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**ATOMIC ENERGY
OF CANADA LIMITED**



**L'ÉNERGIE ATOMIQUE
DU CANADA LIMITÉE**

PROCEDURE FOR OXIDIZING ZIRCALOY-2 AND ZIRCALOY-4

Méthode pour oxyder Zircaloy-2 et Zircaloy-4

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Chalk River, Ontario

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R.D. Watson

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Mechanical Equipment Development Branch
Chalk River Nuclear Laboratories
Chalk River, Ontario K0J 1J0
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Résumé

On a développé une méthode pour produire une épaisse couche d'oxyde, uniforme et continue, à la surface des alliages Zircaloy-2 et Zircaloy-4. Cette couche est dure et elle résiste à l'usure. Elle a de bonnes propriétés pour l'isolation électrique et thermique ainsi qu'une bonne résistance à la corrosion dans l'eau.

Des méthodes permettant de calculer l'épaisseur de l'oxyde et les changements dimensionnels dus à l'oxydation sont également indiquées.

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SYNOPSIS

A procedure for producing a uniformly thick continuous oxide layer on the surface of Zircaloy-2 and Zircaloy-4 has been developed. This coating is hard and wear resistant; it has good electrical and thermal insulating properties, and good corrosion resistance in water.

Methods of calculating the oxide thickness and the dimensional changes due to oxidation are also provided.

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PROCEDURE FOR
OXIDIZING ZIRCALOY-2 AND ZIRCALOY-4

1. SCOPE

This report describes a procedure for oxidizing Zircaloy-2 and Zircaloy-4 and contains a method for calculating oxide thickness and dimensional changes due to oxidation. It is not to be used on Zr-2.5 wt% Nb or other zirconium alloys.

1.1 Oxidation Process

The material is fully annealed, machined to size, degreased, washed, glass-shot blasted and heated in air in an electric furnace. The preferred heating temperature is 650°C but the material can be oxidized at higher or lower temperature according to Figure 1. The oxidation curves are not absolute and should be used with the knowledge that they may be displaced slightly from that shown in Figure 1 because of differences in the purity of Zircaloy-2 and the amount of shot blasting done.

1.2 Oxide Thickness

This process produces oxide coatings 0.013 mm (0.0005 in.) to more than 0.227 mm (0.009 in.) by heating in air at 650°C. The thickness is almost proportional to the heating period. A layer of 0.076 mm (0.003 in.) requires about 48 h at 650°C.

1.3 Application

Oxidized Zircaloy-2 and Zircaloy-4 may be used for:

- a) A corrosion resistant surface in cold or hot water.
- b) Thermal insulation in pressure tubes.
- c) Electrical insulation where the radiation level is too high for organic materials.
- d) A wear surface in water lubricated mechanisms.
- e) Stiffening thin walled tubing.
- f) Valve stem material.

This report does not specify the oxide thickness for these applications. The purchase order specifies oxidizing temperature and specific weight gain.

It is difficult to say what oxide thickness is best because it depends to some extent on the application. For friction and wear parts an oxide thickness of 0.051 mm (0.002 in.) to 0.076 mm (0.003 in.) is most frequently used. For thermal insulation a much thicker coating would probably be specified. For electrical insulation the coating might be thick or thin depending on the application.

2. APPLICABLE DOCUMENTS

- 2.1 Watson, R.D., Forming Uniform Thick Oxide Layers on Zircaloy-2 for Friction and Wear Applications in High Temperature Water, Atomic Energy of Canada Limited, Report AECL-2542, March 1966.
- 2.2 Celli, A., Heat Transfer Characteristics of Oxidized Zircaloy-2 Sheets, Unpublished Information, July 1967.
- 2.3 Dunn, J.T., Wear Rates of Metals and Oxides in 80°F and 160°F High Purity Water, Atomic Energy of Canada Limited, Report AECL-2602, August 1966.
- 2.4 Watson, R.D. et al., Forming Uniform Thick Oxide Layer of Material, United States Patent 3,615,885, Patented Oct. 26, 1971.
- 2.5 Watson, R.D. et al., Forming Uniform Thick Oxide Layer on Material, Canadian Patent 770,080, Filed Sept. 19, 1966.
- 2.6 Watson, R.D., On the Oxidation of Zirconium Alloys in Air and the Dimensional Changes Associated with Oxidation, Atomic Energy of Canada Limited, Report AECL-3375, June 1969.

3. REQUIREMENTS

3.1 Annealing

If flatness or straightness after oxidizing is critical, fully anneal parts before oxidizing to minimize warping.

a) Rods

To produce straight rods anneal as follows:

- i) Start with material 1.59 mm (1/16 in.) larger in diameter than required. Place in an electric furnace at 650°C +10, -0°C on a piece of clean fire brick with a V-groove in the surface to prevent the rod from rolling off.
- ii) Leave in the furnace for at least 16 hours.

- iii) Remove the fire brick and rod from the furnace while still at temperature and allow to cool in still air.

Remove out-of-straightness in rods during machining to size (see Section 3.2). If out-of-straightness is more than machining tolerance, bend straight and repeat annealing.

b) Rings

Where rings for shaft seals must not be more than 0.003 mm (0.0001 in.) out-of-flat after oxidizing, anneal as follows:

- i) Machine ring roughly to size leaving 1.59 mm (1/16 in.) machining allowance all over.
- ii) Insert in an electric furnace at 650°C +10, -0°C on a piece of clean fire brick.
- iii) Leave in furnace at least 16 hours.
- iv) Remove fire brick and ring from furnace while still at temperature and allow to cool in air.

Remove out-of-flatness during machining to finished size.

3.2 Machining

Machine parts after annealing to a surface finish of 0.8 to 1.6 μm (32 to 63 $\mu\text{in.}$) AA. Better finishes are not required because the glass-shot blasting exceeds 0.8 μm (32 $\mu\text{in.}$) AA. As grinding Zircaloy-2 and Zircaloy-4 is difficult and may introduce residual stresses, it is not recommended. Check marks indicate plastic flow. They cannot be tolerated on machined parts.

To machine rods or rings flat and straight after annealing hold them in special devices which will not deform them elastically or plastically. For example, support a ring in a brass holder with a dozen equally spaced plastic tipped screws tightened lightly against the OD of the ring. Locate the screws so their axes pass approximately through the centroid of the ring.

3.3 Degreasing

Degrease material to be oxidized in clean trichloroethylene liquid or vapor and dry thoroughly.

3.4 Washing

After degreasing thoroughly wash the material in soap and water, rinse in demineralized water and dry in a blast of oil free air from an air hose.

3.5 Shot Blasting

3.5.1 Glass Shot Size

Purchase 0.089 mm (0.0035 in.) nominal diameter glass shot.

Cataphote Corporation Glass-shot (glass spheres) size ML supplied by Ritchey Supply Ltd. is satisfactory. Blast-O-Lite glass beads size No. BT-11 supplied by Ritchey Supply Ltd. should also be satisfactory.

Slightly larger glass shot than that specified above may be used when agreed to by the customer.

3.5.2 Procedure

Shot blast all surfaces with conventional grit blasting equipment. Air pressure must be 0.62 to 0.69 kN (90 to 100 lbf/in²) to shot blast with sufficient intensity. Lines to the cabinet and nozzle must be at least 13 mm (1/2 in.) ID to minimize pressure drop. Figure 2 shows a typical shot blast nozzle with a 10 mm (3/8 in.) opening at the exit end.

Continue shot blasting until the surface is uniformly covered with a dull nonreflecting matte finish. A little extra shot blasting is better than not enough. Uniformly blast lapped surfaces to ensure they remain flat. When shot blasting by hand follow a systematic procedure to ensure surfaces are covered uniformly. Wipe off dust afterwards with a clean cloth.

3.6 Weighing

Weigh the specimen on an analytic balance to an accuracy of +0.2 mg. If the sample is too heavy to weigh prepare in a similar manner a small control piece of the same material about 13 mm (1/2 in.) square x 3 mm (1/8 in.) thick. Oxidize the control piece with the specimen and determine the oxide thickness of the specimen from the specific weight gain of the control piece.

3.7 Oxidizing

3.7.1 Oxygen Requirements

If a large number of parts with a large total surface area are being oxidized in a small, fairly well sealed furnace,

it may be necessary to replenish the oxygen in the air by opening the door periodically or by providing a small flow of air through the furnace.

The weight of oxygen required is almost equal to the total weight gain of the specimens. If the furnace is sufficiently large to supply this weight of oxygen without reducing the oxygen level in the furnace air by more than 10% then there should be no problem.

3.7.2 Oxidizing Procedure

Oxidize parts in air in an electric furnace, preferably at 650°C. This is the temperature at which most information on dimensional changes has been obtained (see section 6.1).

To produce a uniformly thick oxide and minimize distortion, each surface of each piece must get the same dose of heat. This can be provided by:

- a) Heating in a furnace that has little or no temperature gradient across that part of the furnace in which the piece is situated.
- b) Turning, rotating and moving the part regularly or continuously in a furnace that has large thermal gradients.

In a), because the oxidation rate almost triples every 50°C between 600°C and 700°C, the temperature variation across the heating zone of the part must not be greater than 5°C to prevent the oxide thickness varying widely. To decrease the temperature gradient in a furnace, circulate the air with a fan.

In b), to oxidize a long tube with a uniformly thick coating, pull it through the hot zone at a constant rate and continuously rotate it. Also in b), to produce the same coating thickness on several small parts or a large part, regularly or continuously turn, rotate and move them so all surfaces receive the same dose of heat.

Insert the parts after the furnace has reached the appropriate temperature. Do not insert them prior to this. Remove the parts and the fire brick on which they are sitting while the furnace is still at temperature. Cool them in still air on the fire brick.

Locate the furnace in a room free of vapors from cleaning solvents and grinding lubricants. Trichloroethylene vapor reduces oxidation of Zircaloy-2 at 650°C to about 20% of the values in Figure 1.

Support parts to be oxidized on something inert such as clean fire brick (Babcock and Wilcox No. K28 or equivalent). Do not support them on metal surfaces, which may contaminate the Zircaloy-2 or Zircaloy-4 surfaces and cause an inferior oxide layer to form.

Determine from Figure 1 the time required to form an oxide of specified thickness.

3.8 Weighing after Oxidation

Reweigh the specimen after oxidation and determine the weight gain and corresponding oxide thickness according to Section 4.1.

4. QUALITY ASSURANCE REQUIREMENTS

4.1 Calculating Oxide Thickness

Determine oxide thickness as follows:

- a) Calculate the surface area of the specimen in dm^2 (both inside and out).
- b) Weigh specimen before and after oxidation.
- c) Calculate the specific weight gain in g/dm^2 .
- d) A weight gain of $1 \text{ g}/\text{dm}^2$ is equivalent to an oxide thickness of 0.070 mm ($2.76 \times 10^{-3} \text{ in.}$).

4.2 Oxide Appearance

A properly oxidized specimen should be uniformly covered with a light brown oxide.

5. PREPARATION FOR DELIVERY

Pack the parts in cellular material and waterproof wrapping to prevent:

- a) Physical damage to the fragile oxide coating, and
- b) Contamination of the coating including contamination from the packing material.

6. NOTES

- 6.1 During oxidation, parts such as bushings, plates, sheets, etc. change dimensions. The change is quite significant, especially for tubular shapes and plates having relatively thin walls.

During the oxidation of a tubular shape or plate at 650°C in air the following happens. Oxidation of the surface produces an increase in volume. Some of this increase in volume produces a stretching of the wall, both longitudinally and circumferentially, which manifests itself in an increase in length and width for a plate. The remainder of the increase in volume produces a thickening of the wall, which in the case of the tube tends to reduce the inside diameter and increase the outside diameter.

After oxidizing, the new dimensions are as follows:

$$OD = (\text{mean diam.} + \text{increase in mean diam.}) + (\text{wall thickness} + \text{increase in wall thickness})$$

$$ID = (\text{mean diam.} + \text{increase in mean diam.}) - (\text{wall thickness} + \text{increase in wall thickness})$$

$$\text{Length} = (\text{original length} + \text{increase in length}) + \text{increase in wall.}$$

Small holes in thick material will decrease in size during oxidation by an amount equal to the values given in Figure 4 for increase in wall thickness. Solid rod will increase in diameter by a similar amount.

Quite a lot of experimental data has been obtained on the dimensional changes of tubes and sheets of varying wall thickness. The best available information on the increase in length (or diameter) and wall thickness is given in Figures 3 and 4, respectively.

6.2 Calculating the Changes in Dimensions Due to Oxidation

Problem 1: How much allowance should be made for growth during oxidation to produce a coating 0.051 mm (0.002 in.) thick on a bushing approximately 21.285 mm (0.838 in.) OD x 15.875 mm (0.625 in.) ID x 25.4 mm (1.000 in.) long?

Solution 1: A specific weight gain of 1 g/dm² is equivalent to an oxide thickness of 0.0701 mm (0.00276 in.). Thus an oxide thickness of 0.0508 mm (0.002 in.) is equivalent to $\frac{0.002}{0.00276} \times 1.0 \text{ g/dm}^2 = 0.725 \text{ g/dm}^2$.

$$\text{Mean diameter of bushing} = \frac{21.285 + 15.875}{2} = 18.58 \text{ mm (0.7315 in.)}$$

$$\text{Wall thickness} = \frac{21.285 - 15.875}{2} = 2.705 \text{ mm (0.1065 in.)}$$

Using Figure 3, the line for wall or material thicknesses from 0.100 to 0.125 in. intersects the required specific weight gain of 0.725 g/dm^2 at an increase of 0.22%. This means that the mean diameter of this bushing will increase by about 0.22% or $\frac{0.22}{100} \times 18.58 \text{ mm} = 0.0408 \text{ mm}$ (0.0016 in.). Increase in length due to stretching = $\frac{0.22}{100} \times 25.4 = 0.0559 \text{ mm}$ (0.0022 in.).

From Figure 4, the increase in wall thickness for a specific weight gain of $0.725 \text{ g/dm}^2 = 0.0368 \text{ mm}$ (0.00145 in.).

After oxidizing, the OD of bushing = (mean diam. + increase in mean diam.) + (wall thickness + increase in wall thickness) = $(18.58 + 0.0408) + (2.705 + 0.0368) = 21.3626 \text{ mm}$ (0.8410 in.).

The ID of bushing = (mean diam. + increase in mean diam.) - (wall thickness + increase in wall thickness) = $(18.58 + 0.0408) - (2.705 + 0.0368) = 15.879 \text{ mm}$ (0.6252 in.).

The length of bushing = (original length + increase in length) + increase in wall thickness = $(25.4 + 0.0559) + 0.0368 = 25.4927 \text{ mm}$ (1.0036 in.).

Therefore, in order to get the specified dimensions of the bushing after oxidizing, the bushing must be made 21.209 mm (0.835 in.) OD x 15.870 mm (0.6248 in.) ID x 25.309 mm (0.9964 in.) long.

Problem 2: Suppose the bushing in problem 1 was stepped so that for half its length the bushing was 23.8506 mm (0.939 in.) OD and for the other half was 21.031 mm (0.828 in.) OD, with the bore and the overall length being the same as problem 1.

What is the shape of the bushing after it has been oxidized to produce a coating 0.0508 mm (0.002 in.) thick?

Solution 2: In solving this problem assume that we have two bushings of different OD and wall thickness. Calculate the new dimensions, after oxidizing, for both bushings. The thinner-walled bushing is going to stretch more than the thicker-walled bushing. The dimensions of each end of the original stepped bushing after oxidizing will be the same as the calculated new dimensions of the two separate bushings. The actual ID at the centre of the stepped bushing after oxidizing will be approximately

$$ID_c = ID_1 + \frac{t_1 (ID_2 - ID_1)}{t_1 + t_2}$$

where ID_c = ID at centre of bushing
 ID_1 = ID of thicker bushing
 ID_2 = ID of thinner bushing
 t_1 = wall of thicker bushing
 t_2 = wall of thinner bushing

6.3 Precautions and Suggestions

A clean electric furnace must be used for oxidation. A dirty furnace is likely to produce a poor oxide coating.

Locate the furnace in a room free of cleaning solvent vapors and grinding lubricants, which may prevent or retard oxidation.

The glass-shot blasting is required to produce a uniform oxide coating. If glass-shot blasting is not used, a discontinuous nonuniform coating will result. The size of the glass shot must not be smaller than that specified. Using finer glass shot is likely to produce a nonuniform coating.

The data given for dimensional changes due to oxidation applies only to material heated at 650°C in air. Material that is oxidized at temperatures above 650°C will probably be stretched a greater amount than the curves of Figure 3 indicate, while material that is oxidized at temperatures less than 650°C will probably be stretched a lesser amount.

Where possible use bushings or parts having uniform cross sections to avoid differential growth.

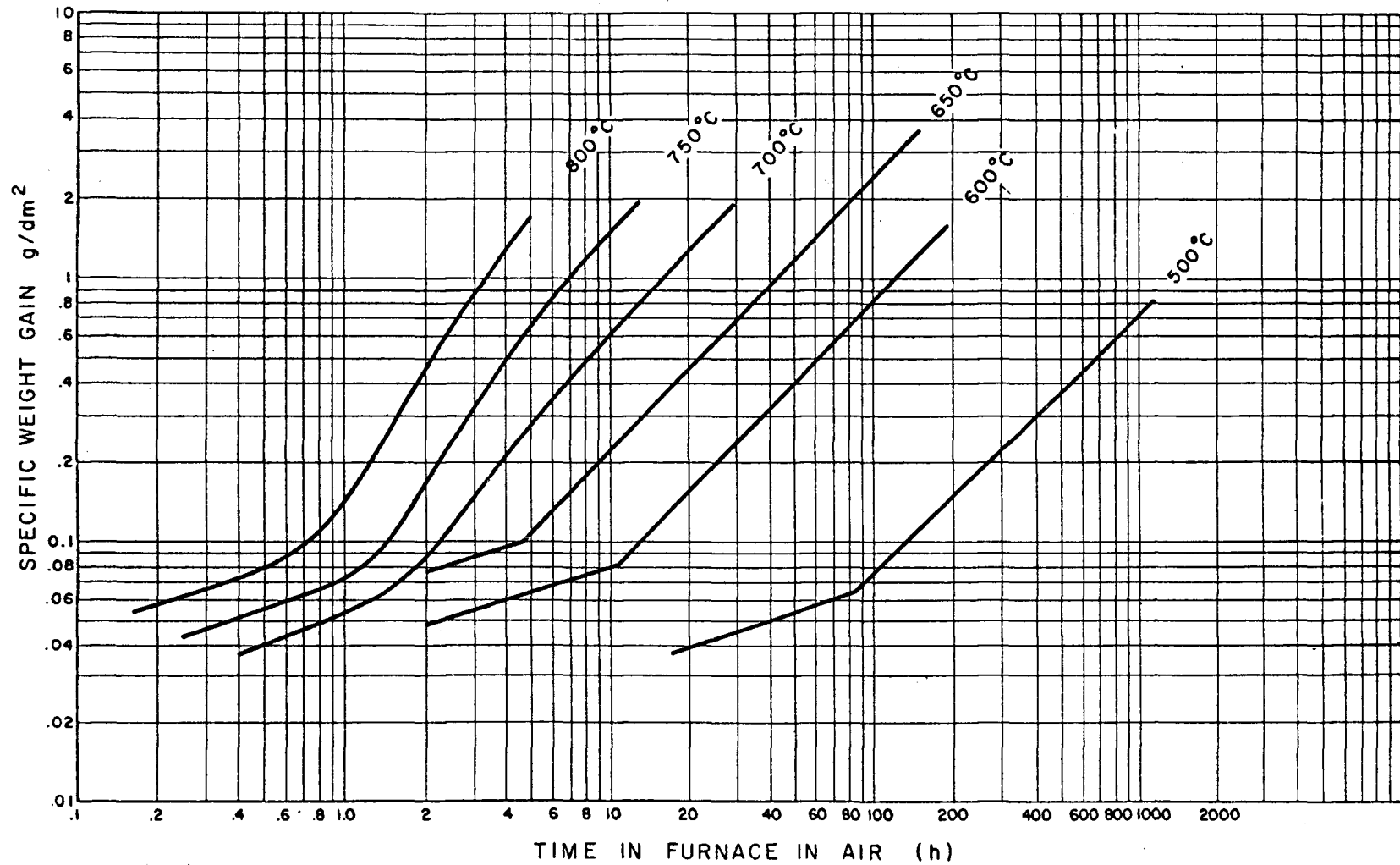
Complicated parts can be oxidized if close tolerances are not required.

Don't use small furnaces for oxidizing large parts or large numbers of small parts, unless special procedures are used to prevent nonuniform oxidation (see Section 3.7).

6.4 Masking

There is no satisfactory way of masking part of the surface during oxidizing. All surfaces exposed to the atmosphere will oxidize to about the same depth, even two surfaces that have been press-fitted together.

Figure 1: Oxidation of Glas-Shot Blasted Zircaloy-2 in Air at Different Temperatures



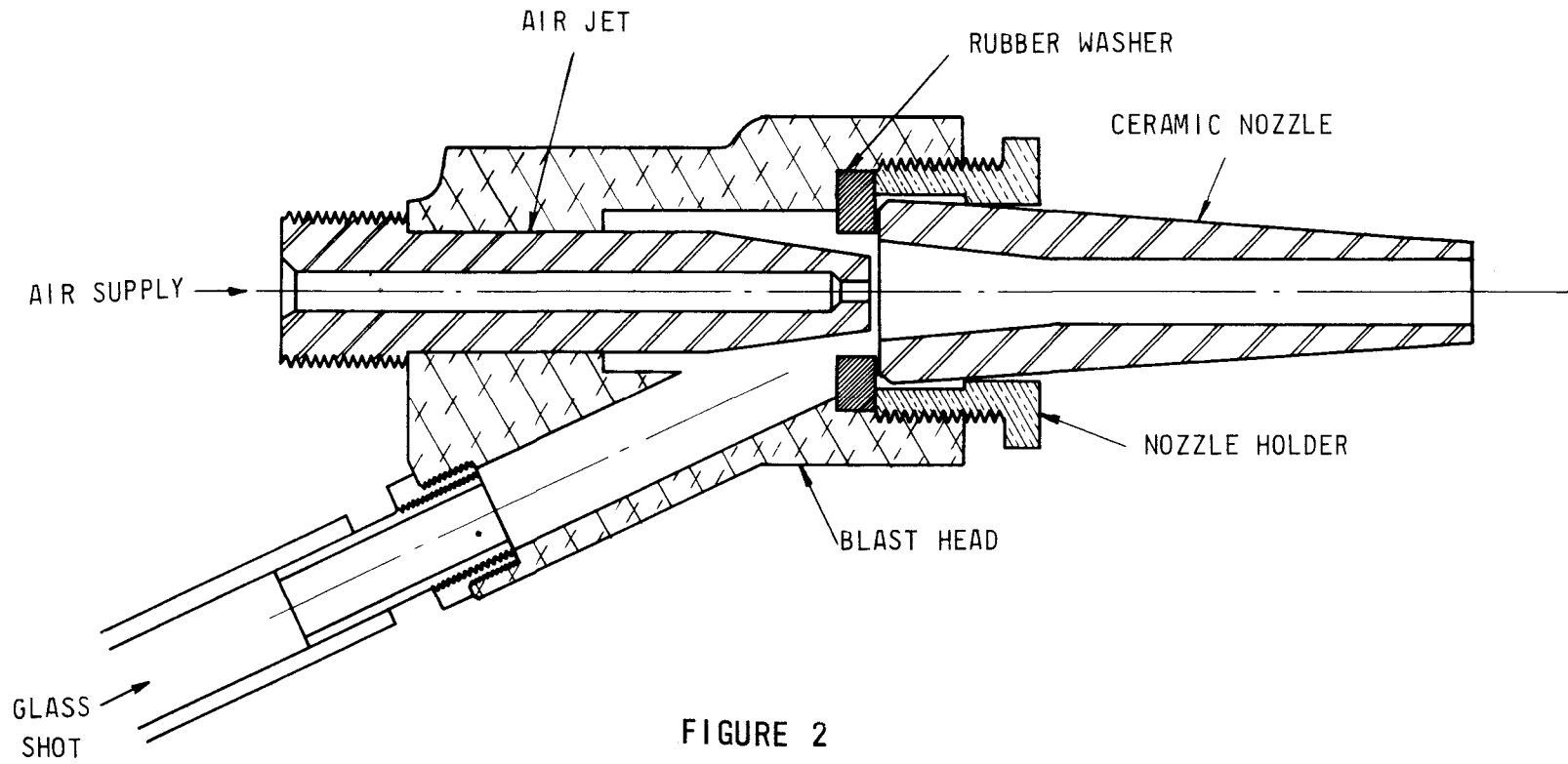


FIGURE 2
TYPICAL SHOT BLAST NOZZLE

Oxidizing Zircaloy-2 and Zircaloy-4

Figure 3: Dimensional Changes of Zircaloy-2 or Zircaloy-4 Parts Oxidized in Air at 650°C

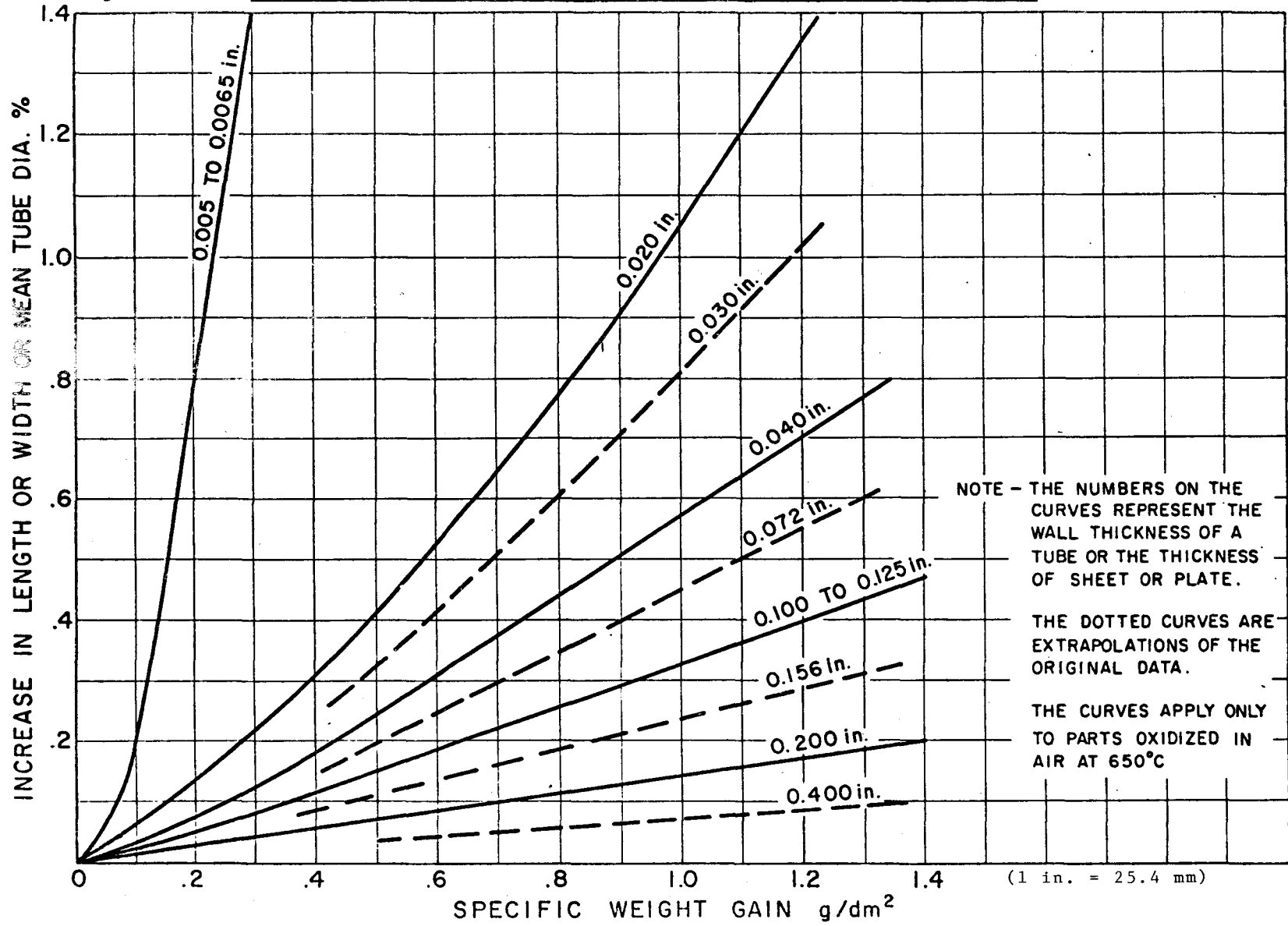
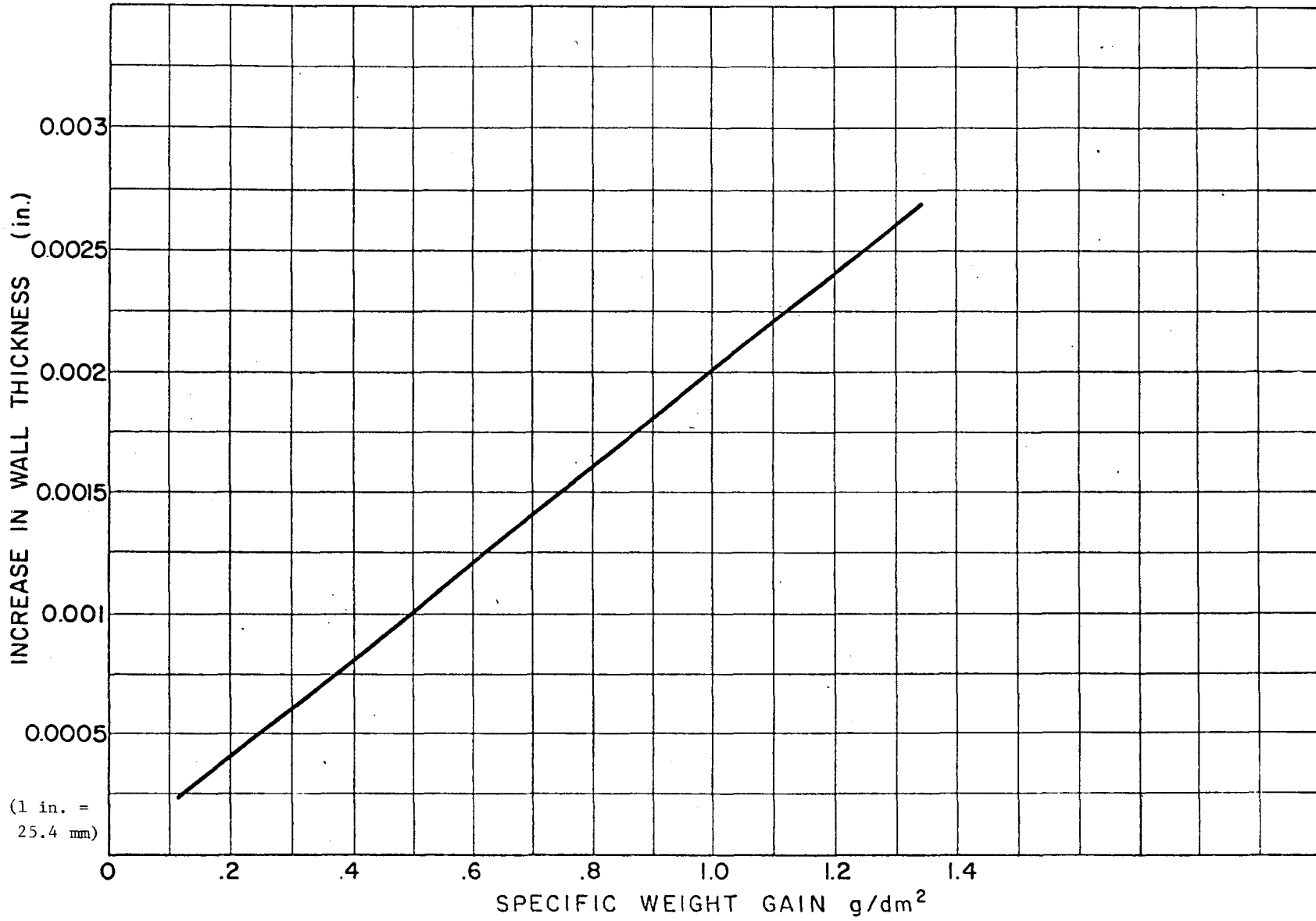


Figure 4: Increase in Wall Thickness of Zircaloy-2 and Zircaloy-4 During Oxidation at 650°C in Air



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