A STUDY OF THE KINETICS OF OXIDATION OF URANIUM-ALUMINIUM COMPOUNDS

A Thesis submitted to the University of London for the degree of Doctor of Philosophy by

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November, 1962.
ABSTRACT

The kinetics of the high temperature oxidation (250 - 600°C), in purified oxygen, of the intermetallic compounds UA12, UA13 and UA14 have been studied using a microbalance and a thermal balance.

The compound UA14 was prepared by an arc melting process, whilst samples of UA13 were supplied by the Metallurgy Division, Harwell. UA14 could not be obtained in a pure form and its behaviour was indirectly assessed by 'extrapolating' the behaviour of uranium-aluminium alloys containing various proportions of UA14 to that of the pure compound.

Alloys containing large amounts of UA14 oxidised linearly over the range 350-550°C, except for the initial stages of film formation. At 600°C a cubic rate of oxidation was observed which gave much smaller weight gains than at lower temperatures. It is suggested that this phenomenon is due to sintering of the oxide film. Alloys containing small proportions of UA14 oxidised in a logarithmic manner over short periods and in a slow linear manner thereafter. Sintering and pre-oxidation experiments were also conducted with the oxide films on UA14 alloys.

UA12 and UA13 oxidised linearly after a short initial period of either increasing or decreasing oxidation rate.

The oxide films produced have been examined chiefly by X-ray powder microscopy and electron microscopy. The only oxide identified was U3O8. The films have few surface features until after prolonged oxidation, when in the case of UA14 and UA13, cracking occurs. A unique system of concentric crack formation occurs in the oxide films formed on UA14 alloys at 500°C, whilst only random cracking occurs at 600°C.
All the linear rates of oxidation are attributed to either the formation of a porous film and a thin coherent barrier film, or to a porous film and a rate determining reaction. These possibilities are fully discussed.
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ACKNOWLEDGMENTS

Special gratitude is expressed to my Supervisor, Dr. L.L. Shreir, for the guidance, advice and encouragement given throughout this work.

The author wishes to thank Mr. O. Flint and Mr. W.B. Mott of the Metallurgy Division, U.K.A.E.A., Harwell for the interest shown in this work and for the guidance given. Acknowledgment is also due to Dr. W.B. Jepson, Mr. A.R. Gibson, Mr. C.T. Thomas and Mr. C.K. Jackson of the Metallurgy Division, Harwell, for their specialised help.

Finally, the author wishes to thank Mr. L.W. Derry, Head of the Metallurgy Department, Battersea College of Advanced Technology, for his interest in this work, and the U.K.A.E.A. for sponsoring and financing it.
The power reactors being built at the present in the United Kingdom are fueled with natural uranium metal and are cooled by carbon dioxide. Although the fuel elements are contained in magnesium alloy (Magnox) cans, the compatibility of the fuel with the coolant can be of great importance in the event of the can being punctured. As uranium oxidises readily in the coolant it is desirable to have a second line of defence which need not necessarily give complete protection, although this would be desirable, but should at least reduce the rate of oxidation of the fuel element. This would allow more time to be taken in dealing with the fault, instead of necessitating the immediate removal of the offending rod which would normally contaminate the cooling system with oxidation products quite rapidly.

The coating of uranium with some form of oxidation-resistant material is an obvious answer to the problem. For such a case, however, two main difficulties exist:

1) Uranium is covered with a natural oxide skin which is very adherent and extremely difficult to remove. Even if this oxide is removed there still remains the problem of re-oxidation as uranium will oxidise even in a very high vacuum. The adhesion of any deposited metal to the oxide film is very poor, particularly during thermal cycling for long periods under the conditions of operation in a pile.

2) Electrodeposition of a metal from an aqueous bath probably leads to the formation of uranium hydrides. These are not stable at elevated temperatures and will decompose to form hydrogen which will weaken the adhesion between the protective metal and the substrate.
The seriousness of these difficulties is underlined by a brief survey of the attempts which have been made to deposit metallic coatings onto uranium. Deposits of Ni, Cu, Pb, Cr, Zn, Co and Sn from aqueous baths have proved unsuccessful. Except in the case of Ni and Cu the deposits peeled off in the bath, whilst only Ni offered protection for any length of time. Nickel coatings will afford protection in boiling water for periods up to 100-200 h, but for not more than 75-100 h when heated in air. Similarly no successful deposit of Co, Be, Cu, Ag, Cd, Fe, or Au has been obtained. Often, even if an apparently adherent coating has been obtained, the coating will fail because of the corrosion of the uranium via "pin hole" defects in the coating. This will produce so much oxide that the coating will be detached from the substrate. Special methods of coating such as solid-solid reactions, solid-liquid reactions, halide decomposition and metal evaporation appear in general to have no particular advantage over electro-deposition whatever the metal used. Failure is always very rapid under test conditions, irrespective of the method of applying the coating.

A protective coating must be adherent and pore-free and should be produced under conditions where hydrides do not form. Although electroplating may introduce the problem of hydride formation, this difficulty can be overcome by using non-aqueous solutions. Such a method of application offers the possibility of an anodic pretreatment of the uranium to activate the surface and to remove the oxide film prior to metallic deposition. After the application of a coating to the uranium, it would be possible to increase the adhesion to the substrate and eliminate any pores by diffusion-bonding the coating and
The uranium base.

An obvious choice for a protective coating would be aluminium or nickel, both of which are extremely resistant to gaseous oxidation and are widely used for protective purposes. Much effort has been extended into the protection of uranium by nickel coatings, but even after the most careful surface preparation of the uranium substrate, it has been found impossible to deposit a coating which affords protection for very long, either in gaseous or liquid environments.\(^1\) Aluminium,\(^{1,4}\) on the other hand, has hardly been studied as a protective coating for uranium, although the metal is extremely resistant to oxidation.

It should be observed, however, that the interdiffusion of aluminium and uranium at the temperature of pile operation (approx. 400-450°C) is very rapid, but it can be reduced either by using alloying elements with the aluminium such as silicon, or by means of a diffusion barrier such as nickel. Interdiffusion will, to some extent, enable a good bond to be obtained between the two metals, but if this leads to a total depletion of the aluminium layer, as may be possible, then the resulting diffusion band of uranium-aluminium compounds will govern the behaviour of the coating during gaseous oxidation.

The investigation of the protection of uranium by coatings of aluminium poses two distinct problems:-

1. Method of application of the aluminium\(^{5,16}\), it was decided that electro-deposition from organic solutions offered the most hopeful line of approach.

2) Oxidation behaviour of the intermetallic compounds of uranium and aluminium formed by the interdiffusion of the aluminium coating into the uranium substrate.

The present work deals with the second problem although the first problem was investigated simultaneously.
2. LITERATURE SURVEY

For an understanding and appreciation of the problem to be investigated, it is necessary to consider several topics which are related to the main problem. The topics to be surveyed are:

1) Interdiffusion of uranium and aluminium, 2) oxidation of aluminium and its alloys, 3) oxidation of uranium and its alloys, 4) properties of intermetallic compounds, with special reference to the chemical and physical properties of uranium compounds.

2.1 The interdiffusion of uranium and aluminium

The uranium-aluminium system is one of very limited solubility but contains three distinct intermetallic compounds. These intermediate phases may be observed metallographically and the growth of layers of these compounds can be observed during diffusion experiments. Measurement of the rate of growth of these intermediate layers does not permit any estimation of the rate of diffusion of the elements in the separate phases to be made. When an intermediate phase C is formed between two metals A and B the boundary motion between C and A will depend on both the diffusion rates in C and A, and the change in width will depend on the diffusion rates in all three phases. The rate of phase boundary migration is some average rate that only rarely permits the rate of diffusion in the separate phases to be estimated, especially when more than one intermediate phase is formed.

The growth and penetration of intermetallic phases in the uranium-aluminium system can generally be represented by an equation of the form:

\[ X^2/t = A \exp \left( -\frac{\Delta a}{RT} \right) \]

where \( X \) = thickness or penetration of the intermetallic phase.
\( a = \) constant, the growth or penetration coefficient.

\( Q_a = \) activation energy.

\( R = \) gas constant.

\( T = \) absolute temperature.

\( t = \) time.

This has the same form of the equation \( D = D_0 \exp \left( \frac{-Q}{RT} \right) \) where, from Fick's Law

\[ m = A \cdot D \frac{dc}{dt} \]

where \( m = \) amount of solute diffusing through a cross section of area \( A \) per second, and

\[ \frac{dc}{dt} = \) concentration gradient at cross section \( A \).

\( D = \) diffusion coefficient.

Although the forms of the equations are similar, the parameters do not necessarily have the same significance.

The interdiffusion of uranium and aluminium occurs very rapidly at elevated temperatures. From the uranium-aluminium phase diagram shown in Fig. 1 it may be seen that the formation of three intermetallic compounds is possible: \( \text{UA}_1, \text{UA}_2, \text{UA}_3, \text{and UA}_4 \). It has been found experimentally, however, that in the case of solid/solid diffusion, i.e. below 640°C, \( \text{UA}_2 \) and \( \text{UA}_3 \) predominate and \( \text{UA}_4 \) forms the greater proportion of the diffusion band. The presence of \( \text{UA}_4 \) is controversial - if any does occur, the amount formed is probably very small.

Data on the solid/solid diffusion of uranium and aluminium is only in approximate agreement and there is a wide discrepancy in the values for the diffusion constants (See Table 1).
This is almost certainly due to the difficulty in obtaining clean diffusion couples, as oxide films on uranium and aluminium are both very adherent and difficult to remove permanently, and their presence will greatly influence the diffusion kinetics.

Bierlein and Green took great precautions to clean their specimens by vacuum cathodically etching in a dynamic krypton atmosphere; the specimens then being joined to form the couple in an inert atmosphere using either pressure alone or a combination of pressure and temperature. They showed that cleaning of specimens, which were subsequently used in diffusion couples, by ordinary chemical means reduced the width of the diffusion zone to half the value obtained by adopting their standard procedure. They obtained a value of 14.3 kcal/g atom for the activation energy over the temperature range 200 - 390°C. Because of the precautions taken in couple preparation it is reasonable to assume that this value is as accurate as any obtained.
LeClair and Bear confined their experiments to the range 480 - 620°C but took less precautions than Bierlein and Green over oxide film prevention and removal. Their value for $Q_a$ was $14.3 - 16.0 \text{ kcal/g atom}$, depending on the temperature range. Two interesting features of their work were: 1) They found that during the formation of the diffusion zone the penetration of aluminium into uranium was only half as great as the penetration of uranium into aluminium, 2) the effect of pressure on the couple was to increase the extent of the diffusion zone and the magnitude of this effect varied with temperature.

The very unusual dependence on applied pressure has since been observed by other workers, and in general it has been found that the effect was most marked above 400°C when pressures as small as 5 to 10 t.s.i. were sufficient to cause an increase in the thickness of the diffusion zone. No satisfactory explanation for these observations is yet available, but it seems probable that the effect is in some way associated with the formation of intermediate phases as it has never been observed in simple solid-solution diffusion.

All investigations confirm that the main product of diffusion in the uranium-aluminium system is the compound $\text{UA}_3$. It is reported that in the very early stages of diffusion $\text{UA}_2$ is formed first, and that diffusion of aluminium and uranium through this layer leads to the formation of $\text{UA}_3$ and $\text{UA}_4$. $\text{UA}_2$ is only found in definite layer form at the higher temperatures of diffusion. Castleman reported that he found $\text{UA}_2$ in layer form very infrequently, but often as a dispersion with $\text{UA}_3$. The formation of $\text{UA}_4$ has never been definitely observed but indirect evidence for its formation does exist.
Kirkendall marker experiments by several workers have indicated that aluminium penetrates into uranium approximately twice as fast as uranium into aluminium.

2.2. The oxidation of aluminium and its alloys

Theoretical

The oxidation of aluminium has been the subject of many experimental and theoretical investigations. It has been found experimentally that aluminium very rapidly builds up an oxide film to a limiting thickness, and that after this further oxidation proceeds extremely slowly. The theoretical treatment of this phenomena, and similar phenomena in very thin films on copper, iron and gold is due to Cabrera and Mott\(^{20,21}\).

Whilst the Wagner mechanism assumes that there is an even distribution of charge in thick films, Cabrera and Mott assume that in very thin films a very intense electrical field is set up. At low temperatures ionic diffusion would not be possible through the film, but it is supposed that electrons can pass from the metal to adsorbed oxygen on the surface film either by thermionic emission or by the quantum mechanical "tunnel effect". This would enable cations to be formed at the metal/oxide interface and oxygen anions at the oxide/gas interface.

Let \(n_i(e)\) and \(n_e(e)\) be the concentration of ions and electrons at a distance \(e\) from the metal/oxide interface. If:-

\[
\begin{align*}
W_i &= \text{energy to remove an ion from the oxide} \\
\Phi &= \text{energy for electron to pass from the metal to the oxide conduction band.} \\
N_i &= \text{number of interstitial positions per unit volume} \\
N_e &= \text{number of electrons per unit volume, which is given by} \\
&\quad 2(2\pi m k T/h)^{3/2}
\end{align*}
\]
m being the electron mass and $k_T$, $h$ having their usual meaning.

Then at the interface the concentrations $n_i(0)$ and $n_e(0)$ are given by:

$$n_i(0) = N_i \exp (-W_i/kT)$$

and

$$n_e(0) = N_e \exp (-\phi/kT)$$

At large distances, $e$, $n_i(e) = n_e(e) = n$ (say) and $n = \sqrt{N_i N_e} \exp (-\frac{1}{2}(W_i + \phi/kT))$.

At smaller distances $E$, $n_i(e)$ and $n_e(e)$ can be related to the electrostatic potential $V$ by Boltzmann's Law.

$$n_i(E) = n \exp (-eV/kT)$$

and

$$n_e(E) = n \exp (eV/kT)$$

By using Poisson's equation and applying the conditions of large $E$ and small $V$ the solution which is obtained is:

$$V = \text{const.} \exp (-E/E_0) \text{ where } E_0 \text{ is a constant}$$

By considering the relative magnitudes of $E$, $E_i$, and $E_0$ a number of distinct cases emerge.

1. $E \gg E_0$. The electrostatic potential is very small - the Wagner mechanism is applicable.

2. $E \ll E_0$. An electrostatic field $E$ is set up, where $E = V/E$. This field enforces directional movement of ions across the film at temperatures where normal diffusion is too small to accomplish this.

3. $E_i < E < E_0$. In this case the rate of diffusion of ions is proportional to the field strength. When $E \gg E_i$ a parabolic law results, not to be confused with the parabolic law of Wagner.

4. $E_i > E < E_0$. Here the field strength is so great that it is not permissible to assume that the ionic migration rate is proportional to the field strength (i.e. no longer inversely proportional to the film
The probability of an ion overcoming a potential barrier $U$ is $\mathcal{U} \exp \left( -\frac{U}{kT} \right)$ where $\mathcal{U} =$ frequency factor; in the case of a field being present however, the potential barrier is lowered and the probability of migration along interstitial lattice sites is increased to $\mathcal{U} \exp \left( -\left( U - \frac{1}{2} Z e a \bar{E} \right) / kT \right)$, where $Ze =$ ionic charge $a =$ barrier constant

Assuming $\bar{E} = \mathcal{U}/E$ it may be shown that $\frac{dE}{dt} = \mathcal{U} \exp \left( \frac{E_i}{E} \right) \left( U = \text{const. at given temp.} \right)$, where $E_i = ZeaV/kT$. For $E \ll E_i E_i/E = \text{const.} - \log e t$.

This equation predicts an inverse logarithmic relation between $E_i$ and $t$ which is rarely observed in practice. The explanation of the direct logarithmic law is due to a modification proposed by Hauffe and Ilschner$^{22}$. They assume that the rate determining factor is not the ionic but the electronic current provided by the "tunnel effect".

In this case, $j_e \ll \exp \left( - E/E_{0'} \right)$ where $E_{0'} = \hbar/4 \pi 2 m \phi^* \phi^* =$ height of potential barrier. Using this assumption it may be shown that $\frac{dE}{dt} = k \exp \left( -E/E_{0'} \right)$ which leads to $E = E_{0'} \log t \sim C$

As the film thickens the rate determining factor changes to that of ionic current and the logarithmic law changes over to the inverse logarithmic law.

This theory distinguishes between thin and very thin films. For the thin film range a parabolic and cubic relationship may be derived, depending on the type of conductor represented by the metal oxide.

In the very thin film range of room temperature oxidation or the first stage of high temperature film formation, a logarithmic relationship is obtained.
Experimental work

The kinetics of aluminium oxidation have been studied by Gulbransen, Smeltzer, Cochran and Sleppy, Dignam and Aylmore and Gregg in the temperature range 350 - 640°C in purified oxygen. Gulbransen studied the behaviour for periods up to only two hours and found that the rates obeyed a parabolic law over the range 350 - 475°C with an activation energy of 22.8 kcal/mol. At 500 - 550°C only linear rates were observed. In Smeltzer's short term studies he found that the rate of oxidation decreased to a very low value after a formative stage of a few hours. This formative stage was parabolic in nature with an activation energy of 37.2 kcal/mol. Cochran and Sleppy, and Dignam also confined themselves to short term tests. They found that the oxidation curves did not exactly fit any well known law over their full range, but that either a linear or parabolic law described at least part of their curves. The very great drop in rate after the formative stage was observed after a few hours oxidation. These workers prepared their specimen surfaces by either chemical or electropolishing, and because such a preparation produced a very smooth surface their weight gain values were much lower than results used by workers who prepared the specimens by mechanical polishing. The work of Lewis and Plumb showed that the true surface area of aluminium could be as much as 25 times the geometric area, depending on the type of polishing used. Aylmore et al conducted experiments for times up to 200 hours and divided the oxidation curves into three distinct stages:

1. An initial pre-linear branch over which the rate decreased with time.
2. A linear branch with an activation energy of 51.9 kcal/mol.
3. A region of decreasing rate which finally led to extremely slow oxidation.

An explanation of these stages was offered in terms of the crystallization and sintering of the oxide film from an amorphous to crystalline structure. As crystallization occurred the resistance of the film to ionic diffusion increased until oxidation virtually ceased when crystallization was completed. Annealing of the thin non-crystalline film "in vacuo" allowed crystallization to proceed and when oxidation was resumed it was found that the final region of very slow oxidation was attained without any transitional stages.

The nature of the oxide film formed on aluminium during high and room temperature oxidation has been frequently investigated.\textsuperscript{29-31} In both instances it was found that the film was initially amorphous. Wilsdorf\textsuperscript{29} has interpreted the halo patterns to which the amorphous structure is attributed as arising from totally disordered groups of Al\textsubscript{4}O\textsubscript{6}. High temperature films usually crystallize to $\gamma$-Al\textsubscript{2}O\textsubscript{3} if held at an elevated temperature for a sufficiently long time.

**Aluminium alloys**

Since pure aluminium forms a very protective film very little work has been performed on the oxidation of its alloys and Al/Mg is the only system which has been thoroughly investigated. The work of de Brouckere\textsuperscript{32}, Preston and Bircumshaw\textsuperscript{33} and Dobinski\textsuperscript{34} on 2.4 - 8\% Mg alloys was concerned with the nature of the oxide film formed. The composition of the film depended very much on the temperature of formation. In the range 120 - 350°C $\gamma$-Al\textsubscript{2}O\textsubscript{3} was formed; above 350°C Mg O was formed preferentially whilst slow heating of an alloy to 400°C produced MgO and Al\textsubscript{2}O\textsubscript{3}.
Smeltzer studied 2.9% Mg - Al alloys at 200 - 550°C. The oxidation curves in purified oxygen were of the paralinear type, the change from parabolic to linear occurring at a film thickness of approximately 1000 Å. Further kinetic studies have been carried out by Cochran and Sleppy, and Hine and Guminiski. The former workers used a 2.35% Mg/Al commercial alloy, and investigated its behaviour in pure oxygen over the range 450 - 640°C for several hours. A parabolic law, with minor deviations was observed and the only product of oxidation was MgO. Hine and Guminiski used dry air, undried air and air plus CO₂ as their oxidizing atmospheres. In dry air a paralinear curve was obtained, but in wet air blisters formed after 90 h which led to an increase in the linear rate. It was found also that the presence of CO₂ tended to inhibit oxidation. As with other workers MgO was found to be preferentially formed and its concentration was found to increase with time.

Fueki and Ishabashi investigated the oxidation of Ni/Al alloys containing up to 12 mole % Al. Parabolic laws were obtained over the temperature range 700 - 900°C. The oxide scale formed had a layer structure, consisting of Al₂O₃, NiO.Al₂O₃ and finally NiO on the outer surface.

An explanation of the behaviour of Al/Mg and Al/Ni alloys may be made in terms of the formation of a layered oxide film. The inner layer of this structure will consist of Al₂O₃ because of its high heat of formation. Whilst the outer layers will be either MgO or NiO, or mixtures of these with Al₂O₃, the inner layer is assumed to be adherent and non-porous, but the outer layer may have porous (as in the case of Al/Mg) or non-porous (as in the case of Al/Ni) structures.

Small additions of Al have improved the oxidation resistance of the following: Ti, Ni, Fe, Cu, Zn and Pb.
2.3 The oxidation of uranium and its alloys

Uranium

Uranium is known to possess pyrophoricity comparable to that of cerium and the effect of specimen self-heating during oxidation is important under certain circumstances. This effect ultimately governs the temperature range over which oxidation may be conveniently observed. In pure oxygen it is difficult to avoid the effect of self-heating above 300°C, although in CO₂ the range may be increased to 700°C before the effect begins to be important. The heats of formation of the various oxides in the uranium-oxygen system are given in Table 2.

Table 2. Heats of formation in the uranium-oxygen system

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Heat of formation (kcal/g mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>272.0</td>
</tr>
<tr>
<td>UO₁.₇₅-₂.₀₀</td>
<td>259.₀</td>
</tr>
<tr>
<td>UO₂.₆₄-₂.₆₇</td>
<td>1080</td>
</tr>
<tr>
<td>U₃O₈</td>
<td>853.6</td>
</tr>
<tr>
<td>UO₃</td>
<td>292.₀</td>
</tr>
</tbody>
</table>

In oxygen the film which is formed at temperatures up to 140 - 150°C is of the parabolic type, i.e. \( W² = kt \). This has been independently established by Cubbicciotti, Spedding and Loriers who found that above this temperature oxidation proceeded according to a linear law. Cubbicciotti postulated that the change from parabolic to linear oxidation was due to film cracking, whilst Loriers favoured the change being due
to self-heating. It is certainly self-heating which causes the combustion of a solid specimen at approximately 360°C and at 245°C for a powdered one. Catastrophic oxidation of a specimen occurs at 300°C the reaction rate only being controlled by the rate at which oxygen can reach the surface. In static gas conditions rates as great as $2\text{mg cm}^{-2}\text{min}^{-1}$ can be achieved. Recent studies by Leibowitz on the oxidation of uranium in the range 125 - 250°C showed that there are two linear portions to the oxidation curve. The first linear stage commenced almost immediately on oxidation; when approximately $50\text{ mg} \text{O}_2/\text{cm}^2$ of surface had been consumed there was a gradual change to a greater linear rate. Only the first linear stage was followed quantitatively and over the temperature range mentioned the activation energy was 10.7 kcal/mol. The change to the second linear rate was thought to be due to the increase of oxide surface area which can be attributed to microscopically observable oxide nodules whose initiation was observed at this point. These nodules increased in area as the oxidation proceeded and usually originated at inclusions or scratches in the metal surface. Leibowitz suggested that the controlling mechanism of the reaction is not that of diffusion, but of a reaction at the gas-oxide interface. Such a reaction could be that of ionization or ionic dissociation or migration.

Unlike most metal-oxide systems the diffusing species during oxidation is the oxygen ion. The diffusion of the oxygen anion inwards through the film is surprising as its ionic diameter of 1.40Å is very large, larger even than that of the uranium cation 0.97Å.
Oxidation products

Up to 1400°C the f.c.c. structure of UO₂ is found on the surface of uranium. When transition has occurred to the linear type of oxidation it is observed that two oxide layers are formed. The outer layer is porous and the inner one compact, but this inner layer decreases as the temperature increases and finally disappears at approximately 230°C. 

Estimations of pore size and the fraction of the oxide volume constituted by voids have been made by Aylmore, Gregg and Jepson for the oxide formed during linear oxidation. Above 230°C the orthorhombic structure of U₃O₈ begins to be evident and the oxide then becomes very loose and flaky. Underneath the non-adherent layers U₃O₈ new cubic layers of UO₂ continue to exist.

The transformation of the oxide to U₃O₈ is accomplished in the presence of non-stoichiometric UO₂. The process of the transformation of UO₂ to U₃O₈ has been investigated by Aberman and Anderson. Their results showed that up to 230°C the dioxide took oxygen into its structure up to UO₂.₂ without appreciable structural change. Above 230°C a phase change occurred and normal UO₂ in the presence of excess oxygen changed to UO₂.₂ and U₃O₈. The system was nucleated by U₃O₈ as oxidation proceeded. This has been confirmed by Aronson et al who concluded that the phase change UO₂ → U₃O₈ occurred both in oxygen and air. Similar conclusions have also been reached by Hering and Perio.

Carbon dioxide

As carbon dioxide is used as a pile coolant its compatibility with uranium is of importance. The first study of the oxidation of uranium in carbon dioxide was due to Allen who noted that appreciable oxidation
occurred in a few hours above 500°C, but not at temperatures below 350°C where prolonged exposure was necessary. Uranium dioxide was the main product of oxidation, but traces of $\text{U}_3\text{O}_8$ and UC were also found. Reduction of $\text{CO}_2$ to CO also occurred and up to 1% of the emerging gas stream at 655°C was CO.

In 1954 more extensive experiments were performed by Huddle$^{54}$. In all cases oxidation was linear with only slight deviations. Up to temperatures of 275°C an induction period exists during which there was virtually no oxidation. The length of this period decreases with rising temperature, which also causes the linear rates to increase after the induction period.

Detailed investigations of the oxidation of uranium in carbon dioxide have been conducted by Antill, Peakall et al$^{55}$ since 1957. They have confirmed that the main product of oxidation is $\text{UO}_2$, both in "moist" and "dry" $\text{CO}_2$. The effect of the moisture content of the gas has been found to be important as uranium oxidizes more rapidly in moist $\text{CO}_2$ than in the dry gas. Over the range 500 - 800°C the reaction obeyed a linear law, although self heating sometimes caused a non-linearity in the weight gain-time relationships. In the range 500 - 725°C the activation energy was 26±10 kcal/mol which is consistent with diffusion of $\text{O}^{2-}$ ions, being the rate controlling mechanism.$^{56}$ Over the range 700 - 1000°C appreciable self-heating occurred and in this range the rate of oxidation decreased with increasing temperature due to the formation of a thick barrier oxide between the gas and the metal.
Uranium alloys

Investigations have been conducted by Silvester\textsuperscript{57} and Antill and Peakall\textsuperscript{58} into the oxidation behaviour of uranium alloys in air and CO\textsubscript{2} over a wide temperature range. Silvester\textsuperscript{57} chose a temperature of 500°C and a carbon-dioxide atmosphere in which to study the effect of various alloying elements with uranium. He divided his results into three groups:

1) Elements Te, V, Fe, Cu, Zr, Nb, Ta, Cr, Mn, Sn, Mb, W and Th reduced the oxidation rate by a factor of 3 - 5 compared to pure uranium.

2) Elements Be, Al, Si, Ni, Pd, Ce and Pb showed no improvement in oxidation behaviour.

3) Elements Co, Pt and Au gave an acceleration in the oxidation rate. In every case additions of not more than 3 weight percent were made, and the product of oxidation was always UO\textsubscript{2}.

Following from the work of Silvester\textsuperscript{57}, Antill and Peakall\textsuperscript{58} investigated in greater detail the effect of Ti, Mo, Nb and Cu alloying elements up to concentrations as great as 15 weight percent. These elements decreased the oxidation rate in air at 500°C or in carbon dioxide between 680 - 1000°C by factors of 200 - 500. These investigators have concluded that as yet there is no satisfactory explanation of the effect of alloying additions and that factors such as oxide solubility, oxide plasticity or lattice defect concentration do not provide any consistent explanation. Study of a 50 weight percent U/Zr alloy has been conducted by Barnartt et al.\textsuperscript{59} A porous oxide was produced which gave rise to a linear oxidation rate, greater than that of pure zirconium but very much less than that of pure uranium.
2.4 Intermetallic compounds and their oxidation behaviour

Types of compound

An intermetallic compound may be defined as a compound in which different metallic elements are bonded together in a stable structure. This definition is usually further restricted by considering only two different metallic elements in each compound, although this need not necessarily be so. The identity of the constituent elements in an intermetallic compound has an important influence on the type of bonding which occurs, which in its turn must influence the physical and chemical properties of the compound. For a complete understanding of the bonding mechanism in these compounds it is necessary to consider the atomic size, valency and electrochemical interaction of the combining elements. These factors govern the type of bonding to be expected and consequently the crystallographic arrangement of the constituent atoms. Virtually every possible type of binding is known to operate either singly or in a mixed form in various specific compounds. Thus pure covalent, metallic or ionic bonding is known to exist in certain compounds although very often it is natural that an overlapping of types occur and compounds with some type of intermediate bonding are formed.

Many compound constituents do not have their normal valencies when in compound form, but there is a large group of compounds where the elements assume their normal valencies. All elements form normal valency compounds with elements from Groups IVB, VB or VIB of the Periodic Table and such compounds are stable if the metal is the electropositive constituent and the element from one of the groups mentioned is the electronegative constituent. Such compounds have the same structure as simple ionic or homopolar compounds of the type AB, A\textsubscript{2}B or A\textsubscript{3}B\textsubscript{2}. 
Compounds such as MgSe, PbTe or Cu$_2$Se are ionic in nature having a high specific resistance and an electrical conductivity which increases as the negative nature of the metalloid elements decreases. In the case of PtSn$_2$ or AuAl$_2$ the compounds are typically metallic and exhibit corresponding properties.

A large class of compounds possesses bonding midway between homopolar and metallic. Such compounds are often formed between electro-negative elements and the transitional metals which have incomplete shells of electrons in the outer ion shell. Structural arrangements in such compounds are often similar but slight modifications in structure can give rise to comparatively large variations in bonding mechanism. This type of compound is typified by NiAs; other examples are CoSe, NiTe, CrSb and MnBi.

Compounds possessing metallic characteristics, and whose elements do not obey the normal valency rules may be classified as "electron compounds". The structure of these depends on the accommodation of the particular number of valency electrons per atom possessed by the phase in the electron energy states of the lowest equilibrium energy. According to Hume-Rothery's rule such compounds will be formed if the electron-atom ratio is 3:2, 21:13 or 7:4. Other factors which must also be considered are that the atomic sizes should not differ by > 15% and that of the electrochemical factor. Examples are Au$_3$Fe, Cu$_5$Cd$_8$, Pd$_5$Zn$_{21}$ and Ag$_3$Sn.

The final type of compound is that known as Laves' phases. These are formed when the difference in atomic diameter is intermediate and usually $A_a:A_b = 1.2:1$. Simple atomic ratios usually occur and the
structures are isomorphic with MgCu₂, MgZn₂ or MgNi₂. The class includes a large number of phases of the composition AB₂ where A and B may be chosen from any group in the Periodic Table. Uranium forms Laves' Phases with Os or Ir but not with Pt, Pd or Ru. The compound UA1₂ is also a Laves' Phase and is isomorphic with MgCu₂.

Experimental Work

In general very little work has been performed upon the chemical properties of intermetallic compounds or allied systems such as carbides, borides, nitrides, etc. Chief interest in such compounds has been in semi-conductors and in their associated physical properties.

Rosenberg has investigated the oxidation of AIII-V compounds such as InSb, GaSb, AlSb, InAs, GaAs and InP. The oxidation curves for InSb were parabolic after an initial short period of rapid oxidation. He found that (Sb₂O₅)₂ was preferentially formed and evaporated from the surface to leave In₂O₃. This crystallized and brought the reaction under diffusion control. Elemental Sb was formed and as it cannot be accommodated in the InSb lattice it accumulated at the In₂O₃ - InSb interface. Oxide formation on all the above-mentioned compounds has been studied at room temperature. Except for InP each curve was characterised by a region with negative curvature followed by a transitional region into positive curvature. The results were interpreted in terms of the formation of metastable surface complexes which preceded the initiation of true oxide growth. The kinetics depended symmetrically on the AIII atoms and the rate of complex formation decreased in the order Al > In > Ga, whilst the rate of oxide formation decreased in the order In > Ga > Al.
Oxidation of the compounds \( \text{Mg}_2\text{Sn} \) and \( \text{Mg}_2\text{Sb} \) in both dried and undried oxygen in the temperature range 350 - 500°C has been studied by Robertson and Uhlig who have also studied the action of moist air at 20°C. At elevated temperatures both compounds oxidised linearly in oxygen with \( \text{Mg}_2\text{Sn} \) being more rapid than either \( \text{Mg}_2\text{Pb} \) or pure Mg. The oxidation products were not identified in this instance but the products of oxidation in moist air at 20°C were hydrated magnesium, tin and lead oxides. The disintegration of \( \text{Mg}_2\text{Pb} \) in air at room temperature is well known; this compound being the most sensitive of Tammann's so called "Zerrieselnden Verbindungen". The corrosion of e.g. \( \text{Mg}_3\text{Sb}_2 \), \( \text{Mg}_3\text{Bi}_2 \), \( \text{MgCd}, \text{Mg}_2\text{Sn}, \text{AlSb} \) was re-investigated by Lohberg together with \( \text{Al}_2\text{Cu}, \text{AlCu}, \text{Al}_4\text{Cu}_9 \), \( \text{Al}_3\text{Mg}_2 \), \( \text{Mg}_2\text{Si}, \text{MgZn}_2 \) and \( \text{Mg}_2\text{Cu} \) in air, water and steam.

Investigations of refractory uranium compounds have been conducted by Snyder & Duckworth and Albrecht and Koohl. The compounds investigated were \( \text{UA}_1\text{}_{2} \), \( \text{UB}_{2} \), \( \text{Be}_{13} \), \( \text{UC}_{2} \), \( \text{U}_3\text{Si}_2 \), \( \text{USi}, \text{USi}_2, \text{USi}_3 \). They were prepared by powder metallurgical techniques which seldom gave attainment of the theoretical density of any particular compound, thus indicating the presence of porosity. Besides being porous the compounds were only nominally pure and often contained 5 - 10% weight of other phases.

**Table 3:** Oxidation properties of uranium compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical density g/cc</th>
<th>Experimental density g/cc</th>
<th>Type of curve</th>
<th>Temp. Range °C</th>
<th>Activation energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{UA}<em>1\text{}</em>{2} )</td>
<td>8.14</td>
<td>6.13</td>
<td>Cubic</td>
<td>200-250</td>
<td>26.0</td>
</tr>
<tr>
<td>( \text{UB}_{2} )</td>
<td>12.8</td>
<td>12.4</td>
<td>Linear</td>
<td>200-400</td>
<td>16.1</td>
</tr>
<tr>
<td>( \text{UBe}_{13} )</td>
<td>4.37</td>
<td>4.46</td>
<td>Linear</td>
<td>300-600</td>
<td>26.2</td>
</tr>
<tr>
<td>( \text{UC}_{2} )</td>
<td>11.7</td>
<td>10.4</td>
<td>Parabolic</td>
<td>150-250</td>
<td>21.2</td>
</tr>
</tbody>
</table>
Table 3. Oxidation properties of uranium compounds - contd.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical density g/cc</th>
<th>Experimental density g/cc</th>
<th>Type of curve</th>
<th>Temp Range °C</th>
<th>Activation energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>U₃Si₂</td>
<td>12.2</td>
<td>12.1</td>
<td>Parabolic</td>
<td>250-400</td>
<td>10.6</td>
</tr>
<tr>
<td>USi</td>
<td>10.4</td>
<td>9.9</td>
<td>Linear</td>
<td>150-300</td>
<td>8.6</td>
</tr>
<tr>
<td>USi₂</td>
<td>8.98</td>
<td>8.91</td>
<td>Parabolic</td>
<td>250</td>
<td>No data</td>
</tr>
<tr>
<td>USi₃</td>
<td>8.15</td>
<td>7.21</td>
<td>Parabolic</td>
<td>300-400</td>
<td>23.6</td>
</tr>
</tbody>
</table>

A summary of results obtained by oxidation of the compounds in oxygen is shown in Table 3. In no case could anything other than UO₂ be detected in the oxidation products.

Although nitrides, carbides, borides and silicides are not true intermetallic compounds, the silicides of the transitional metals have been studied by Kieffer, Benesovsky and their associates in air between 1000 - 1500°C. The maximum oxidation resistance in the systems Mo - Si, Ti - Si, W - Sc, and Cr - Si was found to be at the approximate composition MeSi₂ (Me - metal). Both titanium carbide and nitride have been extensively studied and have been found to oxidise parabolically (TiC) or paralinearly (TiN). The outer layer of the oxide scale was TiO₂ and between this outer layer and the substrate was a solid solution of either TiO₂ - TiC or TiO₂ - Ti N. The boride, TiB₂ oxidised parabolically and between 800 - 1000°C the scale consisted of an outer layer of B₂O₃ and an inner one of TiO₂.

From the information available, it is impossible to generalise on the oxidation behaviour of intermetallic compounds. It does appear evident, however, that the behaviour depends very much on the relative...
reactivity of the constituent elements. One of the components may be so reactive that a protective film is immediately formed preferentially. Conversely, although an oxide may be formed preferentially it may well allow diffusion of ions and the subsequent formation of a complex double oxide system. Other factors of importance will be the formation of oxide solid solutions or spinels and the possibility of one of the uncombined constituent elements being accommodated in the compound lattice or at the oxide-metal interface.
3. EXPERIMENTAL TECHNIQUES

Introduction

The preparation of uranium-aluminium intermetallic compounds and alloys will be described in section 4, and the present section will be confined to a description of the apparatus. As at least some of the compounds were expected to be highly resistant to oxidation, it was necessary to have means available of detecting very small weight increases. For tests to be conducted over long periods of time, and also for preliminary experimental work on some of the alloys, it was decided to use a simple thermal balance. Although this would be less sensitive than a microbalance, the fact that it was intended to be used mainly for long term tests would, to some extent, compensate for this.

A variety of techniques is available for measuring the growth of thin oxide films on metallic specimens. Several of these methods, although extremely sensitive, may only be used in certain cases and are not generally applicable. Methods, for example, such as film stripping, electrical resistance measurement, the use of polarised light, interferometry, or electrometric techniques, have all been employed successfully in certain cases.

The two most widely used kinetic methods are:

1) microbalance techniques,

2) manometric methods.

Both give a measure of the weight increase of a specimen rather than the thickness of the film formed. Conversion to film thickness requires a knowledge of the density of the oxide produced; if this is not available then only the weight increase per unit area of specimen can be evaluated.
Vacuum microbalance

The vacuum microbalance pioneered by Gulbransen is well-known and is very often used in oxidation and similar studies. Briefly, the principle of the balance is to note by means of a travelling microscope the movement of a balance beam which is attached to a horizontal torsional fibre. The specimen is suspended from one arm of the beam and the other is counterweighted. Such a balance is versatile, extremely sensitive, and can easily be made small enough to be totally enclosed in a reaction system. It has very small temperature and pressure coefficients and may be employed for use in a variety of atmospheres and over a very wide range of temperatures.

The manometric method is very simple in principle as it measures the consumption or rate of consumption of the reacting gas with the metallic specimen by observation of the pressure variation in a closed system. The design of such arrangements has been described by Hinshelwood, Wilkins et al., Portevin et al., Cambell et al., and Kubaschewski et al. Such arrangements are not quite as flexible and as widely used as microbalance systems as they have the following disadvantages:

1) Very accurate temperature control of the reaction vessel is needed, as the pressure inside the vessel is a direct function of the temperature;

2) At low pressures (< 1 mm Hg) a correction for thermomolecular flow may have to be applied.

3) No secondary gaseous reactions must occur.

As it was intended to follow the kinetics of oxidation as completely as possible, and as it was probable that mixed oxides of unknown optical properties would be formed on the specimens it was considered impossible...
to employ any of the more specialised techniques. The choice lay therefore between the gravimetric or the manometric technique. As the gravimetric vacuum microbalance method is more flexible and has no serious disadvantages, it was decided to adopt this method of weight measurement in preference to the manometric method.

3.1 Thermal Balance

The thermal balance consisted essentially of a specimen suspended by an inert suspension from the arm of a chemical balance into the hot zone of a vertical tube furnace. The characteristics of such a balance have been listed by Kubachewski and Hopkins79: -

1) The balance should give accurate readings, say to 0.1 mg.

2) The space between the balance and furnace should be well insulated and the holes through which the suspension wire passes should be very small, i.e. only large enough to allow the wire free play.

3) The suspension wire should be well shielded to prevent disturbance by draughts.

The method may be used for oxidation measurements other than in air if a sufficiently rapid and constant gas stream is passed into the closed furnace tube. The gas is allowed to leave through the hole provided for the passage of the suspension wire. To prevent counterdiffusion of the outside air into the chamber, it is necessary to lengthen the hole by means of a suitable narrow tube.

Balance design

The thermal balance built to incorporate the above features is shown in Fig. 2 and was designed to enable a specimen to be oxidised in an oxygen atmosphere at a controlled temperature. The balance
ARM OF CHEMICAL BALANCE

DRAUGHT SHIELD

THERMAL SHIELD

DRIED OXYGEN

B34 CONE & SOCKET

SILICIA TUBE

FURNACE

THERMOCOUPLE LEADS

THERMAL BALANCE

FIGURE 2
used, which had a sensitivity of 0.1 mg, was a Stanton Air Damped Model.

The balance was mounted well above the furnace on a "Dexion" framework with about three feet between the bottom of the balance case and the furnace. In this space insulating sheets of asbestos were placed and the spaces between such sheets were filled with glass wool. This provided a very satisfactory means of thermal insulation and the ambient air temperature in the balance housing during an experiment never rose by more than 1°C above the outside air temperature.

A silica fibre, which hung from the balance arm through a small hole in the balance case, was used for holding the specimen container. This fibre was protected from draughts by a surrounding glass tube. Before entry into the reaction tube the suspension passed through a very narrow hole in a movable metal plate which acted as a baffle against gas emerging from the reaction vessel. From the lower end of the silica fibre a platinum crucible was suspended so as to be just above the re-entrant thermocouple pocket. The specimen to be oxidised was placed in this crucible, as it was possible that during very long term tests a non-adherent oxide might be formed.

The silica glass reaction system consisted of two concentric chambers which ensured that the reacting gas was properly preheated to the desired temperature, even though the system were a dynamic one. The outer tube (A) was fitted with a B34 socket at one end and had a re-entrant thermocouple pocket at the other. The inner tube (B), the second half of the system, consisted of a smaller diameter tube than the first fitted with a B34 cone having two open ends. The end above the cone was extended by a narrow tube to provide an entrance
for the suspension fibre and an exit for emerging gas. An entrance for incoming gas was also provided just above the cone. When the two parts were fitted together they formed a double walled reaction vessel. Dried oxygen entered at the top, flowed down the outer tube, up through the inner one, past the specimen suspended from the balance and then emerged from the top of the vessel through the lengthened exit port.

The furnace which surrounded the greater part of the reaction tube was wound with Nichrome wire. It was controlled by means of an 'Ether Transitrol Anticipatory Indicating Temperature Controller, Type 991' used in conjunction with a 'Gibbs-Engel Mercury Trip Switch.' The controller had a calibrated accuracy of ± 1% and gave control over a band width of ± 2% of the set temperature which was measured with a chrome-alumel thermocouple.

To ensure no back diffusion of air into the system a flow rate of 500 cc/min was used for the dried oxygen. The gas flow rate was measured by means of a "Rotameter" and the flow controlled by means of coarse and fine valves on the oxygen cylinder head. The oxygen was dried by passing the gas through columns of silica gel, anhydrone and phosphorus pentoxide. As this was the only impurity likely to have a marked effect on the oxidation rate and as the balance was relatively insensitive, it was considered unnecessary to use more elaborate techniques for gas purification.

In using the balance experimentally the specimen was placed in the platinum crucible and the balance counterweighted. Dried oxygen was then passed for at least half an hour to ensure good displacement of all the air from the tube. The furnace was then placed in position and allowed to heat up 'in situ'. As temperatures of up to 600°C
were attained within 15 min and the usual time of a complete run was 200-300 hours, it was considered that the effect of this 'warming up' time would not influence the overall oxidation behaviour. When the desired temperature was reached, the balance was read and subsequent readings then taken at appropriate intervals.

3.2 Microbalance System

1. Introduction

The whole system was designed so that weight changes as small as 1 μg could be detected using a 2-3g specimen in a given purified atmosphere, at a constant temperature for any length of time. The system may be conveniently divided into the following units: gas purification, microbalance and control system, reaction chamber and furnace control, and high vacuum system. Each of these units will now be described in detail in the following sections.

2. Gas Purification and Storage

The techniques used for the producing of highly purified oxygen from cylinder oxygen have become quite standardized amongst workers investigating gas-solid reactions. The impure gas is passed through a purification train which successively removes all of the possible impurities except the inert gases.

The purification train used is shown in Fig.3. The rate of gas flow was roughly controlled by a coarse valve on the cylinder head and more finely by a needle valve. Measurement of the gas flow rate was performed by means of a "Rotameter" which had a range of 0 - 500 cc/min.

Oxidizable impurities were removed by passing the gas over hot platinized asbestos (A); products of combustion and acid constituents
such as CO₂, were removed by passing over asbestos coated with sodium hydroxide (B); water vapour by trains of anhydride (magnesium perchlorate) and phosphorous pentoxide (C) and (D); and finally any remaining condensible constituents by passing through a liquid air trap (E).

The purified gas was stored in a five-litre glass bulb attached to the main part of the apparatus. The storage bulb could be connected to the reaction chamber containing the microbalance, a high vacuum pumping system or to a gas exit via two bubblers containing liquid paraffin (F), as required.

In practice an appropriate gas flow rate was selected using the rough and fine needle valves and the gas was allowed to escape via the bubblers (F). The storage bulb was isolated from the gas purification system and connected to the high vacuum pumping unit. When a high vacuum had been attained the system was isolated from the vacuum pump, and purified oxygen allowed to fill the storage vessel instead of being allowed to escape into the atmosphere. When the vessel was full and at atmospheric pressure as indicated by the mercury manometer (G) the gas flow was stopped.

When the rest of the system was ready for the admission of pure oxygen it was leaked from the storage bulb into the reaction system. A slow leak was used so as not to cause violent oscillations of the microbalance and the required amount of oxygen was usually admitted within two minutes. The leaking device consisted of a very fine capillary tube placed in the oxygen admission line to the reaction system which only permitted a slow rate of entry of purified oxygen.
3. The Microbalance and Control System

The balance used was a modified form of the original Gulbransen type balance due to Daane and Edwards & Baldwin. In this form of microbalance the displacement of the beam is not used as a direct measure of weight change, but instead the beam is magnetically restored to a zero position for each reading of weight gain. Such a balance has the advantages of being damped by the magnetic restoring field so that the beam rapidly attains a steady position which is an advantage where rapid reactions are being followed. A further advantage is the large range of weight increase over which a reaction can be followed.

The principle of magnetic restoration is to allow magnetic interaction between two magnets on the balance beam and a controlled external magnetic field. The magnets are placed vertically on either side of the beam axis and the direction of the controlling field is arranged to be perpendicular to their axis but in the same vertical plane. If the field direction is chosen so that the restoring couple tends to oppose the beam displacement caused by the weight change of a specimen suspended from it, then it is possible to keep the beam in a fixed zero position by varying the magnitude (and possibly the direction) of the field.

Manufacture

The balance beam was constructed of silica rod, mainly of 1mm diameter (see Fig.4). The magnets 2mm diameter and 15mm long were of "Ticonel G", a special alloy of high stability and permeability. They were housed in two cylindrical silica capsules (A), affixed to the beam on either side of the beam axis (B) and in such a way as to be vertical when the beam was horizontal. The beam axis (B) consisted
SILICIA BALANCE BEAM

SILICIA SUPPORTING FRAME

MICROBALANCE X 1

FIGURE 4
of a short piece of narrow bore silica tubing fixed at right angles to the plane of the beam.

The beam cradle was constructed from 2mm silica rod (Fig. 4) and for ease of attachment of the torsion wires the tops of the main supporting posts (G) were flattened and enlarged. The beam stops (F) were provided to prevent the beam from excessive movement during handling of the balance assembly.

The balance beam was mounted in the frame by means of a horizontal tungsten wire (H) of 0.001 in diameter which was attached to the beam axis by means of Araldite. The beam with attached wire was then mounted in the frame, across the supporting posts, and under tension applied by two 50g weights hanging from each end of the fibre. The wire was attached to the supporting posts by means of Araldite and the tension was applied for 20 hours during which the Araldite set.

As the magnets were heated during sealing in their silica capsules, and consequently became demagnetised, it was necessary to remagnetise them after the beam had been mounted in its cradle. The beam was immobilised and fixed rigidly by "fusing" it with picein wax to the beam stops; after magnetisation the wax could be removed completely by burning it off with a small flame. The assembly was then placed between the poles of an electromagnet with the magnets in the field direction, and symmetrically situated in the strongest part of the field. A field of 4000 - 6000 oersteds was applied for several hours, and then the assembly was left to magnetically stabilise for 24 hours in a field of 300 oersteds.
Adjustment

When the beam had been freed from the stops the position of its centre of gravity had to be adjusted to give the required sensitivity. For maximum sensitivity it is necessary to have the centre of gravity coincident with, or just below, the tungsten torsional wire. The position of the centre of gravity was raised or lowered by sticking small amounts of platinum wire with adhesive to the beam either above or below the axis. A rough estimate of the sensitivity of the balance could be quickly made by noting the deflection of one end of the beam by means of a travelling microscope when a rider of say 100 μg was placed on one arm of the beam. Adjustments were made until, on a rough estimate, the balance had the desired sensitivity, i.e. 1 μg.

In practice, when a specimen of weight 1 - 2g was used it was necessary to counterbalance the beam by adding small pieces of platinum wire or foil to the platinum pan (D) suspended from one end of the beam.

It was necessary to ensure that there was no movement of the balance system relative to the observational microscope through which the movement of one end of the balance beam was observed, since this would give rise to a spurious weight gain or loss. Check was kept upon this possibility by observing the movement, if any, of a particular reference pointer in the balance system. This pointer was arranged to be in the field of view at the same time as the beam end, but was independent of the balance assembly. If any movement did occur during an experiment it was possible to compensate for this by "re-zeroing" the position of the travelling microscope cross wires relative to the fixed pointer.
The balance manufactured in this manner was adjusted to have a sensitivity of approximately 1 μg. This was sensitive enough to follow the slower reactions up to periods of 10 h, and the 5 mg range of the balance was sufficient to allow the more rapid reactions to be followed for a commensurate period. Tests were conducted upon the stability of the balance using a platinum specimen. No spurious weight changes were observed over the temperature range 300 - 600°C for times up to 50 h using an atmosphere of purified oxygen at a pressure of 7.6 cm of mercury.

**Electrical circuit**

The coil which supplied the magnetic field needed to restore the balance to a null position was wound on a brass spool which could just slide over the glass envelope housing the balance and was co-axial with the balance beam. Ten thousand turns of 22 s.w.g. enamelled copper wire were wound on the spool which was then positioned in the reaction system as shown in Fig.6, so that almost the whole of the balance was in the magnetic field of the coil.

The coil, which had a resistance of approximately 70 ohms, was connected into the controlling circuit. This circuit supplied current to the coil by means of six 2V accumulators; the magnitude of the current could be varied by a set of variable resistors (see Fig.5). A reversing key was included in the circuit together with an on/off switch and a standard 10 ohm resistor. The magnitude of the applied current was measured by finding the potential drop across the standard resistor with a Tinsley Potentiometer (Type 3387B) capable of measuring to 1 μV over the range 0 - 2V.
MAGNETISING COIL CIRCUIT FOR MICROWAVE BALANCE

FIGURE 5
Calibration

The balance was brought to a null position, as observed through the travelling microscope (B) in Fig.6 by adjusting the variable resistors to pass the required current. Calibration of the balance was achieved by observing the change in potential difference across the standard resistor to restore the balance to a null position when a small platinum weight was added to the beam pan. As the weight applied/restoring potential graph is linear, the greatest accuracy of calibration was obtained by using a large weight. Suitable weights were prepared from pieces of platinum wire (500 - 1500 μg) using a chemical balance of 5 μg sensitivity for determining the weight. Thus the absolute accuracy of calibration was within ± 1% and, as the reproducibility of weighing was also of this magnitude, the maximum error to be expected in any weighing was ± 2%.

As errors are sometimes caused by the accumulation of static electricity on the balance, the build up of static charge was avoided by the use of a 2 mc source of thallium 204 which was placed in the balance housing adjacent to the microbalance.

4. Reaction chamber and furnace

The system is shown in Fig.6 and was constructed entirely from Pyrex glass with the exception of the silica tube (L) which entered the moveable furnace.

The microbalance was housed at the top of the chamber and the specimen hung from its beam into the silica tube (L).

Around the horizontal chamber which housed the microbalance was a brass spool (A) which carried the magnetising coil. The end of the balance chamber was closed by means of a sheet of plate glass (C).
WATER → WATER

VACUUM SYSTEM

MERGENCY MANOMETER

PURIFIED OXYGEN SUPPLY

FURNACE

MICROBALANCE & REACTION SYSTEM

FIGURE 6
and a rubber "O" ring (D) was placed between this plate and the flanged end of the chamber. This provided a vacuum tight de-mountable seal which allowed rapid access to the balance for any adjustments that were necessary. Further access to the balance was possible by removal of a sealed cone (M) from a socket just above the end of the beam from which the specimen was suspended. The movement of the balance arm was observed through the plate glass port (C) by means of the travelling microscope (B). Illumination for observation through the microscope was provided by means of a 40 watt bulb (K) placed outside the system. The balance chamber also contained the radioactive source for the dispersal of static electricity.

To prevent undue heating of the balance and balance housing by the furnace thermal shields (F) were placed between the balance housing and the furnace. To eliminate any heat conduction through the glass from the furnace, and to ensure that the gas in contact with the balance was cool, a water cooled jacket (J) was fitted between the silica tube (L) and the balance chamber.

The system was evacuated by means of a high vacuum pumping system described in the following sub-section. Provision was also made for the admission of highly purified oxygen (see Fig.3). When the pressure in the system was greater than that which could be recorded by the gauges of the pumping system, it was registered on a mercury manometer connected to the reaction chamber.

The silica tube (L) was connected to the rest of the system by means of a B34 cone and socket. In the bottom of the tube there was a thermocouple pocket which projected four inches into the tube.
The specimen hung from the balance arm just above this pocket which housed a chrome-alumel thermocouple connected to the temperature-controlling unit.

The furnace used for heating the silica reaction tube could be drawn up around the tube by means of a system of pulleys and counterweights. The furnace was wound with Nichrome wire on a silica former, and ran directly from the mains. Temperature control was achieved by means of an Ether Transitrol used in conjunction with a Gibbs-Eingel Mercury Trip Switch. The controller has a calibrated accuracy of ± 1% and gave control over a band width of ± 3% of the set temperature.

In practice the furnace was brought up to the required temperature before being drawn up to the silica tube. The furnace temperature was noted on a subsidiary thermocouple and temperature indicator. As the position of the controlling thermocouple did not exactly correspond to the specimen position in the reaction system, it was necessary to determine the temperature difference between these two positions. This was accomplished by using a second thermocouple placed in the position of the specimen whilst the furnace was set at a particular temperature. In this way it was possible to apply the slight correction necessary to the temperature controller setting to ensure that the exact specimen temperature was known.

As all the specimens used were regularly shaped solids and the oxide formed on them was very adherent, it was not necessary to suspend them in crucibles to catch any spalled oxide. Instead, simple platinum wire stirrups were used and the specimens were suspended in these from the balance arm. Silica fibres were used as suspension wires between the balance arm and specimen.
5. High vacuum system

A conventional high vacuum pumping system was used to evacuate both the reaction chamber containing the microbalance and also the oxygen storage vessel with its associated parts.

The rotary pump used was a "Metrovac" Rotary Pump, Type DRI, which had an ultimate vacuum of 0.5 mm Hg and a displacement of 1 l/s. This was used to back a 4-stage "Speedivac" Mercury Vapour Pump, Model 2M 4A of ultimate vacuum $5 \times 10^{-7}$ mm Hg.

The vacuum detection system consisted of "Speedivac" Pirani and Penning Gauge. The Pirani Gauge was used between the backing and diffusion pump and the Penning Gauge on the high vacuum side. Provision was made for the pumping unit to evacuate either the oxygen storage globe or the reaction system singly, or both of them together.

With the system described pressures of better than $10^{-5}$ mm Hg could be attained in both systems.

6. Mode of operation of complete system

After a particular specimen had been prepared by techniques described in Section IV it was fitted in a suitable platinum stirrup and suspended from the balance arm by means of a silica fibre. The balance was then counterweighted using platinum weights until the balance was swinging freely. The position was further adjusted until both the arm of the balance and the reference pointer could be seen in the field of view of the travelling microscope. This was usually done by using both gravitational and magnetic forces on the balance beam. When this had been attained the system was sealed, and it and the associated gas storage system evacuated. Evacuation of the system was continued overnight to ensure good degassing.
When the systems had been degassed, oxygen was passed through the purification train and out into the atmosphere. The storage system was isolated from the pumping system and purified oxygen allowed to pass into it until atmospheric pressure was attained. When the reaction system furnace had attained the required temperature it was slid into position around the silica tube. After 30-60 minutes the system achieved a constant uniform temperature and the specimen had been completely degassed. The experiment was initiated by ceasing evacuation of the system and admitting oxygen from the storage globe until there was a pressure of 7.6 cm of Hg in the reaction system. Oxidation of the specimen was followed by adjusting the beam position to its null point at chosen intervals by means of the magnetic control circuit, the potential difference then being measured across the standard resistor. After the experiment had run for its chosen time the system was evacuated, the furnace switched off and slid away from the silica tube. When the temperature of the system was near that of room temperature, air was admitted and the specimen removed.
4. PREPARATION OF URANIUM-ALUMINIUM COMPOUNDS AND ALLOYS

Introduction

Examination of the uranium-aluminium phase diagram shown in Fig. 1 shows that three compounds exist: UA\textsubscript{12}, UA\textsubscript{13} and UA\textsubscript{14}. Working from the uranium rich end of the diagram the first compound to be found is UA\textsubscript{12}, which has a melting point of 1590°C. Formation of the second compound, UA\textsubscript{13}, results from a peritectic reaction with UA\textsubscript{12} and an uranium-aluminium alloy liquid containing 60 wt.% of uranium. The melting point of UA\textsubscript{13} is 1350°C. The third compound, UA\textsubscript{14}, which is formed by a peritectic reaction between UA\textsubscript{13} and an aluminium rich liquid containing 18 wt.% of uranium, has a melting point of 730°C.

The occurrence of peritectic reactions in the system makes the preparation of compounds which are formed via these reactions extremely difficult. The probability of the reaction:

\[ \text{solid (1) + liquid} \rightarrow \text{solid (2)} \]

proceeding to completion is small, as the production of solid (2) itself tends to hinder the transformation of further amounts of solid (1). For the reaction to approach anything like completion it is necessary to anneal specimens for a very long time at a suitable temperature. This treatment has not been found to be satisfactory and homogeneous samples of UA\textsubscript{13} and UA\textsubscript{14} cannot be prepared by melting the appropriate amounts of uranium and aluminium and then annealing the resulting alloy.

As no peritectic reaction is involved in the production of UA\textsubscript{12} it should be possible to prepare this compound by melting the appropriate amounts of uranium and aluminium. As a temperature of at least 1590°C is needed for the compound to form, care must be taken to see that evaporation of aluminium is avoided as at 1830°C aluminium has a
vapour pressure of one atmosphere. Loss of Al by evaporation could be avoided by melting the components in a high pressure furnace.

4.1 Literature survey

Several successful attempts have been made to prepare uranium-aluminium compounds. Eding and Carr, Snyder and Duckworth, and Ivanov have successfully prepared all three compounds using a solid-solid reaction below the melting point of the compound in question. The constituent metals are used in a finely divided form, uranium as the hydride UH$_3$ and aluminium as the powdered metal, and are mixed in the appropriate quantities and then heated in vacuo to about 400°C. At this temperature decomposition of the hydride occurs to give an intimate mixture of finely divided uranium and aluminium. When a temperature of about 700°C is reached an atmosphere of argon is substituted for the high vacuum so as to suppress vaporization of aluminium on further heating. Heating then proceeds until a temperature suitable for the production of the specific compound is reached. For UA$_2$ (m.p., 1590°C) this is approximately 1400°C, for UA$_3$ (m.p., 1350°C) it is 1300°C and for UA$_4$ (m.p., 730°C) it is 700°C. After the sample has been held at this temperature for some time it is cooled to room temperature and examined.

All authors reported that the products, although substantially single phased, were extremely porous. Porosity can be reduced by grinding up the sample followed by compacting and sintering, but it is inevitable that a certain porosity remains. From the point of view of oxidation studies it was considered highly desirable to be able to prepare compounds in a non-porous form. (If pores are present in a sample then it is obviously impossible to either prepare the entire
surface metallographically or to be certain of the true surface area). Furthermore, kinetic studies which are conducted with porous specimens are likely to give an entirely false impression of the kinetics. During oxidation the oxide thickens and pores may become blocked isolating the underlying metal from the reacting gas and causing a diminution in the specimen surface area.

It was thus considered essential to secure non-porous samples of the compounds for oxidation experiments and in the following sections the methods used for obtaining non-porous samples of compounds, together with the apparatus used, are described.

4.3 Experimental methods

Introduction

1. Materials used. The uranium was supplied by the U.K.A.E.A., Harwell, in the form of sheet 1/16" thick. A spectrographic analysis of a typical specimen is given below:-

<table>
<thead>
<tr>
<th>Element</th>
<th>p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>870</td>
</tr>
<tr>
<td>Al</td>
<td>700</td>
</tr>
<tr>
<td>Fe</td>
<td>370</td>
</tr>
<tr>
<td>Si</td>
<td>180</td>
</tr>
<tr>
<td>N</td>
<td>25</td>
</tr>
<tr>
<td>Cr</td>
<td>20</td>
</tr>
<tr>
<td>Mn</td>
<td>15</td>
</tr>
<tr>
<td>K</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Ni</td>
<td>7</td>
</tr>
<tr>
<td>Tl</td>
<td>6</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt; 7</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Co</td>
<td>&lt; 2</td>
</tr>
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</tr>
<tr>
<td>Li</td>
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</tr>
<tr>
<td>B</td>
<td>&lt; 0.06</td>
</tr>
<tr>
<td>Ga</td>
<td>&lt; 7</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.02</td>
</tr>
</tbody>
</table>

U = 99.78%

The "as supplied" metal was covered with a thick black adherent oxide film which had to be removed prior to its use for compound preparation. This was achieved most conveniently by electrolytic dissolution of the film and surface uranium substrate using an apparatus identical to that described by Sykes et al.\(^85\). This was essentially an electro-polishing unit fitted with means for continually circulating the electrolyte past the specimen. The scrubbing action of the stream of electrolyte removed
any anodic film formed without causing any flow line patterns on the specimen. As most of the solutions used in uranium electropolishing are highly corrosive, the parts of the apparatus which came in contact with the electrolyte were manufactured from polythene.

Several solutions are available for the polishing of uranium (see Holden, Sykes et al. and Saller and Rough) and the most efficient for the removal of oxide film was found to be the orthophosphoric/sulphuric acid mixture of Sykes et al.

**Polishing Solution**

Sulphuric acid (S.G. = 1.84) 200 ml
Orthophosphoric acid (S.G. = 1.56) 100 ml
Water 200 ml

Using a current density of 500 mA/cm² of specimen area, removal of oxide film was completed within one minute, and a good polish given to the specimen. Unlike mechanically polished uranium which tarnished very rapidly, electropolished specimens retained their surface lustre for much longer, probably because of the presence of a thin anodic film on the specimen. This was considered to be an advantage as it enabled specimen preparation for compound manufacture to be performed without the disadvantage of subsequent rapid tarnishing.

After electropolishing the only treatment needed was for the uranium to be rinsed several times in distilled water, degreased for twenty minutes in acetone, and then dried with a cold air blower.

The aluminium used was supplied by the Aluminium Laboratories Ltd., Banbury, Oxon. Superpurity metal in the form of ¼" square rods was used, and spectroscopic analysis of a typical specimen is given below:
Aluminium Analysis (p.p.m)

Fe 75   Si 150   Mn < 10   Cu < 10

Al > 99.97%

Preparation of aluminium for compound production was achieved by cleaning the aluminium in concentrated caustic soda solution for a few minutes, followed by repeated rinsing in distilled water, degreasing in acetone for twenty minutes, and then drying by means of a cold air blower.

2. Metallography of the uranium-aluminium system

In the course of uranium-aluminium alloy and compound manufacture it was necessary to identify the various phases and structures in the system. The chief interest lay in the identification of the uranium-aluminium compounds present and whether they were in the form of primary crystals or present as an eutectic with aluminium or uranium.

Metallography. Various authors have briefly dealt with the metallography of the uranium-aluminium system (Gordon & Kaufmann\textsuperscript{87} and Saller\textsuperscript{88}) but the most comprehensive study is due to Hills\textsuperscript{89}. He divided the system into three regions and dealt with each of these in turn.

The first region was that containing Al and UA\textsubscript{14}, i.e. alloys with over 31.2 wt % of Al. In practice fast cooling may lead to the suppression of the peritectic reaction which gives UA\textsubscript{14} so that UA\textsubscript{13} may also be present. The best etches for alloys produced in this region were:

a) 50% nitric acid and 50% water

b) 40% chromic acid, 50% acetic acid and 10% water (used as an electrochemical polish).
Both etches enabled UA\textsubscript{13} to be distinguished from UA\textsubscript{14}. Gordon and Kaufmann\textsuperscript{87} and Saller\textsuperscript{88} used caustic soda or 1% hydrofluoric acid in this region and although these are satisfactory they do not enable UA\textsubscript{13} to be distinguished from UA\textsubscript{14}. If cooling has been slow enough to give complete formation of UA\textsubscript{14} then these etches are as effective as those used by Hills\textsuperscript{89}.

In the second region which contained only UA\textsubscript{13} and UA\textsubscript{14}, or UA\textsubscript{12} and UA\textsubscript{13}, the 40% chromic/50% acetic acid, the 50% nitric acid and the hydrofluoric acid etches all allow differentiation between the two compounds present.

The last region of the system is the U-UA\textsubscript{12} region. Although not mentioned by Hills\textsuperscript{89} or any of the other authors it was found that any of the standard aluminium etches proved satisfactory.

A final aid to microscopic examination in the system was the use of polarized light. Of the three compounds that may be formed, only UA\textsubscript{14} is anisotropic and should, therefore, respond to polarized light examination. In practice, this was not successful unless the UA\textsubscript{14} was present in a massive form.

Preparation of specimens for metallographical examination was not difficult, especially for alloys containing large amounts of intermetallic compounds. Such specimens were mounted in Bakelite or cold setting resin, abraded down to "600 grit" silicon carbide paper under water and then polished with 6µ and 1µ diamond on a polishing wheel. For very soft alloys containing very little compound the specimens were abraded under oil and then polished with "Bluebell" on a wheel.
As discussed previously the preparation of pure UA$_12$ should be possible by direct melting of the appropriate amounts of pure aluminium and uranium as long as care is taken to prevent the evaporation of aluminium during heating. Attempts to prepare UA$_12$ in the manner described were conducted in the Metallurgy Division of the U.K.A.E.A. Harwell using an argon-arc furnace.

This type of furnace is capable of producing very high temperatures in small specimens very rapidly, as heating is due to the passage of an intense high voltage discharge between a carbon electrode and a water cooled copper electrode. The specimen to be melted is contained in a small depression in the water cooled plate, whilst the other electrode is a short distance vertically above it. This discharge is operated in an argon atmosphere of several atmospheres pressure which effectively prevents the evaporation of aluminium even at the high temperatures reached ($>2000^\circ$C). To ensure that the atmosphere is absolutely oxygen free, the system is first evacuated by means of a diffusion pump and then argon is admitted to the required pressure. To "getter" any oxygen from the argon, the arc is always initially played on a small specimen of zirconium metal which resides in a depression in the copper electrode adjacent to the sample. The method of preferential oxygen absorption by molten zirconium is one of the most powerful "getters" of oxygen known. Since the system is at a positive pressure with respect to its surroundings there is no possibility of diffusion of air from the atmosphere into the system.

After "gettering" the atmosphere the discharge is allowed to melt the specimen. Stirring of the melt may be accomplished by a slight
movement of the carbon electrode. This causes a pronounced disturbance of the melt surface and ensures good homogeneity of the sample. To further the attainment of homogeneity the sample is allowed to solidify and then the solid button is "flipped" over with the electrode and remelted. This procedure is repeated several times.

With this furnace and by means of the techniques described attempts were made to manufacture samples of UAl₂. As this compound corresponds to a composition of 18.5 wt % aluminium, samples were prepared with compositions of 16.5, 17.0, 18.5, 20.0 and 21.5 wt % of aluminium to ensure a straddling of the compound composition. The constituent metals were cleaned and prepared by the methods mentioned and then melted in the manner described. The resultant buttons had a volume of approximately 0.75 c.c. since roughly six grams total of aluminium and uranium were used and the density of UAl₂ is 8.2 gm/c.c.

For purposes of comparison, attempts were also made to manufacture UAl₃ and UAl₄ in this manner. The procedure used was exactly the same as for UAl₂, save that slightly less starting material was used as the density of UAl₃ is 6.4 gm/c.c. and that of UAl₄ is 5.7 gm/c.c. whilst the optimum volume for operation in the furnace was a little less than 1 c.c.

3. Preparation of UAl₃

Details of this method are not available until the method is patented by U.K.A.E.A. Harwell.

4. Preparation of UAl₄ and UAl₄/Al alloys

As was anticipated, the arc melting method, which was satisfactory for the preparation of UAl₂, was not successful. Multiphase composites always resulted and heat treatment was only found to be partially
successful as a means of homogenisation,

Leaching

A method which has been used for the separation of intermetallic phases from a metal or alloy substrate is that of preferential dissolution. It is very often possible to find a reagent which will attack the base metal or alloy but not the intermetallic compounds and inclusions present. If this is possible then the particular compound may be obtained in a finely divided state and then pressed and sintered to give a solid specimen. Accelerated dissolution may often be achieved electrochemically providing a particular reagent is suitable. Such a method was used by Petty in the preparation of some of his binary intermetallic compounds of aluminium. By dissolution of the alloy matrix he was able to obtain crystals of the compounds NiAl₃, MnAl₄, MnAl₆, FeAl₃, Cr₂Al₁₁ and Co₂Al₉ which could then be compacted and sintered into suitable specimens.

In a study of the crystal structure of UA₁₄, Borie stated that small crystals of UA₁₄ were obtained from an aluminium rich matrix by preferential dissolution of the matrix with caustic soda. Attempts to repeat this experiment using 25 and 50 wt % aluminium-uranium alloys did not prove successful. Initial experiments were conducted using 1N and ION caustic soda for dissolution of the two compositions of alloys, but this yielded only a grey-black powder which was identified by X-ray powder photography to be UO₂ with only traces of UA₁₄. Further experiments using more dilute solutions of caustic soda, and also dilute solutions electrolytically, only yielded the same results as before.

A search for a solution which would dissolve only the matrix was not successful although a great variety of solutions were tried.
All of the following solutions yielded \( \text{U}_2\text{O}_3 \) and faint traces of \( \text{UA}_4 \) on dissolution of the alloy:—

1) Dilute and concentrated \( \text{HCl} \), \( \text{HNO}_3 \) and \( \text{H}_2\text{SO}_4 \).
2) Metallic salts, e.g. \( \text{CuSO}_4 \), \( \text{SnCl}_4 \) and \( \text{HgCl}_2 \).
3) Various carbonates, bicarbonates and organic compounds such as bromoethane and solutions of iodine in alcohol.

This line of investigation was not pursued further as the possibility of finding a successful leaching agent did not seem very likely. Coupled with this was the knowledge that even if a successful method had been found, compacting of the resulting crystals would have been necessary, and this would have inevitably produced a porous specimen.

**Al-rich alloys**

In view of these difficulties it was decided to conduct experiments on the oxidation properties of alloys containing varying amounts of \( \text{UA}_4 \), starting with the pure \( \text{Al/UA}_4 \) eutectic and finishing with an alloy containing a high proportion of compound. This was undertaken for two reasons:—

1) It was of interest to correlate the behaviour of alloys containing various proportions of \( \text{UA}_4 \) with their oxidation properties.
2) It was considered that although it might not be possible to prepare pure samples of \( \text{UA}_4 \) it might be possible by studying the behaviour of alloys containing various amounts of compound to "extrapolate" the results to 100% pure \( \text{UA}_4 \).

The intention was therefore to prepare a series of alloys in the \( \text{Al/UA}_4 \) region and study their oxidation behaviour on the microbalance. The first alloy in the series was to have the composition of the \( \text{Al/UA}_4 \) eutectic, i.e. 13 wt % uranium. Subsequent alloys were to contain
increasing amounts of UA\textsubscript{4} finishing with an alloy containing as much UA\textsubscript{4} as possible. It was intended to prepare alloys having, say 30, 60 and 90 per cent of their surface area occupied by massive UA\textsubscript{4} in an Al/UA\textsubscript{4} eutectic. The oxidation behaviour of the eutectic could be studied separately and it should be possible by "difference" to study the behaviour of UA\textsubscript{4}. It is of course evident that this argument hinges on the supposition that the primary crystals of UA\textsubscript{4} and eutectic in any alloy oxidize entirely independently of each other.

The easiest method of preparation of UA\textsubscript{4}/Al alloys was by dissolution of uranium in molten aluminium. This method has been used by Saller\textsuperscript{88} and it quite successful for comparatively dilute uranium alloys. Melting of the constituents may be achieved in a vacuum furnace without the attainment of high temperatures and, therefore, without the danger of serious aluminium evaporation.

\textbf{Vacuum furnace}

The vacuum furnace built for the production of these alloys is shown in Fig. 7. The sample to be melted was contained in an alumina crucible which rested on the re-entrant thermocouple pocket of the silica tube. Around the lower half of this tube there was a "Nichrome" wire wound furnace which ran directly from the mains. Control of the furnace was achieved by a system similar to that used for the microbalance and thermal balance systems. A Chrome-Alumel thermocouple resided in the pocket in the silica tube and was connected to the temperature controller. The upper half of the silica tube which terminated in a B34 socket, projected from the furnace and fitted into a B34 cone of the vacuum system. The vacuum system was similar to that used in the microbalance system. As it was also intended
Figure 7

Vacuum & Controlled Atmosphere Furnace

Source of Purified Oxygen

Detachable Glass/Metal Coupling

Silica Tube

Vacuum System & Measuring Gauges

Mercury Manometer

Furnace

Thermocouple Leads
that the furnace should be capable of oxidising specimens in an atmosphere similar to that used in the microbalance system, provision was made for the entry of purified oxygen from the purification train used in the microbalance system. A mercury manometer was attached to the system to enable the correct pressure of oxygen to be admitted for oxidation experiments.

Procedure

The experimental procedure in alloy preparation was as follows. The required amounts of aluminium and uranium were prepared by the procedures already described and then placed in the alumina crucible. The crucible was placed in the silica tube on top of the thermocouple pocket and then the whole system was sealed. Evacuation was commenced and when a vacuum of $10^{-5}$ mm had been reached the furnace was switched on and heating commenced. As aluminium melts at 660°C it was not necessary to use a high temperature - if 730°C is exceeded then care has to be taken in cooling the melt down as the peritectic transformation

$$\text{UA}_3 + \text{Al} = \text{UA}_4$$

occurs at 730°C. The choice therefore was between keeping the aluminium just molten, i.e. 700°C or exceeding the peritectic temperature and having then to take care of the transformation at 730°C. It was found best to use a temperature of 800-850°C for preparation, especially when alloys containing a large amount of UA$_4$ were being manufactured, as better dissolution of the large amounts of uranium required was attained. Having taken the furnace temperature up to 800-850°C it was kept there for 1 - 2 h to ensure complete reaction and then allowed to slowly cool to 750°C. The temperature was then allowed to drop in 5°C steps and
held at each temperature for half an hour. The slow cooling was achieved by cutting out the "Ether" temperature controlling unit and using a "Sinnvic" controller. This process was continued until the temperature was 10 or 15°C below the peritectic temperature and then the furnace was allowed to cool naturally to room temperature.

It was observed that preparation in this manner gave alloys with a non-uniform distribution of UA1₄ in the eutectic matrix. Gravity segregation in this system would be expected to be quite serious as the density of aluminium is 2.7 gm/cc, whilst that of UA1₄ is 5.7 gm/cc. This effect was not unduly troublesome as thin sections could be taken in a plane perpendicular to the direction of segregation and as long as the specimen was not very thick (i.e. not greater than 1 mm) the difference in distribution of UA1₄ between opposite faces was found to be negligible.

The presence of this effect did however suggest that it might be possible to obtain alloys containing high proportions of UA1₄ if natural segregation could be increased. An obvious way of effecting this would be by some form of centrifugal separation whilst the eutectic was molten and the primary crystals of UA1₄ were solid.

Centrifuging

To test the feasibility of this idea some preliminary experiments were conducted in which an alloy was melted in an open furnace at 900°C in a narrow alumina crucible. The size of the crucible was chosen so that it would fit into the bucket of a bench model centrifuge, the other arm of which was suitably counterweighted. When the alloy had attained the furnace temperature it was transferred rapidly from the furnace to the centrifuge and the centrifuge was operated until the alloy had
solidified. The results obtained were surprisingly good even though the alloy had been subjected to high "g" forces for only 10 sec before it solidified. On the basis of these preliminary experiments a more refined apparatus was built capable of centrifuging molten alloys at any desired temperature for more prolonged periods of time.

A general view of the apparatus built is shown in Fig. 8. Essentially the apparatus consisted of a centrifuge with a furnace attached to the end of one of its arms, the other arm being balanced by an equal weight. The current for the furnace entered via slip rings on the driving shaft.

To drive the apparatus a 3/4 h.p motor was used which was controlled by a "Variac". A cylindrical steel container housed the furnace which was suspended from one arm of the centrifuge whilst the other arm was suitably counterweighted. Both containers were free to swing so that as the centrifuge rotated they rose from a vertical to horizontal position. The slip rings which allowed current to be fed to the furnace during rotation were sited on the driving shaft beneath the arms of the centrifuge. Current was supplied to these rings by means of a circuit containing a "Variac" ammeter and ballast resistance.

Details of the rotating contacts may be seen in Fig. 9. The contacts (C) were circular brass discs, insulated from the driving shaft by an anulus of p.t.f.e. and fixed to the driving shaft by a screw(D) which tightened up against the p.t.f.e. insulation. The brass discs were separated from each other by a disc (E) of p.t.f.e. The current leads to the furnace were soldered to the underside of each disc, and the lead to the upper brass disc was led through an insulated hole (F) in the lower one to reach the furnace at the end.
CENTRIFUGE MOTOR

V.A.

MAINS

PLATINUM FURNACE

DUMMY FURNACE

BEARINGS

CURRENT CONTROL CIRCUIT FOR FURNACE

MAINS

V.A.

A

CENTRIFUGAL FURNACE

FIGURE 8
DETAILS OF ROTATING CONTACTS FOR CENTRIFUGAL FURNACE

FIGURE 9

DETAILS OF CENTRIFUGAL FURNACE

FIGURE 10
of the rotor arm. Contact was made with the brass rings by means of two spring loaded carbon brushes (A,B) and the current for these brushes was fed from a Variac (See Fig.9). The contacts were placed underneath the rotor arms as there was less heating of them by thermal convection currents from the furnace.

Details of the furnace used are shown in Fig.10. Because of the requirements of small volume, very little insulation could be used and consequently a furnace with a high heat output was required. This necessitated winding the furnace with platinum wire as no other winding could carry the required current. The platinum wire was wound on a piece of silica tube as a former and was surrounded by a thin layer of "Pyruma" cement (E) which provided good electrical insulation. The top and bottom of the furnace tube were closed with circular blocks of asbestos (D) and the tube itself was sufficiently large to accommodate a small alumina crucible (F). The furnace just fitted into a cylindrical steel bucket (G) which was free to swing by a crosspiece (C) from the rotor arm (A). Both the furnace leads emerged from the top of the furnace and were connected by means of insulated connectors to the brass slip rings.

It was estimated that a heat output of between 500-1000 watts would be required to maintain the crucible at a temperature of 700-900°C. This estimate took into account the large heat losses which would occur because of the very small amount of thermal insulation and also for the fact that rotation of the centrifuge would cause cooling by forced convection.

It was decided to wind the furnace with 0.009" diameter platinum wire which would allow a maximum current of approximately 10A to be passed.
Sufficient wire was used in the construction of the furnace to give a room temperature resistance of 3 ohms. Now

\[ R_T = R_0 (1 + \alpha T) \]

where \( R_T \) = resistance at temperature \( T \)°C.

\[ R_0 = \quad " \quad " \quad 0 \text{°C} \]

\( \alpha = \) temperature coefficient of resistance

For platinum, \( \alpha = 0.004/\text{o°C} \)

hence at 800°C

\[ \frac{R_{800}}{R_0} = (1 + 800 \times 0.4 \times 10^{-3}) \]

i.e. \[ \frac{R_{800}}{R_0} \sim 4. \]

Thus when at 800°C the furnace resistance would have increased to roughly 12 ohms. Using

\[ W = I^2 R \]

where \( W = \) wattage

\( I = \) current

\( R = \) resistance

and putting \( W = 1000 \) and \( R = 12 \), it may be seen that \( I = (1000/12)^{1/2} \).

This gives a value of \( I \sim 10 \) amps to maintain the furnace at 800-1000°C during conditions of high heat loss, which was within the current carrying capacity of the wire employed.

The speed of rotation which could be used with the centrifuge had a maximum value of 3000rev/min. A precise determination of the maximum value achieved was made with a stroboscope. Higher speeds could not be used owing to excessive vibration of the apparatus and its associated bearings. Satisfactory results were obtained with speeds of revolution of up to 3000rev/min.
The distance from the axis of rotation to the bottom of the crucible was approximately 15 cm. Using

\[ f = rw^2 \]

where \( f \) = outwards acceleration (cm/sec\(^2\))
\( r \) = radius of revolution (cm)
\( w \) = angular velocity (rad/sec)

and taking \( r = 15 \) cm, \( w = 3000 \pi/60 \) rad/sec leads to \( f = 4.10^5 \text{cm/sec}^2 \) or \( \sim 400 \text{ g.} \)

The main factors which could influence the efficiency of separation by this method were:-

1) temperature of the melt - this would control the viscosity of the UA\(_4\)/Al eutectic and hence the speed with which primary crystals of UA\(_4\) would segregate,

2) speed of centrifuge - the force on each elemental particle of UA\(_4\) would be proportional to the square of the speed of rotation,

3) time of centrifuging,

4) initial composition of the melt.

In practice alloy compositions of between wt. of aluminium in alloy/wt. of uranium in alloy = 0.7 to 1.1 were used, temperatures were 800-900°C, speeds of revolution up to 3000 rev/min and time of centrifuging up to 20 min. Under these conditions it was found that the composition and compound distribution in the resulting centrifuged alloys did not critically depend on any of the above factors showing that the temperature, time of centrifuging and speed of rotation were of the right magnitude to ensure good separation. The initial composition of the alloy influenced only the thickness of the UA\(_4\) layer; the larger the amount
of uranium in the alloy and hence of UA\textsubscript{14}, the greater the thickness of the layer of compound which separated.

**Results**

1) UA\textsubscript{12}. The method of preparation already described gave almost completely homogeneous specimens of UA\textsubscript{12}. The melts containing 18.5 and 20.0 wt % of aluminium were examined metallographically and were almost entirely single phase with the exception of slight amounts of a second phase along the grain boundaries (See Fig. 30). X-ray examination of powdered samples of compound gave only lines which corresponded to UA\textsubscript{12}.

Depending on which side of the 18.5 wt % of aluminium the true composition of the alloy lay determined whether the phase present along the grain boundaries was the UA\textsubscript{12}/U eutectic or a mixture of UA\textsubscript{12} and UA\textsubscript{13}. The presence of free uranium would have been disastrous as it would have oxidized more rapidly than UA\textsubscript{12} and have led to spurious results. To avoid this possibility it was decided to choose a sample composition for oxidation tests corresponding to 20.0 wt % aluminium. Such a composition would ensure that no uncombined uranium was present, and that the slight amount of any second phase present would be UA\textsubscript{13} or some complex mixture of UA\textsubscript{12}, UA\textsubscript{13} and aluminium. It was considered that there would not be any undue influence on the overall oxidation rate of UA\textsubscript{12} resulting from these minor constituents.

As the amount of material available was limited, specimens in the form of small blocks were used. Their dimensions were approximately $1 \times \frac{1}{2} \times \frac{1}{2}$ cm giving a surface area of $2\frac{1}{2}$ cm$^2$.

2) UA\textsubscript{12}. Specimens were available in a powdered and a solid form but as the amount of material available was limited it was only
possible to use small specimens. Metallographic examination of the solid specimens gave indication of the presence of only small amounts of other phases and showed that the porosity was slight (see Fig. 30). X-ray powder photography of both the powdered and solid specimens gave only lines corresponding to $\text{UA}_3$.

3) $\text{UA}_4$ and alloys. By means of the techniques described it was possible to prepare almost pure specimens of $\text{UA}_4$ and of a whole range of $\text{UA}_4/\text{Al}$ alloys.

$\text{UA}_4$ specimens obtained by centrifugal separation were usually in the form of discs 1 mm thick and 1 cm in diameter. Metallographic examination showed that the specimens were substantially pure $\text{UA}_4$ with not more than 10% of the surface being the $\text{UA}_4/\text{Al}$ eutectic (see Fig. 31). This corresponded to 96 wt% $\text{UA}_4$. X-ray powder photography showed only the presence of $\text{UA}_4$ and aluminium. No lines other than these were detected. Alloys with approximately 30 and 60% of their surface area as $\text{UA}_4$ were also prepared, as well as the $\text{UA}_4/\text{Al}$ eutectic. These specimens were available as thin sheets, 1 mm x 2 cm x 1 cm being the maximum size. The method used for an exact determination of the ratio of $\text{UA}_4$ to eutectic area will be described in a later section.
5. OXIDATION OF UAl₄/Al' ALLOYS IN THE RANGE 400-600°C

5.1 Introduction

The preparation of alloys containing various proportions of primary crystals of UAl₄ has been dealt with in Section 4. By means of the centrifuging technique already described samples were obtained having approximately 90% of their surface area as primary crystals of UAl₄. In addition, specimens of almost pure UAl₄/Al' eutectic were obtained in a similar way by centrifugal separation of the primary crystals of UAl₄. Intermediate alloys containing 30 or 65% of their surface area as primary UAl₄ were manufactured by melting the appropriate amounts of uranium and aluminium in a vacuum furnace (see Section 4).

Area Determination

Determination of the ratio of the area of primary UAl₄ to UAl₄/Al eutectic in any specimen was determined photographically. The specimen was prepared metallographically by the methods described in Section 4. A series of photomicrographs was then taken of the specimen surface, the photographs were cut up and the amount of each separate phase weighed. If the weight per unit area of the photographic paper is constant, then the weight of each phase cut from the photograph is directly proportional to its area.

For an accurate result to be obtained it was necessary to have an alloy of uniform composition and to take a large number of photographs. The lower the magnification the better as a larger and more representative surface area could then be surveyed. The lower limit of magnification was that which gave a structure on the photograph which was too small to
Text cut off in original
be accurately cut up by means of scissors. The upper limit was that at which the features on the photograph became unrepresentative of the whole surface.

For each specimen used, 25-30 photomicrographs of the surface were taken at a magnification of between 250-500 dia. It was considered that this procedure gave a value for the ratio of the relative areas of the two phases having an error of not more than ± 5%.

**Specimen Designation**

The designation of the amount of primary UA1₄ in any alloy was given thus:- 30% UA1₄/Al. The 30% refers to the amount by area of primary UA1₄ expressed as a percentage of the total surface area of the particular alloy in question. The second phase present in such an alloy is the UA1₄/Al eutectic which contains 13 wt.% of uranium (see Fig. 1). Similar considerations apply to the 65 and 90% UA1₄/Al' alloys. The eutectic specimen referred to previously was as near as could be obtained to the ideal composition of 13 wt.% of uranium and contained only very small amounts of primary UA1₄.

**Preparation**

Preparation of specimens for oxidation experiments was achieved by abrading them under water down to "600 grit" silicon carbide paper, degreasing in acetone and drying with a cold air drier. The area of each specimen (rectangular or square sheets) was measured with a micrometer.

After surface preparation the specimens were suspended in a platinum stirrup from the arm of the microbalance in readiness for an experiment (experimental procedures employed in using the microbalance and its associated gas purification train are described in Section 3).
Each specimen was oxidised for a suitable time at a selected temperature in an atmosphere of 7.6 cm Hg purified oxygen (7.6 cm Hg being the standard pressure used in such work). Experiments were also performed in which the temperature was altered to a different pre-determined value during the course of an experiment and in which oxidation was interrupted to sinter the oxide film 'in vacuo'.

Reproducibility

In the initial experiments with the various UA14/Al' alloys several specimens of each different alloy composition were used. Generally, three experiments were performed at any one temperature employing a different specimen in each case and the average of these three runs was taken as representative of the behaviour of the alloy. The reproducibility of the present results (Table 4) lay between those obtained by previous workers for pure aluminium (+15%) and for pure uranium (very large) and depended on the temperature used.

Table 4. Reproducibility of UA14/Al' alloy oxidation experiments

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Reproducibility (max. limits)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>± 10%</td>
</tr>
<tr>
<td>450</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>± 20%</td>
</tr>
<tr>
<td>550</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>± 10%</td>
</tr>
</tbody>
</table>

5.2 Results of short term experiments

1. Eutectic Alloy

A photomicrograph of a typical specimen is shown in Fig.11a. Oxidation studies were conducted on the microbalance over the temperature range 400-600°C for times up to 10 h. The resulting weight gain/time graphs which are shown in Fig.12 indicate that the oxides are all protective in nature.
Fig. 11. Photomicrographs of UA₁₅/Al alloys.

a) UA₁₅/Al eutectic, Unetched (X250).

b) 30% UA₁₅/Al alloy, 1% HF etch (X250).
c) 65% UA$_4$/Al alloy. 1% HF etch (X250).

d) 90% UA$_4$/Al alloy. 1% HF etch (X250).
Fig. 12. Weight gain/time graphs for the UA14/Al eutectic alloy, in oxygen between 400-600°C
The most striking feature of Fig. 12 is that the curve representing oxidation at 600°C is below that at 500 or 550°C. Over the first few minutes of an experiment, oxidation at 600°C is very rapid, but as shown in Fig. 12, subsequent oxidation is extremely slow, being less than comparable stages in the temperature range 450-550°C.

Fig. 13 shows the results of Fig. 12 plotted semi-logarithmically, i.e. W/log t. Each curve consists of two linear parts; the first line corresponds to an initial period of comparatively rapid oxidation, whilst the second and steeper line corresponds to a period of less rapid oxidation. The transition from the first to second line occurs after a time of between 40-250 min. No relation between this transition time and the temperature of oxidation is apparent. Attempts to obtain an activation energy for the oxidation process from the slopes of the graphs in Fig. 13 at different temperatures did not give a very reliable result as the variation with temperature was erratic.

2. 30% UA11/Al alloy

A photomicrograph of a typical specimen is shown in Fig. 11b. The same experimental procedure was adopted as in Part 1 and the resulting weight gain/time graphs are shown in Fig. 14. All the curves show the films to be protective in nature and it is evident that the oxidation curve at 600°C is again below that at 450, 500 or 550°C.

Fig. 15 shows these results plotted semi-logarithmically, i.e. W/log t. Each curve can be divided into two parts: an initial stage of continuously increasing slope corresponding to the early stages of oxidation, and a second linear portion corresponding to the remainder of the oxidation. The second stage of oxidation can be represented by the equation:-
Fig. 13. Oxidation of the UA14/Al eutectic alloy in oxygen between 400-600°C.
Fig. 11. Weight gain/time graphs for 30% Zn-Al alloys in oxygen, between 350-600°C.
Fig. 15  Oxidation of 30% UA1\textsubscript{4}/Al alloys in oxygen between 350-600°C

(t = min)
\[ W = k \log t \]

where \( k = A \exp \left( -\frac{E}{RT} \right) \)

and \( t = \) time, \( W = \) weight gain/unit area

\[ E = \text{activation energy}, \ A = \text{constant} \]

Thus \( W = A \exp \left( -\frac{E}{RT} \right) \log t \)

and hence \( \log \left( \frac{W}{\log t} \right) = \log A - \frac{E}{RT} \).

A graph of \( \log \left( \frac{W}{\log t} \right) - \frac{1}{T} \) is shown in Fig. 16 and from its slope the activation energy for the second stage of the oxidation process between 400-550°C was found to be 7.4 kcal/mol.

All the curves shown in Fig. 14 have a tendency to linearity as the time of oxidation increases and this linearity becomes established in long term tests (see Part 5 of this section). Over short times and with \( W/\log t \) plots any evidence of such tendencies becomes obscured by the logarithmic plot which is insensitive to minor variations in the graph slope. Thus, although the graphs in Fig. 15 and 16 enable the activation energy of the initial part of the oxidation process to be found, this activation energy does not represent the later stages.

Use of the final linear (or approximately linear) section of each graph in Fig. 14 enables a plot to be made of \( \log \left( \frac{W}{t} \right) - \frac{1}{T} \) which represents the later stages of oxidation. Fig. 16a shows such a graph and from its slope an activation energy of 12.9 kcal/mol was obtained.

3. **65% UAl\(_1\)/Al alloy**

A photomicrograph of a typical specimen is shown in Fig. 11c. The same experimental procedure was adopted as in Part 1 and the resulting weight gain/time graphs are shown in Fig. 17.

Each graph in Fig. 17 with the exception of the curve at 600°C is characterized by a short period of rapid but decreasing oxidation
Fig. 16. Oxidation of 30% UA14/Al alloys in oxygen between 350-500°C
Fig. 15a. Oxidation of 30% UAl₄/Al alloy in oxygen between 350-550°C
Fig. 17. Weight gain/time graphs for 65% UA14/Al alloys in oxygen between 400-600°C
rate, followed by a linear rate. In the case of the curve at 600°C there is a rapid initial build up of an oxide film and then very little oxidation after this.

From Fig.17 it follows that the main process of oxidation up to 550°C obeys the law:

\[ W = kt \]

where the symbols have the same significance as given above.

In Fig.18 the values of \( W/t \) obtained from Fig.17 are plotted against \( 1/T \) for the temperatures 400-550°C. From the slope of this graph the activation energy was calculated to be \( 21.4 \text{ kcal/mol} \).

4. 90% UAl₁/Al' alloy

A photomicrograph of a typical specimen is shown in Fig.11d. The same experimental procedure was adopted as in Part 1 and the resulting weight gain/time graphs are shown in Fig.19.

The form of the graphs is very much the same as for the 60% UAl₁/Al' alloys, i.e. after a rapid short formative period the weight gain/time relation is linear. The only exception to this is the curve at 600°C which is characterised by a continuously decreasing oxidation rate. As this suggested a relation of the form:

\[ W^\gamma = kt \]

\( \log W \) was plotted against \( \log t \). If the above equation is true then:

\[ \gamma \log W = \log k + \log t \]

and the value of \( \gamma \) can be obtained from the slope of the graph.

Fig.20 shows a graph of \( \log W/\log t \) for a typical experiment at 600°C and from its slope \( \gamma = 2.96 \). The value of \( \gamma \) obtained by averaging the slopes of all \( \log W/\log t \) graphs is \( 3.0 \pm 0.1 \). A more accurate
Fig. 18. Oxidation of 65% UA$_4$/Al alloys in oxygen between 400-600°C

\[ W = \mu g/cm^2; \ t \ = \ min \]
Fig. 19  Weight gain/time graphs for 90% UA\textsubscript{14}/Al alloys in oxygen between 400-600°C.
Fig. 20 Typical graph for the oxidation of 90% UAl₄/Al alloys at 600°C in oxygen

\((W = \mu g/cm^2; \ t = \text{min})\)
assessment of whether the equation:
\[ W' = kt \]

is accurately obeyed can be obtained by plotting \( W'^3/t \), once a value of \( \eta \) has been determined. It was found that taking \( \eta = 3 \) and plotting \( W'^3/t \) gave a good straight line graph in which there were no significant deviations throughout the experiment. Thus at 600°C the oxide on the 90% \( \text{UA}14/\text{Al}1 \) alloy is very protective and obeys a cubic law.

As the weight gain/time curves are linear up to 550°C a graph of \( \log (W/t) - 1/T \) enables the activation energy to be calculated. Such a graph is plotted in Fig. 21 and from its slope an activation energy of 33.4 kcal/mol was obtained for oxidation in the temperature range 400-550°C. From the intercept of this graph with the y-axis the constant \( A \) in the equation \( W = A \exp (-E/RT)t \) was found to be \( 1.1 \times 10^9 \, \mu g \cdot cm^{-2} \cdot sec^{-1} \).

5.3 Long term tests

As it was of importance to determine whether the behaviour of the various \( \text{UA}14/\text{Al}1 \) alloys was the same during short term tests (i.e. not longer than 10 h) and long term tests (200 h or more) a series of experiments was performed using the thermal balance described in Section 3. Each alloy was tested over the range 400-600°C in dried oxygen for times up to 200 h. As every run took a considerable time it was not possible to perform any experiment more than once.

1. Eutectic alloy

The weight gain/time graphs for the \( \text{UA}14/\text{Al}1 \) eutectic alloys are shown in Fig. 22. At 500-600°C the graphs are linear, but at lower temperatures the weight gains are so small that the form of the curve could not be determined. No anomalous effect at 600°C was observed.
Fig. 21. Oxidation of 90% UA14/Al alloys in oxygen between 400 - 600°C

\( w = \mu g/cm^2; \ t - \text{min} \)
Fig. 22. Long term oxidation experiments with UA14/Al eutectic alloys in oxygen at 500 and 600°C
As only small weight gains were observed, experimental errors were large and no attempt was made to calculate an activation energy.

2. 30% UA14/Al alloy

The weight gain/time graphs for the 30% UA14/Al alloys are shown in Fig. 23 and it is evident that after a period of between 50-100 h the graphs become linear and remain so for the duration of the experiment. The anomalous effect at 600°C which had been observed in short term tests was not present.

From the linear part of each curve in Fig. 23, a plot of log (W/t) -1/T was made as in Fig. 23a. From the slope of this graph the activation energy of oxidation between 400-600°C was calculated to be 15.4 kcal/mol.

3. 65% UA14/Al alloy

The weight gain/time graphs for the 65% UA14/Al alloys are shown in Fig. 24. The main aim of this series of experiments was to ascertain if the anomalous effect at 600°C, observed in short term experiments, was present over long times, and therefore experiments were only performed at 500 and 600°C.

The major portion of the curve at 600°C is represented by a slow linear rate of oxidation. At 500°C the curve has two linear branches, the change from one slope to another occurring after approximately 90 h of oxidation. The rate of oxidation represented by both of these branches at 500°C is much greater than at 600°C.

4. 90% UA14/Al alloy

The weight gain/time graphs for the 90% UA14/Al alloy are shown in Fig. 25. As in the case of the 65% UA14/Al alloys curves were obtained at only 500 and 600°C and the behaviour of the two sets of
Fig. 23. Long term oxidation experiments with 30% UA1$_4$/Al alloys in oxygen between 400–600°C
Fig. 23a. Long term oxidation experiments with 30% UAl₄/Al alloys in oxygen between 400 - 600°C

\( w = \text{mg/cm}^2; \ t = \text{hours} \)
Fig. 24. Long term oxidation experiments with 65% UAl₄/Al alloys in oxygen between 500-600°C.
Fig. 25. Long term oxidation experiments with 90% UAl₄/Al alloys in oxygen at 500 and 600°C
alloys at these temperatures were analogous. The oxidation curve at 600°C shows a very slow linear rate, whilst that at 500°C is very much more rapid and consists of two branches, the transition from one linear rate to a greater linear rate occurring after approximately 50 h.

The results presented so far represent a wide range of behaviour, but common to almost all experiments performed on UA\(^4\)/Al\(^{1}\) alloys is the anomalous temperature effect at 600°C, or what may be termed a 'temperature inversion'. Such an effect in oxidation phenomena has been previously reported in the case of other metals and has been explained in terms of physical changes occurring in the oxide film. The following series of experiments was designed to test whether or not such a hypothesis could be applied to the present case. A more complete discussion of this phenomena will be presented later.

5.4 Pre-oxidation experiments

As the oxidation curves at 600°C have been almost always observed to represent a more protective oxide than those at lower temperatures, it was considered of interest to see if an alloy which had been oxidised at 600°C would retain its protective nature at lower temperatures, where a more rapid rate was usually observed.

1. Experimental procedure

The procedure adopted was to suspend a specimen from the micro-

balance arm and oxidise it for a specified time at 600°C. The temper-

ature was then dropped to 500°C (this took not more than 5 min) and the subsequent oxidation of the specimen was then observed for several hours.

As the anomalous effect was not observed with the 30% UA\(^4\)/Al\(^{1}\)
alloys during long term tests, experiments were confined to 65 and 90% UA14/Al' alloys. Each experiment was performed twice, and agreement was to within ±10%. Each curve in Figs. 26 and 27 is an average of two experimental determinations.

2. Results

1. 65% UA14/Al' alloys

Using the above procedure alloys were oxidised for T minutes at 600°C (T = 4 - 67 min). The subsequent oxidation at 500°C is shown in the weight gain/time graphs of Fig. 26. For clarity the graphs have been vertically displaced from each other, although in practice the initial portions of the graphs for T = 1), 37 and 67 min would be almost co-incident.

On lowering the temperature each graph (except T = 4 min) is characterized by a period in which oxidation was either undetectable or very small. Following this there is a short period of increasing rate and finally a constant rate of oxidation for the remainder of the experiment. This rate, except in the case of the longest time of oxidation at 600°C is approximately half the normal rate at 500°C (see broken line in Fig. 26). For the longest time of pre-oxidation at 600°C (65 min) the subsequent linear rate at 500°C after the period of 'zero oxidation' is about one quarter of the normal rate.

It was noticed in some of the experiments that deviations from linearity occurred in the final portion of the plots at 500°C. Although most experiments ceased after 6-7 h several were extended to 24 h and these showed that there was a slow but steady reversion to the original oxidation rate of 500°C. For short pre-oxidation times (T = 10) the normal rate was reached within this time, but for
Fig. 26. Pre-oxidation experiments with 6% YAl₃/Al alloys.
longer times (T = 65) the final observed rate was somewhat below the normal one.

The period of zero oxidation was roughly proportional to the time of oxidation at 600°C in the case of T = 10, 37 and 65 min. For T = 4 oxidation continued and a constant rate of about half the normal one at 500°C was observed.

2. 90% UA1₄/Al' alloys

Exactly comparable experiments to those in the case of the 65% UA1₄/Al' alloys were performed. The resulting weight gain/time graphs for oxidation at 500°C after pre-oxidation at 600°C are shown in Fig. 27.

In this case, occurrence of a period of zero oxidation and the linearity of the subsequent oxidation is not so apparent. It is clear however that over the first 100 min of oxidation at 500°C little oxidation occurs and in the case of T = 10-200 min only approximately 1/10 - 1/40 of the normal oxidation occurs (see broken line in Fig. 27 for normal rate).

For T = 20, 45 and 223 min the curves have a slow but continuous increment in rate and approach half the normal rate after 5 h oxidation. For T = 2½ and 10 h a linear rate is more evident, but it is still less than the normal one.

To ensure that the observed effects for the 65 and 90% UA1₄/Al' alloys did not occur at other temperatures, several experiments were performed in which, after oxidation at 550 or 450°C, the temperature was dropped to 500 or 400°C respectively. In every case no anomalous effect was observed and there was always a rapid change to a new linear oxidation rate characteristic of the particular temperature employed.
Although the last two sets of experiments indicated that pre-oxidation at 600°C altered the subsequent oxidation behaviour at 500°C they did not provide an understanding of the reason for the alteration. Thermodynamically, it may be possible that the composition of the film at 600°C is different from that at 550°C or below and this might provide an explanation of the anomalous temperature effect. An alternative explanation may be suggested in terms of a critical temperature effect on the physical nature of the film which has the same chemical composition over the entire temperature range. Such an effect could be the crystallization or sintering of the film.

It should be possible to distinguish between those two possible explanations by treating an oxide film formed at 500°C in vacuo at 600°C. If after this treatment no further oxidation occurs it follows that any changes in the film properties are most likely to be of a physical nature, as it is unlikely that any change in the chemical nature of the film due to the loss of oxygen would occur at such low temperatures.

5.5 Vacuum Annealing Experiments

Experimental procedure

In these experiments an alloy was oxidised for a certain time at 500°C, the system evacuated and the temperature of the system raised to 600°C. The specimen was then vacuum annealed at 600°C for a set time whilst still suspended from the micro-balance beam. The temperature was then dropped to 500°C, oxygen admitted to the system and the subsequent oxidation observed.

Results

To avoid needless duplication experiments were confined to 90% UAl₄/Al alloys. The procedure described previously was adopted and
Fig. 28 shows the final stage of the experiment after oxidation for 1 or 5 h at 500°C and annealing 'in vacuo' at 600°C for T hours.

The curves marked with continuous lines are experiments in which the period of oxidation at 500°C was 1 h. The time of annealing (T) was 3, 15½ or 110 h. All these curves especially those for T = 15½ or 110 h show an initial period of up to 4 h during which the oxidation rate is much less than normal - after this time the rate gradually increases and tends to approach the normal rate.

The curves marked with a broken line are experiments in which the period of oxidation at 500°C was 5 h, and the time of annealing (T) was 18 or 90 h. These curves are linear over the first few hours with a rate of only half that of normal, but towards the end of the experiment they exhibit a tendency to higher rates.

To ensure that the above effect did not occur at other temperatures several experiments were performed which were identical to those previously described except that the film was annealed in vacuo at 500°C instead of 600°C. Annealing at this temperature had no influence whatsoever on subsequent oxidation at 600°C.

Reproducibility of these experiments was to within ± 10%.

As it has been shown that the oxidation behaviour of UA14/411 alloys can be altered by thermal treatment of a pre-formed oxide film, it was decided to form an oxide film on the alloys chemically and then to observe the effect on the subsequent behaviour during thermal oxidation.

5.6 Chemical polishing experiments

It is known that both chemical and electrochemical treatment of a metal produces a thin anodic oxide film on the surface. In this case chemical polishing with a solution similar to that used for aluminium
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and its intermetallic compounds was employed - the solution used consisted of 25 ml of sulphuric acid, 70 ml of phosphoric acid and 5 ml of nitric acid at 85°C. Specimens were immersed in it for one minute. After washing and drying, the specimens were oxidised and their kinetics followed on the microbalance. As in the case of the pre-oxidation experiments 65 and 90% UA14/Al' alloys were used.

The results obtained for the 65% UA14/Al' alloy are shown in Fig. 29. At temperatures of 450 and 500°C practically no oxidation was observed for up to 5 h. Above 500°C the effect was less marked. At 550°C the rate was initially very slow and was followed by a slow reversion (over several hours) to the normal rate, whilst at 600°C the behaviour was unaffected by polishing.

The results obtained for the 90% UA14/Al' alloy were less marked. At 450°C the rate was approximately halved, but at 500°C there was a much smaller decrease.

5.7 Discussion

This will be confined to a consideration of the preceeding results in general terms leaving a more fundamental interpretation until after the results of X-ray diffraction and electron microscopy experiments have been presented.

Form of Curves

1. UA14/Al' Eutectic

All the curves exhibit logarithmic growth during short term tests (Fig.13) although after several hours of oxidation it is very difficult to distinguish between this and a very slow linear rate of oxidation. However, the transition from logarithmic to linear oxidation must eventually occur as long term tests (Fig.22) indicate that a linear mode
Fig. 29. Chemical polishing experiments with 65% UA\textsubscript{4}/Al alloys
of oxidation is eventually established at all temperatures.

Such a transition might well be heralded by the discontinuity observed in the $W/\log t$ curves of the short term tests. Although the curve still appears to follow a $W = k \log t$ relationship after the discontinuity, the slope is greater and transition to a linear rate might be occurring too slowly for it to be shown by the $W/\log t$ plot.

Over the range 400 - 550°C there is insufficient data to obtain an accurate activation energy value as only four possible points were available. This difficulty is increased by the fact that the oxidation rates increase with temperature over the range 400 - 500°C and then decrease over the range 550 - 600°C. Using the data in the range 400 - 500°C a very approximate value of 22 kcal/g·mol was obtained for the activation energy. This value for the activation energy is of limited value as its probable error is large and it applies to a restricted temperature range; it does however, enable a rough comparison to be made with the activation energy of oxidation of other UA14/Al' alloys.

The position of the curve representing oxidation at 600°C with respect to the other curves is a feature common to all alloy compositions and its significance and interpretation will be discussed in a later section.

2. 30% UA14/Al' alloys

As with the UA14/Al' eutectic all the curves exhibit logarithmic growth in short term tests (Fig.15) with a tendency to linearity as time progresses. Such linearity becomes well defined in long term tests.
The $W/\log t$ curves are slightly different from those obtained with the eutectic as after an initial period of increasing slope the graphs become linear for the remainder of the experiment. The slopes of the linear portions of these curves are greater than those of the second stage of the eutectic alloy oxidation. Probably the linear portion of the $W/\log t$ plot for the $30\% \text{UAL}_4/\text{Al'}$ alloy corresponds to the second portion of a similar plot for the eutectic specimen, whilst the initial stage present in the eutectic specimen is hardly obvious in the $30\% \text{UAL}_4/\text{Al'}$ alloy.

It is considered that the discontinuous nature of the oxidation curves indicate that two different types of oxidation occur thus resulting in two different activation energies of oxidation. Over the early stages of oxidation the curve is definitely logarithmic and over this stage the activation energy was obtained from the slopes of the $W/\log t$ plots at different temperatures (Fig.16) (the first linear portion of each $W/\log t$ curve was used). In the later stages of oxidation a transition to a linear rate becomes evident and the slopes of the $W/t$ curves at different temperatures were used (Fig.16a). During the earlier stages of oxidation the activation energy was 7.4 kcal/g.mol—in the final linear stage of oxidation a larger energy of 12.9 kcal/g.mol was obtained. The agreement between short and long term tests for the activation energy of the linear rate of oxidation is quite good (12.9 compared with 15.4 kcal/g.mol).

3. $65\% \text{UAL}_4/\text{Al'}$ alloys

In this case all the graphs are predominantly linear, and only in the early hours of oxidation does any non-linearity exist (Fig.17). In this first stage there is evidence of a partially protective oxide
film being formed which then acts as a barrier film and leads to linear rates of oxidation in later stages.

In this particular alloy 35% of the surface area is occupied by the UA14/Al eutectic and in the early stages of oxidation (i.e. the first hour) the oxidation of this portion will be important as the eutectic alloy oxidises in a logarithmic manner which means that the bulk of the oxidation occurs early in time. As time progresses the importance of the contribution from the eutectic portion will diminish and after several hours will be negligible (assuming the two phases oxidise independently). Although this contribution is important in the preliminary stages, other factors are also present.

In the first 50 min of oxidation at 500°C the pure eutectic has a weight gain of \( \sim 40 \mu g/cm^2 \), whilst the 65% UA14/Al alloy gains 55 \( \mu g/cm^2 \). Only 35/100.40 \( \sim 14 \mu g/cm^2 \) of the weight gain can have been contributed by the eutectic. Hence the remainder, 55 - 14 \( \sim 40 \mu g \), must have come from the UA14. This gives a weight increment of 40.100/65\( \mu g/cm^2 \) for the pure UA14 during the first 50 min of oxidation, i.e. \( \sim 60 \mu g/cm^2 \). As the final rate of oxidation at 500°C is \( \sim 0.5 \mu g/cm^2 \) min\(^{-1} \) and the rate of oxidation of the pure eutectic is only 0.06 \( \mu g/cm^2 \) min\(^{-1} \), its contribution to the above figure can be neglected. Hence on comparing the average rate of increment at 500°C of the primary UA14, i.e. 60/50 \( \mu g/cm^2 \) min with the final rate of 1/2 \( \mu g/cm^2 \) min\(^{-1} \) it can be seen that the rate of oxidation of the primary UA14 phase has decreased, i.e. it attains its linear rate after an early period of more rapid but decreasing rate.

Similar considerations also apply to other temperatures. From the deductions made from such considerations it would appear likely
that as long as there is no interference between the oxidation of the two phases it can be postulated that pure UA\textsubscript{14} oxidises in a linear manner (up to 550°C) after an initial period of decreasing oxidation rate.

4. 90\% UA\textsubscript{14}/Al\textprime alloy

The curves obtained for the 90\% UA\textsubscript{14}/Al\textprime alloy, which should be substantially the same as pure UA\textsubscript{14}, tend to confirm the above predictions (Fig.19). Even during the early period of oxidation any contribution from the eutectic portion of the specimen will be very small and the curves should represent approximately the behaviour of pure UA\textsubscript{14}. Although the early stages of oxidation (25 - 50 min) are non-linear, indicating the formation of some type of barrier film, the remainder of the oxidation curve is linear throughout.

Considerations of the change in the activation energy of oxidation with alloy composition and of the forms of the oxidation curves obtained should make it possible to advance a quantitative explanation of these phenomena. Only a semi-quantitative explanation will be advanced, however, as the kinetic data available is not sufficiently accurate for a more precise explanation. Furthermore, the discussion will be limited to explaining the transition from one type of curve to another over the range of UA\textsubscript{14}/Al\textprime alloys employed in short term tests and no attempt will be made to give a fundamental explanation of the mechanism underlying each type of curve.

Use will be made of the following experimentally determined facts:

1. The pure UA\textsubscript{14}/Al\textprime eutectic oxidises logarithmically for short times and any further oxidation (if not logarithmic) is of a very slow linear rate.
2. The oxidation curves for 30, 65 and 90% UA14/Al' alloys all eventually become linear.

The following assumptions are made:-

1. Pure UA14 crystals and the UA14/Al' eutectic oxidise independently of each other.

2. Primary crystals of UA14, when in alloy form with the UA14/Al' eutectic, oxidise in a linear manner (after possibly a short formative period of decreasing oxidation rate) in the temperature range 400 - 550°C.

Semi-Quantitative Analysis

In the oxidation of the alloys two types of oxidation were observed:-

1. Linear, i.e. \( W = k_1 t \)

2. Logarithmic, i.e. \( W = k_2 \log t \)

where \( W = \text{weight gain/cm}^2 \), \( t = \text{time} \), \( k_1 \) and \( k_2 \) - constants.

In a non-homogenous sample where one phase oxidises according to 1 and the other phase according to 2, the total weight gain per cm\(^2\), \( W_t \), is given by:-

\[
W_t = xk_1 t + yk_2 \log t
\]

where \( x \) and \( y \) represent the fraction of the total surface area occupied by each phase.

Depending on the relative values of \( (xk_1) \) and \( (yk_2) \) will depend the type of oxidation law obeyed by the whole surface. If:-

1. \( (xk_1) \gg (yk_2) \) - linear law.
2. \( (xk_1) \ll (yk_2) \) - logarithmic law
3. \( (xk_1) \sim (yk_2) \) - 'mixed' curve, i.e. composite logarithmic - linear law which will have a tendency to linearity as time increases.
Let a fraction of the alloy surface, \( f \), be occupied by primary crystals of UA\(_4\), whilst the remainder \((1-f)\) is the UA\(_4\)/Al'eutectic. Assuming no interference between the two modes of oxidation, the weight gain \( W_t \) of the whole surface after a time \( t \) is given by:

\[
W_t = (1-f) k_2 \log t + k_1 ft
\]

\[
\frac{dW_t}{dt} = (1-f) \frac{k_2}{t} + k_1 f
\]

The magnitude of the ratio of the two terms in the expression for \( \frac{dW_t}{dt} \), \( F \), will govern the type of law observed.

Then

\[
F = \left[ \frac{(1-f) k_2}{k_1} \right] / f
\]

\[
= \frac{[1-f] k_2 / k_1}{1/t}
\]

For \( F \) to be a maximum, and hence for a logarithmic law to hold, one or more of the following conditions must hold:

1. \( f \to 0 \)
2. \( k_2 \gg k_1 \)
3. \( t \to 0 \)

Conversely for a linear law to hold the reverse of the above conditions must apply.

In the case of the oxidation of 90% UA\(_4\)/Al' when linearity has been established and the contribution of the eutectic can be neglected, the constant \( k_1 \) lies between 1 and 0.01 \( \mu g \) cm\(^{-2}\) min\(^{-1}\) depending on the temperature. To a first approximation this may be taken as the value of \( k_1 \) for pure UA\(_4\). For the eutectic UA\(_4\)/Al', \( k_2 \) lies between 10 - 20 \( \mu g/cm^2 \). Hence the limits of the ratio \( \frac{k_2}{k_1} \) lie between 20/1 and 10/0.01

\[
\text{i.e. } 20 - 1,000
\]

Using the above limits for the value of \( \frac{k_2}{k_1} \) the case of the 30% and 65% UA\(_4\)/Al' alloys can be considered and their behaviour predicted.
**30% UA\textsubscript{14}/Al\textsubscript{11} alloy**

In this case \((1-f)/f \sim 2/3 \times 1/3 \sim 2\).

Hence \(F = 2 \times (20 - 1,000)/t\)

\[= (40 - 2,000)/t\]

For the logarithmic law to predominate \(F\) must be at least 5 (say) and hence \(t = 8 - 400\) min. Thus, depending on the temperature the logarithmic law will predominate for between 8 - 400 min. Until \(F = 1/5\) (say) i.e. after 200 - 1,000 min the linear law will not be strongly evident, and the intervening region between \(F = 5\) and 1/5 will give more linear curves as time increases.

These predictions are fairly well borne out by Fig.14. At 350 - 450\textdegree{}C linearity is not at all evident until 300 min and is not even well established after 400 min. At 500 and 550\textdegree{}C linearity commences to be evident after 350 and 200 min respectively and in the case of the curve at 550\textdegree{}C is fairly well established after 400 min.

**65% UA\textsubscript{14}/Al\textsubscript{11} alloy**

In this case \((1-f)/f \sim 1/3 \times 2/3 = \frac{1}{2}\)

Hence \(F = \frac{1}{2} \times (20 - 1,000)/t\)

\[= (10 - 500)/t\]

For the logarithmic law to predominate \(F\) must be at least 5 (say) and hence \(t = 2 - 100\) min, whilst for the linear law to predominate \(F = 1/5\) (say) giving \(t = 50 - 2,500\) min. From Fig.17 it can be seen that definite linearity of oxidation is established at all temperatures, after at the most 300 min of oxidation, whilst a decreasing rate does not persist for much more than 150 min, even at the lowest temperature. As mentioned in an earlier part of the discussion some of the non-linearity in the early stages of oxidation can be attributed to the
primary UA14 rather than the UA14/Al eutectic, but such an effect does not seriously alter the preceding argument.

**Activation energy**

Besides considering the variation of the type of curve with the alloy composition and temperature it is also possible to consider the variation of activation energy (obtained from the linear part of each curve) with alloy composition.

If it is assumed that all oxidation curves for alloys having 30% or more of primary UA14 eventually become linear, then the variation of this linear slope with temperature will give the activation energy.

\[ W_t = (1-f)k_2 \log t + k_1 ft. \]

Once linearity has become established the second term predominates and the first term can be neglected.

Hence \( W_t \sim k_1 ft. \)

Now the activation energy \( E \) for pure UA14 is given by:

\[ E = \log \left( \frac{W}{t} \right) RT \]

This gives the activation energy for the oxidation of pure UA14 which in fact occupies a fraction \( f \) of the total surface area of the alloy.

The weight gain of this fraction \( f \) is \( W \) and \( W \sim W_t \) as long as the contribution from the logarithmic oxidation of the eutectic can be neglected.

Hence \( E = \log \left( \frac{W_t}{ft} \right) RT \)

\[ = \log \left( \frac{W_t}{t} \right) RT - \log f RT \]

But \( \log \left( \frac{W_t}{t} \right) RT \) is the activation energy \( E^1 \), obtained by experiment from each alloy.

\[ E = E^1 - RT \log f \]

or \( E^1 = E + \alpha \log f \)  \( (\log f \leq 0 \text{ since } f \leq 1) \)

From the last equation it may be seen that a graph of \( E^1/\log f \) will
enable E to be obtained and the validity of the equation to be checked. Such a graph is shown in Fig. 29a and the data used is summarized below. The fact that the three points

<table>
<thead>
<tr>
<th>Fraction f of area as pure UA14</th>
<th>log f</th>
<th>Activation energy E₀ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>-0.48</td>
<td>12.7</td>
</tr>
<tr>
<td>0.65</td>
<td>-0.23</td>
<td>21.4</td>
</tr>
<tr>
<td>0.90</td>
<td>-0.046</td>
<td>33.4</td>
</tr>
</tbody>
</table>

in Fig. 25a accurately lie on a straight line confirms the assumptions made in deducing the relationship between E₀ and log f, and in predicting the form of the oxidation curves for 30 and 65% UA14/Al alloys.

The value of 36.5 kcal/mol for E obtained from the intersection of the graph with the y-axis in Fig. 25a represents, on the basis of the assumptions made, the activation energy of oxidation of pure UA14 in oxygen between 400 - 550°C.

Further discussion of the oxidation of UA14/Al alloys will be given in Section IX after the presentation of X-ray diffraction and electron microscopy experiments.
Fig. 29a. Graph to determine the activation energy of oxidation of pure UAl₄.

\[ f = \text{fraction by area of UAl₄ in alloy} \]

\[ E = \text{kcal/mol} \]

Activation energy, \( E \).
6. OXIDATION OF UA13 AND UA12 INTERMETALLIC COMPOUNDS

6.1 Introduction

The preparation of the intermetallic compounds UA13 and UA12 has been described in detail in Section 4. The surface preparation prior to oxidation and the experimental procedure adopted was similar to that employed for UA14/Al alloys (Section 5).

As already mentioned, only small specimens (approx. area 2-4 cm²) of each compound were available. Although each face of the specimen was planar the boundary of each face was irregular in shape so that area determination by direct measurement was impossible. The specimen area was determined by placing one face of the specimen on a sheet of squared paper and outlining its boundary with a sharp pencil. This procedure was adopted for each face in turn, and then the total surface area found by counting the number of squares within each outline.

For the compound UA13 the temperature range of investigation was the same as that for the UA14/Al alloys, i.e. 350-600°C but in the case of UA12, where oxidation was extremely rapid, investigations were restricted to the range 250-350°C. In this case temperature intervals of 25°C were employed in studying the temperature/oxidation rate relation rather than the 50°C interval used with UA13 and UA14/Al alloys.

The reproducibility of experimental results is roughly the same as for the UA14/Al experiments. Every curve presented in the results represents the average of three experiments, each of which was performed on a different specimen. For UA13 the reproducibility lay between 10-15%, and for UA12 between 10-20%, depending on the temperature.
Fig. 30. Photomicrographs of UA$_3$ and UA$_2$.

a) UA$_3$. Unetched (X250).

b) UA$_2$. 1% HF etch (X250).
6.2 Results

1. UA13

Specimens were oxidised in pure oxygen over the temperature range 350-600°C for times up to 6 h, depending on the temperature employed. The resulting weight gain/time graphs are shown in Fig.31. Every curve is predominantly linear with an early stage of decreasing rate before linearity is established. The time taken for the graphs to become linear varies with temperature, being approximately 100 min at 450-500°C but only 5-10 min at 550-600°C.

As the oxidation is mainly linear, the activation energy of the oxidation process can be obtained from a plot of \( \log \left( \frac{W}{t} \right) - \frac{1}{T} \). Such a plot is shown in Fig.32 and from its slope the activation energy for oxidation between 350-600°C was found to be 23.6 kcal/mol. From the intercept of this graph with the y-axis the constant \( A \), in the equation \( \frac{W}{t} = A \exp \left( -\frac{E}{RT} \right) \) was found to be \( 1.7 \times 10^5 \mu g \cdot cm^{-2} \cdot sec^{-1} \).

2. UA12

Specimens were oxidised in pure oxygen in the temperature range 250-350°C. As oxidation occurred very rapidly even at these low temperatures, experiments were not conducted for more than 20 min and it can be seen that the weight gain/time graphs (Fig.33) are predominantly linear. At the higher temperatures of this range, oxidation during the first 6-8 min occurred at a slowly increasing rate, after which however the curves became linear. This effect is not observable at lower temperatures where the weight gains are much less and the graphs are linear throughout.

From the linear portion of each curve a graph of \( \log \left( \frac{W}{t} \right) - \frac{1}{T} \) was plotted as in Fig.34. From its slope the activation energy of
Fig. 31. Weight gain/time graphs for UAl_3 in oxygen between 350-600°C
Fig. 32. Oxidation of UA1\textsubscript{3} in oxygen between 400-600°C

\[ W = \mu g/cm^2, \ t = \text{min} \]
oxidation was calculated to be 22.1 kcal/mol. The intercept of the graphs with the y-axis gave the value of the constant $A$ in the equation $W/t = A \exp(-E/RT)$ to be $1.0 \times 10^8 \mu g.cm^{-2} \text{sec}^{-1}$.

3. Sintering experiments

The anomalous temperature effect which was observed with UA$_{14}$/Al alloys has been described previously and vacuum sintering experiments on pre-oxidised alloys were conducted to determine whether the physical nature of the oxide influenced the kinetics of the process. With this in mind similar experiments were conducted with the compounds UA$_3$ and UA$_2$. In this instance a wider range of sintering temperatures was available as both these compounds have higher melting points than UA$_{14}$ (640°C).

The compound UA$_3$ was vacuum sintered at 600 or 700°C for 10 h after oxidation for 1 h either at 400 or 600°C. Subsequent oxidation at 400 or 600°C showed that this procedure produced no change in the oxidation rate. Similar results were obtained with UA$_2$ oxidised at 250 or 350°C, sintered at 600 or 700°C and subsequently oxidised at 250 or 350°C.

6.3 Discussion

1. UA$_3$

The majority of the results on oxidation of this compound can be represented by linear weight gain/time graphs, except for the initial period of oxidation in the case of temperatures up to 500°C. These results can be interpreted therefore in terms of the formation of a cracked or porous oxide film, possibly after an initial stage during which the scale remains coherent.

Such an explanation would be consistent with the formation of
$\text{U}_3\text{O}_8$ as the main oxidation product, as this possesses a low volume ratio on $\text{UA}_1\text{Al}_3$ (see calculation in Section 8). A low volume ratio indicates that a strained film will be formed and it is possible that such strains could lead to film cracking.

2. $\text{UA}_1\text{Al}_2$

As with $\text{UA}_1\text{Al}_3$, the major portion of each curve is linear except for the early stages of oxidation where a gradual increase in oxidation is observed. The cause of such an increase is not certain but two possible explanations are:

1. The increase in rate prior to linearity being established could be due to specimen self-heating. If this is the case then it is difficult to explain why this occurs only during the first few minutes of oxidation.

2. The non-linear stage of oxidation could represent the accelerated build up to a barrier film of constant thickness, after which oxidation obeys a linear law. Why the build up of such a barrier film should occur at an increasing rate is not clear.

As with $\text{UA}_1\text{Al}_3$ the formation of $\text{U}_3\text{O}_8$ as the main oxidation product could lead to a cracked film, and hence a linear oxidation rate.

3. Activation energy

The similarity between the activation energy for the oxidation of $\text{UA}_1\text{Al}_3$ (23.6 kcal/mol) and $\text{UA}_1\text{Al}_2$ (22.1 kcal/mol) suggests that the rate controlling mechanism is the same in each case. This is not surprising as each compound contains a large proportion of uranium and it is likely that oxidation will be the rate controlling mechanism in both cases. The only difference in behaviour is reflected in the values obtained for the constant $A$; $1.7 \times 10^5 \mu g \cdot cm^{-2} \ sec^{-1}$ in the case of
UA1₂₃ and $1.0 \times 10^8 \mu g. cm^{-2} \sec^{-1}$ in the case of UA1₂. This difference merely expresses the fact that UA1₂ oxidises much more rapidly than UA1₃, although both processes have similar activation energies.

4. Sintering experiments

The failure to find any effect caused by sintering the film was not unexpected. The oxidation curves for UA1₂₃ and UA1₂ gave no indication that any effect was heralded by a marked change in oxidation rate and in the anomalous oxidation rate observed between 550 and 600°C. The failure to find any effect indicates that the phenomena is directly or indirectly associated with the proportion of aluminium in each compound.
7. X-RAY AND ELECTRON DIFFRACTION STUDIES OF OXIDE FILMS

7.1 Introduction

This section deals with the methods employed to determine the composition of the oxidation products of UA14/Al alloys and of the compounds UA12 and UA13. In the case of UA14/Al alloys great difficulty was experienced as, even after very prolonged oxidation, very little oxide was produced on the alloy surface. The compound UA13 presented a somewhat easier case, whilst with UA12 no difficulty was experienced as the oxidation rate was rapid.

The primary tool for oxide identification was X-ray powder microscopy. This was employed in every instance and in the case of crystalline oxides provided an easy means of identification.

In the case of thin film formation where it was difficult to scrape off enough oxide for X-ray microscopy, an X-ray glancing angle technique was employed. This lacked the precision and convenience of the former method, but allowed identification of oxidation products by comparison with photographic standards of the suspected oxides.

It should be observed that when several oxides are produced, or where the powder consists of a mixture of oxides and metal from the substrate, it is possible that only the major constituents will be identified by this technique. A further limitation applies when the lines of different oxides which may be produced tend to coincide, as in this case it may be impossible to distinguish one from another, especially if only a few lines of each is present.
As the oxide on UA14/Al alloys was very thin and extremely adherent it was difficult to scrape off sufficient oxide for X-ray analysis. In such cases it is preferable to study the oxide 'in situ' by electron diffraction*. It should be emphasized that whereas X-ray diffraction owing to the great depth of penetration of X-rays usually deals with the bulk oxide, electron diffraction is confined to the surface layers of the oxide as the depth of penetration of electrons into an oxide film is very small. Ideally, any oxide film should be examined by both methods to enable the bulk and surface composition to be obtained independently.

To supplement the X-ray examination of bulk oxides attempts were also made to chemically analyse the films. These were confined to tests for the detection of the presence of Al either as elemental aluminium or as an aluminium oxide (probably Al₂O₃).

7.3 X-ray powder photography

Experimental procedure

The oxide to be examined was obtained by scraping the film from the metal substrate with a sharp razor blade. If sufficient powder were available it was ground up with an agate pestle and mortar.

The specimen of the oxide was attached to a fine glass fibre with Durofix and then mounted in an X-ray camera. In early experiments a 9cm Hilger camera was used; whilst this proved very satisfactory it was considered unnecessarily refined for non-quantitative work so that in subsequent experiments a 9cm Unicam camera was used. This had a less accurate collimation system but allowed a much more intense beam

* The work on electron diffraction was limited owing to lack of facilities.
to be employed with a consequent increase in line intensity and decrease in exposure time.

The position of the fibre was adjusted by means of centring screws so that on rotation of the fibre in the camera little lateral displacement about the axis of rotation could be detected. The camera was then loaded with X-ray film and a diffraction pattern obtained using a Cu target and Ni filter. The tube was operated at 15 mA, 40 kV and the camera was positioned so that the shadow of the rotating glass fibre was visible on the fluorescent window. The exposure time varied according to the sample used but was usually between 2-4 h.

Interpretation of photographs

Two methods are available:

1) If it is suspected that the sample examined contains certain substances, standard photographs can be prepared of these and then directly compared with the original specimen photograph.

2) The 'd' value of each line on the photograph can be measured, either directly on a 'd' scale or calculated from measurements taken on the film with a film measurer. Such 'd' values, together with estimated intensities can be tabulated and identified by means of the A.S.T.M. index.

It was considered for the present purposes that the first method was preferable as substrate lines were invariably present in the oxide and, in addition, the possibility that more than one oxide was present could not be precluded. This resulted in a complex line system on the photograph in which most of the lines were those of the substrate. Identification by procedure (2) would have proved time consuming and difficult.
As all the compounds or alloys contained only the elements uranium or aluminium (combined or free) the only oxidation products possible were uranium or aluminium oxides, or the free elements produced by the selective oxidation of one of the constituent elements of an aluminium/uranium compound. No system of double oxides is likely as it is known that the UO₂/Al₂O₃ oxide system does not form a single phase until above 2000°C⁹¹ and a similar situation probably exists in the U₃O₈/Al₂O₃ system.

The uranium oxides to be expected are UO₂ and U₃O₈ but where oxidation occurs for an appreciable period in oxygen the product of oxidation of uranium and its alloys is always U₃O₈⁵₀⁻⁵₂. The only aluminium oxide which forms in high-temperature oxidation studies is Al₂O₃²⁹⁻³³; it is initially formed in the amorphous state and crystallization to Y-Al₂O₃ occurs during oxidation.

Oxide standards of Al₂O₃, UO₂ and U₃O₈ were produced chemically, as well as standards of the compounds UA₁₂ and UA₁₃, the alloy UA₁₄/Al¹ and the elements uranium and aluminium. All the photographic standards were taken using a Unicam camera which was subsequently used for the diffraction photographs of the unknown oxide films.

7.3 Experimental results

1. UA₁₄/Al¹ system

As most interest lay in identifying the products of oxidation of UA₁₄, experiments were mainly conducted with the 90% UA₁₄/Al¹ alloys which also gave the maximum amount of oxide for powder diffraction studies.

The main object of this investigation was to establish if the anomalous temperature effect (see Section 4) was due to chemical differences in the oxide film. Experiments were performed, therefore, mainly on oxides produced at 500 or 600°C after oxidation of the 90% UA₁₄/Al¹ alloy.
for 5, 50, 200 and 400 h.

500°C. For times up to 200 hours the only lines recorded were those of the substrate alloy UA14/Al. As the time of oxidation increased within this range, the oxide thickened and the lines of the alloy became more obscure with their weaker members totally disappearing. This may be seen by comparing Fig.35a (pure UA14/Al alloy) with Fig.35c (UA14/Al alloys oxidised for 50 h at 500°C). After 400 h of oxidation the lines of the alloy were eliminated and several other faint lines appeared (see Fig.35d). These were identified as most probably belonging to U₃O₈ (Fig.35b) although it was not possible to be definite owing to the low intensity and lack of numbers of the lines.

600°C. In the case of oxidation at 600°C only the UA14/Al lines were observed and there was no evidence of U₃O₈ even after 400 h oxidation. As the time of oxidation was increased within this time the intensity of the weaker lines of the alloy became less and were in certain cases completely obscured.

65% UA14/Al

The behaviour of the 65% UA14/Al alloy differed only slightly from that of the 90% alloy at 500°C. Up to 50 h only UA14/Al lines were observed but after 200 h these lines were generally obscured save for the presence of a few lines which were identified as belonging to elemental aluminium. At 600°C the only lines observable belonged to the substrate alloy, although the line intensity was reduced compared to the unoxidised alloy.

Glancing angle experiments

Experiments were also conducted using a glancing angle technique for examination of the oxide films in situ. A 5.7 cm diameter oscill-
Fig. 35. X-ray powder Photographs.

a) Unoxidised UAl$_4$/Al alloy.

b) U$_3$O$_8$.

c) 90% UAl$_4$/Al alloy oxidised for 50h at 500°C.

d) 90% UAl$_4$/Al alloy oxidised for 400h at 500°C.
ation camera was used, which gave a fine X-ray beam and also enabled the glancing angle to be set with accuracy. An oxidised specimen was set in the camera at 15-20°C to the collimated beam and the specimen was exposed to the beam for up to 6 h.

In the case of thick oxide films (i.e. films produced by oxidation up to 550°C for 100 h or more) U₃O₈ was observed to be present together with the substrate lines. Thin films produced by short times of oxidation at temperatures up to 550°C or for long times at 600°C did not give any lines other than those of the UA₁₃/Al substrate.

UA₁₃. Oxidation products were obtained over the temperature range 400 - 600°C for times between 3 - 100 h. It was found that scraping of the oxide from the substrate compound resulted in the appearance of substrate lines on an X-ray photograph. As it appeared that this could not be avoided most of the investigations were conducted using powdered UA₁₃. The sample of powder was oxidised under the required conditions and then mounted on a glass fibre for X-ray examination. In this way an experiment could be conducted under specified conditions using a very small amount of powdered sample.

It was generally observed that under all conditions of oxidation the only product was U₃O₈ and that this very quickly obscured any lines from the UA₁₃ substrate. Fig. 36a shows the lines of the compound UA₁₃ whilst Fig. 36b shows a powdered sample which has been oxidised for 5 h at 400°C and in which the UA₁₃ lines predominate, but in which are also present a few lines of U₃O₈. After oxidation for 7 h at 500°C (Fig. 36c) U₃O₈ lines predominate and UA₁₃ lines appear only faintly. Prolonged oxidation results in only U₃O₈ being detected, as in Fig. 36d where a powdered UA₁₃ sample had been oxidised for 100 h at 600°C. No lines
Fig. 36. X-ray powder Photographs.

a) Unoxidised \( \text{UAl}_3 \).

b) Powdered \( \text{UAl}_3 \) oxidised for 5h at 400°C.

c) Powdered \( \text{UAl}_3 \) oxidised for 7h at 500°C.

\( \text{UAl}_3 \) oxidised for 100h at 600°C.
corresponding to free aluminium were detected even after prolonged oxidation at 600°C.

UA12. Experiments were conducted over the temperature range 300 - 600°C for varying times. Except for short oxidation times (less than 30 min) at low temperatures, the substrate lines were always obscured and the only product observed was \( \text{U}_3\text{O}_8 \). Figs. 37a and 37b show photographs of oxidation products produced by 1 h oxidation at 400 and 600°C respectively. Oxidation at 600°C for 100 h failed to produce any pattern other than that of \( \text{U}_3\text{O}_8 \).

3. Electron diffraction

As access to an electron diffraction unit was limited only two sets of photographs were taken using such an apparatus. The first set corresponded to oxidation of 65% UA14/Al' alloy at 500°C for 1 h, whilst the other corresponded to oxidation at 600°C for 1 h. These two temperatures were chosen because of the anomalous temperature effect.

Experimental procedure

Two identical specimens of a 65% UA14/Al' alloy were used. They were abraded down to '600 grit' silicon carbide paper and then polished with 6, 1 and \( \frac{1}{4} \) \( \mu \) diamond paste on a polishing wheel. As great care had to be taken in seeing that no diamond particles became embedded in the alloy surface during polishing a very wet polishing wheel was used with \( n \)-Propanol as a lubricant as this had a higher boiling point than paraffin and was less likely to evaporate away during polishing.

After surface preparation one specimen was oxidised in pure oxygen for 1 h at 500°C and the other at 600°C. The surface oxide films were examined using an electron diffraction unit of the Metallurgy Division.
Fig. 37. X-ray powder Photographs.

a) Unoxidised UAl₂.

b) Powdered UAl₂ oxidised for 1h at 400°C.

c) Powdered UAl₂ oxidised for 1h at 600°C.
of the U.K.A.E.A. Harwell. A reflection method was used in which the electron beam grazes the flat oxide surface at a small angle (≈1°). The operating conditions used are given below:

- Camera length \( L = 304 \text{ mm} \)
- Accelerating voltage \( = 80 \text{ kV} \)

If \( D \) = the pattern diameter on the photographic plate and \( d \) = lattice parameter of examined substance, then \( d = \frac{2A\lambda}{D} \) where \( \lambda \) is the wavelength of the electron beam.

### Results

As the specimens were heterogeneous six different areas on each oxide surface were examined. Only a few photographs gave results which could be identified as being produced by an oxide surface, the remainder gave pictures difficult to interpret and which probably arose from stray reflections from the uneven oxide surface.

Two such photographs are shown in Figs. 38a and 38b, the former from the 500°C film and the latter from the 600°C film. No difference could be detected in the two sets of photographs. The spacing of the spots on the pictures is not sufficiently great to enable measurements to be made and lattice parameters to be deduced accurately. Thus it is impossible to say whether the pattern arises from \( \text{Al}_2\text{O}_3 \) or from a form of \( \text{U}_3\text{O}_8 \) as the data fits either of these reasonably well.

#### 4. Chemical analysis

As so little data concerning the composition of the oxide films on the compounds (especially the UA\(_{14}/\text{Al}^1\) alloys) could be obtained by the aforementioned methods, it was hoped that it would be possible to chemically analyse (qualitatively at least) some of the oxide films.

In the case of UA\(_{14}/\text{Al}^1\) alloys, the oxide is so firmly adherent and
Fig. 38. Electron Diffraction Photographs.

a) 65% UA14/Al alloy oxidised for 3h at 500°C.

b) 65% UA14/Al alloy oxidised for 3h at 600°C.
present in such small quantities that it was difficult to secure sufficient material. For chemical analysis it was not practicable to scrape off the oxide owing to the possibility of removing some of the substrate.

The only way of avoiding this difficulty is by the technique of film stripping, which in some cases allows complete separation of an oxide film from its substrate. The technique is to dissolve away the layer of metal or alloy immediately next to the oxide film in a suitable solution and so 'float' off the film.

**Film stripping attempts on UAl_{x}/Al alloys**

The alcoholic iodine stripping method of Vernon, Wormwell and Nurse is well known and has been used to strip films from various types of steels. Following the procedure of these authors a solution of dried Analar iodine was prepared in water-free methyl alcohol. The solution was kept in a dry box under an atmosphere of dried argon at a positive pressure with respect to the atmosphere. The specimen with attached oxide film was placed in the solution and left for times between 2-20 h. In the procedure of Vernon, Wormwell and Nurse the specimens were attacked for 30 - 90 min in alcoholic iodine, washed with alcohol and then the oxide film detached by shaking the specimen in a dish of dry alcohol.

In the present study of U/Al alloys this procedure was not found to be effective. Although dissolution of the alloy occurred the oxide appeared to be so adherent that separation of the oxide film was impossible. No evidence could be seen of even a disintegrated film, although such a film might well have been lost amongst the dissolution products of the alloy.

A method which is sometimes used for stripping oxide films from
aluminium substrates for examination by electron microscopy is that of substrate dissolution with mercury salts or caustic soda. Both of these techniques resulted in the dissolution of the substrate without oxide film removal.

UA12 and UA13 oxides

Film stripping techniques proved to be unsuccessful in these cases as well. In the case of UA12, however, where oxidation was rapid, it was possible to scrape the comparatively thick oxide film from the substrate very easily although, as before, it was impossible to be certain that no substrate had been removed.

The oxide from UA12 was tested for the presence of the Al by dissolving in concentrated NaOH and then testing the solution for the presence of the Al. The test reagent used was Alizarin (Sensitivity 0.15 μg Al; concentration limit = 1 in 333,000) and the procedure employed was that recommended by Vogel. The test indicated the presence of aluminium in all cases.

A similar procedure was adopted with finely powdered specimens of UA13 and UA12 which had been completely oxidised by treatment in oxygen at 600°C for 100 h. (X-ray analysis of these oxides showed only the presence of U3O8). Again the presence of aluminium was detected.

Due to the uncertainty of the origin of the aluminium detected no attempt was made to perform any quantitative analysis.

7.4 Discussion

1. General considerations

The number of substances which may be present in the oxide film on UA14/Al alloys or the compounds UA13 or UA12 is limited. If the formation of a double oxide is discounted then the possibilities are:
Although other uranium oxides do exist, $\text{U}_2\text{O}_3$, $\text{UO}_2$, $\text{U}_3\text{O}_8$ and Al. Although other uranium oxides do exist, $\text{UO}_2$ or $\text{U}_3\text{O}_8$ is invariably produced during high-temperature gaseous oxidation of pure or alloyed uranium. Since all the cases of oxidation occurred in an unlimited supply of oxygen the most likely uranium oxide to be expected would be $\text{U}_3\text{O}_8$. This has always been observed to be the product of oxidation of pure or alloyed uranium in air or oxygen$^{50-52}$, whereas the formation of $\text{UO}_2$ is usually confined to oxidation in carbon dioxide $^{53-55}$. As may be seen from Table 2, $\text{U}_3\text{O}_8$ has an extremely high heat of formation and is formed extremely rapidly during the oxidation of uranium in oxygen.

Oxidation of uranium in any of the compounds automatically frees the aluminium ions. The free aluminium may then be oxidised to $\text{Al}_2\text{O}_3$ or may remain uncombined, in the latter case three possibilities exist:

1) aluminium ions may pass into the $\text{U}_3\text{O}_8$,
2) " " may become accommodated in the $\text{UA}_x$ lattice giving rise to a non-stoichiometric form of the compound,
3) aluminium ions may form a metallic layer at the $\text{U}_3\text{O}_8$/UA$_x$ interface.

If the first or third possibility occurs then it should be possible to detect the presence of uncombined aluminium in the oxide layer. The results obtained will be discussed in the light of the above considerations.

$\text{UA}_x$/Al alloys

Very little evidence can be supplied as to the nature of the oxide film on these alloys. From the evidence available it would appear that after long periods of oxidation at 500°C $\text{U}_3\text{O}_8$ can be detected by X-ray powder diffraction or glancing angle techniques, whereas oxidation at
600°C produces a film so thin that oxide lines were not detectable. Although investigation of the early stages of oxidation at 500 and 600°C by electron diffraction did not permit identification of the product it did show that the oxide was crystalline and that there was no significant difference between the products of oxidation obtained at 500 and 600°C.

The fact that UA1₄/Al' lines are present in nearly all the oxide photographs can be explained in two ways:

1) In removing the firmly adherent oxide from its substrate by scraping it is inevitable that some of the substrate is also removed.

2) The oxide will penetrate more deeply into the massive crystals of UA1₄ than into the UA1₄/Al' eutectic and hence the oxide/metal interface will not be planar. In removing the oxide it is possible that some of the eutectic could become trapped in the oxide and removed with the UA1₃O₈.

All that can be said with certainty is that until the oxide becomes quite thick, UA1₄/Al' lines predominate. Oxidation at 600°C for 400 h produced a very thin film in which only UA1₄/Al' lines were observable. It follows therefore that film thickness is the factor which determines that the pattern revealed by X-ray diffraction and with very thin films the line intensity of UA1₃O₈ is very weak and the presence of only a small amount of UA1₄/Al' is needed to swamp any other lines which may exist.

The absence of UA1₃O₈ lines until the later stages of oxidation can be argued from another viewpoint and, for example, it could be assumed that the oxide formed initially is amorphous. The appearance of the UA1₃O₈ lines may then correspond to crystallization of the UA1₃O₈.
The formation of $U_3O_8$ in an amorphous form followed by slow crystallization is contrary to most of the evidence available from oxidation studies of uranium and its alloys. However, Barnartt et al.\textsuperscript{59} found that the oxide produced from the oxidation of a 50 wt % U-Zr alloy for times up to 400 h in the temperature range 300-500°C produced X-ray diffraction lines too diffuse to be identified, although chemical analysis indicated the presence of $U_3O_8$. As electron diffraction experiments indicate that the oxide surface is composed of a crystalline oxide the above explanation seems unlikely unless only the surface oxide layers are crystalline.

The presence of aluminium lines in the oxide produced on 65% UAl\textsubscript{4}/Al\textsubscript{1} alloys after prolonged oxidation at 500°C is significant. These lines could have originated either from free aluminium in the UAl\textsubscript{4}/Al\textsubscript{1} eutectic or from the reaction

$$3\text{ UAl}_4 + 4\text{ O}_2 = U_3\text{O}_8 + 12\text{ Al}$$

It is unlikely that aluminium was removed from the substrate during removal of the oxide as if this were the case UAl\textsubscript{4} lines would have appeared with those of the aluminium. The fact that aluminium was only observed in the 65% UAl\textsubscript{4}/Al\textsubscript{1} and not in the alloys containing higher proportions of UAl\textsubscript{4} indicates that it probably originated from the free aluminium in the eutectic as a 65% UAl\textsubscript{4}/Al\textsubscript{1} alloy contains roughly $4\frac{1}{2}$ times as much free aluminium as a 90% UAl\textsubscript{4}/Al\textsubscript{1} alloy. With the 90% UAl\textsubscript{4}/Al\textsubscript{1} alloy, free aluminium and UAl\textsubscript{4} are both evident. As the oxide thickens the UAl\textsubscript{4} lines disappear and there is probably insufficient aluminium present to be detected so that only $U_3O_8$ is observed.

It would appear that aluminium can exist in the oxide in the elementary form and that very little Al\textsubscript{2}O\textsubscript{3} is formed. It is suggested therefore...
that the above equation probably represents the mode of oxidation of $\text{UA}_4$ in a $\text{UA}_4/\text{Al}$ alloy.

$\text{UA}_{3}$ and $\text{UA}_{2}$

The mechanism suggested above for $\text{UA}_4$ will, if valid, occur all the more readily in the case of the other two compounds which contain correspondingly greater proportions of uranium than $\text{UA}_4$.

X-ray diffraction studies indicate that at all temperatures $\text{U}_3\text{O}_8$ is the major product of oxidation for both compounds. The presence of free aluminium could not be detected by X-ray analysis although the amount expected to be formed from the reaction is 21.5 wt % in the case of $\text{UA}_3$ and 15.5 wt % in the case of $\text{UA}_2$ compared with 28 wt % for $\text{UA}_4$. However, chemical analysis indicated that aluminium was present in the oxide although it was not possible to differentiate between Al and $\text{Al}_2\text{O}_3$. No mechanism can be postulated at present as to how the aluminium arrived in the film.

To summarize the results obtained and the deductions made appear to support the view that the reaction:

$$3 \text{UA}_x + 4\text{O}_2 = \text{U}_3\text{O}_8 + 3x\cdot\text{Al}$$

(where $x = 2$, 3 or 4)

is the most likely one to occur during the oxidation of U/Al intermetallic compounds.
8. ELECTRON MICROSCOPE EXAMINATION OF THE OXIDE FILMS ON U/Al COMPOUNDS AND ALLOYS

8.1 Introduction

The electron microscope was used to examine oxide films produced by the oxidation of the compounds UA12 and UA13 and of the 90% UA14/Al alloys.

Specimens were prepared by abrading them down to 600 'grit' silicon carbide paper under water, and then by polishing down to ½ µ diamond paste on a polishing wheel. The specimens were degreased in acetone and dried with a cold air blower. They were then oxidised under controlled conditions in the vacuum/purified atmosphere furnace described in Section 4.

Replica preparation

The aim of replica preparation is to produce a copy of a specimen's surface topography in a substance which is transparent to electrons. The replica produced can then be examined in the electron microscope. As many replicas give very low contrast when examined with an electron beam it is often necessary to increase this by means of "shadow casting". This consists of evaporating a thin film of electron dense material obliquely onto the specimen or replica surface.

Replicas may either be prepared by a one or two stage technique. In the single stage method a substance is deposited onto the specimen surface and then removed and examined in the electron microscope. In the two stage method a preliminary impression is taken in one material and a final impression taken from this with a different material.

Although the single stage process is generally more satisfactory such a process usually involves the destruction of the specimen or at
least its surface topography. Two stage methods overcome this difficulty and are more generally employed for the surface examination of bulk specimens.

A wide range of plastic or vacuum deposited materials can be used for the production of preliminary impressions in multi-stage replica techniques. The choice of material for the preparation of the final replica is limited to either formvar or collodion for low resolution work, or vacuum deposited carbon, silicon oxide or silica for high resolution purposes. The most commonly used shadowing materials are carbon/platinum or gold/palladium both of which may be vacuum deposited.

The formvar/carbon replica method

This was the first method used for the preparation of replicas of oxidised compound and alloy surfaces.

The procedure used was to coat the specimen with a formvar film by flooding with a 2% solution of the plastic in chloroform and then draining the excess vertically onto a filter paper. The film was thoroughly dried by placing it near a 100 watt lamp for at least 10 min. A short length of Sellotape on which moisture had been condensed by breathing heavily on it, was pressed against the plastic film. The Sellotape was then sharply pulled from the specimen and the plastic replica carried with it. The film was mounted on a glass slide and 100-200 Å of carbon deposited onto the structure surface of the film. The Sellotape, formvar and carbon deposit were cut into squares of approximately the same size as the mounting grids and immersed in a bath of petroleum ether. This dissolved the adhesive from the Sellotape and allowed the formvar with its carbon deposit to be freed. The
formvar was then dissolved away in chloroform to leave the carbon replica which was mounted on a copper support grid ready for shadowing or immediate examination.

Although this and minor variations of this method were tried repeatedly little success was obtained with replica production. Failure seemed to be due to two causes:

1) Great difficulty was experienced in stripping the formvar film from the oxide surface with Sellotape.
2) In the few cases where the formvar film was successfully removed from the oxide surface it was found that the carbon replicas produced from it tended to disintegrate in the chloroform bath.

The Bex film/carbon replica method

In view of the failure of the first method of replication a second method was tried. This method involved the softening of a sheet of 0.002 in. Bex film (cellulose triacetate) in acetone for 5-7 sec. The soft film was then quickly placed onto the specimen surface and the film allowed to dry for at least twenty minutes, during which time it hardened and conformed to the surface topography of the specimen. After drying the film was easily pulled away from the specimen and fixed to a glass slide. A carbon deposit of 100-200 Å was evaporated onto the surface of the film and the film was then cut into small squares. The film was removed by acetone leaving the carbon replica which was mounted on a copper grid so that it could be either examined directly or shadowed.

Although films could be easily stripped from the specimen by this method, great trouble was still experienced with the disintegration of the carbon replicas during immersion in acetone. This difficulty
was eventually overcome by using a modified version of the above process. After carbon deposition the film and carbon deposit was smeared with a thin layer of vaseline which was softened on the film by placing it under a 100 watt lamp for a short time. The film was then cut up into small squares which were immersed in acetone. After the Bex film had dissolved away, the carbon replicas were left with a thin vaseline film on one side. This film was removed by immersing the squares in a bath of carbon tetrachloride, and then the carbon replicas were mounted on copper grids. By adopting this modified technique it was found that very few replicas disintegrated and that a consistent standard of preparation was achieved. Experience showed that care had to be taken to ensure that the Bex film or vaseline was washed away from the replicas. A double wash system was used in which a replica was immersed in a bath of acetone or carbon tetrachloride for 10 h and then transferred to a bath of a fresh solution for a further 3 h. This method produced clean replicas with no surface contamination.

**Shadowing and carbon deposition**

Carbon deposition and shadowing was performed in a 'Speedivac' High Vacuum Coating Unit, Model 12E6.

Carbon was deposited by evaporating carbon at normal incidence onto the Bex film replica. This process was carried out under vacuum by passing a suitable current (approximately 60 A) through two 5 mm diameter pointed carbon rods, the points of which were kept lightly pressed together. On passing a current, intense local heating occurred at the points, carbon evaporated and was deposited on the specimen. The deposit could be detected by the formation of a brown film on a piece of white glazed porcelain located below the points. A drop
of Apiezon B oil was put on the porcelain to emphasize the darkening of the porcelain. Normally, a light brown deposit of about 50 Å in thickness was just detectable under these conditions and a grey-brown deposit corresponding to approximately 200 Å was obtained within a few seconds.

A normally deposited carbon replica of this thickness gives little contrast in the electron microscope. Contrast between adjacent regions of the replica may be enhanced considerably by a process known as "shadow casting" in which a suitable heavy metal is deposited obliquely on the carbon replica. This can be accomplished in a deposition unit by using carbon rods containing a granulated platinum core or by evaporating a suitably heavy metal. Only a very thin film of 15-30 Å which is deposited at an angle of approximately 45° for coarse surface structure, but as low as 10° for fine surface detail is necessary to provide good contrast.

In many cases it was found that a similar contrast could be obtained by preparing "self shadowed" carbon replicas rather than using carbon/platinum shadowing. This procedure simplified the shadowing technique and, as long as not too low an angle was used for the shadowing, little distortion of the specimen shape, due to pile up of carbon on the side facing the course, was obtained. For revealing fine surface details the former procedure was preferred to the simpler self-shadowing technique.

Electron microscope

The microscope used for the examination of replicas was the "Tronscope" Model TRS-50EL which is manufactured by the Akashi Seisakusho Co. Ltd., Tokyo, Japan. This is a general purpose instrument with a maximum
magnification of x 30,000 and an ultimate resolution of about 20 Å.

8.2. Results

Interpretation of photographs

Many of the photographs show evidence of definite cracking of the oxide. In others it would appear that in addition to cracks there are series of partially resolved dots (see Fig. 42b, 42c, 43b, 44b, 44c). It is considered that the latter are caused by the edges of small uneven cracks which when shadowed at an angle enable agglomerates of deposited material to collect in them, thus resulting in the observed effect.

UA1\textsubscript{4}/Al\textsubscript{1} alloys

Experiments were confined to 90\% UA1\textsubscript{4}/Al\textsubscript{1} alloys so as to study as far as possible the behaviour of the oxide film on pure UA1\textsubscript{4}. Temperatures of 500 and 600°C were chosen for the production of oxide films because of the 'anomalous' temperature effect observed previously. Replicas were taken from specimens oxidised for 3, 20 and 120 h respectively.

1. Oxidation at 500°C for 3 h

Except for discontinuities or scratches which were present in the original metal surface, the oxide film produced under the above conditions exhibits no discernable surface detail (see Fig. 39).

2. Oxidation at 600°C for 3 h

Under these conditions an oxide film was produced whose surface exhibits no gross surface structure. However, at a magnification of 17,000 the appearance of small randomly dispersed cracks is evident (Fig. 40).

3. Oxidation at 500°C for 20 h

The replicas now show a series of 'terraces' on the oxide surface.
Electron micrographs of the oxidised surface of 90% UAl₆/Al alloys

Fig. 39. 3h at 500°C (x13,000)

Fig. 40. 3h at 600°C (x17,000)
The terraces partially or wholly isolate areas of oxide from one another and give the appearance that some areas of oxide are growing from the substrate surface more quickly than others. Examination of the 'terraces' in detail as in Fig. 41a and 41b shows that the lines defining the terraces consist of cracks and fissures. The main cracks observed tend to spread outwards in a roughly concentric manner and define an inner area of continuous and almost planar oxide, whilst the oxide beyond the outer cracks is also fairly smooth with only minor surface uneveness.

4. Oxidation at 600°C for 20 h

Replicas of oxide films produced under these conditions show two distinct types of surface feature. The majority of the surface is composed of areas which show pronounced cracking whilst minor portions show an almost planar surface (Fig. 42a). The cracking observed seems to be of a different type from that observed earlier as the orientation of cracks with respect to each other is completely random within each area of cracking (Fig. 42b). Several cracks (usually 3) seem to propagate outwards from a selected point and this system either exists in isolation or tends to link up with other similar systems to form a network. Fig. 42c shows the border between an intensely cracked and a smooth region. As this and Fig. 42a show the major cracks or fissures in the system appear to be those demarking the cracked and smooth oxide areas.

5. Oxidation at 500°C for 120 h

Replicas show an intense system of cracking of the oxide surface. Fig. 43a shows that the 'terrace' effect observed earlier now almost completely occupies the whole oxide surface and that a series of concentric cracks can be observed to be growing outwards from various centres in the
Electron micrographs of the oxidised surface of 90% UAl$_{2}$/Al alloys

Fig. 41a. 20h at 500°C. (x5,000)

Fig. 41b. 20h at 500°C. (x15,000)
Electron micrographs of the oxidised surface of 90% UA1/Al alloys

Fig. 42a. 20h at 600°C. (x2,700)

Fig. 42b. 20h at 600°C. (x6,400)
Electron micrographs of the oxidised surface of 90% UA1/Al alloys

Fig. 42c. 20h at 600°C. (x17,000)

Fig. 43a. 120h at 500°C. (x3,000)
film. The areas of almost smooth oxido are now very much less obvious and tend to be 'squeezed' in between the concentric crack systems. Fig.43b shows the centre of one of these systems and clearly illustrates the concentric nature of the major cracks, with the occurrence of a few 'cross' cracks linking the various peripheral cracks. Fig.43c shows part of the crack system in detail and emphasises the smooth nature of the surface between the crack network.

6. Oxidation at 600°C for 120 h

As in the case of 20 h oxidation two types of surface structure are visible on the replicas. A random cracking occupies the major areas of the surface and these areas are delineated from smaller smooth areas by major fissures (Fig.44a). Fig.44b shows an area composed entirely of this random cracking whilst Fig.44c shows the dividing fissure between a cracked and uncracked area of oxide.

Up to at least 30 h of oxidation replicas from the oxide surface show very little surface detail. After 80 min the oxide surface is slightly roughened (Fig.45a), but this roughness appears to decrease with increasing oxidation time, and after 9 h (Fig.45b) is not very pronounced. Prolonged oxidation (108 h) is necessary before any cracks appear (Fig.45c) and in this case the surface between the cracks appears to be smooth.

The oxide surface exhibits very similar features during all periods of oxidation between 5 min - 45 h. The majority of the oxide surface is quite smooth but in certain selected areas small disruptions of the surface occur (Fig.46a). These disruptions are shown in greater detail.
Electron micrographs of the oxidised surface of 90\% UA1\textsubscript{4}/Al alloys

Fig. 43b. 120h at 500°C. (x8,000)

Fig. 43c. 120h at 500°C. (x37,000)
Electron micrographs of the oxidised surface of 90% UAl₁₁/Al alloys

Fig. 44a. 120h at 600°C. (x2,600)

Fig. 44c. 120h at 600°C. (x18,000)
Electron micrographs of the oxidised surface of 90% Al₄/Al alloys.

Fig. 44b. 120h at 600°C (x8,000).
Electron micrographs of the oxidised surface of UA13

Fig. 45a. 80 min at 500°C. (x13,000)

Fig. 45b. 9h at 500°C. (x19,000)
Electron micrographs of the oxidised surfaces of UA$_1\!$ and UA$_2\!$. 

**Fig. 45c.** UA$_1\!$. 108h at 500°C. (x16,000)

**Fig. 46a.** UA$_2\!$. 3h at 350°C. (x6,000)
in Fig. 46b and 46c. They are always roughly circular in shape with an outer protruding lip and an inner area of slightly roughened oxide.

8.3 Discussion

Oxidation of UAl₄/Al alloys: 500°C

As the time of oxidation progresses and the oxide thickens the formation of cracks in the oxide commences to become obvious. Initially, these cracks appear to define the periphery of various areas (Fig. 41a) but in time fill the entire specimen surface (Fig. 43a). The surface then has the appearance of a system of concentric but independent crack systems which originate and propagate from randomly scattered centres on the oxide surface.

It is suggested that the origin of such systems may be explained in the following way:— Kinetic experiments (Section 5) have already clearly shown that at temperatures up to 550°C the UAl₄/Al eutectic oxidises much more slowly than primary crystals of UAl₄ in a UAl₄/Al eutectic. A 90% UAl₄/Al alloy surface will consist of large areas of UAl₄ and small areas of eutectic, and such an alloy when oxidised will have most of its weight gain attributed to the oxidation of primary UAl₄. If, as is most likely, the oxide formed on primary UAl₄ is U₃O₈ (see Section 7) having a volume ratio on a UAl₄ surface of 0.59 (see Section 8), then such an oxide will be formed under great tension, and as well as being porous is likely to crack. As each oxidised area of UAl₄ is surrounded by areas of UAl₄/Al eutectic possessing a much thinner oxide film (for example, at 500°C the ratio of film thicknesses is roughly 8:1), it will be possible for stresses to be relieved by the oxide cracking and bursting outwards. As the oxide appears to be firmly keyed to the substrate the release of tensile forces will cause...
Electron micrographs of the oxidised surface of UA1$_2$

Fig. 46b. 5 min at 350°C. (x24,000)

Fig. 46c. 45h at 350°C. (x42,000)
cracking and will result in sections of oxide splaying outwards.
The outer oxide blocks of each area will be able to tilt forwards
the most whilst those nearer the system centre will be less disturbed.
Thus, originating from the centre of each oxidised UA14 surface there will
be a radial system of stress relaxation. This system will manifest
itself by the appearance of a system of cracks perpendicular to the stress
direction which will spread radially outwards.

Oxidation of UA14/Al alloys: 600°C

Kinetic experiments (Section 5) indicate that at 600°C oxidation
of both primary crystals of UA14 and the UA14/Al eutectic occurs extremely
slowly. Thus, there will be comparatively little difference in the
oxide thickness of eutectic and primary UA14 areas. The cracking which
occurs over the majority of the surface (assumed to correspond to areas
of primary UA14) does not show the concentricity of crack propagation
observed at 500°C (compare Fig. 44a and 43a), but is entirely random
in nature. It is suggested that the change in type of cracking between
500 and 600°C is due to the change in the relative levels of oxide on
the eutectic and primary UA14 phases. At 600°C the mode of crack
propagation must be different from that suggested for 500°C as the oxide
stress cannot decrease in a radial manner so readily since there will
be little difference in oxide levels on different phases. Cracking
could, in this case, occur due to the presence of random local weaknesses
in the film. Each weakness could act as a crack source and thus a
system of entirely random cracking would occur.

If the above explanations are true it is still rather difficult
to account for the presence of uncracked areas of oxide at 600°C but
not at 500°C after prolonged oxidation. These areas form a minor part
of the surface area of a specimen and presumably correspond to areas of UA₄/Alₑutectic. Possibly as stresses in the oxide on primary UA₄ are much higher at 500 than 600°C, such stresses are more readily communicated in the former case to adjacent areas of lowly stressed oxide on the UA₄/Alₑutectic. Thus oxidation at 500°C produces a thicker and more highly stressed oxide than at 600°C with the result that complete stress distribution, and hence cracking, is more readily achieved at 500 than at 600°C.

Although cracking occurs at both temperatures investigated it is difficult to understand how it influences oxidation kinetics. At 500°C a linear rate of oxidation is observed, except for an early period of non-linearity (see Section 5) which lasts for only a short time. As cracks are not clearly observed until after 20 h of oxidation it is clear that linearity of oxidation and the specimen's appearance cannot be directly related. At 600°C cracks again appear, but as virtually no oxidation occurs after a few hours at 600°C these cracks cannot penetrate deeply or a linear rate of oxidation would be observed.

In both cases it would appear that the different types of cracking observed are only secondary effects and cannot be used as a direct explanation of the observed kinetic behaviour. Similarly the 'anomalous' temperature effect cannot be explained in terms of different oxide surface structures at 500 and 600°C as these only begin to be evident after several hours of oxidation, whereas kinetic experiments show an almost instantaneous change of behaviour with temperature. It may be possible that the surface changes observed are slowly produced secondary effects of an unknown but rapidly operating mechanism which operates within the oxide film.
Little surface details is observable on the oxide films until cracking begins to be evident after prolonged oxidation (Fig. 45c).

Prior to the onset of cracking a certain surface roughness is discernable, especially after short times of oxidation (Fig. 45a). The apparent decrease in surface roughness as oxidation proceeds cannot be readily explained.

The cracking of the oxide film (U₃0₈) after prolonged oxidation is presumed to be due to the formation of a highly stressed (tensile) oxide film. Cracking in such a film occurs when a critical thickness is reached and the film is no longer able to bear the stresses produced by the formation of an oxide with a very low volume ratio. The film thickness at which cracking occurs for the oxide on UA1₃ is much greater than for the 90% UA1₄/Al alloy under comparable conditions. This is probably because in the former case an even homogeneous oxide layer is produced, whilst in the latter the difference in oxide levels between phases will encourage cracking.

Kinetic experiments show that linear oxidation predominates at all temperatures. It might therefore be expected that a cracked or porous oxide is being formed. Electron micrographs show that the oxide might well be porous in the early stages of oxidation (Fig. 45a) but that the oxide surface appears perfectly smooth and non-porous after prolonged oxidation (Fig. 45c), although by this time surface cracks begin to appear. Possibly the oxide film always possesses extremely small micro-pores and observations with the electron microscope revealed a genuine surface roughness rather than a cross section of a pore system.
The disruptions which appear over various areas of the surface are thought to be due to impurities gathered along the grain boundaries, as they appear to have the same form and density of distribution over the compound surface as the impurities (see Fig. 30a). It is suggested that the impurities oxidise more rapidly than the surrounding UA12 and consequently the oxide film on them tend to push away the surrounding oxide film on the UA12. This disrupted oxide forms a lip around the perimeter of the oxide on the impurity and gives rise to the type of feature observed in Fig. 46c.

The oxide produced on the pure UA12 surface is featureless at all stages of oxidation. Thus, unless very small micro-pores exist, the linearity of oxidation rate observed in kinetic experiments (Section 6) cannot be due to the formation of a porous or cracked film.
9. GENERAL DISCUSSIONS

9.1 Introduction

The aim of the following discussion is to explain as fully as the experimental evidence allows:

1. The oxidation of UA14/Al alloys and compounds UA12 and UA13 considered as separate entities.
2. The oxidation characteristics of the class of compounds UA1x where x = 2, 3 or 4.

9.2 General thermodynamic considerations

These considerations are intended to predict on a thermodynamic basis, the possible products of oxidation of the U/Al compounds. Such considerations are limited by the fact that any calculation based solely on thermodynamic reasoning is not capable of describing the kinetics of a process, but only the initial and final states of the reactants and products and their associated thermodynamic properties. Knowledge of the heats of formation of the intermetallic compounds and the free energies of the oxides produced allows certain calculations to be made regarding ionic activities.

Ionic activities

A comparison of the activities of uranium and aluminium ions in UA14, UA13 and UA12 with the activities of similar ions in UO2, U3O8 or Al2O3 enables an estimate to be made of the oxides which can be formed on any compound. The possible oxides that can be produced are UO2, U3O8 and Al2O3.

Figures 47b, c and d show the integral free energy diagrams of the U/Al, U/O and Al/O systems. Such diagrams are constructed by plotting the heat of formation per gram atom of a particular binary compound.
Fig. 47. Integral Free Energy diagrams.

a) System A/B.

b) System U/Al.

c) System U/O.

d) System Al/O.
against the atomic percentage of one component (A or B) of the compound. Neglecting the entropy change in compound formation which should be small, the second term on the L.H.S of the equation:

$$\Delta G = \Delta H - T \Delta S$$

may be neglected (the symbols have their usual significance).

Hence $\Delta G \sim \Delta H$

Dividing both sides by $n$, the number of atoms per molecule of the compound referred to, the relation:

$$\frac{\Delta G}{n} = \frac{\Delta H}{n}$$

is obtained where $\Delta H/n = \text{heat of formation per g. atom}$ and $\Delta G/n = \text{free energy of formation per g. atom}$.

Since $\Delta H \sim \Delta G$, the tangent to any point on the diagram cuts the $\Delta H/n$ ordinates at the partial free energies of A and B. In Fig. 47a, $N_B$ is the mole fraction of B so that A is 100% A and B is 100% B. Thus in Fig. 47a, an imaginary system containing two inter-metallic compounds:

$$\Delta H_1/n = \text{heat of formation of } AB \text{ per g. atom}$$

$$\Delta H_2/n = \text{heat of formation of } AB_3 \text{ per g. atom}$$

$\Delta G_1$ is the free energy of reaction of $1B + \infty (x AB + y AB_3)$

$\Delta G_2$ is the free energy of reaction of $1A + \infty (x AB + y AB_3)$

The $\infty$ sign denotes an infinite amount of a particular system, such that the addition of a further atom of A or B does not change the overall composition. Using $\Delta G = RT \ln a$ enables the activity, $a$, to be calculated.

Substituting the values of $\Delta G_1$ and $\Delta G_2$ in the above equation yields:

$$a_1 = \text{activity of } B \text{ in } \infty (x AB + y AB_3)$$

$$a_2 = \text{activity of } A \text{ in } \infty (x AB + y AB_3)$$

The values of $\Delta H$ used in constructing Figs. 47b, c and d are taken
from the references listed below:

UO$_2$, U$_3$O$_8$ and Al$_2$O$_3$ - reference 116
UA1$_2$, UA1$_3$ and UA1$_4$ - reference 83

By extrapolation of these graphs to the appropriate ordinates, a table of uranium and aluminium activities may be drawn up for various systems at selected temperatures. In this case 500°C is taken as a reference temperature.

Table 6. Activities of uranium and aluminium at 500°C

<table>
<thead>
<tr>
<th>System</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al in $\infty$ (x UA$_13$ + y UA$_14$)</td>
<td>$5.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>Al in $\infty$ (x UA$_12$ + y UA$_13$)</td>
<td>$2.7 \times 10^{-1}$</td>
</tr>
<tr>
<td>Al in $\infty$ (x U + y UA$_12$)</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>U in $\infty$ (x UA$_13$ + y UA$_14$)</td>
<td>$1.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>U in $\infty$ (x UA$_12$ + y UA$_13$)</td>
<td>$3.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>U in $\infty$ (x Al + UA$_14$)</td>
<td>$4.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>(\frac{4}{3}O_2) in $\infty$ (x U$<em>{3O_8}$ + y U$</em>{3O_0}$)</td>
<td>$\sim 10^{-37}$</td>
</tr>
<tr>
<td>(\frac{4}{3}O_2) in $\infty$ (x U$<em>{3O_8}$ + y U$</em>{3O_0}$)</td>
<td>$\sim 10^{-10}$</td>
</tr>
<tr>
<td>(\frac{4}{3}O_2) in $\infty$ (x U$_{3O_8}$ + y UO$_3$)</td>
<td>$\sim 10^{-7}$</td>
</tr>
<tr>
<td>(\frac{4}{3}O_2) in $\infty$ (x Al$_2$O$_3$ + y (\frac{4}{3}O_2))</td>
<td>$\sim 10^{-40}$</td>
</tr>
<tr>
<td>Al in $\infty$ (x Al$_2$O$_3$ + y (\frac{4}{3}O_2))</td>
<td>$\sim 10^{-50}$</td>
</tr>
</tbody>
</table>
From Table 6 it may be seen that the activities of the uranium and aluminium when in compound form are much greater than the corresponding activities when in oxide form. It should be observed that as activities are greater at the metal side of the oxide/metal interface than at the oxide side of the same interface the activities at the actual interface at any instant of time will be greater than the minimum required for the production of any of the oxides.

As would be expected the aluminium activity is greatest at the aluminium end of the U/Al system, but varies surprisingly little over the entire system. A greater variation is shown by the uranium whose activity varies by a factor of $10^{-7}$ between opposite ends of the system. All uranium, aluminium and oxygen activities are very low in their appropriate oxide systems.

The above analysis is not very useful as it shows that thermodynamically all oxides are capable of being formed. Whether or not this will occur depends on the kinetics of the oxidation process and on the physical properties of the oxidation products.

9.3 UAl₄/Al' alloys

It was proposed in Section 5 that the oxidation of the various UAl₄/Al' alloys could be considered as being the sum of the individual oxidation characteristics of the primary crystals of UAl₄ and of the UAl₄/Al eutectic.

Eutectic

Very little is known about the oxidation of the UAl₄/Al eutectic. Its highly protective mode of oxidation can probably be attributed to the high percentage of aluminium it contains (87 wt.%) but no indication can be given as to the chemical nature of the oxide formed.
micrographs indicate that the oxide surface is uncracked and apparently non-porous.

**UA1₄: General**

The oxidation of UA1₄ has been studied by using alloys containing large amounts of UA1₄ (98 wt.%) and also by extrapolating the results obtained with alloys containing varying amounts of UA1₄ to a composition of 100% UA1₄ (see Section 5).

From these results and deductions it appears that the compound oxidises linearly over the temperature range 400 - 550°C, with the exception of the early stages of oxidation where a partially protective film is formed. However, the protection conferred by this initial film is small and, depending on the temperature, is soon replaced by a linear rate of oxidation. The special case of oxidation at 600°C will be discussed subsequently.

The products of oxidation can only be identified with any certainty after prolonged oxidation, but it is inferred that the main product of oxidation at all stages is U₃O₈ (Section 7), and that aluminium released from the compound by preferential oxidation of uranium is left in a virtually unoxidised state. This would be in agreement with the work of Albrecht and Koehl on the oxidation of the intermetallic compounds of uranium with Be, B, Si and C and Al (only UA1₂ was studied). It was found that except for UC₂, where UC and CO/CO₂ were produced, the only oxide produced by oxidation was UO₂ or U₃O₈ and there was no evidence of the formation of an oxide corresponding to the metal combined as a compound with the uranium.

**UA1₄: Early oxidation**

The early stages of oxidation of UA1₄ may be explained by assuming
that a coherent non-porous oxide is formed. As the film thickens
the resistance to ionic diffusion increases and the rate of oxidation
decreases. The time for which this stage persists depends on temperature
but the protection afforded by this film soon ceases and a linear rate
of oxidation is observed.

If the initial stage of oxidation is parabolic followed by a tran-
sition to a linear stage, then the overall oxidation is said to be
"paralinear" in character. The transition from parabolic (protective)
to linear (non-protective) has been dealt with both theoretically and
practically by Loriers, 108 Haycock, 109 Aylmore et al, 113 and Webb et
al 111. The generally accepted mechanism of paralinear oxidation is
that an inner compact layer of oxide forms at a parabolic rate and
transforms to an outer porous layer at a linear rate. In such circum-
stances the oxidation tends to linearity as time proceeds, with non-
linearity evident in the early stages. The time taken for linearity
to be established depends on the parameters governing the two types
of oxidation and their temperature dependence.

In the case of UA1 alloys it is difficult to test if the initial
stage of oxidation is parabolic as the situation is complicated by the
presence of the UA1/Al eutectic and in many cases, by the short time
of existence of the protective period. For the purposes of this dis-
cussion, however, it will be assumed that the protective period of
oxidation observed is essentially parabolic in nature and is merely
indicative of the formation of a coherent oxide film.

UA1: Linear oxidation

The "paralinear" mechanism would appear to fit the experimental
results reported in Section 5. In such a case the linear rate of
oxidation observed in the second stage would be due to the presence of cracks or pores in the oxide film although a coherent film would still exist at the metal/oxide interface.

Alternatively, the reaction could be rate controlled either at the gas/oxide or metal/oxide interface. If a porous oxide is formed then the reaction would always occur at the metal oxide interface (or more probably through a thin oxide film of constant thickness at this interface) and very little ionic diffusion would be necessary in the oxide film.

Cracking of the oxide certainly occurs after prolonged oxidation although in the early stages the film surface shows no discontinuities (see Section 8). There is thus an intermediate period of oxidation in which linear oxidation occurs - the surface of the oxide formed during this stage shows virtually no porosity or cracking under the electron microscope. This does not, however, preclude the possibility of cracks or pores being present as they may be so extremely small that they are not resolvable even with an electron microscope. The occurrence of systems of micro-cracks and micro-pores in oxide films has been suggested by Ing et al. who measured the gas permeation characteristics of thin SiO₂ films. The permeation constant \((\text{cm}³ \cdot \text{cm}.\text{sec}^{-1} \cdot \text{cm Hg})\) which is a measure of the film permeability was divided into three ranges of values:

1) \(10^{-3} - 10^{-5}\) - permeation due to micro-cracks, pores and crystalline boundaries.

2) \(10^{-7} - 10^{-10}\) - microchannels

3) \(\sim 10^{-15}\) - true diffusion

The range of values represented by 2 and 3 was produced by films in
which the electron microscope produced no discernable surface features.

a) Porosity calculation

Some idea of the relation between pore size, number of pores and total pore area in a porous oxide film may be obtained from the following considerations.

Let \( n = \text{number of pores/cm}^2 \) of oxide surface

\( r = \text{average pore radius} \)

\( l = \text{pore depth} \).

It is assumed that the pores are evenly distributed over the oxide surface, circular in cross section, and penetrate the total thickness of the film (i.e. in the present calculation no barrier film is assumed to be present). If a fraction \( y \) of the surface area is occupied by pores, then for 1 cm²

\[
\frac{n \pi r^2}{l} = y \quad \text{(1)}
\]

where \( n \) is the number of pores/cm².

By Stokes' Law, the amount of gas available at the metal/oxide interface due to flow through a single pore of length \( l \) is given by

\[
V = p \frac{\pi r^4}{8l \eta}
\]

where \( p \) = pressure difference across pore length.

\( \eta \) = viscosity of gas at the temperature in question

Therefore the total volume \( V_t = nV \)

\[
= p \frac{\pi r^4 n}{8l \eta} \quad \text{(2)}
\]

Substituting from 1 for \( n \) gives \( V = yr^2 p/8l \eta \) \quad \text{(3)}

Now for any gas \( V_t = xM/22.4 \cdot 10^3 \) \quad \text{(4)}

where \( x = \text{weight gain of specimen oxidised in the gas in question} \) (gm.cm⁻².sec⁻¹)

\( M \) = molecular weight of gas
Hence equating 3 and 4:-

\[ \frac{xM}{22.4 \times 10^3} = \frac{yr^2p}{81n} \]

Therefore:

\[ r = \left( \frac{81n \times m}{22.4 \times 10^3 \times yp} \right)^{\frac{1}{2}} \]

(5)

Now, \( x, M \) and \( n \) are accurately known, whilst \( l, y \) and \( p \) may be estimated and hence \( r \) calculated approximately.

Putting:

\[ l = 1000 \, \text{Å} \] (estimated from weight gain of 90% UA14/Al alloy after 2 h at 500°C)

\[ p = 1 \, \text{mm Hg} \] (very small pressure drop assumed for high porosity film)

\[ M = 16 \] - the molecular weight of oxygen, the oxidizing gas

\[ x = 0.01 \, \mu g \cdot cm^{-2} \cdot sec^{-1} \] (estimated from same source as \( l \))

\[ = 400 \times 10^{-6} \, \text{poise at 500°C} \]

\[ y = 10^{-8} \] (taken from Ing's work on SiO2 films)

Substituting these values in 5 gives \( r \approx 15 \, \text{Å} \).

Hence \( n \) from 1 is found to be \( \approx 10^5 \) pores cm\(^{-2} \).

The value obtained for \( r \) is reasonable as \( 15 \, \text{Å} \) is less than the resolution of the electron microscope, yet larger than the molecular diameter of the oxygen molecule (collision diameter of oxygen molecule is \( 3.61 \, \text{Å} \)). Hence gas flow could occur through pores too small to be observed with the electron microscope. The value of \( n \) which follows from \( r \) is also felt to be reasonable, and is roughly 10 times that which may be calculated from Ing's work.

It is realised that many approximations have been made in the above analysis and that the figures quoted may contain large errors. However, although these errors may substantially alter the values of \( r \) and \( n \), this approach indicates that gas will be able to flow through the porous film at sufficient rate to maintain the reaction.
b) Volume ratios

The likelihood of a porous oxide being formed appears all the more probable when the volume ratios of the products of oxidation are considered. Although $U_3O_8$ when formed on uranium, has a high volume ratio (2.77) this will not necessarily be the case when the oxide is formed on uranium-aluminium compounds.

The volume ratio $\phi$, is defined as:-

Molecular volume of oxidation product/atomic volume of metal.

\[ \phi = \frac{\text{molecular weight of oxide/density of oxide}}{\text{density of metal/formulae atomic weight of metal}} \] ........................... (6)

For the formation of two products from the same metal or compound, $\phi$, is given by:

\[ \phi = \frac{AX + BY}{C} \]

where $X =$ fraction by weight of product whose molecular volume is $A$

where $Y =$ fraction by weight of product whose molecular volume is $B$

$s = \frac{C}{C}$ = metal or compound, atomic or molecular volume.

As long as the equation of reaction is known the fractional proportions of $A$ and $B$ produced can be calculated from the ratio of the molecular weights of each product to the total molecular weights of all products.

Thus for the reaction:

\[ 3UA1_x + 4O_2 = U_3O_8 + 3x Al \] .................................(7)

the percentage of $U_3O_8$ is \( (238.3) + (16.8)/(3x.27)+(238.3)+(16.8) \)....(8)

and that of $Al$ is \( (3x.27)/(238.3)+(16.8)+(3x.27) \).................................(9)

The following densities are used in the calculations: $7,8,127$

$U_3O_8 = 8.3; \ U = 18.7; \ Al = 2.7; \ UA14 = 5.7; \ UA13 = 6.4; \ UA12 = 8.2.$
c) Molecular volumes

Using the above figures the following values are obtained:

\[ 3UA1_4 = 181 \quad 3UA1_3 = 149 \]
\[ 3UA1_2 = 107 \quad U_3O_8 = 101 \]
\[ y.Al = 10y \]

Using the value \( x = 2, 3 \) or \( 4 \) in equation 7 the weight percentage of \( U_3O_8 \) and \( Al \) can be found from 8 and 9. These values, when substituted in 6 with the appropriate molecular volumes given above, yield the volume ratios of the oxide \( U_3O_8 \) and of the \( Al \) when produced in the oxidation of \( UA1_2, UA1_3 \) and \( UA1_4 \). The values obtained are:

\[ UA1_4 = 0.59 \]
\[ UA1_3 = 0.66 \]
\[ UA1_2 = 0.88 \]

These figures indicate that the films formed on all the compounds will be porous, especially those on \( UA1_4 \) where the volume ratio is the lowest in the series. It is not surprising that cracking of the oxide film is observed in such circumstances, although prolonged oxidation is necessary before it becomes evident. The form and mode of such crack propagation has been dealt with in Section 8 and will not be discussed further.

d) Porosity measurements

Although no measurements were made of the surface area or porosity of the oxide films formed, such measurements have been made on oxidised uranium surfaces. Jepson and Aylmore \(^{110}\) made measurements on uranium which had been oxidised at \( 2400^\circ C \). The composition of the oxide formed was not known with certainty but probably consisted of mainly \( UO_2 \) with higher uranium oxides possibly also present. Surface areas were measured...
by gas adsorption methods, and porosity measured by determining oxide
densities in CCl₄ and mercury.

It was found that the total porosity (open and closed) of such films
was 26.3% and of this 14.9% could be attributed to pores of less than
5Å diameter. A surface area of 6.5 m²/g of oxide was found, indicating
a porous open surfaced oxide.

e) Rate controlled reaction

Alternatively a linear rate may arise because of a rate controlled
reaction at one of the interfaces. Such a reaction could be ionization,
dissociation or migration, as was suggested by Leibowitz⁴⁷ for the
oxidation of uranium. A further possibility exists, in that the rate
controlled reaction may be entirely due to chemical kinetics of the
process.

i.e. the kinetics of the reaction:

$$3 \text{UA}_14 + 4\text{O}_2 = \text{U}_3\text{O}_8 + 12\text{Al}$$
could govern the reaction rate rather than the rate being governed
by the physical properties of the oxide film produced.

It is possible that in the case of UA₁₄ the oxide film produced
possesses not only a network of micro-channels which allows gas pene-
tration to the oxide/metal interface, but that a rate controlled reaction
occurs at this interface.

f) Volatile products

A linear oxidation rate is sometimes explained by the formation
of volatile oxidation products. Even if the product does not disappear
at once, or if formed simultaneously with less volatile products, the
continuous break up of the surface layer due to partial vapourization
would expose new metal surface to the attacking atmosphere. Such
reactions take place at the metal interface since the oxide produced will be broken and porous. This mechanism is applicable in the case of the oxidation of W\textsuperscript{114} and Mo\textsuperscript{115}, but is thought to be improbable in the oxidation of uranium since the U\textsubscript{3}O\textsubscript{8} produced is fairly stable up to 1350°C at atmospheric pressure although a slow loss of oxygen occurs above 650°C.\textsuperscript{116}

g) Metal diffusion

It may be deduced from the fact that oxidation is always linear that the rate of diffusion of uranium ions (or aluminium) in the compound to the metal/oxide interface is not a controlling factor. If such a factor were important, then a parabolic rate of oxide growth would be expected throughout oxidation rather than a linear one. Assuming the only oxide produced is U\textsubscript{3}O\textsubscript{8} the unoxidised Al ions have three possible courses open to them:

1) Passage into the alloy from the oxide/metal interface to form a non-stoichiometric compound.

2) Formation of a layer at the substrate/oxide interface.

3) Formation of a mixture with U\textsubscript{3}O\textsubscript{8} (suboxide).

It is not possible to decide which of these is the most likely on the evidence available. However, it has often been observed that when an alloy containing a noble and base metal is oxidised, the noble metal remains unoxidised and is found present in the oxide of the base metal. Such a situation could well exist in the present case, i.e. Al would be present mixed with U\textsubscript{3}O\textsubscript{8}.

\textbf{UA\textsubscript{11}: Anomalous temperature effect}

This type of effect is by no means confined to the U/Al system but has been observed to occur in the oxidation of Ca\textsuperscript{95}, Cd\textsuperscript{96}, Pb\textsuperscript{97},
The oxidation of calcium in water vapour over the temperature range 20-70°C was investigated by Svec and Apel\textsuperscript{95}. Although a logarithmic law was obeyed at all temperatures the rate decreased with increase of temperature and reached a minimum at 50-70°C. At higher temperatures the rate increased again. The effect was explained in terms of the increase of cohesion of small crystallites and of a healing of discontinuities in the oxide coating as the temperature increased.

In the case of Nb the anomalous effect has been noted by several workers\textsuperscript{98}, but only Aylmore et al have advanced a possible explanation. They tentatively suggested that the effect might be explained by a change in the growth mechanism from predominately anionic to predominantly cationic diffusion.

The oxidation of Cu\textsubscript{2}O to CuO has been investigated by Meijering and Verheijhe\textsuperscript{99} who found that a cubic law held over the temperature range 600-1000°C. The temperature variation of the rate constant over the temperature range 800-1000°C was found to be abnormal and yielded an activation energy of -15 kcal/mol. The results were explained by postulating a change in the permeability of the oxide film being formed. Defining the permeability $D$, by the equation:

$$\frac{dw}{dt} = K \cdot \frac{D}{W}$$

where $W$ = weight gain/cm$^2$, $t$ = time, $K$ = constant.

It may be shown that if a suitable time dependence is chosen for $D$, a cubic oxidation law results. By assuming that the change of permeability more than compensates for the increased ionic diffusion as the temperature increases, it is possible to explain the decrease in oxidation rate with
increasing temperature.

The anomalous effect observed with zinc by Vernon, Akeroyd and Stroud\textsuperscript{100} was explained in terms of film recrystallization which caused an increase in the resistance to ionic diffusion. The crystallization and sintering of an amorphous oxide film was also suggested by Aylmore et al\textsuperscript{27} to explain anomalous effects in the oxidation of aluminium.

The little evidence that is available concerning the structure of the film on UA\textsubscript{14} suggests that it is crystalline from a very early stage over all temperatures of oxidation (see Section 7). It is however possible that the oxide could change its physical characteristics above a critical temperature due to a sintering process. The experiments performed indicate that such a sintering effect would have to become operative in the region of 600\textdegree C in the case of UA\textsubscript{14}. At such a low temperature it is unlikely that major cracks or pores would sinter, but micro-channels or micro-pores whose existence is suspected would possibly be able to do so.

\textbf{Sintering}

No direct experimental evidence is available concerning the sintering characteristics of U\textsubscript{3}O\textsubscript{8} but a great deal of work has been performed on the related oxide, UO\textsubscript{2}, as this has potentialities as a high temperature reactor fuel. Most investigations have been conducted in the temperature range 800-1000\textdegree C as the process occurs most readily at these temperatures\textsuperscript{117-119, 121}. In an inert or oxidising atmosphere sintering commences between 550-600\textdegree C, but in a reducing atmosphere temperatures of more than 800\textdegree C are required\textsuperscript{118}.

The difference in the sintering behaviour in different atmospheres is readily explained by using the two theories of sintering. The first
theory assumes that the process is a result of bulk diffusion in the oxide lattice, whilst the second assumes that viscous or plastic flow of the oxide occurs\textsuperscript{119,120}. It is assumed that sintering which occurs in the presence of oxygen or in a vacuum is dominated by the former mechanism which has an activation energy of approximately 30 kcal/mol, whilst sintering in a reducing atmosphere is dominated by the second mechanism which has an activation energy of 76 kcal/mol\textsuperscript{120}.

The most direct evidence of sintering of U\textsubscript{3}O\textsubscript{8} comes from studies of the oxidation of UO\textsubscript{2}\textsuperscript{119}. Up to 300°C UO\textsubscript{2}\textsuperscript{12,13} has a negligible rate of oxidation (0.3 mg cm\textsuperscript{-2} h\textsuperscript{-1} at 300°C). Above 300°C it rapidly increases with temperature and reaches a maximum of 160 mg cm\textsuperscript{-2} h\textsuperscript{-1} at 700°C - at higher temperatures the rate decreases to a very low value again. It is suggested that the peak in the rate/temperature curve can be accounted for by assuming that U\textsubscript{3}O\textsubscript{8} (which is formed by the reaction 3 UO\textsubscript{2} + O\textsubscript{2} = U\textsubscript{3}O\textsubscript{8}) begins to sinter at about 600-700°C. Completely crystallised U\textsubscript{3}O\textsubscript{8} has a much smaller surface area than UO\textsubscript{2} (1 m\textsuperscript{2}/g compared with 20-30 m\textsuperscript{2}/g) and its crystallization will cause a marked reduction in surface area as well as causing the disappearance of micro-pores.

A solid is usually capable of rapid sintering above a critical temperature \( T_c \), which is characteristic of the solid but lies within the temperature range 0.37 - 0.53 \( T_f \), where \( T_f \) = melting point of solid on the absolute scale\textsuperscript{123}. Hence \( T_c \) for UO\textsubscript{2} = 800-960°C as \( T_f \) for UO\textsubscript{2} = 2176°C. The estimation of a similar temperature for U\textsubscript{3}O\textsubscript{8} is more difficult as U\textsubscript{3}O\textsubscript{8} is thermally unstable between 600-1400°C and oxygen is slowly evolved, whilst at 1450°C decomposition into a lower oxide occurs\textsuperscript{122}. However, taking \( T_f \) for U\textsubscript{3}O\textsubscript{8} to be 1450°C gives \( T_c \) as lying between
Thus $\text{U}_3\text{O}_8$ would be expected to sinter at about $750^\circ\text{C}$; it is not surprising however that lower temperatures are found capable of promoting sintering as the above relationship is only approximate, and the fact that oxygen is evolved from $\text{U}_3\text{O}_8$ between $600-1400^\circ\text{C}$ indicates a high mobility of oxygen ions in the oxide lattice which would promote sintering.

By using a sintering mechanism to explain the anomalous temperature effect an explanation of the results of vacuum sintering and pre-oxidation experiments (see Section 5) can be advanced. It was found that both vacuum sintering at $600^\circ\text{C}$ of an oxide film formed at $500^\circ\text{C}$, or forming an oxide film at $600^\circ\text{C}$ and then continuing oxidation at $500^\circ\text{C}$, greatly decreased the normal oxidation rate at $500^\circ\text{C}$. Such an effect was not permanent and a slow reversion to the original oxidation rate was observed. The period of 'zero' oxidation was longer and the rate of reversion slower with preformed films as compared to vacuum annealed films (see Section 5).

As sintering is accelerated by the presence of oxygen it is to be expected that the process will be more effective if conducted in the presence of $\text{O}_2$ rather than in a vacuum. Thus a film will slowly sinter at $600^\circ\text{C}$ 'in vacuo' but the process will be more effective if oxygen is present, although oxidation will occur at the same time. Therefore, pre-oxidation at $600^\circ\text{C}$ followed by oxidation at $500^\circ\text{C}$ would be expected to yield a more sintered film than sintering a film formed at $500^\circ\text{C}$, 'in vacuo' at $600^\circ\text{C}$.

After sintering, when the temperature is dropped to $500^\circ\text{C}$ it is assumed that no further sintering occurs. The sintered film protects the substrate from oxidation but slowly loses its protective nature.
Possibly the loss in protective nature is due to the slow evaporation of oxygen from the film, causing some type of structural change in the film and hence a loss of its protective nature.

Although a sintering mechanism is favoured for an explanation of the anomalous temperature effect another possibility does exist. It could be postulated that up to temperatures of 550°C only U₃O₈ is produced, but that at 600°C, Al₂O₃ is also manufactured. A coherent film of Al₂O₃ would form near the metal/oxide interface due to aluminium ions diffusing outwards through a thin barrier film, meeting oxygen molecules at the start of the porous oxide, and then forming Al₂O₃. As in the case of the oxidation of pure aluminium this film would crystallise and form an efficient barrier to ionic diffusion. It is assumed that the type of diffusion which occurs is of the same type as in the oxidation of the pure metal, i.e. anionic for uranium⁴⁸a and cationic for aluminium.¹⁰²

If this is the case it is difficult to understand some of the results of vacuum sintering and pre-oxidation experiments. Vacuum sintering at 600°C (of a film formed at 500°C) only allows physical changes to occur and thus if the above mechanism applies, should result in no change in the subsequent oxidation characteristics. Likewise if a coherent Al₂O₃ film is formed at 600°C, the gradual breakdown of this film during oxidation at 500°C, which is indicated by the gradual reversion to a linear oxidation rate, remains unexplicable. It should be noted however that a similar objection applies to the proposed sintering mechanism and there seems little reason for a sintered film to revert to its porous state.
9.4 UA1$_2$ and UA1$_2$

The mechanism of oxidation of these compounds appears to be similar. Both oxidise in a linear manner, giving U$_3$O$_8$ as the only oxide detectable. In the case of UA1$_3$, linearity is achieved after an initial period of more protective oxidation, whilst in the case of UA1$_2$, the oxidation rate increases gradually over the first few minutes and then passes into a linear oxidation rate (see Section 6). As viewed under the electron microscope the surface of both oxides is virtually featureless until after very prolonged oxidation. In the case of UA1$_3$, the slight surface roughness disappears as oxidation proceeds whilst with UA1$_2$, no roughness or porosity was observed, (except for discontinuities due to impurities). In both cases no anomalous temperature effect was observed.

The linearity of oxidation rate suggests that either the oxide is porous or else that the reaction is rate controlled (or both). Either possibility could apply to UA1$_3$, but for UA1$_2$, a rate controlled reaction is more likely as linearity is established without the formation of a barrier film. The absence of surface features in the two oxides suggests, as in the case of the oxide on UA1$_4$, that any pores which are present must be of very small dimensions.

Comparison of results

The linearity of oxidation rate found for UA1$_2$ disagrees with the results of Albrecht and Kohl$^{64}$ who investigated the oxidation characteristics of several refractory uranium compounds, amongst which was UA1$_2$. They found a cubic rate of oxidation which gave weight gains 10-15 times as great as those observed in the present investigation (figures obtained by comparing weight gains at 250°C after 16 min of
oxidation). The agreement in activation energy is much better, however, and the value of 22.3 kcal/mol calculated from the present results is in reasonable agreement with 26 kcal/mol of Albrecht and Koehl's. It is probable that, as these workers determined the activation energy from the slope of a line passing through only two points, their value could contain an error more than large enough to account for the difference between the two values.

The difference in the type of oxidation observed between this and previous work could be due to the porous nature of the samples used by the other investigators. As all the compounds of Albrecht and Koehl were manufactured by powder methods, some porosity was inevitable. In the case of the manufacture of UA12 compacts only 75% of the theoretical density was attained, hence porosity was very high as was shown by microscopic examination.

During oxidation, open pores in the specimen will tend to be isolated from the reacting gas by the oxide film blocking the pore entrances and this will be rapid if the rate of oxidation is appreciable, as it is for UA12. As oxidation proceeds the area of specimen available for oxidation will rapidly decrease. Suppose, in an idealised case,

\[ \frac{dA}{dt} = k_1 t \]

where \( A \) = area of specimen which continues to oxidise

\[ t = \text{time} \]

\[ k = \text{constant} \]

i.e. the rate of decrease of area is linear with time

then \( A = k_1 t^2 \)

For linear oxidation \( W/A = k_2 t \) (\( W \) = total weight gain)

Hence \( W = k_1 k_2 t^3 \)
If a constant area of $A_c$ is assumed then:

$$\frac{W}{A_c} = kt^3 \quad (A_c \ll A)$$

Thus in an idealised case of a specimen oxidising in a linear manner and possessing a rate of surface area decrease proportional to time, a cubic rate of oxidation would be observed. This type of situation could apply to the experiments of Albrecht and Koehl in which very porous specimens were sometimes used. Assuming a variation of pore size in the specimen it is clear that initial oxidation will close only the smallest pores, but that as time proceeds larger pores will be isolated and hence greater decreases in area may occur. This type of phenomena will then lead to the type of relationship assumed to exist between $A$ and $t$.

The fact that the magnitude of the weight gain per geometric area of specimen observed by Albrecht and Koehl is much greater than observed in this investigation supports the above contentions. Much greater weight gains per unit geometric area would be expected with a porous rather than a non-porous specimen. Such a change in area with time of oxidation would not alter the activation energy obtained in the two investigations as long as samples of comparable porosity were used in different experiments. Hence, although different rate laws may be observed the activation energy obtained in both cases should be the same. This was indeed found to be so.

**Sintering of the oxides on UA1$_3$ and UA1$_2$**

The anomalous temperature effect observed with UA1$_4$, which has been explained on the basis of sintering of the oxide, does not occur with UA1$_3$ and UA1$_2$. As similar (but less porous) films are found on the latter compounds a similar anomalous temperature effect might be expected.
The differences between the oxidation of UAl₄ and the other compounds can be summarized as follows:

1) The amount of aluminium assumed to be produced and to be present in the U₃O₈ film varies from compound to compound.
2) The rates of oxidation vary considerably.
3) The activation energy for UAl₂ and UAl₃ are approximately the same whereas that for UAl₄ is much higher (35 kcal/mol).

It is difficult to see with certainty why any of the above facts should cause sintering to occur in one case but not in the others. Possibly the rate of oxide formation must be relatively slow before the whole film can sinter effectively, otherwise rapid oxidation causes film breakdown before sintering can occur to a great extent. Alternatively the explanation may lie in a consideration of activation energies. For sintering to occur by oxygen ion diffusion the energy required is approximately 28 kcal/mol. Now the activation energy for oxidation of UAl₂ and UAl₃ is lower than this value, whereas for UAl₄ the activation energy is 34 kcal/mol. This may explain why the sintering effect postulated is confined to the latter compounds.

9.5 Comparison of results

The most significant point regarding the oxidation of the various compounds is the variation of activation energy of oxidation. Table 7 shows the activation energy of oxidation of the compounds UAl₂, UAl₃ and UAl₄ together with the published data on the oxidation of other compounds.
Table 7. Properties of intermetallic compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of formation $\Delta H$ (kcal/mol)</th>
<th>Activation energy of oxidation $\Delta E$</th>
<th>Type of oxidation</th>
<th>Ref to $\Delta H$</th>
<th>Ref to $\Delta E$</th>
<th>Products of oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>UAl$_2$</td>
<td>22.3</td>
<td>22.1</td>
<td>L</td>
<td>)</td>
<td>)</td>
<td>U$_3$O$_8$</td>
</tr>
<tr>
<td>UAl$_3$</td>
<td>25.2</td>
<td>23.6</td>
<td>L</td>
<td>) 83</td>
<td>)</td>
<td>Unknown</td>
</tr>
<tr>
<td>UAl$_4$</td>
<td>31.2</td>
<td>34.7</td>
<td>L</td>
<td>) work</td>
<td>)</td>
<td>&quot;</td>
</tr>
<tr>
<td>USi</td>
<td>9.55</td>
<td>8.6</td>
<td>L</td>
<td>)</td>
<td>)</td>
<td>&quot;</td>
</tr>
<tr>
<td>UBe$_{13}$</td>
<td>-</td>
<td>26.2</td>
<td>L</td>
<td>) 127</td>
<td>) 64</td>
<td>Unknown</td>
</tr>
<tr>
<td>UB$_2$</td>
<td>-</td>
<td>16.1</td>
<td>L</td>
<td>)</td>
<td>)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mg$_2$Sn</td>
<td>18.3</td>
<td>22.1</td>
<td>L</td>
<td>)</td>
<td>)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mg$_2$Pb</td>
<td>12.6</td>
<td>10.3</td>
<td>L</td>
<td>) 128</td>
<td>) 61a</td>
<td>&quot;</td>
</tr>
<tr>
<td>UC$_2$</td>
<td>39</td>
<td>21.2</td>
<td>P</td>
<td>129</td>
<td>)</td>
<td>CO/CO$_2$, UO$_2$, UC</td>
</tr>
<tr>
<td>U$_3$Si$_2$</td>
<td>8.16</td>
<td>10.6</td>
<td>P</td>
<td>)</td>
<td>)</td>
<td>UO$_2$</td>
</tr>
<tr>
<td>USi$_2$</td>
<td>10.4</td>
<td>-</td>
<td>P</td>
<td>) 127</td>
<td>) 64</td>
<td>&quot;</td>
</tr>
<tr>
<td>USi$_3$</td>
<td>7.9</td>
<td>23.6</td>
<td>P</td>
<td>)</td>
<td>)</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

L = linear mode of oxidation

P = parabolic mode of oxidation

From Table 7 it may be seen that when a linear rate of oxidation is obeyed by a compound, the heat of formation of the compound and its activation energy of oxidation are approximately the same. However, there is insufficient data for an accurate assessment to be made and it is quite possible that the correlation is coincidental.

If a relationship does exist its occurrence can only be explained in terms of the chemical kinetics of the reaction occurring, as it is difficult to imagine any other way in which the heat of formation of the compound could be linked to the activation energy of oxidation.
Although this is possible, it is unlikely, as the oxide films formed are not thought to be totally porous and it is more probable therefore that a barrier film in the oxide controls the oxidation kinetics.

The variation of the frequency factor $A$ (linear oxidation is represented by $W/t = A \exp (-E/RT)$, where the symbols have their usual significance) throughout the series of compounds is small. It may however, be significant that the minimum value of $A$, i.e. $A_{UA13}$, occurs in the approximate position of maximum aluminium activity in the U/Al system.

<table>
<thead>
<tr>
<th>Frequency Factor, $A$</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^8$</td>
<td>UA12</td>
</tr>
<tr>
<td>$1.7 \times 10^5$</td>
<td>UA13</td>
</tr>
<tr>
<td>$1.1 \times 10^9$</td>
<td>UA14</td>
</tr>
</tbody>
</table>

Since the maximum aluminium activity lies in the range $UA12 - UA13$, rather than $UA13 - UA14$ or $U - UA12$ it would be expected that in a reaction resulting in predominance of $U3O8$ the uranium activity would be all-important. Although this decreases with increasing aluminium content it is always sufficient for the formation of $U3O8$. Hence it appears that the activity of the aluminium plays an important part in the formation of $U3O8$ and the greater its value the lower the value of $A$.

If the activation energies of oxidation obtained represent the energy of ionic diffusion through a barrier film, it is likely that the diffusing species is the oxygen ion, which requires an energy of 29 kcal/mol for diffusion through a film of $UO2^{56}$. Although $U3O8$ is formed in the present cases this probably forms via nucleation of $UO2^{50}$ and it is not unreasonable to assume the existence of a thin $UO2$ layer at the reaction interface.
Although the activation energies obtained vary between 22 - 34 kcal/mol they could all represent a process of oxygen ion diffusion through a barrier film. Considering the probable errors in the activation energies determined (these are likely to be in the order of ± 20%), all three values obtained could represent the same process. However, a variation of activation energy for the same process in the different cases could be possible owing to:

1) The films formed in each case (U$_3$O$_8$) differ in the amount of aluminium they are thought to incorporate. Such differences could influence the energy needed for a diffusion process.

2) According to Peakall and Antill the observed activation energy, $E$, is a function of the energy of diffusion $E_d$, and of the plastic deformation of the oxide, $E_p$, both of which are thermally activated processes. The plasticity may be influenced by the amount of aluminium present in the film and would then vary from film to film. This would, in its turn, influence the value of $E_p$ and ultimately $E$. 

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NOTE

B.M.I - Battelle Memorial Institute.


C.T. - University of Chicago Metallurgy Lab.


H.W. - Hanford River Research Lab.


A.N.L. - Argonne National Lab.
