First Results of U_3Si_2 Production and its Relevance in the Power Scale-up of IPEN Research Reactor IEA-R1m

Saliba-Silva, A.M[1].; Souza, J.A.B[1].; Frajndlich, E.U.C.[1]; Perrotta, J.A[2].; Durazzo,M.[1]

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Abstract

The own supply of LEU U_3Si_2 is crucial for IPEN, since the whole scale-up of IPEN MTR IEA-R1m reactor will rely on it. The Brazilian request for radioisotopes production is fully linked with the already made power scale-up from 2 to 5 MW for this reactor. IPEN now depends on fuel element material upgrading from U_3O_8 towards LEU U_3Si_2. The fuel plate productive technology from the powdered material is already well established, only needing simple making of minor adjustments, but to reach the stage of producing U_3Si_2 we need a fully settled chemical pilot plant in order to reach a LEU UF_4 productive routine. Complementing this process, it was also needed to scale down the previous practice of uranium magnesiothermic reduction to around a sub-critical safe uranium mass of approximately 3000g. To complete the metallurgical processing, it is being developed the production of U_3Si_2 in a vacuum induction furnace. Some experiments to get this intermetallic, using natural uranium, have already been carried out in order to build up a general idea of the future process of LEU U_3Si_2. These experiments are described in this paper and also some of the initial characterization results, such as the qualification pattern of the ingot. It is also discussed some new features of inhomogeneity of solidified phases that may be deleterious to future production routine.

[1] Departamento do Ciclo do Combustivel, Instituto de Pesquisas Energeticas e Nucleares (IPEN/CNEN-SP), Cidade Universitaria (USP) , Travessa R, 400 CEP05508-900 Sao Paulo (SP) Brasil - email: adonis@net.ipen.br

[2] Divisão de Engenharia do Nucleo, IPEN/CNEN-SP

IEA-R1m Research Reactor

Since the Brazilian request for radioisotopes has increased vigorously in recent years, for medical diagnosis and therapy, IPEN decided to increase IEA-R1m[3] power from 2 MW towards 5 MW and to operate it continuously throughout the week. This is effective since September 16th, 1997. The pair ^{99}Mo-^{99}Tc will be the main radioisotope to be produced, for this, other projects have been developed in the last three years: structure and component modifications of IEA-R1m; adequacy of reactor systems; adequacy of radioisotope production and finally the adequacy and new fuel material development. That is the main approach of nowadays concern of IPEN.

Recently, in the last RERTR Seoul meeting, it was presented a paper[1] with a full description of our reactor IEA-R1m main history, showing a sequence for fuel utilization. Reviewing and expanding it, we have now:

(a) *First Stage - Since September 16th, 1957 (first criticallity), the IEA-R1m reactor operated under the nominal power, designed for 5MW, but always operated as 2MW one. The charged fuels, during this period, was 20wt% enriched U-Al alloy fuel, made by B&W. 19 curved plates were used. These fuel failed in the earlier stage due to pit corrosion and replaced by new ones in 1958. All this material worked well until discharge.*

(b) *Second Stage - (1968) The fuel was based in a loading of U-Al alloy, 93% enriched, having 18 flat fuel plates bought from UNC (USA). At this time, the core was transformed from LEU to HEU. Some of this fuel were until recently operating in the reactor. The control fuel element assembling were fabricated by CERCA (France), using the same material concept.*

(c) *Third Stage - (1981) Due to the restriction to HEU, IPEN bought from NUKEN (Germany), 5 fuel elements of UAl$_x$-Al dispersion type, with 20 wt% enrichment and having 18 flat fuel plates per fuel element. The amount of ^{235}U in this LEU fuel plate was almost the same as the HEU fuel plate and the the geometry was the same. With this partial LEU core load, the HEU fuels, that stayed in core, began to have a higher burn-up and the pieces of elements inside the reactor core increased ever since.*

(d) *Fourth Stage - (1988) This stage started with IPEN deciding to fabricate its own LEU fuel and to replace gradually the high burn-up HEU fuels in the core. This stage has been most characterized by the continuous replacing of old fuel elements by the IPEN U$_3$O$_8$-Al type using 1.9 gU/cm^3.*

(e) *Fifth Stage -(1995 till presently)Recently, the amount of the last assemblies passed from a concentration of 1.9 gU/cm^3 to 2.3 gU/cm^3 (1996 - Elements 153-161). Since Sep. 16th 1997, re-inauguration day for the fully 5MW reactor, denominated ever since by IEA-R1m ("m" for modified), the whole reactor core is fed with IPEN own produced U$_3$O$_8$-Al dispersion.*

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[3] "m" stands for modified, IEA-R1m is now the official name of this MTR reactor of IPEN.

(f) Sixth Stage - (1998?) The sixth stage is programmed to start replacing the elements based on U_3O_8-Al dispersion by LEU U_3Si_2-Al (3.0 gU/cm³). Initially using CERCA material and, from 2001 on, using IPEN production of this intermetallic.

Fuel Material

At the time being, there is a whole project, which has already started in order to develop skills on U_3Si_2 fuel fabrication technology, sponsored by IPEN/CNEN and Brazilian Government. So, many of the present citations in this paper, may change in future, because our production basis has not been fully established yet. The main object of this paper is to describe our present activities in LEU U_3Si_2 fuel development.

Plate Fabrication

The fuel plate fabrication itself has already been well clarified and there are, as far as we foresee, no major questions about its technology. Some new equipment are being purchased, such as rolling mill and quality control devices; some adaptation in the facilities will be made and some crew training is envisaged.

Our present major concern is the area ahead of plate fabrication, because this last stage depends on several internal developments to be reached. First of them is the chemical process development based on stannun chloride route to get UF_4 from UF_6 20wt% enriched in ^{235}U. This is followed by magnesiothermic reduction to obtain LEU metallic uranium and then also the U_3Si_2 alloy fabrication and preparation to be employed in the fuel plate meat. The chemical and metallurgical processes are under development and will be commented bellow in more detail.

Chemical Process

Since 1993, IPEN produces the raw material to fabricate the fuel based on U_3O_8, in order to supply its reactor IEA-R1m. It was chosen the route through hydrolysis of enriched UF_6 with subsequent precipitation of ammonium diuranate (ADU). After calcination of this material we can get the product U_3O_8.

Knowing the necessity to replace the U_3O_8 by U_3Si_2, to face the needs of scaling up the reactor power to 5MW and relying on a previous experience of acquired skill in hydrolysis process and ADU precipitation, it was decided to obtain UF_4 by a route starting with hydrolysis solution. The main reason for that was the possibility of keeping up using the available facilities and equipment. The adopted route uses hydrolysis solution treated with $SnCl_2$, where occurs the reduction of U^{6+} to U^{4+}, with a subsequent precipitation of UF_4 with HF. The Fig.1 shows the sequence of previous operation to get U_3O_8 and the proposed one to get U_3Si_2.

The hydrolysis is essentially based on aqueous dissolution of UF_6. The UF_6 is a crystalline substance in normal conditions of pressure and temperature, for this the process heats the UF_6 to 90°C, reaching a pressure of 3 kgf/cm² and then passing to the gaseous state. The cylinder of UF_6 is placed inside an autoclave which is connected to a stainless steel reactor, which is chemically protected internally. This reactor has a continuous re-flow of distilled water. From an injection nozzle, the UF_6 enters in contact with the water, promoting the following reaction:

$$UF_6 + H_2O \rightarrow UO_2F_2 + 4HF \qquad\qquad (1)$$

Once with the ion U^{+6} in solution, it is necessary that the chemical reduction towards U^{-4} uses addition of a reductant agent solution. Several reductant agents have been tested, such as: $SnCl_2$, $CuCl$, $FeCl_2$, $Na_2S_2O_4$. The most interesting reductant agent was $SnCl_2$.

This solution is heated to a pre-determined temperature under constant solution re-flow. The reductant agent is added, followed by the gradual addition of the precipitation agent HF. The reaction of precipitation is:

$$UO_2F_2 + SnCl_2 + HF \rightarrow UF_4 + SnCl_2 + 2H_2O \qquad\qquad (2)$$

Once the precipitation of UF_4 is made, the suspension pulp is left to rest until it reaches the room temperature. After 12 hours, the separation solid/liquid is made by a vacuum filtering.

The UF_4 humidity is very deleterious for the yield performance in metallic uranium reduction, so a project of UF_4 drying is being carried out for the time being, using basically three possible routes: controlled heating under vacuum, heating with flowing of inert gas (argon) and microwave drying. Those studies are just in the beginning.

This process aiming at producing UF_4 has been developed since 1995, using natural UF_6. A batch of obtained UF_4 has already been used in the reduction process with a fair result in terms of yield (60%), probably due to a higher humidity. The product UF_4 obtained is passing nowadays for a rigorous evaluation test in order to furnish better understanding of its behavior during metallic uranium production.

Metallurgical Process

Uranium Magnesiothermic Reduction

Since 1995, we have made experiments in order to produce metallic uranium. The reduction bomb used for these experiments is shown in Fig.2. The charge of the mixture (UF_4 + Mg in excess of 16wt%) was prepared as cylindrical briquettes with $\varnothing$100mm x 50mm compacted under a pressure of 64kgf/cm^2. The apparent density of this briquette is around 2.6 g/cm^3. The whole load for each batch is 7 of those briquettes, which makes an average total load of 6000g.

The heating follows a sequence of 8 hours in two stages of 4 hours each, with the temperature set, for each plateau, at 550°C and 1000°C. The product is delivered in two days, after opening the bomb and collecting the metallic uranium. The metallic yield results, for the whole set of experiments ranged from 50 to 90%. We had many unsuccessful experiments, which are probably due to the humidity of the material (in the earlier experiment lots we had around 10% of free water, presently we are working in a 3% level) and also an unbalanced heat supply to the load inside the bomb. We know that in a smaller scale such as ours, the yield should not be expected very high, but as we obtained in a few cases higher yields as 90-92%, we think it is possible to reach this point. We established, as a guide, our starting metallic yield to be 80%.

We also have developed a routine to recover back the metallic uranium from the slag of MgF_2, which will bring us back to around 97% of metallic recovering in total. We think that our productive routine of uranium, once fully operative, will lead to a better skill with a reasonable performance in terms of yield. The dingots presented a macroscopic appearance as expected, but

some of the dingots presented a heavy interpenetration of slag within the dingot top. Since we used all the time only crucibles made of graphite, the pick-up of carbon was not so high. It was less than 1000ppm.

IPEN used to produce previously, natural uranium in higher weight scale (up to 100kg dingots), but it has not been easy to re-achieve our previous skill in this metallurgy, since the downscaling of the process requires new plant adaptations and more advanced controlling equipment.

After a year and so of the recent practice, we can say that many improvements have been made, but there a plenty of parameters to control, mainly in preparing the charge and crucible and bomb design. The major drawback has been the process yield, for its heavy economical factor. In the area of process control, we are also trying to study a heat transfer modeling in order to get a fully controlled advancing thermal front inside the bomb during process. Controlling and data acquisition system for the reduction plant will be installed in future to provide a more adequate reduction process control.

U_3Si_2 Experiments

We aim to have IPEN production routing in a vacuum induction furnace. Nowadays, our available furnace needs a fully revamp in terms of new control facilities. This is a 40kW furnace, working in a fixed 10 kHz frequency as indicated in Fig.3. Some experiments using this equipment have been made with interesting results in terms of the aimed alloy U_3Si_2. The most representative of them was the UNSI02 that we consider to be closer to the product we aim to produce. So it has been studied in order to characterize it.

The experiment UNSI02 was made with a direct load of the whole charge inside the crucible. The charge was 2622g Uranium (<762ppm C) + 228g Silicon (8wt%), in form of chunks with less than 50mm in diameter. The fusion followed a pattern of 10min at 20kW, 8min at 40kW. After 2 min. at 40kW, we have the whole bath fully molten. The melt was kept under 40kW till the casting. The product was poured into a cylindrical copper mould of 29mm of internal diameter. The total mass obtained was 2810g, corresponding to 96.6% of weight yield. A chemical analysis revealed that the material was in average with 7.64 wt%Si. There was no serious silicon segregation from top to bottom of the rod (±0.05wt%Si, from 7.62 to 7.68wt%Si).

The chemical analysis of the product revealed a high pick-up in carbon (aprox.2000ppm). The product was cut in radial directions and prepared in metallographic specimens revealing the radial section of U_3Si_2 rod for analysis. Those specimens have been microanalysed using EDAX MEV Phillips XL30. Some powdered material was analysed in x-ray diffractometry and revealed the major phase presence for U_3Si_2, but also minor presence of U_3Si and USi.

EDAX microanalysis in a pace of 800μm, analyzing individual macro-areas of $6.10^5 μm^2$, throughout the radial direction, revealed a decreasing variation of silicon content from the ingot border towards the center, as shown in figure 4d. In this figure, three representative micrographic pictures are shown (fig.4a, 4b, 4c). Figure 5 and 6 show the variation of EDAX silicon content in the nominated phases USi and U_3Si_2, from the border until it was reached 2000μm in the radial direction. The fig.7 shows the radial direction path composition of a 50μm-band micrographs in order to characterize the microstructure evolution of the material formation from the border to the

center of the rod.

Table 1 - U_3Si_2 Physical and chemical specification for nuclear use in MTR IEA-R1m and the results for an experiment UNSI02

Elements	Specification	Exp. UNSI02
Uranium	balance	91.45%
Si	7.50% +0.40% -0.10%	7.64%
U_3Si_2	>80 wt%	Mainly U_3Si_2 phase
Al	600 ppm	20 ppm
B	10 ppm	0.7 ppm
C	2000 ppm	2665 ppm
Cd	10 ppm	0.1 ppm
Co	10 ppm	10 ppm
Cu	500 ppm	60 ppm
Fe+Ni	1500 ppm	150 ppm
H	200 ppm	
Li	10 ppm	
N	2500 ppm	
O	7000 ppm	
Zn	1000 ppm	10 ppm
Others	500 ppm individually, 2500 ppm in total	Mg = 3.24 ppm F = 3.15ppm
Isotopic Concentration	19.75% +/-0.20% for [235]U	Natural uranium
Density	11.7 g/cm^3	11.67 g/cm^3
Particle Size	44-89μm with max.20wt% <44μm	not available

Gathering the obtained information, we came to the conclusion that most of the present phase in the structure is U_3Si_2. The x-ray diffraction results is fairly coincident with the observed metalography. Some of the information shown above reveal an interesting arrange of phase microstructures, that the authors could not understand very well in the light of the described microstructures in the literature(2,3,4). Snelgrove(4) and Domagala(3) comments the impossibility of having in practice a theoretical homogeneous and monophase U_3Si_2 due to the presence of impurities. In our case, carbon is pretty much high and typically non-equilibrium process. Durand(5) showed recently that a new phase exists in between U_3Si_2 and USi, which is U_5Si_4 under 1200ºC, which also shows an eventual unstable structure for U_3Si_2 in a over stochiometric area under special conditions. Most of the literature is based on arc melted (and many times remelted) U_3Si_2, which displays a much more continuous phase formation different from the one we got, since it is closier to the equilibrium

situation. But we did not come across to analyses of non-equilibrium microstructures and no comments have also been furnished for eventual varition in silicon content in U_3Si_2

In our case, we had, during solidification (continuous temperature gradient) of the rod ingot, a silicon gradient from the border towards the center (macro-areas – fig 4d). Some may argue saying that this feature is a inhomogeneity in the bath, having not enough agitation before casting, which caused a probable segregation. This is not the case since there was no major segregation of silicon from the top to the bottom of the ingot. It was in fact a minor variation (less than 0.05% ([4])).

We had a very big variation in silicon percent from border to center (varying from 43 to 37 at%Si). Without much ground on the subject on our own, we register that we came across to a potential instability of U_3Si_2 chemical composition in a non-equilibrium situation, which vary strongly with the directional cooling imposed during the casting of molten alloy inwards of a copper mould. We hope that much more scientific work should be done to prove that, since its technologically very important.

Another relevant experimental fact is the variation of EDAX silicon content in nominated USi phase which varied not much around the expect 50at%. If we compared with its neighbor phase in the same region of analysis, U_3Si_2 phase should be very close to 40 at%Si (figure 6), but varied dramatically along the cooling direction. Commenting about the microstructure observation, we also saw a region of heavily cracked microstructure in a internal ring ranging from 600-2000μm from the border. This area were most of time 40at%Si, as shown by EDAX evaluation, in total agreement with the brittle nature of the equilibrium U_3Si_2. We are not assuring that the existence of this chemical tendency is a general rule, we are just registering it for further future scientific analysis.

In the more inner core of our solidified rod (>7000μm from the border) we found a much more constant microstructure of a EDAX Si-poor(around 38-37atwt%Si) U_3Si_2 surrounded by smaller regions of intergranular structures containing uranium rich phase and a nominated U_3Si. Describing this structure as shown in figure 4c, we can notice an interface (gray) between an almost full uranium material in the interior of the region (white) and the external grains of U_3Si_2.

The EDAX analysis for this material denotes the presence of U_3Si. Formed by $U_3Si_2 + U^o \rightarrow U_3Si$. It would be expected to have this reaction in a more time-temperature dependent way, but it appeared to happen much more promptly in a solidification cooling pattern.

All this lead us to the point to have problems of homogeneity if we really decide for induction route with casting, but the produced cast ingot of U_3Si_2 in the present experiments of IPEN already revealed our possibilities of reaching the aimed fuel material in future adopting this route.

Acknowledgements

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[4] In case of serious inhomogeneity due to bath lack of agitation, we would certainly get a gravitational segregation inside de ingot having the lightier (more silicon) material floating in the top of the ingot and the alloys with more uranium content aggregating towards the botton. In the case of our tests we had nothing similar to that.

References

(1) Perrota, J.A. , Lainetti, P.E.O. - Program of Converting IEA-R1 Brazilian Reasearch Reactor from HEU to LEU, 1996 RERTR Oct 7-10, 1996 Seoul, Korea.

(2) Wiencek, T.C. - Summary Report on Fuel Development and MiniPlate Fabrication for The RERTR Program, 1978 to 1990, August 1995, ANL/RERTTR/TM-15.

(3) Domagala, R.F. – Phases in U-Si Alloys – Research Reactor Core Conversion Guidebook – Vol:4: Fuels – IAEA , April 1992

(4) Snelgrove, J.L., Domagala, R.F., Hofman, G.L. and Wincek, T.C. – The Use of U3Si2 dispersed in aluminum in Plate-type fuel elements for research and test reactors, ANL/RERTR/TM-11, October 1987.

(5)Durand, J.P., Olagnon, G., Colomb, P. Lavastre, Y., Grasse, M. – Leu Fuel Development at CERCA – U5Si4 – A New Phase in the U/Si Diagram – Proceedings of RERTR Meeting, Oct 7-10, 1996, Seoul, Korea
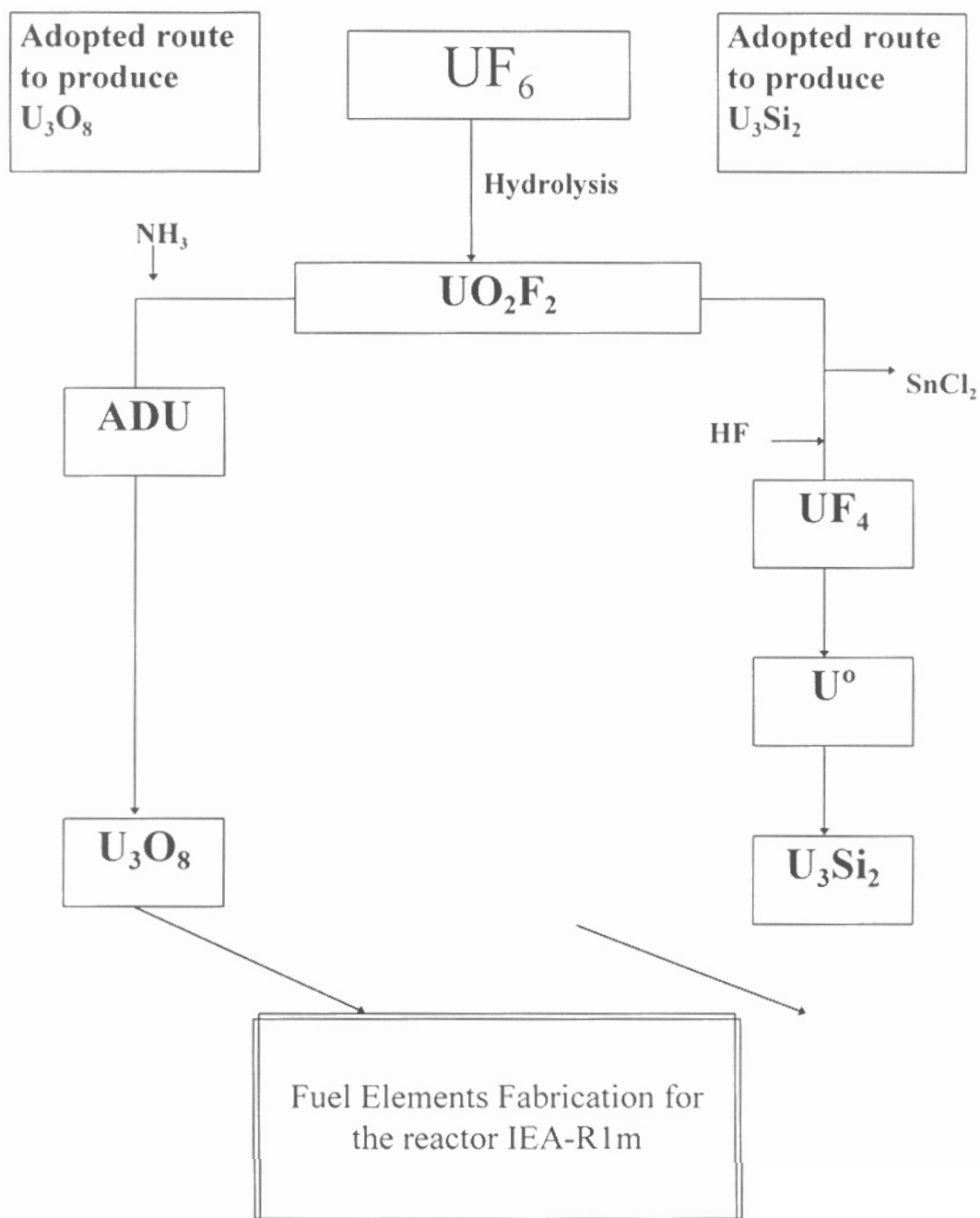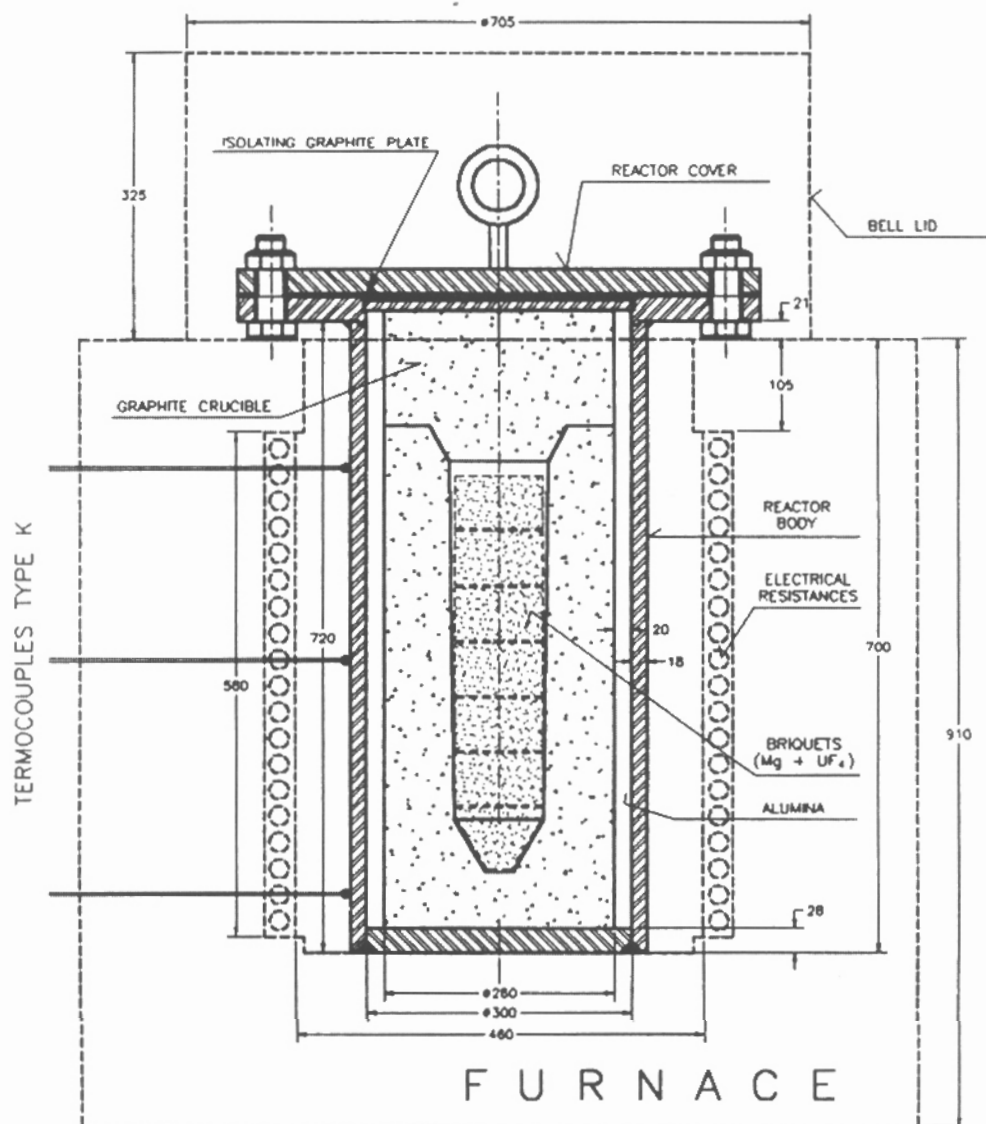
Fig.1

Routes used to produce fuel raw material U_3O_8 and UF_4
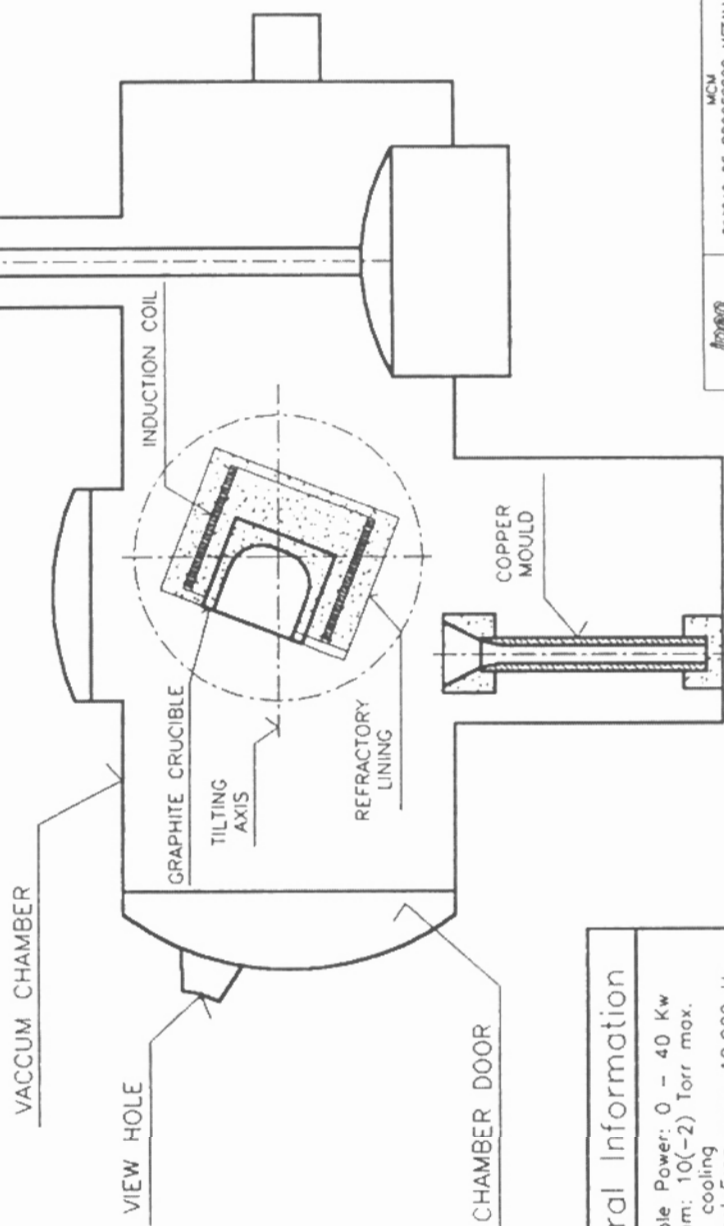
ASSEMBLING OF URANIUM REDUCTION BOMB

ISOLATING GRAPHITE PLATE

REACTOR COVER

BELL LID

GRAPHITE CRUCIBLE

TERMOCOUPLES TYPE K

REACTOR BODY

ELECTRICAL RESISTANCES

BRIQUETS (Mg + UF₄)

ALUMINA

F U R N A C E

ipen	MCM DIVISAO DE PROCESSOS METALURGICOS	
Design: Eneas Tavares de Oliveira		DATE 09/19/97

Fig.2 - Reduction Bomb for magnesiothermic reduction of UF_4 to produce metallic uranium.

SCHEMATIC DRAWING OF INDUCTION FURNACE
(SINDUS)

VACCUM CHAMBER

VIEW HOLE

INDUCTION COIL

GRAPHITE CRUCIBLE

TILTING AXIS

REFRACTORY LINING

COPPER MOULD

CHAMBER DOOR

General Information

- Variable Power: 0 – 40 Kw
- Vaccum: 10(-2) Torr max.
- Water cooling
- Nominal Frequency: 10.000 Hz
- Nominal Tension: 500V

Ipen

MCN
DIVISAO DE PROCESSOS METALURGICOS

Design: Eneas Tavares de Oliveira

DATE
09/17/97

Fig.3- Schematic drawing of Vacuum Induction Furnace (SINDUS) to fabricate the intermetallic U₃Si₂.
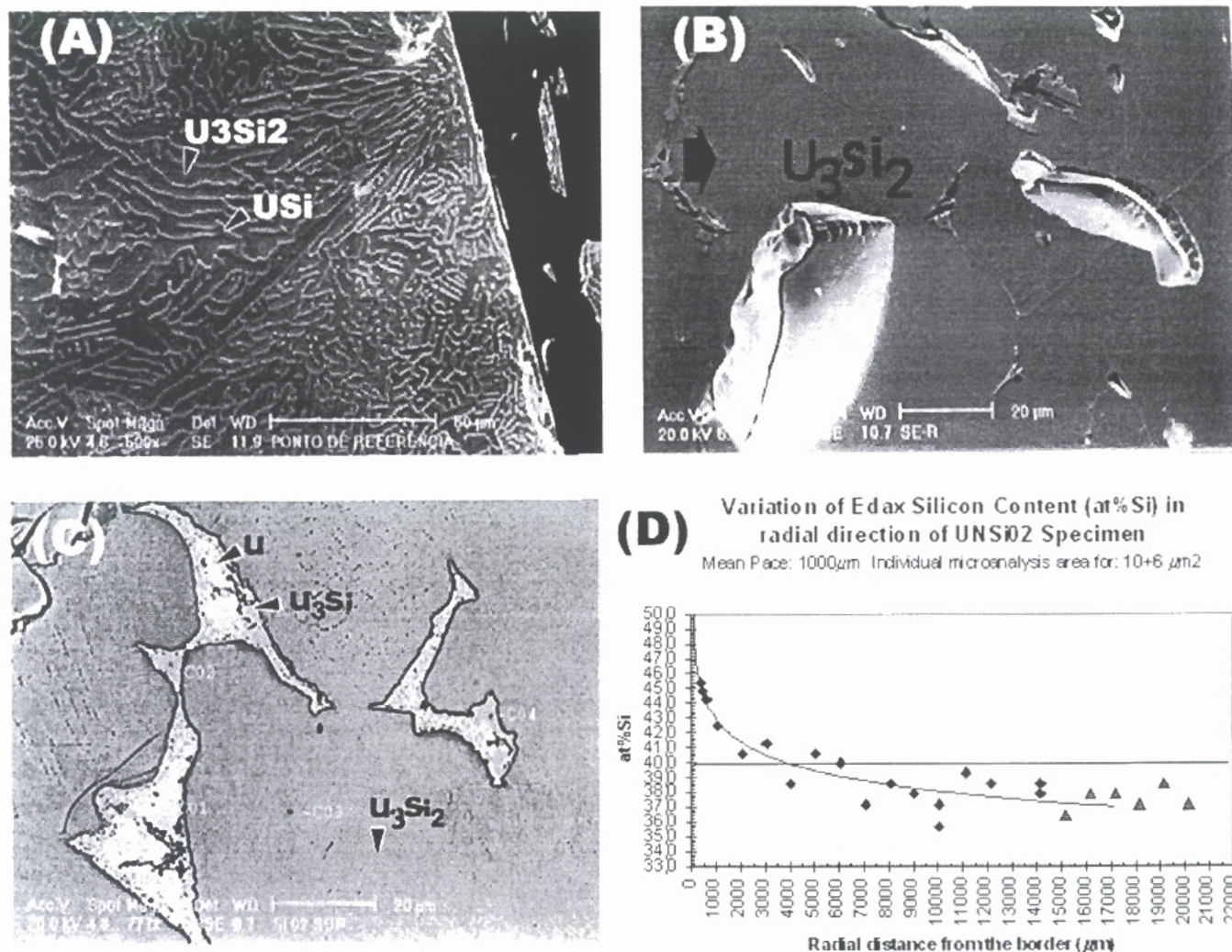
Fig.4- Samples of microstructure along the radial direction of specimen from experiment UNSI02. (a) border (b) 2067μm from border (c) center of the specimen (d) variation of at%Si throughout the radial direction from the border.
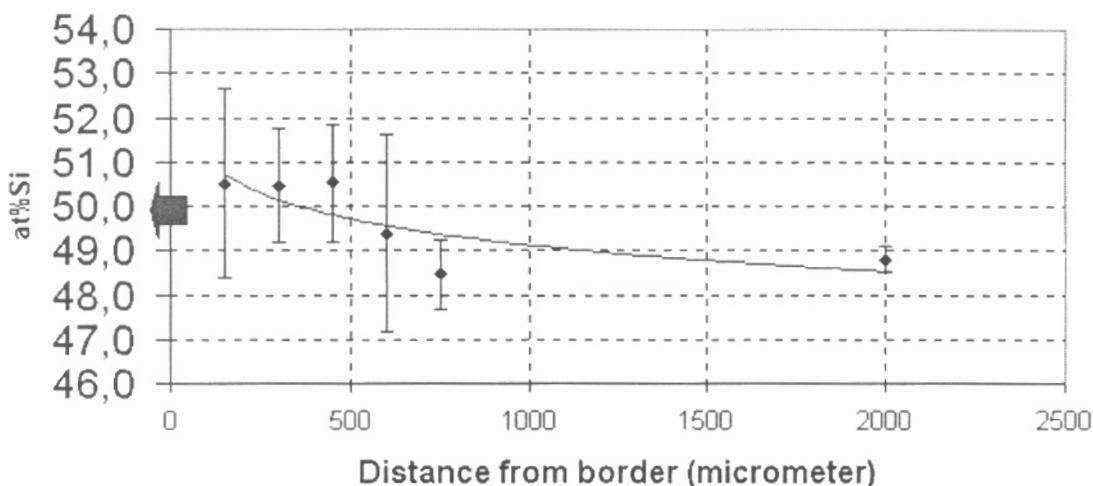
USi Phase - Dispersion of EDAX at% Silicon

Fig.5- Dispersion of EDAX at%Si in USi phase in the first 2000μm
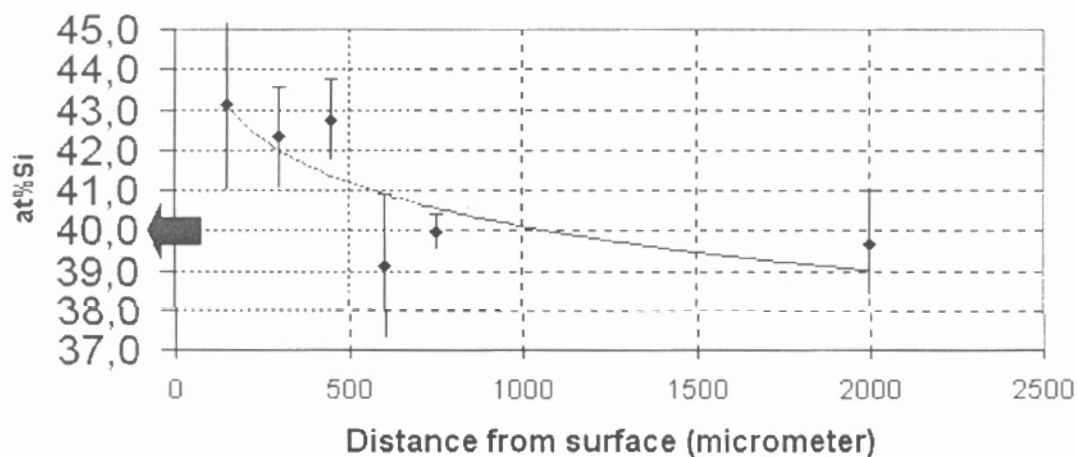
U3Si2 Phase - Dispersion of EDAX at% Silicon

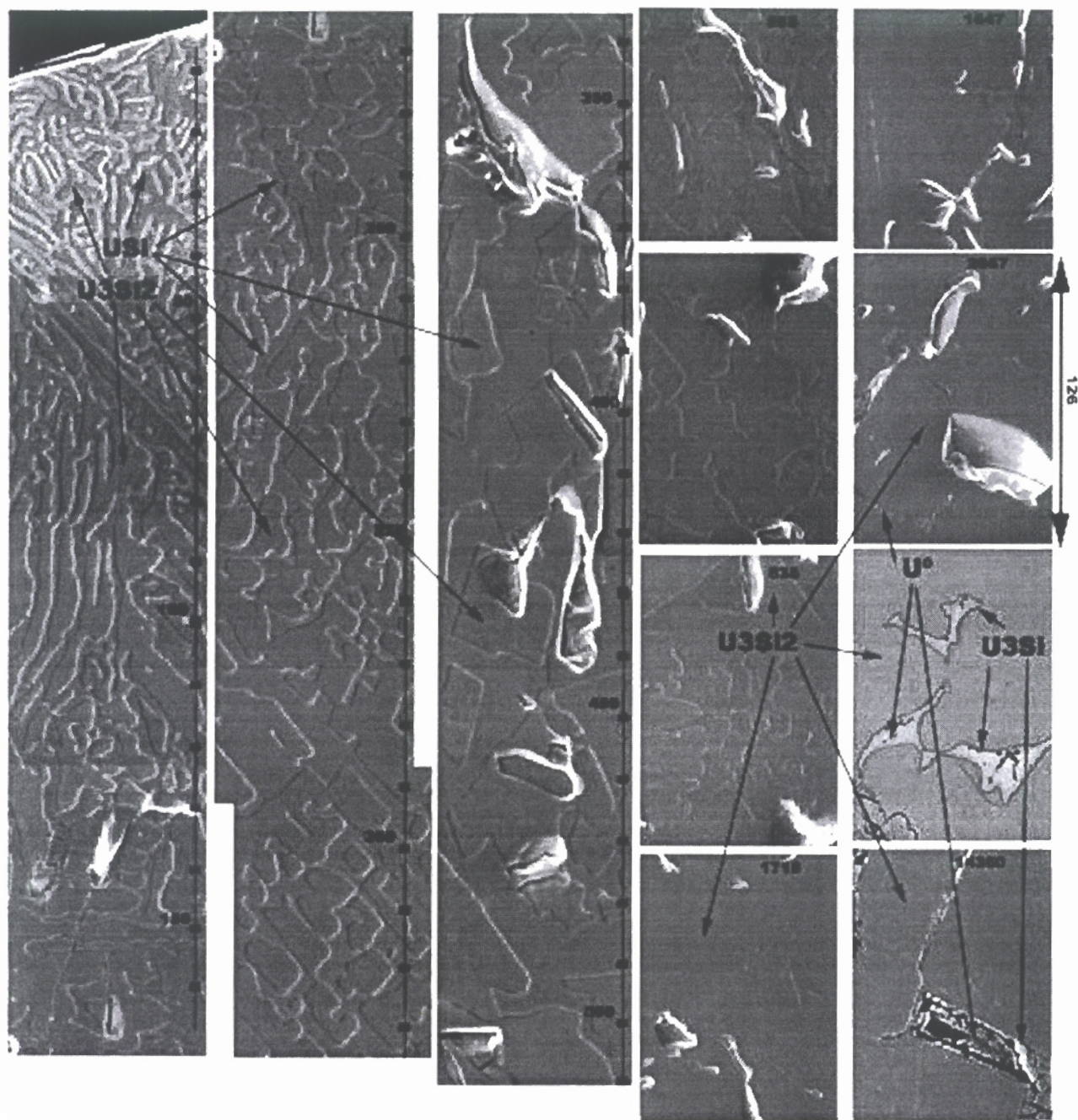Fig.6- Dispersion of EDAX at%Si in U_3Si_2 phase in the first 2000μm

Fig.7- Assembling of micrographs to show the path of EDAX analysis along the radial direction in the specimen from experiment UNSI02

References

[1] **Perrota, J.A. , Lainetti, P.E.O.** - Program of Converting IEA-R1 Brazilian Reasearch Reactor from HEU to LEU, 1996 RERTR Oct 7-10, 1996 Seoul, Korea.

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