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DIOXIDE-ALUMINUM FUEL PLATES AND COMPACTS

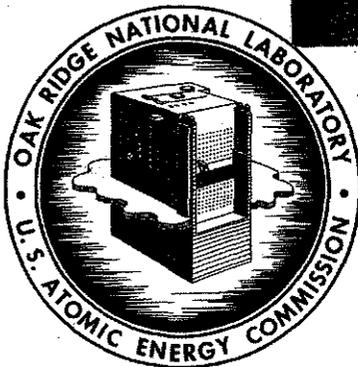
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THE REACTION AND GROWTH OF URANIUM DIOXIDE-
ALUMINUM FUEL PLATES AND COMPACTS

Roger Conant Waugh

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TABLE OF CONTENTS

CHAPTER	PAGE
I. SUMMARY	1
II. INTRODUCTION	3
III. OBJECTIVES	5
IV. REVIEW OF PREVIOUS WORK.	6
V. EXPERIMENTAL PROCEDURE AND EQUIPMENT	7
VI. RESULTS AND DISCUSSION.	20
VII. CONCLUSIONS:	61
LIST OF REFERENCES.	63

CHAPTER I

SUMMARY

The reaction of dispersed uranium dioxide in an aluminum matrix in pressed compacts and fuel plates has been studied at 500 - 600°C. Correlation of reaction with the accompanying volume increase was made and a growth mechanism proposed.

Uranium dioxide reacts slowly with aluminum in 50 weight per cent UO_2 pressed compacts at 600°C to form UAl_3 and Al_2O_3 . Seventy-five per cent reaction is attained in 80 hours and is accompanied by swelling.

Uranium dioxide reacts with aluminum in 52.3 weight per cent UO_2 fuel plates to form UAl_4 and Al_2O_3 . Intermediate reaction products are UAl_2 and UAl_3 . Reaction is rapid at 600°C, attaining 90 - 100 per cent completion in 10 hours, and moderate at 500°C, attaining 50 - 70 per cent completion in one week. Three reaction product zones, tentatively identified as containing UAl_2 , UAl_3 , and UAl_4 , are visible by electron microscopy. No evidence of diffusional porosity is noted. Volume increases of 20 - 30 per cent accompany reaction. The rate of volume increase decreases with heat-treatment temperature.

The observed volume increase cannot be explained on the bases of specific volume changes associated with the solid-state reaction, a Kirkendall mechanism, or the presence of hydrogen chemisorbed on the UO_2 surface. A growth mechanism is proposed and supported which is

based upon gas generation within the fuel plate core during reaction,
thus causing growth by creep due to internal pressure.

CHAPTER II

INTRODUCTION

Aluminum-base, plate-type fuel elements are attractive for use in high-flux research reactors, such as the Materials Testing Reactor. In this application, highly enriched uranium containing greater than 90 per cent U-235 is used in the form of 10 - 20 weight per cent U-Al alloy. The method of fabrication of such fuel elements has long been established.¹ The composite fuel plates are fabricated by roll cladding at 590°C, and subsequently assembled by brazing into a fuel element.

In the spring of 1955, the Oak Ridge National Laboratory was requested by the Atomic Energy Commission to construct a pool-type reactor for display at the Geneva Conference in August, 1955. The uranium for use in the fuel elements, however, was limited to 20 per cent U-235 by Congressional restriction. The urgency of time also precluded the investigation of major design alterations. These factors necessitated increasing the total uranium content of the fuel-bearing core of the composite plate by a factor of approximately five, so that a 50 per cent U-Al alloy was thus required. The established inhomogeneity and lack of ductility in such high-concentration U-Al alloys at that time indicated that considerable fabrication difficulty would be encountered. The unproved, yet promising, technique of incorporating the uranium as a UO_2 dispersion in aluminum powder was, therefore, selected. Problems soon developed, however, in

the use of this approach. Fuel plates showed abnormal dimensional growth during the elevated temperature fabrication procedures. Examination revealed the dispersed UO_2 particles were reacting with the aluminum matrix to form the uranium-aluminum intermetallic compounds and aluminum oxide. Fortunately, as a result of an intensive development program, an acceptable number of UO_2 -bearing fuel elements were prepared. This was accomplished, however, without obtaining an understanding of the UO_2 -Al reaction itself.

An increasing number of research reactors using fuel enriched to 20 per cent U-235 are presently being planned and constructed abroad under the Atoms-for-Peace Program of the United States. Although alternate fuel systems are now available, it is important to try to establish the soundness of the UO_2 -Al fuel component for this application, by obtaining a basic understanding of the conditions and mechanism of the undesirable reaction which has been observed. This study is an attempt to accomplish these objectives.

CHAPTER III

OBJECTIVES

The objectives of this study are to obtain a basic understanding of the conditions and mechanism of the UO_2 -Al reaction in pressed compacts and fuel plates. This study should permit evaluation of the growth mechanism by correlation of extent of reaction with the accompanying volume increase of fuel plates. The following factors were selected for evaluation:

1. the reaction in pressed compacts at 600°C ,
2. the effect of atmosphere in the reduction of $\text{UO}_3 \cdot \text{H}_2\text{O}$ to UO_2 on the subsequent reaction and growth characteristics of fuel plates, and
3. the reaction in and growth of fuel plates heat treated at $500 - 600^\circ\text{C}$.

CHAPTER IV

REVIEW OF PREVIOUS WORK

A literature survey indicated that limited and, in general, qualitative work has been reported on the reaction of UO_2 with aluminum. Waugh and Cunningham have reported the difficulties encountered in the fabrication of the UO_2 -Al fuel elements for the 1955 Geneva Conference display reactor.² Picklesimer has reported on the reaction rate in pressed compacts at 615°C .³ The uranium-aluminum intermetallic compounds UAl_3 and UAl_4 and aluminum oxide were identified as reaction products, and U_3O_8 was postulated to be an intermediate reaction product. The primary cause of the growth of compacts and fuel plates which had been observed was attributed to the release of hydrogen which had been previously chemisorbed by the UO_2 during its preparation. Later, Waugh detected trace amounts of UAl_2 during the early stage of reaction in fuel plates.⁴ Waugh and Beaver have reported the growth characteristics at 600°C of aluminum fuel plates containing 52.3 weight per cent UO_2 prepared by several methods.⁵ No reaction-rate data were given. The reaction rate of UO_2 prepared by various methods in aluminum fuel plates has been evaluated metallographically at $500 - 600^\circ\text{C}$ by Eiss.⁶ Williams has reported that aluminum will react with UO_2 to form the U-Al intermetallic compounds, accompanied by a volume increase.⁷ In the solid state, this reaction is sluggish and needs an inoculation time of more than a day at 600°C .

CHAPTER V

EXPERIMENTAL PROCEDURE AND EQUIPMENT

Two types of UO_2 were used in this study and both were prepared from $\text{UO}_3 \cdot \text{H}_2\text{O}$. The $\text{UO}_3 \cdot \text{H}_2\text{O}$ had been grown in an autoclave at 250°C from a UO_4 hydrate (peroxide cake)-nitric acid aqueous solution. For the first type, the $\text{UO}_3 \cdot \text{H}_2\text{O}$ was thermally reduced to UO_2 , high fired at 1700°C , and cooled in a high-purity-argon atmosphere. This material is referred to subsequently as A- UO_2 . The purity of the argon used, as determined by mass spectrographic analysis, is given in Table I. For the second type of UO_2 , the $\text{UO}_3 \cdot \text{H}_2\text{O}$ was reduced to UO_2 , high fired at 1700°C , and cooled in a dry-hydrogen atmosphere. It is referred to subsequently as H- UO_2 . The as-received A- UO_2 and H- UO_2 , both -100 +325 mesh (44 - 149 microns), are shown in Figures 1 and 2, respectively. The A- UO_2 particles were angular and had a vitreous appearance. The H- UO_2 particles were angular and had a generally rough surface which was locally faceted. The lattice parameters of the A- UO_2 and H- UO_2 were determined from a slow-scan diffractometer trace, using nickel-filtered copper K_α radiation, to be 5.469 ± 0.002 and $5.466 \pm 0.001 \text{ \AA}$, respectively. These results are in excellent agreement with the accepted value of $a_0 = 5.4691 \pm 0.0005 \text{ \AA}$.⁸ The stoichiometry of each UO_2 was determined by a method based on the determination of the excess oxygen content by polarographic measurement of the Uranium VI.⁹ Compositions determined for the A- UO_2 and H- UO_2 were $\text{UO}_{2.017}$ and $\text{UO}_{2.018}$, respectively. The chemical purity of each UO_2

TABLE I

MASS SPECTROGRAPHIC ANALYSIS OF ARGON

Constituent	Composition (Wt %)
A	99.995
N ₂	0.0034
CH ₄	0.0006
O ₂	0.0003
Hc	0.0002

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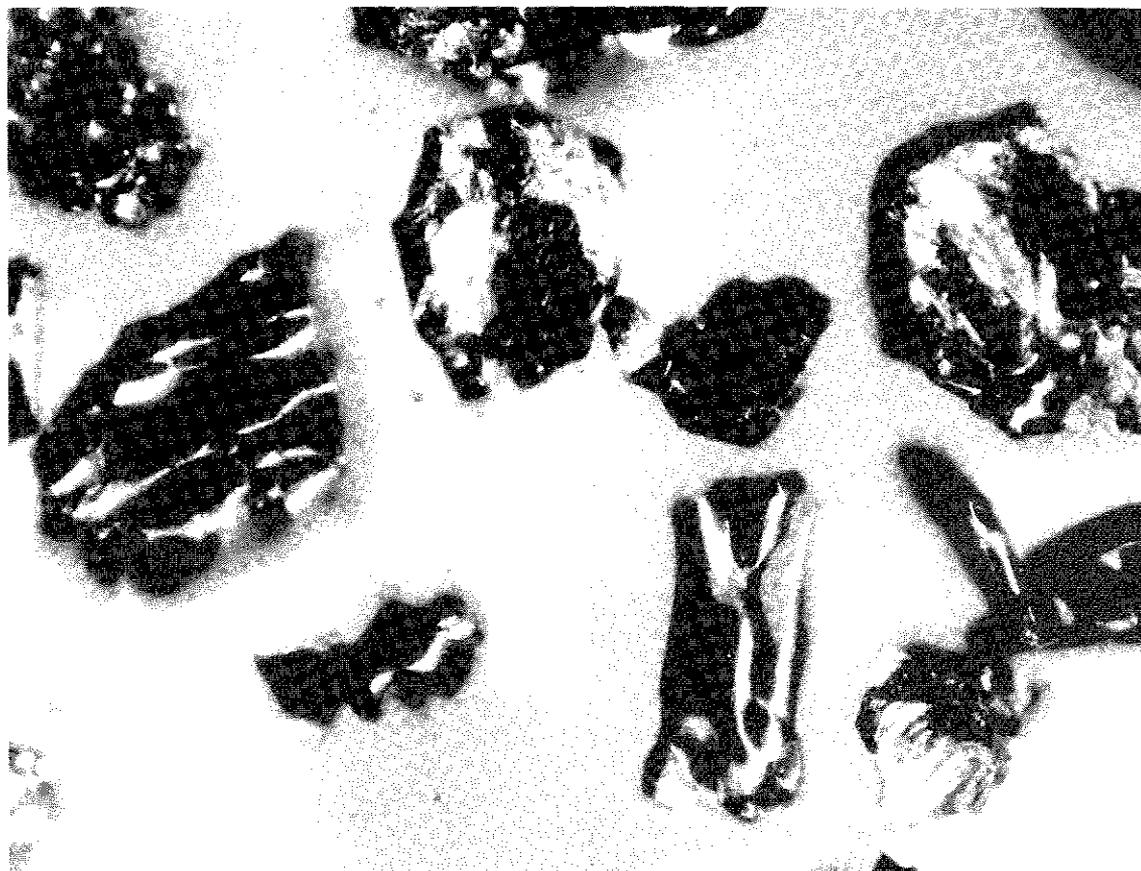


Figure 1. As-Received, -100 +325 Mesh UO_2 Reduced from $UO_3 \cdot H_2O$ in High Purity Argon (A- UO_2). 250X.

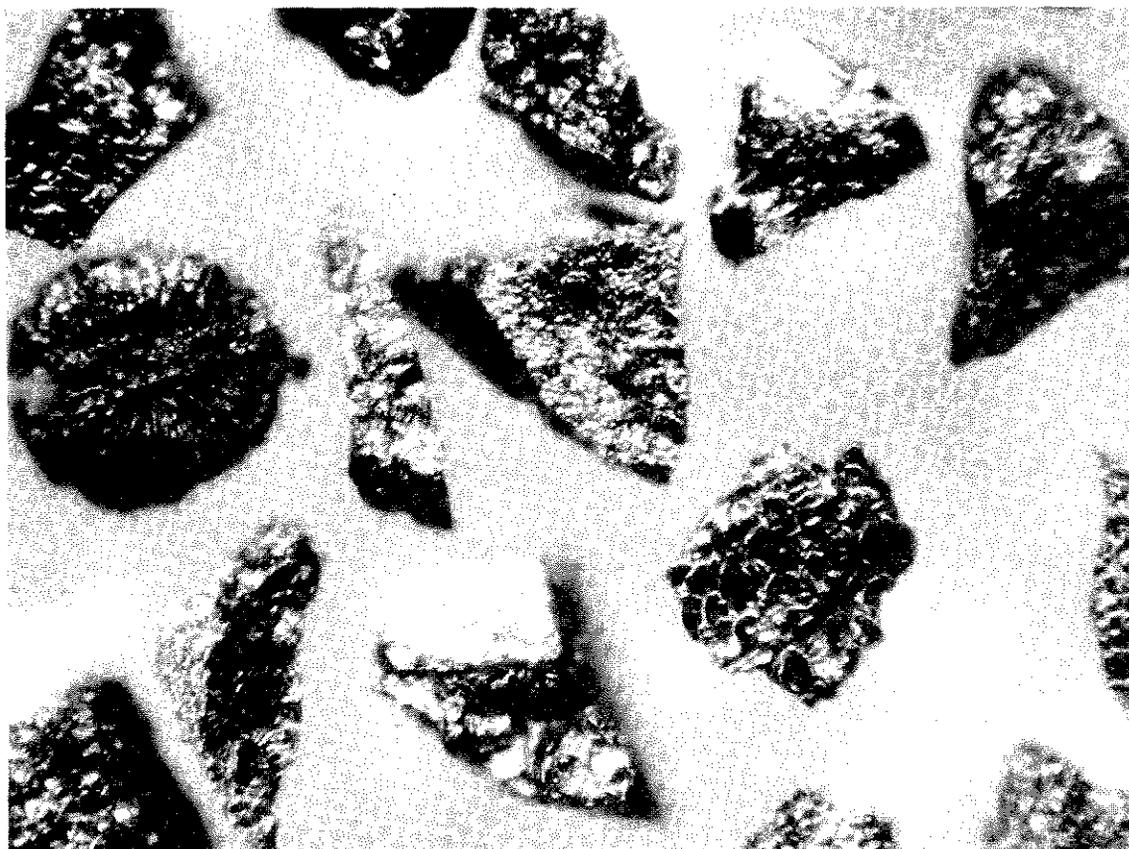
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Figure 2. As-Received, -100 +325 Mesh UO_2 Reduced from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in Hydrogen (H-UO_2). 250X.

was determined by quantitative spectrographic analysis and the data are presented in Table II. Combined differential thermal analysis and weight change determination during oxidation from UO_2 to U_3O_8 were performed on each UO_2 . The curves obtained are presented in Figures 3 and 4 for the A- UO_2 and H- UO_2 and are typical of coarse-grained, dense UO_2 .

The aluminum powder used was Grade MD-101, atomized powder manufactured by Metal Disintegrating Company, Elizabeth, New Jersey. It was -100 mesh with approximately 85 per cent -325 mesh. The powder was vacuum sintered at less than ten microns of Hg pressure for two hours at $600^\circ C$ prior to analysis and use. The results of a semi-quantitative spectrographic analysis are given in Table III. The major elements were determined by wet chemical methods to be 99.4 per cent total aluminum, 0.2 per cent iron, and 0.1 per cent silicon.

Wrought, 1100-grade aluminum, supplied by the Aluminum Company of America, was used for the frame and cover-plate material in the fuel plate fabrication.

Fuel Plate Fabrication

The fuel-bearing core sections of the composite plates were prepared by powder-metallurgy techniques. The composite plates were fabricated by roll cladding at elevated temperature. The procedure used is described in detail below.

TABLE II

QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF
AS-RECEIVED A-UO₂ AND H-UO₂ POWDERS

Element	Composition (Wt %)	
	A-UO ₂	H-UO ₂
Al	0.00012	0.0010
B	0.00025	0.00017
Ca	0.0017	0.002
Cr	0.00063	0.00065
Cu	0.0013	0.0013
Fe	0.0068	0.0046
Mg	0.00047	0.00036
Mn	0.000077	0.000095
Ni	0.00054	0.0034
Si	0.00034	0.00013

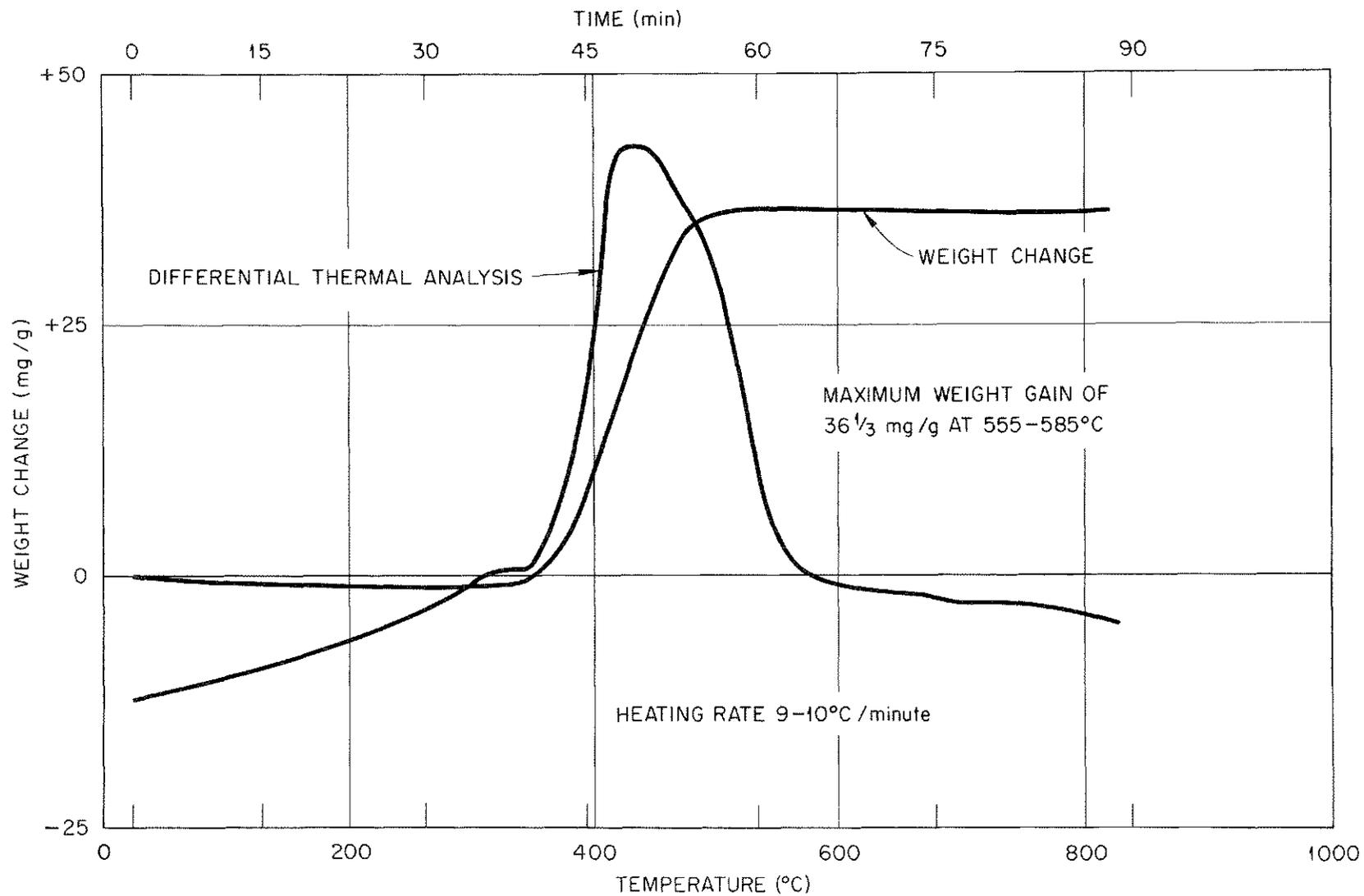


Figure 3. Combined Differential Thermal Analysis and Weight Change from UO_2 to U_3O_8 for -100 +325 Mesh UO_2 Reduced from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in High Purity Argon.

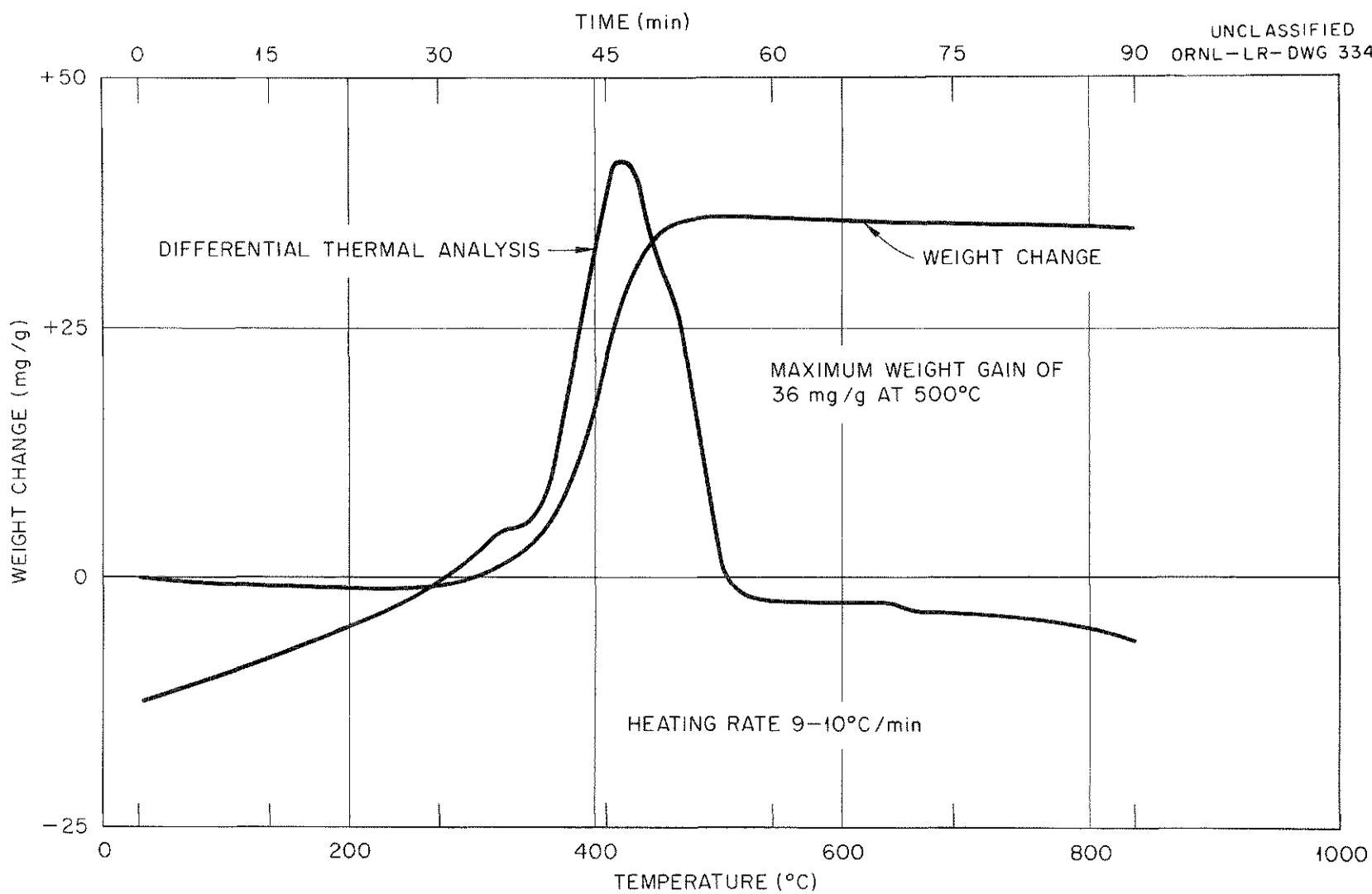


Figure 4. Combined Differential Thermal Analysis and Weight Change from UO_2 to U_3O_8 for -100 +325 Mesh UO_2 Reduced from $UO_3 \cdot H_2O$ in Hydrogen.

TABLE III

SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS
OF ALUMINUM POWDER

Element	Wt %	Element	Wt %
Ag	< 0.0002	Mn	0.001 - 0.01
Al	10 - 100	Mo	< 0.003
As	< 0.1	Na	< 0.05
Au	< 0.004	Ni	< 0.001
B	< 0.006	P	< 0.2
Ba	< 0.2	Pb	< 0.02
Be	< 0.0002	Pd	< 0.0004
Bi	< 0.002	Pt	< 0.009
Ca	0.001 - 0.01	Ru	< 0.004
Co	< 0.0005	Si	0.1 - 1.0
Cr	0.0001 - 0.001	Sn	< 0.003
Cu	0.001 - 0.01	Sr	< 0.1
Fe	0.1 - 1.0	Ta	< 0.3
Ga	< 0.004	Ti	0.01 - 0.1
Ge	< 0.003	V	0.01 - 0.1
Hg	< 0.14	W	< 0.1
Li	< 0.02	Zn	< 0.02
Mg	0.001 - 0.01	Zr	< 0.008

The standard A-UO₂- and H-UO₂-bearing fuel cores were 52.3 weight per cent UO₂ - balance aluminum and weighed 103.3 grams. The uranium dioxide and aluminum were blended in a 4-ounce glass jar for 3 hours on an oblique-type blender and compacted cold in a double-acting die at 33 tsi to approximately 95 per cent of theoretical density. A piece of 0.002-inch-thick aluminum foil was pressed on the top and bottom surfaces of each core to assist in attaining sound core-to-clad bonding during hot rolling. The core was deliberately made 0.025-inch thicker than the picture frame. Prior to billet assembly, the core was inserted into the frame cavity and hydraulically pressed to give an intimate fit. This step minimized the possibility of subsequent blistering due to misfit. Cover plates and evacuation stem were added and the composite billet assembled by heliarc welding. The billet was initially evacuated cold, degassed for 1 hour at 300°C at 5 microns of Hg pressure, and the evacuation stem forged shut.

The billet was preheated at 590°C for 60 minutes and hot rolled in 9 passes from an initial billet thickness of 0.754 inch to 0.072 inch. It was reheated for 5 minutes between each pass. Excess aluminum was sheared after fluoroscopy. The flux-annealing operation consisted of coating the plate surfaces with a slurry mixture of alcohol and Eutectic 190 brazing flux and annealing for 35 minutes at 604°C. The water-soluble flux was removed by a scrub wash. The plates were dipped in an acid bath of 15 volume per cent HNO₃-1 volume per cent HF-balance water, rinsed in hot water and dried. The plates were reduced cold in several passes to a nominal thickness of 0.060

inch. They were flattened by roller leveling prior to fluoroscopy and shearing.

The plates were machined to a width of 2.916 ± 0.002 inch and a length of 28.625 ± 0.016 inch. The nominal core dimensions in the finished plate were 2.5 inches wide and 22 inches long. The clad and core thicknesses were 0.0175 and 0.025 inch, respectively. This procedure will be referred to subsequently as the standard fuel-plate-fabrication procedure.

A reference plate containing an aluminum core was prepared by compacting 62.5 grams of aluminum powder at 33 tsi. The standard fabrication procedure was used through the roller-leveling operation, except for the elimination of the fluoroscopic marking steps. The nominal core dimensions and clad and core thicknesses were the same as those of standard fuel plates. The over-all plate dimensions were 30 inches long and 3.5 inches wide.

Fuel Plate Heat Treatment and Growth Measurement

The A-UO₂ and H-UO₂ fuel plates fabricated by the standard procedure were heat treated for selected times at 500, 525, 550, 575, and 600°C in a resistance-heated tube furnace. The plate containing an aluminum core was heat treated for 40 hours at 600°C in the same furnace. Volume changes which occurred during heat treatment were determined by the displacement method using distilled water containing Aerosol OT wetting agent.

Evaluation of Reaction in Fuel Plates

The distortion which occurs during heat treatment was removed by cold rolling the fuel plates to a 0.002-inch reduction in thickness. The cladding was removed from a sheared portion of the flattened plate, and the desired core specimen obtained in the form of fine chips by machining. The sample obtained was used for the chemical and x-ray diffraction analyses.

A complete constituent analysis was performed on the A-UO₂ and H-UO₂ fuel plate cores which had been heat treated at 600°C. The method of analysis consisted of sequential, selective leaching of the constituents in the sample.^{9,10} Basically, the steps were as follows: the unreacted aluminum was dissolved in 1 M NaOH, the uranium-aluminum intermetallics dissolved in 1 M H₂SO₄, the unreacted UO₂ dissolved in HNO₃, and the Al₂O₃ residue ignited. The amount of uranium in the uranium-aluminum intermetallics relative to the total uranium recovered is defined as the degree of reaction. The amount of each constituent present is expressed as a percentage of the total weight recovered, which was generally greater than 97 per cent of the original weight. The partial chemical analysis required to determine the degree of reaction was performed only for the standard A-UO₂ and H-UO₂ fuel plates heat treated at less than 600°C.

The constituents present in A-UO₂ and H-UO₂ fuel plates heat treated at 600°C were identified by diffractometer trace using nickel-filtered, copper K_α radiation. The 2θ values for the UAl₄ formed in

the H-UO₂ plates were examined for evidence of the range of aluminum content, UAl_{4.5} to UAl_{4.9}, which has been reported.¹¹

Procedure for Pressed Compacts

The reaction of H-UO₂ with aluminum in pressed compacts was studied during vacuum heat treatment at 600°C. The compacts were 50 weight per cent UO₂-balance Al and weighed 0.80 gram. The UO₂ and Al were preblended for 0.5 hour on an oblique-type blender, one drop of carbon tetrachloride added to the blend, and the mixture blended for an additional three hours. The core was compacted cold in a double-acting cylindrical die at 30.8 tsi to approximately 92 per cent of theoretical density. The compact dimensions were 0.252 inch diameter and 0.242 inch high.

Each compact was individually encapsulated cold, and groups of 4 - 7 heat treated for 24, 32, 40, 48, 72, and 80 hours at 600°C. The identity of the constituents present was established by x-ray diffraction for a number of the compacts, and the degree of reaction determined for all compacts. One compact from each group was checked for Uranium VI by a polarographic technique after initial dissolution in phosphoric acid under an argon blanket.

CHAPTER VI

RESULTS AND DISCUSSION

Reaction in Pressed Compacts

A summary of the data on the extent of reaction at 600°C in pressed compacts containing 50 weight per cent H-UO₂-Al is presented in Table IV. Each compact had been individually encapsulated cold prior to vacuum heat treatment for selected times. The data show considerable scatter for compacts which had been prepared and processed in an identical manner. The reason for this scatter was not established. The average deviation within each group decreases, with a single exception, with increasing time of heat treatment. The significance of the observed decrease also is not understood.

In spite of the scatter within each group, the average degree of reaction for each group generally increases with increasing heat treatment, as expected. The reaction-rate data are plotted in Figure 5. An average degree of reaction of 75.7 per cent is attained after 80 hours at 600°C. As will be discussed in a subsequent section, fuel plate cores containing 52.3 weight per cent H-UO₂ will react completely in 10 hours at 600°C (see Figure 12). Pressed compacts react, therefore, markedly slower than fuel plate cores. This result is reasonable, however, considering the greater continuity of the aluminum oxide film on the matrix particles and the lower densification of the reacting specimen. Pronounced swelling of the compact

TABLE IV

REACTION IN 50 WEIGHT PER CENT H-UO₂-AL COMPACTS
AFTER VACUUM HEAT TREATMENT AT 600°C

Heat Treatment at 600°C (Hr.)	Degree of Reaction (%)	Average Degree of Reaction for Group (%)	Average Deviation from Average Degree of Reaction for Group (%)
24	52.3	23.4	14.4
	16.7		
	11.6		
	13.0		
32	69.6	57.8	9.0
	64.0		
	57.1		
	40.6		
40	69.7	52.9	9.6
	55.3		
	51.2		
	35.5		
48	86.4	75.0	5.8
	70.3		
	73.5		
	69.6		
72	71.3	77.8	5.1
	84.3		
	73.8		
	74.1		
	79.4		
	81.2		
80	80.2	75.7	3.0
	79.0		
	69.7		
	77.2		
	77.0		

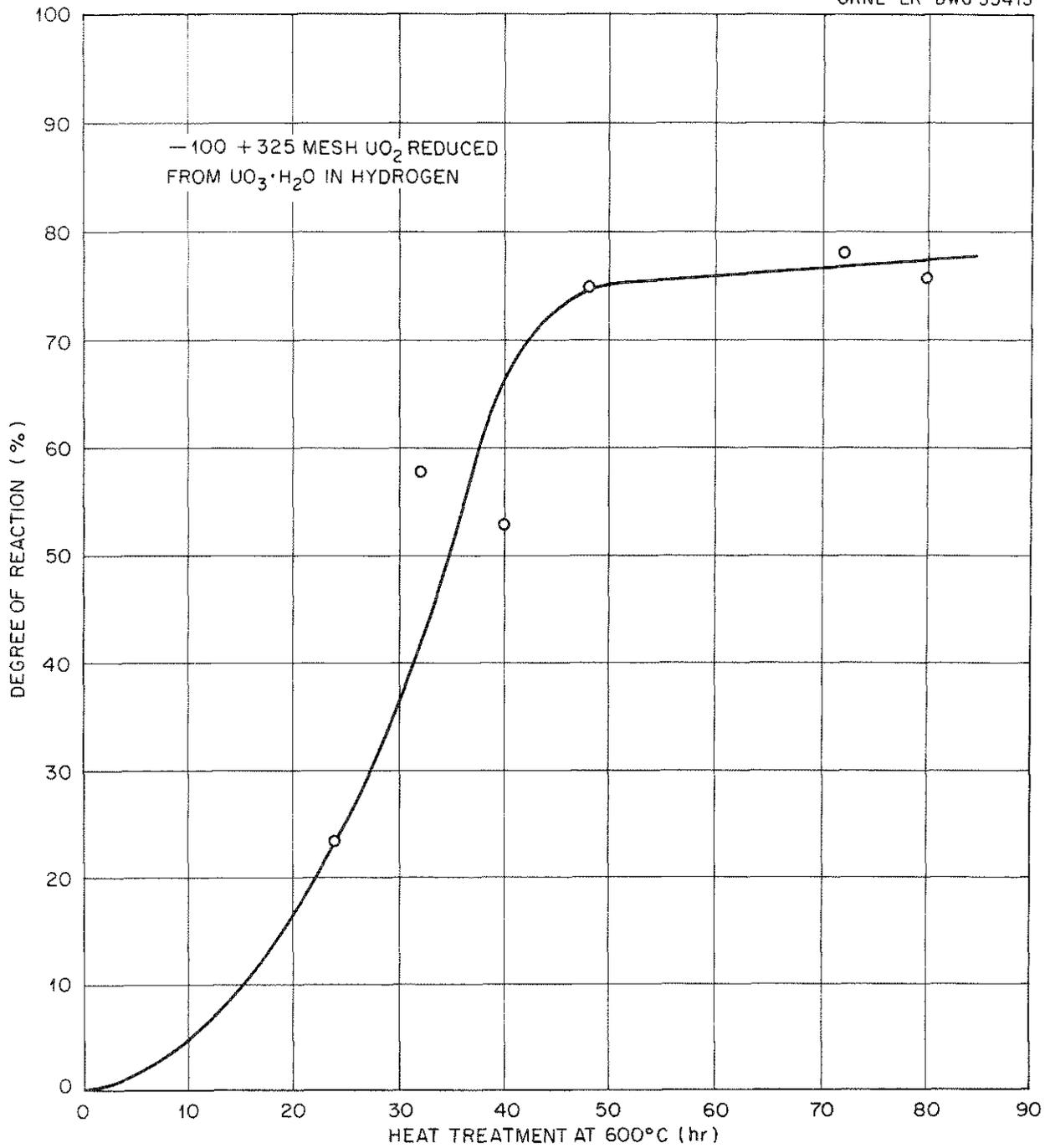
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Figure 5. Reaction Rate in 50 Weight Per Cent H-UO₂ + Aluminum Compacts Heat Treated at 600°C.

accompanies reaction. The friable nature of the reacted compact prevented measurement of the swelling which had occurred.

The change in compact composition with degree of reaction, as determined by chemical analysis, is shown in Figure 6. The curves obtained for the individual reactants and reaction products are linear. It is apparent that the initial 50 weight per cent aluminum investment is approximately 100 per cent in excess of that required for reaction. Minor inhomogeneity of the dispersed UO_2 would therefore not affect the degree of reaction obtained on heat treatment.

One compact from each of five groups was examined by x-ray diffraction to identify the constituents present. The results are summarized in Table V. It is significant to note that UAL_3 is the principal U-Al intermetallic compound formed. A trace of UAL_2 was detected in one compact and small amounts of UAL_4 in two compacts. By way of contrast and as will be discussed in a subsequent section, UAL_4 is the principal and equilibrium U-Al intermetallic compound formed during reaction in fuel plate cores. The latter condition would be expected at equilibrium since reference to the aluminum-uranium phase diagram, shown in Figure 7, indicates that UAL_4 is the equilibrium U-Al intermetallic compound present at these conditions. It is pertinent to note that DeLuca reports a supporting situation in U-Al diffusion couples.¹² His x-ray diffraction studies revealed that UAL_3 was the main diffusion product at all temperatures and that traces of UAL_2 and UAL_4 were detectable at 475°C and above. No explanation was given.

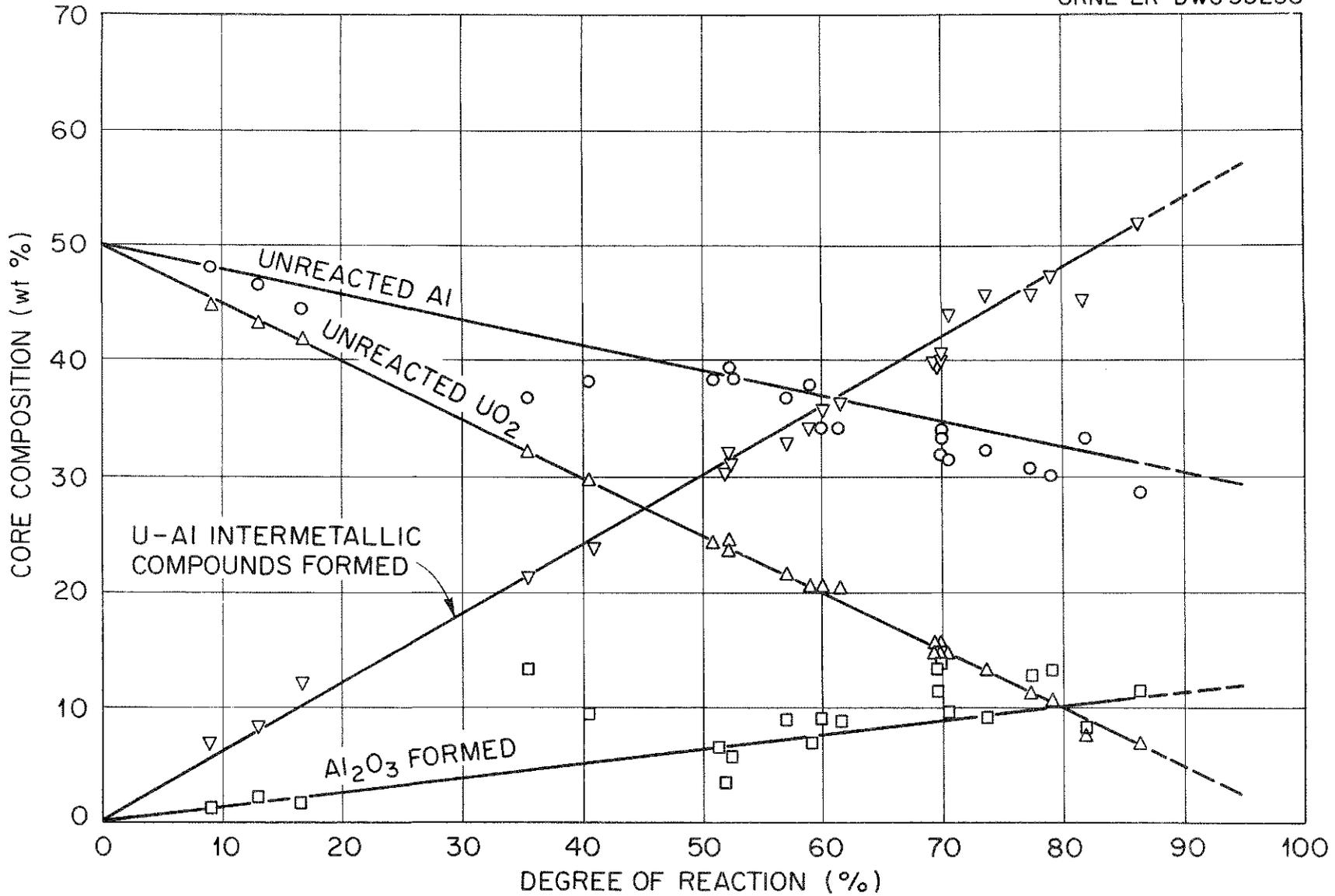


Figure 6. Composition Change During Reaction of 50 Weight Per Cent H-UO₂ + Aluminum Compacts at 600°C.

TABLE V

X-RAY DIFFRACTION IDENTIFICATION OF CONSTITUENTS
PRESENT IN H-UO₂-AL COMPACTS AFTER
VACUUM HEAT TREATMENT AT 600°C

Heat Treatment at 600°C (Hr.)	Constituents Present				
	Al	UO ₂	UAl ₂	UAl ₃	UAl ₄
24	Yes	Yes	Trace	Yes	Yes
32	Yes	Yes	-	Yes	-
40	Yes	Yes	-	Yes	-
48	Yes	Yes	-	Yes	-
80	Yes	Yes	-	Yes	-

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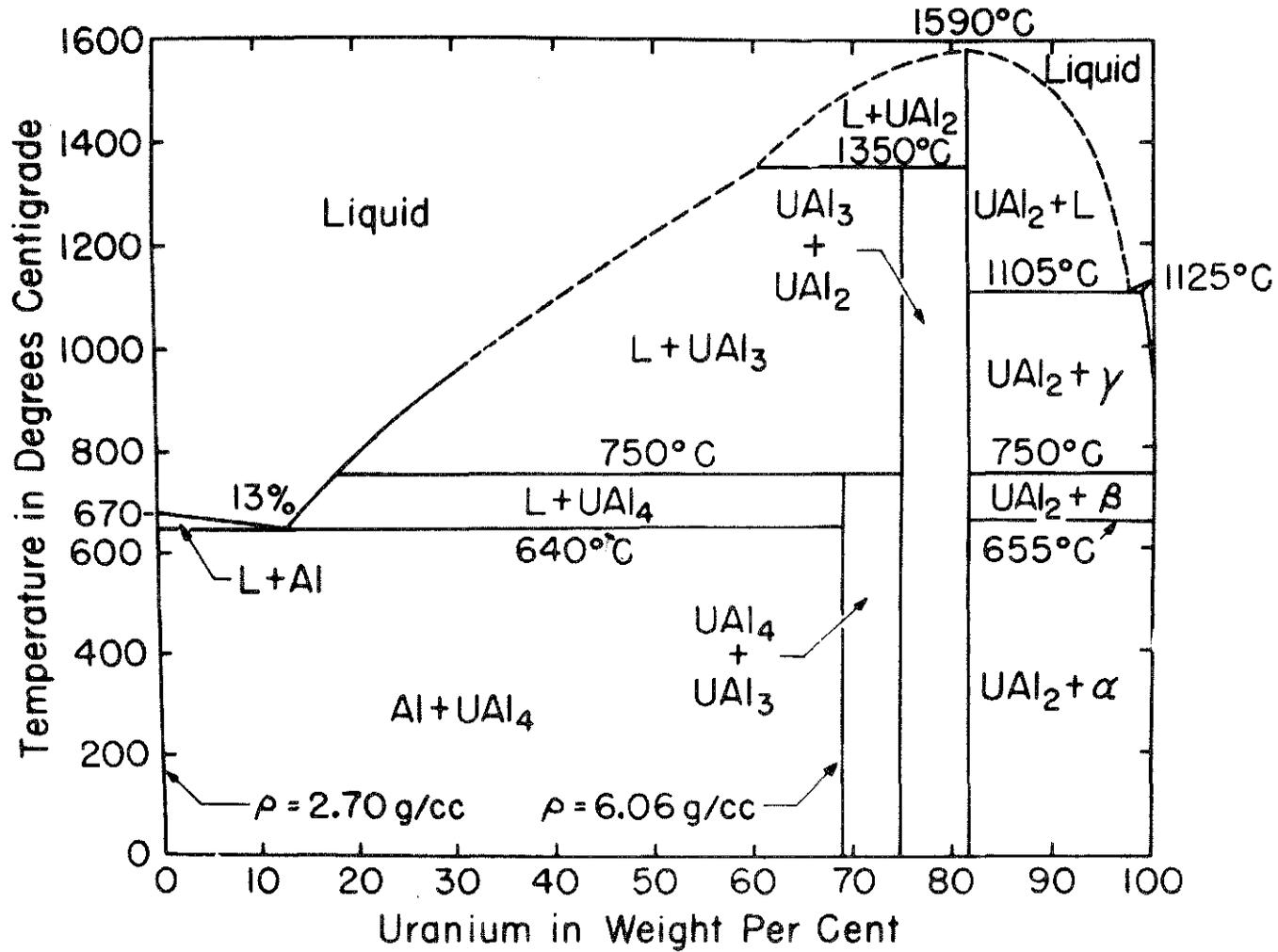


Figure 7. Aluminum-Uranium Phase Diagram.

One compact from each group was examined for Uranium VI in an attempt to verify the postulate that U_3O_8 was an intermediate product. In no case, however, were amounts of Uranium VI greater than that associated with the excess oxygen of the UO_2 found. Neither was the presence of U_3O_8 detected in any of the x-ray diffraction analyses of compacts or fuel plate cores. The data, therefore, do not verify the presence of U_3O_8 as an intermediate reaction product.

Reaction in Fuel Plates

The reaction which occurs during heat treatment of A- UO_2 and H- UO_2 fuel plates at 500 - 600°C has been evaluated by a similar chemical analysis. The change in core composition with degree of reaction during heat treatment of A- UO_2 and H- UO_2 fuel plates at 600°C is shown in Figures 8 and 9. The UO_2 curve of each is linear by its definition. The fact that the Al_2O_3 curve is linear, and that a reasonably good oxygen balance is obtained for the H- UO_2 fuel plates heat treated at 600°C by using UO_2 and Al_2O_3 as the only oxygen-containing constituents, is additional verification that U_3O_8 is not an intermediate product.

The rate of aluminum consumption increases at an intermediate point. In the case of the H- UO_2 fuel plates, this increase occurs at approximately 35 per cent reaction. This increase would be due to increase in the UAl_x -Al side reactions, because it will be shown subsequently (see Figure 12) that the UO_2 reaction rate at 600°C is constant through approximately 90 per cent reaction. These side reactions

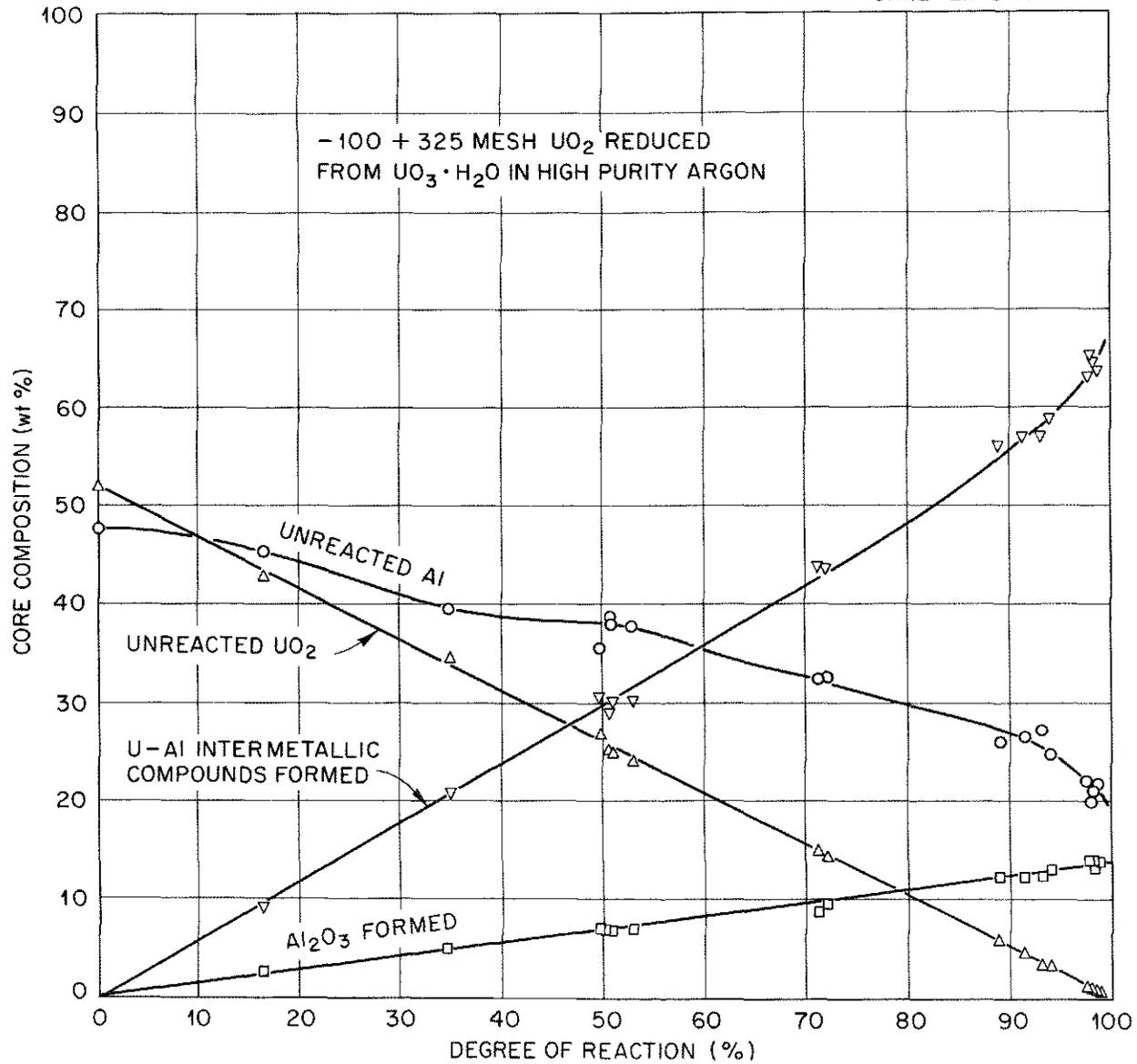


Figure 8. Change in Core Composition During Reaction of 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates at 600°C.

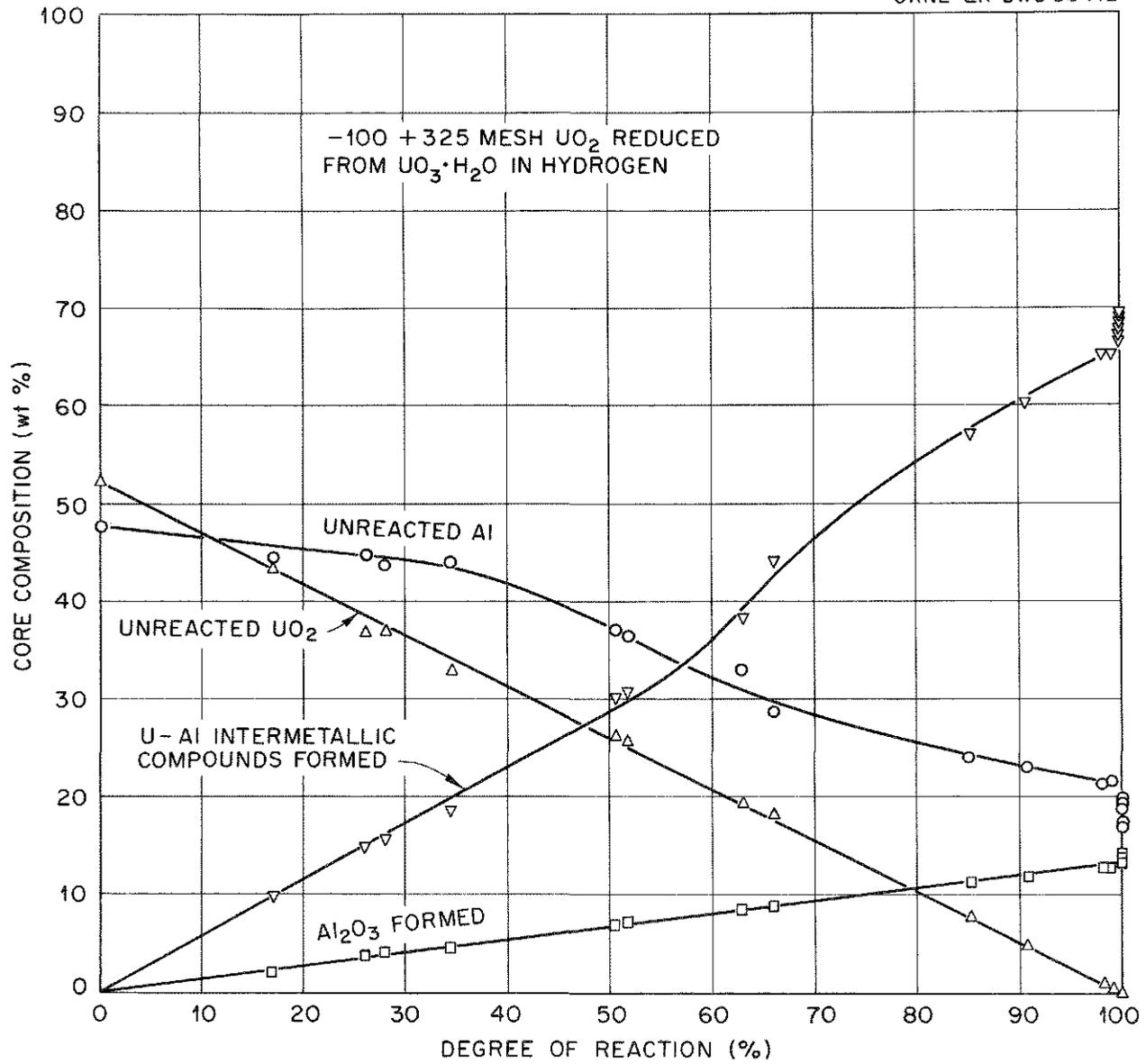


Figure 9. Change in Core Composition During Reaction of 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates at 600°C.

are discussed further in a subsequent section. Figure 10 is a replot of the Al and U-Al intermetallic compound curves for each UO_2 . A significant deviation exists between the respective curves for each UO_2 , starting at about 50 per cent reaction. The data indicate that the U-Al side reactions occur at a faster rate for the H- UO_2 . Toward completion of the UO_2 -Al reaction, however, the respective curves rejoin, indicating that the same U-Al intermetallic compound (UAL_4) is formed.

A generally sharp increase in the U-Al intermetallic compound curve and decrease in the Al curve at completion of reaction occurs for each UO_2 and indicates increase in the aluminum content of the UAL_4 . The data for the H- UO_2 fuel plates heat treated at 600°C were evaluated to ascertain the variation with time in the aluminum/uranium mole ratio in the U-Al intermetallics. The individual scatter was fairly large, however, and thus inconclusive. The cause of the scatter appeared due to prior leaching of some of the aluminum of the intermetallic compounds during the initial NaOH leaching step of analysis. This effect may be seen in Figure 10.

The UO_2 -Al reaction rates in A- UO_2 and H- UO_2 fuel plates heat treated at $500 - 600^\circ\text{C}$ are shown in Figures 11 and 12. The reaction rate is moderate at 500°C and rapid at 600°C for each UO_2 . A striking difference in the reaction rates, however, is apparent. The H- UO_2 has reacted faster at every point of comparison. For example, reaction in the H- UO_2 plates is complete in 10 hours at 600°C , whereas in the A- UO_2 plates reaction is 98.7 per cent complete after 32 hours. The faster

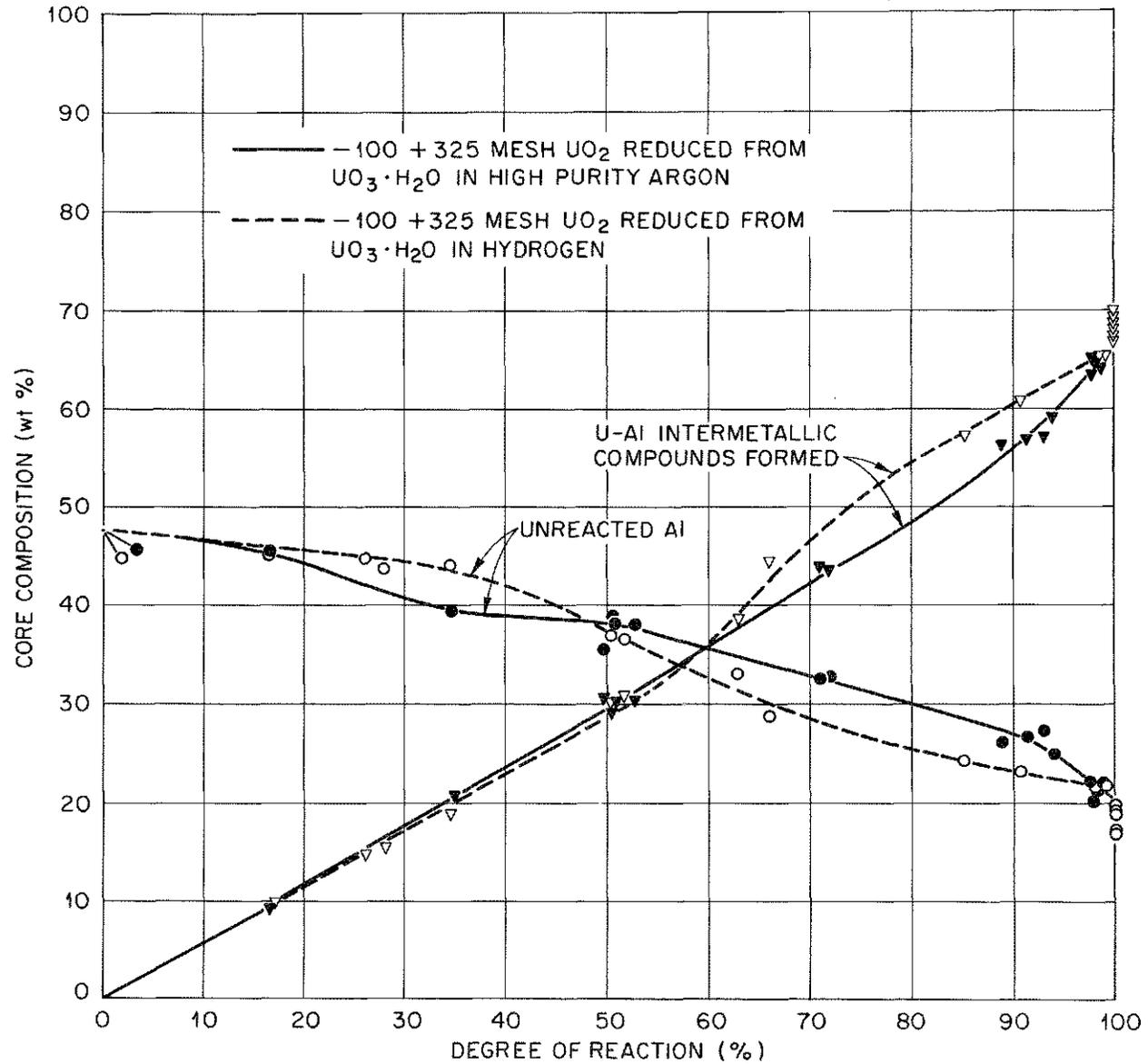


Figure 10. Comparison of Selected Composition Changes During Reaction of 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates at 600°C.

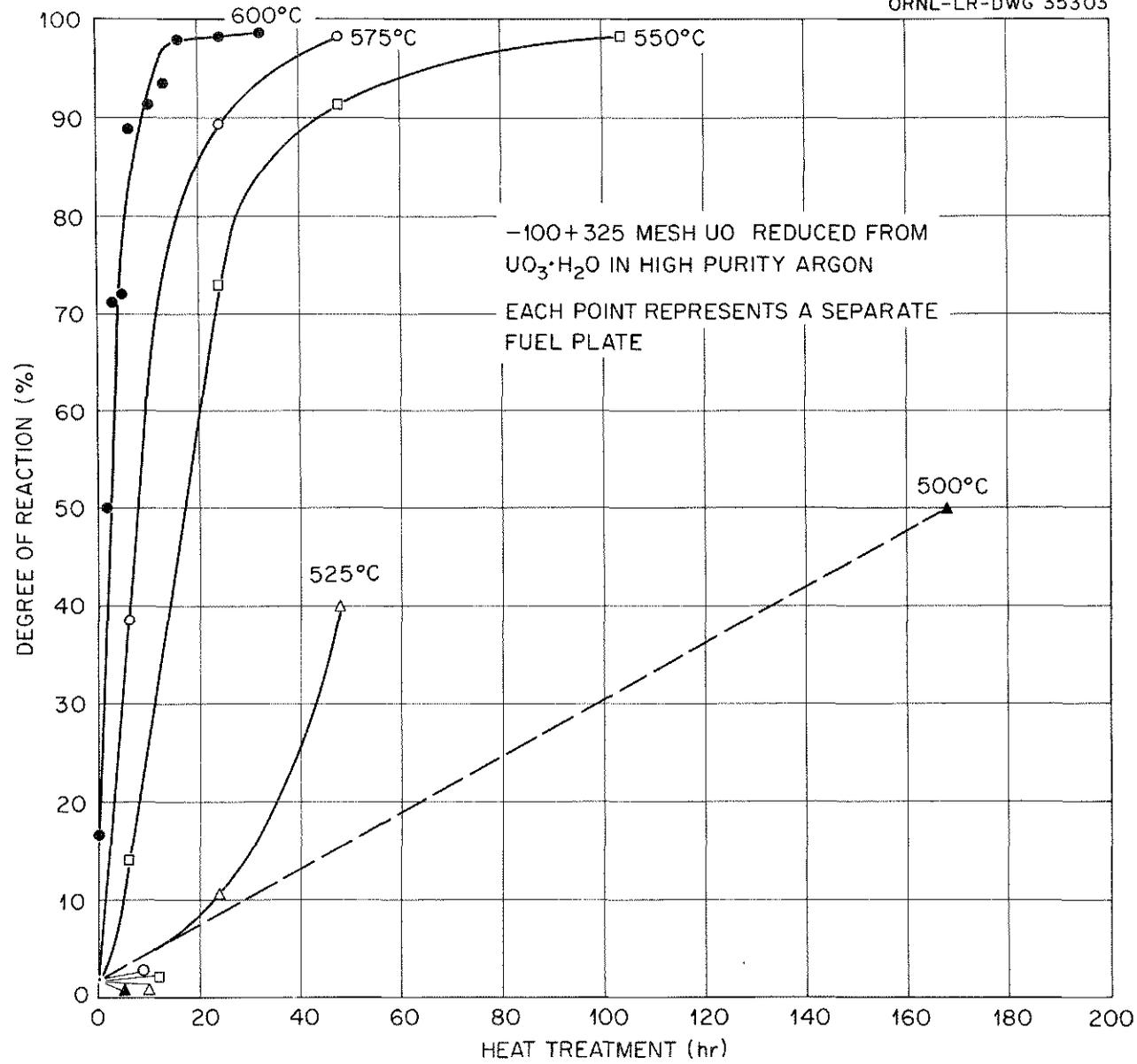


Figure 11. Reaction Rate of 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates at Selected Temperatures.

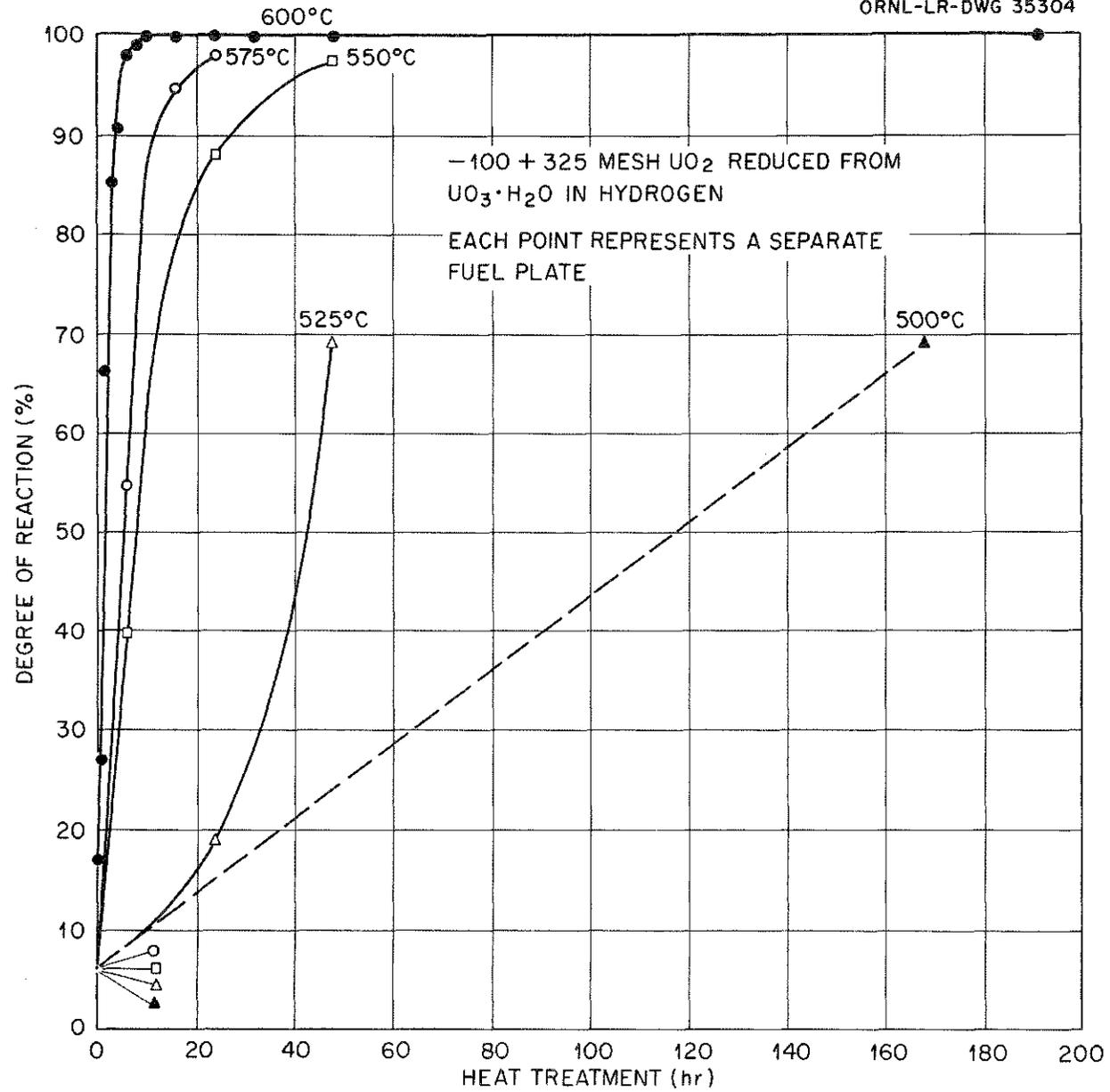


Figure 12. Reaction Rate of 52.3 Weight Per Cent UO₂-Aluminum Fuel Plates at Selected Temperatures.

reaction rate observed in the H-UO₂ plates appears to be due to greater stringering and fragmentation of the UO₂ during fabrication, as well as the presence of a larger fraction of UO₂ particles in the lower end of the 44 - 149 μ size range. Both factors produce a larger UO₂ surface/volume ratio in the H-UO₂ plates, and thus a faster reaction rate would be expected.

X-Ray Diffraction Analysis of Reacted Fuel Plates

The A-UO₂ and H-UO₂ fuel plates which had been heat treated at 600°C were examined by x-ray diffraction for identity of the constituents present. The data are summarized in Tables VI and VII. Aluminum was present in each plate and UAl₂ was not detectable in any plate. Trace amounts of UAl₂ had been detected, however, in several earlier fuel plates which had been heat treated for 1 - 2 hours at 600°C. The formation of all three of the U-Al intermetallic compounds, UAl₂, UAl₃, and UAl₄, is predicted by the U-Al equilibrium phase diagram. Kiessling and LeClair have reported in their respective studies of U-Al couples that the three are present in the diffusion zone.^{13,14} In the case of the UO₂-Al reaction in fuel plates, the UAl₂ diffusion layer is at the limit of detection by x-ray diffraction. The UAl₂-Al side reaction which produces UAl₃ may also be very rapid. As will be discussed in a subsequent section, however, electron microscope studies have shown the existence of an extremely thin diffusion layer adjacent to the reacting UO₂ particle (see Figure 16). This layer is

TABLE VI

X-RAY DIFFRACTION IDENTIFICATION OF CONSTITUENTS
PRESENT IN A-UO₂ FUEL PLATES HEAT
TREATED AT 600°C

Heat Treatment at 600°C (Hr.)	Constituents Present				
	Al	UO ₂	UAl ₂	UAl ₃	UAl ₄
As-Fabricated	Yes	Yes	-	-	-
1.5	Yes	Yes	-	Yes	Yes
3	Yes	Yes	-	Yes	Yes
4.5	Yes	Yes	-	Yes	Yes
6	Yes	Yes	-	Yes	Yes
10	Yes	-	-	-	Yes

TABLE VII

X-RAY DIFFRACTION IDENTIFICATION OF CONSTITUENTS
PRESENT IN H-UO₂ FUEL PLATES HEAT
TREATED AT 600°C

Heat Treatment at 600°C (Hr.)	Constituents Present				
	Al	UO ₂	UAl ₂	UAl ₃	UAl ₄
As-Fabricated	Yes	Yes	-	Yes	-
0.5	Yes	Yes	-	Yes	Yes
1.5	Yes	Yes	-	Yes	Yes
3	Yes	Yes	-	Yes	Yes
4.5	Yes	Yes	-	Yes	Yes
6	Yes	-	-	Trace	Yes
8	Yes	-	-	-	Yes
10	Yes	-	-	-	Yes

therefore, tentatively identified as containing UAl_2 . Two thicker layers containing UAl_3 and UAl_4 , respectively, exist adjacent to it. The x-ray data show that UAl_3 and UAl_4 co-exist in the presence of UO_2 during reaction. The UAl_3 quickly converts to UAl_4 by a UAl_3 -Al side reaction after the UO_2 has completely reacted.

No change should occur in the UAl_4 lattice parameters when aluminum atoms are added to the defect structure. This was verified experimentally.

Optical and Electron Microscopy

The nature of the reaction occurring in fuel plates has been studied by optical and electron microscopy. Figures 13 and 14 show representative areas of as-fabricated A- UO_2 and H- UO_2 fuel plates. Approximately the same degree of reaction has occurred in each during fabrication. The degree of reaction determined by chemical analysis is 16.5 per cent in the A- UO_2 fuel plate and 17.0 per cent in the H- UO_2 plate. Minor fragmentation and stringering of the UO_2 has occurred. The larger UO_2 particles generally show slight peripheral reaction, whereas fragmented and stringered areas exhibit considerably greater reaction. Figure 15 shows a section of an H- UO_2 fuel plate which has been heat treated for 0.5 hour at 600°C. The degree of reaction has increased to 27.1 per cent. The fragmented and stringered areas show severe reaction. An apparent increase in the porosity of some of the

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Figure 13. As-Fabricated A-UO₂ Heat Treat Control Plate Showing Typical Structure; 16.5 Per Cent Reaction. As-Polished. 500X.

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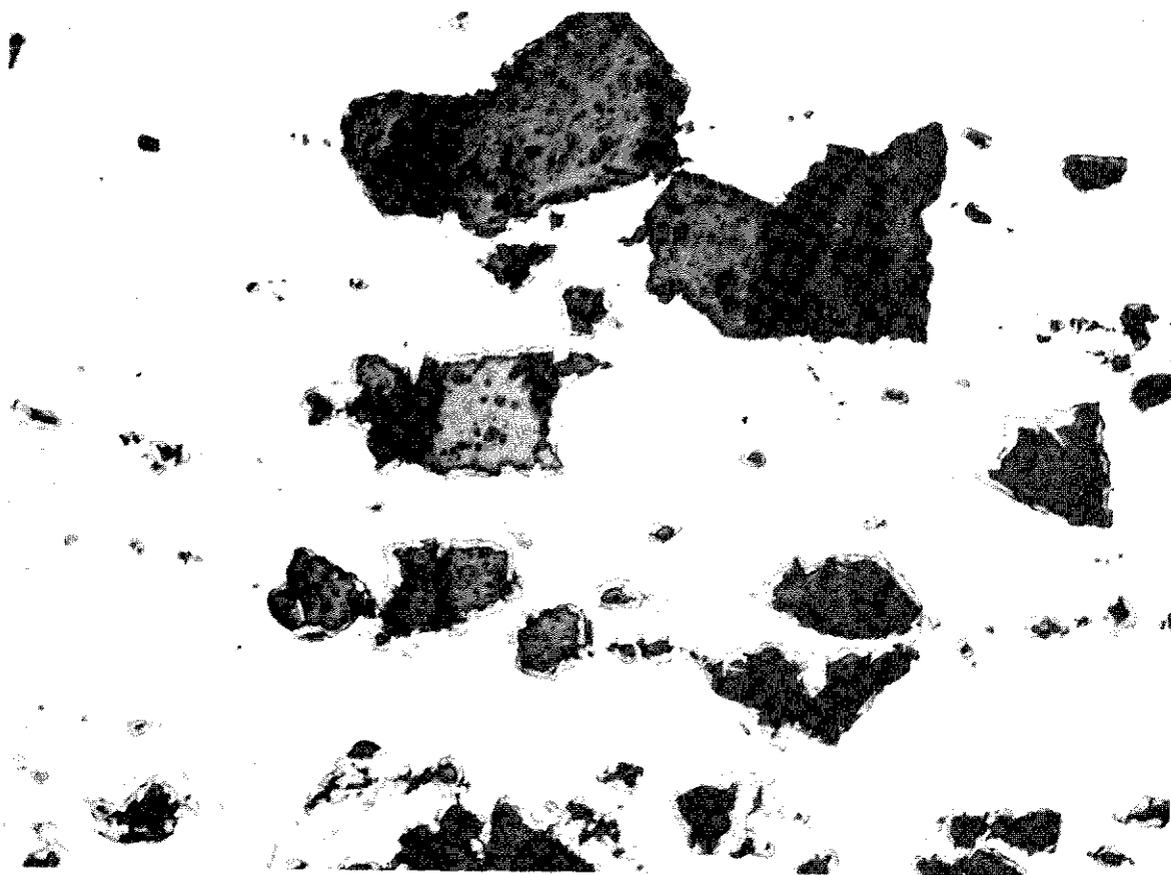


Figure 14. As-Fabricated H-UO₂ Heat Treat Control Plate Showing Typical Structure; 17.0 Per Cent Reaction. As-Polished. 500X.

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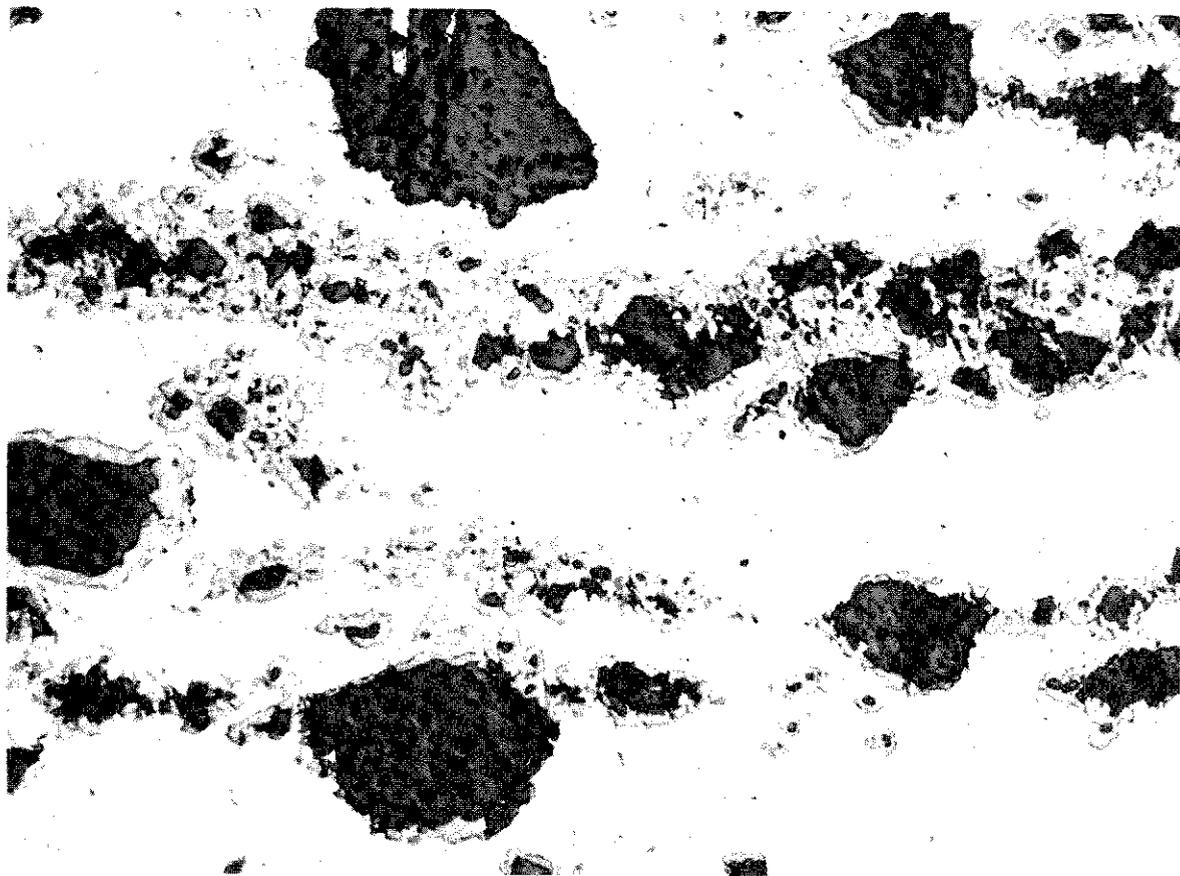


Figure 15. H-UO₂ Plate Heat Treated for 0.5 Hour at 600°C. Note increased reaction of fragmented UO₂ stringers and apparent lack of reaction of some UO₂ particles; 27.1 per cent reaction. As-Polished. 500X.

UO₂ particles is seen. This is not a general observation, however. It is interesting to note the apparent lack of reaction of several UO₂ particles.

The nature of the reaction products formed was defined by electron microscope studies. An unusual view of a reacting interface is shown in Figure 16. Two distinct reaction product zones are visible, and adjacent to the UO₂ particle is an apparently third diffusion zone. From U-Al couple studies and phase diagram considerations previously discussed, it logically follows that the diffusion zones are identified as containing UAl₄, UAl₃, and UAl₂ and are so labeled. Each zone would contain Al₂O₃ also. The UAl₄ + Al₂O₃ zone appears as a continuous region adjacent to the aluminum matrix. The UAl₃ + Al₂O₃ zone has a lamellar structure (see Figure 17) with the two phases showing a tendency to align parallel to the reacting UO₂ interface. The UAl₂ + Al₂O₃ zone was seen in only one other field. This zone is apparently extremely thin and consequently, visible only in rare, high angle cuts of polish through it. A supporting observation has been made of U-Al couples, in which a thin UAl₂ zone is formed at 600°C.¹³

A typical section of a reacting UO₂ particle is shown in Figure 17. Note the absence of the UAl₂ + Al₂O₃ diffusion zone. A short separation of the aluminum matrix and reaction diffusion zone is visible. Such separations have been observed at the aluminum-UAl₄ + Al₂O₃ and UAl₄ + Al₂O₃-UAl₃ + Al₂O₃ interfaces, but not at the UAl₃ + Al₂O₃-UO₂ particle interface. No porosity was noted in the diffusion zone or matrix aluminum, and no increase in the small amount of

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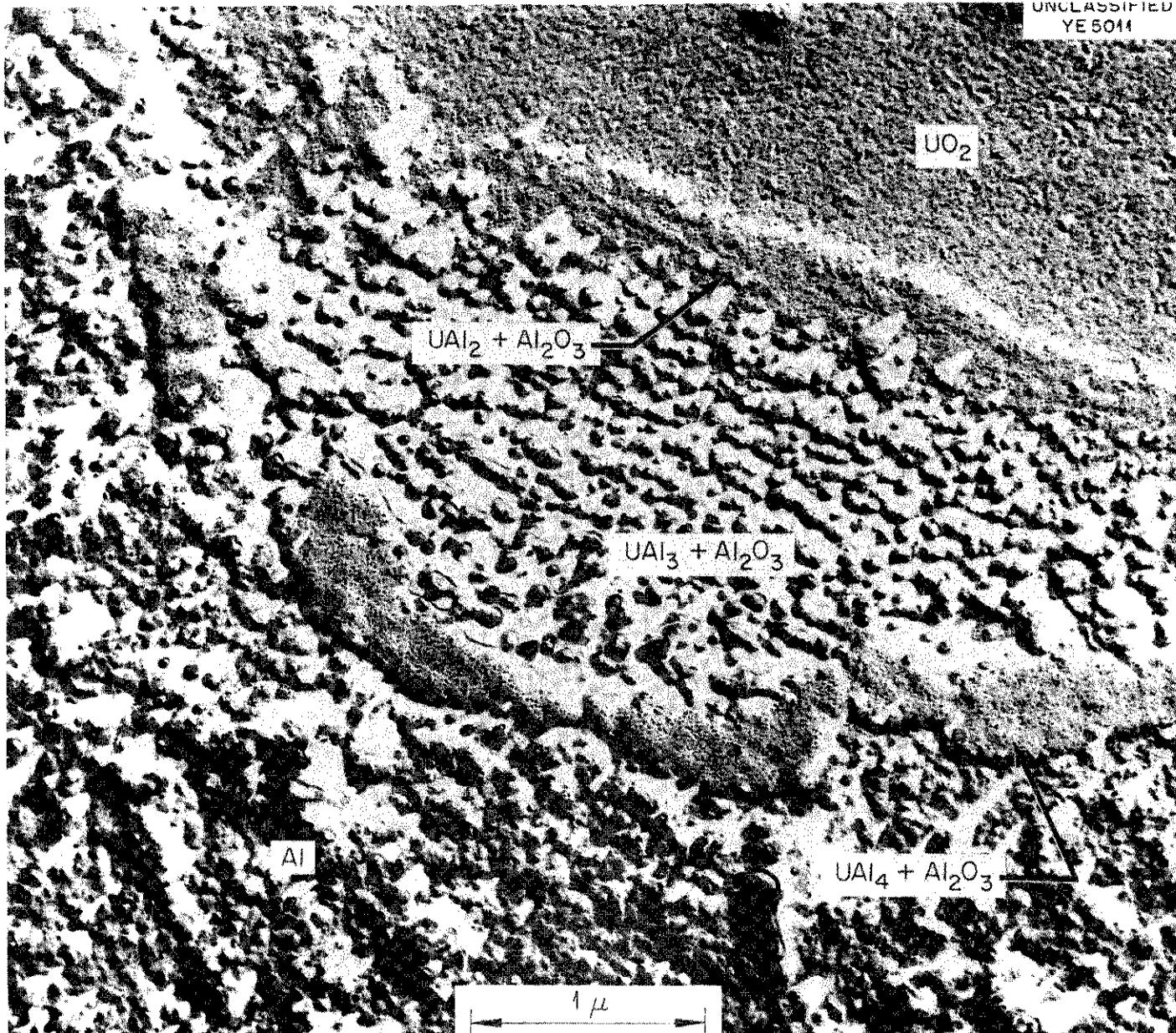


Figure 16. As-Fabricated H-UO₂ Heat Treat Control Plate. Etched with 85 parts H₃PO₄-15 parts H₂SO₄. Fax film, Pd shadowed carbon negative replica.

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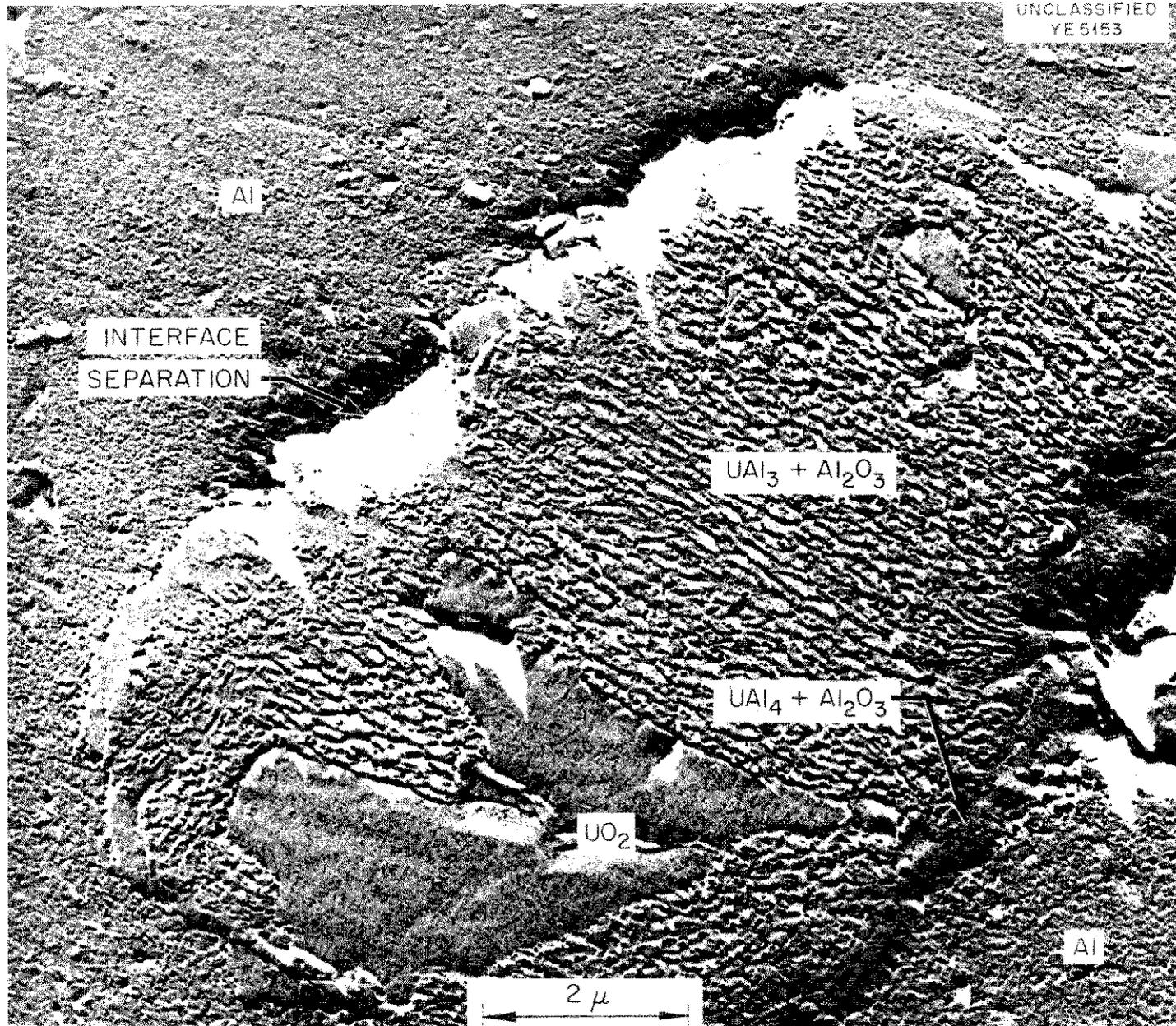


Figure 17. H-UO₂ Fuel Plate Heat Treated for 0.5 Hour at 600°C. Etched with 20 parts H₂O₂-5 parts H₂SO₄-balance water. Fax film, Pd shadowed carbon negative replica.

porosity present in the as-received UO_2 of either type was observed. Electron microscope examination of as-polished fields comparable to that shown in the etched condition in Figure 17 showed no porosity in either reaction zone, and also verified that the observed lamellar structure is an etching effect. It should be emphasized that the total growth observed was only 0.4 per cent. The interface separation noted may represent a part of this small increase in core porosity. It is unfortunate that specimens which have reacted to a greater extent are so difficult to process metallographically.

Fuel Plate Growth

Roberts has reported that hydrogen is chemisorbed on UO_2 in the temperature range of $400 - 700^\circ\text{C}$.¹⁵ The hydrogen probably reacts with the surface oxygen atoms, and at least one complete layer can be formed. Increased hydrogen adsorptions were observed, however, thus suggesting the possibility of solubility of hydrogen in the bulk UO_2 . Possible mechanisms include lattice solubility and the mobility of $(\text{OH})^-$ ions into the lattice. This information was the basis for a prior explanation of the volume increase of UO_2 -Al compacts and fuel plates which has been observed. It also was the reason for preparing UO_2 from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in both hydrogen and argon in this study. The argon has no tendency to chemisorb on the UO_2 surface during cooling from high firing, and thus it would be anticipated

that subsequent growth of A-UO₂ fuel plates during reaction would be greatly reduced.

The reproducibility of growth during heat treatment of similar fuel plates was found to be quite good. Growth data for A-UO₂ and H-UO₂ fuel plates heat treated for 24 hours at 600°C are summarized in Table VIII. The growth of individual fuel plates in each group is accurate within plus or minus four per cent of the average growth of the group.

Significant growth occurs during heat treatment of A-UO₂ and H-UO₂ fuel plates at 500 - 600°C, and the data are plotted in Figures 18 and 19. The A-UO₂ plates reach a maximum growth of approximately 25 per cent in about 16 hours at 600°C, while the H-UO₂ plates attain approximately 19 per cent in about 20 hours. These values represent an experimentally significant difference in the levels of maximum growth. Plates of each UO₂ show greater growth during heat treatment at 550 and 575°C than was attained at 600°C.

The results of heat treating a second group of A-UO₂ and H-UO₂ fuel plates for extended times at 550, 575, and 600°C are shown in Figure 20. Maximum growth was attained in the plates heat treated at 575 and 600°C. The two plates heat treated at 550°C failed in-test due to localized cladding rupture, and thus maximum growth was not attained. Both plates heat treated at 575°C attained experimentally significant, greater growth than those heat treated at 600°C, with the A-UO₂ plate growing more than the H-UO₂ plate at each temperature. The two plates heat treated at 550°C grew more than those at 600°C

TABLE VIII

REPRODUCIBILITY OF FUEL PLATE GROWTH AFTER
HEAT TREATMENT FOR 24 HOURS AT 600°C

Type UO ₂ in Fuel Plate	Growth Attained (%)	Average Growth for Group (%)	Deviation from Average Group Growth (%)
A-UO ₂	25.28	26.23	- 3.8
A-UO ₂	26.94		+ 2.6
A-UO ₂	26.46		+ 1.2
H-UO ₂	19.68	19.83	- 0.8
H-UO ₂	20.40		+ 2.8
H-UO ₂	19.96		+ 0.8
H-UO ₂	19.26		- 2.8

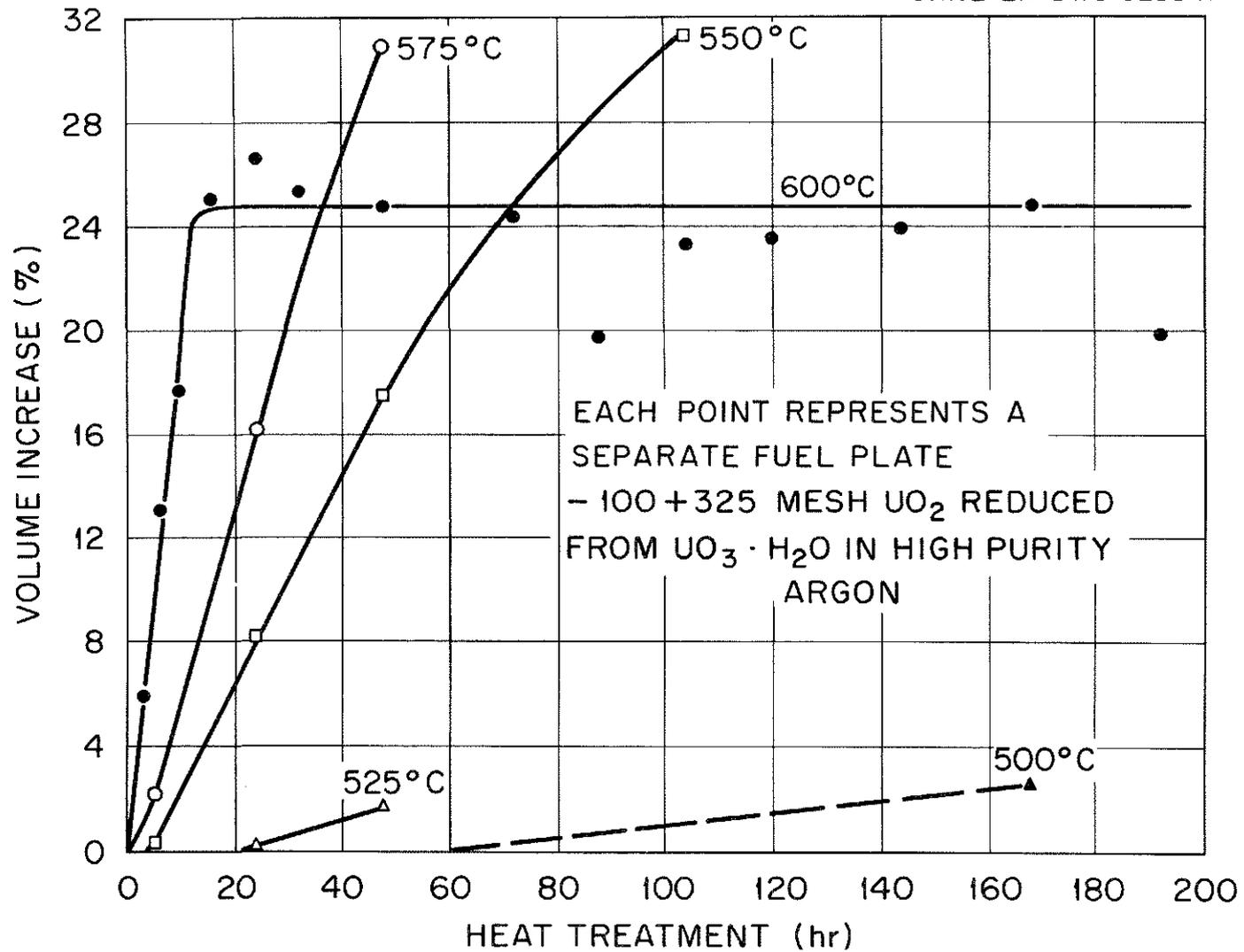


Figure 18. Growth Characteristics of 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates at Selected Temperatures.

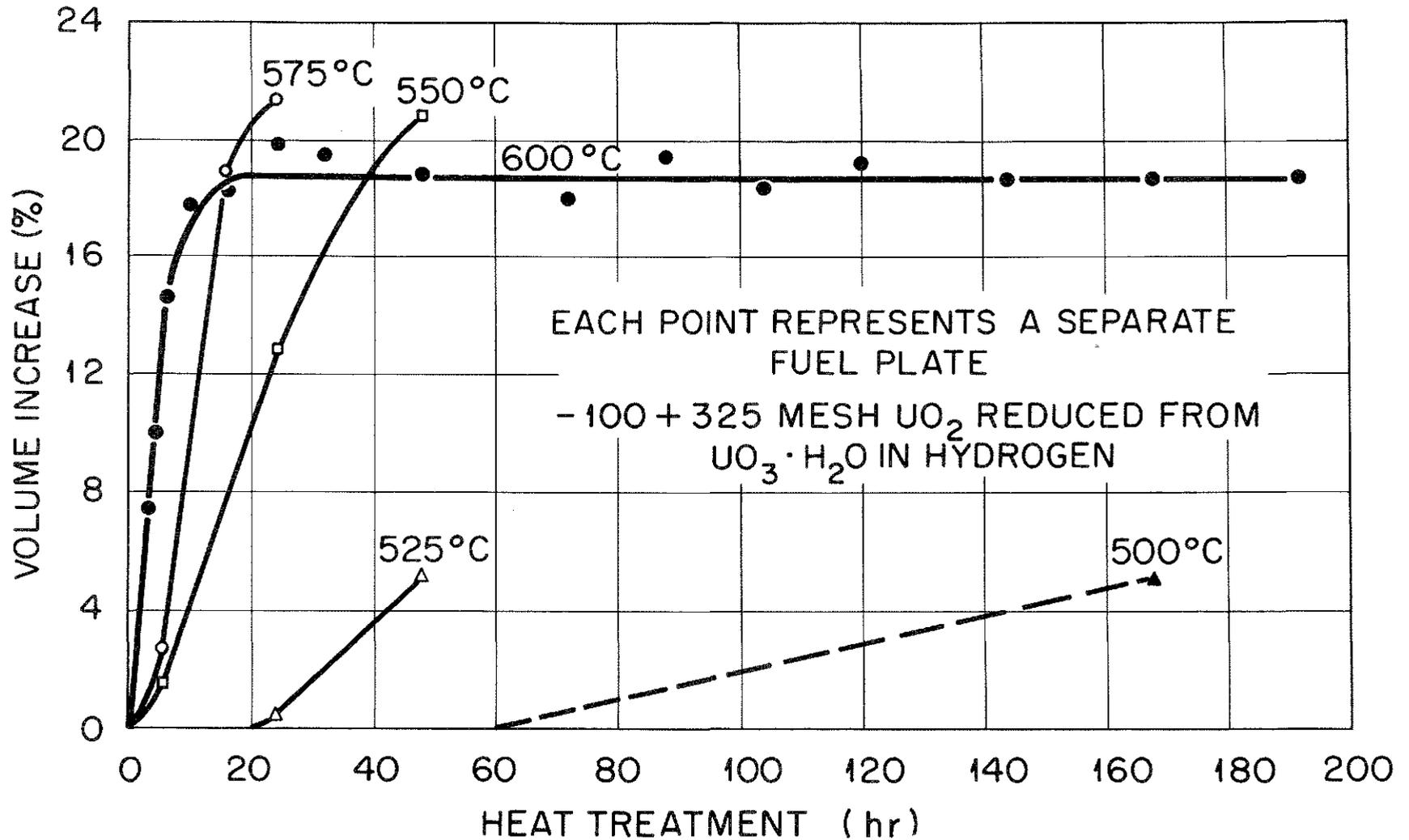


Figure 19. Growth Characteristics of 52.3 Weight Per Cent UO₂-Aluminum Fuel Plates at Selected Temperatures.

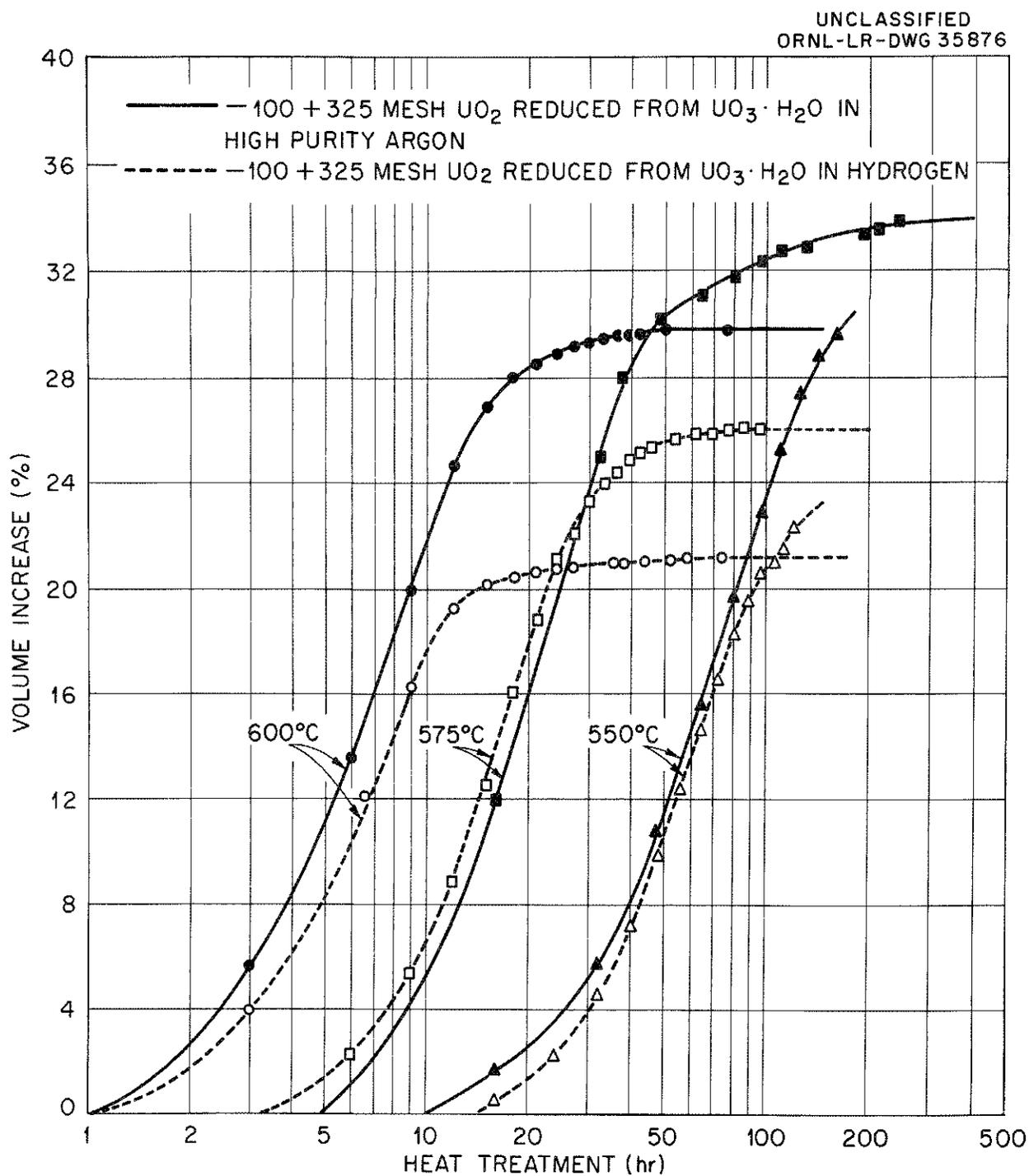


Figure 20. Growth Characteristics of 52.3 Weight Per Cent UO₂-Aluminum Fuel Plates at Selected Temperatures.

but less than those at 575°C, and the A-UO₂ plate had grown more than the H-UO₂ plate at the time of failure. The extent of additional growth, had they not failed, is uncertain. Growth takes longer to start at the lower heat-treatment temperatures. The growth rates of the A-UO₂ and H-UO₂ plates at each heat-treatment temperature are approximately the same and they both decrease significantly with temperature.

It is evident that the A-UO₂ and H-UO₂ plates of this second group heat treated at 600°C have attained significantly greater growth than the comparable plates shown in Figures 18 and 19. The reason for the difference in growth levels is that the as-fabricated, un-heat treated plates of the second group had 10 - 15 per cent less reaction. Growth therefore could be observed over a greater span of reaction. The significance of these observations with regard to a postulated mechanism of fuel plate growth will be discussed in the following section.

The severe distortion which accompanies growth of plates of each UO₂ during heat treatment at 600°C is shown in Figures 21 and 22. Distortion is seen to increase with growth.

The reference plate containing an aluminum core instead of the dispersed fuel showed no growth after heat treatment for 40 hours at 600°C. It is evident, therefore, that fuel plate growth is not caused by heat treatment of the aluminum matrix itself.

The degree of reaction-volume increase relationship during heat treatment at 500 - 600°C is shown for A-UO₂ and H-UO₂ plates in

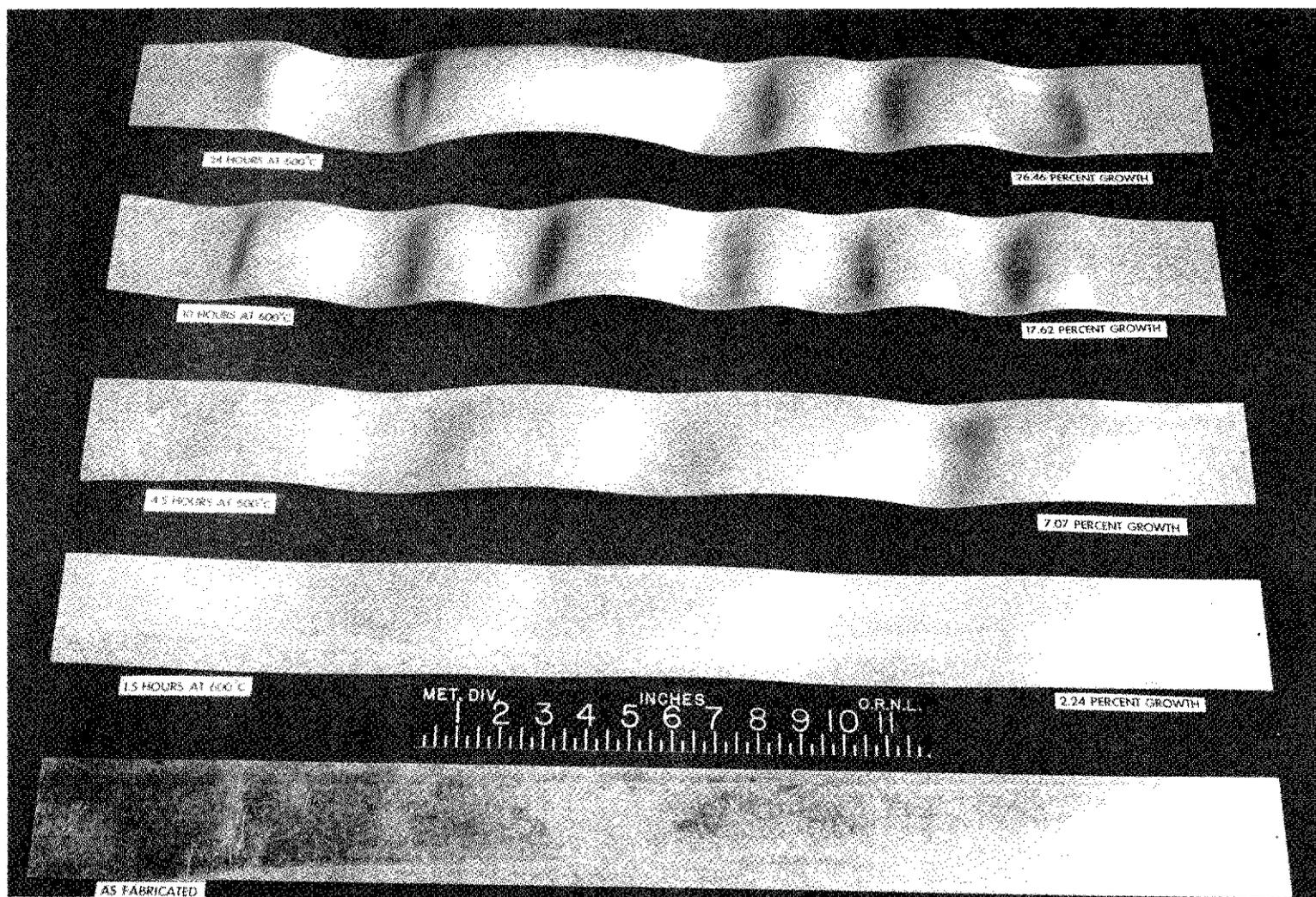


Figure 21. Distortion of A-UO₂ + Al Fuel Plates Due to Reaction During Heat Treatment at 600°C.

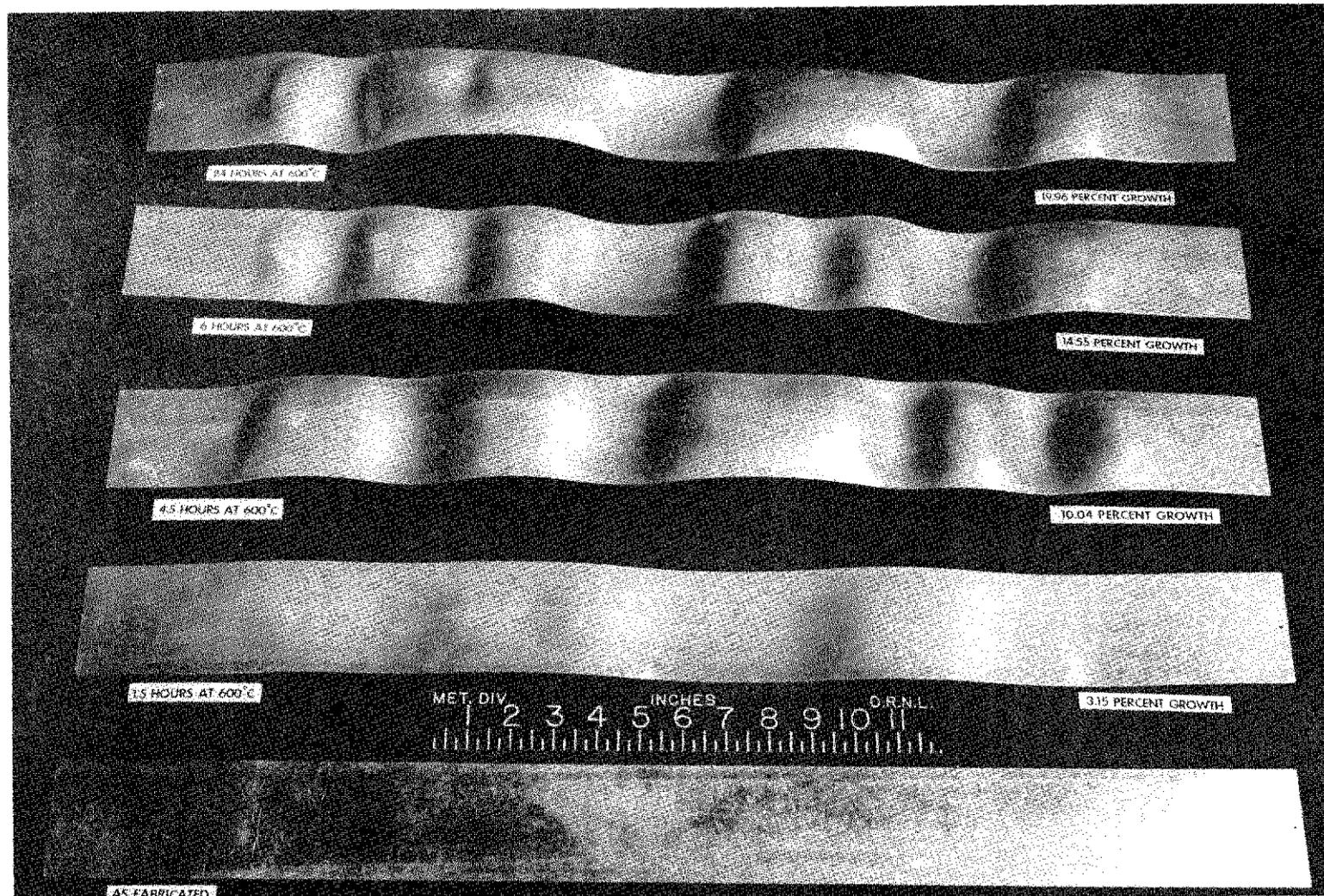


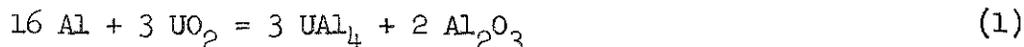
Figure 22. Distortion of H-UO₂ + Al Fuel Plates Due to Reaction During Heat Treatment at 600°C.

Figures 23 and 24. The increased fuel plate growth with increased degree of reaction is apparent. The relationship of growth to reaction will be discussed in detail in the following section.

Proposed Mechanism of Fuel Plate Growth

The absence of growth during heat treatment of the plate containing an aluminum core indicates that growth is not caused by heat treatment of the aluminum matrix itself. Two potential mechanisms by which a solid-state reaction could exhibit a volume increase are as follows: first, the reaction products could occupy a greater specific volume than the reactants consumed, and second, a Kirkendall effect could be operative. The feasibility of each of these mechanisms has been evaluated in detail and, as shown below, neither was found applicable to the phenomenon under consideration.

Consider the following equation for the stoichiometric reaction of UO_2 to UAl_4 :



Using theoretical density values of 2.68 g/cc for Al, 10.9 for UO_2 , 6.0 for UAl_4 , and 4.0 for Al_2O_3 , it may be shown that a 5 per cent volume decrease should accompany the solid-state reaction - not volume increases of 20 - 30 per cent as were observed. Similarly, and using a theoretical density value of 6.7 g/cc for UAl_3 , no volume change should occur when UAl_3 converts to UAl_4 . It is apparent, therefore, that volume increase encountered during reaction in fuel plates cannot

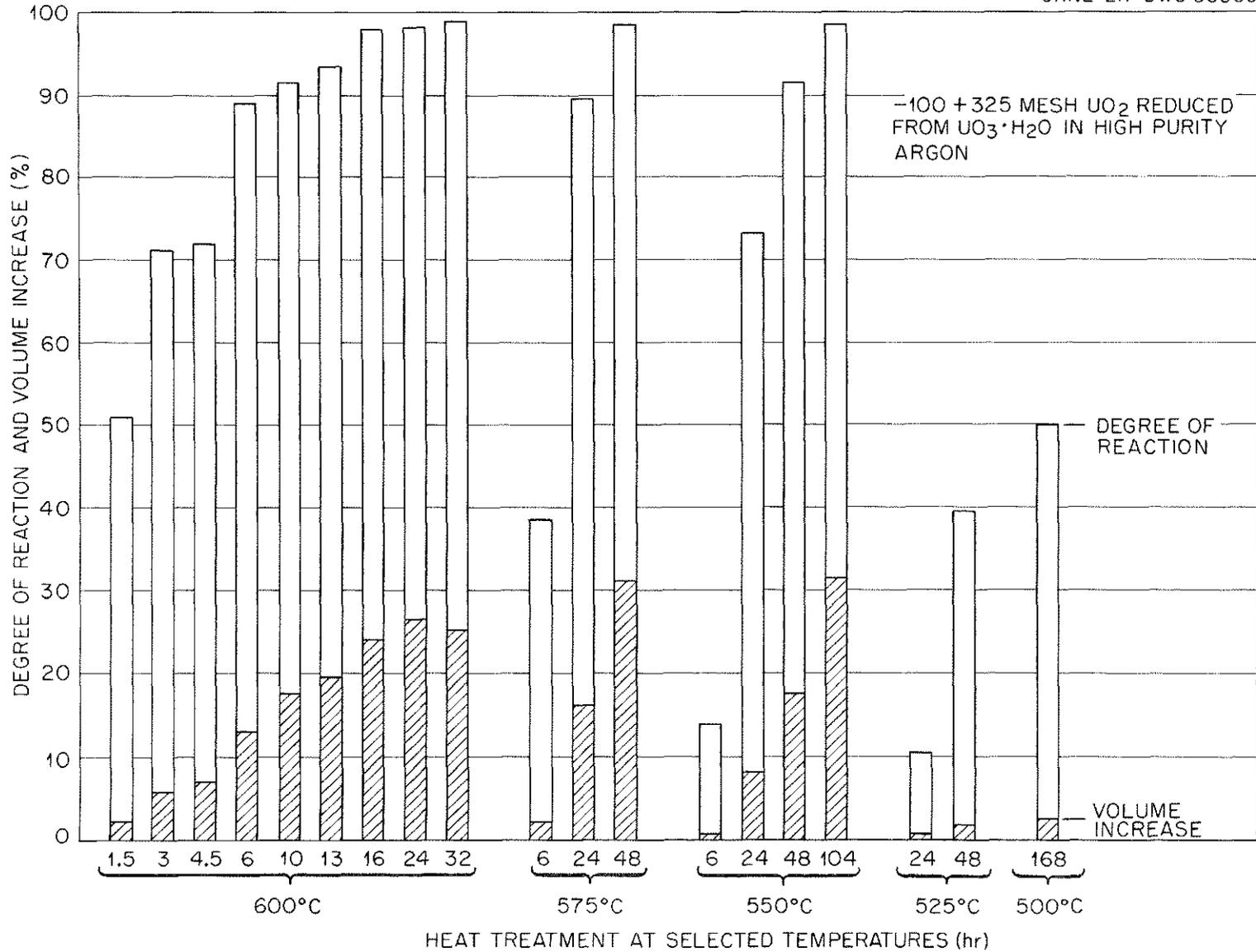


Figure 23. Degree of Reaction-Volume Increase Relationship at Selected Heat Treatment Times and Temperatures for 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates.

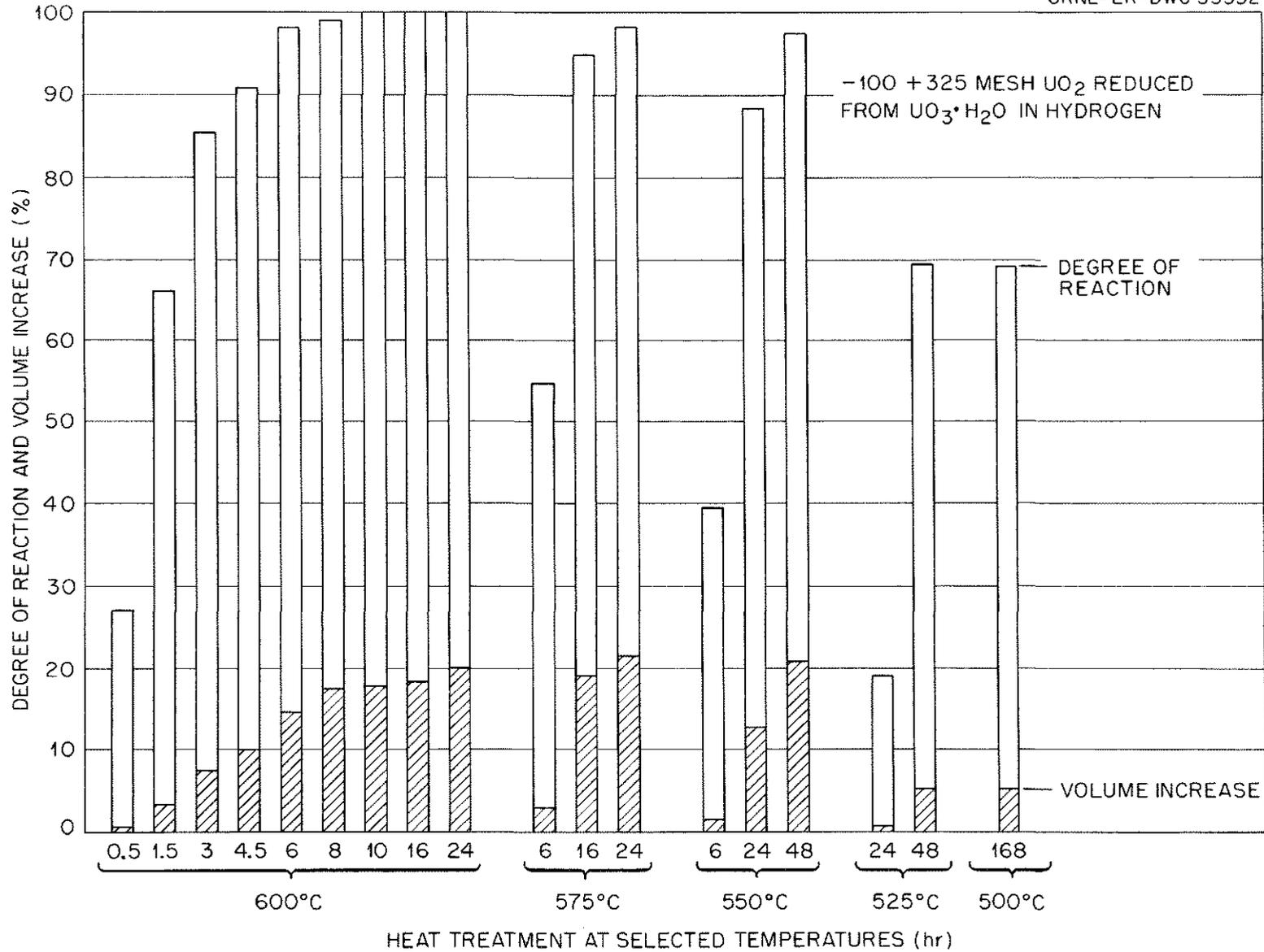


Figure 24. Degree of Reaction-Volume Increase Relationship at Selected Heat Treatment Times and Temperatures for 52.3 Weight Per Cent UO_2 -Aluminum Fuel Plates.

be explained on the basis of change in specific volume during reaction.

Large volume expansions of 50 - 180 per cent during the solid-state reaction of various binary metal systems, such as U-Al, Be-U, and Be-Th, have been reported by Williams.¹⁶ The volume changes observed were far greater than the maximum of approximately 5 per cent which would be expected from volume changes associated solely with the phase changes accompanying the formation of alloys. The expansion was attributed to the Kirkendall effect, in which an excess of vacancies are formed when there is an appreciable difference in the diffusion rates between the component atoms of a system. Volume expansion was thus associated with the formation and growth of voids on the side of the diffusion interface which contained the more rapidly diffusing component. For a phase to exhibit diffusional porosity, it must be stable over a range of composition.

Williams has reported that sintering compacted U-Al mixtures of composition UAl_3 at $1100^\circ C$ gave very friable, swollen compacts which contained UAl_3 and UAl_4 .¹⁶ Both hot and cold compacted mixtures containing 18 weight per cent uranium gave no anomalous expansions upon sintering between $400 - 600^\circ C$. The final structure consisted of UAl_4 in a matrix of aluminum. For compacted mixtures, the maximum expansion upon sintering occurred around the composition UAl_3-UAl_4 . They feel that diffusional porosity may be the cause of swelling, and that UAl_4 may be the phase responsible since it apparently has a range of homogeneity.

Kiessling has made a detailed study of U-Al couples.¹³ Reaction starts by formation of nuclei of UAl_2 in the uranium phase near the interface. The UAl_2 grains grow into the uranium, and UAl_3 and UAl_4 are formed on the aluminum side. Some UAl_3 also grows on the uranium side of the initial boundary and in close contact with UAl_2 . The UAl_4 grows into the aluminum, forming a rather coarse and porous structure. Porosity is attributed to the Kirkendall effect.

The diffusion characteristics of the UO_2 -Al reaction appear to differ, however, from that observed in U-Al couples because the UAl_4 formed does not exhibit porosity. Possibly, the net difference in the aluminum and uranium diffusion rates, or the driving force for the Kirkendall effect, is less in the case of the UO_2 -Al reaction, thus accounting for the apparent lack of diffusional porosity. In any case, however, electron microscope examination of reacted fuel plates has not revealed evidence of porosity either in the UO_2 particle, the reaction product zone, or the matrix aluminum. The fact that A- UO_2 and H- UO_2 fuel plates heat treated to maximum growth at $575^\circ C$ attain significantly greater growth than those heat treated at $600^\circ C$ (see Figure 20) is inexplicable by the Kirkendall effect. It was concluded, therefore, that the volume increase observed during reaction in fuel plates was not caused by the Kirkendall effect.

It is known that the matrix aluminum and each type of UO_2 studied incorporate significant gas in the fuel plate core.⁴ The hydrogen available from the reacted aluminum alone is sufficient to create a maximum pressure of 960 psi at $600^\circ C$ in a volume equal to the

original fuel-plate-core porosity, and thus cause growth. The implications of this mechanism of growth will now be discussed in detail, and an attempt will be made to explain the experimental observations on this basis.

A co-plot of the growth and reaction rates at 600°C for the A-UO₂ and H-UO₂ fuel plates, Figure 25, shows that the growth of both types of fuel plates continues for an extended period of time after the UO₂ reaction is essentially complete. In the case of the H-UO₂ plates, reaction is complete after 10 hours, but growth slowly continues for an additional 10 hours. Similarly, reaction is 90 per cent complete in the A-UO₂ plates after 6 hours, but only 13 per cent growth has been attained; growth continues for 10 more hours, at which time a maximum growth of 25 per cent--almost double that at 90 per cent reaction--has occurred. This behavior is consistent with the postulate of growth by internal-gas-pressure buildup during reaction. Growth occurs when the internal pressure exceeds the creep strength of the cladding, and would be expected to continue after completion of reaction until the internal pressure was reduced by increase in the core volume to the point where creep effectively ceased.

The postulate that growth was due to hydrogen chemisorbed on the UO₂ surface is incorrect. If growth resulted from the release of chemisorbed gases, the A-UO₂ fuel plates should have grown less than the H-UO₂ plates during reaction, based upon relative pressure considerations. The data show, however, (see Figures 18 - 20) that the A-UO₂ plates grow significantly more at 575°C and 600°C than

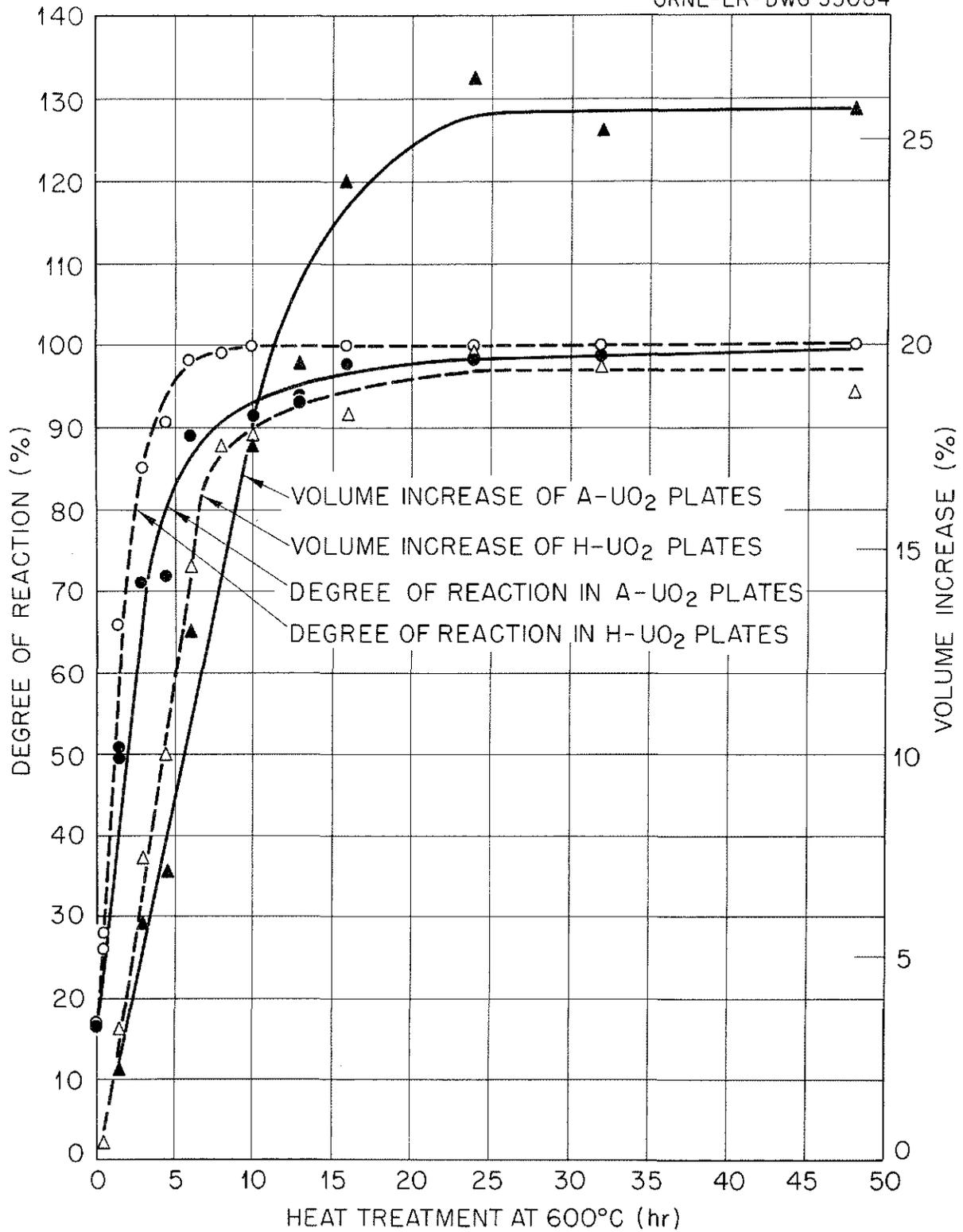


Figure 25. Reaction Rate and Growth Characteristics of 52.3 Weight Per Cent UO₂-Aluminum Fuel Plates.

do the H-UO₂ plates. Some hydrogen actually may be chemisorbed on the UO₂ surface and ultimately released during reaction, but its effect on growth should be small.

Greater growth also occurs on heat treatment at the lower temperatures. Figures 18 - 20 show that the A-UO₂ and H-UO₂ plates heat treated at 550 and 575°C consistently grew more than those heat treated at 600°C.

The observed effects of type of UO₂ and of temperature on growth are not inconsistent with the proposed growth mechanism. The difficulty of explaining the observed effects with the available data is a result of the numerous variables involved. The variables include relative amounts of gas associated with each UO₂, reaction rate, diffusion of hydrogen through the cladding, strain rate (growth rate), and the effects of temperature upon these.

A detailed investigation and verification of the proposed mechanism of fuel plate growth was beyond the scope of the study described. Such an investigation is, however, presently underway at the Oak Ridge National Laboratory. The results to date support the mechanism proposed.⁴

CHAPTER VII

CONCLUSIONS

The following conclusions can be stated as a result of the reported investigation:

1. Uranium dioxide reacts slowly with aluminum at 600°C in 50 weight per cent UO_2 pressed compacts, attaining 75 per cent completion after 80 hours in static vacuum. The primary reaction products are UAl_3 and Al_2O_3 . The absence of UAl_4 is not understood. A volume increase accompanies the reaction.

2. Uranium dioxide reacts with aluminum in 52.3 weight per cent UO_2 fuel plate cores to form UAl_4 and Al_2O_3 . Intermediate reaction products are UAl_2 and UAl_3 . Reaction is rapid at 600°C, attaining 90 - 100 per cent completion in 10 hours, and moderate at 500°C, attaining 50 - 70 per cent completion in one week.

3. Three reaction product zones are visible in reacted fuel plate cores by electron microscopy. The zones are tentatively identified as containing UAl_2 , UAl_3 , and UAl_4 , respectively. The extremely thin UAl_2 zone generally is not detectable by x-ray diffraction. No evidence of diffusional porosity is noted.

4. Volume increases of 20 - 30 per cent accompany reaction in fuel plates. Plates containing UO_2 reduced from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in argon attain greater total growth during heat treatment at 575 and 600°C than do plates containing UO_2 reduced from $\text{UO}_3 \cdot \text{H}_2\text{O}$ in hydrogen. Plates containing both types of UO_2 attain greater growth during heat

treatment at 550 and 575°C than at 600°C. The rate of fuel plate growth decreases with heat-treatment temperature.

5. The observed volume increases cannot be explained on the bases of specific volume changes associated with the solid-state reaction or a Kirkendall mechanism. A prior explanation that growth is due to hydrogen chemisorbed on the UO_2 surface is shown to be incorrect.

6. A growth mechanism based upon gas generation within the fuel plate core during reaction is proposed. Growth occurs by creep due to the large internal pressure which is developed. The observed effects of type of UO_2 and of temperature on growth are not inconsistent with the proposed growth mechanism. The difficulty of explaining the observed effects with the available data is a result of the numerous variables involved. Supplementary investigation supports the proposed growth mechanism.

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