Final Report

THERMAL EXPANSION OF URANIUM DIOXIDE

TID-5722

Prepared for:

Metallurgy and Materials Branch Division of Research
United States Atomic Energy Commission Washington, D. C.

STANFORD RESEARCH INSTITUTE

Applied Research Center of the West

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Approved:

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O. F. Senn, Chairman Department of Chemistry

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PREFACE

This report has been prepared in a manner suitable for publication in the Journal of the American Ceramic Society. The preface is intended to present conclusions pertinent to the sponsored research program and to indicate regions which appear to warrant additional exploration.

In this investigation an attempt was made to obtain high temperature thermal expansion data on uranium dioxide actually employed for reactor fuel elements. For this reason specimens were obtained from a commercial supplier. In order to determine the influence of changes in the sintering process samples were prepared to provide variation in density and grain size. Although no firm answer was obtained to the problem of the volume change of uranium dioxide on melting, several significant results can be determined from this work.

1. Thermal expansion data have been extended from the region of 900 to 1000°C to the melting point of uranium dioxide.

2. An expansion anomaly was observed in the region of 1000 to 1500°C. Further study would be required to determine if this is a result of nonstoichiometry of uranium dioxide or an actual structural change occurring at these temperatures.

3. The thermal expansion of large grain, dense uranium dioxide, sintered for an extended period, was somewhat less than that of material having the same density but with a normal grain size.

4. Unique heating techniques for obtaining high temperature physical data have been explored, and their advantages and limitations more fully defined.

5. Exploration of the temperature region around the melting point of uranium dioxide has suggested that the volume change on melting is probably less than three percent. Further refinement of the techniques explored should permit improved measurement of this change.

THERMAL EXPANSION OF URANIUM DIOXIDE

ABSTRACT

The thermal expansion of commercial uranium dioxide specimens have been measured up to the melting point. The linear expansion of dense, normal grain size UO_2 follows closely the equation:

$$L = L_o(1 + 6.0 \times 10^{-6}t + 2.0 \times 10^{-9}t^2 + 1.7 \times 10^{-12}t^3)$$

An anomalous expansion was noted in the temperature range of 1000 to 1500°C. Above 2500°C the rapid vaporization and crystal growth of UO_2 necessitate the application of heating techniques which provide rapid heating and quenching in order to obtain reliable data. The use of solar and arc-melting furnaces for this type of measurement is described.

Final Report

THERMAL EXPANSION OF URANIUM DIOXIDE

Introduction

The desire to operate nuclear reactors at increased temperatures has in the past ten years stimulated extensive research on ceramic fuel element materials. Numerous investigations have been devoted to phase studies on the uranium-oxygen system, preparation of sinterable powders, and fabrication techniques, in addition to determination of thermal conductivity, thermal expansion, and irradiation effect. However, knowledge of the properties of uranium dioxide at temperatures above 1000°C is still quite limited.

Calculations of thermal stresses and heat transfer at elevated temperatures require accurate knowledge of thermal expansion and thermal conductivity. It has been suggested that some failures of fuel elements may have occurred as a result of the volume change of uranium dioxide upon melting in the core[1]. This investigation was initiated to explore unique heating techniques for obtaining thermal expansion data up to the melting temperature of uranium dioxide, with particular emphasis on the determination of volume change of uranium dioxide on melting.

Method

The technique used for measuring thermal expansion was to heat specimens of known densities and dimensions under atmospheres of argon, helium, or hydrogen and to photograph the profile of these specimens by their emitted light at temperature. These photographs were then enlarged, approximately ten times specimen size, on glass plates to prevent dimensional changes that normally occur with the use of photographic paper. The profile dimensions were measured with a traveling microscope calibrated to 1 mil.

It was proposed that if liquid UO_2 formed a contact angle greater than 90° on a leveled tungsten plaque, it should be possible to calculate the density of molten uranium oxide as well as its surface tension by the sessile drop technique described by Kingery and Humenik[2]. If wetting on tungsten does occur, it was felt that this information might still be obtained by melting the top portion of a UO_2 cylinder to form a self-supported bead.

Equipment and Procedure

In order to meet the heating requirements for measurements of this type at temperatures around 2860°C (melting point of UO_2)[3] a solar furnace was employed in this investigation. The solar furnace at Stanford Research Institute, shown in Figure 1, has been described in previous publications[4]. A diagram of the furnace chamber employed is shown in Figure 2. Two 24-inch focal length cameras, placed 90° apart, were employed to photograph the specimen at elevated temperatures and to indicate uniformity of the specimen shape.

In such a furnace, only the specimen under investigation is heated directly; the furnace chamber remains just above ambient temperature. Thus, many of the difficulties encountered at these temperatures with conventional furnaces, such as insulation requirements, sagging of structural components, atmosphere contamination due to outgassing of hot elements, etc., are eliminated. Close observation of the specimen is possible through glass windows. In addition, as a result of the low thermal inertia of such a furnace, the specimen can be heated rapidly and quenched -- a consideration of particular importance for materials having high vapor pressures where it is desirable to minimize weight loss during heating (v. p. UO_2 = 1 mm at melting temperature[5]).

One major limitation in the use of a solar furnace for this type of investigation is the difficulty in making accurate temperature measurements. Normal optical techniques are unsuited because of reflections from the sun; calibrations of flux with materials of varying melting points are unsuited because of temperature dependence on the emissivity of the specimen. Some attempts were made to employ two-color pyrometry, but the complex optical requirements placed development of this technique out of the scope of this program. For this reason the solar furnace was considered to provide data only in the region of the melting point of UO_2.

To determine the suitability of the solar furnace for sessile drop measurements, a 1-gram nickel specimen was melted in argon on a Morganite plaque and photographed. Surface tension, density, and contact angle of molten nickel were calculated from the tables of Bashforth and Adams[8]. The surface tension was found to be 1375 $\pm$ 20 dynes/cm compared to the reported value[2] of 1615 dynes/cm. A density of 7.36 $\pm$ 0.14 gm/cm^3 was obtained as compared to 8.0 gm/cm^3 reported in the literature[9]. The contact angle was 125 $\pm$ 3 degrees. These values appear quite reasonable considering that no attempt was made to obtain

extremely pure nickel or aluminum oxide or to purify the argon atmosphere employed. In addition, no particular care was taken to maintain the nickel temperature at the melting point; consequently, it may have been considerably higher.

To obtain thermal expansion data below 2500°C, the tungsten resistance furnace illustrated in Figure 3 was constructed. The all-tungsten heating chamber consists of top plate, side spacers, and a slotted 0.050-inch base plate 1-inch square. The heating chamber rests on two upright 0.050-inch tungsten plates fitted into 1/2-inch tungsten electrodes. The top plate and side spacers of the heating chamber were ground to thicknesses that provided a total electrical resistance equal to that of the base plate. The entire chamber was held in position by 1/8-inch diameter tungsten springs, as shown. In this way, a uniform temperature chamber 1 inch square by 1/4 inch high was provided. A thin slit in one side spacer permitted temperature measurement of the specimen while maintaining essentially black body conditions. The 1/4-inch square openings on opposite faces permitted profile photographs to be taken of the heated specimens. The hot chamber was surrounded with molybdenum radiation shields and a water-cooled shell. Power was provided by a transformer variable autotransformer combination supplying a maximum of 1500 amps at 14 volts. During operation this furnace was normally heated to red heat in hydrogen and then flushed with argon for high temperature measurements. In order to assure thermal equilibrium at each temperature, the specimen was held at constant temperature for ten minutes before taking photographs. Temperature measurements were made with a standardized optical pyrometer. A 13 degree temperature correction was made for the Pyrex furnace window.

Materials

The uranium dioxide employed in this investigation was obtained from the Nuclear Materials Corporation of Appollo, Pennsylvania in the form of cylinders 3/16 inch in diameter and 1/4 to 1 inch long. This material was fabricated by normal cold pressing and sintering techniques. Specimen densities of 77 and 93 percent of theoretical were obtained, with the high density material sintered in a manner to provide specimens of normal and large grain size. Density values for the three types of uranium dioxide, measured on all specimens by direct dimensional measurement and mercury immersion techniques, are shown in Table I.

Table I

DENSITY OF UO_2 SPECIMENS

Low density, normal grain	8.45 ± 0.10 gm/cm³
High density, normal grain	10.19 ± 0.11 gm/cm³
High density, large grain	10.19 ± 0.12 gm/cm³

Microphotographs of typical polished sections of the three types of specimens are shown in Figure 4. Emission spectrographic analysis revealed the presence of 100 ppm silicon, 15 ppm aluminum, and 2 ppm copper. X-ray diffraction patterns showed a lattice constant of 5.47 ± 0.01 Å.

Results

Linear thermal expansion data for uranium dioxide are plotted in Figures 5 through 8. During the initial heating, each specimen was heated to 2000°C. Typical expansion values for these runs are shown in Figure 5. Considerable scatter of data points was found during these tests in the case of the two dense grades. The scatter for the high density, normal grain material was so great that it is not shown in Figure 5. Sintering was observed above 1400°C in all cases on the low density material, and during these initial runs the density increased from 8.45 to 9.33 gm/cm³. The shaded points indicate data obtained during cooling. Thermal expansion data of Bell and Makin[6] and Murray and Thackray[7] to temperatures of 1000°C and 900°C, respectively, are shown for comparison.

Upon reheating these specimens to 2500°C the thermal expansion curves in Figures 6, 7, and 8 were obtained for the three types of uranium dioxide pellets. Typical data points for individual runs are shown. These values were highly reproducible. The low density material further sintered at elevated temperatures and then during cooling followed closely the expansion curve of the large grain, dense material, reaching a room temperature density of 10.27 gm/cm³. No sintering was observed in the normal grain, dense material, and the linear thermal expansion is represented by the equation:

$$L = L_o(1 + 6.0 \times 10^{-6}t + 2.0 \times 10^{-9}t^2 + 1.7 \times 10^{-12}t^3)$$

The large grain, dense UO_2 increased slightly in density to 10.25 gm/cm³.

In all cases, during heating and cooling of dense uranium dioxide, an irregularity was noted in the expansion curve between 1000 and 1500°C. No attempt was made to explore this region in detail.

The volume expansion of uranium dioxide up to the melting point is presented in Figure 9 for the two dense grades studied. These data were calculated from the linear expansion values of the previous curves and illustrate more clearly the large increase in volume occurring at temperatures above 2000°C.

Above 2450°C excessive vaporization and crystal growth on the surface of the specimens were observed in the tungsten furnace. A polished section of this crystal growth is shown in Figure 10. At temperatures of approximately 2700°C in helium or hydrogen, weight loss was very rapid and whiskers of UO_2 up to 1/8 inch long appeared. An argon atmosphere reduced this vaporization somewhat, and at a temperature slightly above 2810°C (maximum reading on optical pyrometer) UO_2 melted and completely wet the tungsten plaque.

During this investigation it was found that uranium dioxide could not be melted in a controlled manner in the solar furnace. One of the principal reasons for this was the high vapor pressure of UO_2 near the melting point. As the melting point was approached a considerable amount of vapor was observed to form which acted as a filter for the solar energy and coated the glass cover on the furnace chamber. Excessive crystal growth occurred on the specimen, and melting started on the top surface, but before sufficient melting could occur to permit measurement, the surface resolidified. It is probable that with a larger collector mirror the radiant flux would be sufficient to accomplish melting in spite of this difficulty. Attempts to force vapor out of the solar radiation path by means of argon circulation were unsuccessful. Modifications of the furnace chamber by providing a thin-wall glass hemisphere top or by removal of the top glass plate to locate the specimen in an open column of argon did not significantly increase the temperature.

In order to obtain values of the volume of UO_2 at the melting point several tests were made using an arc-melting furnace, available in the laboratory. A diagram of this furnace is shown in Figure 11. For this work, the viewing port and cover were replaced with a polystyrene plate so that photographs of the drop profile could be taken. This general technique for measuring the volume change of UO_2 on melting was first proposed by Dr. L. M. Pidgeon of the University of Toronto and is being studied in detail there at the present time.

The method employed in this program consisted of placing a 1/4-inch-thick tungsten electrode on the water-cooled copper hearth in order to reduce the temperature gradient through the UO_2 specimen. The d. c. arc was directed onto the top of a 1/2-inch UO_2 cylinder (3/16 inch diameter) placed on the tungsten plaque. When a molten bead was formed on the top of the UO_2, high speed movies (32 frames/sec) were taken as the arc was turned off and the specimen cooled. Measurements were then taken of the maximum bead diameter and distance from the equator to the top of the bead during cooling. Pictures were also taken of the bead at room temperature in order to calculate the volume change on cooling.

In each case, when the arc was placed on the specimen, the UO_2 cylinder fractured. Consequently the molten bead formed was not symmetrical and calculations of surface tension were not possible. Measurements of the bead profile during cooling are shown in Figure 12. These values are normalized on the room temperature measurements. It can be seen that during arc cutoff a large volume change occurred. Prior to this time the dimensions varied considerably, probably due to stirring of the melt by the arc. Following the arc cutoff, the bead dimensions remained constant for approximately three seconds and then started contracting without a sharp discontinuity. This constant region is felt to be a temperature arrest point where solid and liquid are in equilibrium and it was used to calculate the expansion of solid UO_2 at the melting point (Figures 7 and 8).

The initial volume change during arc cutoff does not appear to be a change due to solidification. Rather, it more likely is caused by the action of the arc on the melt, by superheating of the melt surface, and by overexposure of the film due to the bright arc flame around the bead. If this change were a true volume change it would mean a change of 40 to 50 percent, which appears unreasonable from past observations[1].

If solidification actually occurred during the uniform-volume period it would indicate that the volume change on solidification must be less than three percent (the estimated accuracy of these measurements). If it exceeded this, some distortion of the drop surface should have occurred during solidification, or a hollow zone should have formed in the bead. This was not observed on the bead surface. However, extensive internal fracture occurred in the bead, which was revealed by polished sections, so that the latter possibility cannot be eliminated.

CONCLUSIONS

The thermal expansion of uranium dioxide has been measured at temperatures up to the melting point (2860°C). The linear expansion of dense, normal grain size UO_2 follows closely the equation:

$$L = L_o(1 + 6.0 \times 10^{-6}t + 2.0 \times 10^{-9}t^2 + 1.7 \times 10^{-12}t^3)$$

An anomaly was observed in the expansion curve in the region of 1000 to 1500°C. At temperatures above 2500°C vaporization of UO_2 is extremely rapid in inert atmospheres and hydrogen.

ACKNOWLEDGEMENT

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FIGURES

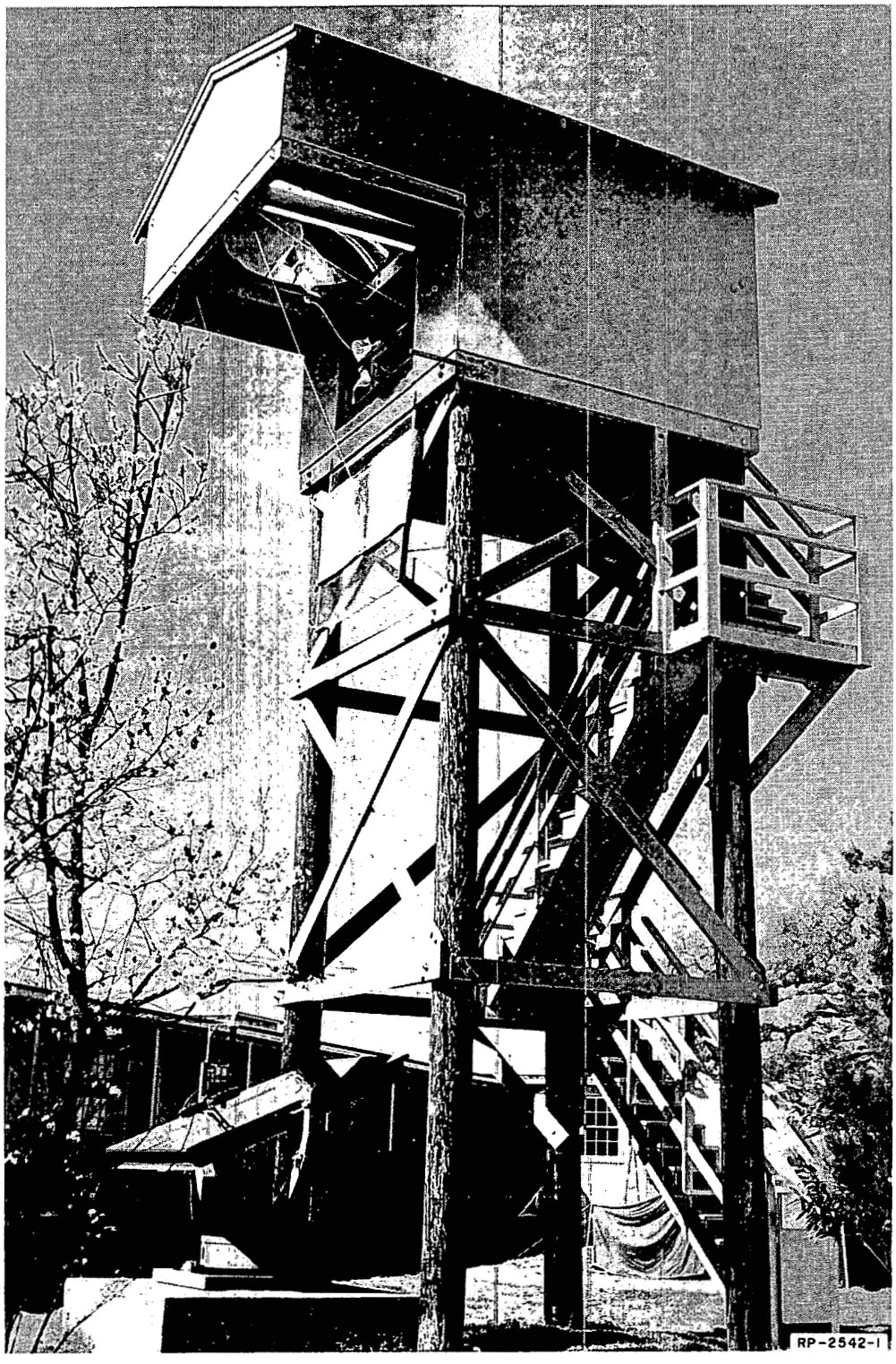

FIG. 1

SOLAR FURNACE AT STANFORD RESEARCH INSTITUTE

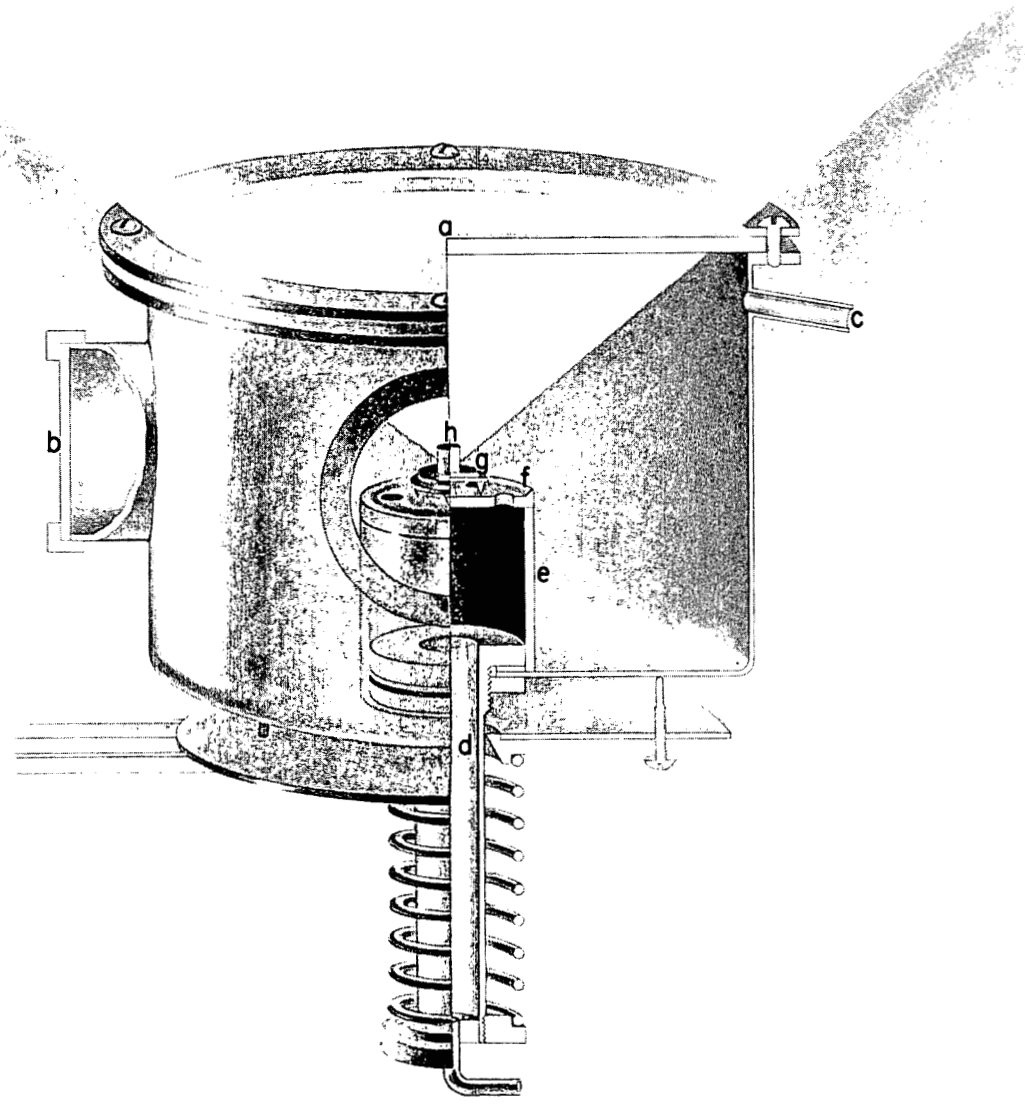

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FIG. 2

SOLAR FURNACE SPECIMEN CHAMBER: (a) PYREX OPTICAL PLATE, (b) SIGHT PORT, (c) GAS INLET, (d) GAS OUTLET, (e) COPPER SUPPORT, (f) GRAPHITE BASE PLATE, (g) TUNGSTEN SETTER PLATE, (h) UO_2 SPECIMEN

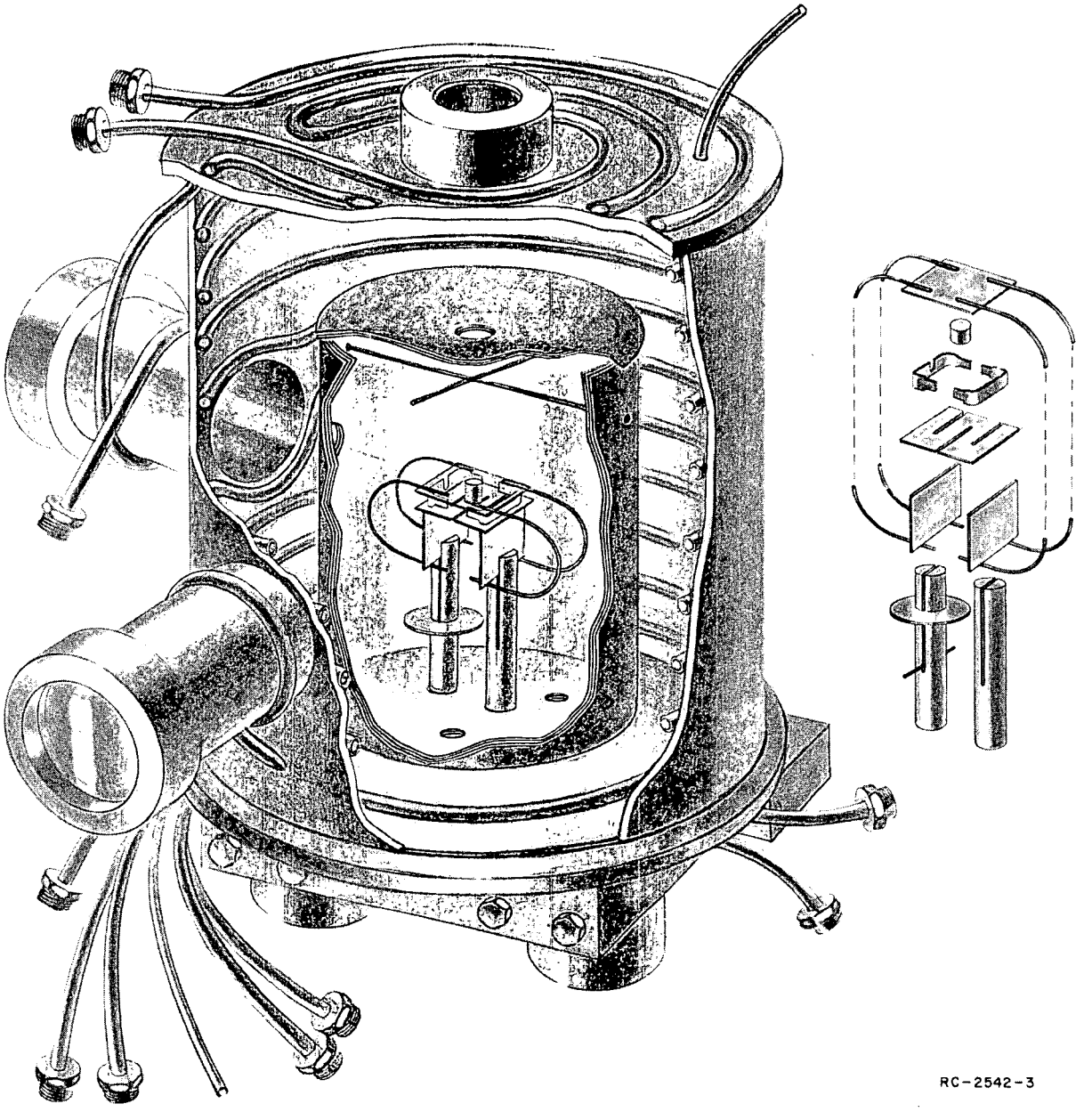
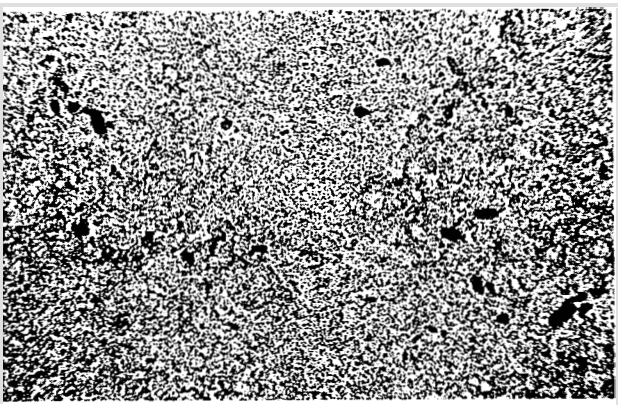
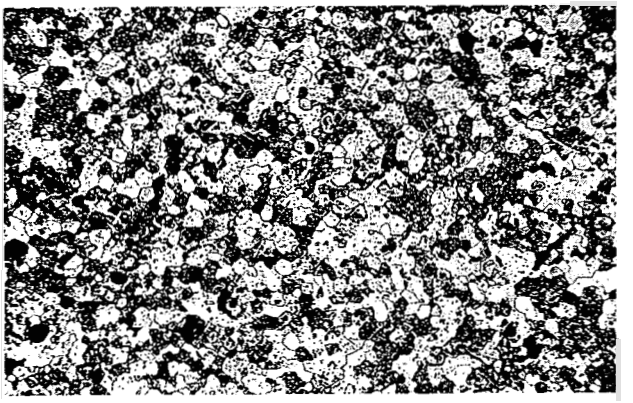


FIG. 3
TUNGSTEN RESISTANCE FURNACE



(a)



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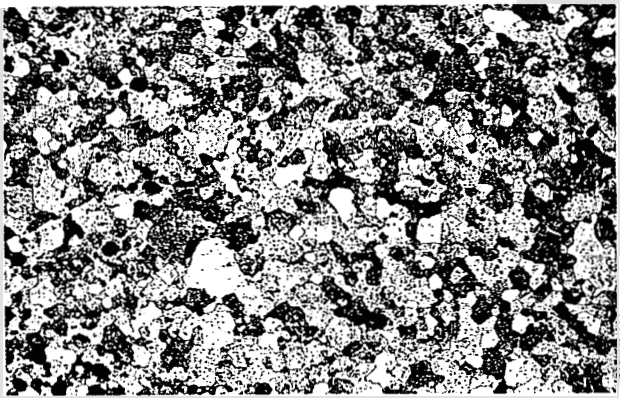

(c)

RP-2542-4

FIG. 4

PHOTOMICROGRAPHS OF URANIUM DIOXIDE SPECIMENS AS RECEIVED: (a) LOW DENSITY, NORMAL GRAIN, (b) HIGH DENSITY, NORMAL GRAIN, (c) HIGH DENSITY, LARGE GRAIN (80X)

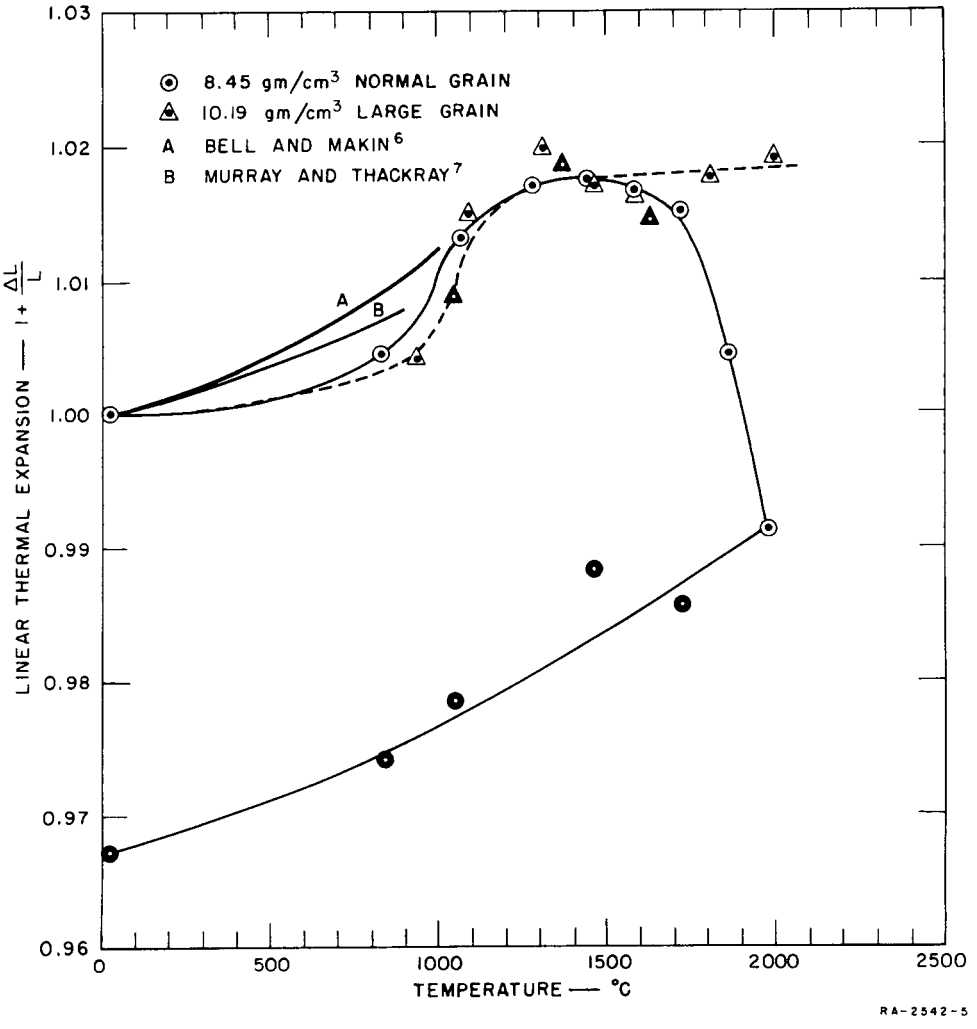

FIG. 5

LINEAR THERMAL EXPANSION OF UO_2: INITIAL HEATING AFTER FABRICATION
(Shaded points indicate measurements on cooling)

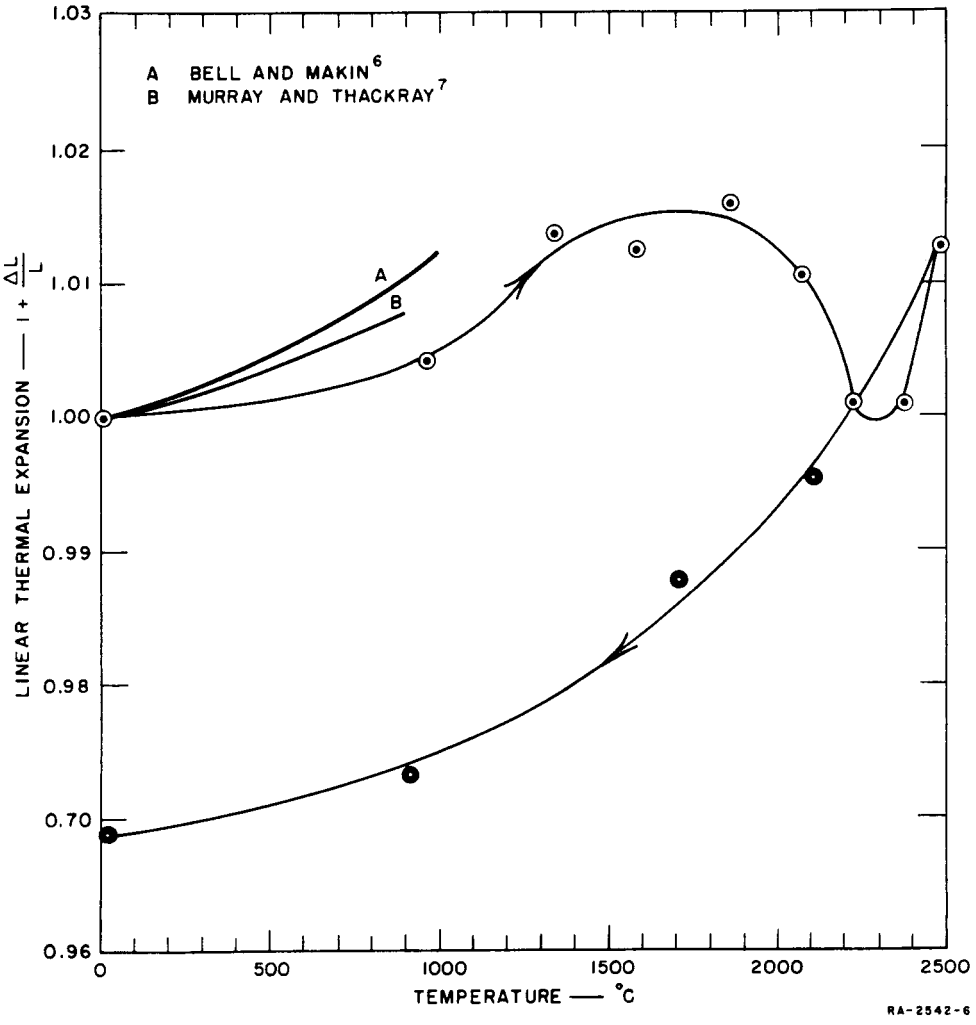

FIG. 6

LINEAR THERMAL EXPANSION OF LOW DENSITY UO_2 UPON REHEATING TO 2500°C
(Initial density, 9.33 gm/cm3)

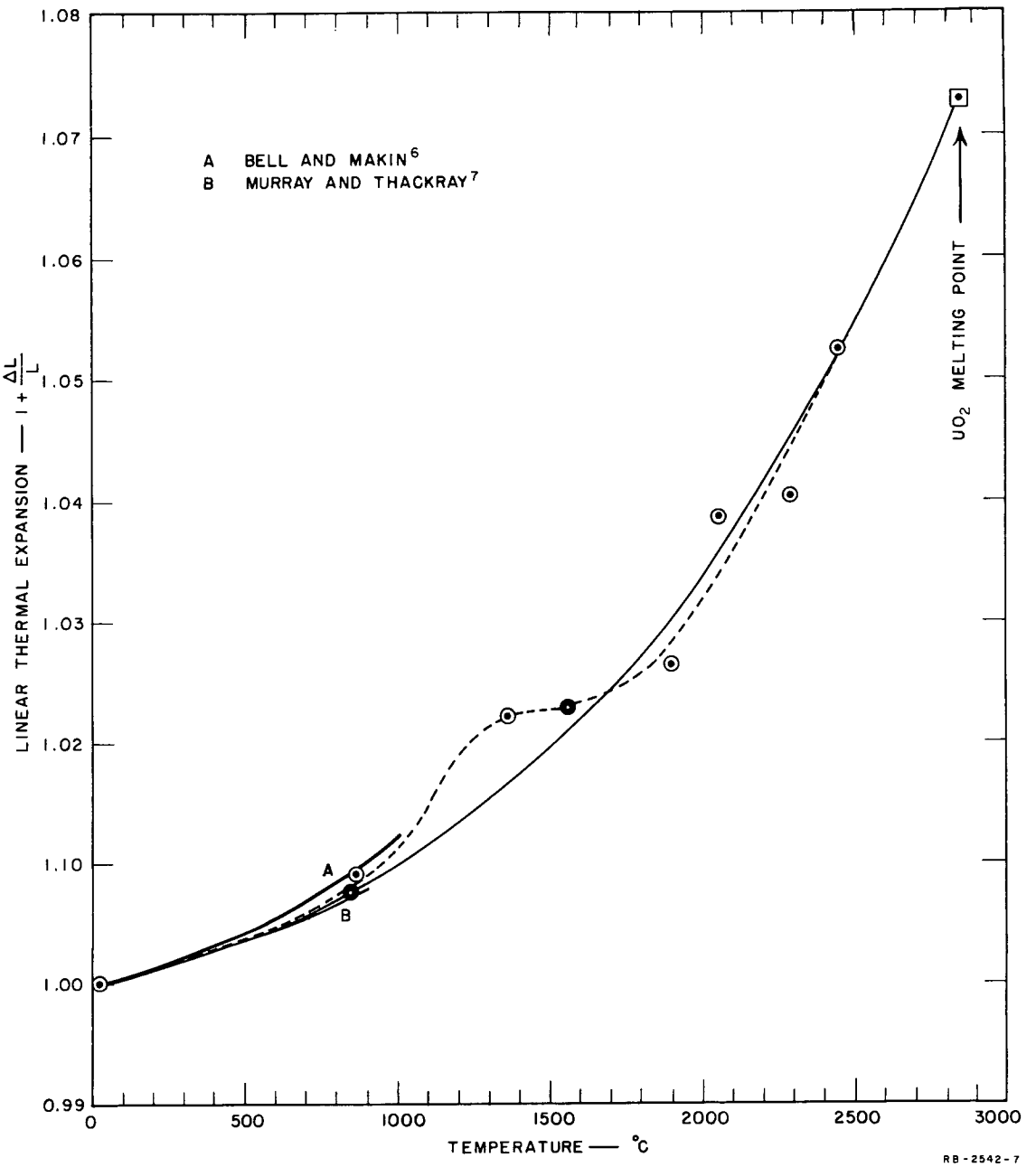

FIG. 7

LINEAR THERMAL EXPANSION OF DENSE (10.19 gm/cm^3), NORMAL GRAIN SIZE UO_2 UPON REHEATING

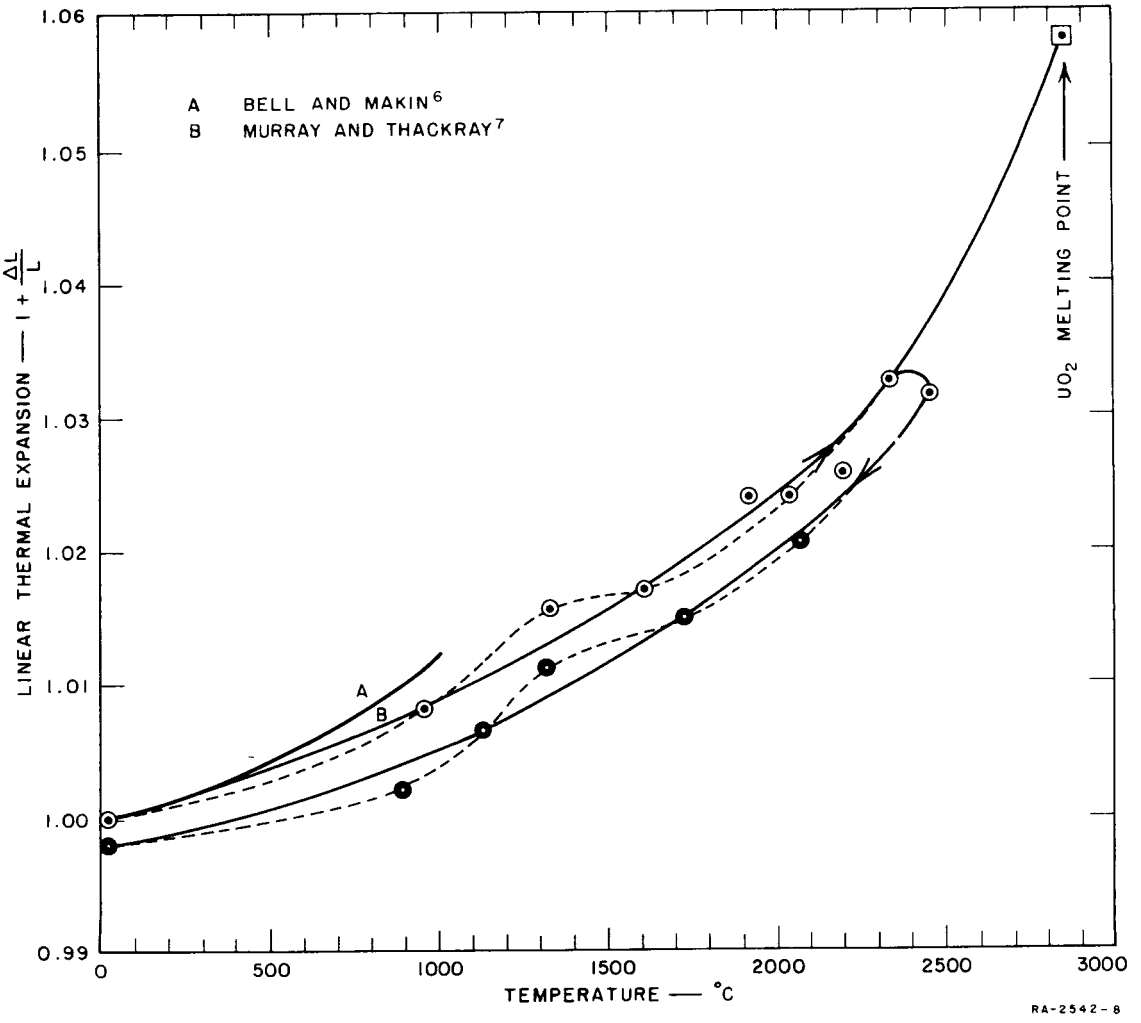

FIG. 8

LINEAR THERMAL EXPANSION OF DENSE (10.19 gm/cm^3), LARGE GRAIN SIZE UO_2 UPON REHEATING

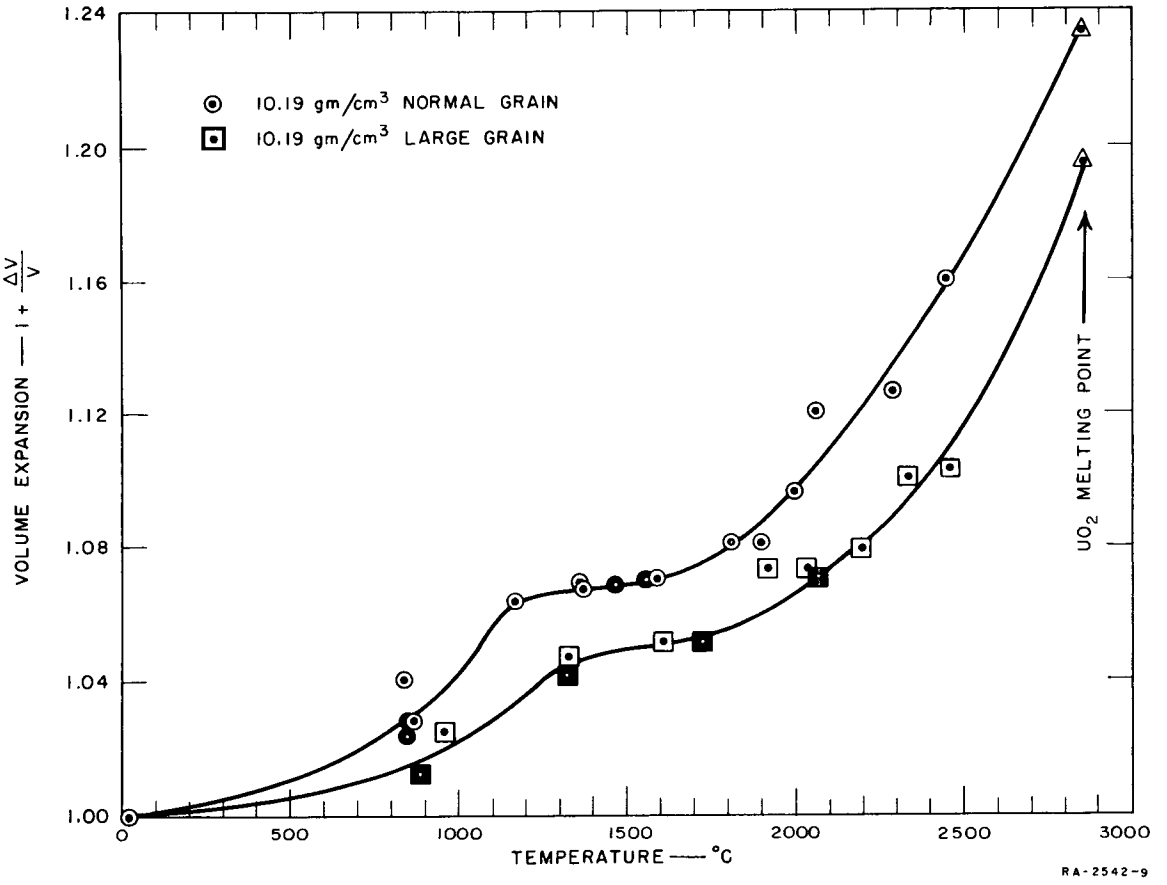

FIG. 9

VOLUME EXPANSION IN HEATING UO_2 TO THE MELTING POINT
(Shaded points indicate measurements on cooling)

FIG. 10

PHOTOMICROGRAPH SHOWING CRYSTAL GROWTH AT THE SURFACE OF UO_2 SPECIMEN HEATED ABOVE 2500°C (80X)

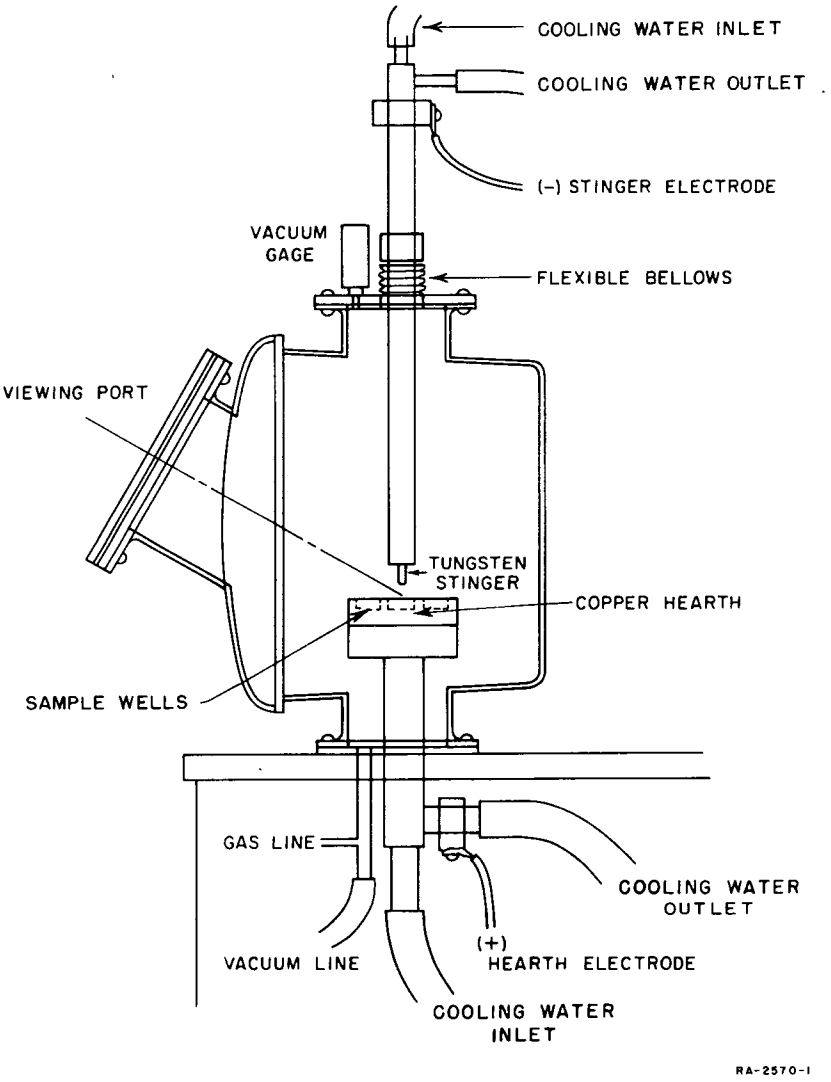

FIG. 11
ARC-MELTING FURNACE

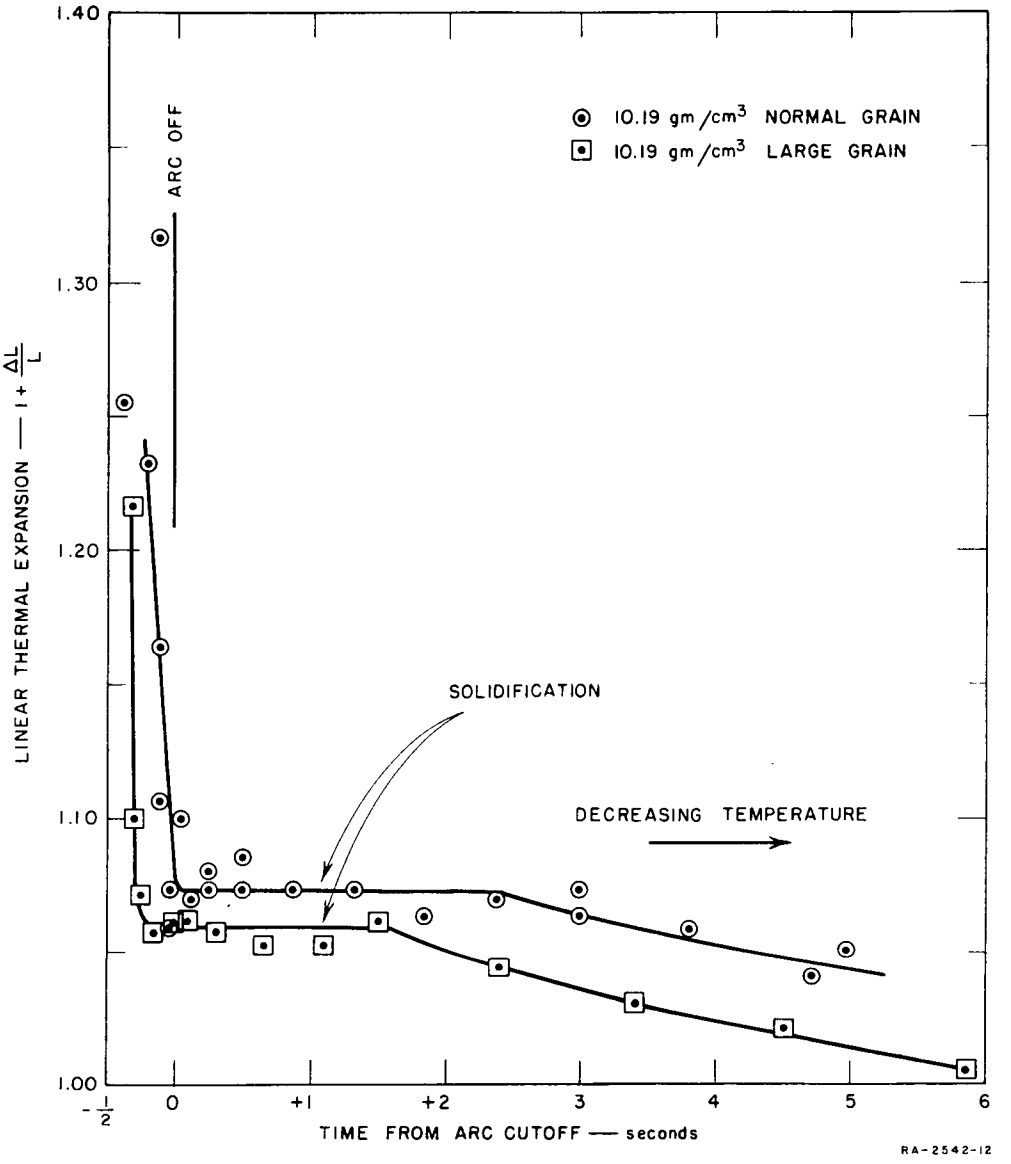

FIG. 12

LINEAR DIMENSIONAL CHANGE OF UO_2 IN COOLING THROUGH THE MELTING POINT

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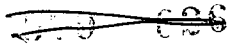

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