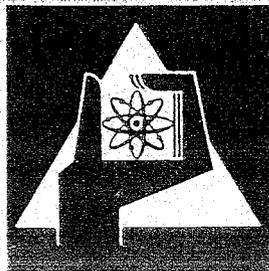# KERNFORSCHUNGSZENTRUM

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UAl$_2$-Al Instead of UAl$_3$-Al in Fuel-Element Plates for
Advanced Test-Reactors

F. Thümmler, H. E. Lilienthal, S. Nazare

UAl₂-Al INSTEAD OF UAl₃-Al
IN FUEL-ELEMENT PLATES FOR ADVANCED
TEST-REACTORS*

By Professor F. THÜMMLER,† H. E. LILIENTHAL,‡
and S. NAZARE†

ABSTRACT

The existing literature on UAl₂-Al dispersions is surveyed and a comparison with similar data for UAl₃-Al dispersions is attempted. The experimental work included the preparation of a practically single-phase UAl₂ compound by induction-melting and its grinding to a pre-determined particle size. The blending of UAl₂ and aluminium powders into suitable dispersions and their compaction by cold pressing to the densities required for roll-bonding are described. The picture-frame technique was used to clad the dispersions with aluminium to produce test-plates for irradiation experiments.

The kinetics of the UAl₂ and UAl₃ solid-state reactions with aluminium are dealt with on a qualitative basis. Throughout, comparison is made with the known technology of UAl₃-Al dispersions, taking into consideration uranium densities, production aspects, pyrophoricity, volume changes, &c.

It is concluded that UAl₂-Al dispersions have potential applications as fuels for advanced test reactors.

I.—INTRODUCTION

RESEARCH reactors with neutron fluxes of $\sim 10^{15}$ n cm^{-2} sec^{-1} utilize plate-type fuel elements having a high uranium content and, in most cases, an aluminium matrix and cladding.

Up to ~ 25 wt.-% uranium, U–Al alloys can be produced by melting and casting and hot rolled without difficulty into fuel-element plates. At higher uranium concentrations, homogeneous distribution of the fissile phase in the matrix and the hot-rolling process present problems. By adding ~ 3 wt.-% Si to the melt, fuel elements containing 48 wt.-% uranium can be made by conventional melting.[1] The presence of silicon, however, complicates the chemical reprocessing of the fuel.[2]

In recent times, with the development of dispersion fuels such as U₃O₈–Al and UAl₃–Al, an increase in the uranium content to the extent

of 45–50 wt.-% was achieved. By powder-metallurgical fabrication methods a homogeneous distribution of the fissile phase is obtained, and it also becomes possible to distribute evenly a burnable poison (e.g. B$_4$C), which is added to control the reactivity. Finally, as a result of powder-metallurgical compaction the retained porosity seems to reduce the swelling rate by trapping the fission gases.[3]

While some years ago U$_3$O$_8$–Al fuel elements were well to the fore, UAl$_3$–Al is preferred today in reactors running at low cooling-water temperatures (H$_2$O or D$_2$O), since its behaviour is more favourable at high burnups.[2,4,5] The exothermic reaction of U$_3$O$_8$ with aluminium is an additional hazard as far as reactor safety is concerned.[6] The employment of UAl$_2$–Al dispersions has hardly been considered in this context, especially because of the greater pyrophoricity of UAl$_2$.[7] However, the few irradiation tests carried out on fuel plates of UAl$_2$–Al (44 wt.-% UAl$_2$) seem to indicate that the irradiation behaviour of this dispersion is as good as that of UAl$_3$–Al. Should it be possible to fabricate plate-type fuel elements of UAl$_2$–Al successfully, the following obvious advantages would be gained:

(1) The higher uranium content (6·64 as compared with 5·07 g cm^{-3}) and the greater material density (8·14 as compared with 6·8 g cm^{-3}) results in a further increase in the uranium content of the plate without the necessity of raising the content of the brittle dispersed phase.

(2) Owing to its congruent melting the preparation of UAl$_3$ is much simpler than that of UAl$_3$. The homogenization step that is necessary for the preparation of UAl$_3$ is not required for UAl$_2$.

Owing to their high melting points and good thermal conductivities UAl$_2$ and UAl$_3$ are also attractive as fuels for rod-type fuel elements. In addition, they could be used as dispersion fuels with a matrix metal having a high melting point.[8]

The experimental work described here deals with the preparation of UAl$_2$ on a laboratory scale and its use in a UAl$_2$–Al dispersion in plate-type elements with dimensions smaller than those envisaged for the original fuel elements. As far as these can be judged from the present work, the advantages and disadvantages of the UAl$_2$–Al and UAl$_3$–Al elements are discussed.

II.—REVIEW OF EXISTING DATA

1. *Preparation of UAl$_2$*

In general, UAl$_2$ can be prepared by the same methods as UAl$_3$, i.e. by melting or by solid-state reactions. Because of the congruent melting of UAl$_2$, the easier melting procedures offer advantages.

(a) *Melting Procedures*

In the case of induction- or arc-melting, uranium and aluminium are weighed-in stoichiometrically. The crucible material used is graphite, sometimes with a magnesium zirconate coating, or vacuum-annealed Al_2O_3. Melting is carried out in air, in vacuum (5×10^{-3} torr), or in an inert gas (argon). The melt can be poured into graphite or preheated steel moulds. In arc-melting, homogenization is achieved by repeated melting.[9,11-13] The carbon content of the melt is ~ 0.1–0.4 wt.-%. Owing to the relatively high melting temperatures, losses by evaporation and soaking into the crucible of ~ 10 wt.-% occur.[11]

(b) *Reactions in the Solid State*

These procedures, while somewhat more complicated than melting methods, yield single-phase substances of high purity (especially in the case of UAl_3). In this context, the question arises as to whether the effort is justified, since, owing to the presence of aluminium in the dispersion, reactions to UAl_3 or UAl_4 will at least partly occur during hot rolling.

In the hydride process,[14] uranium hydride is mixed with a stoichiometric amount of aluminium powder and heated in vacuum (700°C, 4 h). During this period the liquid aluminium reacts with the very finely distributed uranium to form uranium aluminide. A subsequent annealing (1300°C, 13 h) in inert gas (argon) completes the reaction.

The fluidized-bed technique has so far been used to prepare UAl_3. However, it should also be applicable to other uranium aluminides. Spherical aluminium powder is heated in air (350°C) in a reaction vessel and sprayed with a solution of uranyl nitrate ($UO_2(NO_3)_2$) by means of an atomizing nozzle. The UO_3 produced forms a coating on the aluminium particles. Spraying is continued until the desired U/Al ratio is attained.

The second stage is the reduction of UO_3 to UO_2 with a mixture of argon and methanol, again at 350°C. In this way undesirable side reactions during the subsequent chlorination are minimized. Chlorination is carried out at 350°C in a stream of argon and carbon tetrachloride, the UO_2 layer being thus converted to UCl_3. Finally, argon is introduced, the temperature is raised to 600°C, and the following reaction takes place:

$$UCl_3 + 4\ Al \xrightarrow{\ 600°C\ argon\ } UAl_3 + AlCl_3$$
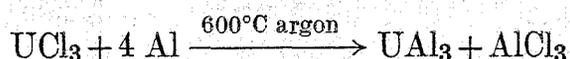
The resulting UAl_3 particles are nearly spherical, but hollow. They could be densified in a plasma flame, though the incongruent melting of UAl_3 and UAl_4 would probably lead to a two-phase product. The

advantages of the fluidized-bed technique are elimination of the crushing process, control of particle shape and size and, above all, obviation of the need to reduce the uranium to metal during reprocessing.[15]

2. *Fabrication of* UAl_2–Al *Dispersions and Fuel Plates*

The individual technological steps are similar to those for UAl_3–Al, though on account of the pyrophoricity of UAl_2 the crushing process must be modified.

If the compound is not available as a powder, crushing is carried out in an inert gas (argon) or a protective liquid (petrolether) in ball- or hammer-mills.[10] UAl_2 (~ 125 μm) and aluminium (44 μm) powders are blended mechanically (3 h) and pressed into highly dense pellets at ~ 5 Mp cm^{-2}.

For the fabrication of fuel-element plates by the well-known picture-frame technique, rectangular pellets are required.   No data are available in the existing literature on the fabrication of such pellets or of clad fuel-element plates.   However, it can be assumed that procedures that are suitable for UAl_3–Al dispersions can be applied to UAl_2–Al dispersions also.[4, 5, 13]

3. *Structure and Properties of* UAl_2 *and* UAl_3

UAl_2 and UAl_3 have a cubic lattice and, according to the equilibrium diagram, no homogeneity range.[16]   However, recent measurements indicate a homogeneity range ($> 2\cdot 7$ wt.-%U) for UAl_3.[17]   In the presence of aluminium both compounds form an unstable dispersion. While UAl_3 reacts at $\sim 450°C$ with aluminium to form UAl_{4+x},[18, 19] little is known about the course of the UAl_2–Al reaction.   It can, however, be assumed that UAl_2 also reacts to form UAl_{4+x} when aluminium is present.   If as a first step UAl_3 was formed at the particle boundary it would immediately react further to UAl_{4+x}.   The diffusion of aluminium to the unreacted zone would not be restricted since UAl_3 as well as UAl_4 can hold aluminium in solution.[4, 17]

Only limited data are available on the properties of UAl_2– and UAl_3–Al dispersions, though some data exist for the components (Table I).

With regard to the pyrophoricity of both aluminides the following considerations seem to be useful: U_3O_8 and Al_2O_3 are the products of oxidation of UAl_2 and UAl_3 in air at 550°C, as determined by X-ray diffraction.   With the help of the known thermodynamic data the affinity of the two compounds for oxygen can be estimated.

$$3\, UAl_2 + 8\cdot 5\, O_2 \rightarrow U_3O_8 + 3\, Al_2O_3 \qquad . \quad . \quad (1)$$

TABLE I.—*Properties of UAl_2, UAl_3, and Aluminium*

Properties	UAl_2	Ref.	UAl_3	Ref.	Al	Ref.
Lattice parameter, Å	7.744 ± 0.001	20	4.254 ± 0.001	20	4.0493	
Melting point, °C	1620		1350		660	
Density, g cm^{-3}	8·14		6·8		2·7	
Standard enthalpy (H_{298}), kcal mole^{-1}	22.3 ± 5.0	21	25.2 ± 5.0	21		
Standard entropy (S_{298}), cal degC^{-1}	25.5 ± 3	21	32.5 ± 3	21		
Free enthalpy of formation (ΔG), kcal mole^{-1} (calculated)	$-27.4 + 9.9 \times 10^{-3}T$	22	$-32.9 + 13 \times 10^{-3}T$	22		
Thermal conductivity, cal cm^{-1} degC^{-1} sec^{-1}: estimated by extrapolating values of U–Al alloys and U	0·119 (at 200°C)	23	0·151 (at 200°C)	23	0·55 (at 20°C)	
measured at 94°C with hot-pressed pellets of 98% T.D.	—		0·024	22	—	
Electrical resistivity, Ω cm, at room temperature of unsintered pellets (63–90 μm), 90% T.D.	6×10^{-3}	24	3.0×10^{-3}	24		
Temperature coefficient of the electrical resistance (measured on unsintered pellets)	1.8×10^{-4}	24	2.2×10^{-4}	24		
Linear thermal-expansion coefficient deg^{-1} 0–300°C	14.7×10^{-6}	10	16.8×10^{-6}	25	25.8×10^{-6}	26
0–400°C	15.0×10^{-6}		15.8×10^{-6}		26.8×10^{-6}	
0–500°C	15.1×10^{-6}		15.2×10^{-6}		27.9×10^{-6}	
0–600°C	15.2×10^{-6}		14.9×10^{-6}		28.5×10^{-6}	

$$3 \text{ UAl}_3 + 10\cdot75 \text{ O}_2 \rightarrow \text{U}_3\text{O}_8 + 4\cdot5 \text{ Al}_2\text{O}_3 \qquad . \quad . \quad (2)$$
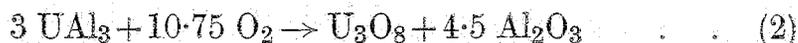
For the oxidation of UAl₂ the free enthalpy of formation per mole of oxygen is

$$\Delta G_{\text{UAl}_2} = \frac{1}{8\cdot5} [\Delta G \langle \text{U}_3\text{O}_8 \rangle + 3 \Delta G \langle \text{Al}_2\text{O}_3 \rangle - 3 \Delta G \langle \text{UAl}_2 \rangle] \quad (3)$$

In the case of UAl₃ it is

$$\Delta G_{\text{UAl}_3} = \frac{1}{10\cdot75} [\Delta G \langle \text{U}_3\text{O}_8 \rangle + 4\cdot5 \Delta G \langle \text{Al}_2\text{O}_3 \rangle - 3 \Delta G \langle \text{UAl}_3 \rangle] \quad (4)$$

Equations (3) and (4) show that (e.g. at 300°K) UAl₂ has a greater affinity for oxygen ($\Delta G = -218$ kcal mole^{-1} O₂) than UAl₃ ($\Delta G = -182$ kcal mole^{-1} O₂). The resulting reaction products are in addition poor heat conductors, so that the heat produced is insufficiently removed. Using the Neumann–Kopp rule, a smaller molar specific heat (18 cal deg^{-1} mole^{-1}) can be predicted for UAl₂ than for UAl₃ (24 cal deg^{-1} mole^{-1}). The lower specific heat of UAl₂, combined with the higher production of heat occurring during its crushing or oxidation, would lead to a greater increase in temperature and, hence, to more rapid attainment of the "autogenous-ignition temperature".[27]

III.—EXPERIMENTAL WORK

The following investigations had as their aim the preparation of pure, single-phase UAl₂ and its powder-metallurgical processing into UAl₂–Al irradiation test-plates containing ~ 50 wt.-% UAl₂ (24·9 vol.-%) or 40·75 wt.-% U in the core. For the purpose of making comparisons with the technology of UAl₃–Al dispersions,[13] the fabrication parameters were kept constant as far as possible. The fabricated fuel-element plate should have the characteristics (distribution of uranium, bonding, dimension tolerances) required for irradiation experiments.[19]

1. *Preparation of UAl₂ Powder*

For the preparation of UAl₂ the induction-melting procedure was the same as that used for UAl₃. Compared with arc-melting, this method permits the production of larger melts. The crucible material chosen was vacuum-annealed Al₂O₃ (1500°C, 10^{-5} torr),[13] which has already been satisfactorily used for melting UAl₃. The metallic uranium (rod or strip) was rinsed with carbon tetrachloride and propanon and subsequently etched in a mixture (1:1) of nitric and acetic acid. The components were weighed-in stoichiometrically (81·52 wt.-% uranium, balance aluminium). As a precaution against segregation, the alu-
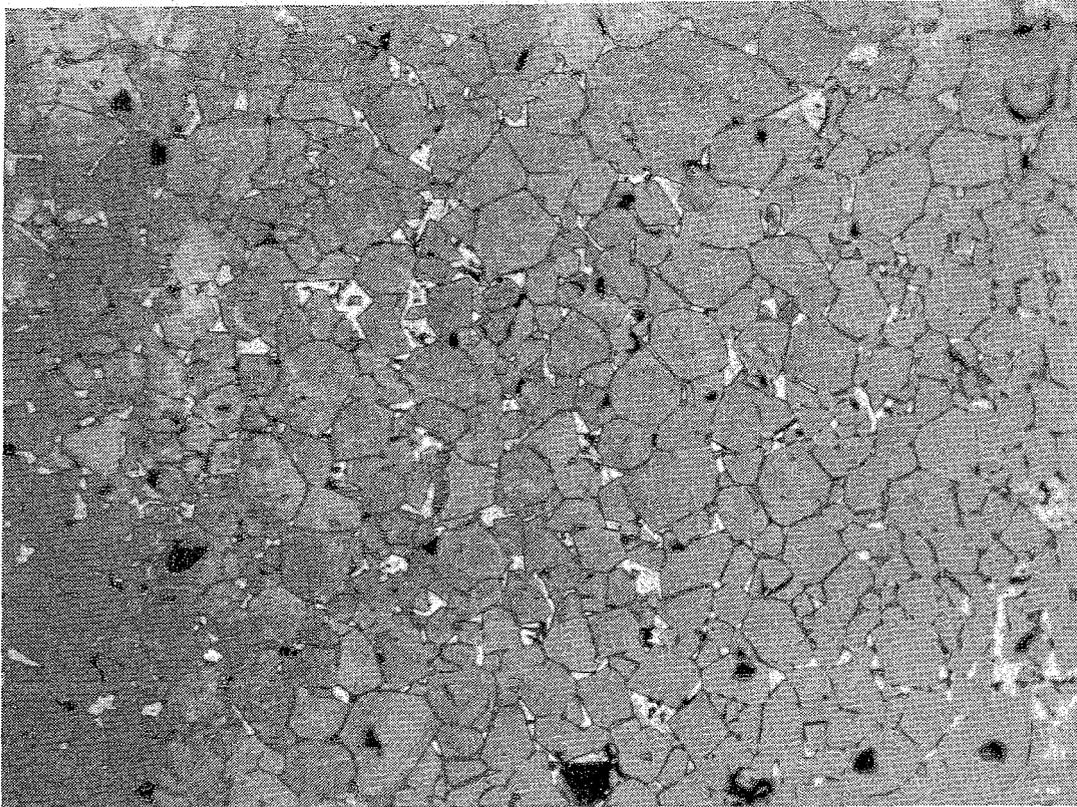
(a)
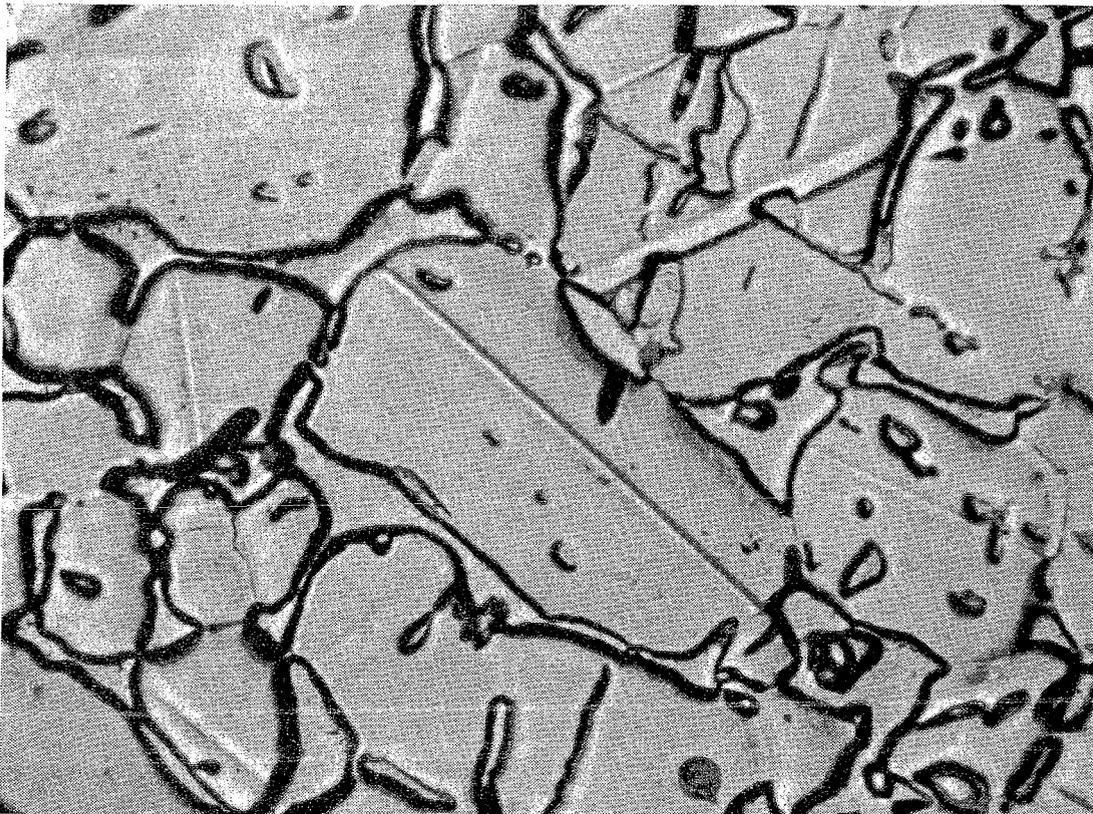
(b)

FIG. 1.—UAl$_2$, as cast, containing UAl$_3$. Etched with 50% HNO$_3$ solution.
(a) ×100; (b) ×500.

—P.M.

minium was always placed at the bottom of the crucible, with the uranium on top. The following melting conditions appear to be suitable:

Atmosphere:	helium, 400 torr.
Heating rate:	50 degC min^{-1}.
Melting temperature:	1620°C.
Cooling:	optional.

Under these conditions, a relatively porous product is obtained that can be easily separated from the crucible.

The density of UAl_2 is much higher than that of the other aluminides or aluminium, so that if segregation took place the uranium content would be expected to decrease from the bottom to the top of the regulus. To determine this point two samples from the melt were chemically analysed. The sample taken from near the bottom showed a very small difference in uranium content (0·1 wt.-%) as compared with that taken from the regulus surface.

Various samples from the melt were also examined metallographically. The three uranium aluminides yield typical colours after etching. The structure (Fig. 1) reveals a two-phase product. The main component is UAl_2 (dark). The small fraction of the UAl_3 phase (light) has solidified from the residual melt at the grain boundaries.

The product was also analysed by X-ray diffraction. To obtain representative samples, the whole regulus was crushed in inert gas (helium) and the fine-grain fraction (< 25 μm) was used. Oxidation during analysis was prevented by soaking the sample in paraffin. The goniometer patterns ($CuK\alpha$ radiation) confirmed the metallographic examinations and also revealed a small quantity of UAl_3. Owing to the difference between the lattice structures of the two phases (UAl_2, $MgCu_2$-type; UAl_3, $AuCu_3$-type) a comparison of the intensities of the diffraction patterns cannot be used to obtain a reliable quantitative analysis.

To prepare UAl_2–Al dispersions the molten product must be crushed to a coarse particle size. This requirement arises out of the following considerations.

Optimum behaviour of dispersion fuel elements under irradiation seems, in general, to require that recoil and reaction zones, if any, do not interact. An undamaged portion of the matrix is then available for the transport of fission heat. This condition is partly met if the fissile phase is in the form of a coarse powder, so that the interparticle spacing is large.

The distance between particles in the dispersion as a function of particle size can be calculated from geometrical relations. Fig. 2 shows

these functions for UAl_2– and UAl_3–Al dispersions containing 40 wt.-% U. The average path of the fission fragments in aluminium is ~13·7 μm.[28] Since UAl_2 has a higher uranium content and density than UAl_3, the recoil-zone requirement can be met by using a somewhat finer grain (~62 μm) in the dispersion than in the case of UAl_3 (~73 μm). Because of technological problems (mixing, pressing, and rolling) the upper limit should in both cases be~150 μm.
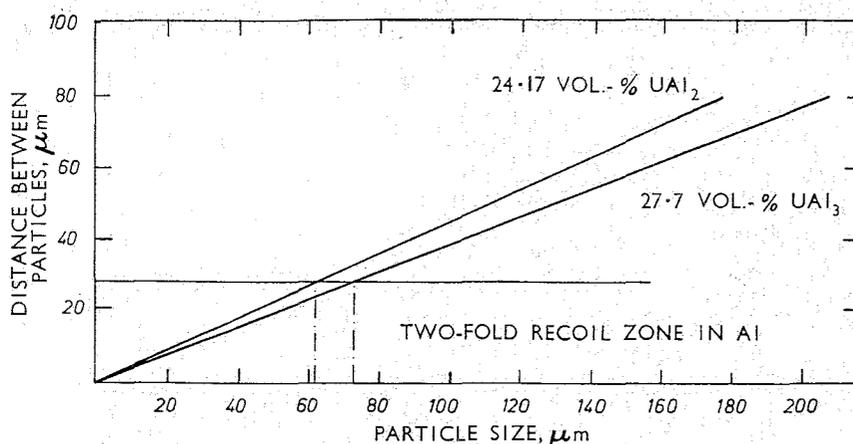

FIG. 2.—Minimum particle size of the dispersed phase for no recoil-zone interaction with a uranium content of 40 wt.-% and a uniform distribution of spherical particles.

With the object of obtaining a high yield covering a relatively narrow range of grain size (63–90 μm), the crushing of UAl_2 was studied under different conditions. Crushing was carried out with a "pulverisette", supplied by Messrs. Fritsch, Idar-Oberstein, Germany. To avoid oxidation the experiments were performed in inert gas (helium). The starting material was a precrushed and screened fraction of 1–1·6 mm. Table II shows the results. It can be seen that with this method a satisfactory yield of the desired fraction cannot be achieved. In this respect UAl_2 behaves similarly to UAl_3.[13] Experiments are in progress to increase the yield by crushing by means of a spindle rotating in a conical vessel, but despite some improvement a considerable amount is undersize. It can be recycled by melting or by hot pressing.

The hot pressing of UAl_2 powder (< 63 μm) in graphite dies should be carried out at a temperature sufficiently low to avoid excessive carbon impurities.[29] It was found that highly dense (93% T.D.) pellets could be obtained by hot pressing in vacuum (10^{-4} torr) at 1220°C and 0·19 Mp cm^{-2}. Metallographic examination (Fig. 3) reveals a compact body with a very small amount of UAl_3, which is discernible as a light phase. The dark spots are pores and breaks produced during the metallographic preparation. These pellets can be easily crushed again and thus recycled.
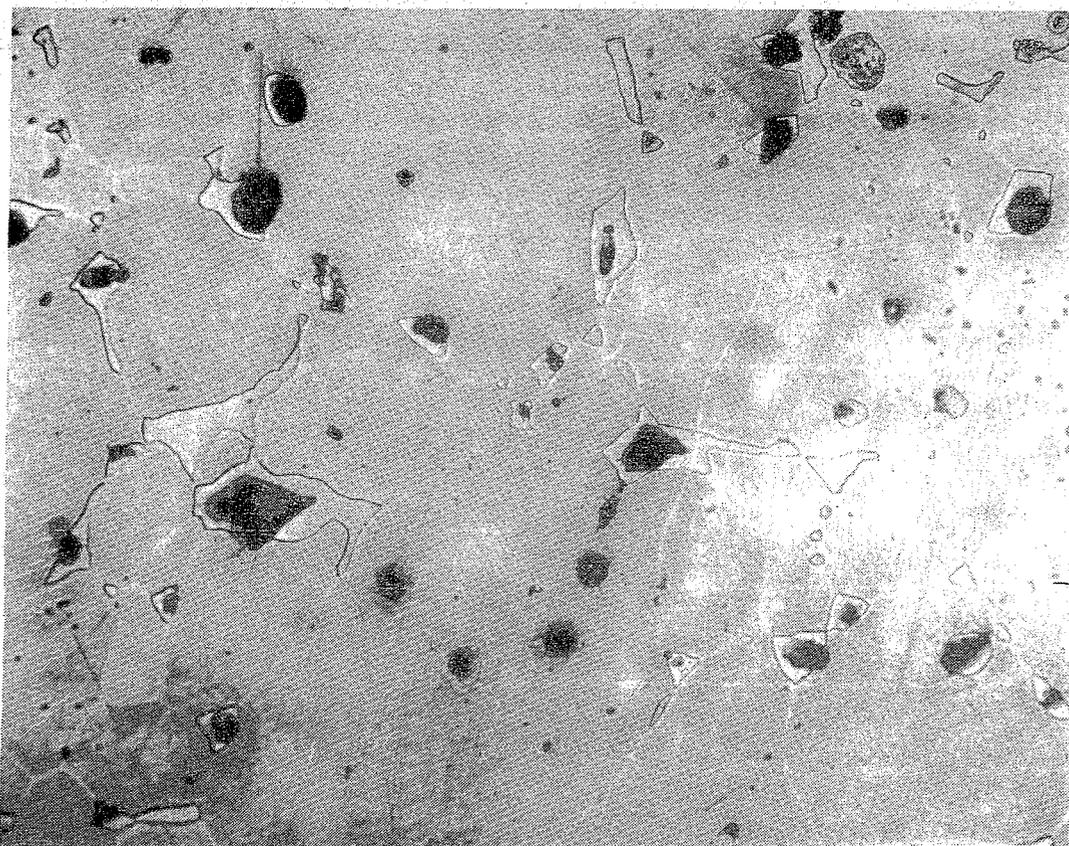
FIG. 3.—Structure of hot-pressed UAl_2. Density 93% T.D. Etched with 50% HNO_3 solution. $\times$ 500.

TABLE II.—*Screen Analyses of UAl_2 Powder under Various Crushing Conditions in the " Pulverisette" (3 min at Three Different Frequencies)*

Grain Size, μm	Quantity, wt.-%	Quantity, wt.-%	Quantity, wt.-%
< 90	59·76	32·35	24·32
< 90 > 63	12·00	16·27	18·65
< 63	28·34	51·38	57·03
Frequency position	6	8	10

The analysis of the aluminide powders (UAl_2 and UAl_3) after crushing is shown in Table III. The amount of each phase was calculated from the chemical analysis by applying the lever law. Thus, the resulting values are average values that permit local fluctuations. In fact, the amount of second phase present should be somewhat higher than calculated. Basically UAl_2 and UAl_3 powders do not differ significantly

TABLE III.—*Analysis of UAl₂, UAl₃, and Aluminium*

Composition, wt.-%	UAl₂	UAl₃	Al (Alcoa 101)
Al	18·26	25·15	99·5
U	79·96	72·43	—
Impurities, wt.-%			
O₂		0·88	0·29
N₂		0·0225	—
H₂	1·78	0·0088	—
C		0·198	—
Remainder		1·13	
Fe			0·13
Si			0·07
Cu			0·01
Average aluminide content (wt.-%) in UAl$_x$ (calculated)	98·2	93·4	—
Particle size, μm	63–90	63–90	18·6 (mean value)

in quality. Because the peritectic reaction is incomplete, the amount of the second phase is slightly higher in the case of UAl₃.

2. *Preparation of UAl₂–Al Dispersions*

The aim was to obtain a very homogeneous distribution of the UAl₂ particles in the aluminium. Dry- and wet-mixing methods were investigated. Wet mixing in trichlorethylene showed that owing to the difference in the density and particle size of the components sedimentation clustering took place. To achieve equal fall rates in the mixing medium would require either a reduction of the UAl₂ particle size or an increase of the aluminium particle size. The first alternative is not feasible on account of recoil zones, while an increase in the aluminium particle size would probably affect compaction adversely. The degree of distribution (degree of homogenization) obtained by dry mixing was calculated from chemical analysis, applying the following equation.[31]

$$V_g = \left(1 - \frac{|f|}{x_s}\right) \times 100(\%)$$

where $f = \sqrt{\dfrac{1}{N-1}\sum_{i=1}^{N}(x_i - x_s)^2}$

x_s = weighed-in ratio of UAl_2 to Al.

x_i = ratio of UAl_2 to Al determined by chemical analysis.

V_g = degree of distribution.

N = number of analyses.

f = mean-square deviation.

The variation of the degree of distribution with mixing time, determined on samples of 0·5 g, is shown in Fig. 4. It can be seen that a longer mixing period does not significantly improve the degree of distribution. The probable reason is that equilibrium is reached between
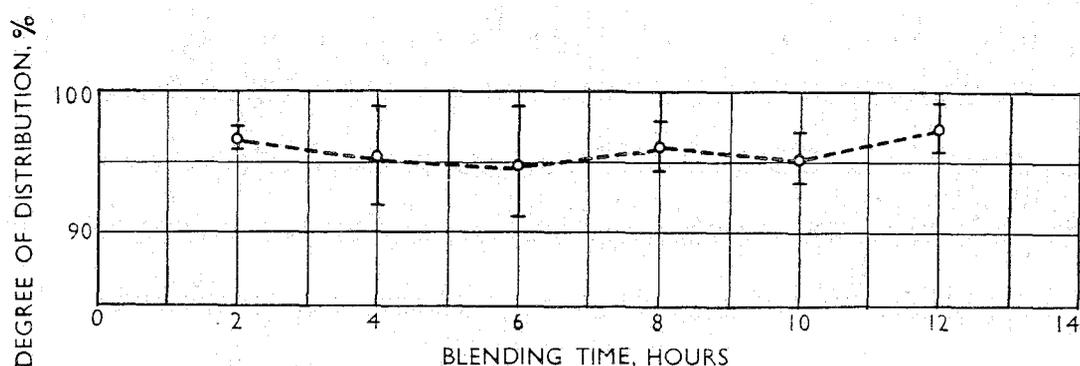
FIG. 4.—Degree of distribution (degree of homogenization) of UAl_2/Al powder mixtures blended with tumbler movement at 70 rev/min. Ratio of powder volume to container volume = 1:4.
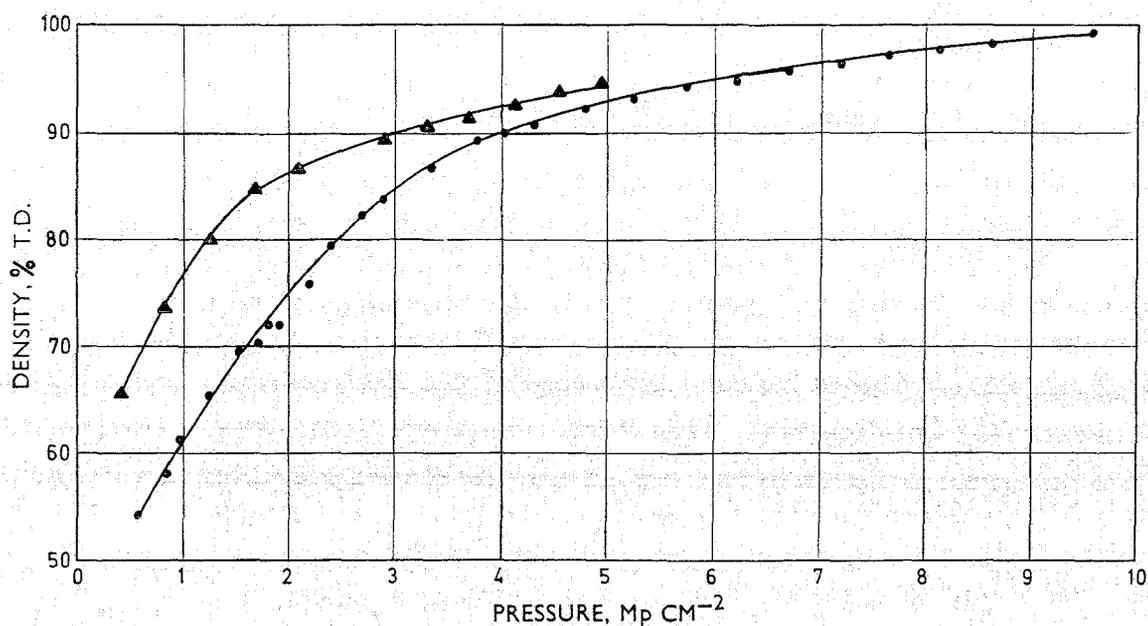
FIG. 5.—Density of a 20 vol.-% UAl_2–Al dispersion as a function of pressure. ● Cylindrical pellets, H/D = 1; ▲ rectangular pellets, 30 × 40 × 2·5 mm.

Fig. 6.—Compacting behaviour of UAl_2–Al dispersions as a function of pressure. Measured on cylindrical pellets with $H/D = 1$.
Volume fraction of UAl_2 (%)

△ 10   ○ 20   □ 30   ▽ 40
▲ 50   ● 60   ■ 70   ▼ 100
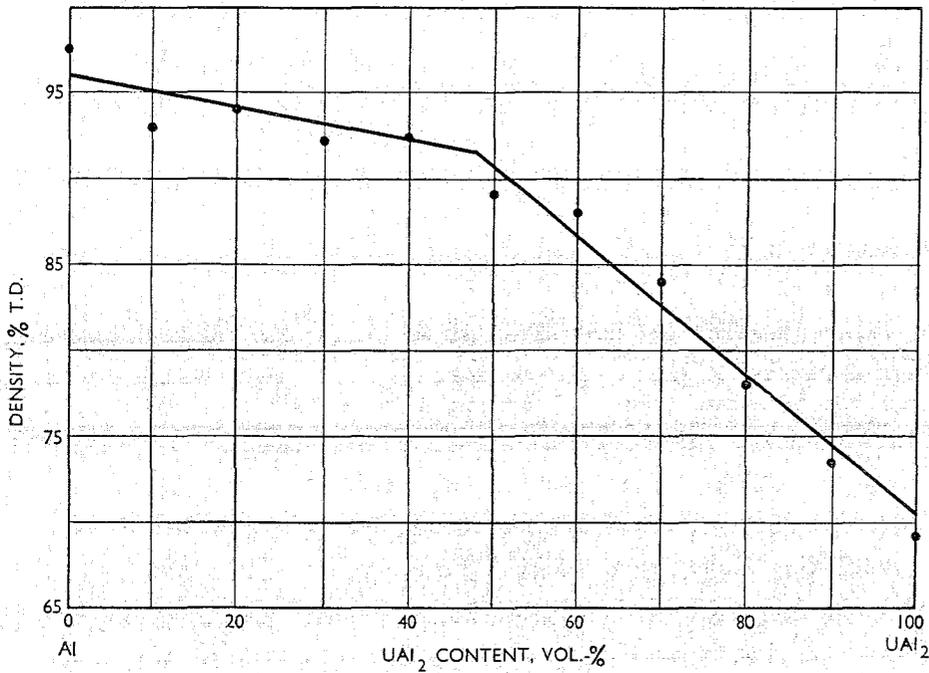
Fig. 7.—Density of pellets as a function of UAl_2 concentration. Measured on cylindrical pellets with $H/D = 1$, pressed at 5 Mp cm^{-2}.

mixing and clustering, so that an increase in the mixing time does not result in an improvement of homogenity. Somewhat different is the case of mixing UAl_3 with aluminium.[13] Because of the smaller differences in density ($\rho_{UAl_3}: \rho_{Al} = 2.52$ as compared with $\rho_{UAl_2}: \rho_{Al} = 3.01$) there is a decreased tendency towards clustering, so that an increase in mixing time results in an improvement in distribution. However, the homogenity achieved by dry mixing of UAl_2 with aluminium is sufficient to guarantee an adequate distribution of the fissile material in the fuel-element plate.
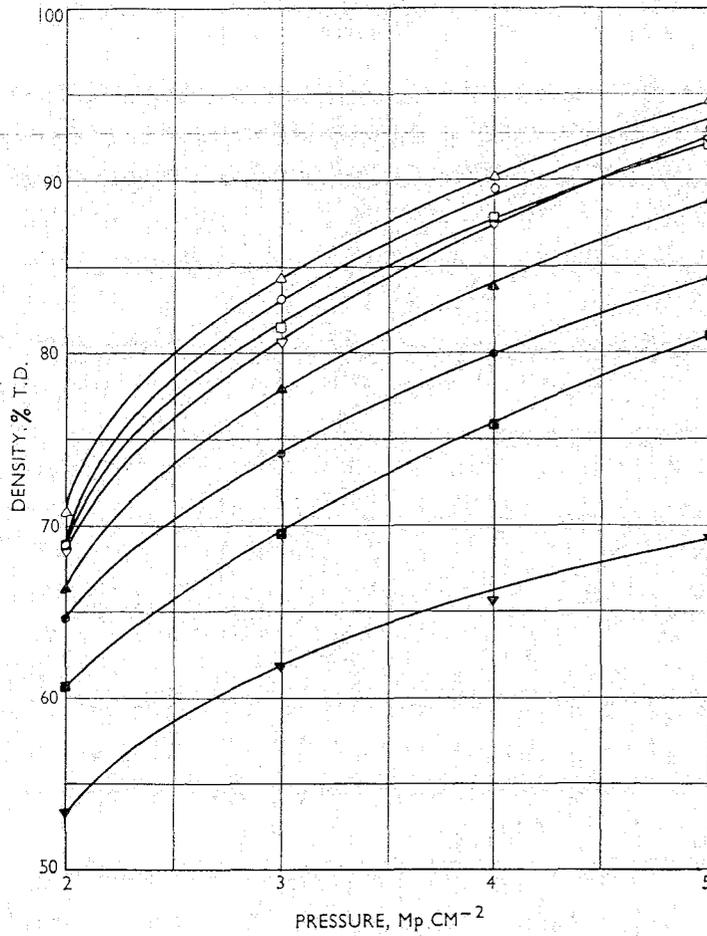
The compacting behaviour of a UAl_2–Al dispersion was studied on cylindrical pellets and also (with regard to the fabrication of fuel elements) on rectangular pellets. A solution of stearic acid and petrol-ether was used as a die lubricant. Fig. 5 shows the density attained as a function of pressure. It is apparent that the pressing behaviour of rectangular pellets is better than that of cylindrical ones. The reason is to be found in the more favourable ratio that exists between their height and dimensions, which results in reduced wall friction. The densities achieved (94% T.D.) are so high that such pellets can be processed into fuel elements without sintering.

An increase in the volume fraction of the dispersed phase (UAl_2) is possible only up to the point where a change in the matrix occurs. To determine this change the compaction behaviour of UAl_2–Al dispersions was investigated as a function of the volume concentration of the dispersed phase (Fig. 6). The curves show that at 50 vol.-% UAl_2 an unsteady variation of behaviour during pressing occurs, indicating the onset of a UAl_2 matrix. This is still more obvious from Fig. 7, in which the density of compacts is plotted as a function of the UAl_2 concentration.

UAl_3–Al dispersions[13] behave similarly. This is to be expected, since in both cases the aluminium matrix primarily determines behaviour during compaction.

3. *Fabrication of UAl₂–Al Irradiation Test-Plates*

The plate dimensions for the irradiation tests were: plate $220 \times 40 \times 1.3$ mm; core $200 \times 30 \times 0.5$ mm.

The UAl_2 fraction in the core was 50 wt.-% (24.9 vol.-%). Aluminium and also $AlMg_2$ were employed as cladding materials. Pure aluminium seems to have a greater resistance to corrosion than the AlMg alloy, but it is inferior to the latter in strength at higher temperatures. The irradiation test-plates were fabricated according to the scheme given in Fig. 8. The radiographs (Fig. 9) show a uniform distribution of the fissile material. The fuel geometry in the plate is in conformity
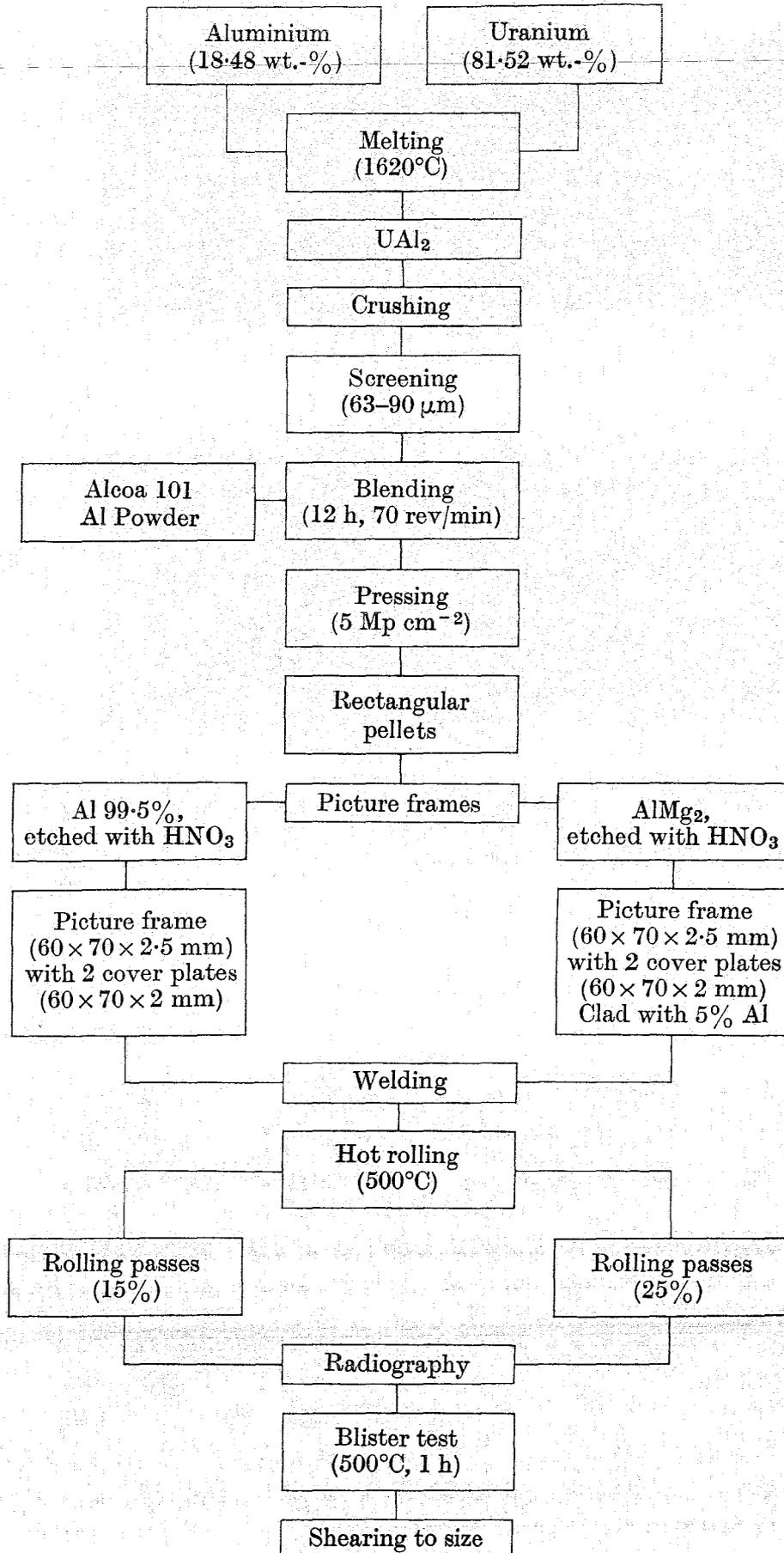
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┌─────────────────────┐        ┌─────────────────────┐
│     Aluminium       │        │      Uranium        │
│   (18·48 wt.-%)     │        │   (81·52 wt.-%)     │
└─────────────────────┘        └─────────────────────┘
              │                       │
           ┌─────────────────────┐
           │      Melting        │
           │     (1620°C)        │
           └─────────────────────┘
                      │
           ┌─────────────────────┐
           │       UAl₂          │
           └─────────────────────┘
                      │
           ┌─────────────────────┐
           │     Crushing        │
           └─────────────────────┘
                      │
           ┌─────────────────────┐
           │     Screening       │
           │    (63–90 μm)       │
           └─────────────────────┘
                      │
┌──────────────┐  ┌─────────────────────┐
│  Alcoa 101   │  │     Blending        │
│  Al Powder   │──│  (12 h, 70 rev/min) │
└──────────────┘  └─────────────────────┘
                      │
           ┌─────────────────────┐
           │      Pressing       │
           │   (5 Mp cm⁻²)       │
           └─────────────────────┘
                      │
           ┌─────────────────────┐
           │    Rectangular      │
           │      pellets        │
           └─────────────────────┘
                      │
           ┌─────────────────────┐
           │   Picture frames    │
           └─────────────────────┘
```

Flow diagram boxes:

- **Aluminium (18·48 wt.-%)** — **Uranium (81·52 wt.-%)**
- **Melting (1620°C)**
- **UAl_2**
- **Crushing**
- **Screening (63–90 μm)**
- **Alcoa 101 Al Powder** → **Blending (12 h, 70 rev/min)**
- **Pressing (5 Mp cm^{-2})**
- **Rectangular pellets**
- **Picture frames**
- **Al 99·5%, etched with HNO_3** / **$AlMg_2$, etched with HNO_3**
- **Picture frame (60 × 70 × 2·5 mm) with 2 cover plates (60 × 70 × 2 mm)** / **Picture frame (60 × 70 × 2·5 mm) with 2 cover plates (60 × 70 × 2 mm) Clad with 5% Al**
- **Welding**
- **Hot rolling (500°C)**
- **Rolling passes (15%)** / **Rolling passes (25%)**
- **Radiography**
- **Blister test (500°C, 1 h)**
- **Shearing to size**

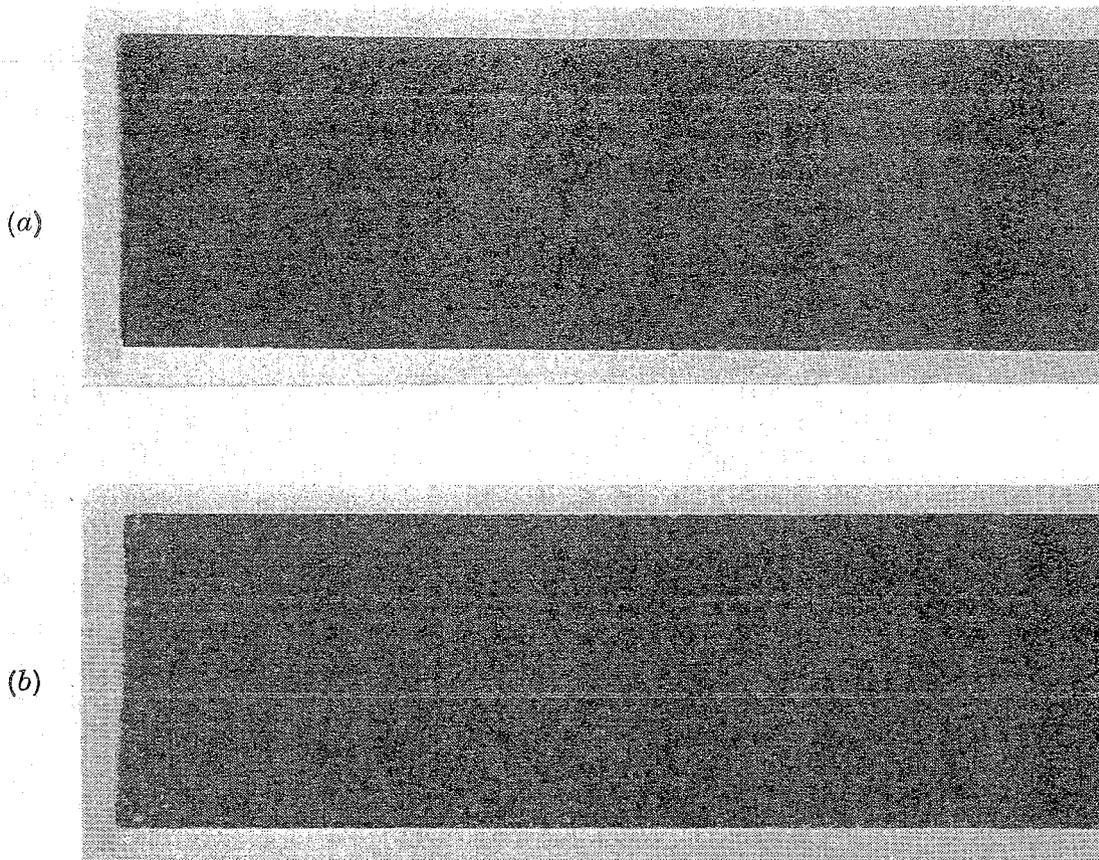FIG. 8.—Schematic diagram of UAl_2–Al plate fabrication.

FIG. 9.—Sections of radiographs of clad UAl₂–Al fuel-element test-plates.   UAl₂ content in the dispersion 50 wt.-% = 24·9 vol.-%.   (a) With aluminium cladding; (b) with AlMg₂ cladding.
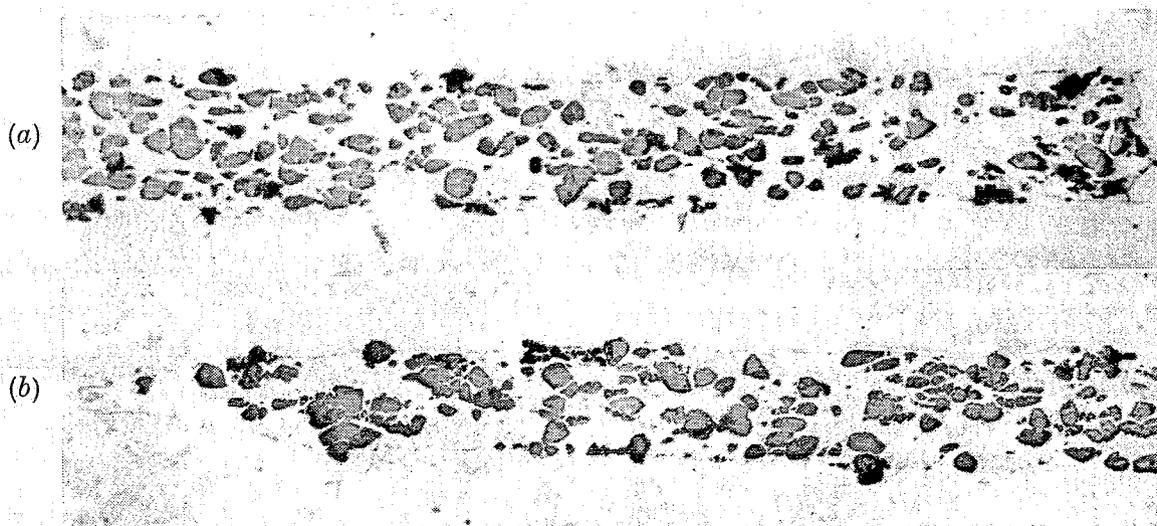

FIG. 10.—Metallographic structure of aluminium-clad fuel plates.   (a) Transverse section; (b) longitudinal section.   Unetched.   × 25.

with the required tolerance. To find possible defects (e.g. dog-boning, tapering) and to determine the thicknesses of fuel and cladding, transverse and longitudinal sections of the plate were metallographically examined (Fig. 10). Here too, the quality of the plates is in conformity with requirements. The blister test did not indicate any bond defects in the fuel plates clad with either aluminium or $AlMg_2$. The UAl_2–Al irradiation test-plates fabricated in this way are of the same standard of quality as the UAl_3–Al plates prepared by similar means.

It can therefore be concluded that UAl_2–Al and UAl_3–Al fuel-element plates can be fabricated on a laboratory scale by basically the same procedure. Though the pyrophoricity of UAl_2 causes certain difficulties, the problem is not insurmountable.

IV.—INTERACTION BETWEEN UAl_2 AND UAl_3 AND THE ALUMINIUM MATRIX

The thermodynamic data for the two aluminides indicate that reactions with aluminium can be expected. The course of these reactions is interesting from the viewpoint of fabrication technology as well as of operational behaviour. Under irradiation the reactions will probably take place at even lower temperatures.

To simulate the operating conditions of fuel plates, the following studies were carried out exclusively with highly dense pellets. Aluminium was always present in excess. The reactions were investigated qualitatively by hot-stage microscopy and quantitatively by dilatometry. The quantitative experiments will be described later.[30] The optical contrast between UAl_2, UAl_3, UAl_4, and aluminium is sufficient for any changes that might occur to be observed. Cylindrical pellets were used (20 vol.-% dispersed phase, pressure 5 Mp cm^{-2}, dia. 8 mm, UAl_2 particle size 63–200 μm). During the experiments the temperature was measured directly on the sample by means of calibrated thermocouples. The tests were carried out in vacuum ($< 10^{-4}$ torr) at a low heating rate (~ 5 degC min^{-1}).

The course of the reactions is shown in Figs. 11 (a)–(d). For the particle size in question, the reaction "starts" in both cases at $\sim 400°C$ (Fig. 11(b)). At this temperature the reaction rate is very low; consequently the temperature had to be increased to permit the observation of the process within a reasonable period of time (3 h). At 500°C (Figs. 11 (c) and (d)) the reaction has progressed considerably in the case of the fine particles, while the coarser ones are "beginning" to react. Microprobe analysis showed that UAl_{4+x} was the reaction product in both cases. The course of the reaction can be explained as follows: At a certain temperature ($\sim 400°C$) a reaction-product growth nucleus

UAl$_2$–Al   UAl$_3$–Al

(a)

(b)

UAl$_2$–Al   UAl$_3$–Al

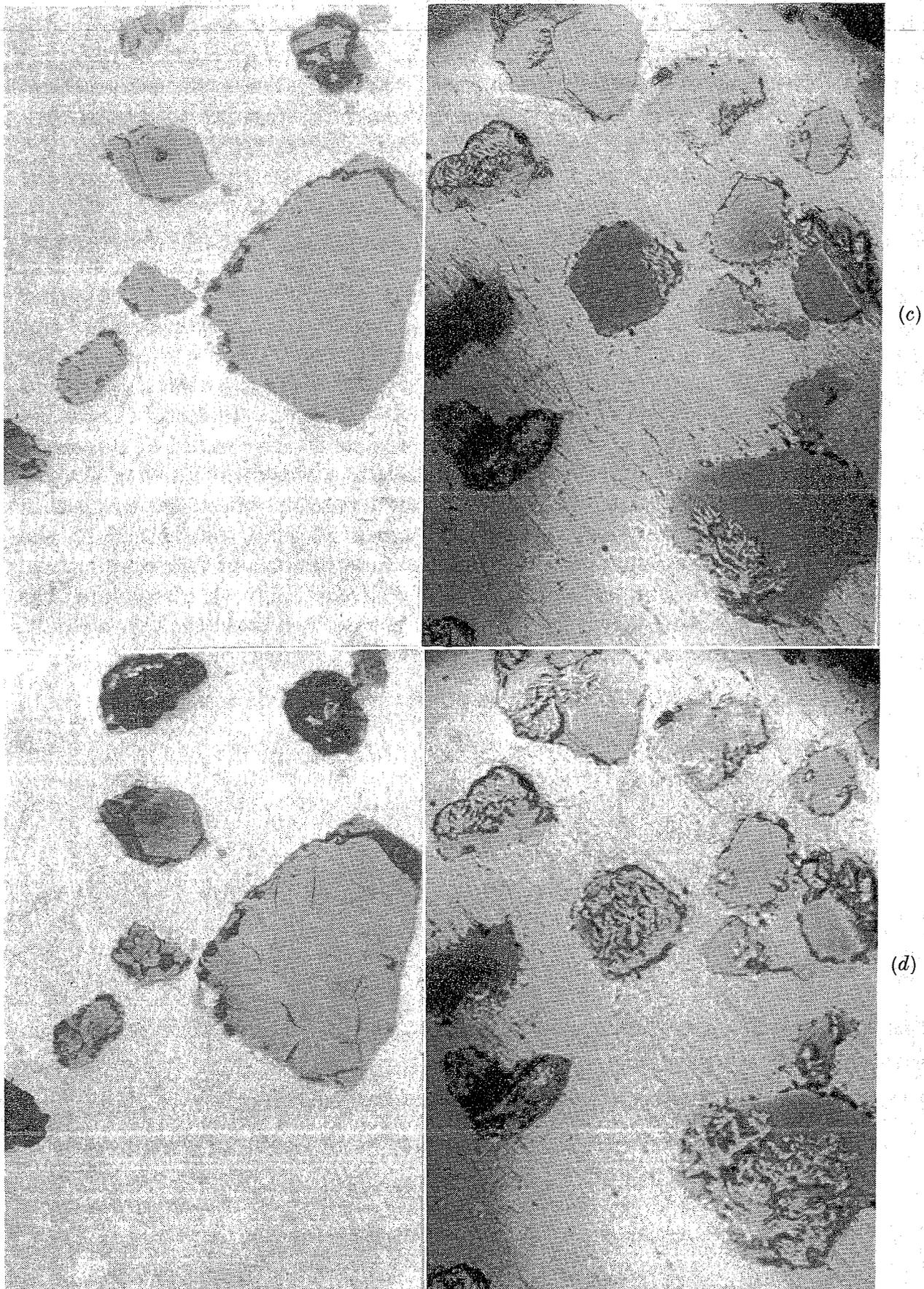UAl$_2$–Al   UAl$_3$–Al

(c)

(d)
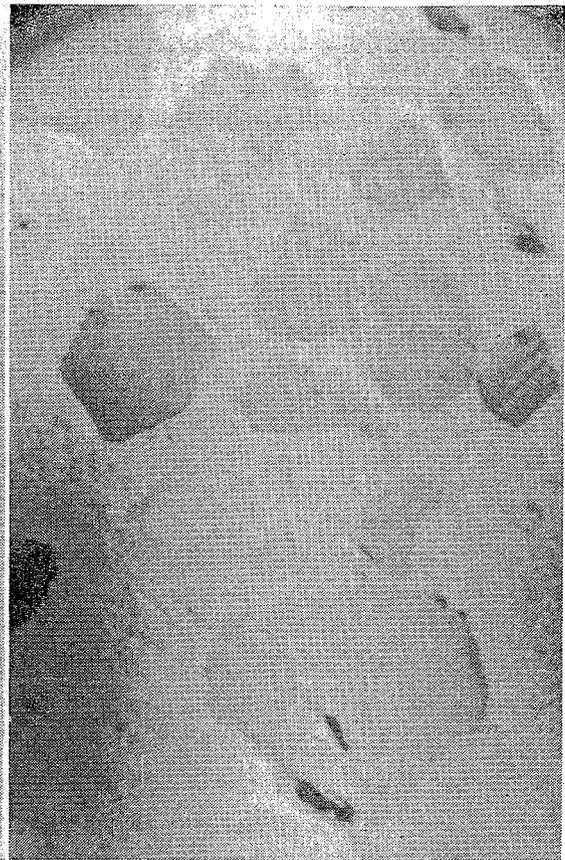
Fig. 11.—Hot-stage metallography of the UAl$_2$ and UAl$_3$ reaction with aluminium.
(a) Room temperature; (b) 410°C; (c) 500°C; (d) 520°C.   × 100.

is formed after an incubation period. In the case of UAl_2 the formation of UAl_3 as a short-lived intermediate product cannot be ruled out, whereas UAl_{4+x} is formed immediately in the case of UAl_3. It seems that nucleation is the rate-determining factor for the reaction. As expected, nuclei are formed at regions that are advantageous both geometrically and energetically. Once the reaction has begun the diffusion of aluminium through the UAl_{4+x} layer formed is decisive for the kinetics. The reaction is probably accelerated by the heat released. As a result, UAl_2 reacts at a faster rate than UAl_3. This would agree with the heat of reaction being higher in the UAl_2 reaction (9 kcal mole^{-1}) than in the UAl_3 reaction (6 kcal mole^{-1}).[21] Assuming that the heat produced is not removed by the aluminium matrix, and assuming further a molar specific heat of 30 kcal deg^{-1} mole^{-1} for UAl_4, a temperature rise of 300 degC as compared to 200 degC would occur in the immediate vicinity of UAl_2 particles. In fact, in hot-stage experiments temperature increases of some 30 degC could be measured at the "start" of the reaction when UAl_{4+x} was formed out of UAl_3.[18]

Apparently, these reactions do not adversely affect the irradiation behaviour, especially since UAl_{4+x} can at least partly satisfy the volume requirements of fission fragments because of its defect lattice. Furthermore, in contrast to the U_3O_8 reaction with aluminium, the above reactions do not yield ceramic phases such as Al_2O_3. As a result, the transfer of fission heat is not seriously affected.
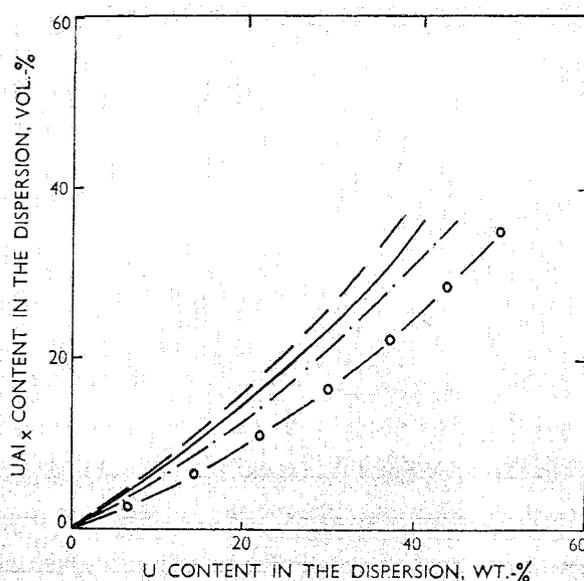

Fig. 12.—Reduction of the aluminium matrix fraction due to reactions (matrix content = 100 − UAl_x content)

— · — · UAl_3 before reaction
— — — — UAl_3 after reaction
— o — o — UAl_2 before reaction
—————— UAl_2 after reaction

A decrease in the dispersion strength must, however, be expected as a consequence of the reactions, since a part of the matrix is consumed. For total reaction the consumption of aluminium is greater with UAl_2 than with UAl_3 (Fig. 12); however, this is more than compensated by the fact that, for a given uranium content, the UAl_2–Al dispersion contains more aluminium from the start. These considerations apply to compact stoichiometric reactants and reaction products. Any existing porosity, or porosity generated by the reaction (Kirkendall effect), and volume increases are not taken into account.

A theoretical calculation of the volume changes resulting from the reactions is difficult since the density of UAl_{4+x} is still a matter for debate. Its preparation in pure form is problematic because of the low peritectic temperature (730°C). Experiments have, however, shown[30] that the reactions are accompanied by an increase in the volume of the dispersion (~1·6% for UAl_2–Al and ~4·6% for UAl_3–Al). Such volume increases would be undesirable if they resulted in a change in the core geometry or in the narrowing of the cooling gap in the reactor core, which consists of a bundle of plates. A cyclic heat-treatment (530°C, 1 h, 6 cycles) of the UAl_2–Al and UAl_3–Al fuel-element plates after hot rolling did not, however, cause any volume changes.

V.—CONCLUSIONS

Comparison between UAl_2–Al and UAl_3–Al dispersions can be summarized as follows:

The preparation by induction-melting of UAl_2 is simpler than for UAl_3, since it can be obtained directly from the melt without homogenization. Aluminium losses due to evaporation are practically eliminated and charging can therefore be stoichiometric. On the other hand, crushing of UAl_2 presents problems. Because of its pyrophoricity it must be crushed in helium; this is, however, technically feasible. The amount of fine powder formed, but not desired (< 63 μm), is similar for both aluminides; it can be recycled by hot pressing and repeated crushing. The UAl_2 obtained has a slightly higher purity than the corresponding UAl_3 powder. The procedure for mixing with aluminium, as well as pressing and cladding by the picture-frame technique, is similar for both dispersions. The reaction with aluminium leads to a smaller increase in volume for the UAl_2–Al combination. However, after an appropriate annealing treatment, deformation of either UAl_2–Al or UAl_3–Al fuel plates was not measurable.

Considering the higher uranium content of UAl_2 and its greater crystal density, from the existing data UAl_2–Al dispersions compare very favourably with UAl_3–Al dispersions. They could, in fact, be

judged to be slightly superior. A final assessment can be made only on the basis of comparative irradiation tests. Known data, however, do not indicate any unfavourable irradiation behaviour for UAl$_2$–Al dispersions.

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