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EFFICIENCY OF DIFFUSION BARRIERS
FOR ALUMINIUM-CANNED
URANIUM FUEL ELEMENTS

by

F. BROSSA, H. W. SCHLEICHER and R. THEISEN

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ORGEL PROGRAM

Joint Nuclear Research Centre
Ispra Establishment (Italy)
Materials Department
Metallurgy and Ceramics Division

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In the frame of the Orgel project, different barriers have been studied. Deposition methods have been developed and the diffusion behaviour of the respective couples and triplets has been evaluated by metallographic, micro-hardness and electron microprobe analyses. Ni, Cr, V, Nb and multiple barriers such as Si-V and Si-Cr seem up to now to show the greatest promise for practical applications.

The paper describes the results obtained thus far and compares the different barriers with respect to deposition procedures, diffusion rates, formation of intermetallic compounds and uranium concentration gradients. On the basis of these phenomena, the thickness of the diffusion barrier needed under specific reactor conditions (pressure, temperature and lifetime of fuel element) can be determined.

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CENTRE COMMUN DE RECHERCHE NUCLÉAIRE D'EURATOM
ISPRA, ITALY

Abstract — Résumé — Аннотация — Resumen

EFFICIENCY OF DIFFUSION BARRIERS FOR ALUMINIUM-CANNED URANIUM FUEL ELEMENTS. The use of aluminium-canned metallic uranium fuel elements is limited to relatively low temperatures if no special means are provided to inhibit the intermetallic diffusion between fuel and can. Intermediate layers should be efficient diffusion barriers but should, at the same time, effect a good bonding and exhibit a good thermal conductivity. This restricts these barriers practically to metallic layers.

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EFFICACITÉ DES BARRIÈRES CONTRE LA DIFFUSION DANS LES ÉLÉMENTS COMBUSTIBLES D'URANIUM GAINÉS D'ALUMINIUM. On ne peut utiliser des éléments combustibles d'uranium métallique gainés d'aluminium qu'à des températures relativement basses, si l'on ne prend pas des précautions spéciales pour inhiber la diffusion intermétallique combustible-gaine. Les couches intermédiaires devraient constituer des barrières efficaces contre la diffusion, mais aussi assurer une bonne liaison et présenter une bonne conductivité thermique. Pratiquement de telles barrières ne peuvent être que métalliques.

Dans le cadre du projet Orgel, les auteurs ont étudié divers types de barrières. Ils ont mis au point des procédés de déposition et étudié le comportement des différents doublets et triplets au point de vue de la diffusion en procédant à une analyse métallographique, à une analyse de la microdureté et à une analyse par microsonde électronique. Des barrières de Ni, Cr, V, Nb ainsi que des barrières multiples telles que Si/V, Si/Cr semblent offrir les meilleures perspectives d'application pratique.

Les auteurs exposent les résultats obtenus jusqu'ici et comparent les différentes barrières quant aux procédés de déposition, aux vitesses de diffusion, à la formation de composés intermétalliques et aux gradients de concentration de l'uranium. En tenant compte de ces phénomènes, on peut déterminer l'épaisseur de la barrière nécessaire pour empêcher la diffusion dans les conditions particulières d'un réacteur donné (pression, température et durée de vie de l'élément combustible).

ЭФФЕКТИВНОСТЬ ДИФФУЗИОННЫХ БАРЬЕРОВ ДЛЯ ТЕПЛОВЫДЕЛЯЮЩИХ ЭЛЕМЕНТОВ ИЗ УРАНА С АЛЮМИНИЕВОЙ ОБОЛОЧКОЙ. Применение тепловыделяющих элементов из металлического урана с алюминиевой оболочкой лимитируется сравнительно низкими температурными режимами, если не предусмотрены специальные меры, препятствующие диффузии между топливом и оболочкой. Промежуточные прослойки должны быть эффективными диффузионными барьерами, одновременно должны обеспечивать прочную связь и иметь хорошую теплопроводность. Это практически ограничивает выбор таких барьеров металлическими прослойками.

В рамках проекта Оргель были изучены различные барьеры и разработаны их нанесения. Путем металлографического и электронного микрованализа и определения микротвердости были оценены диффузионные свойства соответствующих пар и триплетов.

В настоящее время Ni, Cr, V, Nb и многослойные барьеры вроде Si/V, Si/Cr являются самыми перспективными для применения на практике.

Дается описание результатов, достигнутых до сих пор, и сравниваются различные барьеры с точки зрения технологии их нанесения, скорости диффузии, образования межметаллических соединений и градиентов концентрации урана. На основе таких данных можно определить толщину диффузионного барьера, необходимую при определенных условиях реакторного режима (давление, температура и срок службы теплоделяющего элемента).

EFICACIA DE LAS BARRERAS DE DIFUSIÓN PARA ELEMENTOS COMBUSTIBLES DE URANIO ENVAINADO EN ALUMINIO. Si no se recurre a medios especiales tendientes a evitar la difusión intermetálica combustible vaina, los elementos combustibles de uranio metálico revestidos de aluminio sólo pueden utilizarse a temperaturas relativamente bajas. Esas barreras intermedias deberían inhibir eficazmente la difusión y, al mismo tiempo, constituir una unión resistente y buena conductora del calor. Por tales motivos, la elección se limita en la práctica a los metales.

En el marco del proyecto Orgel, los autores han estudiado diversos inhibidores. Perfeccionaron procedimientos de depósito y evaluaron las propiedades de difusión de los pares o tripletes respectivos por medio de determinaciones metalográficas y de la microdureza, así como por análisis electrónico de micromuestras. A parecer, los mejores resultados se obtienen con Ni, Cr, V y Nb, así como con barreras múltiples del tipo Si/V y Si/Cr.

La memoria describe los resultados obtenidos hasta el presente, y compara los diversos inhibidores en cuanto a los procedimientos de depósito, velocidades de difusión, formación de compuestos intermetálicos y gradientes de concentración del uranio. Sobre la base de estos datos, puede determinarse el espesor de la barrera de difusión que se requiere para condiciones determinadas de funcionamiento del reactor (presión temperatura y vida útil de los elementos combustibles).

1. INTRODUCTION

In the development of a nuclear fuel element, special attention has to be paid to the compatibility between fuel and can. In the ORGEL reactor (organic-cooled, heavy-water-moderated natural uranium reactor), one possible fuel type could consist of a metallic uranium rod canned with aluminium. Fuel surface temperatures will be around 430°C. At this temperature a direct contact between uranium and aluminium would result in excessive interdiffusion between the metals and limit the lifetime of an element to a very short period. It is thus clear that a diffusion barrier is required between the two metals.

Such a diffusion barrier has to fulfil certain conditions:

1. It must prevent the penetration of uranium to the outer surface of the can.
2. It must establish a good bonding between fuel and can.
3. It should have a good thermal conductivity.
4. Neutron absorption must be kept as low as possible.

On the basis of these considerations several types of barriers have been studied in detail with the aim of evaluating a conveniently applicable barrier which would work for at least one year at 450°C. This paper describes the results obtained and compares the different barrier types. The results of the diffusion studies on binary systems with the barrier metal and uranium or aluminium, respectively, which preceded normally the study of the combined systems, are however only briefly cited and reference is made to the respective reports describing this work in detail.

The work on which this paper is based has only partially been done at Euratom's own laboratories; the most important contributions came from the Metallurgy Department of the Nuclear Research Centre of Belgium (Centre d'étude de l'énergie nucléaire (C.E.N.), Mol), as well as from the

laboratories of CERCA (Compagnie pour l'étude et la réalisation de combustibles atomiques), Bonneuil, which both worked under contract. The preparation of the diffusion layers was made at the above laboratories. Electron microprobe analyses were made at Ispra.

2. MATERIALS, PREPARATION AND EVALUATION

2.1. Materials

After preliminary tests with a number of different metals, Ni, Cr, V and Nb were selected for a detailed study. To these have been added recently multiple barriers composed of V-Si and Cr-Si, Si being in both cases situated on the aluminium side. These combinations have been chosen, as there is only a very small solubility of Si in Al and of V or Cr in U [1]. The uranium was reactor-grade material, containing 120 ppm (Fe + Si); the aluminium was 99.5% pure, with 0.5% (Fe + Si) as main impurities.

2.2. Preparation and treatment of the samples

In the case of the nickel and chromium barriers, which were deposited electrolytically, cylindrical samples of 8-mm diam. were used. For the study of the barriers consisting of V, Nb or multiple layers, however, the evaporation unit, which was used for their preparation, was not equipped with the necessary rotating device, so that flat sandwich-type samples had to be used.

Details of the deposition procedures are mentioned in the sections dealing with the special barriers. The cylindrical samples were autoclaved to achieve a good contact between the different metals. The sandwich-type samples were normally clamped together by stainless steel screws, the creep of the aluminium at high temperatures limited the pressure during the diffusion treatment, which was done in an argon atmosphere in quartz capsules. Other samples were prepared by roll-milling.

2.3. Examination

Diffused samples were examined by metallography, by electron microprobe analysis and by microhardness testing. In the case of the chromium barriers also X-ray radiography was done and thermal cycling was employed to determine the mechanical rigidity of the bond.

The metallographic preparation and examination of the samples were often very difficult because of the brittleness of the intermetallic compounds, the differences in the hardness of the different layers and the failure to find etching solutions which develop all the phases equally well. Furthermore, the identification of the appearing phases is sometimes difficult because of the absence of some intermetallic phases which should be thermodynamically stable but, for kinetic reasons, do not develop during the diffusion process.

All these problems may have contributed to the contradictions found in earlier work. In such cases the electron microprobe analyser is the most powerful tool to get precise information.

In our work a Cameca microprobe analyser was used, on samples polished on diamond ($1/4 \mu\text{m}$) without or with only a very slight chemical attack. As the normally used correction calculations [2] are insufficient for the analysis of phases containing elements with X-ray absorption coefficients as different as those of the system U-Ni-Al, new correction formulas have been developed [3] and used for the calculations. As the determined values of the aluminium concentration depend strongly on the acceleration of the excited electrons, the analysis of aluminium in the different phases has been accomplished by measurements of the $\text{AlK}\alpha_1$ line intensities at different acceleration voltages between 5 and 10 kV and extrapolation of the obtained values (after correction for the mass absorption) to the critical acceleration of the $\text{AlK}\alpha_1$ line (where no retrodiffusion of electrons occurs). The concentration values thus obtained are quoted in the figures and tables of this paper.

2.4. Evaluation of the quality of the barriers

Up to now, the lifetime of the diffusion barriers was normally considered to be the time during which undecomposed, pure barrier metal is still present in the bond. Our examination showed, however, that the diffusion of uranium in the aluminium phase of the can is very restricted, even if the barrier metal is totally transformed to intermetallic compounds. That means that there is still a barrier effect after consumption of the pure barrier metal and this permits an increase in the life of the barrier. The criterion for the efficiency of a special type of diffusion barrier can therefore not be quoted as "lifetime" of pure metal as a function of the temperature, but has to take into account the thickness of the penetration zone. In view of the special conditions of the ORGEL project, where the canning thickness may be about 1 mm of aluminium, we consider as lifetime of a barrier the time after which a diffusion zone of about $750 \mu\text{m}$ will be visible under the microscope.

Microprobe analysis has shown that the uranium concentration in the aluminium phase comes down to undetectably low values within a few microns of distance from the visible phase boundary.

3. THE DIFFUSION BEHAVIOUR OF ELEMENTS WITH DIFFERENT BARRIER SYSTEMS

3.1. Study of the diffusion in elements U-Ni-Al

The practical interest of a nickel barrier is shown by several publications concerning the diffusion in the systems Al-Ni [4-6], Ni-U [7, 8] and Al-Ni-U [9-11]. However, the data of these papers are not sufficient to allow definite conclusion as to the applicability for the ORGEL project.

The study described here has been carried out in close collaboration with the Nuclear Research Centre of Belgium at Mol, and much of the data communicated here was taken from the report issued on this work [12].

As a knowledge of the binary system is the only satisfactory basis for the study of the ternary system, these binary systems are treated briefly before proceeding to the ternary. The preparation methods, which are largely the same for both studies, are described together with the binary systems.

3.1.1. The study of the couples U-Ni-and Ni-Al

3.1.1.1. U-Ni

The tests have been limited as it was found that the diffusion rate in the ternary system is determined rather by the interdiffusion Al-Ni than by the interdiffusion U-Ni. The tests showed that the methods of etching and nickel deposition have a strong influence on the diffusion rate and the homogeneity of the diffusion layers. Among a number of methods, the subsequently described procedure gave the best results [13].

- (a) Anodic etching of the uranium in an aqueous solution, containing 10% nitric acid.
- (b) Nickel deposition in an aqueous solution containing:
- | | |
|----------------------------|-----------------------|
| Nickel sulphate | 200 g/l |
| Sodium citrate | 40 g/l |
| Ammonium chloride | 5 g/l |
| Wetting agent ("Lissapol") | 2 cm ³ /l |
| pH | 4-5 |
| Temperature | 25°C |
| Current density | 1,5 A/dm ² |
- (c) Degassing in vacuum (slow temperature rise (100°C/h) up to 350°C, maintaining the final temperature for about 1 h).

After a treatment of 1 h at 500°C, no diffusion was found; at 540°C, however, a diffusion layer of about 3- μ m thickness had appeared after the same time. No detailed study has been done on either the determination of the phases formed or the kinetics of the process. The results induced us, however, to specify a pre-treatment of 1 h, 575°C for all ternary U-Ni-Al samples.

3.1.1.2. Ni-Al

The study of this binary system was limited to solid samples of the sandwich-type, clamped together by a titanium screw. The nickel, as well as the aluminium, had been etched in a solution after JACQUET [14] (HClO₄ and CH₃COOH).

Diffusion treatments have been carried out at temperatures from 370°C to 520°C and durations from 2 × 10⁵ to 5 × 10⁶ s. Two intermetallic phases Al₃Ni₂ and Al₃Ni have been found.

The diffusion follows the expression

$$X^n = kt, \quad (X = \text{thickness of diffusion layer in cm}) \quad (1)$$

$$(t = \text{time in s})$$

where n is approximately 2. The temperature influence is described by

$$k = k_0 e^{-Q/RT}, \quad (2)$$

with

$$k_0 = 7.3$$

$$Q = 38\,500 \text{ cal/M}.$$

3.1.2. Multiphase diffusion studies in U-Ni-Al elements

The following procedure was employed for the preparation and treatment of the ternary U-Ni-Al elements, consisting of a uranium rod (8-mm diam.), a nickel layer (thickness between 9 and 37 μm) and an aluminium can (1-mm thickness):

- (a) Nickel deposition by the described procedure.
- (b) Vacuum degassing with temperature rise to about 350°C (see 3.1.1.1).
- (c) Pre-diffusion for 1 h at 575°C.
- (d) Canning, electron bombardment welding.
- (e) Autoclaving at different temperatures (475–600°C) and pressures (50–1000 atm), normally 525°C, 700 atm.
- (f) Sealing in quartz capsules.
- (g) Diffusion treatment between 400 and 520°C.

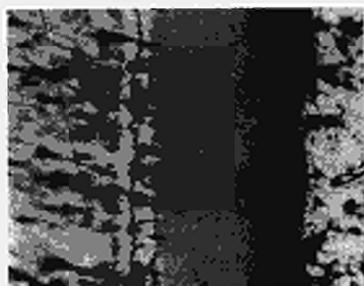
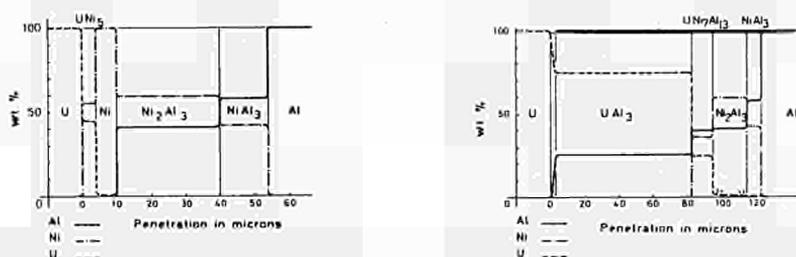
The aim of the different autoclaving treatments (mentioned as (e)) was to determine the best conditions for an intimate contact of can and barrier and for a regular development of the diffusion between the nickel and both its adjacent metals. It was found that at least 525°C and 350 atm are necessary to have an efficient bonding, but best results were obtained at 535°C with 500 atm.

Depending on time and temperature of the diffusion treatment, microscopical and X-ray microprobe analysis showed a different composition of the samples. Three main stages may be distinguished, as follows:

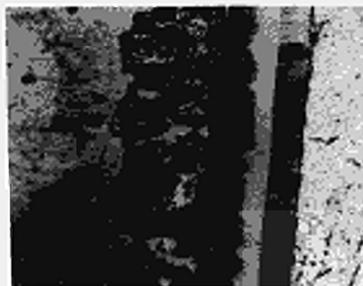
- (i) There is still a pure, undecomposed nickel barrier (Fig. 1(a)).

Diffusion proceeds as described for both binary systems U-Ni and Ni-Al, with parabolic rate laws and formation of very brittle intermetallic compounds (especially on the U-Ni side).

- (ii) All the nickel is consumed, but a binary U-Al compound has not yet formed.



(a)



(b)

Fig. 1

Multiphase diffusion in uranium-nickel-aluminum samples

(a) Diffusion of U-Ni-Al, 10^5 s at 520°C ($25\ \mu\text{m}$ Ni)

(b) Diffusion of U-Ni-Al, 3×10^5 s at 520°C ($28\ \mu\text{m}$ Ni)

The aluminium comes into contact with the UNi_5 and forms with it a ternary layer of variable composition (two phases in one diffusion layer are thermodynamically possible in a system of three components).

(iii) Formation of a ternary layer of a composition of nearly $\text{UNi}_7\text{Al}_{13}$ and appearance of the binary compound UAl_3 (Fig. 1(b)).

Stages (i) and (ii) are relatively rapid. The formation of UAl_3 then becomes the most apparent feature of the process. This phase grows rapidly, preferentially in the form of tendrils entering in the grain boundaries of the uranium and then expanding laterally. The thickness of this phase exceeds in a relatively short time the thickness of all other diffusion layers together.

The concentration of the third element has been measured in some of the binary phases. In the UAl_3 the Ni content drops from 0.4% at the interface with the ternary phase to practically zero within about $80\ \mu\text{m}$. The phases adjacent to the aluminium, NiAl_3 and Ni_2Al_3 contain about 0.3 and 0.4% uranium, respectively. Uranium is detectable in the Al within about $50\ \mu\text{m}$ from the Al- Al_3Ni interface.

A ternary compound corresponding approximately to the formula $\text{UNi}_7\text{Al}_{13}$ has been found adjacent to the UAl_3 . Attempts have been made to prepare this compound synthetically but without success. Always two phases Ni_2Al_3 and UNiAl_4 were formed. It seems therefore that this phase is formed only

at low temperature by diffusion processes and that it decomposes at higher temperatures by the mechanism



This decomposition has been confirmed by X-ray projection microscopy, achieved by a special accessory in the electron micro-analyser [15] (see Fig. 2).

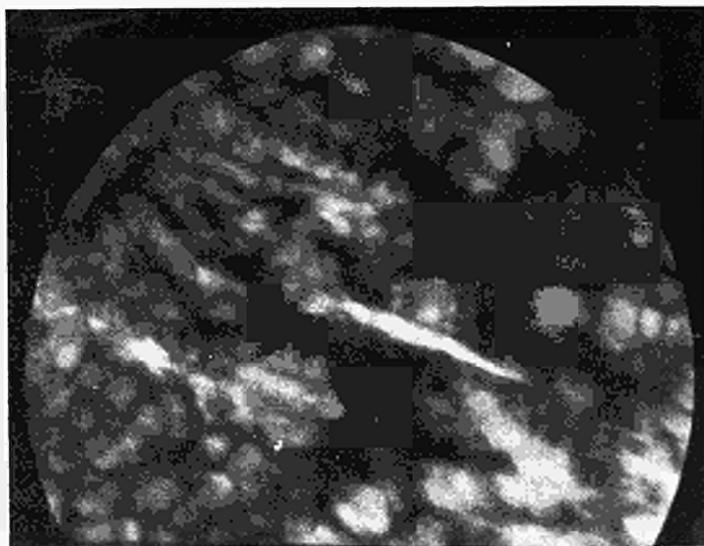


Fig. 2

Decomposition of ternary $\text{UNi}_7\text{Al}_{13}$ diffusion layer after annealing above 650°C
 (X-ray projection microradiograph, $\times 250$)
 UNiAl_4 = dark zone.
 Ni_2Al_3 = bright grey dendrites.

The compounds formed during stage (iii) seem to be less brittle than those formed previously. Table I summarizes the main compositions of the diffusion layers.

The experimental results show that the logarithm of the total diffusion layer thickness is a linear function of the logarithm of the time for given temperature and initial nickel layer thickness, so that

$$X^n = kt; \quad (1)$$

k depends on temperature by the equation

$$k = k_0 e^{-Q/RT}, \quad (2)$$

and k_0 and Q have been found to be

TABLE I

MEAN COMPOSITION OF DIFFUSION
LAYERS IN THE SYSTEM Al-Ni-U
(Corrected values, adjusted to 100%)

| Al (wt. %) | Ni (wt. %) | U (wt. %) | Phase |
|---------------|---------------|--------------|-----------------------------------|
| 0.2 | 41.7 | 58.1 | NiAl ₃ |
| 0.4 | 58.8 | 40.8 | Ni ₂ Al ₃ |
| 34.8 | 40.7 | 24.5 | UNi ₇ Al ₁₃ |

$$k_0 = 2.75 \times 10^{-2}$$

$$Q = 23\,500 \text{ cal/M}$$

when t is measured in seconds and X in centimetres.

As it has been found that for given times and temperatures the logarithm of the total thickness X is a linear function of the initial barrier thickness E (cm) X may be expressed by the formula

$$X = C_1 t^{C_2} e^{C_3/T_e} C_4 E \quad (3)$$

for which the following values have been determined by the method of least squares, using all measured values:

$$C_1 = 0.32$$

$$C_2 = 0.716$$

$$C_3 = -8350$$

$$C_4 = -740$$

3.2. Study of the diffusion in elements U-Cr-Al

The study concerning the chromium as a diffusion barrier was carried out in collaboration with CERCA, Bonneuil. The final report on this work under contract is in press [16]. Again, the binary systems are shortly treated at first.

3.2.1. The study of the couples U-Cr and Cr-Al

3.2.1.1. U-Cr

The chromium barrier was deposited electrolytically. The uranium was etched anodically by a treatment in a solution of 10% HCl followed by etching in 30% HNO₃, 90°C, with ultrasonic agitation. The uranium surface

becomes quite rough in this treatment. For the electrolytic chromium deposition two solutions have been applied:

- (a) Solution of Passal [17]
- | | |
|---------------------------------|--------|
| CrO ₃ | 300 g |
| SrSO ₄ | 15 g |
| K ₂ SiF ₆ | 40 g |
| H ₂ O | 1000 g |
- (b) Solution of BORNHAUSER [18]
- | | |
|--------------------------------|---------|
| CrO ₃ | 330 g/l |
| NaOH | 48 g/l |
| Cr ₂ O ₃ | 6 g/l |

The adherence of both deposits is good, however corrosion tests show the existence of cracks. Tests are underway to prevent them by multistage deposition.

Diffusion experiments have been run with solid sandwich-type samples. No diffusion has been found with α -uranium, i. e. at temperatures up to 600°C, even after very long times. At higher temperatures (β - and γ -uranium) the diffusion becomes quite important. Differences have been found in the diffusion rate using different types of chromium (Passal or Bornhauser deposits or solid samples). However, as the diffusion with β - or γ -uranium is not of practical interest for the ORGEL project (because of too high temperatures), the study of the U-Cr diffusion has not been continued further. Differential electron beam scanning pictures show that no diffusion layer is formed. Uranium and chromium are present as pure elements (Fig. 3).

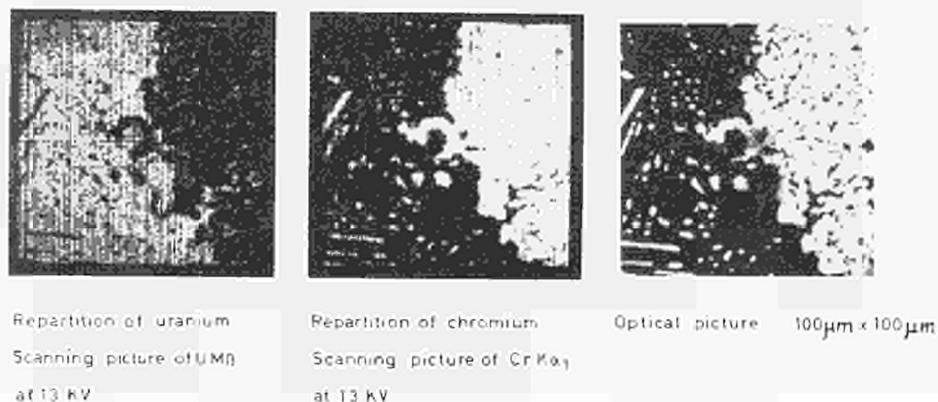


Fig. 3

Diffusion of uranium-chromium couples after annealing 15 h at 825°C
(Optical and scanning electron microprobe picture)

3.2.1.2. Cr-Al

The diffusion has been studied with chrome-plated aluminium samples. The most characteristic results are:

- (a) High sensibility to the applied pressure.
(b) Without application of pressure, the diffusion does not start at

temperatures beyond 430°C, but is highly accelerated when passing from 450 to 500°C.

- (c) Only two of the intermetallic phases given by the phase diagram (1) appear as diffusion layers. The compound adjacent to the chromium forms a relatively flat layer (Vickers hardness 650 kg/mm²), the other one shows a toothed band (Vickers hardness 350 kg/mm²). The junction between aluminium and this compound is the most brittle interface in the system.

A comparison of the systems Cr-Al and Ni-Al shows that the interdiffusion of chromium and aluminium is initially more important than that of nickel and aluminium, but continues at a smaller rate. At 450°C, for instance, the following rate laws have been found:

$$\begin{aligned} x &= 1.64 t^{0.32} && \text{for Cr-Al, and} \\ x &= 0.26 t^{0.59} && \text{for Ni-Al.} \end{aligned}$$

The Vickers hardness (V. H.) of the hardest compounds forming during the diffusion in both systems is

$$\begin{aligned} 650 \text{ V. H.} &&& \text{for Cr}_2\text{Al}_{11}, \text{ and} \\ 860 \text{ V. H.} &&& \text{for Ni}_2\text{Al}_3. \end{aligned}$$

3.2.2. Multiphase diffusion studies in U-Cr-Al elements

As the deposition of chromium barriers is more difficult than that of nickel barriers and as the results of the ternary diffusion examinations show a much bigger scatter, the preparation and treatment pattern was sometimes changed during the course of the study. However, the general line may be described similarly to that of the nickel barriers.

- (a) Deposition of the chromium in the solution after Passal (cf. 3.2.1).
- (b) Degassing for 3 h at 200°C and 10⁻⁵ torr.
- (c) Canning, electron bombardment welding.
- (d) Autoclaving, generally at 450°C and 200 atm, however also for some tests at higher temperatures and pressures.
- (e) Diffusion treatment at temperatures between 450 and 600°C, either in vacuum or under argon pressure in autoclaves.

As described above, the chromium deposits are generally sound and adherent after the vacuum treatment. However, they do not look brilliant and exhibit a slightly rough, coarse surface.

Diffusion at 450°C

No diffusion could be detected, either after treatments without pressure, or after 200 h at 40 atm. Even a previous autoclaving of 1 h at 535°C and 650 atm did not produce diffusion after annealing during 360 h.

Dismantling of the samples shows the complete absence of bonding between chromium and aluminium. This corresponds nearly to the binary Al-Cr diffusion studies which showed that diffusion starts only at about 440°C.

Diffusion at 500°C

The tests demonstrate a considerable influence of the pressure. After 15 h, a diffusion layer of 10 μm was observed when the treatment was done in vacuum and a layer of 25 μm , when a pressure of 40 atm was maintained. In this latter case diffusion peaks reached nearly the uranium (initial chromium thickness 30 μm). After 60 h under 40 atm, chromium layers of 30-50 μm had reacted almost completely with the aluminium.

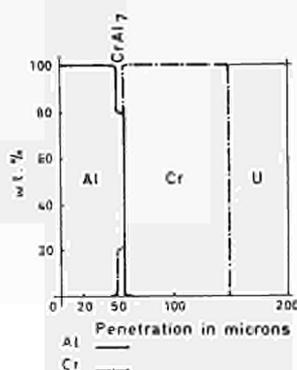


Fig. 4

Diffusion of chromium-aluminium after annealing 5 h at 500°C

The microprobe analysis of a sample treated during 5 h at 40 atm showed that a layer smaller than 10 μm consists in only one compound, CrAl_7 (Fig. 4).

Diffusion at 550°C

Diffusion without applied pressure is irregular. After 25 h, a maximal thickness of about 25 μm was measured.

Table II summarizes the mean compositions of the diffusion layers. As it is shown by Fig. 5(a), the layer of CrAl_3 disappears in contact with UAl_3 when the chromium is completely consumed.

The composition of Fig. 5(b) has been determined in the zone where the chromium layer was still present. The presence of uranium in the phase CrAl_3 and $\text{Cr}_2\text{Al}_{11}$ indicates that there has been a horizontal diffusion of uranium behind the barrier. The concentration of uranium in the compound CrAl_3 has been found to decrease from 0.3 wt. % at the contact $\text{UAl}_3\text{-Cr-CrAl}_3$ (near the "break-through") to 0.17 wt. % at the interface $\text{CrAl}_3\text{-Cr}_2\text{Al}_{11}$. In the $\text{Cr}_2\text{Al}_{11}$ the uranium concentration is constant and equal to 0.17 wt. % and in the CrAl_7 no uranium was detectable.

In spite of the sometimes very irregular test results, the following characteristic features of the chromium barriers were well established:

- (a) The diffusion starts only when the temperature exceeds 450°C. Once initiated, it proceeds quite irregularly but when external pressure is applied, more rapidly than that of a Ni barrier.

TABLE II
 MEAN COMPOSITION OF DIFFUSION
 LAYERS IN THE SYSTEM Al-Cr-U
 (Corrected values, adjusted to 100%)

| No. | Al (wt. %) | Cr (wt. %) | U (wt. %) | Phase |
|-----|---------------|---------------|--------------|----------------------------------|
| 1 | 78.6 | 21.4 | - | CrAl ₇ |
| 2 | 72.5 | 27.3 | 0.2 | Cr ₂ Al ₁₁ |
| 3a* | 61.6 | 38.1 | 0.3 | CrAl ₃ |
| 3b* | 26.9 | - | 73.1 | UAl ₃ |

* Layers 3a or 3b are formed when chromium is still present or consumed, respectively.

- (b) The diffusion of the uranium most probably does not penetrate the last layer of CrAl₇ and does not reach the aluminium can.
- (c) The mechanical behaviour of miniature fuel elements which were prepared by canning threaded uranium rods with an aluminium can using an intermediate chromium layer of 30 μm has been acceptable, even after a strong thermal cycling treatment (100 rapid cycles between 15 and 350°C).

3.3. Study of the diffusion in sandwiches U-V-Al

As already mentioned, the study of the vanadium barrier has been limited to flat samples, as it was up to now not possible in the apparatus employed by C.E.N., Mol, to evaporate the vanadium on cylindrical samples. As for the preceding barriers, the main deposition procedures are described in the section dealing with the binary systems.

3.3.1. Study of the couples U-V and V-Al

3.3.1.1. U-V

As no suitable electrolytic deposition process for vanadium had been found, evaporation by electron bombardment heating has been adopted [19]. The vanadium was carefully degassed and the uranium was anodically etched in a 10% HNO₃ solution. The uranium substrate must be maintained at about 400°C during evaporation if good adherence is requested. This determines a lower limit of the distance between the vapour source and the uranium. One hundred mm was chosen as the separation still permitting good efficiency. The heating of the uranium produces oxidation however, visible as a layer of about 2- μm thickness by micrography, but not preventing the diffusion.

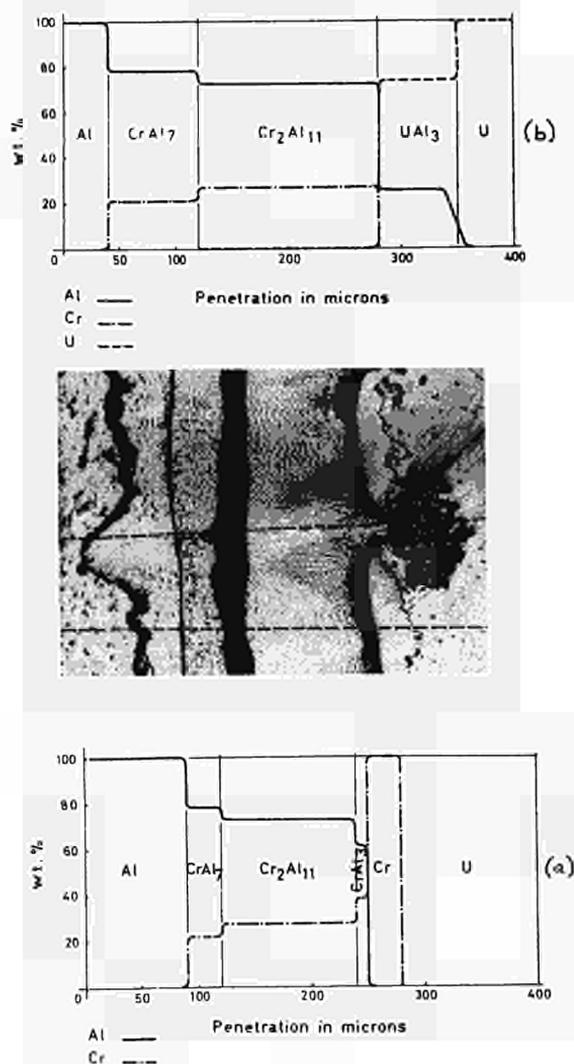


Fig. 5

Ternary diffusion uranium-chromium-aluminum

- (a) Diffusion 85 h at 500°C, applied pressure 40 kg/cm²
 (b) Diffusion 85 h at 500°C, applied pressure 40 kg/cm²

However, to exclude any possible influence of an oxide film a very faint nickel layer was deposited electrolytically on several samples before evaporation of the vanadium. After evaporation, the samples were maintained for 16 h at 600°C under vacuum, in order to decrease internal tensions and to improve the adherence. No diffusion was found between vanadium and α -uranium, even after heat treatments (up to 3 months).

3.3.1.2. V-Al

Different procedures were used to prepare the diffusion couples: evaporation of vanadium onto aluminium, roll-milling of units consisting of an aluminium rod surrounded by a vanadium tube, combining aluminium and vanadium disks by titanium screws and spot-welding. Both metals were etched anodically, the aluminium in a mixture of HClO_4 and CH_3COOH , the vanadium in a solution containing HF , CH_3COOH and H_3PO_4 .

Diffusion tests were run at temperatures between 460 and 610°C and durations between 3 h and 3 months.

The coefficients of the equation

$$X^n = kt = k_0 e^{-Q/RT} t, \quad (4)$$

where

X = total thickness of diffusion layers (cm)

T = temperature (°K)

t = time (s),

have been calculated by the method of least squares.

The following values have been found for the samples with evaporated vanadium:

$$n = 1.42$$

$$k_0 = 270$$

$$Q = 43\,000 \text{ cal/M}$$

For the rolled samples the diffusion is more rapid and it has been found

$$n = 1.48$$

$$k_0 = 7.7$$

$$Q = 36\,600 \text{ cal/M}$$

The microprobe analyses carried out on samples treated for 5×10^5 s at 610°C revealed the presence of four intermetallic compounds: V_5Al_8 , VAl_3 , VAl_6 and VAl_7 (Fig. 6).

3.3.2. Multiphase diffusion studies in the U-V-Al system.

Vanadium layers of 10- to 22- μm thickness were evaporated onto uranium disks by the previously described procedure. The coated samples were clamped with titanium screws to aluminium disks and heat treated in argon-filled quartz capsules at temperatures between 460 and 610°C and times between 3×10^4 and 1.2×10^7 s.

Differing from what was found for the solid binary couples of Al-V, the two phases VAl_7 and V_5Al_8 were not detected in the ternary samples with evaporated V; however, besides the two compounds VAl_3 and VAl_6 , in most samples a small UO_2 layer was found (Fig. 7(b) which had been formed during the evaporation procedure. This layer blocks during a certain period the reaction between VAl_3 and the uranium. After a long period of diffusion

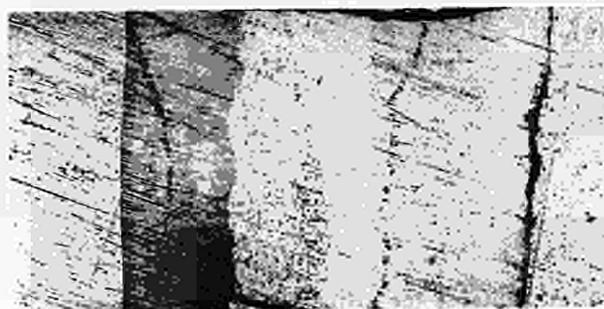
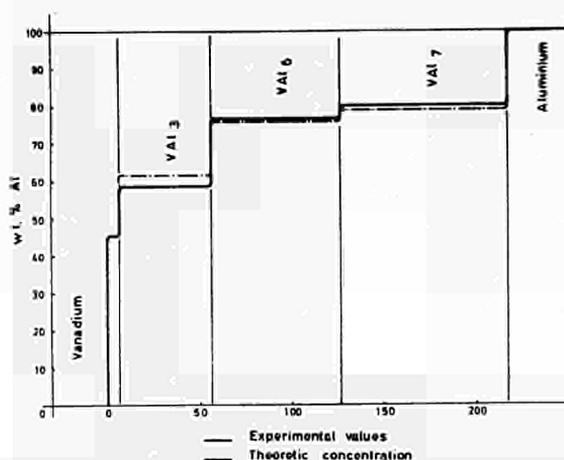


Fig. 6

Diffusion of vanadium-aluminium for 5×10^5 s at 610°C

($t > 10^6$ s) this layer disappears completely, but it may probably be – together with the limited solubility of the vanadium in the uranium – the reason for deviations in the diffusion law, when the aluminium begins to penetrate into the uranium. Samples which had received a faint nickel layer before the vanadium evaporation (see 3.3.1.1) showed a more regular and a slightly enhanced diffusion, which however does not influence remarkably the general results.

The penetration of the aluminium through the barrier produces, as in the case of the other barriers, the compound UAl_3 . The penetration of the uranium towards the aluminium is practically stopped before it reaches the canning metal, even when both the vanadium and the UO_2 are totally consumed.

As shown by Fig. 7, there exists, after a treatment of 3×10^6 s at 580°C , a gradient of the uranium concentration in the VAl_3 phase, ranging from 1.6 wt. % at the interface $\text{UAl}_3/\text{VAl}_3$ to 0.6 wt. % at the interface $\text{VAl}_3/\text{VAl}_6$; 0.3 wt. % uranium was determined in the VAl_6 .

The mean composition of the diffusion layers, after a total consumption of metallic vanadium (and UO_2) is summarized in Table III.

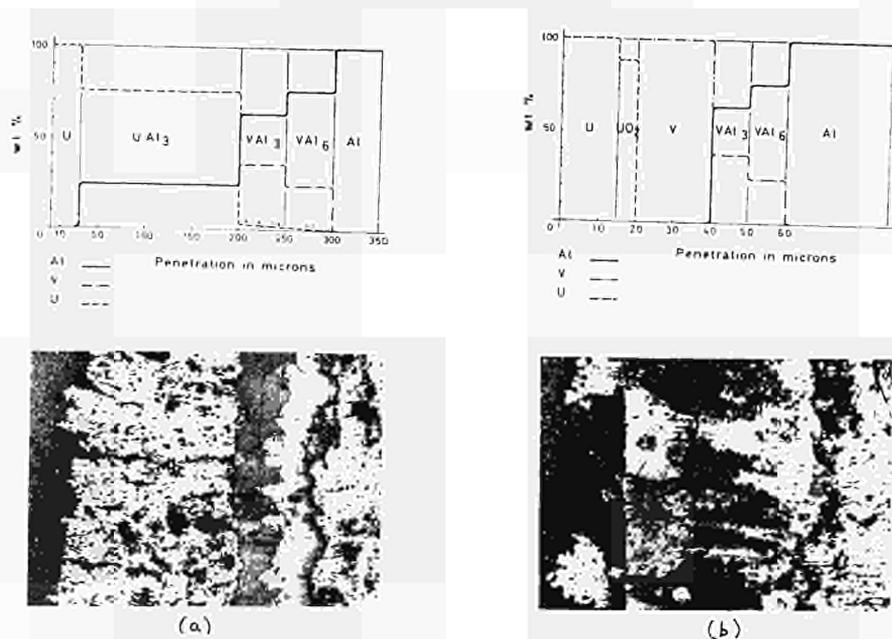


Fig. 7

Ternary diffusion of uranium-vanadium-aluminium

(a) Diffusion U-V-Al, 3×10^6 s at 580°C (b) Diffusion V-Al, 5×10^5 s at 610°C

The coefficients of the expression

$$X = C_1 t^{C_2} e^{C_3/T} e^{C_4/E}, \quad (3)$$

where

X = total diffusion thickness (cm)

t = time (s)

T = temperature ($^\circ\text{K}$)

E = initial V thickness (cm),

were calculated by the method of least squares. Using the experimental results obtained for the later stage of the diffusion process and neglecting those for shorter times, the following values were determined:

 $C_1 = 0.88$ $C_2 = 0.40$ $C_3 = -6600$ $C_4 = -260$.

If a total diffusion zone of $750 \mu\text{m}$ is acceptable, it follows that an initial vanadium barrier of $10 \mu\text{m}$ will be sufficient for one year of operation at 450°C . For the temperature of 470°C , $20 \mu\text{m}$ are required for the same duration.

TABLE III

MEAN COMPOSITION OF DIFFUSION
LAYERS IN THE SYSTEM Al-V-U
(Corrected values, adjusted to 100%)

| Al (wt. %) | V (wt. %) | U (wt. %) | Phase |
|---------------|--------------|--------------|------------------|
| 75.5 | 24.2 | 0.3 | VAL ₆ |
| 61.7 | 37.0 | 1.6-0.6 | VAL ₃ |
| 24.8 | - | 75.1 | UAL ₃ |

3.4. Study of the diffusion in the system U-Nb-Al

As the deposition of niobium onto metals is even more difficult than that of vanadium, the study of the niobium barrier has been very much delayed and no definite test results can be given at present.

The deposition was done by C.E.N., Mol, using evaporation by means of electron bombardment heating. The procedure was similar to that employed for the evaporation of vanadium. Very careful degassing was necessary and, because of the higher temperature of the evaporation source, the distance between this and the uranium had to be raised to 160 mm. After a thermal treatment of the covered samples for 3 h at 600°C the niobium deposits show a good adherence.

Preliminary binary diffusion tests have been run with samples prepared by roll-milling. No reaction has been detected between uranium and niobium below 600°C. Between niobium and aluminium a eutectic alloy is formed, mostly in the grain boundaries of the aluminium at temperatures above 610°C. At 640°C NbAl₃ appears and grows quite rapidly in thickness.

3.5. Study of the diffusion in U-V-Si-Al system

A somewhat different possibility for the solution of the diffusion barrier problem consists in the application of double layer barriers, in which both components show a good resistance to their adjacent metals respectively and a low solubility for uranium and aluminium of the intermetallics formed between them. Several tests run up to now with the system U-V-Si-Al have given quite encouraging results. Samples were prepared by evaporation as described for V and Nb. V and Si were deposited successively. Much care had to be taken to avoid cracking of the Si during the outgassing procedure.

The diffusion mechanism in the system U-V-Si-Al seems to be very complex. Thermodynamically, the "driving forces" for the diffusion are the differences in the chemical activities of the diffusing species. As the activity coefficients, which combine activity and concentration, normally do not differ too much in the various parts of a system, this is in most cases

equivalent to the statement that the diffusion follows the concentration gradient. This is, however, not a necessary conclusion and it is thermodynamically quite possible that diffusion occurs against a concentration gradient ("up-hill diffusion"), for instance when the diffusion crosses the interface of two phases with a very limited miscibility [20]. Such a case exists apparently for the system in question.

By microprobe analysis of samples treated at different temperatures for different durations, the phases indicated in Table IV have been identified (UAl₃ is formed only after quite heavy thermal treatments).

TABLE IV
MEAN COMPOSITION OF DIFFUSION
LAYERS IN THE SYSTEM Al-Si-V-U
(Corrected values, adjusted to 100%)

| Al (wt. %) | Si (wt. %) | V (wt. %) | U (wt. %) | Phase |
|---------------|---------------|--------------|--------------|------------------------------------|
| < 0.4 | 38.3 | 61.7 | - | (VSi ₂ +V) |
| 44.2 | 8.7 | 47.1 | - | VSi ₂ +VAl ₃ |
| 59.8 | 0.4 | 40.2 | - | VAl ₃ |
| - | - | 99.4 | 0.6 | V |
| - | - | - | 83.8 | UO ₂ |
| 25.0 | - | - | 75.0 | UAl ₃ |

Referring to the data of Table IV and to Figs. 8 and 9, the following remarks can be made:

- (a) The phase (VSi₂+V) is only visible after a strong etching treatment (5% HF). The layer, which is partially penetrated, is 2-3 μm thick. The phase diagram (1) indicates that the existence of a phase VSi₂ containing vanadium in solid solution is probable.
- (b) The adjacent layer (visible here and there on Fig. 8) has a metallographic aspect corresponding to a mixture of two phases (VSi₂ and VAl₃). In spite of its placement between the aluminium and the foregoing layer, which is nearer to the aluminium, this layer contains more aluminium and less vanadium than the foregoing one, and also less aluminium and more vanadium than the following one. Its concentration of silicon varies strongly and the indicated value has to be considered as a mean value. The strong variation of the Si concentration supports, together with its aspect, the hypothesis that the layer contains two phases (VSi₂ (+V) and VAl₃).
- (c) The low concentration of silicon in the following layer (VAl₃) may be due to the presence of particles of VSi₂. The aspect of the layer - a brown colour after the HF etch - corresponds to that found for VAl₃ in the binary V-Al couples.

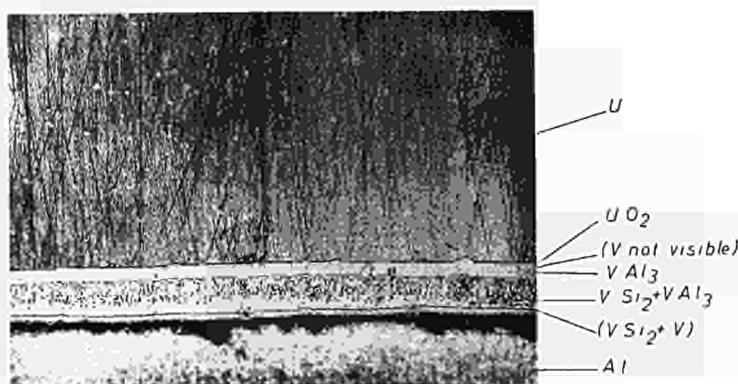


Fig. 8

Multiphase diffusion of U-V-Si-Al samples

- (d) The pure vanadium layer of 0-to 6- μm thickness contains a small concentration of uranium and is separated from the uranium by a thin grey layer, 2-3 μm thick, consisting most probably of UO_2 . At some places, this layer is absent however and here the aluminium reacted with the uranium forming UAl_3 which penetrates sometimes deeply into the uranium (Fig. 9).

Table V summarizes the results obtained up to now with diffusion treatments at 550, 520 and 490°C.

As can be seen, approximate values for n and k have been calculated for special cases. The number of experimental results is however still too small to draw more general conclusions, as to the dependence on temperature or relative thickness of initially deposited layers. It seems, however, that the multiple layer barriers in question produce much smaller diffusion zones than the previously studied barriers.

4. DISCUSSION

As shown above, the characteristics of the barrier types studied are quite different. A final decision for practical application in a special case has to take account of a large number of factors of which only a few are known up to now with certainty. Knowledge of the behaviour of the barriers under thermal gradients and under irradiation are completely missing. However, the results obtained up to now give a very strong basis for the final evaluation, as they allow comparison of the most important characteristics such as temperature limits, mechanical stability and diffusion rate. The study of the deposition procedures has been up to now only a means to produce good, sound samples and was not influenced by questions of practical interest. Other possible deposition procedures may produce improvements, as, for instance, in the case of silicon, which may perhaps be deposited much easier by a gas phase decomposition than by evaporation.

Table VI gives a very abridged comparison of the most important features of the different barriers.

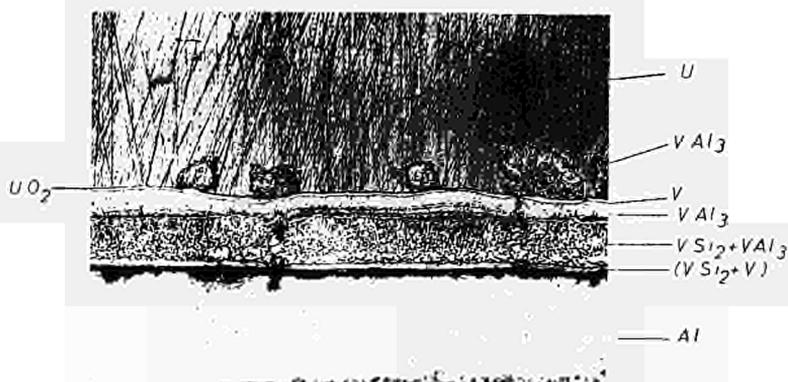


Fig. 9

Multiphase diffusion of U-V-Si-Al samples
Presence of UAl_3 tendrils.

As may be seen, the nickel barrier is the most convenient one from the point of view of the deposition. However, its relatively high diffusion rate makes it unsuitable for applications at about 450°C when low neutron absorption is required. The applicability of the chromium barrier is doubtful, owing to the high influence of the pressure on the diffusion rate, which may lead to dangerous consequences in the case of hot spots and owing to failures in the deposited Cr layer. All the following barriers could be deposited up to now only by vacuum evaporation, which means that they are costly. The evaporation of niobium is very difficult, and as there are, for the time being, no other procedures of deposition working at relatively low temperatures of the substrate, this barrier shows an important disadvantage from the technical point of view. As its efficiency seems to be outstandingly good, application in solid form (foils) may be advantageous in special cases [21]. Vanadium may work satisfactorily; its evaporation is easier than that of niobium. The influence of pressure on diffusion has still to be examined. The Si-V double barrier shows great promise judging from the still limited experimental results. Diffusion rates are low, neutron absorption acceptable and mechanical bonding properties probably satisfactory. Experiments are continuing for further information on this barrier type.

5. CONCLUSION

Among the different diffusion barriers (Ni, Cr, N, Nb, Si-V) studied with the aim of minimizing the diffusion between uranium and aluminium in a fuel element working with about 430°C surface temperature, the most promising ones seem to be vanadium and Si-V barriers. Nickel shows too high diffusion rates, chromium is very sensitive to pressure variations and niobium presents for the time being too many difficulties in respect to deposition.

TABLE V

THICKNESS OF DIFFUSION LAYERS AND DIFFUSION
CONSTANTS IN THE SYSTEM Al-Si-V-U

| Temp. (°C) | Time (s) | Thickness of diffusion layers (μm) | | | Approximative values of the diffusion constants | | | | |
|---------------|-----------------|---|----------------------------|-----------------------------|--|---------------------|------|---------------------|-----|
| | | I | II | III | I | | II | | III |
| | | Si = 10 V = 10 Ni = 0 | Si = 5 V = 10 Ni = 0 | Si = 20 V = 10 Ni = 2 | n | k (10^{-10}) | n | k (10^{-10}) | |
| 550 | 5×10^5 | 50 | 30 | - | | | | | |
| | 2×10^5 | 53 | 38 | - | | | | | |
| | 10^6 | 70 | 40 | 120 | 1.64 | 4.9 | 1.19 | 16 | |
| | 2×10^6 | 78 | 55 | - | | | | | |
| | 5×10^6 | 175 | 120 | - | | | | | |
| | 8×10^6 | - | 425 | - | | | | | |
| 520 | 7×10^5 | 35 | 25 | - | | | | | |
| | 10^6 | 38 | 35 | 37 | | | | | |
| | 2×10^6 | 58 | 43 | 100 | 1.52 | 2.6 | 1.25 | 9.5 | |
| | 5×10^6 | 110 | - | - | | | | | |
| | 8×10^6 | 200 | 320 | - | | | | | |
| | 10^7 | 200 | - | - | | | | | |
| 490 | 2×10^6 | - | - | 95 | | | | | |
| | 4×10^6 | 80 | 36 | - | | | | | |
| | 5×10^6 | 100 | 55 | - | | | | | |

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TABLE VI

COMPARISON OF DIFFERENT BARRIER TYPES

| Barrier | Deposition method | Judgement on deposition method | Temp. of start of binary diffusion (°C) | Properties of diffusion layers | Approximate thickness of barrier to resist 450°C for 1 yr (μm) | Remarks |
|---------|-------------------------------------|--|---|---|--|--|
| Ni | Electrolysis | Easy (attention to H ₂ uptake). | UNi: 500 < T < 540 NiAl: < 350 | Numerous different intermetallics. Brittle. | > 30 | Not interesting for ORGEL because of too high diffusion rate. |
| Cr | Electrolysis | Easy, but danger of porosity and cracks. | UCr: > 600 CrAl: < 440 | Less layers than for Ni. Not too brittle. No penetration of U in the can. | Comparable to Ni. Depends on pressure. | Applicability doubtful, high influence of pressure at temp. > 450°C (hot spots). |
| V | Evaporation by electron bombardment | Satisfactory, but costly. | U-V: > 600 V-Al: ~450 | Regular, practically no penetration of U to Al. | ~ 10 | May be satisfactory; influence of pressure? |
| Nb | Evaporation by electron bombardment | Difficult, costly. | U-Nb; > 600 Nb-Al: ~ 610 | Diffusion mostly in grain boundaries of Al. | Most probably < 10 | Deposition difficult; pre-diffusion difficult (temp. too high for Al). |
| Si-V | Evaporation by electron bombardment | Satisfactory, costly. | U-V: > 600 | Not very brittle. Complex diffusion mechanism. | << 15 | Promising, good efficiency at relatively high temperatures. Other Si deposition methods seem possible. |

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