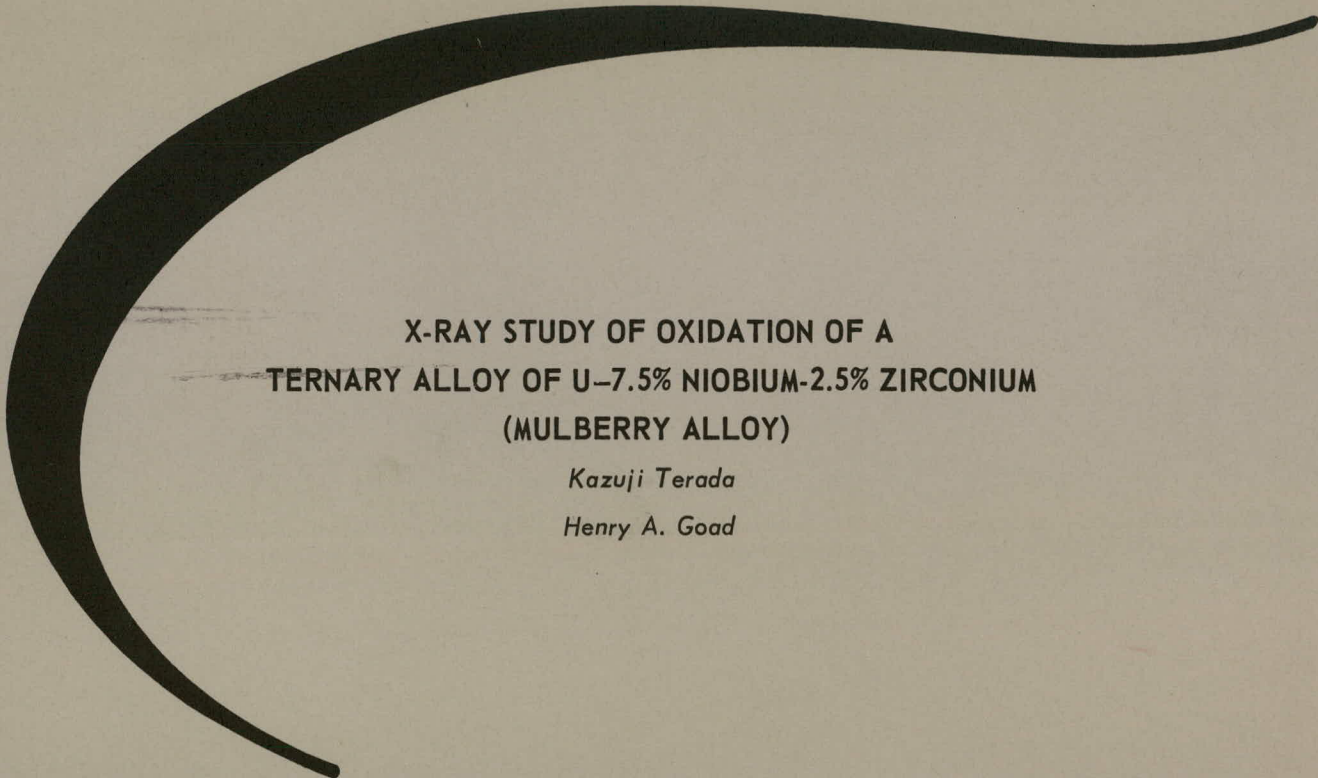194/
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X-RAY STUDY OF OXIDATION OF A
TERNARY ALLOY OF U–7.5% NIOBIUM-2.5% ZIRCONIUM
(MULBERRY ALLOY)

Kazuji Terada

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June 23, 1970

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Kazuji Terada and Henry A. Goad

Abstract. The x-ray diffraction study of the oxidation of Mulberry alloy is described. Experiments were performed at 150°, 250°, 400°, 500°, and 600°C in both dry and wet air, and with different surface preparation of the samples. Only UO_2 was formed at 150° and 250°C. At 400°C, U_3O_8 was also formed after induction periods ranging from one-quarter to 10 hours. U_3O_8 was formed almost immediately at 500° and 600°C. The moisture content of the oxidizing atmosphere and the surface sample pretreatment did not appear to have any effect on the results.

INTRODUCTION

This investigation concerning the oxidation of Mulberry alloy (U–7.5% Nb—2.5% Zr) was started when interest developed in the role of U_3O_8 in stress corrosion cracking of Mulberry alloy. If U_3O_8 influenced the initiation and/or propagation of stress corrosion cracking, it is important to know under what conditions and how the compound was formed.*

There is no published literature on oxidation of Mulberry alloy; therefore, this study will be compared with the oxidation of uranium. While there are a number of reports on the oxidation of uranium alloys, most are primarily concerned with reaction rates rather than reaction products.

The uranium-oxygen system is very complex, and UO_2 and U_3O_8 are only two of a number of uranium oxides. During the oxidation of uranium to U_3O_8, the formation of oxides such as U_3O_7, U_4O_9, and U_2O_5, are frequently reported in addition to UO_2 and U_3O_8. These oxides have structures very similar to those of either UO_2 or U_3O_8 and they are distinguished by slight shifting or splitting of the X-ray diffraction peaks. In Mulberry alloy, this is complicated since the effect of Zr and Nb on the X-ray diffraction patterns cannot be precisely predicted. Therefore, discussion in this work will be confined mainly to UO_2 and U_3O_8 because we cannot, by X-ray diffraction, distinguish between the effect of the alloying element and the effect of the small changes in the uranium oxide stoichiometry.

According to the early report by Wathen,[1] only UO_2 was formed on uranium metal exposed to air at temperatures up to 100°C. Above 100°C, both U_3O_8 and UO_2 were formed and from 200°C to 500°C the product was practically pure U_3O_8. However, his conclusions were

obtained by the questionable process of deducing stoichiometry by combining data from weight-gain measurement and preferential dissolution of the oxides in 50% HNO_3 solution. Results of similar work by Hilliard[2] led him to conclude that at 300°C, and below, UO_2 was produced, and at above 300°C U_3O_8 was produced.

Hart[3] observed by electron diffraction that U_2O_5 and U_3O_8, on uranium surfaces, electropolished at 15°C. However, mechanically polished surfaces showed only UO_2, and the same results were obtained when samples were oxidized in air at 300°C for 5 minutes. Similarly, Waber, Olsen and Whyte[4] detected only UO_2, or uranium, by electron diffraction when the metal was polished in air with 240-grit silicon-carbide paper on a wheel. However, they did find U_3O_8 on the surface of U-6 wt % Nb alloy similarly pretreated. They suggested that the U_3O_8 formation was due to local heating during the polishing process.

In investigations where the oxide products were identified by X-ray diffraction, Loriers[5] reported that U_3O_8 was formed when the metal was heavily oxidized at temperatures above 240°C. The oxide formed as superficial layers, which easily scaled off from the rest of the specimen. Bagley and Oliver[6] reported U_3O_8 formed at temperatures as low as 200°C. Workers at Argonne National Laboratory[7,8] found U_3O_8 at 400°C only after extensive oxidation of the metal. When a thin film of the oxide is formed on the metal surface, no U_3O_8 is found even at 600°C. On the basis of this investigation and that of Loriers, an induction period might be expected between the beginning of oxidation of uranium and the appearance of U_3O_8 at temperatures above 200°C.

In this report, the results of X-ray diffraction studies of the oxidation of Mulberry alloys are discussed. Experiments with an X-ray unit, having a high temperature-high vacuum sample holder attachment, were the primary source of data. This techique had not been applied in earlier work on the oxidation of uranium or Mulberry alloy.

SUMMARY AND CONCLUSIONS

The experimental data on Mulberry oxidation experiments were consistent with those found for uranium

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metal with respect to the formation of U_3O_8. With both materials the low temperature limit of U_3O_8 formation is between 240° and 400°C. Both exhibit induction periods between the beginning of oxidation and when U_3O_8 begins to form. Except during the incipient growth period, U_3O_8 is found as loose, non-adherent substance on surfaces of the alloy and pure metal.

Two possible explanations for the induction period, in the formation of U_3O_8 during oxidation of Mulberry, were discussed. One was that the UO_2 film must grow to a certain thickness on the substrate alloy before U_3O_8 can begin to form. The other was that the induction period in the oxidation of UO_2 to U_3O_8 was responsible for that observed in the oxidation of the alloy. At this time, there is insufficient evidence to favor one mechanism over the other. Possibly, both play a role in the induction period.

No evidence has been found that U_3O_8 could be formed at temperatures below 200°C. On the basis of the experimental results and the literature, our conclusion is that U_3O_8 does not form under normal storage conditions and therefore plays no part in the mechanism of stress corrosion cracking of Mulberry alloy.

EQUIPMENT AND SUPPLIES

The experiments were performed mainly in a Materials Research Corporation Model X-86G High Temperature-High Vacuum Horizontal X-Ray Diffractometer Attachment. This attachment consists of a chamber which permits a sample to be heated in a controlled atmosphere, or vacuum, and analyzed by X-ray diffraction simultaneously. The mount for the attachment was a Picker Horizontal Biplane Diffractometer. A high intensity X-ray tube with a copper target was used with a Picker Generator. A schematic diagram of the system is shown in Figure 1.

Figure 1. High Temperature-High Vacuum X-Ray Diffraction apparatus

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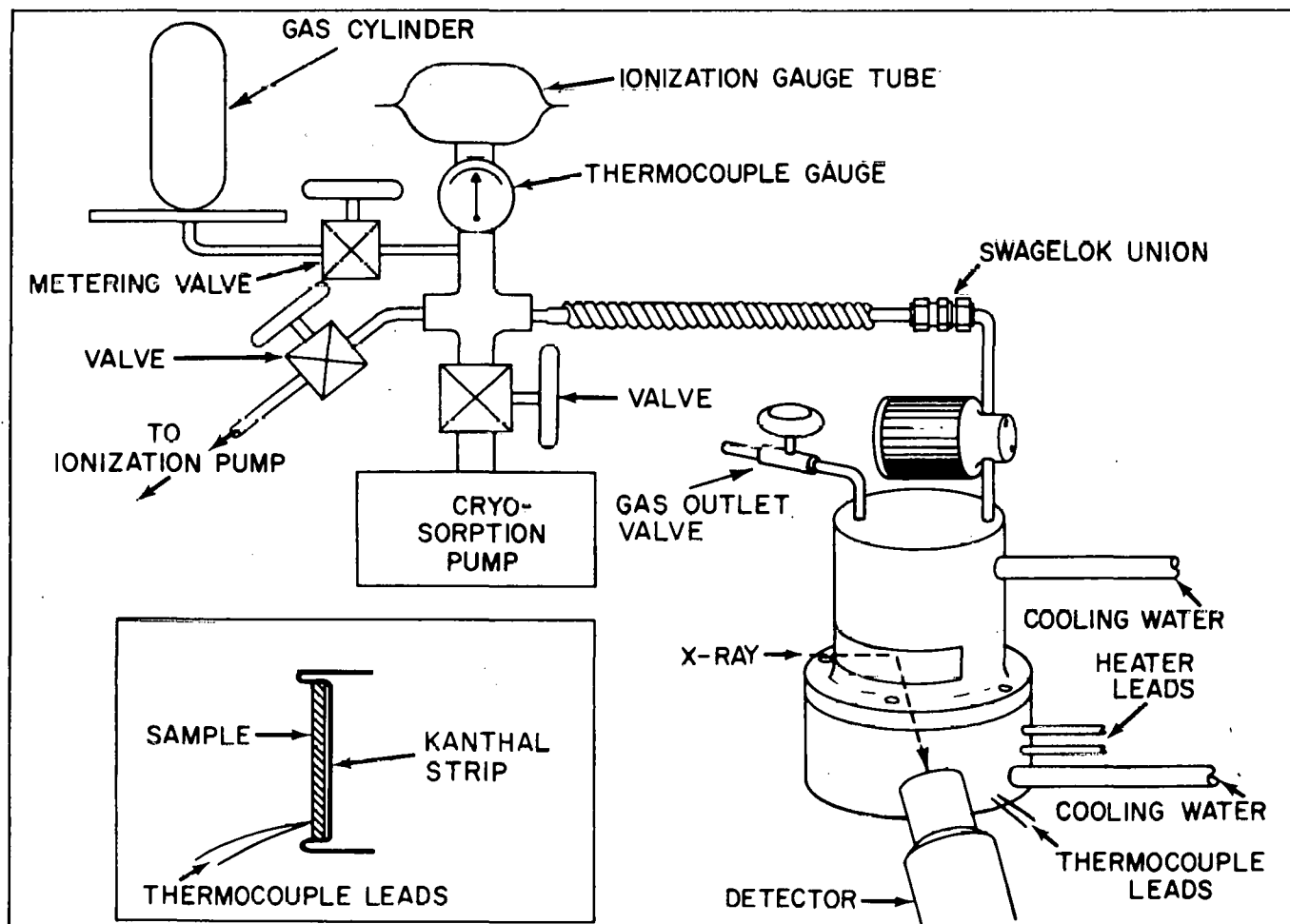
A Trub Tauber KD3 High Energy Electron Diffraction
Unit was utilized to examine the topmost surface
oxide films of some of the oxidized alloys.

The Mulberry specimens were disks 1 inch in diam-
eter and 1/16-inch thick. They were machined from
a rolled sheet and were obtained from the Y-12 Divi-
sion of ORNL via Sandia Laboratories, Albuquerque,
New Mexico.

Several of the specimens, requiring more than a week
of reaction time, were oxidized in the apparatus shown
in Figure 2. They were removed from this apparatus
and periodically examined by X-ray diffraction.

EXPERIMENTAL PROCEDURE

Low Temperature Experiments:

Initially, oxidation experiments were planned at 50°,
100°, and 150°C in relative humidities ranging from
0 to 100%. However, because of the very slow oxida-
tion rate observed at 150°C and 100% relative humidity
the remaining experiments of the planned series were
cancelled.

An as-received coupon was initially oxidized in the
sample holder attachment to the X-ray diffraction unit
(Figure 1). The temperature was measured with a
Platinel II thermocouple, spot welded on the sample
face. X-ray diffraction scans were made periodically
to follow the course of the oxidation. The sample was
transferred to the auxiliary system (Figure 2) after
7 days to continue the oxidation. It was oxidized for
a total of 5 months before the experiment was terminated.

High Temperature Experiments:

The experimental conditions planned for this series
were 250°, 400°, and 600°C in 650 torr of dry air and
at 100% relative humidity. Specimen surfaces were
polished in water with 600-grit sandpaper. Some of
the experiments were performed with coupons in the
as-received condition, or after being given an alcohol
rinse, to examine the effect of surface pretreatment.
For experiments at zero-percent relative humidity,
the reaction chamber was evacuated to at least 10^{-5}
torr before 600 torr of dry gas was introduced. Then
the heat was applied. It required approximately
5 minutes to bring the sample to within 25°C of the
desired reaction temperature. The final temperature
adjustment usually required about 3 to 5 minutes
after which time the pressure was brought up to
650 torr. The initial X-ray scan was usually made

Figure 2. Auxiliary Oxidation System
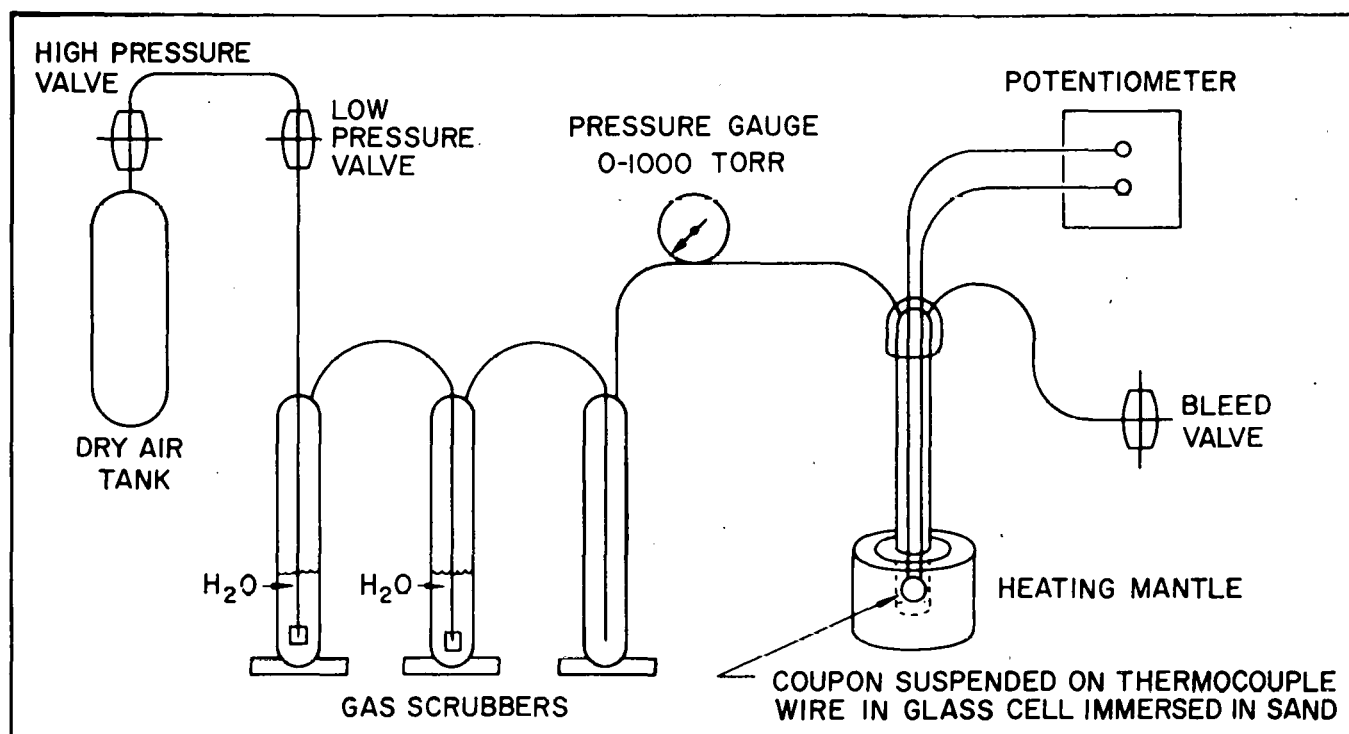
when the temperature reached within 2% of the final temperature (°K). In one experiment, in an effort to decrease the time lag between the start of oxidation and the first X-ray diffraction scan, the gas was added after the sample had reached temperature under vacuum. The gas had a large cooling effect and there was no time advantage in using this procedure.

The oxidation experiments at 150°C and 250°C for extended durations were conducted mostly in the auxiliary system (Figure 2); the samples were removed periodically and x-rayed.

EXPERIMENTAL RESULTS

Low Temperature Experiments:

Since preliminary experiments had shown Mulberry to be quite resistant to oxidation, the first experiment was under the most corrosive condition of the planned series; that is, 150°C in 650 torr of air at 100% relative humidity.

Formation of UO_2 was observed immediately but the growth of the oxide film proceeded at an extremely slow rate. When the experiment was terminated 5 months later, UO_2 was the major substance on the coupon surface. Gamma-metal peaks were still quite prominent and no other metal phase was detectable. There was no evidence of any U_3O_8. Electron diffraction examination of the surface yielded poor patterns of what appeared to be UO_2.

In accord with the literature on uranium oxidation, no U_3O_8 was found at 150°C. The oxides were quite adherent when the experiment was terminated.

High Temperature Experiments:

250°C TEMPERATURE

Two samples were oxidized at 250°C in 650 torr of dry air. One was oxidized in the as-received condition and the other was polished with a 600-grit sandpaper. The results are shown in Table I.

Column 3, in Table I, lists the time required for the gamma-metal peak to disappear from the X-ray diffraction pattern of the alloy surface. The loss of metal-diffraction peaks is the result of oxide film overlying the alloy and phase transformation. This is discussed further in another section.

Oxide films on both samples appeared compact at the end of the experiments. However, while the as-received sample was being cooled for the last time, some of the oxide flaked off the surface.

400°C TEMPERATURE

A number of experiments were performed at 400°C because this was the ideal temperature at which to observe the formation and growth of U_3O_8. The reaction rates were slow enough to enable a great number of scans to be made of the reaction progress. Also, the reaction rates were large enough to complete an experiment in one day.

At 400°C we first observed the formation of U_3O_8. UO_2 was formed first and the initial appearance of U_3O_8 occurred on the surface of adherent, compact UO_2 film. As oxidation continued, the formation rate of U_3O_8 increased and the surface oxides became increasingly friable. These observations were in agreement with those reported by Leibowitz and his co-workers[8]

The U_3O_8 was identified as the hexagonal phase. This was the case at all temperatures at which the compound was formed. However, relatively minor amounts of the orthorhombic phase were probably present also. Resolution of the two phases in the diffraction scans are difficult because of the similarity of their structures and the effect of the alloying elements on the diffraction patterns. Future references to the compound will be simply by the formula U_3O_8.

Table I. X-Ray Diffraction of Mulberry Oxidation at 250°C

Sample No.	Surface Preparation	Days to disappearance of (110) gamma-metal peak	Total Heating Time (days)	Final X-ray	Products HEED**
1551	As-received	18	42	UO_2	UO_2
1579	Polished*	8	46	UO_2	

*All polished samples were finished on a wheel using 600-grit sandpaper and water.

**HEED - High energy electron diffraction.

Table II shows the conditions and results of experiments performed at 400°C temperature. The times listed in the table were obtained by periodic X-ray scans of values where the most intense diffraction peaks of the gamma-metal phase, and the UO_2 and the U_3O_8 occurs. The loss of the metal peak was not entirely caused by the growth of the overlying oxide film exceeding the penetration limit of CuK_α radiation. Much of the loss was due to the transformation of the γ phase to α'' phase. However, if it is assumed that at any given temperature the rate of phase transformation is reproducibe then the time to the disappearance of the metal peak from the diffraction patterns should yield information on the effect of surface pretreatment and humidity on oxidation rates.

It can be seen from the results shown in Table II, that wide variations in the apparent oxidation rate occurred. Therefore, any effects from surface pretreatment and humidity could not be distinguished. With few exceptions, the appearance of U_3O_8 in the diffraction pattern always occurred after the metal peaks were no longer detectable. There is an apparent induction period in the U_3O_8 formation, and this is shown in Figure 3. Plots of the areas under the (d=3.37Å) peaks of U_3O_8 against time show the induction periods.

500°C TEMPERATURE

Experiments were performed at 500°C to bridge the gap between the experimental results at 400° and at 600°C. Table III lists the experiments and the data. The results did not vary much from those at 600°C shown in Table IV.

600°C TEMPERATURE

The results of the experiments at 600°C are listed in Table IV. In almost every case, the U_3O_8 is detectable in the first X-ray diffraction scan within a few minutes at 600°C. The metal peaks were not scanned at the very early stages of these experiments because interest was primarily focused on the U_3O_8. However, the experiments were usually terminated immediately after the U_3O_8 peak was observed during the first scan. The subsequently cooled specimens at no time exhibited any metal peaks by X-ray diffraction.

Oxidation Products

The only oxidation products definitely identified were UO_2 and U_3O_8. Careful examination of the diffraction scans showed no real evidence of tetragonal U_3O_7. Slight shifting and broadening of the diffraction peaks could be seen at times but it was not possible to isolate these effects from the effects of heat and the alloying elements.

No oxides of niobium and zirconium were identified.

DISCUSSION

The experimental results, for the most part, are self-explanatory and not many additional comments are necessary. At 150° and 250°C, no U_3O_8 was formed. At 400°C, U_3O_8 was observed after induction periods which ranged from one-quarter to 10 hours. The

Table II. X-Ray Diffraction of Mulberry Oxidation at 400°C

Sample No.	Surface Preparation	RH(%)	Hours to Disappearance of (110) Gamma Peak	Hours to Appearance of (d=3.37Å) U_3O_8 Peak
1552	As-received	0	1	4
1555	Polished	0	1	4
1557	Polished	100	1 1/2	>8
1559	Polished	100	1 1/2	7
1561	As-received	100	1/2	3/4
1562	Alcohol Wash	100	1 1/2	6 to 12
1563	Alcohol Wash	100	1 1/4	2 1/2
1564	As-received	100	1 1/2	10
1565	As-received	100	1	1
1569	As-received	100	1/4	1/4
1570	As-received	100	1/2	1 1/4
*1575	Polished	0	1/2	2 3/4
1583	Polished	0	1/3	1/2
1584	Polished	0	1 1/4	2

*Oxidized in 20 torr of O_2

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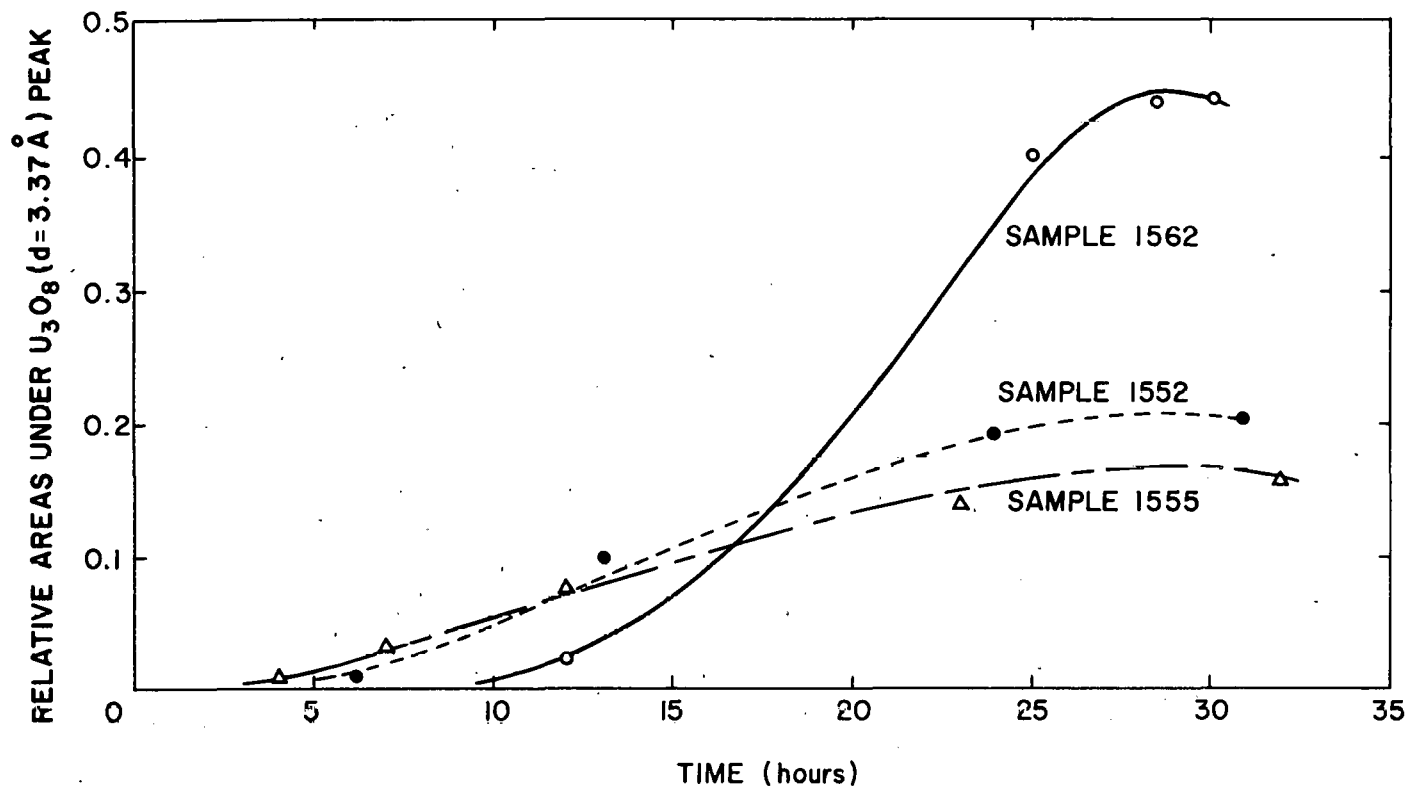
Figure 3. Growth Curve for the Formation of U_3O_8 on Mulberry Surface at 400°C.

Table III. X-Ray Diffraction of Mulberry Oxidation at 500°C

Sample No.	Surface Preparation	RH%	Minutes to Disappearance of (110) Gamma Metal Peak	Minutes to Appearance of (d=3.37Å) U_3O_8 Peak
1566	As-received	100	10	<5
1567	As-received	100	<10	15
1568	As-received	100	5	10
*1576	Polished	0	4	6

*Oxidized in 20 torr of O_2

Table IV. X-Ray Diffraction of Mulberry Oxidation at 600°C

Sample No.	Surface Preparation	RH%	Minutes to Appearance of (d=3.37Å) U_3O_8 Peak
1553	As-received	0	immediate
1554	As-received	0	immediate
1560	Polished	100	<2
*1574	Polished	0	8
*1577	Polished	0	<4
1581	Polished	0	<5
*1582	Polished	0	<2

*Oxidized in 20 torr of O_2

iduction periods were small or practically nonexistent the 500° and 600°C experiments. Any effects on the oxidation as the result of differences in humidities of the oxidizing atmosphere, and in the surface pretreatment of the samples, were not distinguishable. At all temperatures except 400°C, the data are generally reproducible. The 400°C results are characterized by their variability. The times from the beginning of oxidation to when U_3O_8 become detectable by X-ray diffraction ranged from 15 minutes to more than 7 hours. Experiments varying surface preparation and relative humidities of the oxidizing gas did not indicate that these variables have any influence on the oxidation rate.

Except at the earliest stage in the appearance of U_3O_8, the oxide is loose and is nonadherent to the specimen. The loose oxide could be easily removed from the oxidized surface, thereby leaving only UO_2 on the metal surface.

Nucleation and Growth Theory of U_3O_8 Formation

On the basis of our observation, we thought that the onset of U_3O_8 formation depended on the thickness of UO_2 film over the substrate metal. As the oxide film grew, the rate of diffusion of oxygen away from the film surface decreased. This can cause a net increase in surface oxygen concentration as gaseous oxygen continued to be adsorbed. It was hypothesized that, at a certain oxide film thickness, the oxygen concentration on the surface reaches a level whereby the oxidation of UO_2 to U_3O_8 can proceed. An increase in the oxygen concentration on the surface can also be accelerated by disruption of the oxide film such as horizontal or diagonal cracks, to prevent the diffusion of oxygen away from the oxide surface. However, the literature on the oxidation of powdered UO_2 to U_3O_8 also shows an induction period. [9,10,11,12] The oxidation proceeds in two distinct steps. The first step is a diffusion controlled oxidation of UO_2 to U_3O_7, and this is followed by the further oxidation of U_3O_7 to U_3O_8.

Weight gain versus time plots (Figure 4) by Aronson, and others,[9] show the two-step oxidation process. Note that at 299°C, U_3O_8 is not formed immediately. According to those authors, oxidation of U_3O_7 to U_3O_8 is a nucleation and growth controlled process. They arrived at this conclusion when they compared plots of their oxidation data to the family of curves obtained from analytical expressions derived by Johnson and Mehl [13] for the

Figure 4. Experimental rate curves for the oxidation of UO_2.
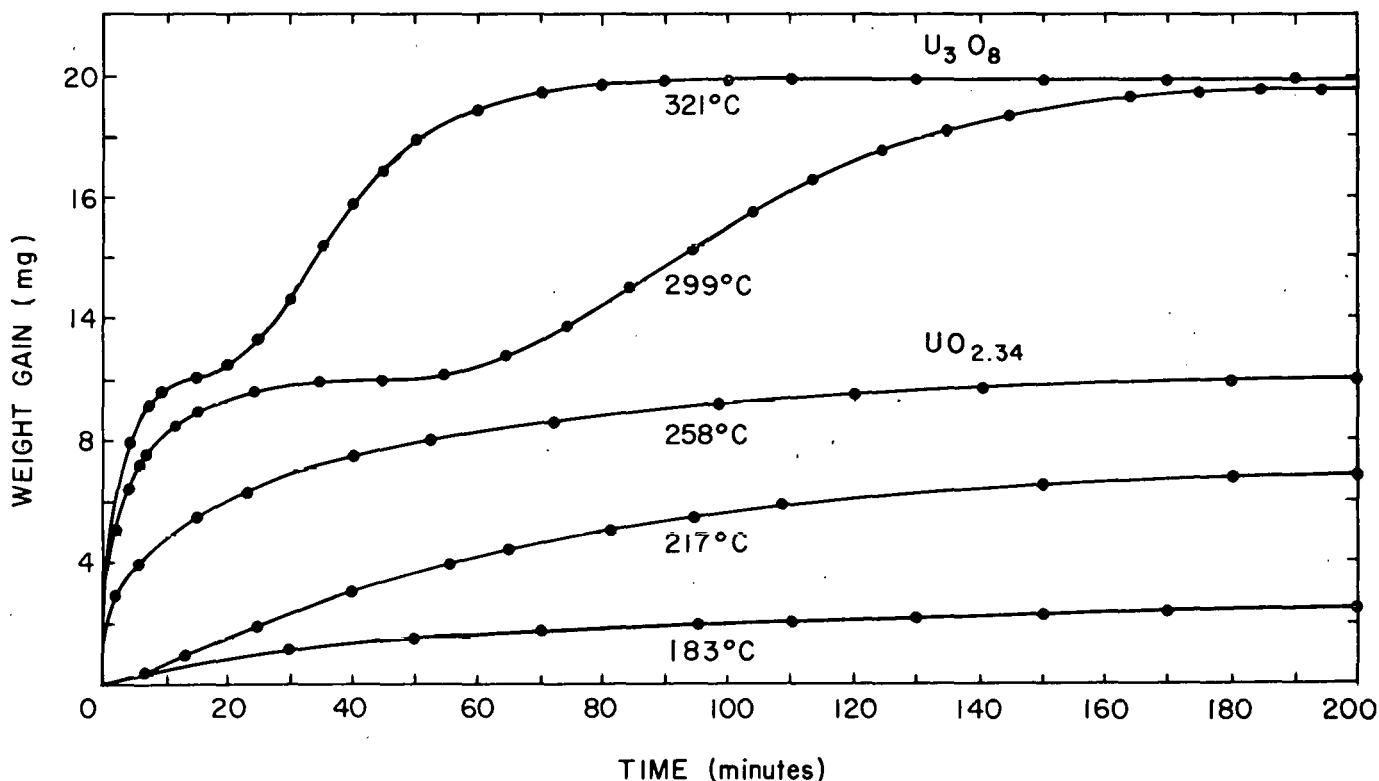
nucleation and growth of pearlite from austenite. Because of the complexities of their equation, Johnson and Mehl plotted a family of theoretical curves in terms of two parameters:

$$Z = \frac{Gt}{a} \text{ and } \lambda = a^3 \frac{Ns}{G}$$

where G = linear growth coefficient
t = time
a = particle radius
$Ns = \dfrac{\text{nucleation rate}}{\text{unit area}}$

The fraction of material transformed was plotted against Z and each curve was associated with a λ value. The family of theoretical curves is shown in Figure 5. Comparison of experimental curves with these theoretical curves allows the calculation of G and Ns. Good coincidence of curves was claimed by Aronson, et al.,[9] and Walker[10] in their UO_2 oxidation experiments. Our plots of formation of U_3O_8 versus time (Figure 3) at 400°C show the sigmoidal-shape characteristics of reaction

kinetics controlled by nucleation and growth. Therefore it appears that the data of our X-ray study of the oxidati of Mulberry alloy reflect the oxidation of UO_2.

Although the nucleation and growth theory is generally accepted, there are differences between our observation and the theory. Aronson, and others,[9] found both U_3O_7 U_3O_8 by X-ray diffraction during oxidation of UO_2 at 300°C. No U_3O_7 was identified in our work. Scott and Harrison[11] reported that UO_2 with surface areas of less than 0.05 m²/g exhibited a one step oxidation to U_3O_8. UO_2 with surface areas of 1.0 m²/g, or more, yielded the characteristic two-step reaction. Aronson worked with oxides having surface areas of 0.6 and 2.4 m²/g. The compact, adherent UO_2 on Mulberry coupon has a comparatively small surface area and would be expected to proceed by the one-step process.

Another area of interest lies in Aronson's suggestion that nucleation and growth of U_3O_8 occurs immediately after UO_2 is exposed to oxygen. It would be expected, then, that the period to detectability of U_3O_8 at a given temperature would be constant within limits. This is not the case in our 400°C experiments.

Figure 5. Master reaction curves for grain-boundary nucleation. Abscissa scale is linear. [*Courtesy* of W. A. Johnson and R. F. Mehl, *Trans. Amer. Inst. Min. (Metall.) Engrs.*, *135*, 416 (1939).]
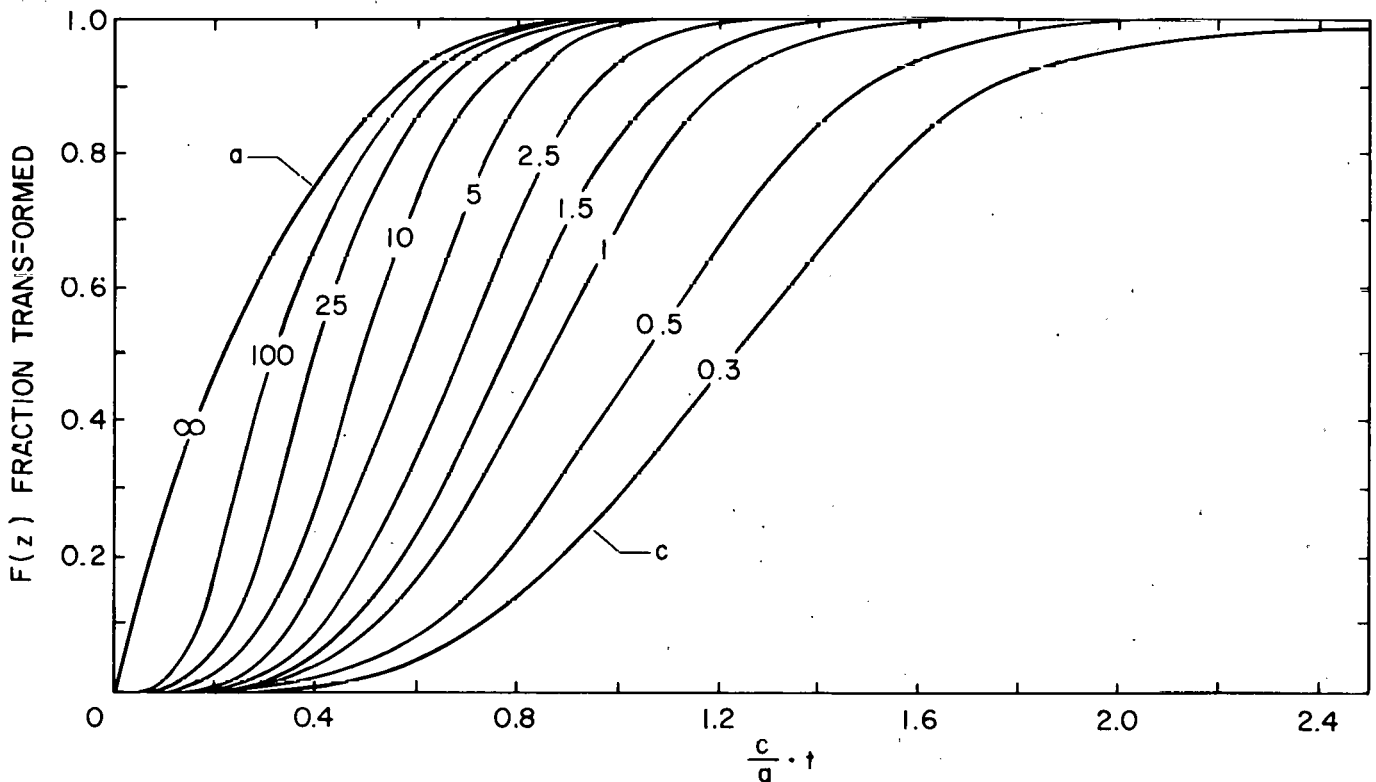
The time for the appearance of U_3O_8 ranged from 15 to over 1 minutes. The data, then indicate that the formation of U_3O_8 is related to the rate at which a given sample is oxidized. When the time to undetectability of the gamma peak is short, then the time to the appearance of U_3O_8 (Column V) is also short. (See Table II.) This interpretation was based on the assumption that the transition of gamma to alpha phase uranium at any given experimental temperature is quite constant. However, the very recent TTT (time-temperature-transformation) diagram by Dean,[14] published after our experimental work was completed, shows a double C curve where the top part of the lower C is a horizontal line at 400°C extending between 8 minutes and 1.5 hours. The diagram is reproduced in Figure 6. The horizontal line at 400°C separates the alpha and gamma alloyed phases of uranium. The diagram shows that if the reaction temperature is above 400°C the gamma phase transformation to alpha is comparatively slow, and if it is slightly below 400°C the transformation 98% complete in less than 8 minutes. Therefore, the time of disappearance of the (110) gamma peak from our diffraction scan in the 400°C experiments would be expected to show large variations since our reaction temperatures may have ranged as much as ±15°C. In

addition, although we elevated the reaction temperatures from ambient to 400°C quite rapidly, our heating temperature curve unavoidably passes the nose of the C curve quite closely. As a result, small differences in the heating rates could cause disproportionate differences in the degree of transformation by the time that the reaction temperature is reached.

This new work of Dean places doubt on the reliability of the time of gamma-peak disappearance as an indicator of oxidation rate. Despite the uncertainty, it is very difficult to ignore its relationship to the time of appearance of the U_3O_8 diffraction peak as shown in Table II.

Influence of Alloy Phase on Oxidation

It was hypothesized earlier that oxide film thickness and cracking may play a role in the oxidation of UO_2 to U_3O_8. The cracks in the oxide result from stresses created by the difference in volume between the alloy and the oxide formed by an equivalent amount of metal. A lower specific volume of alpha phase relative to gamma phase at 400°C would increase the stress as the transformation of Mulberry

Figure 6. Time-Temperature—Transformation diagram for a Uranium-7.5 wt % Niobium-2.5 wt % Zirconium alloy as determined by metallography and hardness. (Courtesy of C. W. Dean, USAEC Y-1694, (1969).
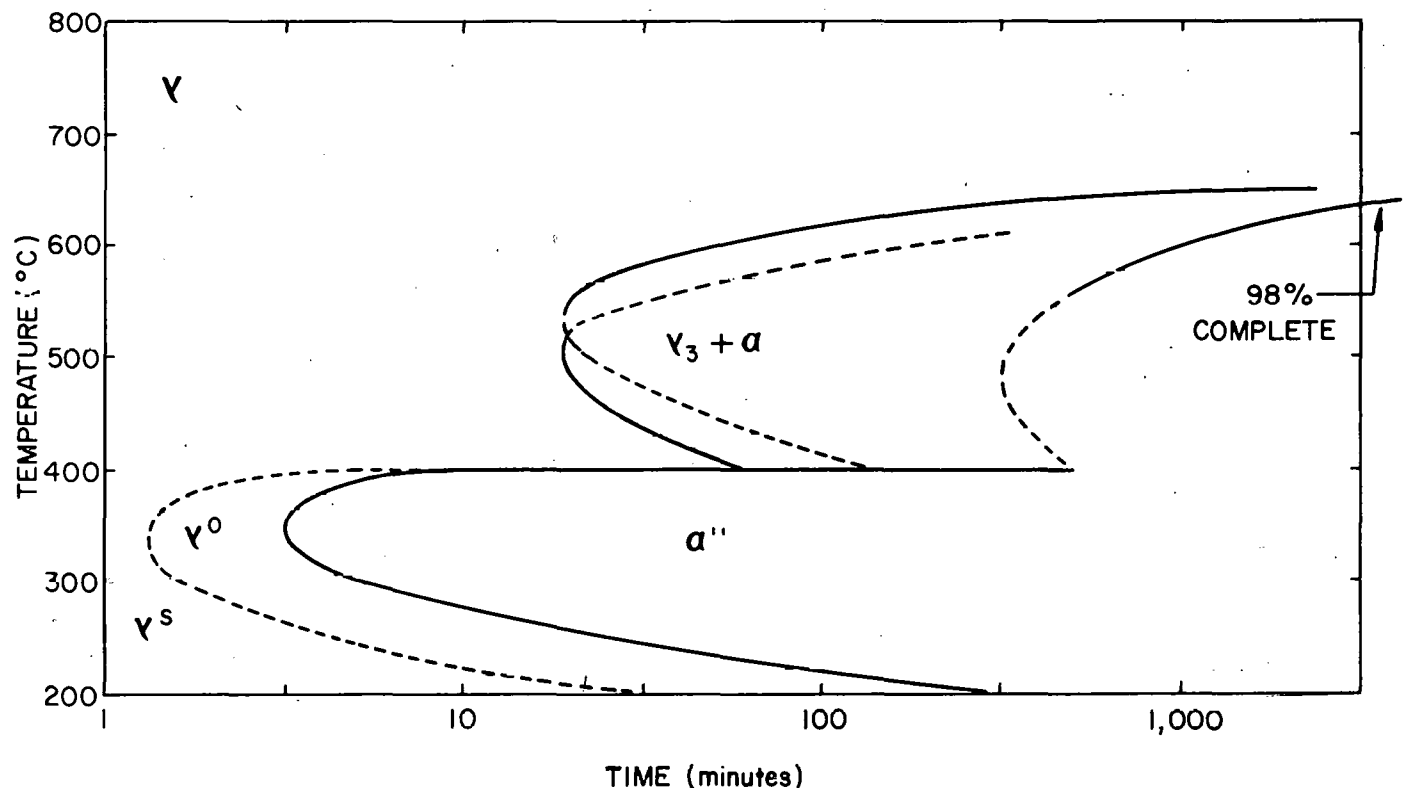
progresses. The linear expansion experiments on Mulberry by Peterson and Vandervoort,[15] shown in Figure 7, indicate that the gamma → alpha transformation does indeed result in a change of the metal volume. Therefore, the increased stress could cause the thinner films to crack, and the result would be shorter induction periods for U_3O_8 formation. To verify this theory, several samples which had different induction periods were examined metallographically to determine the degree of transformation each sample had undergone. If the phase is important in the time required for U_3O_8 to form, a higher degree of transformation would be expected for a sample that exhibited a short induction period compared to one that had a long induction period.

The attempt failed because we were unable to distinguish, by metallography, the different phases in our oxidized samples.

The failure points to an area where further work might be done. Apparently, the phase transformations during oxidation alters the polishing and etching characteristics of the alloy.

Development of a suitable technique to circumvent this would be highly desirable for any future study into the effect of phase transformation on oxidation rates.

Oxidation in 20 Torr of O_2

Several experiments were carried out with 20 torr of high purity O_2. The object was to match the experimental conditions with some of the oxidation studies being done at Sandia Corporation, Albuquerque. It is hoped that our x-ray data can be correlated with the rate data to be obtained.

The results showed that at 20 torr of O_2 the oxide product and the times in which they are formed are the same as that for 650 torr air. The earlier discussions in this report are applicable to oxidation in 20 torr of O_2.

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Figure 7.   Linear expansion of Uranium-7.5 wt % Niobium-2.5 wt % Zirconium.
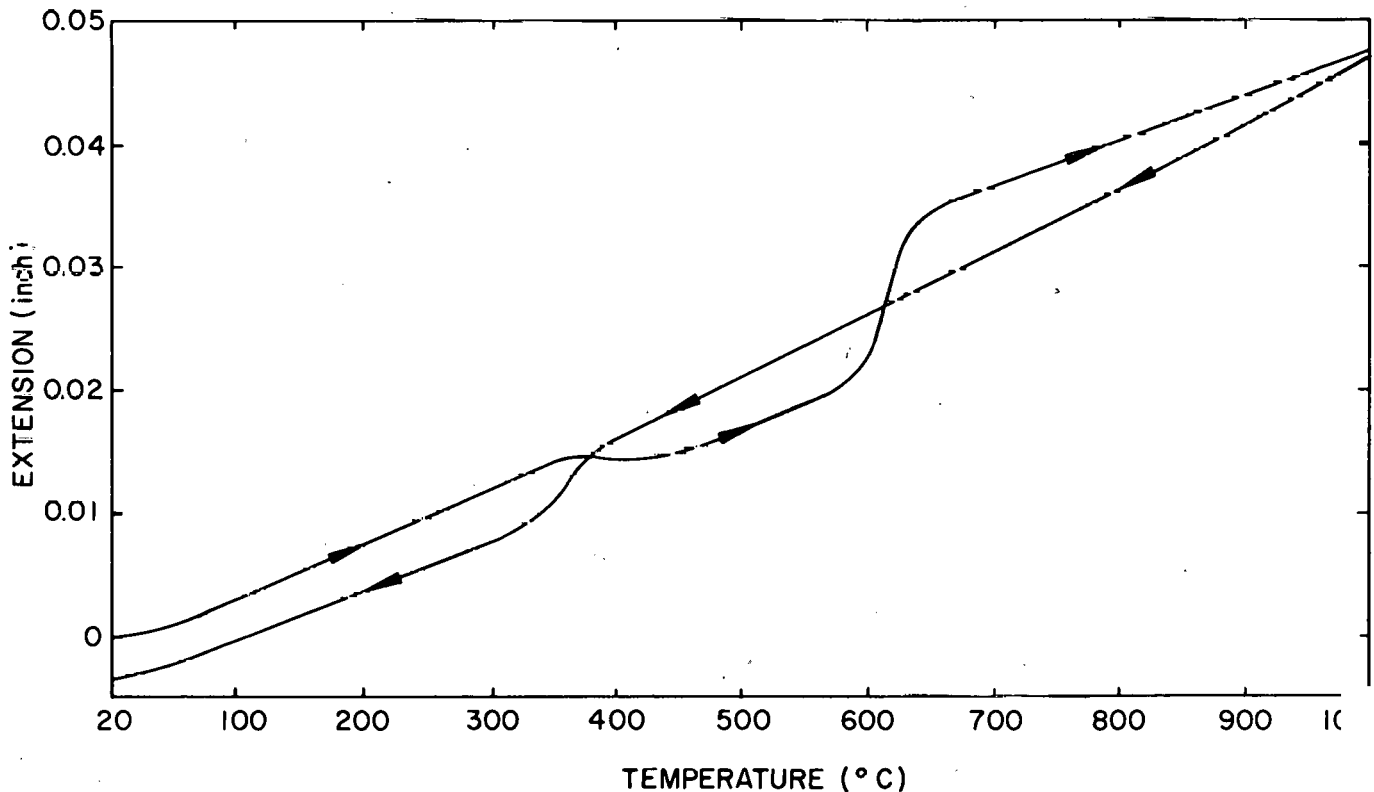
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