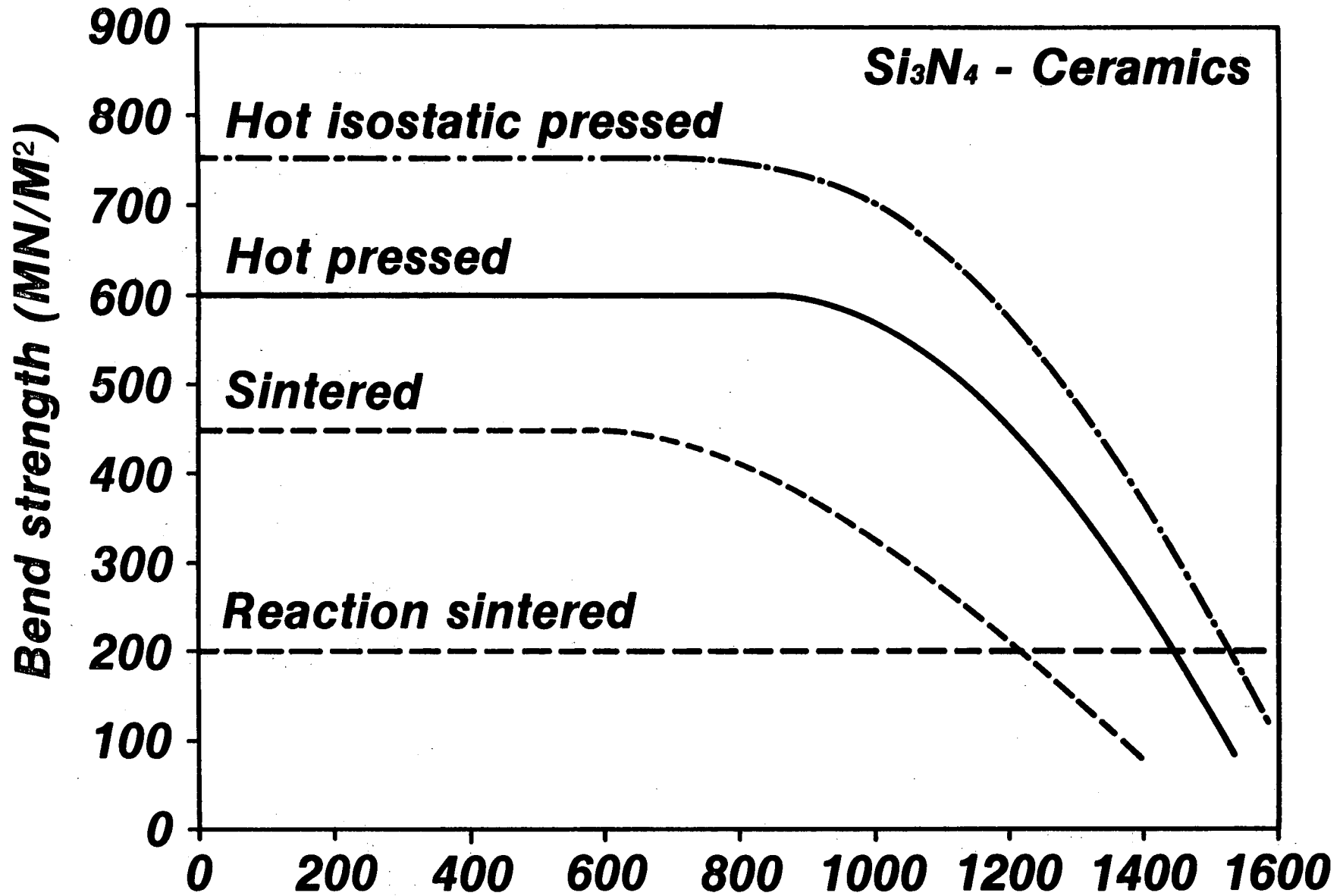


**Fig. 6** *Pre-calcination under wet air during 14 h*

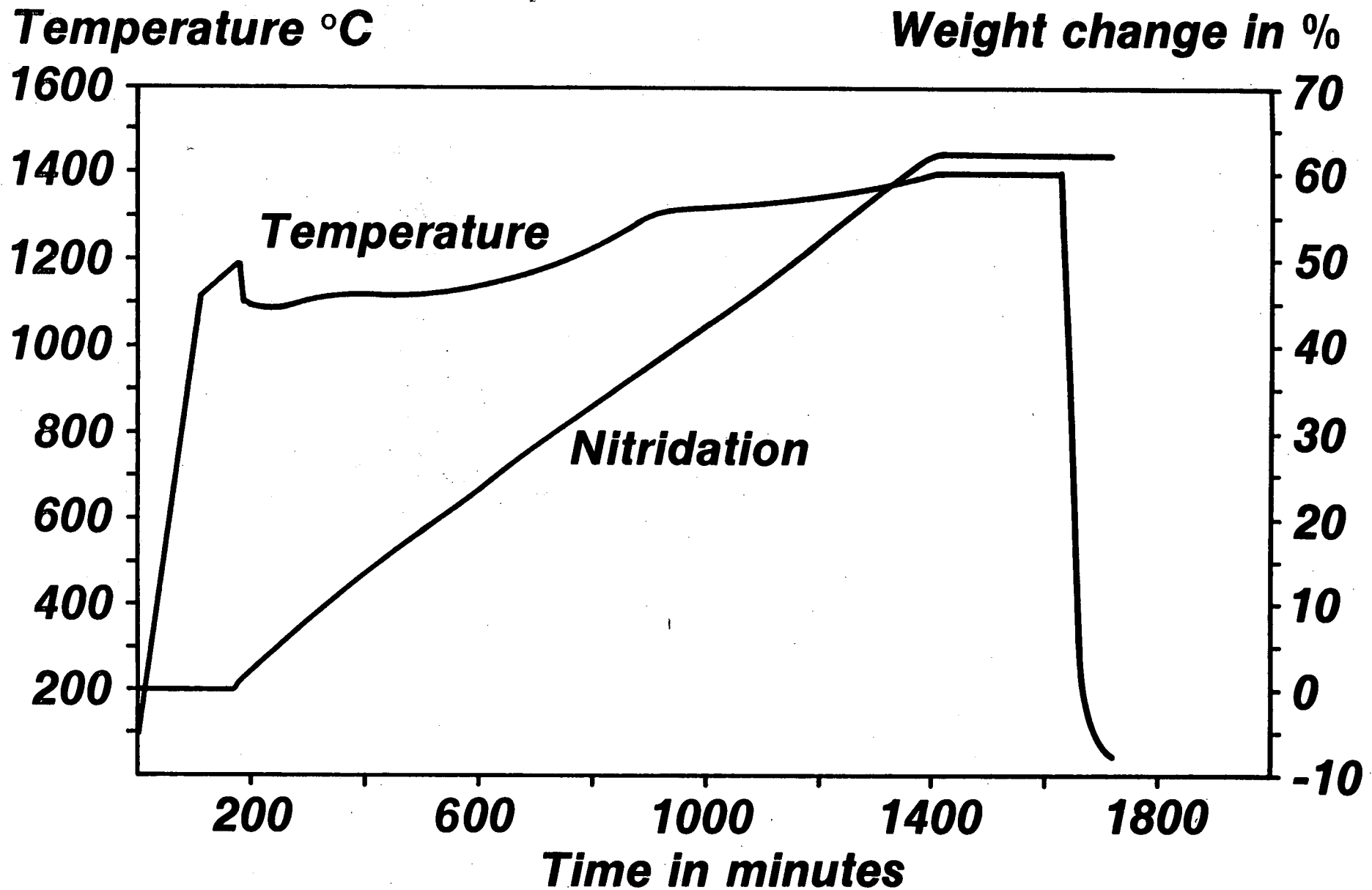
## **Silicon Nitride Ceramics**

<b>Reaction Bonded Silicon Nitride</b>	<b>(RBSN)</b>
<b>Sintered Silicon Nitride</b>	<b>(SSN)</b>
<b>Sintered RBSN</b>	<b>(SRBSN)</b>
<b>Hot-Pressed Silicon Nitride</b>	<b>(HPSN)</b>
<b>Hot-Isostat. Pressed Silicon Nitride</b>	<b>(HIPSN)</b>

**Fig. 7 Densification techniques**



**Fig. 8 Influence of the densification method on the bend strength of Si<sub>3</sub>N<sub>4</sub> samples**



**Fig. 9 Linear nitridation rate of a silicon compact (experiment No 14 STC)**

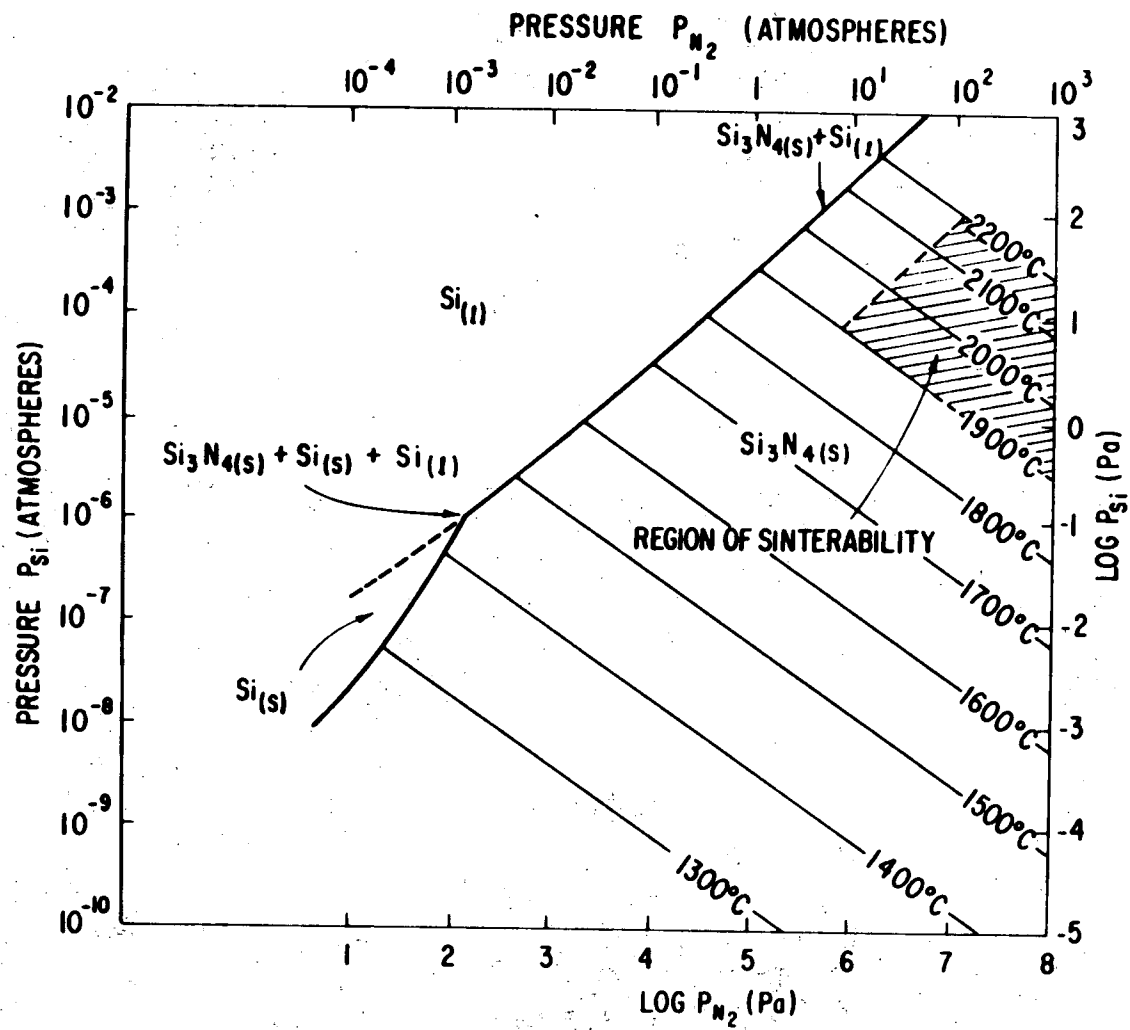
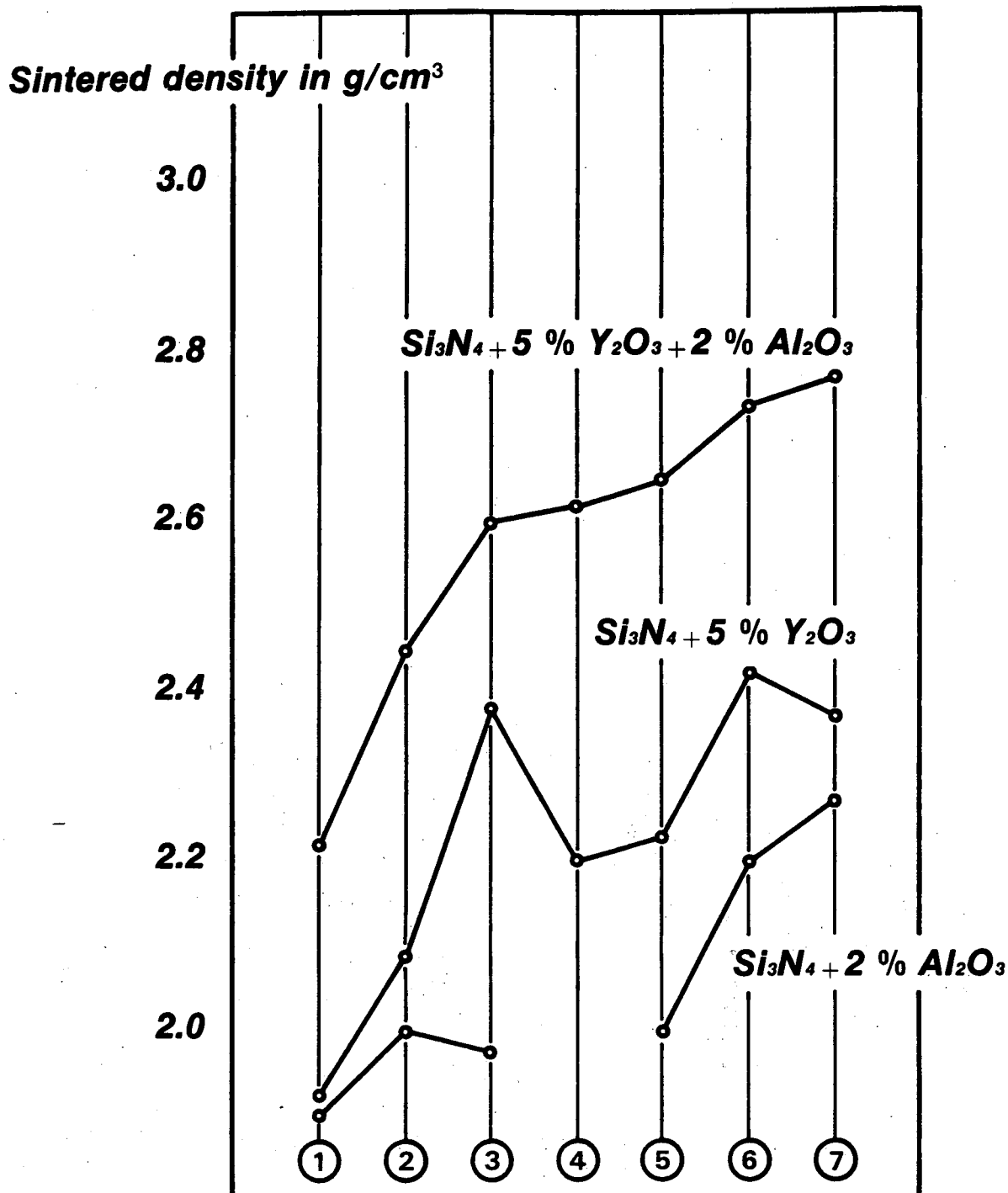


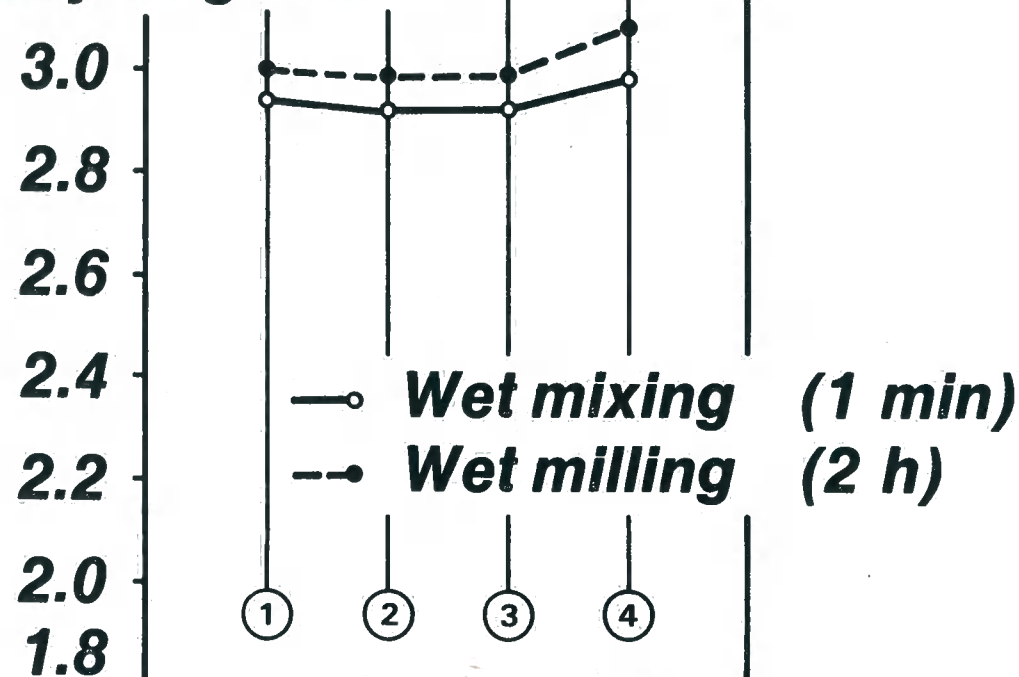
Fig. 10 : Stability diagram for  $\text{Si}_3\text{N}_4$   
 (Greskovich, Prochazka [20])



Experiment number	1	2	3	4	5	6	7
Powder bed	No	No	Pure Si <sub>3</sub> N <sub>4</sub> powder	Si <sub>3</sub> N <sub>4</sub> and additives	Pure Si <sub>3</sub> N <sub>4</sub> powder (pre-sintered)	Impure Si <sub>3</sub> N <sub>4</sub> powder	Impure Si <sub>3</sub> N <sub>4</sub> powder
Heating rate in °C/h	200	1,000	200	200	200	200	1,000

Fig. 11 Effect of additives on the sintered density of Si<sub>3</sub>N<sub>4</sub> pellets sintered 1 h at 1700°C under nitrogen

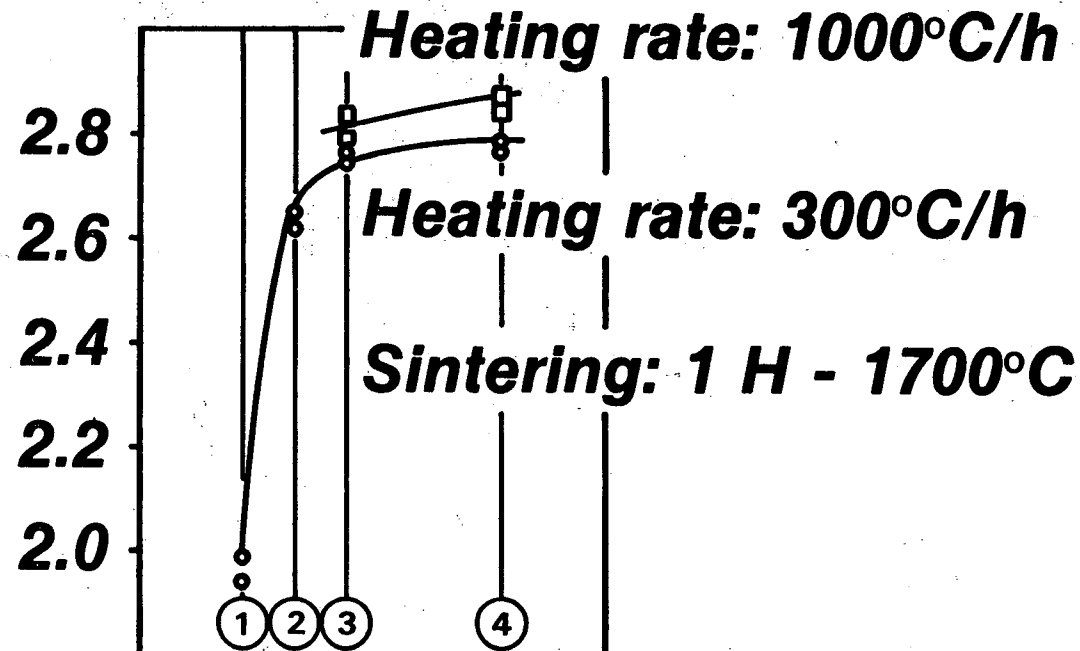
**Sintered density in g/cm<sup>3</sup>**



<b>Experiment number</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>Powder bed</b>	<b>Pure Si<sub>3</sub>N<sub>4</sub> + 5 % MgO</b>	<b>Impure Si<sub>3</sub>N<sub>4</sub> + 5 % MgO</b>	<b>Impure Si<sub>3</sub>N<sub>4</sub> + 5 % MgO</b>	<b>Impure Si<sub>3</sub>N<sub>4</sub> + 10 % MgO</b>
<b>Heating rate in °C/h</b>	<b>200</b>	<b>1000</b>	<b>200</b>	<b>1000</b>

**Fig. 12 Effect of milling on the sinterability of Si<sub>3</sub>N<sub>4</sub> powders doped with MgO. Sintering: 1 h - 1700°C - N<sub>2</sub>**

**Sintered density in g/cm<sup>3</sup>**

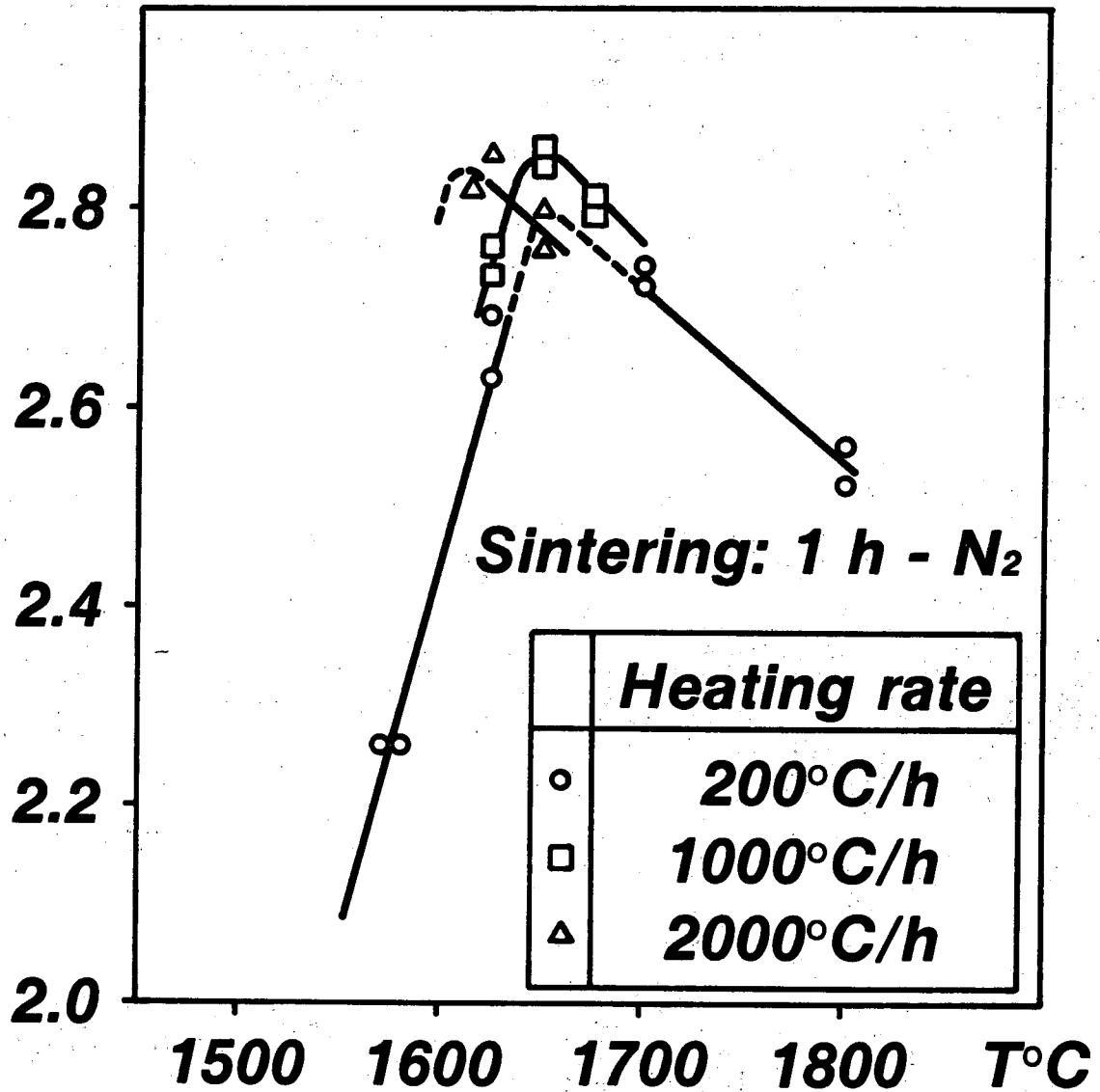


<b>Experiment number</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>Composition of the Si<sub>3</sub>N<sub>4</sub> pellets</b>	<b>Pure Si<sub>3</sub>N<sub>4</sub></b>	<b>Pure Si<sub>3</sub>N<sub>4</sub></b>	<b>Pure Si<sub>3</sub>N<sub>4</sub> + 2 % MgO</b>	<b>Pure Si<sub>3</sub>N<sub>4</sub> + 5 % MgO</b>
<b>Powder bed</b>	<b>Idem</b>	<b>Idem + 5 % MgO</b>	<b>Idem</b>	<b>Idem</b>

**Fig. 13 Influence of the percentage of MgO in Si<sub>3</sub>N<sub>4</sub> on the sintered density**



**Sintered density in g/cm<sup>3</sup>**



**Fig. 14 Influence of the sintering conditions on the final density of Si<sub>3</sub>N<sub>4</sub> pellets doped with 5 % MgO**