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THE DIFFUSION OF URANIUM INTO ALUMINUM

By

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THE DIFFUSION OF URANIUM INTO ALUMINUM

INTRODUCTION

Changes in the properties of reactor materials during irradiation influence the design and successful operation of a reactor. Unfortunately, the mechanism and magnitude of many of the radiation induced and accelerated in-pile reactions are difficult to ascertain and are unknown. In particular, the effect of irradiation on the diffusion rates of the fuel element components, uranium and aluminum, has not been established. Since most reactor fuel elements consist of a fuel core enclosed in a suitable container, diffusion of core and container material may occur to an extent which will markedly alter the performance of a given fuel element. The lack of available data on the effect of irradiation on the diffusion rates of fuel element materials has warranted a systematic comparison of the ex-pile and in-pile diffusion rates of these fuel materials. Such a comparison, however, requires standardized preparation of specimens prior to the diffusion anneals in order to assure valid conclusions. This report presents the methods and techniques used to obtain maximum and reproducible rate coefficients for the penetration of aluminum by uranium, a necessary prerequisite for the proper interpretation of in-pile experiments currently in progress.

SUMMARY AND CONCLUSIONS

The methods used and the results obtained in a study of the maximum rate of penetration of uranium into aluminum in the temperature range 200-390 C (392-734 F) are described in this report. The maximum values for the penetration coefficient, K_T, determined from the relationship $K_T = x^2/t$, are 0.075, 0.50, and 6.1×10^{-6} inches^2/hr at temperatures of 200, 250 and 390 C (392, 482, and 734 F), respectively. The activation energy, Q, from the expression $K = K_o e^{-Q/RT}$ is 14,300 calories per mole.

The maximum penetration of the aluminum by the uranium cited here is generally twice as great in specimens previously cleaned by cathodic vacuum etching, which completely removes surface contaminants, than in specimens cleaned by chemical methods. Couples annealed in the temperature range 200-390 C (392-734 F) fracture at the aluminum-diffusion zone interface when they are pulled apart, whereas couples annealed at higher temperatures fracture within the diffusion zone. Large cone-shaped voids form in the diffusion zone during hot pressing at 450-500 C (842-932 F). The results of this investigation will provide a basis for interpreting and determining the effect of pile irradiation on the maximum diffusion rate of uranium into aluminum.

DISCUSSION

Evaluation

The diffusion of one substance into another can conveniently be considered to occur as a result of some driving force which must overcome obstacles of varying complexities. Fick's laws of diffusion consider this driving force to be a function of the existing concentration gradient, and in some cases, a satisfactory solution of Fick's equations can be obtained and utilized.(1) More frequently, however, approximations must be introduced into the mathematical solution of Fick's laws in order to extend their utility in describing diffusion rates. For the general case of a diffusion experiment in which intermetallic compounds such as UAl_3 are formed, and in which the effect of purity, homogeneity, grain structure, interface conditions, anisotropy or pressure on the overall rates of diffusion are unknown, results and their interpretations suffer from inherent limitations; the magnitude of these limitations depends on the refinements incorporated in the experiments. A survey of the existing literature on

(1) Barrer, R. M., Diffusion in and Through Solids, Cambridge, 1951.

uranium-aluminum diffusion revealed a lack of agreement in the results obtained by various investigations.[2][3] Since the ultimate utility of ex-pile diffusion data is a direct function of its serving as a representative reference for the interpretation of the effect of pile irradiation on the diffusion rates of uranium-aluminum couples, ex-pile diffusion experiments must be conducted in a fashion compatible with in-pile experiments. Application of the Grube or Matano method of determining diffusion coefficients,[4] which is based on the accurate sampling and analysis of the diffusion zone, was not considered because the radioactivity of irradiated couples makes such accurate chemical sampling and analysis impractical.

The diffusion in ex-pile and in-pile couples can, however, be conveniently described by the simple expedient of measuring microscopically the distance between the original uranium-aluminum interface and the terminus of the diffusion zone into the aluminum after a given diffusion anneal. Such penetration measurements can in turn be related to the time of anneal by the approximate expression $x^2 = K_T t$, where x is the maximum penetration of uranium into the aluminum in inches, K_T is the maximum penetration coefficient at a given temperature, and t is the time of anneal in hours. The penetration coefficient, analogous to a diffusion coefficient, can be related to temperature by the expression, $K = K_o e^{-Q/RT}$, where K is the maximum penetration coefficient, K_o the proportionality constant, Q the activation energy in calories per mole, R the gas constant in calories per degree per mole, and T the absolute temperature. The plot of lnK versus $\frac{1}{T}$ provides a convenient basis for expressing and comparing penetration coefficients.

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(2) LeClaire, A. D., and I. J. Bear, AERE-M/R-878, March 5, 1952, (SECRET).

(3) Storchheim, S., and J. Zambrow, SEP-105, October 30, 1952, (SECRET).

(4) Rhines, F. N., and R. F. Mehl, Trans. of A.I.M.E., Inst. of Metals Div., Vol. 128, 185, 1938.

Microscopic Measurements

Uranium-aluminum diffusion couples can be ground, polished, and etched for microscopic examination. The diffusion or intermetallic zone present is very brittle, as can be inferred from the hardness values obtained on a representative specimen illustrated in Figure 1. Since the diffusion zone as it appears on a polished surface perpendicular to the original interface is generally non-uniform, the microscopic measurements in all probability will yield a value of the penetration coefficient less than the maximum value. Microscopic examination of the fracture interfaces of couples that were pulled apart after a vacuum anneal at temperatures in the range 200-390 C (392-734 F) established that they fracture at the aluminum-diffusion zone interface, as illustrated in Figure 2. All fracture interfaces of these couples contained areas in which diffusion had not occurred; such areas established the location of the original uranium-aluminum interface. X-ray diffraction analysis of the fracture surfaces identified UAl_3 on the diffusion zone interface, whereas the adjacent fracture interface contains only aluminum. These observations coupled with the metallographic appearance and the hardness traverse of the diffusion zone cross-section indicate that the fracture interface represents the penetration terminus of uranium into the aluminum. It follows that the maximum penetration, x, of uranium into aluminum can most conveniently be determined after mechanical separation of the couple by a measurement of the maximum height of the UAl_3 peaks above the initial uranium-aluminum interface. This procedure eliminates the necessity for metallographic sectioning and polishing, avoids the ever present possibility of a destructive shearing fracture of the bond, and permits direct measurement of the maximum penetration of uranium into the aluminum.

Preparation of Couples

Reactor grade uranium after beta heat treatment and 2S aluminum were machined into cylindrical disks, 1/2-inch in diameter by 1/4-inch thick, and then vacuum annealed: the aluminum for seven hours at a temperature of 450 C (842 F), and the uranium for thirty hours at 550 C (1022 F). The specimens were then lapped and carefully polished to assure a surface flatness to within 0.0002 inches except in the immediate vicinity of the edges. Soluble surface contaminants were removed with xylene and acetone, and the specimens were cathodically vacuum etched in the apparatus described in a previous report to provide clean metallic surfaces.(5) Four uranium or four aluminum disks were subjected to a simultaneous etching in a dynamic krypton environment at a pressure of 75 microns of mercury, a potential of 1300-2700 volts, and a current density of approximately three milliamperes per square inch of exposed cathode. After a fifteen-minute etching period, the chamber was filled with argon gas previously purified by passage through a zirconium chip furnace with a central zone heated to 600 C (1112 F) and finally through a cold trap. All specimens were transferred in an argon environment into an argon filled glove box equipped with vacuum storage facilities and clean handling equipment to assure freedom from contamination.

Two different methods, hot pressing and mechanical constraining, were used to prepare couples for subsequent final diffusion anneals. In the first case, specimens were joined in an inert atmosphere to form a minimum initial diffusion zone at temperatures of 450-500 C (842-932 F) under a pressure of 11 tons/in^2 and for times of about one minute; in the second case, the specimens were held in intimate contact by means of a constraining clamp which exerted a pressure of about five tons/in^2 measured at room temperature.

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(5) Bierlein, T. K., "Investigations on the Microstructure of Uranium - Replication, Cathodic Vacuum Etching, and Optical and Electron Microscopy," HW-34390, January 18, 1955, (SECRET).

Diffusion Anneal

Since the temperature range of interest in in-pile uranium-aluminum diffusion studies lies in the range 200-400 C (392-752 F), and since the annealing time for in-pile experiments must of necessity be some multiple of the reactor time cycle, ex-pile diffusion anneals were conducted in the equipment illustrated in Figure 3 for comparable times and at comparable temperatures. A platinum-platinum 13 per cent rhodium thermocouple calibrated to ± 0.5 C and an auxiliary chromel-alumel thermocouple were mounted inside the vacuum furnace tube to measure the temperature of the couple; Foxboro controllers were used to control the heaters of the Marshall furnaces. The E.M.F. generated by the platinum thermocouple was applied to a recorder circuit having a deflection sensitivity of 0.1875 inches per degree centigrade at a temperature of 225 C (437 F), full scale of the recorder being equivalent to a ΔT of 100 C (180 F). Figure 4 portrays schematically the arrangement of the controlling and recording circuit which provided and indicated a temperature constancy during the diffusion anneals of ± 2.5 C; pressure in the furnace tube was maintained at less than one micron of mercury by continuous pumping with an oil diffusion pump.

Experimental Results

In the early stages of planning ex-pile control experiments for the evaluation of in-pile diffusion studies, it seemed desirable to irradiate uranium-aluminum couples having an initial minimum diffusion zone. Attainment of suitable prebonded couples was attempted by hot pressing in a helium atmosphere at 450-500 C (842-932 F) under a pressure of 11 tons/in^2 for periods of about one minute. Such couples were examined metallographically and then diffusion annealed; fracture of the couples occurred due to thermal stressing. The appearance of the fracture interfaces of a prebonded couple which was pulled apart after hot pressing is

illustrated by the stereomacrographs and macrograph of Figure 5. It is evident that the aluminum has extruded over the peripheral edges of the uranium during hot pressing at a temperature of 500 C and at a pressure of 11 tons/in^2. The crystalline layer which adheres only partially to the base uranium has been identified as UAl_3 by x-ray diffraction methods. If this layer is broken away from the uranium, an underlying network of dome-shaped holes within the diffusion zone is revealed; such holes have been observed by other investigators.[6] Figure 6, a micrograph of a cross-sectional area of the diffusion zone of a couple hot pressed at a temperature of 500 C (932 F) for a period of one minute under a pressure of 11 tons/in^2, illustrates the typical appearance of the voids which develop during the high temperature anneal. The flat bases of the dome-shaped voids are near the uranium interface and the apices are near the aluminum interface.

The use of prebonded U-Al specimens prepared by hot pressing at elevated temperatures for in-pile and out-of-pile diffusion studies has several severe limitations: (1) a large number of voids exist in the diffusion zone; (2) the applied pressure and temperature of hot pressing produces a diffusion zone the appearance and properties of which differ markedly from those of the diffusion zones obtained at low temperatures; (3) the non-uniform nature of the U-Al diffusion zone prohibits an accurate evaluation of the maximum thickness of the initial diffusion zone prior to irradiation; and (4) the high temperature, hot pressed couples frequently fracture due to thermal expansion during subsequent diffusion anneals. To circumvent these limitations, specimens of uranium and aluminum were not prebonded but were mechanically constrained in the stainless steel specimen clamping container, shown in Figure 3a, and were then subjected to the desired diffusion anneal. The constraining force at room

(6) Bareis, D. W., BNL-38, December 15, 1949, (SECRET).

temperature exerted by the threaded plug of this clamp onto the specimens is 2,200 pounds, equivalent to a pressure of about five tons/in^2 at the specimen interfaces. Examination of various couples indicated that no deformation of the aluminum resulted from this applied pressure.

The effect of surface preparation on the diffusion of uranium into aluminum is illustrated in Figures 7 and 8. If oxide and other contaminating films are not removed from the surface of the uranium and the aluminum specimens, maximum diffusion can not occur; if the surfaces are cleaned by cathodic vacuum etching and maintained free of contamination, maximum diffusion is possible. Figure 8 illustrates the comparative penetration in two couples vacuum annealed at 390 C (734 F) for 119 hours, identically treated with the exception of surface cleaning. In one couple both the uranium and aluminum surfaces were cathodically vacuum etched, whereas in the other the uranium surface was cleaned with 50 per cent nitric acid and the aluminum surface was cleaned with 20 per cent sodium hydroxide prior to rinsing with water and acetone. The penetration of the uranium into the aluminum in the cathodically vacuum etched couple approached 0.027 inches at most points whereas in the chemically cleaned couple it approached 0.011 inches with the exception of one peak, which was 0.026 inches.

Figure 9 is a typical cross-section of a couple annealed at 250 C (482 F) for 263 hours at a pressure of approximately five tons/in^2. The diffusion zone formed at this low temperature is nodular in appearance and contains no voids. The stereomacrographs of Figure 10 illustrate the appearance of the fracture interfaces of a uranium-aluminum couple subjected to an annealing temperature of 200 C (392 F) for a period of 314 hours. The resulting maximum penetration, or maximum height of the UAl_3 mounds above the original uranium-aluminum interface was 0.0048 inches. The original grain structure of the uranium and of the aluminum is readily discernible in regions where improper contact evidently prevented diffusion.

Table I lists the history and resulting diffusion in couples annealed for various times and temperatures in the stainless steel clamp previously described.

TABLE I

Maximum Penetration of Uranium Into Aluminum at Temperatures of 390, 250, and 200 C (734, 482, and 392 F) and at a Pressure of 5 Tons/in^2

Time hours	Temperature C	F	Maximum Penetration $x = (Kt)^{1/2} \times 10^3$ inches	Maximum Penetration Coefficient, $K \times 10^6$ in^2/hr
119	390	734	27	6.1
119	390	734	26	6.1
287	250	482	12	0.5
329	250	482	9.3	0.25
314	200	392	4.8	0.074
330	200	392	3.0	0.027
317	200	392	4.3	0.058

Figure 11, a plot of the logarithm of the maximum penetration coefficient versus the inverse absolute temperature, compares the data of Table I with data obtained at BNL and ORNL;[7] extrapolation is indicated by the dotted lines. At any given temperature in the range 200-390 C (392-734 F), it is evident that the maximum penetration coefficients obtained in this study are appreciably greater than those obtainable from BNL and ORNL data. The explanation for this undoubtedly lies in the method used for preparing the couples and in the method used for determining the maximum penetration values. Cathodic vacuum etching efficiently removes contaminants from the specimen surfaces which, if present, would act as a diffusion barrier and prevent subsequent maximum diffusion.

(7) op. cit. Bareis, D. W., BNL-38, December 15, 1949, (SECRET).

In addition, the method used for measuring penetration, measurement of the maximum peak height of the diffusion mounds adhering to the uranium after fracture of the couple, increases the probability of locating the point of maximum penetration.

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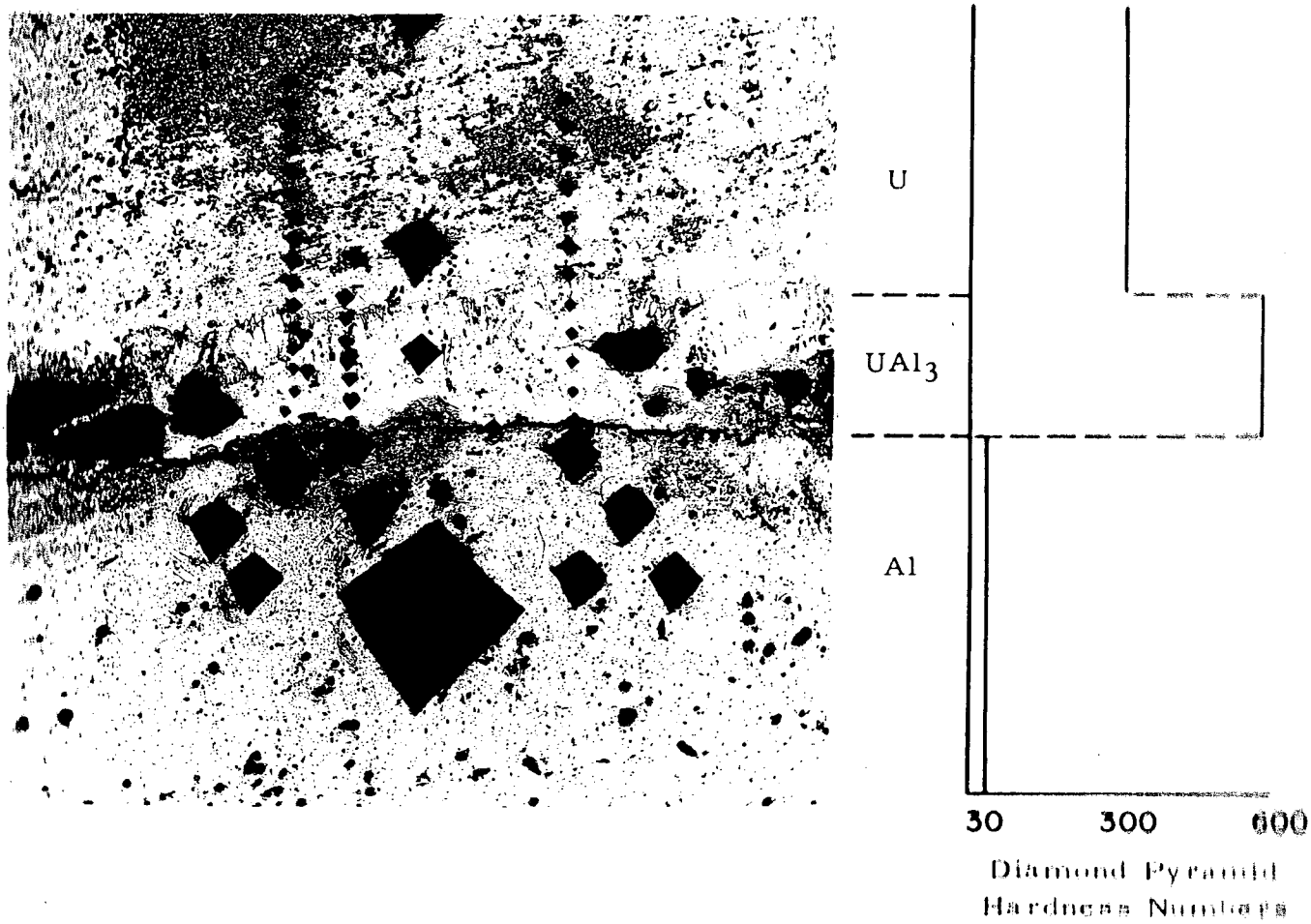

FIGURE 1
MICROGRAPH OF U-Al DIFFUSION COUPLE ILLUSTRATING ABRUPT CHANGES IN HARDNESS AT THE DIFFUSION ZONE INTERFACES. A Particular Load was Used in a Given Traverse. Etchant: 0.05% HF; Magnification: 100X

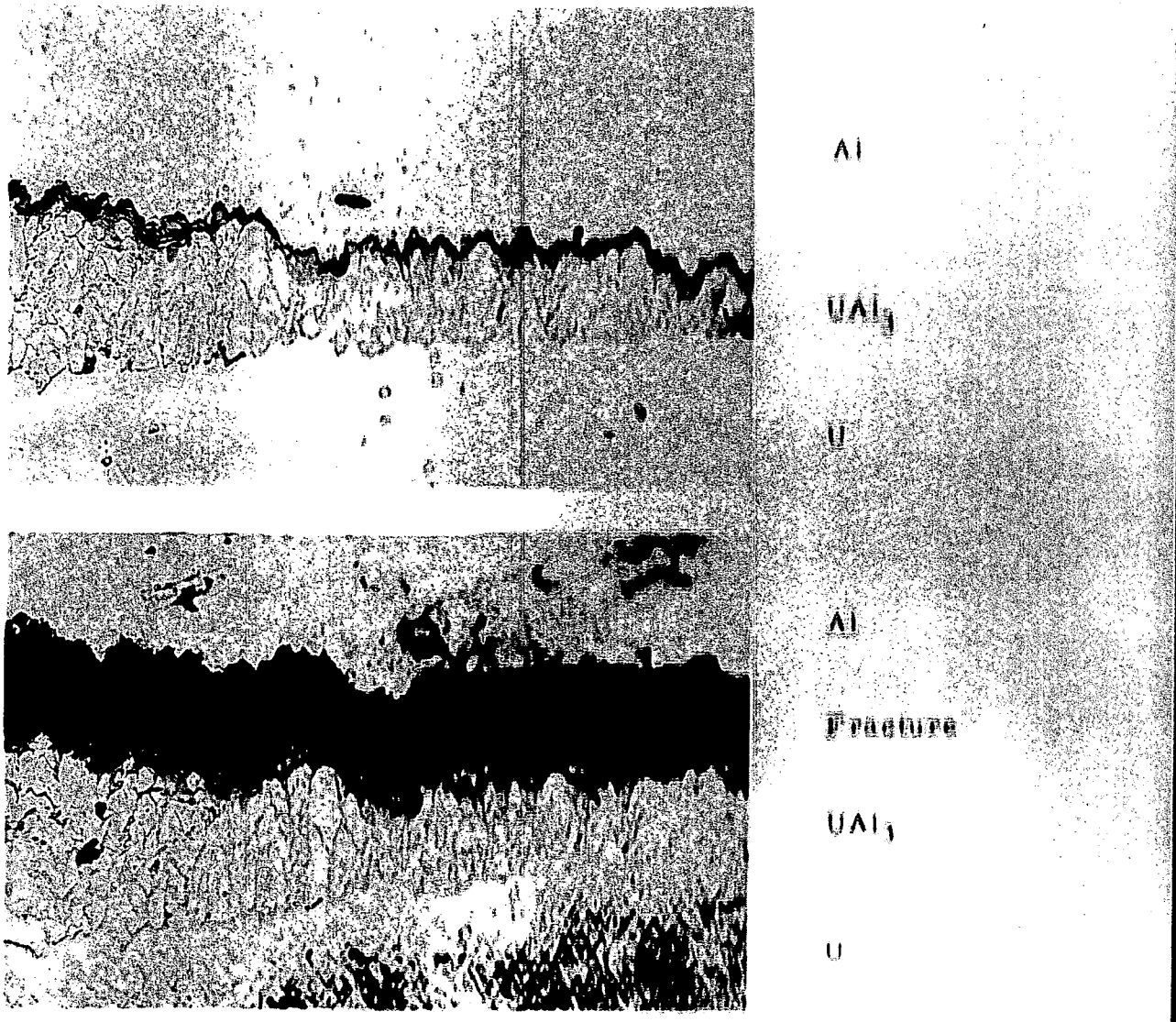

FIGURE 2

MICROGRAPHS OF U-Al DIFFUSION ZONE BEFORE AND AFTER FRACTURE.

Fracture Occurs Between the Diffusion Zone and the Aluminum Interface.
Etchant: 0.05% HF; Magnification: 250X

A.

B.

C.

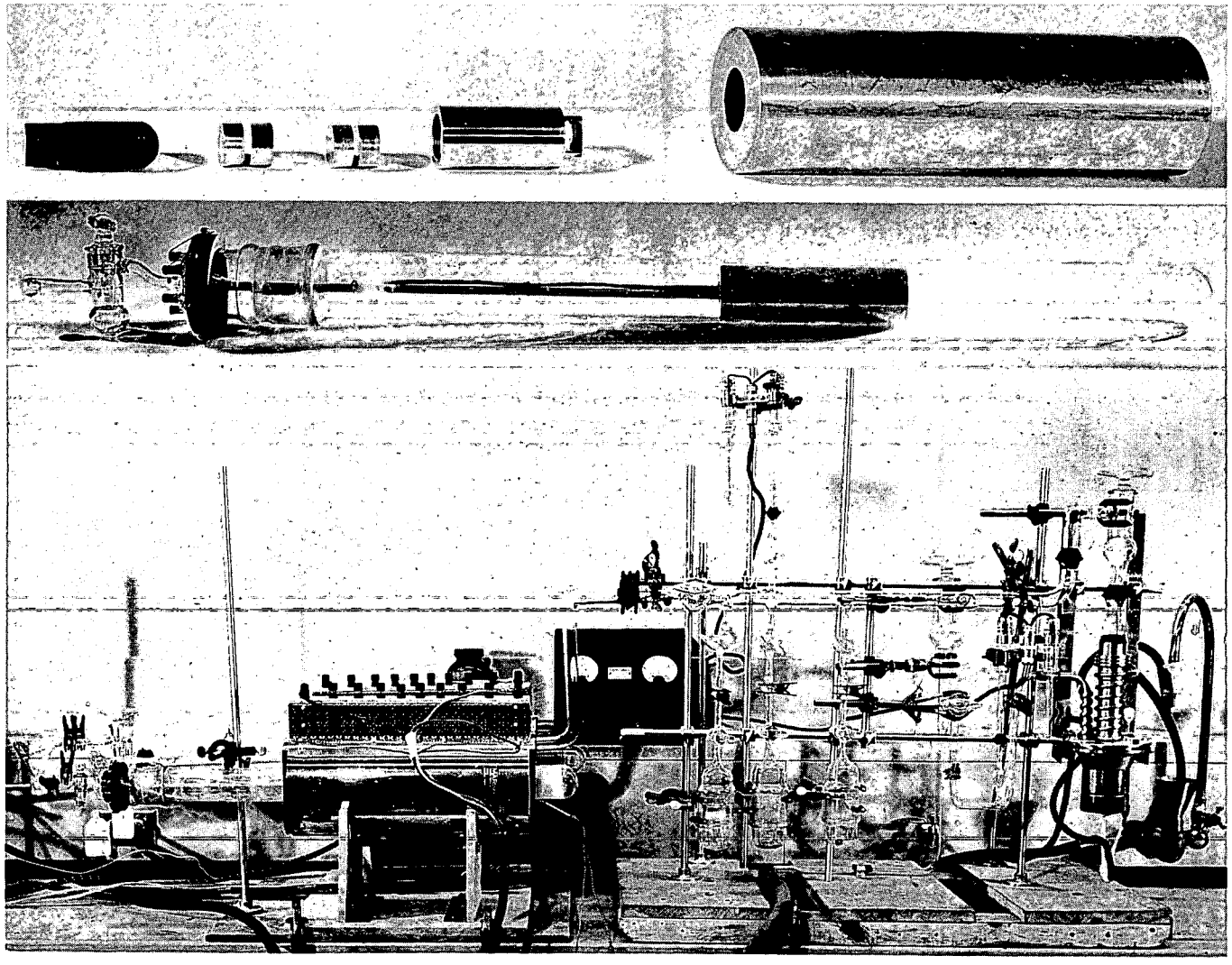

FIGURE 3

APPARATUS USED FOR ANNEALING DIFFUSION COUPLES.

A. Stainless Steel Clamp, Diffusion Couples, and Copper Heat Ballast.
B. Vacuum Furnace Tube with Thermocouples, Clamp, and Ballast.
C. Furnaces and Associated Vacuum Equipment.

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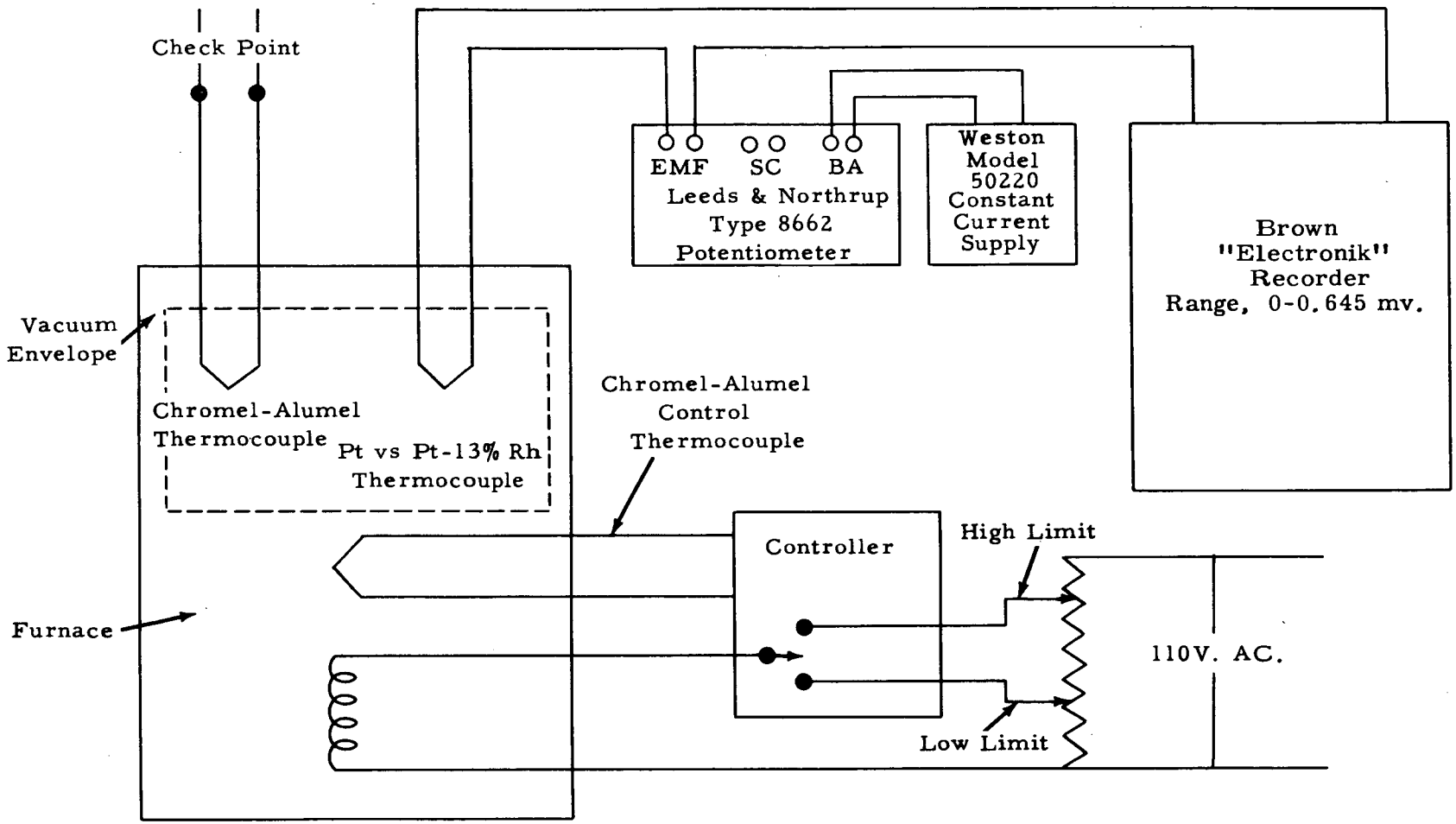

FIGURE 4
SCHEMATIC DIAGRAM OF THE TEMPERATURE CONTROLLING AND RECORDING CIRCUIT.

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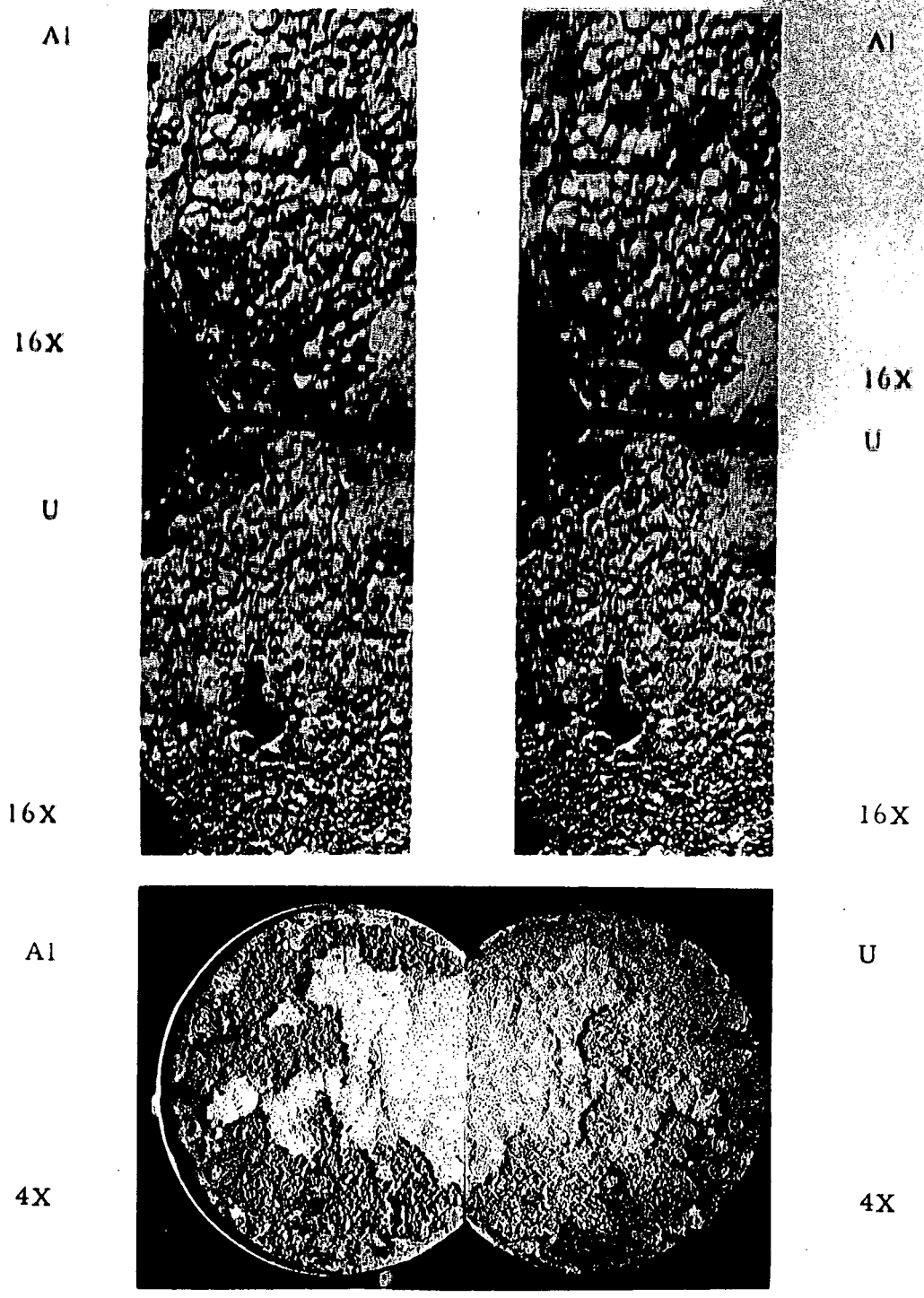

FIGURE 5

APPEARANCE OF THE FRACTURE SURFACES OF A HOT PRESSED U-Al COUPLE - PRESSURE, 11 TONS/in^2 ; TEMPERATURE, 500° C; TIME, 1 MINUTE.

Crystalline Layer Adhering to the Uranium is UAl_3, the Undersurface of Which is Composed of a Network of Voids.

FIGURE 8

MICROSCOPIC CROSS SECTION SHOWING THE ABUNDANCE AND SIZE OF VOIDS FORMED DURING THE HOT PRESSING OF A [illegible] COUPLE-PRESSURE, [illegible] TONS IN^{-2}, TEMPERATURE, [illegible]° C, TIME, 1 MONTH.
Etchant: [illegible] HF; Magnification, [illegible].

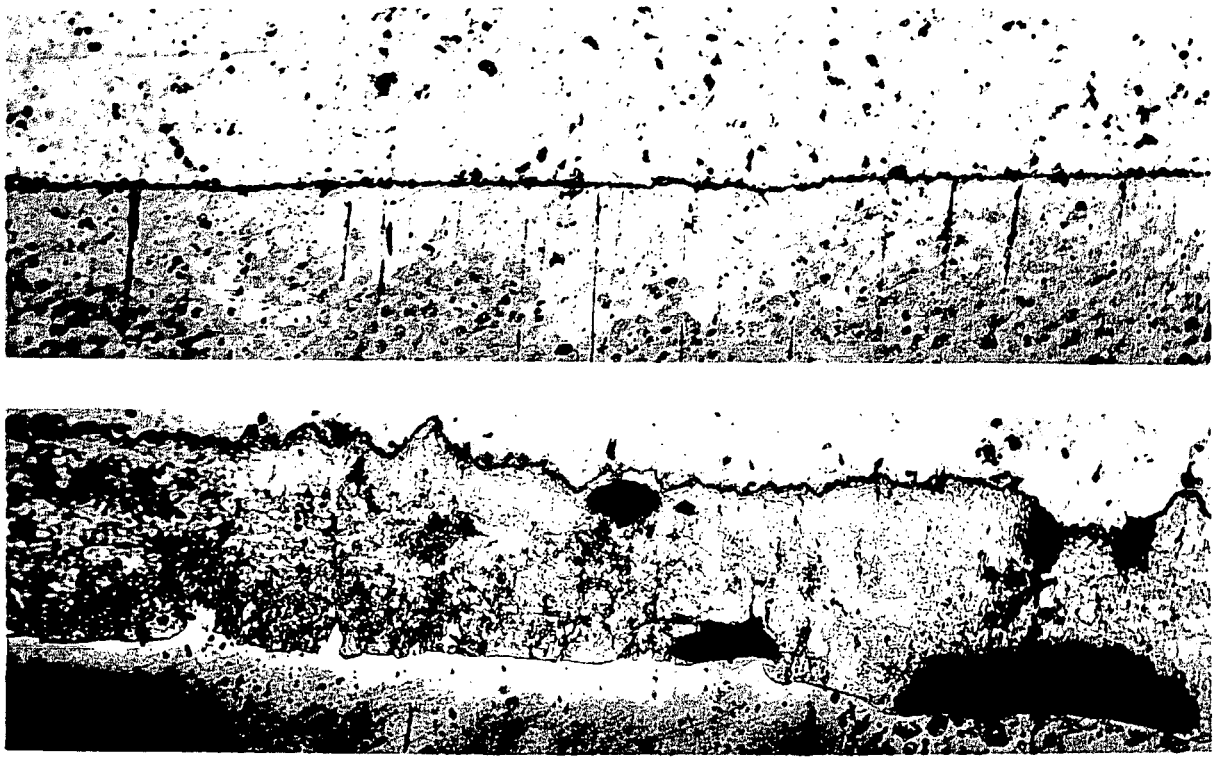

FIGURE 7
THE EFFECT OF SURFACE CLEANLINESS ON THE RATE OF DIFFUSION IN U-Al COUPLES SUBJECTED TO IDENTICAL HOT PRESSING CONDITIONS.
Upper Micrograph Pertains to a Couple Which Had Not Been Cathodically Vacuum Etched. Etchant: 0.05% HF; Magnification: 150X

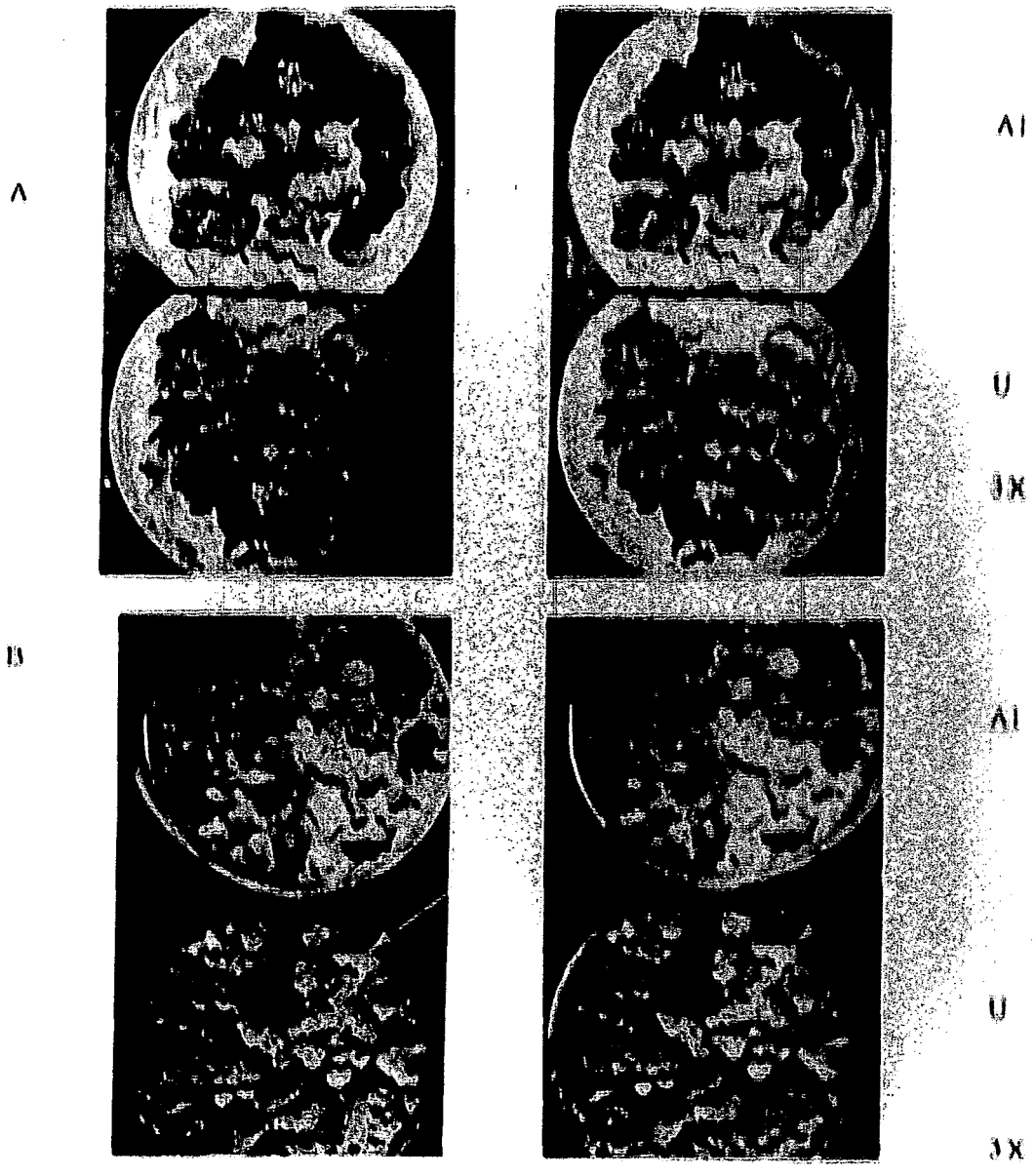

FIGURE 8

THE EFFECT OF INITIAL SURFACE PREPARATION ON THE RESULTING DIFFUSION IN TWO U-Al COUPLES ANNEALED UNDER IDENTICAL CONDITIONS; INITIAL PRESSURE, 5 TONS/in^2; TEMPERATURE, 300°C; TIME, 110 HOURS.

A. Stereograph of the Fracture Interfaces of a Couple Which Had Been Previously Cleaned by Cathodic Vacuum Etching. Most of the Resulting Diffusion Zone Projected A Maximum of 0.037 Inches into the Aluminum.

B. Stereograph of the Fracture Interfaces of a Couple which Had Been Cleaned Chemically. The Resulting Diffusion Zone Projected into the Aluminum Only 0.011 Inches With the Exception of the Indicated Peak Which Projected 0.026 Inches.

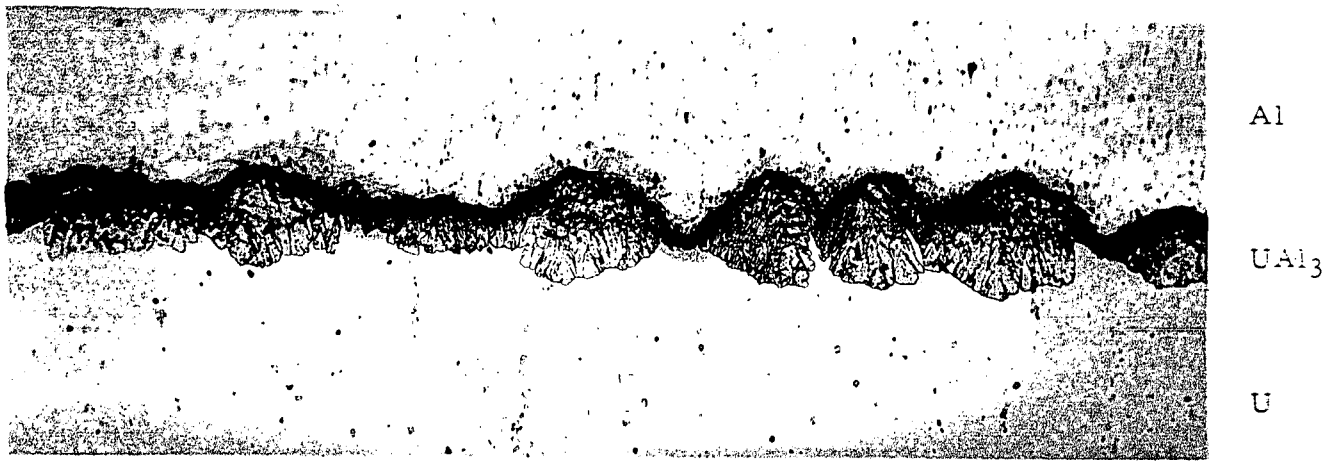

FIGURE 9
CROSS SECTION OF THE DIFFUSION ZONE OF A U-Al COUPLE ANNEALED AT 250° C FOR 263 HOURS AT A PRESSURE OF 5 TONS/in^2
As Polished; Magnification: 150X.

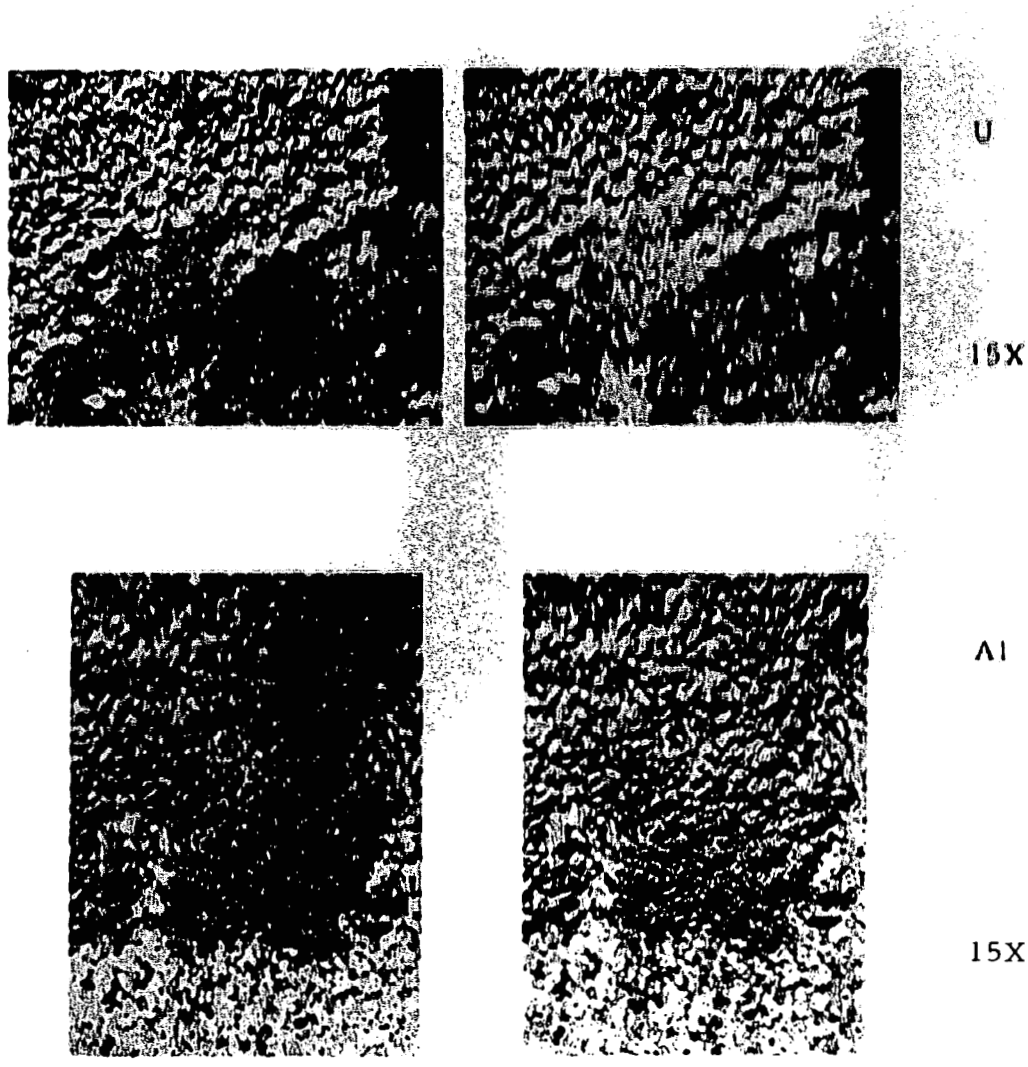

FIGURE 10
STEREOMACROGRAPHS OF CORRESPONDING AREAS IN THE FRACTURE INTERFACES OF A UAl COUPLE ANNEALED AT 200° C FOR 314 HOURS AT ~5 TONS/in^2 PRESSURE.
The Maximum Penetration of Uranium into the Aluminum is 0.0048 Inches.

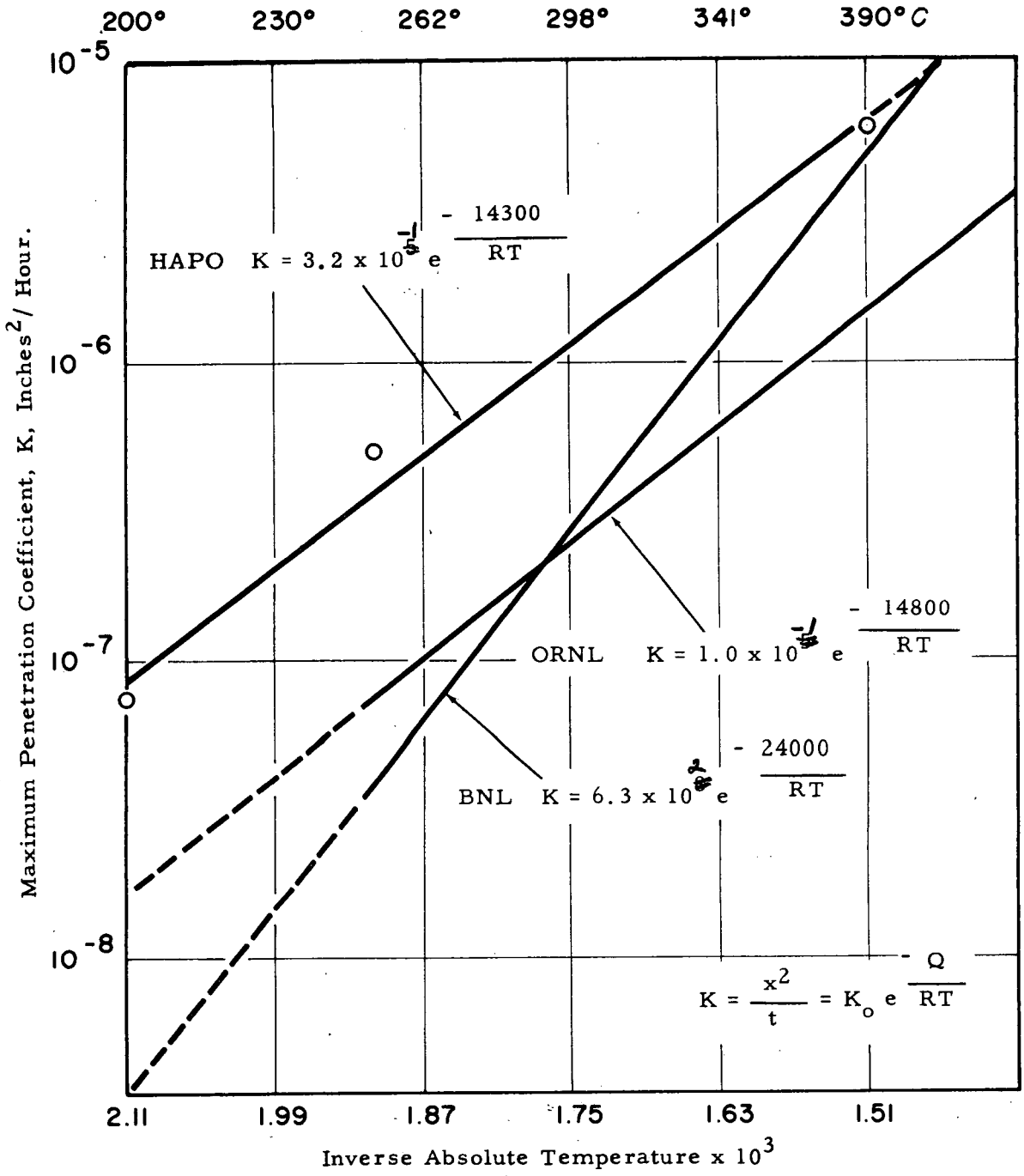

FIGURE 11

LOG OF THE MAXIMUM PENETRATION COEFFICIENT VS INVERSE ABSOLUTE TEMPERATURE.

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ABSTRACT

The maximum penetration of uranium into aluminum in the temperature range 200-390 C (392-734 F) has been investigated. The maximum values for the penetration coefficient K_T, determined from the relationship $K_T = x^2/t$, are 0.075, 0.50, and 6.1×10^{-6} inches^2/hour at temperatures of 200, 250, and 390 C (392, 482, and 734 F), respectively; the corresponding activation energy is 14,300 calories per mole. The utility of cathodically vacuum etching specimens to obtain clean metal surfaces prior to the diffusion anneal is demonstrated. Couples prepared in the temperature range investigated, 200-390 C (392-734 F), fracture by the application of tension between the aluminum and the adjacent UAl_3 diffusion zone interface. Subsequent measurement of the maximum UAl_3 peak heights above the initial uranium-aluminum interface assures a maximum value of the penetration coefficient. The investigation provides a necessary basis for interpreting the effect of irradiation on the diffusion rates of uranium into aluminum.