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THE COLD WORKING OF EXTRUDED ZIRCALOY TUBING

By
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April 30, 1958

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Technical Information Service Extension, Oak Ridge, Tenn.

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Nuclear Metals, Inc.
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Contract No. AT(30-1)-1565

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Technical Director

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I. INTRODUCTION

A. General

Zirconium and its alloys have particularly attractive properties for use in nuclear reactors. They have a relatively low neutron cross section, good mechanical strength at moderate temperatures, and excellent corrosion resistance in high temperature water and steam. The largest demand for small diameter zirconium tubing has been for the cladding of the uranium dioxide type fuel elements. To achieve high thermal efficiency thin walled, small diameter tubing has been required. Demand for such tubing may be expected to continue and in addition, Zircaloy clad metallic fuel elements may require increasing quantities of larger diameter heavier wall tube stock for use in billet assemblies. Following decreasing metal and fabrication costs, it seems clear that the excellent corrosion properties of their alloys, in a wide variety of media, will be utilized for many commercial applications.

This report is primarily concerned with the high quality, small diameter tubing that is presently required for fuel elements. The problems associated with working zirconium alloys are made even more severe by the chemical and dimensional specifications for the final product. Previous development work in this field has mainly centered around a search for satisfactory lubricants for hot and cold working these reactive alloys. A brief summary of the various lubricants which have been investigated is given below.

B. Extrusion Techniques and Problems

In the extrusion operation, care must be taken to prevent:

1. Oxidation and absorption of atmospheric gases
2. Galling with dies and other tools and
3. Poor surface finish on the metal which may be related to method of lubrication. The lubricant techniques which have been attempted are briefly summarized below:

a. Air heating and Oil-Dag lubrication

b. Salt bath (75% $BaCl_2$ and 25% NaCl) heating and extrusion.

c. Salt heating and extrusion in glass (Ugine-Sejournet process).

d. Canning in a metal sheath.

These methods have not been exhaustively investigated and any firm judgment on them may be premature.

The latter procedure is the one now practiced at Nuclear Metals, Inc. in particular, the zirconium alloy billets are inserted into copper cans, which are evacuated, sealed tight and extruded at about 1400°F. Modifications of this technique have included the use of brass and mild steel cans, the latter allowing a somewhat higher extrusion temperature. The formation of a eutectic composition and/or excessive alloying between the zirconium and the canning material limit the maximum extrusion temperature. Since such alloying will affect the quality of the final product, a description of the extent of this interaction is presented in this report. In addition, experiments have been performed to indicate the rate at which the contaminated surface layers may be removed by etching.

The quality of the final product may be effected by conditions other than chemical contamination. The grain size of the extrusion billet is important. It has been clearly demonstrated that pre-extruded or forged billets result in smooth surfaces, while those from as-cast material are coarse, bark-like and sometimes have folds. In addition, salt and glass lubricated extrusions often show rough surfaces which contain pieces of these lubricants.

While other methods of lubrication have shown increasing promise, it appears that the metal sheath is the only one capable of providing consistently high quality extrusions at this time.

C. Cold Working Techniques and Problems

There are higher frictional terms associated with cold drawing than with such other operations as rolling, swaging, cupping and forging.

Therefore, as in extrusion, the major problem centers on finding a satisfactory lubricant. Since even slight metal to metal contact between clean zirconium and the tools will result in pickup on the die and scoring of the tube, it is imperative to introduce a continuous and reliable barrier layer. Most of the conventional metal working lubricants have proven to be inadequate. The following lists contain some of the lubricants which have been attempted with varying degrees of success.

1. Copper powder dispersed in lacquer
2. Moly-Lube No. MW-9 (soluable in water)(Bel-Ray Co., Inc. Madison, New Jersey)
3. Lead powder dispersed in lacquer
4. Kemtone paint diluted 1-1 in water
5. Molykote (MoS_2) dispersed in lacquer (Alpha Corp., Greenwich Conn.)
6. Copper coating from extrusion plus oil lubricant
7. Displacement coating plus soap lubricant
8. Oxidized surface plus "Steelskin" lubricant (R. H. Miller Co., Homer, New York)

The first five lubricants have been found to be not entirely reliable or difficult to remove after drawing, particularly from the inside diameter of long tubes. Lubricant No. 6 is perhaps the most effective and it does allow drawing speeds in excess of those possible with the other methods. However, the resultant surface finish is usually not acceptable. In addition, vacuum annealing with the metal coating results in excessive penetration of copper into the zirconium alloy. The most reliable technique involves the use of a conversion coating and a soap lubricant. This method and a recently developed technique using an oxide coating and "Steelskin" lubricant are described more completely in this report.

II. EXPERIMENTAL DATA

A. Determination of Copper Gradients for Zircaloy-2 Tubing

The present Nuclear Metals method of extruding zirconium alloys makes use of a copper can or sheath. The extrusion temperature, pressure, and time conditions result in sufficient contact between the copper and zirconium to cause surface alloying and folding, as may be seen in Fig. 1, which indicates a diffusion zone between the Zircaloy-2* and copper. Folding is most likely to occur where large grains exist, because of the anisotropy of zirconium. It is believed that such alloying is detrimental to corrosion resistance and weldability and is a source of incipient surface cracking. Most specifications set a maximum limit for permissible copper content, and it is interesting to note that although high copper contents exist at the surface of a tube, due to the extrusion technique, the usual analysis for copper is made by dissolving entire cross-sections. The usual analysis, therefore, does not reflect the more concentrated copper content at the surface.

1. Procedure

Concentration profiles of copper content vs distance from the surface have been obtained for tube sections in the "as-extruded" condition and after various treatments. In order to determine whether there was any difference between the profiles at the outside and inside diameter, only one surface was investigated at a time. While the outside surface was examined, the inner surface was protected from acid attack by rubber stoppers placed into the ends of the tube. The outside was protected by a tight wrapping of cellophane electrical tape.

The following procedure is used for the test purposes after the tube has been processed by various working and chemical treatments. In the pickling(removal of copper) sequence used for these determinations, the first step is the removal, of any copper oxide with a concentrated hydrochloric acid pickle. This is followed by concentrated nitric acid, which removes the unalloyed copper. Both pickling periods are for one minute duration. For purposes of copper analysis, the pickling solutions are combined.

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*Nominal composition (in $^{w}/o$): Sn, 1.2-1.7; Fe, 0.07-0.20; Cr, 0.05-0.15; Ni, 0.03-0.08; N (max), 0.010; N (av), 0.008; O (av), 0.17.

The Zircaloy-2 is etched (removal of Zircaloy-2) for 30 minutes in a dilute hydrofluoric-nitric acid solution (10% HNO_3, 0.25% HF), usually at a temperature of approximately 80^{o}F.

The amount of copper in the etching solution is determined by optical methods with a Beckman Spectrophotometer, and reported in terms of micrograms per gram of Zircaloy removed.

In all cases, the sample (1-inch long tube section) is weighed before and after each etching period. A combination of weight determination for copper in solution and of weight loss during etching yields on average value for the copper content of the zirconium taken into solution. The penetration into the surface of the tube section is determined by calculating the thickness associated with a known weight removal. The relationship between thickness and weight change is:

$$t = \frac{W_L}{A_s L_s \rho}$$

where:
- t = thickness of surface layer removed
- W_L = weight loss from surface
- A_s = surface area of sample
- L_s = length of sample
- ρ = density of Zircaloy-2

As mentioned previously, the composition of the metal removed is averaged in the analysis. In order to plot a copper concentration--distance penetration curve, the analysis is referred to the midpoint of the removed annulus of metal.

The experimental data are presented in Table I. Figures 2 through 9 are the copper profiles of various samples. The sample histories are as follows:

1. As-extruded, one pickle (50% HNO_3, 50% H_2O) — Fig. 2
2. As-extruded, double pickle (50% HNO_3, 50% H_2O) — Fig. 3
3. As-extruded, double pickle 3% HF, 47% HNO_3, 50% H_2O etch for one min pickle — Fig. 4
4. As-extruded, double pickle (50/50 HNO_3), 5% HF etch for one minute, pickle — Fig. 5

5. As-extruded, double pickle, total drawn 36%, anneal 1450°F, total draw 50% — Fig. 6
6. As-extruded, double pickle, draw 36% — Fig. 7
7. As-extruded, pickle, etch 3% HF, pickle (47% HNO_3, 50% H_2O) draw 36% — Fig. 8
8. As-extruded, pickle, total draw 36%, anneal, total draw 50%, belt sand — Fig. 9

2. Conclusions

The observations and conclusions which may be drawn from the data are summarized below:

a. The combination of successively pickling with hydrochloric and nitric acid, both concentrated, results in a total copper content equal to 50% of the weight of material removed, for samples 1, 2, and 6. This copper is in the form of copper oxide, free copper, and probably copper derived from the surface layer of the Zircaloy, which is high in this element. This last source is indicated since the copper (50 $^{w}/o$) containing Zircaloy at the surface may be pickled off due to its inferior corrosion resistance. The actual analysis is too low to be accounted for only by copper and copper oxide being taken into solution. On the basis of copper oxide removal only, the analysis should be at least 80%.

The thickness of material removed, as indicated by the weight loss and density, is approximately 5×10^{-5} inches.

In the case of sample No. 5, which has received a pickling treatment only (as in No. 2), the copper analysis of the pickle solution (combining both HCl and HNO_3 pickling solutions) is considerably lower than the 50% determined for sample Nos. 1, 2, and 6. As noted, this sample has undergone an annealing treatment at 760°C (1408°F) and the surface copper has diffused into the tube. The result is that the amount of copper determined after the two acid treatments is reduced to about 8%, and the copper gradient is considerably less steep (Fig. 6).

Sample No. 8 is similar to No. 6 except that this sample has been belt sanded. In this case sufficient surface volume has been mechanically removed so that the copper content of the new surface area is approximately 2%.

b. In all cases the copper content of the outside surface of the tube is higher than that at the inside surface, presumably due to its severe deformation.

c. The shape of the penetration curves closely resembles that of a diffusion-controlled process.

d. The shapes of curve Nos. 1 and 2 are similar, there being somewhat less surface copper with a double pickle.

e. The double pickled and drawn (36%) sample (No. 6) is similar to sample No. 2 without a draw. The concentration-distance plot reflects the reduction by an appropriate compression of the distance axis of the curve. For instance, the outside surface reaches a 50 ppm copper level at 0.9 mil in sample No. 2, while this level is reached at 0.6 mil in sample No. 6 (drawn).

The inside surface reaches the 50 ppm level at 0.7 mil for sample No. 2 and 0.4 mil for sample No. 6. The outside shows a reduction in penetration of 33% and the inside a reduction of 43%. Within experimental errors, this compares favorably with the 36% reduction during drawing.

f. The effect of annealing on as-pickled, unetched tubing is shown in Fig. 6. This tube has received a total of 50% reduction. It is clear that unetched tubing (containing surface copper) should not be annealed for long periods at elevated temperatures. Penetration of copper is excessive. The surface copper, which acts as a source of copper during annealing, is lower than that observed in sample Nos. 1, 2, and 6.

g. In order to lower the surface copper content to 50 ppm, about 0.9 mil must be removed from the outside surface and 0.7 mil off the inside surface.

h. The tube samples which have been etched reflect the removal of an amount of the surface. It is clear that with both the 3% HF (sample No. 3) and the 5% HF (sample No. 4) treatments the thickness removed by etching is not equal to that cited above to achieve the 50 ppm copper level on the surface. In the case of the 3% HF etch (1 minute), approximately 1/3 of a mil is removed from each surface. A somewhat higher amount is removed with the 5% HF etch (sample No. 4).

B. Etching Conditions

In order to make use of the copper profile data in Section IIA, it is necessary to determine the etching rate for hydrofluoric acid baths. A 3% HF bath (1 minute etching time) has been used for most in-process applications, and a 5% HF bath is used for final etching (before shipment). In the experiments reported here, 3, 5, and 7% HF etching solutions have been investigated.

It is well known that after prolonged use these baths become ineffective, and that a completely fresh bath is more reactive than one which has been used for a moderate period. In the following experiments the etching characteristics of 3, 5, and 7% HF are determined for fresh and depleted solutions. Depleted baths show a lower, etching rate.

1. Procedure

Sections of pickled Zircaloy tubing, 3-inches long, are weighed to the nearest ten thousandth of a gram and their OD and wall dimensions are determined. The section is then submitted to the etchant (volume--600 cc) for a measured 1-minute period. The temperature of the etchant rises rapidly from ambient to $80^{\circ}F$ under these conditions. The weight loss is measured, as well as the dimensional changes. This procedure is repeated and appropriate measurements are taken for the three etch solutions. A total of at least six separate sequences are reported for each concentration of acid. The data for replenished solutions have been obtained by using new baths, and that for depleted solutions by using the same bath for successive treatments.

2. Conclusions

The results of these experiments are summarized in Table II. Included here are data relating to weight and dimensional (OD and wall) changes as a function of the etching operation. Series "C", relating to calculated (see Section IIA for method of calculation) outside diameter change, shows somewhat lower values than those in Series "D" (measured OD changes). This is due to the difference between the outside and inside diameter.

The rate of metal removal per surface is one-half of the diameter or wall changes. Therefore, a 3% etch solution removes approximately 1/3 of a mil in a completely fresh condition and 1/15 of a mil in a depleted solution. A 5% HF bath (50% H_2O, balance HNO_3) removes about 0.6 mil/min with a fresh bath, and 0.15 mil/min with a depleted bath. A 7% HF bath removes 5 mils and 0.15 mil/min for a fresh and depleted bath, respectively.

It is clear that increasing concentrations of hydrofluoric acid result in substantially increased etching rates for fresh solutions, and rates which level off to a constant value for depleted solutions. In commercial practice, when the etch bath is used for an extended period, it seems likely that the data for fresh bath etching is not entirely applicable and that the data for depleted solutions is more realistic. As can be seen in Figs. 10a, b, c, which describe the weight change observed for each of the various baths, there is approximately a 1-minute period during which a maximum rate is observed in a fresh bath. Figure 11 is a plot of the change in OD and wall which results from etching in a 3% HF bath; and Fig. 12 illustrates these dimensional changes for a 5% HF bath. Figures 13a and 13b are for diameter and wall changes, respectively, for a 7% HF bath.

In these tests the ratio of volume etchant to surface area is approximately 8 cc/cm^2.

C. Correlation of Copper Profile with Etching Rate Data

As shown in Section IIA, copper diffuses into the Zircaloy surface in appreciable amounts. A 50 ppm level is reached at a distance of approximately one mil from the surface. It follows, therefore, that at least this amount should be removed if the 50 ppm level is to be obtained. The questionable analytical technique for determining copper by dissolving entire cross sections leaves unsolved the problem of maximum allowable surface copper content. In addition, the effect of surface copper on weldability has never been defined. It is probable that while values of less than 50 ppm are reported for finished tubing, the actual surface content is considerably higher. Experiments reported here, in which the standard etching procedure is followed, show (Figs. 4 and 5) that the surface copper content is in fact higher than 50 ppm. Corrosion data, reported in Section IIF-2, indicates an adverse effect of high copper content. It may be that a more rational specification for copper content is required. In addition, the possibility that the corrosion rate drops to a lower value beyond about 1/2 mil penetration below the surface (i.e., after which the copper content is less than 50 ppm) might be investigated.

Before proceeding with an evaluation, a number of features of the present techniques should be mentioned. First, removal of surface metal by chemical means occurs at a number of stages during the drawing operation. A given copper gradient profile is compressed along the distance axis (as shown in Section IIB) by cold working (during drawing). This is to say that 50 ppm level of copper, which is observed at a one mil level in as-extruded tubing, will be observed at a 1/2 mil level after 50% cold reduction. For a given etching rate (mils/min) it is important, therefore, to note at what stage the etching takes place. When etching occurs after cold working the thickness of metal which must be removed (to reach a given copper content) is reduced in proportion to the cold reduction.

Secondly, the standard procedure at NMI is to belt sand the outside surface of the tube before final etching. Approximately one mil is removed from the OD by this operation (1/2 mil per surface).

Evaluation of actual and required metal removal would be much simplified if only cold working were performed after extrusion. But because annealing extends and reshapes the copper profile curve, it is more difficult to determine the amount of metal that should be removed.

In the first stages of cold working a 3% HF, 4% HNO_3, 50% H_2O etching solution is employed prior to the conversion coating and soap lubrication. Approximately 1/3 of a mil is removed from the surface in this step. The surface copper content is thereby reduced to about 350 ppm on the OD and 150 ppm on the ID. Cold working about 35% is followed by another 3% etch prior to annealing. The copper profile at this stage is compressed, as described previously, and another 1/3 mil is removed from the surface. This is equivalent to removal of about 0.45 mil, in terms of the as-extruded tube. A total thickness of 0.8 mil (in terms of extruded material) is removed by the two 3% HF etches. This reduction lowers the surface content to 60 ppm copper on the OD and 35 ppm copper on the ID.

It can be seen that annealing at this stage will not introduce an excessive amount of copper into the metal by diffusion. It must be remembered, however, that the etching rates cited here are for fresh baths. Since depletion is known to occur these figures must be considered high. In addition, when the procedure is changed, attention must be paid to the effect of this change on the copper content.

D. Lubrication and Annealing

1. Standard Technique

A standard lubrication technique, developed at this laboratory, consists of applying a soap film upon a conversion (probably a phosphate) coating. The coating is obtained after the extruded tube has been pickled, etched, and pickled to insure that the surface is chemically clean. The pickle solution is 50% nitric acid-50% water. The etch is 3% HF - 47% HNO_3 - 50% water used at about $80^{\circ}F$. An acid treatment of one minute duration is used in each case. The conversion coating is obtained with a bath consisting of 5 pounds of a proprietary phosphating product (American Chemical Paint Company-LFN-860) in 40 gallons of water. The bath is operated at room temperature for a one minute soaking period. The required time is indicated by the appearance of a black coating which cannot be readily rubbed off.

A proprietary soap solution (American Chemical Paint Company-Granolube No. 10) is applied to this coating. This bath is operated at 75 to 80°C (167 to 176°F), and tubing is oscillated to insure complete coverage. After immersion the soap coating must be thoroughly dried to insure adequate lubrication. Approximately 2 hours are required for proper drying under normal conditions. Under conditions of high humidity this time is extended, and when infra-red drying lamps are used the required time is reduced.

2. Alternative Technique

Another method of lubrication in the drawing of Zircaloy tubing has recently been developed at NMI. The lubricant is of the solid-powder type and is composed of approximately 2/3 calcium stearate and 1/3 molybdenum disulphide. This material is available from R. H. Miller Co., under their designation No. 120-G5. Like other solid lubricants, it is applied during the drawing operation. The usual preparation procedures associated with the first technique are largely eliminated by the use of this lubricant, and the process is considerably simplified. In particular, the number of steps are reduced, and the possible throughput of tubing increased. Although there is some procedural latitude in its use, two extra considerations which must be taken into account. The first is that the lubricant cannot be applied to an as-etched (HF solution) surface. Secondly, the tubing cannot receive an anneal unless the surfaces are first etched. In the latter consideration, the presence of surface copper after pickling (as shown in Section IIA) would cause excessive penetration of copper during the annealing operation (Fig. 6). Present indications are that the lubricant can be applied to tubing in the as-pickled, or etched and surface-oxidized condition. The high copper and oxide layer on as-pickled tubing serves as an excellent base for the soap-base lubricant, but must be removed before annealing. One possible advantage of accomplishing some cold reduction (about 40% maximum) before etching is that the surface is made smoother and the penetration of copper is less extensive.

Whether the tube is etched before drawing or before annealing (followed by further cold drawing), a method for producing a receptive surface for the lubricant is necessary. Such a method appears to be controlled surface oxidation of the tubing. The oxidized surface is obtained by resistance heating the tube with the electrodes from a direct current welding generator. A current of 700 amps has been found to be a useful base for small diameter (about 1/2 inch) tubing with a 40 mil wall. It should be made clear, however, that only the preliminary work has been performed. A number of questions remain to be resolved including the effects of resistance heating on the impurity level in the metal before these techniques can be considered to be completely reliable. A number of resistance heating sequences have been performed. In all cases, resistance heating provides an oxide layer which is satisfactory as a base for the lubricant described above.

The kind and extent of oxidation associated with resistance heating has been evaluated to a limited degree. It has been found that when current is applied for a long time (20 seconds, as compared to 10 seconds), the resulting higher temperature produces a thicker oxide layer and greater penetration of oxygen and nitrogen into the zirconium. This first effect is shown in Figs. 14a and 14b; the heavier oxide layer formed by resistance heating for 20 seconds is evident at the top of Fig. 14a. Hardness tests (which will be discussed in more detail below) indicate that longer resistance heating periods introduce sufficient oxygen and nitrogen to significantly alter the hardness of the metal. With respect to intermediate annealing during the drawing operation, it has been observed that resistance heating, used to provide an oxide film for a lubrication base, also may serve as a method of annealing.

Table III is a summary of data which indicates that effect of various resistance heating treatments on the hardness of Zircaloy-2 before and after cold working. Resistance heating as-extruded tubing (a) results in some further softening, when a short thermal cycle (10 seconds) is used; whereas, extended heating (20 seconds) results in an increase in hardness. It can be seen in (b) and (c), for 28% and 36% reductions after resistance heating, that a similar effect of heating time is observed. Resistance heating a cold drawn (36%) tube (d) results in a decrease in R_B hardness from 86 to 84 and 77 for long and short cycle heating, respectively. The latter value is that of annealed material.

It appears clear that resistance heating may be a feasible method of annealing Zircaloy tubing (or rod). Further work is required to establish optimum conditions and the consequences of resistance heating. Once a thermal cycle is established, information relating the unit electrical resistivity, the cross section and length of the tube to the applied current will make possible a controlled procedure.

E. Drawing Experiments

Various experiments have been performed in order to determine certain parameters associated with tube drawing with a stationary plug. These parameters, including the draw force, plug force, and frictional terms were investigated under conditions of various reductions, prior states of cold work, drawing speeds, and lubrication procedure. The objectives were to better understand the drawing operation, rationalize certain observed limitations on maximum single and cumulative reductions, and to evaluate other methods of lubrication. Relationships between drawing speed, temperature, and forces required for cold reduction have also been observed.

1. Procedure

Mechanical force (or strain) measurements have been taken during tube drawing on both a Tinius-Olsen Tensile Machine and a standard draw bench. The Tensile Testing Machine provided a readily available and direct means for determining the draw force, and to determine what kind of information could be expected under many conditions with a limited supply of material. With this apparatus the draw force was measured directly, and the plug force by the use of strain gauges. The draw force is defined as that force which must be applied to the tube section at the exit side of the die in order to realize a given reduction. The plug force, the resultant tensile force acting on the drawing plug for a given reduction, is measured by placing a calibrated strain gauge block in line with the plug and suspending rod. The gauge block is calibrated by applying known loads in a tensile machine and recording the gauge readings. In order to establish the validity of such data under commercial drawing conditions (higher drawing speeds), similar experiments have been conducted on a drawbench. Plug force measurements are reported but the draw forces have not been determined. The latter may, to some extent, be extrapolated from the Tensile Machine data wherein a correlation between draw and plug forces has been found to exist.

These force measurements have been converted to stress values, and, by means of known plasticity relationships, various deformation constants and friction factors have been determined. It is appreciated that this data is subject to the limitations inherent in applying mathematical analysis to plasticity problems.

Experiments have been performed to determine a value for the frictional term during tube sinking (reduction of tube diameter with no restriction on wall dimensions). By use of the sinking data in the following relationship it is possible to determine the frictional parameter.

$$\frac{\alpha xa}{\alpha_o''} = \frac{1 + B}{B} \left[1 - \left(\frac{D_A}{D_B} \right)^B \right] + \frac{\alpha xb}{a_o''} \left(\frac{D_A}{D_B} \right)^B \qquad (1)*$$

αxa = stress in exit section of tube during sinking

α_o'' = 1.10 α_o [plasticity factor 1.10 times the yield strength in tension of Zircaloy-2 (66,000 psi)].

B = friction factor, $\frac{f}{\tan A}$

where f is the coefficient of friction between the die and the OD of the tube, and tan A is tangent of the cone angle of the die

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*Introduction to the theory of Plasticity for Engineers, by O. Hoffman and G. Sachs - McGraw Hill Book Co., 1953.

D_A = average diameter of the tube after sinking

D_B = average diameter of the tube before sinking

αxb = stress on tube section before die due to back tension (in this experiment no back tension was applied, and this term is taken as equal to zero).

The plasticity equation for tube drawing with a plug is:

$$\frac{\text{Force}}{\text{Area}} = \alpha xa = a_o \ln \frac{t_o}{t_e} \left(1 + \frac{f_1 + f_2}{\tan A} \right) \qquad (2)$$

t_o = initial wall thickness

t_e = final wall thickness after draw

$\frac{f_1 + f_2}{\tan A}$ = frictional factor. f_1 and f_2 are the coefficient of friction between the tube and the die and plug, respectively. It is assumed that f_1 equals f_2, and that this term is equal to 2B (from the previous sinking data).

2. Discussion of Data

a. Drawing Paramater Determinations

Two sets of data have been obtained for the two lubricants investigated. Table IV presents the data on sinking, and Table V includes the relevant drawing data.

The sinking operation does not require particularly high drawing forces, as can be seen in Table IV. The reasons for this are that the percent reduction in area is not high and the frictional conditions are less severe, since only the die is in contact with the tube. Where there is no restriction on the ID of the tube, the die pressures and, therefore the frictional component are low.

Equation (1) relates the draw stress, reduction in diameter, and frictional factor. In Table IV, the "B" values (equal to f/tan A) are tabulated. In the case of lubricant No. 1 (conversion coating) the "B" term is approximately 2.5. For lubricant No. 2 (oxide base) it can be seen that this value is also about 2.5. In this latter case there is a somewhat higher value for the first draw, and lower value for subsequent draws (after the lubricant film is established). As shown in Table IVC, where lubricant No. 2 is used on an as-etched surface, it can be seen that the frictional term is considerably higher. This lubricant (calicum stearate, MoS_2) can not be used on an etched surface.

It has been assumed that the frictional characteristics between the tube and the die are the same as those between the tube and the drawing plug. In equation (2), the term $(f_1 + f_2)/\tan A$ has been taken to be equal to 2B. For purposes of order of magnitude calculations this term has been set equal to five for drawing with either lubricant. In addition, it is expected, and in part demonstrated, that the friction factor B would be a function of the prior cold work which the tube has experienced and the degree to which the surface lubrication has been disturbed. In either case it is expected that the die pressures and/or metal-metal contact (pickup) would be increased, resulting in a higher value of the frictional term. Presumably the higher than expected flow stress, K, for the drawing sequences 560/498 and 525/480 are due to the above features. The flow stress of an ideally (zero friction) plastic material under deformation is equal to the yield strength. The calculated values are presented in Table V.

b. Effect of Drawing Speed and Reduction on Plug Force

The force acting upon the drawing plug has been measured by means of a strain gauge, which is mounted in line with the plug, and a restraining rod which is connected to the rear of the draw bench. These measurements have been taken at various drawing speeds and it is clear that there is a definite inter-relationship between the drawing speed and plug force. Figures 15 and 16 clearly indicate the type of relationship observed. The load (or tensile force) on the plug is plotted vertically while the horizontal scale is the drawing speed. The curves indicate a falling plug force with increasing drawing speeds. The absolute level of each curve reflects the stresses associated with cold reductions after various amounts of prior cold work. Figure 15 is for drawing with lubricant No. 1 (conversion coating), while Fig. 16 is for the new lubricant, No. 2. In both cases the highest loadings are associated with the last reduction pass (560/498), while the lowest ones are for the first pass (609/530). This condition is also shown in Table VI, where the draw forces increase with successive passes. The mechanical properties of tubing after various amounts of cold work are discussed in Section IIIF-1. The plug and draw forces, mechanical properties and the calculated flow stress are clearly interrelated. In addition, as discussed in the first part of this section, the frictional term is of considerable importance in determining the quantitative relationships involved. Small changes in the frictional factor, B, result in large variations in the observed stresses associated with the drawing process. This last feature must be kept in mind when observations appear to be in error. Under conditions of inadequate or incomplete lubrication, draw or plug forces may become excessive and result in either point breakage or gross metal pickup. These observations might not be expected if only the amount of reduction and the mechanical properties were considered.

After a reduction of 36% (three successive draws with the same lubricant) both lubricants, Nos. 1 and 2, become very thin and some pickup is evident. A limit of approximately 40% total reduction is probably a good level beyond which lubricant failure may account for poor drawing practice. In the case of lubricant No. 2, the use of a lubrication box in front of the die for each draw would increase this figure somewhat. However, a limit will be reached when the oxide becomes sufficiently thin or broken when it would no longer serve as a lubricant base.

The observed decrease in plug force with increasing drawing speed may be attributed to a number of factors. Higher drawing rates result in heating of the tools and the tubes. A temperature of 200°F has been measured with a contact thermocouple at the exit end of the die. This temperature was the result of drawing a short length of tubing at 12 ft/min for a limited period of time. It is expected that at this speed, the temperature may rise to 300°F for extended drawing time. The effect of much higher drawing speeds would be to increase the temperature and thereby further lower the plug force. Commercial drawing may properly be considered warm drawing. There are large changes in physical properties of Zircaloy-2 with increasing temperature. Approximately 7,000 psi are sacrificed in yield and tensile strength for each 100^{o}F up to about 500^{o}F. These lower plug forces reflect the relative ease of "cold" working at these higher temperatures. This advantage could be offset by the weaker nature of the drawn tube at the exit end of the die, and may result in breakage if the draw force is too high. The possibility of cooling the tube as it issues from the die has not been investigated, but such work may be desirable, since it would permit higher stress and therefore, greater reductions. The draw forces reported in Table VI indicate the margin between the required applied stress on the tube, and the strength of such tubing after various reductions. The latter figures are shown in Fig. 17.

Another aspect of high drawing rates and the resultant temperature effect is the probable change in the frictional characteristics and stability of the lubricant. It is possible that very high speeds may require that lubricant No. 2 be modified with more solid content in order to prevent "balling" or melting of the lubricant. These aspects have not been investigated in this work.

F. Product Evaluation

Certain data has been obtained in order to determine product quality and evaluate the various fabrication techniques. Mechanical properties such as tensile and burst strengths, hardness, and residual hoop stress have been determined. Preliminary x-ray analysis (not reported here) has been performed in order to explain certain observed anisotropies. To a limited extent tube cross sections were metallographically examined to observe the effects of resistance heating. Corrosion testing has also been used to determine the product quality.

1. Mechanical Properties

The anisotropy in mechanical properties described in the literature for cold-rolled zirconium sheet is considerably lower than that which has been observed for Zircaloy-2 tubing. In each case, the type of deformation is different. It is expected that if drawing were to take place with only small changes in tube diameter and major reduction in wall thickness, then the anisotropy would more closely resemble that of sheet material. Where considerable changes in diameter occur on cold working, the characteristic "nonisotropic strain hardening" of Zircaloy-2 results in very pronounced directionality in mechanical properties. Figure 17 is a plot of tensile strength vs cold work in the longitudinal and transverse directions. The difference between properties in these two directions increases with successively higher amounts of cold work.

a. Hardness

This data has been previously discussed in the section devoted to annealing. Table III presents the major points of interest.

b. Hoop Stress

In order to determine the magnitude of the hoop stress in cold-worked and as-extruded Zircaloy-2 tubing, the following experiment was performed.

A 1/2-inch length of the tubing is used as the base for a strain gauge. After the gauge is firmly mounted on the OD so that the gauge wires are parallel to the circumference of the tube section, the section is cut perpendicular to the circumference. In this manner the residual compressive strains are relieved, and the initially neutral strain gauge is placed in tension and the reading recorded. The magnitude of this strain is equal to the residual hoop strain; an equivalent hoop stress may be calculated by use of the Young's modulus for Zircaloy-2.

In the case of a 35.8% total reduction (560/498 die-plug combination), a strain of 270 μ in./in. was recorded. With a Young's modulus of 13.8 x 10^6 psi, the hoop stress is 3,725 psi. An "as-extruded" tube section also has a noticeable residual hoop stress. In this case a strain of 92 μ in./in. was recorded, equivalent to a stress of 1,270 psi. In the latter case, the residual stress must be due to thermal stresses and preferred orientation induced during cooling of the extruded tube to room temperature and a hot work texture, respectively.

Interest in this data is primarily centered upon possible dimensional changes which might occur during annealing or in service. It would seem that this effect is of only small importance in this context.

c. Tensile Strength

After various drawing and annealing operations, 5-inch long tube sections were taken for tensile testing. These sections were cut in half along the tube axis, and machined with a 2-inch long reduced section. Supporting pins and serrated rod holding fixtures were used to apply a tensile load to the specimen. Average values of tensile strength are reported in Fig. 17, and a typical fractured specimen is shown in Fig. 18A.

d. Burst Strength

In order to establish the transverse strength of Zircaloy tubing as a function of its processing history, hydrostatic burst tests have been performed. For these tests 6-inch long specimens were prepared. Each specimen was inserted into two rubber "boots", one of which is fixed and the other is free to accommodate various lengths of tubing. The moving carriage head may be locked into place by means of a rack and pinion gear.

In order to minimize the hazards associated with pressure testing, water is used rather than air. The tube is filled with water at city pressure, and various higher pressures are obtained by means of an air operated pump. The pump has a capacity of 20,000 $lb/in.^2$

The pressure required to initiate fracture or to meet minimum specifications is indicated on a Bourdon type pressure gage. The Barlow formula $S = \frac{pd}{2t}$, is used to calculate the stress at fracture or other prescribed specifications. The hydraulic pressure, p; the inside diameter, d; and the wall thickness, t, are used for this calculation.

As in the tensile testing, SR-4 strain gages were used during the burst tests to correlate stress and strain during these tests. This data will be reported when it is more complete.

Figure 17 shows the burst strength of tubing after various reductions. It should be noted that incremental change is not as great for burst strength as it is for tensile strength after cumulative cold reductions above 20%. Figure 18B shows a typical fractured burst specimen.

2. Corrosion Properties

Corrosion testing has been performed to establish the corrosion resistance of Zircaloy-2 tubing as a function of various processing sequences. The media was degassed-steam at 399°C (750°F) and a pressure of 1500 psig; the duration of each set of tests was 14 days, divided into 6 and 8-day intervals. Table VIII is a summary of the results of these tests.

In addition, Table VII presents the results of corrosion testing samples which have received a standard pretreatment, including resistance heating to obtain an oxide film as a lubricant base.

In both cases, as shown in Tables VII and VIII, the results of such testing must be considered in terms of both weight change and visual observation. The kind and extent of corrosion product formation is indicative of product quality as is the weight change. In some cases, where the corrosion product is not sufficiently adherent, the weight gain observed may be misleading, due to the partial loss of the nonadherent (or bulk) oxide product. This is particularly true in the case of sample Nos. 1 and 2, Table VIII; the low corrosion rate observed may be due, in part, to the above and to the fact that an oxide layer already exists on the surface, as a result of resistance heating.

In all cases the corrosion reaction results in a uniform, black tarnish film where the surface layer is removed with an etch. A 5% HF, 45% HNO_3 and 50% H_2O etch provides a more satisfactory film than does a 3% HF-47% HNO_3-50% H_2O etch. The presence of extraneous matter and high copper contents in the surface layer of the tube section is the probable cause of unsatisfactory surface appearance after corrosion.

In all cases, the corrosion rates are considered satisfactory on a weight change basis.

III. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

A. Determination of Copper Concentration Gradient

1. For the extrusion conditions used here, a copper content of 50 ppm is reached at a distance of 0.9 mil from the outside surface and 0.7 mile from the inside surface of the as-extruded tube section.

2. The first few tenths of a mil of the tube surfaces, after free copper has been pickled off, contain large amounts of this element (750-1000 ppm at 0.1 mil). Annealing the tube without prior etching results in excessive diffusion of copper into the Zircaloy, and is not recommended.

3. Cold working results in a predictable compression of the concentration profile along the distance axis.

4. Present specifications which call for copper contents not in excess of 50 ppm may ignore the fact that chemical analysis taken by dissolving entire cross sections masks the high copper content of the surface layers. In this respect, subsequent annealing does, to a large extent, level off the gradient and may therefore be a rationale for such specifications.

B. Etching Rate Data

1. Etching with a fresh bath consisting of 50% water, nitric acid, and 3, 5, and 7% hydrofluoric acid results in metal removal from the surface at a rate of 0.33, 0.6 and 5.0 mil/min, respectively, for solutions of these concentrations at 80^{o}F. The use of ammonium flouride will be worth investigating.

2. Under the conditions used, bath depletion begins after one minute of etching. With a depleted bath, the etching rates are 0.06, 0.15, and 0.15 mils/min,respectively, for the 3.5, 5 and 7% HF solutions.

C. Etching Requirements

The amount of metal to be removed from the surface is dictated by the desired copper level. Consideration must be given the compression of the copper gradient due to cold work. For the conditions of testing described here, it is possible to engineer an etching sequence in order to achieve the required metal removal.

D. Lubrication and Annealing

1. A method of lubrication for the drawing of Zircaloy tubing is presented. Further work on improving the present "Steelskin" lubricant for high speed operation may be worthwhile.

2. Resistance heating appears to be a satisfactory method to obtain an oxide film base for this new lubricant. Other methods using chemical and electrical means to provide an oxide base coating are worthy of investigation.

3. Resistance heating appears to be, under proper operating conditions, a satisfactory method of annealing. Further work in this area is required.

E. Drawing Experiments

1. Significant data has been obtained relating the parameters associated with plug drawing of Zircaloy-2. These parameters have been related to each other, the lubricant used, the drawing speeds, and the mechanical properties of the material. It will be worthwhile to determine similar data for rod drawing, and for fast drawing speeds.

2. A maximum single reduction of approximately 25%, from annealed or as-extruded material, is possible. The maximum cumulative reduction before anneal is approximately 35%. The maximum reductions possible with rod drawing should be determined.

3. Fast drawing results in lower drawing forces due to heating of the metal and increased lubricating efficiency. This advantage is partly offset by a reduction in the mechanical properties of the tube sections at the die exit.

F. Product Evaluation

1. Considerable anisotropy results in plug-drawn tubing after about 20% cold work.

2. The residual hoop stress in tubing drawn 36% is 3,700 psi.

3. Corrosion resistance and characteristics are related to the copper content at the surface. Increased removal of metal from the surface results in improved corrosion resistance.

IV. ACKNOWLEDGEMENTS

The authors wish to express their thanks to all of the employees at NMI who have assisted in this work. Specific mention should be made of Dr. T. T. Magel, who provided valuable discussions, and to Mr. Albert E. Bothe for expert assistance in the experimental work.

V. LIST OF TABLES AND FIGURES

Table I

Summary of Copper Profile Data

Sample No.	Treatment No.1 (1 min, conc. HCl and HNO_3)				Treatment No.2 (30 min, 10% HNO_3, 55 ml + 5 drops HF)			
	Wt. Loss (g)		10^{-6} g Cu		Wt. Loss (g)		10^{-6} g Cu	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
1	0.0113	0.0094	6262	4980	0.0698	0.0455	32.1	12.1
2	0.0082	0.0068	4290	2900	0.0485	0.0391	44.4	18.0
3	0.0002	0.0001	14.7	2.7	0.0408	0.0396	3.5	2.3
4	0.0001	0.0001	9.0	2.3	0.0562	0.0512	7.0	4.9
5	0.0010	0.0002	84.8	16.2	0.0422	0.0462	1460	1861
6	0.0033	0.0042	1012	1951	0.0486	0.0415	53.2	33.8
7	0.0061	0.0091	25.2	24.4	0.0416	0.0539	7.2	7.2
8	0.0046	0.0048	860	904	0.0412	0.0494	409	704

Sample No.	Treatment No.3 (30 min, 10% HNO_3, 55 ml + 5 drops HF)				Treatment No. 4 (60 min, 10% HNO_3, 55 ml + 10 drops HF)			
	Wt. Loss (g)		10^{-6} g Cu		Wt. Loss (g)		10^{-6} g Cu	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
1	0.0685	0.0492	9.4	6.1				
2	0.0577	0.0399	10.2	5.5	0.1219	0.1311	7.63	3.91
3	0.0373	0.0531	3.5	1.6	0.1415	0.1524	5.28	1.57
4	0.0541	0.0496	7.8	3.1	0.1361	0.1470	5.48	1.96
5	0.0371	0.0502	87.9	240	0.1098	0.1341	54.40	65.75
6	0.0343	0.0412	12.9	1.9	0.0945	0.1143	3.72	2.35
7	0.0643	0.0462	7.0	5.3	0.1144	0.1112	4.50	1.96
8	0.0480	0.0380	65.2	47.9	0.1095	0.1381	42.27	45.50

Sample No.	Treatment No.5 (60 min, 10% HNO_3, 55 ml + 10 drops HF)			
	Wt. Loss (g)		10^{-6} g Cu	
	Outside	Inside	Outside	Inside
5	0.0988	0.1222	39.7	36.2

NOTES: (a) Each treatment is performed on samples which have been subjected to all preceding treatments.

(b) Descriptions of the prior treatments for each sample number are given on page 13.

Table II

Etching Rate Data

	50% H_2O, Balance HNO_3 + HF, 80°F					
	Replenished			Depleted		
	3% HF	5% HF	7% HF	3% HF	5% HF	7% HF
A. Weight Loss (g/min)	0.357	0.810	5.670	0.075	0.175	0.183
B. Weight Loss ($g/cm^2/min$)	0.0092	0.0208	0.1460	0.0019	0.0045	0.0047
C. OD Change--Calculated (in./min)	0.00056	0.00126	0.00885	0.00012	0.00027	0.00029
D. OD Change--Measured (in./min)	0.00066	0.00130	0.01200	0.00013	---	0.00031
E. Wall Change--Measured (in./min)	0.00065	0.00126	0.00980	0.00018	0.00035	0.00034

Table III

Effect of Thermal, Mechanical Treatments on Hardness

	Initial Condition	Short time temperature cycles to about 1400°F maximum by resistance heating	Final treatment cold work (percent)	Hardness, R_B
(a)	As extruded	Oxidized 10 sec, once	--	78
	As extruded	Oxidized 10 sec, once	--	74
	As extruded	Oxidized 10 sec, twice	--	77
	As extruded	Oxidized 20 sec, once	--	78
	As extruded	Oxidized 20 sec, twice	--	82
(b)	As extruded	Oxidized 10 sec, twice	28	85
	As extruded	Oxidized 20 sec, twice	28	89
(c)	As extruded	Oxidized 10 sec, twice	36	86
	As extruded	Oxidized 20 sec, once	36	88
	As extruded	Oxidized 20 sec, twice	36	90
(d)	As extruded and drawn at 36% reduction	Oxidized 10 sec, twice	--	77
	As extruded and drawn at 36% reduction	Oxidized 20 sec, once	--	84

Table IV

Tube Sinking Data

	Die	Dimensions		Force	Area	Stress	D_B	D_A	$\frac{D_A}{D_B}$	B
		OD	ID							
	Extruded	0.642	0.548	--	--	--	0.595	--	--	--
A. Lubricant No. 1, conversion coating	0.609	0.609	0.519	1,025	0.0801	12,800	--	0.564	0.948	2.52
	0.560	0.560	0.468	2,380	0.0745	31,900	--	0.514	0.865	2.67
	0.526	0.526	0.434	2,900	0.0694	41,800	--	0.480	0.807	2.48
B. Lubricant No. 2, oxide base	0.609	0.609	0.519	1,030	0.0801	12,860	--	0.564	0.948	2.72
	0.560	0.560	0.468	2,250	0.0745	30,200	--	0.514	0.865	2.44
	0.526	0.526	0.434	2,700	0.0694	38,900	--	0.480	0.807	2.12
C. Lubricant No. 2, on pickled and etched surface	0.609	0.609	0.519	1,500	0.0801	18,700	--	0.564	0.848	3.25
	0.560	0.560	0.468	3,250	0.0745	43,600	--	0.514	0.865	4.00
	0.526	0.526	0.434	3,600	0.0694	52,000	--	0.480	0.807	3.85

Table V

Calculated Flow Stress
(Drawing Speed, 4 in./min)

Draw Set		Cold Drawing Reduction		Draw stress [1]	Flow stress, K [2]	Type of lubricant [3]
Die	Plug	Per individual draw	Cumulative, based on 0.609/0.533 starting section			
0.609	0.533	15.0%		57,200	78,100	1
0.609	0.530	12.1%		36,600	72,500	2
0.579	0.511	14.7%	27.6%	58,800	84,000	1
0.579	0.511	14.7%	27.6%	67,900	77,400	2
0.660	0.498	11.3%	35.8%	63,000	114,000	1
0.560	0.498	11.3%	35.8%	73,400	135,000	2
0.842	0.492	21.3%	49.5%	97,400	75,400	1
0.525	0.480	12.5%	55.8%	91,200	144,000	1
Large single pass from as-extruded condition						
0.585	0.520	29.7%		96,600	58,100	1
0.585	0.520	29.7%		84,300	50,700	2

1. Tensile stress on drawn tube at exit of die

2. Described in text

3. Lubricant No. 1 conversion coating - Soap
   Lubricant No. 2 Oxide Base - (MoS_2 - Soap)

TABLE VI

Slow Drawing Rate Data

	Draw Set		Reduction		Draw Force Pounds	Area $in.^2$	σ_{xa} psi	Plug Force Pounds
	Die	Plug	(Single)	(Cumulative)				
A. Lubricant No. 1	0.609	0.530		13.3%	3250	0.0696	46,700	880
	0.609	0.533		15.0%	3900	0.0682	57,200	770
	0.579	0.511	14.7%	27.6%	3450	0.0582	58,800	980
	0.560	0.498	11.3%	35.8%	3300	0.0516	63,000	1150
	0.542	0.492	21.3%	49.5%	3925	0.0406	97,400	
	0.525	0.480	12.5%	55.8%		0.0355	91,200	930
	0.585	0.520		29.7%	5450	0.0564	96,600	1300
B. Lubricant No. 2	0.609	0.530		13.3%	2600	0.0696	37,000	680
	0.579	0.511	14.7%	27.6%	3950	0.0582	67,900	1135
	0.560	0.498	11.3%	35.8%	3800	0.0516	73,400	1090
	0.585	0.520		29.7%	4750	0.0564	84,300	

Table VII

Corrosion of Zircaloy-2 Tubing

Medium 750°F steam, 1500 psi, 3 days.

Condition: As extruded, pickled (50-50 nitric acid and water), etched (3% HF), pickled, oxidized by resistance heating (20 sec - 700 amp). Lubricant No. 2.

Sample	Treatment	Surface Area	Weight (g)	Weight Δ(mg)	mg/dm^2	Comments
(1A) (1B)	Wash only Lakeseal - Water	0.1576 0.1628	3.6783 3.8881	1.0 1.0	6 6	Entire sample covered by very fine structure of white oxide, grey appearance
(2A) (2B)	Pickle only 50-50 nitric acid and water	0.1678 0.1638	3.9490 3.8276	1.3 1.6	8 10	As in (1A) and (1B) above
(3A) (3B)	Pickle, Etch (3% HF), Pickle	0.1628 0.1601	3.8241 3.6766	1.9 1.6	12 10	Light white oxide structure, streaked, fair appearance
(4A) (4B)	Pickle, Etch (5% HF), Pickle	0.1603 0.1596	3.6474 3.6727	2.2 2.4	14 15	Black tarnish film, good appearance

Table VIII

Corrosion of Zircaloy-2 Tubing

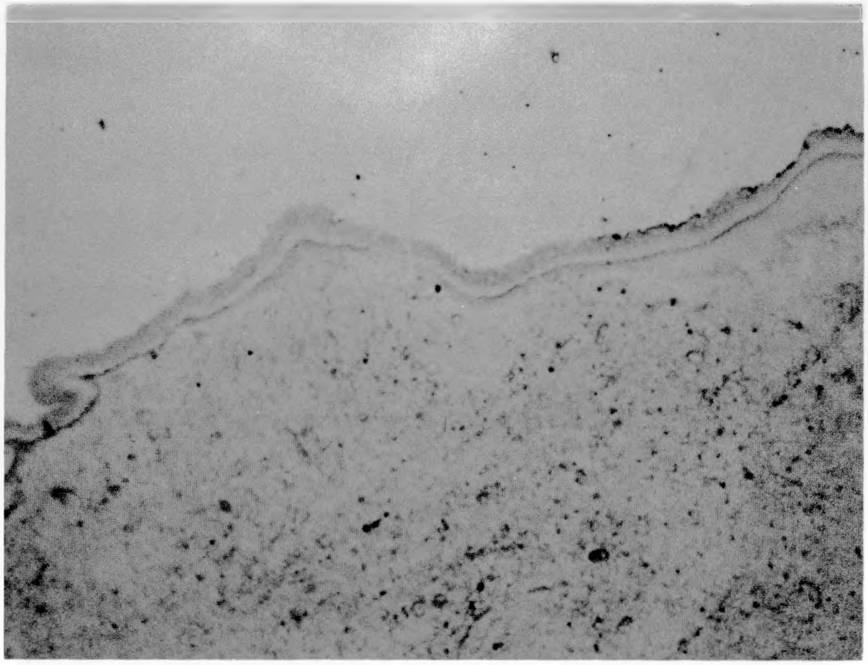
Medium 750°F steam, 1500 psi, 14 days.

Conditions: Various.

Sample	Surface Area	Weight (g)	Weight △(mg)	Weight ∈△(mg)	Time (days)	Time ∈(days)	mg/dm²	Comments
(1) Pickled, lubrication No. 2, Drawn 36%	0.1871	4.3278 4.3315 4.3304	- 3.7 -1.1	- 3.7 2.6	- 6 8	- 6 14	- 20 14	Dull grey with some raised white oxide streaks
(2) As (1)	0.1793	4.2796 4.2839 4.2822	- 4.3 -1.7	- 4.3 2.6	- 6 8	- 6 14	- 24 15	Dull grey with some raised white oxide streaks
(3) As (1), after Anneal, 3% HF Etch, Drawn	0.1704	3.2832 3.2858 3.2865	- 2.6 0.7	- 2.6 3.3	- 6 8	- 6 14	- 15 19	Dull and spotty; large stains on inside
(4) As (3)	0.1668	3.2113 3.2142 3.2150	- 2.9 0.8	- 2.9 3.7	- 6 8	- 6 14	- 17 22	Dull and spotty; large stains on inside; oxide spots on inside
(5) As (3), 5% Etch	0.1753	3.1425 3.1452 3.1458	- 2.7 0.6	- 2.7 3.3	- 6 8	- 6 14	- 15 19	Good

Table VIII (Cont'd.)

Sample	Surface Area	Weight			Time		mg/dm^2	Comments
		(g)	△(mg)	∈△(mg)	(days)	∈(days)		
(6) As (5)	0.1634	3.0738 3.0757 3.0765	- 1.9 0.8	- 1.9 2.7	- 6 8	- 6 14	- 12 16	Good
(6A) As (5), Belt Sanded before 5% Etch	0.1665	3.1007 3.1037 3.1044	- 3.0 0.7	- 3.0 3.7	- 6 8	- 6 14	- 18 22	Good
(6B) As (6A)	0.1601	2.9660 2.9679 2.9687	- 1.9 0.8	- 1.9 2.7	- 6 8	- 6 14	- 12 17	Good
(7) Pickled, 3% HF Etch, Pickled, Drawn 36%, 5% HF Etch	0.1666	3.7844 3.7862 3.7870	- 1.8 0.8	- 1.8 2.6	- 6 8	- 6 14	- 11 16	Good
(8) As (7), 3% HF Etch	0.1756	4.0841 4.0862 4.0871	- 2.1 0.9	- 2.1 3.0	- 6 8	- 6 14	- 12 17	Good. Not as bright as (7)
(9) After Extrusion, Pickled, 3% HF Etch, Pickled	0.2115	6.5535 6.5566 6.5581	- 3.1 1.5	- 3.1 4.6	- 6 8	- 6 14	- 15 22	Good. But not as bright as (1)
(10) As (9), 5% HF Etch	0.2060	6.3665 6.3691 6.3702	- 2.6 1.1	- 2.6 3.7	- 6 8	- 6 14	- 13 18	Good



2000X Bt. Lt. A-1082-1e

2000X Bt. Lt. A-1067(c)

Fig. 1 - Interface in copper clad Zircaloy tube, as-extruded, showing alloying in diffusion zone; two sections, copper at top.

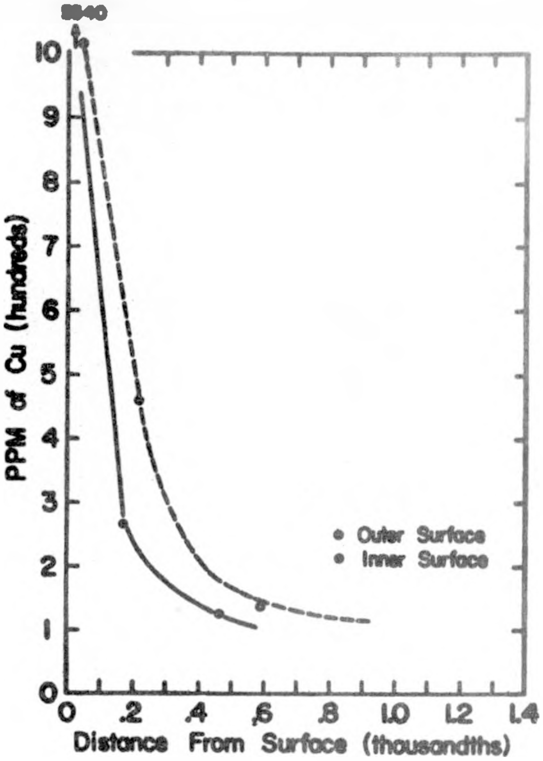


Fig. 2

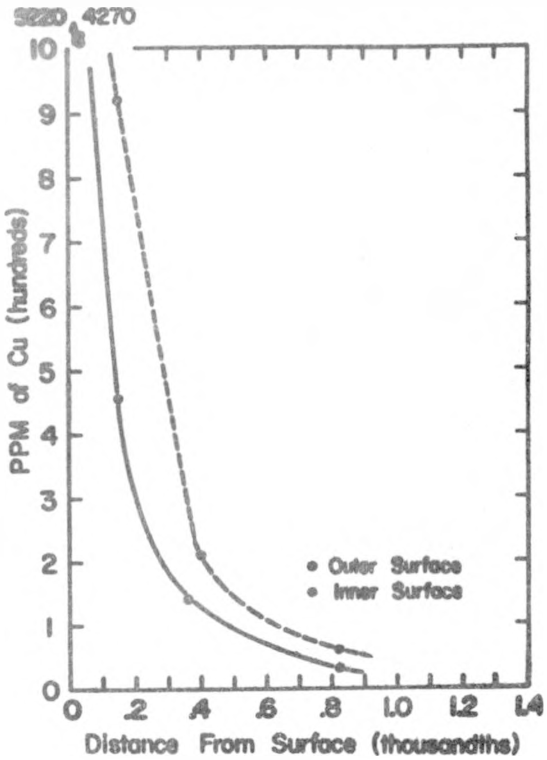


Fig. 3

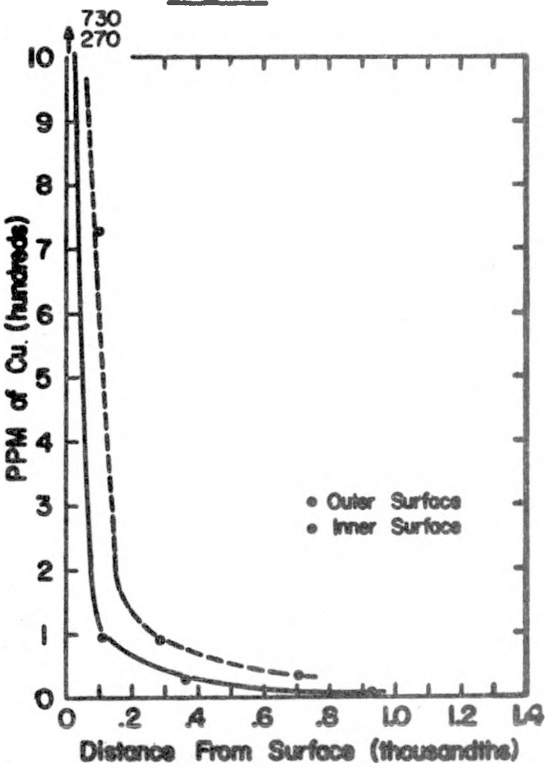


Fig. 4

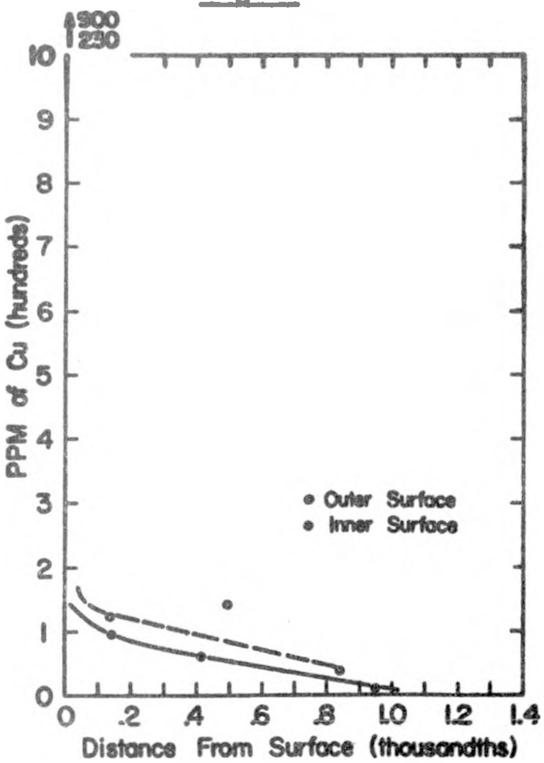


Fig. 5

Profiles of copper content vs distance from surface. (2) as-extruded and given one pickle (50% HNO_3, 50% H_2O) before measurements; (3) as-extruded and given double pickle (50/50 HNO_3) before measurements; (4) as-extruded and given double pickle (50/50 HNO_3), 3% HF, 47% HNO_3, 50% H_2O etch for 1 min, pickled before measurements; (5) as-extruded and given double pickle (50/50 HNO_3), 5% HF etch for 1 min, pickled before measurements.

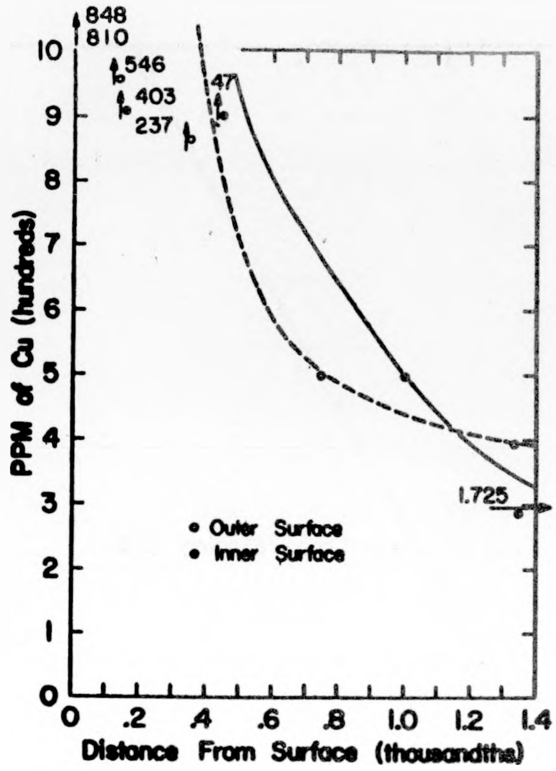


Fig. 6

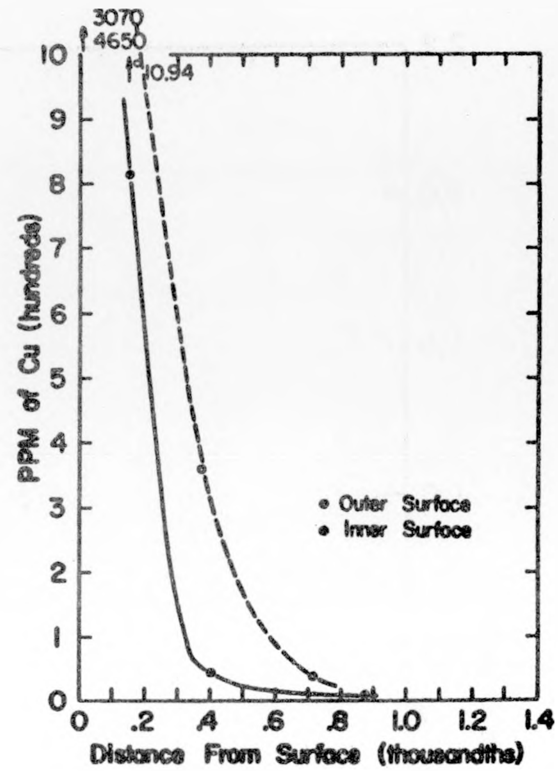
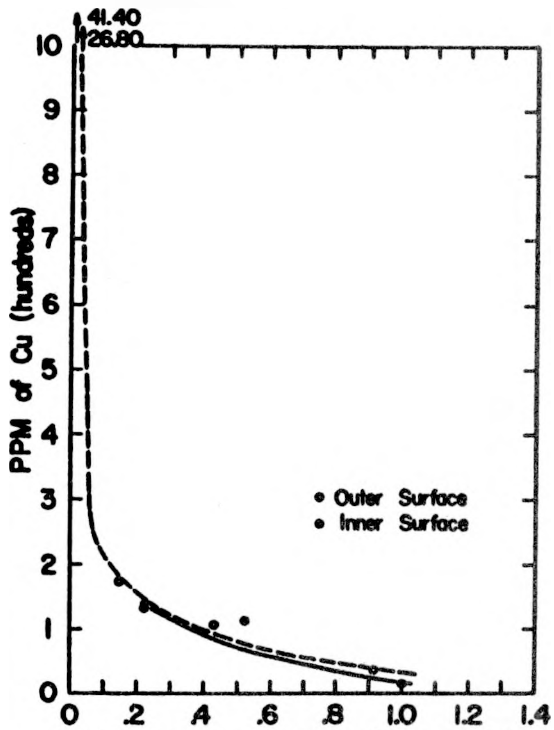
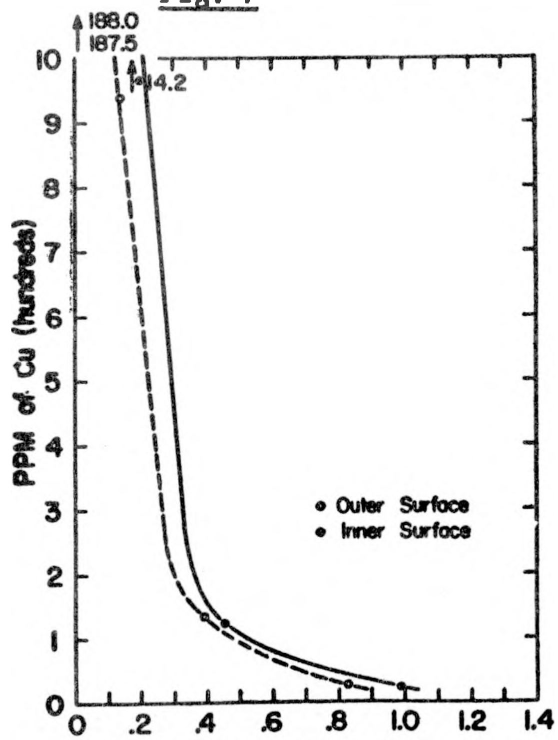


Fig. 7





Profiles of copper content vs distance from surface. (6) as-extruded and given double pickle, total drawn 36%, anneal 1450°F, total drawn 50% before measurements; (7) as-extruded and given double pickle, drawn 36% before measurements; (8) as-extruded and given pickle (50% HNO_3, 50% H_2O), etch 3% HF, 47% HNO_3, 50% H_2O, pickle (50% HNO_3, 50% H_2O), drawn 36% before measurements; (9) as-extruded and given pickle, total drawn 36%, anneal, total drawn 50%, belt sand before measurements.

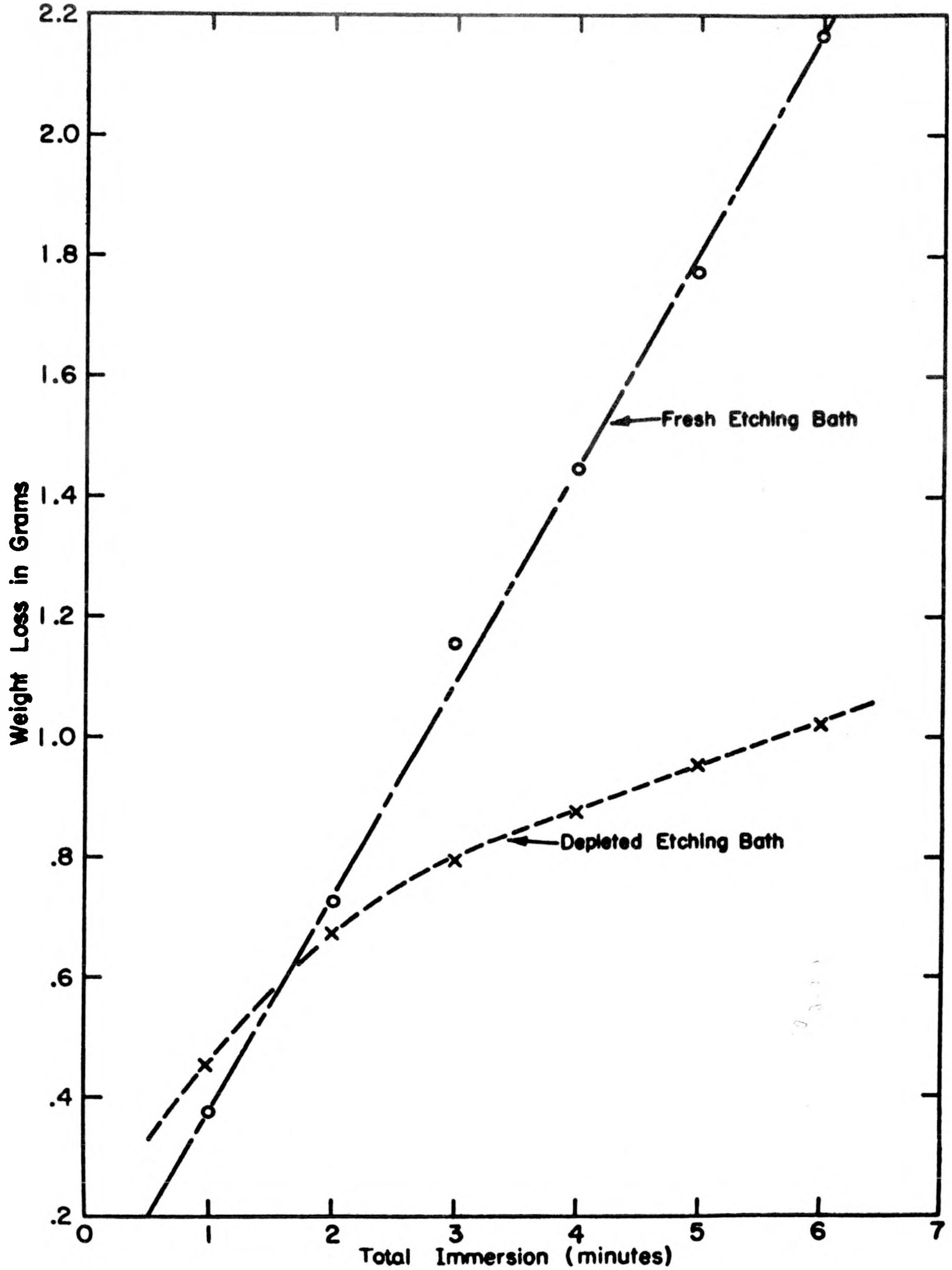


Fig. 10(a) - Cumulative weight losses for Zircaloy-2 immersed in etching bath for 1 min periods; (o) fresh or replenished bath, (x) original or depleted bath; 3% HF, 50% H_2O, 47% HNO_3 etch solution.

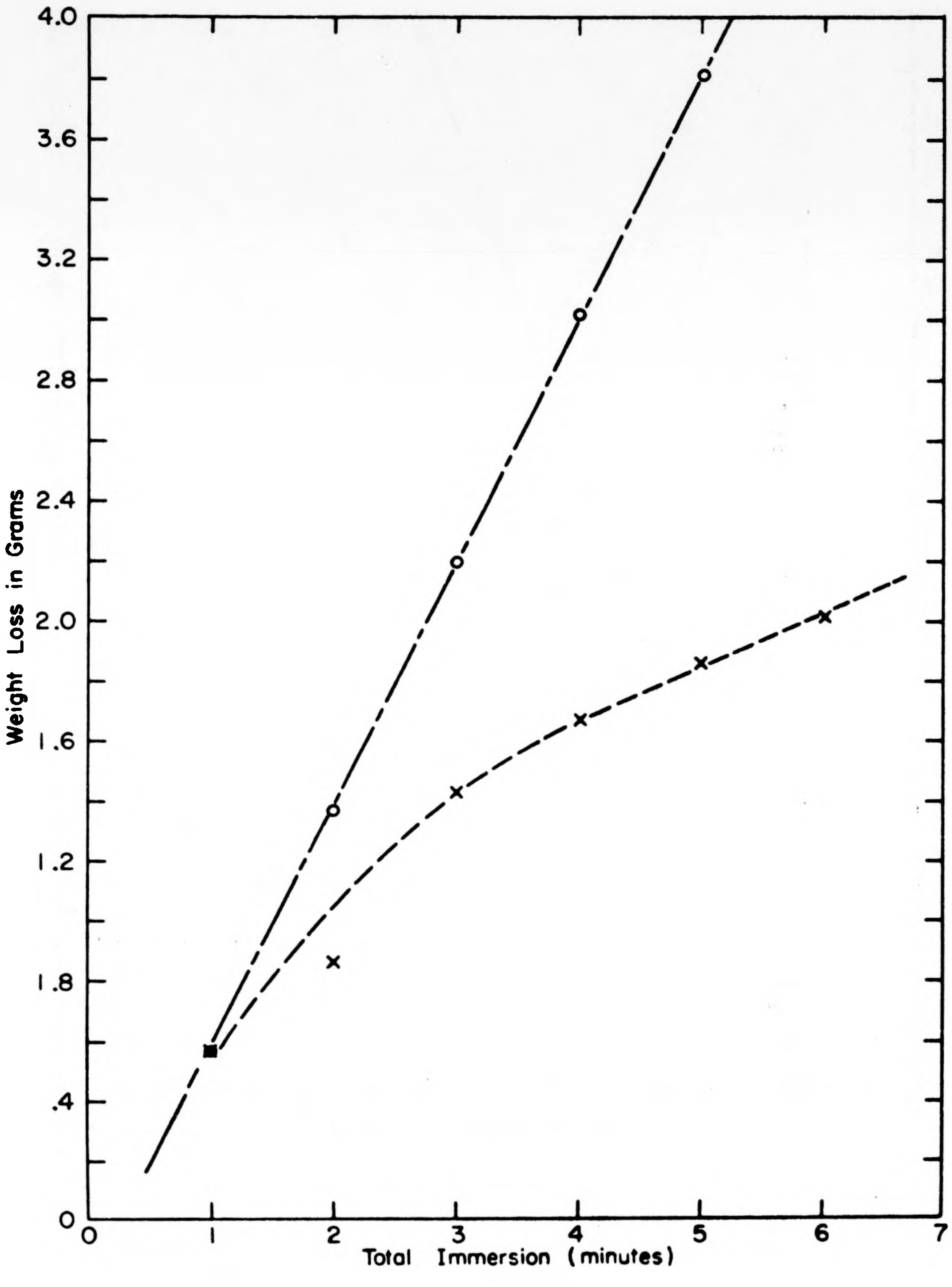


Fig. 10(b) - As (a) 5% HF, 50% H_2O, 45% HNO_3 etch solution.

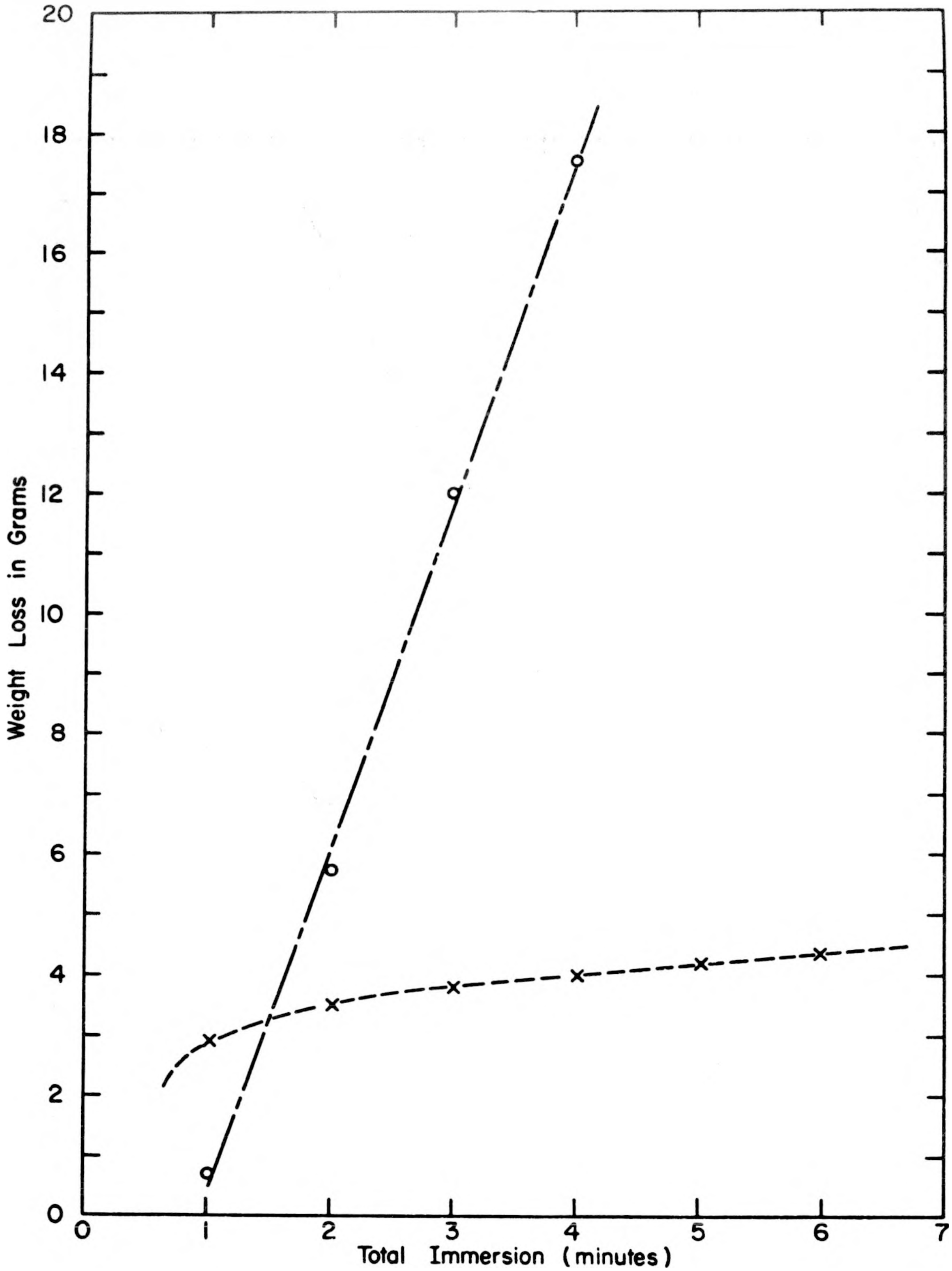


Fig. 10(c) - As (a) 7% HF, 50% H_2O, 43% HNO_3 etch solution.

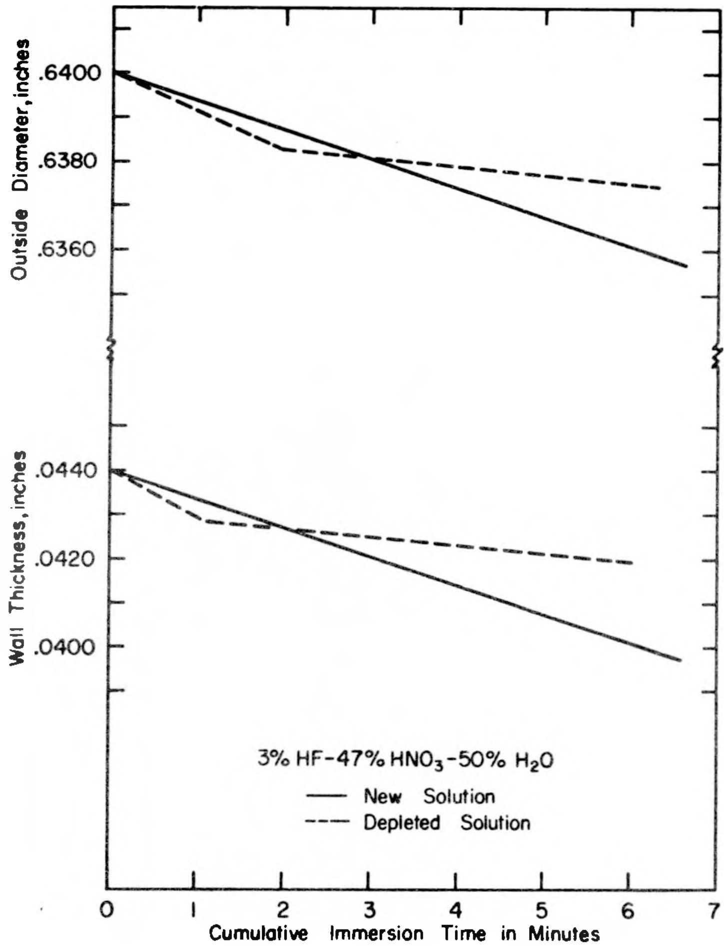


Fig. 11 - The change in OD and wall thickness as the result of etching in a 3% HF bath.

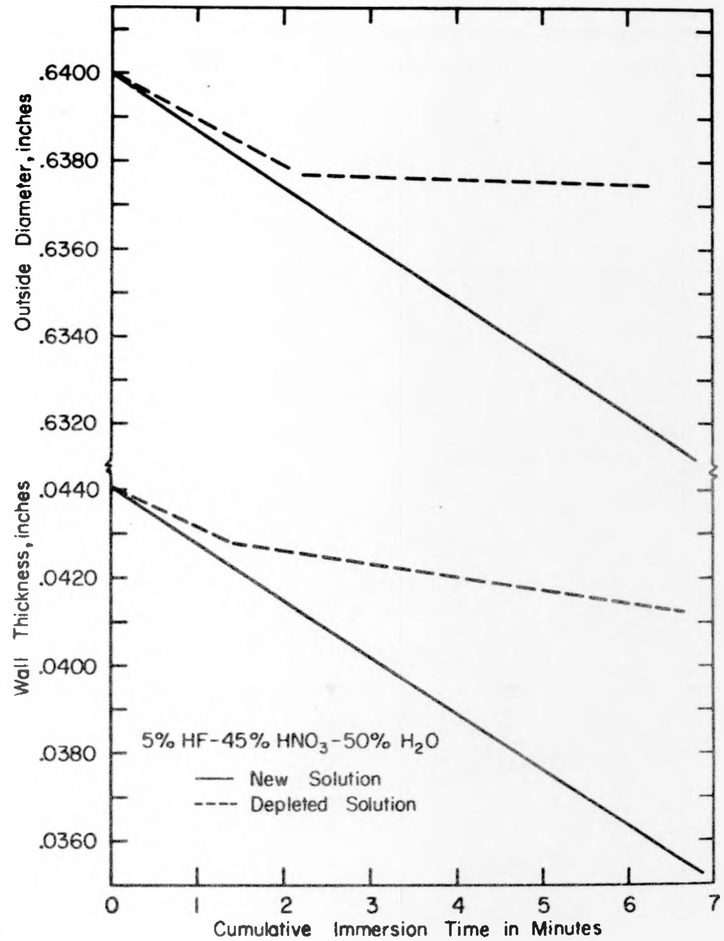


Fig. 12 - The change in OD and wall thickness as the result of etching in a 5% HF bath.

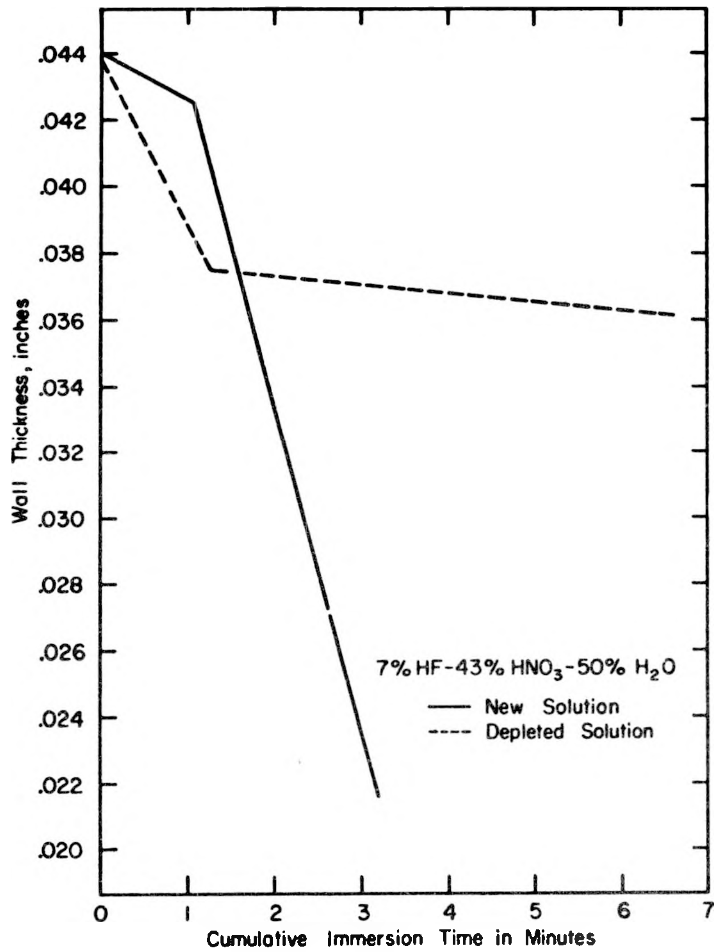


Fig. 13(a) - The change in OD as the result of etching in a 7% HF bath.

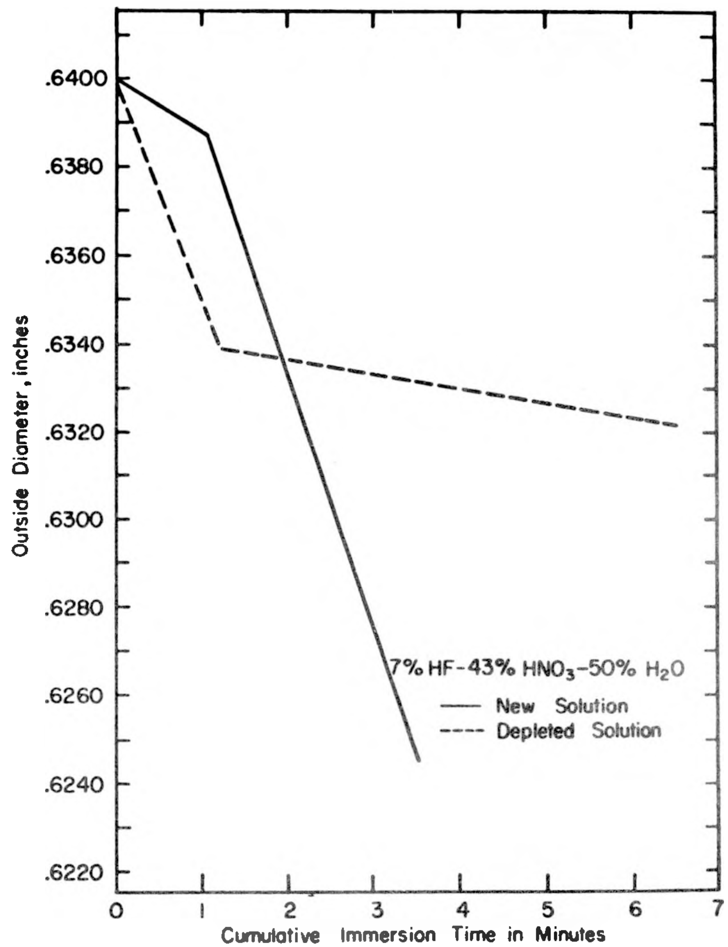


Fig. 13(b) - The change in wall thickness as the result of etching in a 7% HF bath.

100X Pd. Lt.   A-1082-2(f)

Fig. 14(a) - As-extruded sample oxidized by resistance heating for 20 seconds. Marked oxide layer is observable.

100X Pd.Lt. A-1082-3(e)

Fig. 14(b) - Sample cold-drawn 15% and oxidized 10 seconds by resistance heating. No gross oxide layer formed.

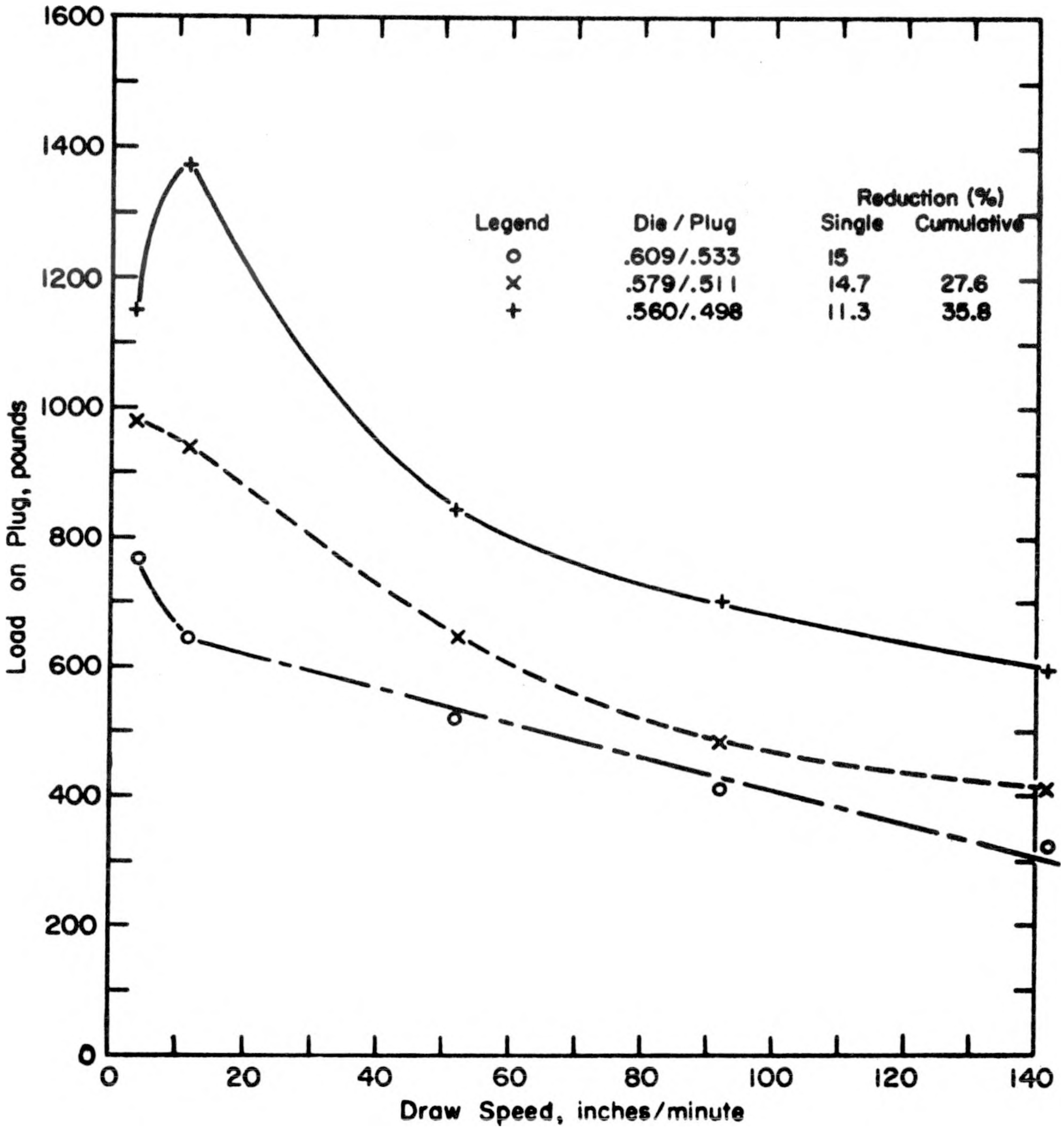
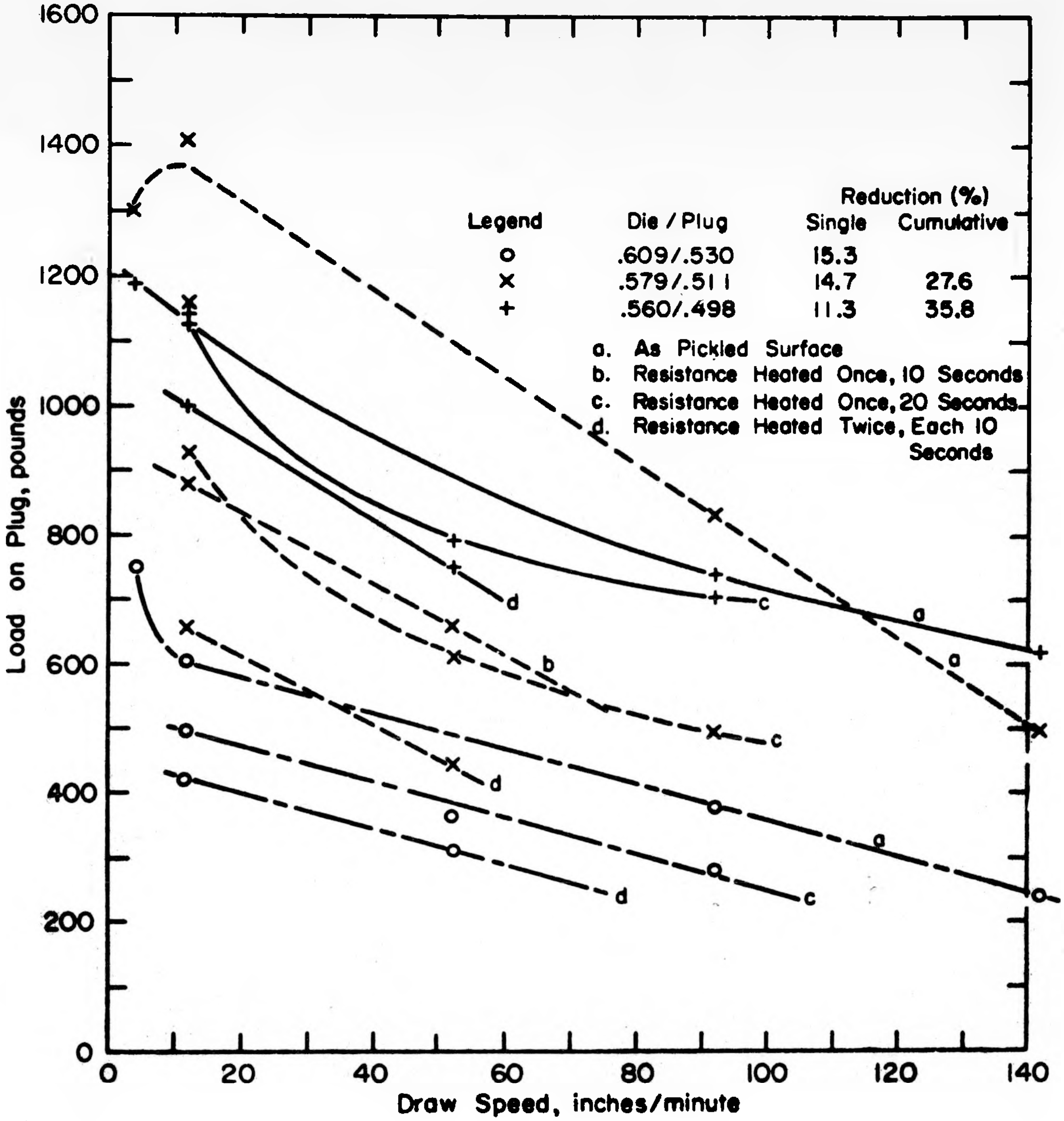
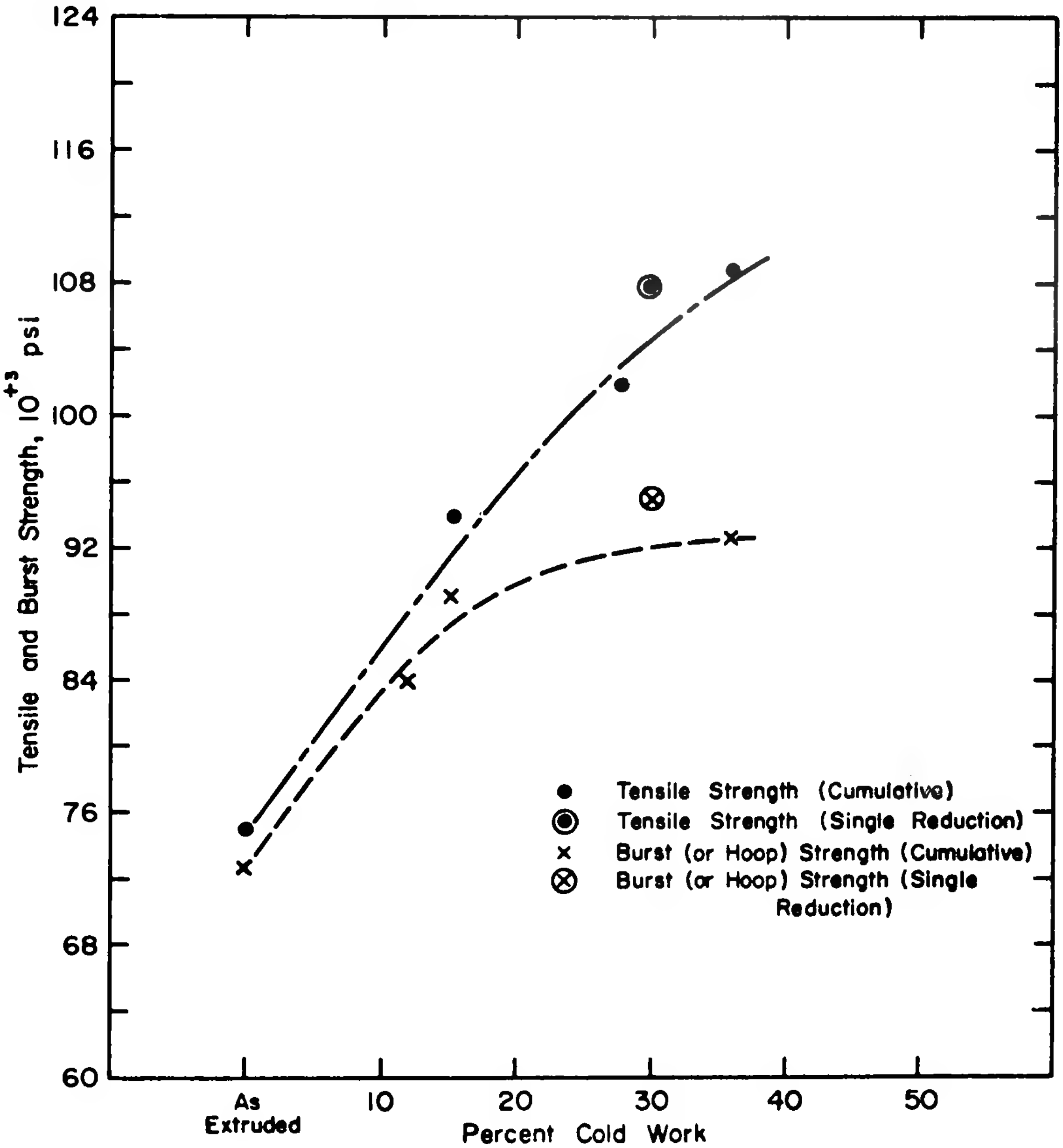


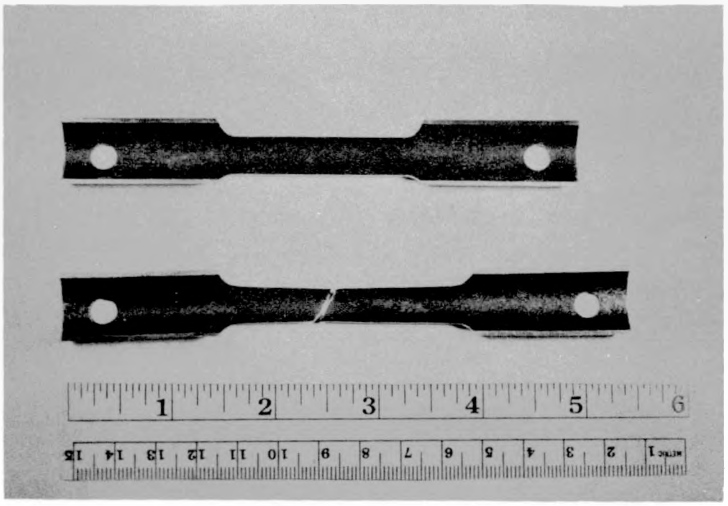
Fig. 15 - Plug force vs drawing speed: conversion coating base, soap as lubricant.



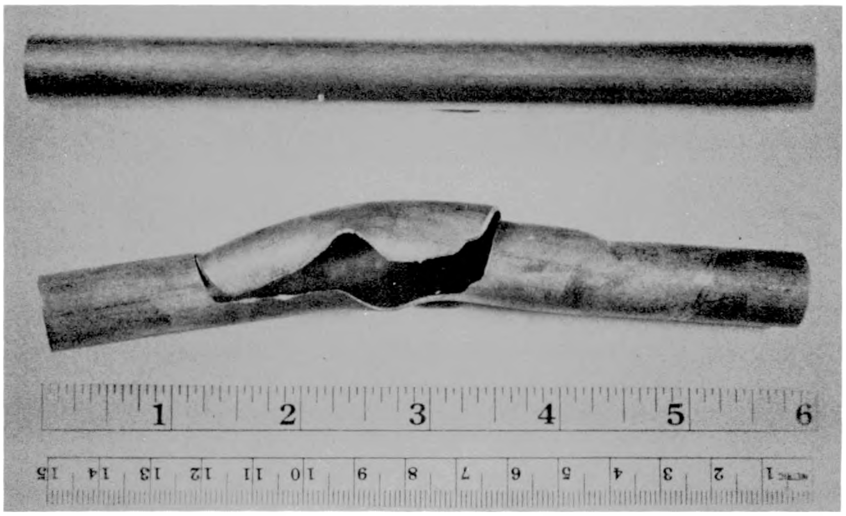
<u>Fig. 16</u> - Plug force vs drawing speed: oxide base, "Steel-skin" as lubricant.



<u>Fig. 17</u> - Tensile and burst strength vs percent cold reduction in the longitudinal and transverse directions.



(a) RF-5635



(b) RF-5634

Fig. 18 - Typical tensile specimen (a) and burst specimen (b), before and after fracture.