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FABRICATION AND PROPERTIES OF EXTRUDED SILVER-CADMIUM CONTROL RODS

by

Austin E. Dwight

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Revere Copper & Brass: Extrusion Technique Development

Rock Island Arsenal: Straddle Milling of Shapes

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FABRICATION AND PROPERTIES OF EXTRUDED SILVER-CADMIUM CONTROL RODS

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Austin E. Dwight

ABSTRACT

The production of cross-type control rods having a span of 4-7/8 in., and an arm thickness of 1/8 in., was studied. Extrusion techniques were developed for producing cross-type control rods from each of two alloys; one containing 75% silver-25% cadmium, and the other containing 67% silver-30% cadmium-3% copper. Fabrication of the extruded crosses into clad control rods for the Mark I naval reactor was attempted. A set of unclad control rods for the Zero Power Reactor was produced.

The effect of copper, nickel, aluminum, palladium, and indium, singly and in various combinations, on the physical and mechanical properties of silver-cadmium was studied. Data are given on the work hardening and annealing of binary silver-cadmium alloys, and on the precipitation hardening of certain complex silver-cadmium alloys.

A materials specification and suggested fabrication procedure were established for nickel-clad extruded silver-cadmium control rods.

I. INTRODUCTION

The development work described in this report was initiated to devise an alternate method of fabricating the control rods for the Mark I naval reactor. In the latter part of 1950, it was not certain that the roll cladding and welding method would be successful. It was decided to develop an alternate method using extrusion as the fundamental process.

During development of the alternate extrusion process, a quantity of data was collected which may be useful for some future fabrication problem. This report is intended both to present these data and to provide a brief history of the development work which was performed. These data can best be presented in two sections, one dealing with the actual fabrication processes used to make a control rod by the extrusion method; and the other dealing with the physical and mechanical properties of the various silver-cadmium base alloys which were tested as core materials.

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The experience which was gained in the attempted fabrication of Mark I control rods made possible the successful production by extrusion of a set of ZPR unclad control rods.

II. SUMMARY AND CONCLUSIONS

1. The flow of silver-cadmium alloys in extrusion is of the type wherein entrained oxide appears as an extrusion defect just under the skin of the shape.

2. An alloy of 75% silver-25% cadmium can be extruded into a cross shape if the extrusion ratio is held below 25:1 and the billet heated to 1300-1400F.

3. An alloy of 67% silver-30% cadmium-3% copper can be extruded into a cross shape if the extrusion ratio is held below 11:1 and the billet heated to 1250-1270F.

4. Cold drawing of an extruded cross did not prove practical, due to distortion of the cross arms.

5. Extruded crosses made of the silver-cadmium-copper alloy can readily be machined to close tolerances by straddle milling.

6. The silver-cadmium-copper alloy is capable of being hardened from Rockwell F 64 to 84 by aging at 600F.

7. An adherent cladding of nickel can be obtained by electroplating. Further development of the plating process is needed.

8. A set of unclad control rods were successfully extruded for the Zero Power Reactor.

III. ATTEMPTED PRODUCTION OF MARK I CONTROL RODS

A. Fabrication of Bare Crosses

1. Casting and Scalping of Billets

The first two billets, 12-1/2 in. long by 5 in. diameter, were cast at the Battelle Memorial Institute. The billets were extruded without machining the surface. Because of bad blisters on the extruded shape, all subsequent billets were scalped to remove surface defects.

Except for the first two billets, all billets were cast at Goldsmith Brothers, Chicago, using a graphite mold. The billet diameter

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as cast was one-half inch larger than after machining, i.e., most of the billets were cast 7 in. OD and machined to 6-1/2 in. OD for use in a 6-5/8 in. ID container. No difficulties were encountered with segregation or with holding the composition within specifications.

The extrusion work was done in two brass mills, Revere Copper and Brass, Detroit, Michigan and Chicago Extruded Metals, Cicero, Illinois. The presses were standard brass mill equipment. The Revere press had a 31.75 in. diameter cylinder and could exert a maximum pressure of 4000 psi or 1580 tons on the ram. The dies used at Revere were of the bell-mouth type. The contour of the die may be estimated from Fig. 1 which shows an extrusion butt after sectioning and etching.

The Chicago Extruded Metals press had a 2000 ton maximum pressure and was of the muzzle-loading type. The dies were of the shear type. The die contour may be estimated from Fig. 2.

2. Extrusion Variables

The variable factors which affect the extrusion process are the temperature of the billet, pressure, extrusion speed, and lubricant. Other factors which are fixed but which affect the process are the composition of the billet, the geometry of the extruded shape, extrusion ratio, and the design of the die. All of these factors are interrelated.

The extrusion ratio proved to be a controlling factor. It is defined as the ratio of the cross-sectional area before extrusion to the area of the extruded shape. The area before extrusion is the area of the container cross section because the billet upsets to fill the container before extrusion starts. In the first extrusion at Revere on November 3, 1950, a 5-5/8 in. container was used. The extruded shape had a cross-sectional area of 1.14 sq. in. and is shown in Fig. 1. Therefore the extrusion ratio was 21.7, and the reduction in area was 95.5%. The extrusion was successful.

In the first extrusion at Chicago Extruded Metals on November 6, 1950, the shape (Fig. 2) had a cross-sectional area of 1.49 sq. in. and the extrusion ratio was 25.9. The extrusion was successful.

On January 5, 1951 a successful extrusion was made at Chicago Extruded Metals with an extrusion ratio of 30.8. However, on February 21, 1951, an attempt was made at Revere to extrude a 6-1/4 in. OD billet in a 6-5/8 in. ID container with an extrusion ratio of 30.2. The billet failed, i.e., the press stalled at its maximum pressure, and no extrusion occurred. The failed billet was turned down to 5-1/2 in. and extruded in a 5-5/8 in. ID container.

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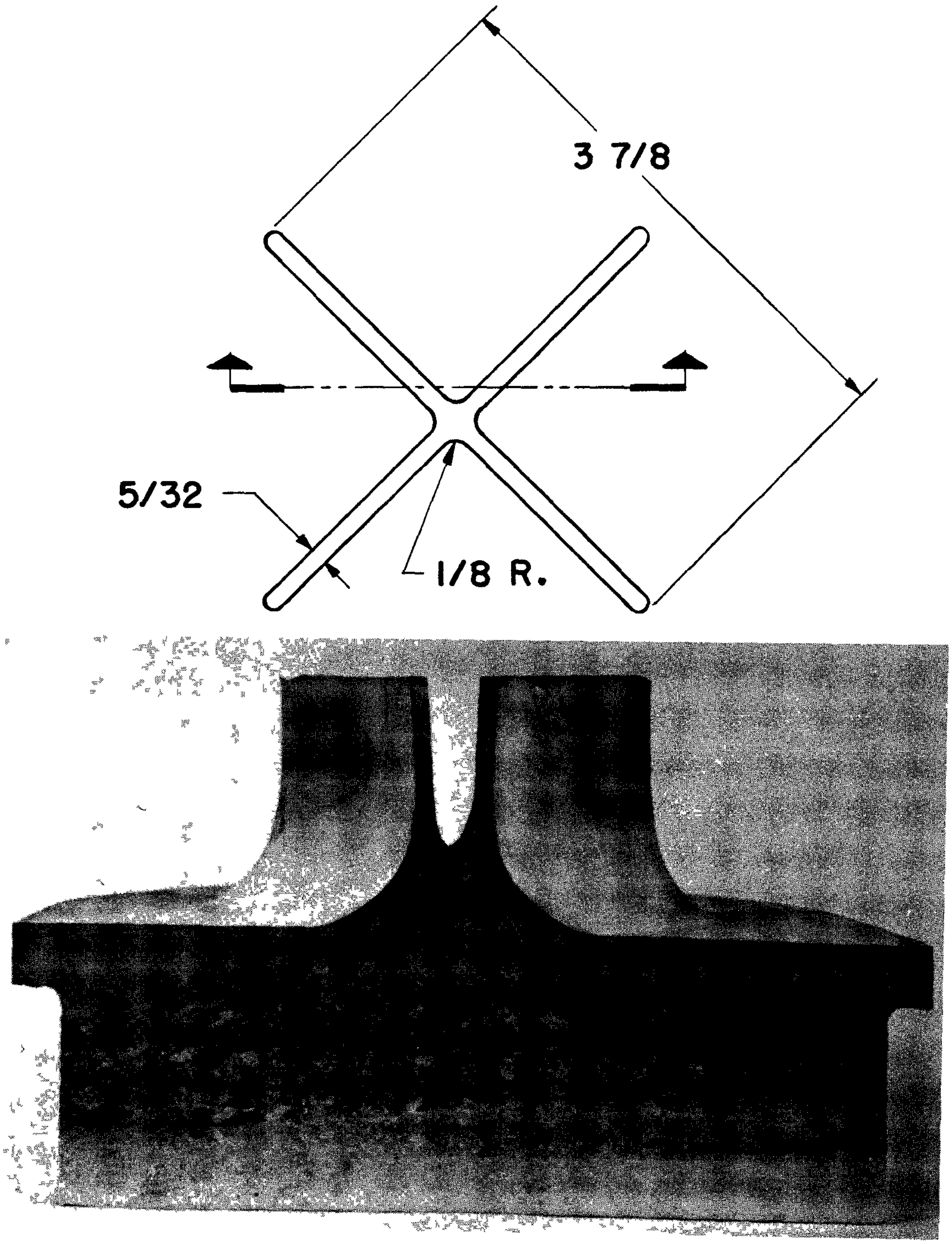

FIG. 1
CROSS-SECTIONAL VIEW OF BUTT
AND SHAPE OF CADMIUM-SILVER CROSS
EXTRUDED BY REVERE COPPER & BRASS CO.

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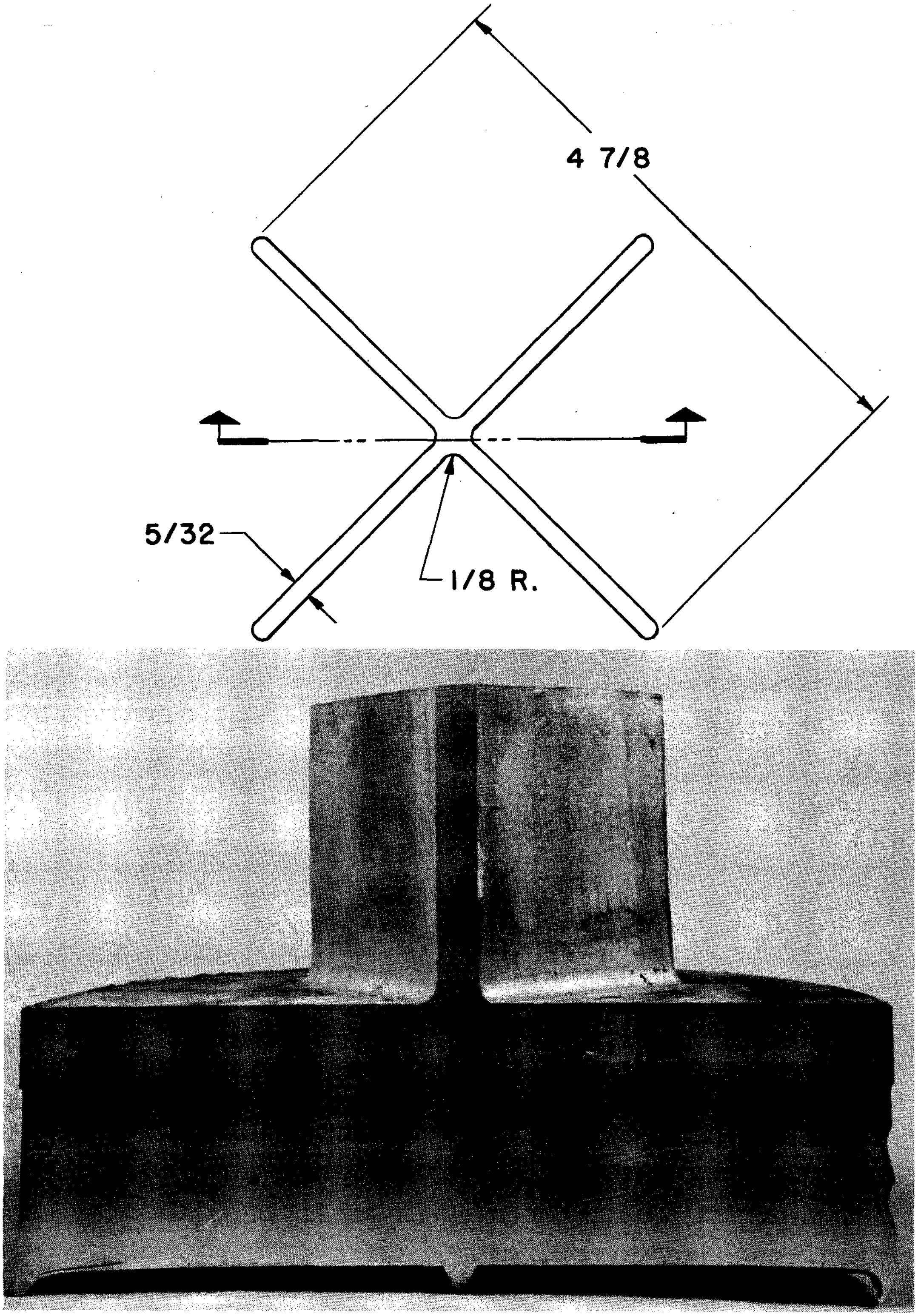

FIG. 2
CROSS-SECTIONAL VIEW OF BUTT
AND SHAPE OF CADMIUM-SILVER CROSS
EXTRUDED BY CHICAGO EXTRUDED METALS CO.

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From the first five extrusion attempts it is apparent that the limiting extrusion ratio lies between 24 and 30 for an alloy of 75% silver, 25% cadmium, extruded into a cross shape. It should be noted that the more powerful press at Chicago Extruded Metals has a higher limiting extrusion ratio than the Revere press.

All subsequent extrusion work was done on a modified composition containing 67% silver, 30% cadmium and 3% copper. The addition of copper necessitated a lower billet temperature, and increased the resistance of the billet to flow through the die.

Two attempts were made to extrude the modified alloy at Chicago Extruded Metals with an extrusion ratio of 30. Both failed, indicating 30 is above the limiting ratio. Chicago Extruded Metals withdrew from the work, and all subsequent extrusion was done at Revere.

An extrusion was attempted May 29 and again on May 30, 1951, using an extrusion ratio of 15 with the modified alloy. The billet failed on both attempts, but, after the extrusion ratio was reduced to 10.9 by reducing the billet diameter to 5-1/2 in., the extrusion was successful. For the copper-bearing alloy the limiting extrusion ratio is apparently between 11 and 15.

The billet temperature is an important variable factor. Most metals and alloys have a hot-short temperature range which must be avoided for successful extrusion. For the alloy containing 75% silver-25% cadmium, successful extrusions were made with billet temperatures of 1340F, 1250F, 1315F, 1335F, and 1400F. In the case of billet failures mentioned above (due to too high extrusion ratios) billet temperatures were 1350F and 1420F. It is apparent that binary 75% silver-25% cadmium can be extruded between 1250F and 1400F, and that raising the billet temperature will not compensate for an excessive extrusion ratio.

For the modified (3% copper) alloy the billet temperature must be lower. An extrusion on March 1, 1951 showed the alloy to be hot short at 1350F. On June 5, 1951 the alloy was successfully extruded into a cross at 1270F. On August 19, 1952 the modified alloy was successfully extruded into crosses at 1250F. The proven temperature range is therefore 1250 to 1270F, but probably is somewhat broader.

The extrusion pressure behaves in the characteristic manner, i.e., it immediately rises to a maximum, falls back to a lower value (called the runout pressure) and very gradually falls during the extrusion. Whether it rises or falls at the end of the cycle depends on the nature of the dummy block which is used.

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The design of the die entrance and throat does not appear to be critical. As shown in Figs. 1 and 2, successful extrusions were obtained with both types of die.

The entrainment of oxides to cause blistering (known in the trade as the extrusion defect) gave much trouble. Because of the close metallurgical similarity between silver-cadmium and alpha brasses, the theory which has been developed by Pearson[1] and Crampton[2] for brass might be expected to apply to the extrusion of silver-cadmium; this proved to be true. Pearson's classification of extrusion defects into three types, A, B, and C, is generally accepted in the industry. No discussion of type A flow will be given as it is not characteristic of any of the silver-cadmium alloys. It is well known that copper extrudes in type B flow. Briefly, type B flow occurs when the restraining effect of friction between the billet surface and the container wall leads to heavy shear along the sides of the billet close to the surface. The effect is to increase the rate of travel of the center part into the die relative to the metal at the outside. In the later stages, the effect of the continued shearing of the billet past its peripheral layers causes the latter to build up at the rear end of the billet in front of the advancing dummy block. In the latter part of the extrusion, this accumulated material bulges inwards and begins to affect the deformation of the metal in the center. Type C flow differs from type B in that the zone of shear in type C formed by the displacement of the center through the outer part retained by friction is now at a greater depth below the surface, leaving a fairly thick rim of dead material. This rim is folded and in the later stages projects tongues into the center stream which enters the die and forms part of the extruded bar. In type B flow the enfolded material appears just under the surface of the extruded section instead of at the center as in type C flow.

Crampton has stated that high-copper alloys consisting entirely of the alpha phase are little subject to the central extrusion defect, but are apt to be unsound at or just below the surface skin of the extruded parts; the latter form of fault may originate when flow follows type B. Pearson states that high-copper alloys are liable to show, usually over the final third of the extruded length, a rough bark-like skin which has to be cleaned up by scalping. The mechanism by which this occurs is that the outer layers of the billet become concertinaed in the deformation zone near the die with the result that oxide is drawn in through this zone, passing out through the die at or just below the surface of the bar.

The 75% silver-25% cadmium alloy is an alpha-solid solution, having the same crystallographic structure as high-copper alloys. The blistering which appeared on the extruded crosses is clearly due to type B flow. The flow type could not be changed with the available extrusion presses, so relief from blistering was attempted by protecting the billets from oxidation (heating them in nitrogen or in graphite cans) and by varying the die lubricant. Oil and graphite was the commonly used lubricant. No better lubricant was found, though probably a development program could discover one.

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The philosophy finally adopted was that subsurface blistering could be held to a minimum, but not eliminated. Therefore, silver-cadmium alloys must be extruded sufficiently oversize to permit removal of the subsurface defective area by machining when 100% prevention of blisters is required in the finished part.

The choice of material for the dummy block affects the amount of useable material obtained per billet. It was found that use of a brass dummy block between the billet and the steel dummy block permitted extrusion of a larger proportion of the billet.

3. Drawing and Straightening

The original plan was to extrude the cross-shaped sections larger than the finished size, so that a cold-drawing operation could be used to obtain the close tolerances required; also to strengthen the rather weak alloy. This is conventional brass mill practice. Difficulty was encountered from two sources. First, the cross shape has much thinner and wider sections than most extruded shapes and therefore was quite susceptible to warping due to slightly unequal reductions of the various fins. Secondly, the blisters which appeared from the extrusion defect were flattened by the drawing operation, but the defect still existed. It was feared that if the flattened blisters were permitted to get into a reactor, they would open up, causing swelling and possible sticking of the control rods.

The first section extruded at Chicago Extruded Metals was given a 12-1/2% minimum cold draw in three steps. The specified camber of ±0.015 in. over a 55 in. length was not held.

The first section extruded at Revere had only a 3-7/8 in. span, compared with approximately 4-7/8 for all other sections. It happened that the specified camber was met on the part after stretcher straightening, drawing, and hand straightening. On the second attempt at Revere, with a 4-7/8 in. cross, too heavy a draw was used, resulting in a wavy surface on some of the fins.

After the work on the 75% silver-25% cadmium alloy was terminated in favor of the 67% silver-30% cadmium-3% copper alloy, no further attempts were made to obtain close tolerances by drawing. However, all of the modified alloy sections were given a light draw, called a forming draw, to insure that the 90-degree angle between fins was not changed when the hot section was cooling on the run-out table.

4. Machining

After it was realized that close dimensional tolerance and good strength could not be obtained consistently by cold drawing, it was decided to use alloying additions to obtain strength, and machining to obtain

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the necessary dimensional tolerances. Straddle milling was selected as the most promising method. The 55 in. length required a rather large milling machine which was located at the Rock Island Arsenal. All subsequent crosses were extruded oversize and straddle milled to size at Rock Island. This method resulted in the elimination of the extrusion defect and satisfactory tolerances were held.

B. Cladding Experiments

After development of the extrusion and straddle milling techniques, the only remaining major problem in the fabrication of control rods was cladding the silver-cadmium crosses. Cladding was necessary to prevent corrosion of the control rods in 600F liquid water and to prevent dissolution of cadmium into the water, where it might be disseminated through the reactor core. The following cladding materials and methods were investigated:

1. Soldering Stainless Steel with Easy-Flo

Stainless steel was the preferred cladding material and Type 347 was considered necessary because welding was involved. Easy-Flo silver solder was spray coated onto a flat plate of Type 347 stainless steel which had been sand blasted. A plate of 75% silver-25% cadmium alloy was clamped to the silver-soldered surface and the sandwich heated to above the flow point of the solder. After cooling, the sandwich broke apart when dropped, apparently due to severe oxidation of the silver solder during the spray-coating operation. No attempt was made to develop this method further.

2. Soldering Nickel with Easy-Flo

A one-inch long section was assembled with a thin foil of Easy-Flo silver solder between the sheet nickel cladding and the extruded cross. A poor bond was obtained, probably due to an inadequate fixture for clamping the assembly together at the soldering temperature.

3. Diffusion Bonding with Gold

A small flat plate of Type 347 stainless steel was plated with approximately 0.001 in. of gold by Gilbertson and Son of Chicago. This amount is an unusually heavy gold plate and was rather rough. A similar gold layer was plated onto a piece of silver-cadmium alloy, and the two metals then were clamped together with the gold layers in contact. After heating at 1350F for several hours a fairly good bond was obtained.

Next, an attempt was made to clad a short section of the extruded cross, approximately 1 in. long, using 0.030 in. Nickel "A" instead of Type 347 stainless steel. For such a short length, it was simple to bend

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the gold-plated nickel to conform to the outside of the gold-plated extruded cross. Four stainless steel triangular-shaped bars were machined to fit into the four angles of the cross, and a heavy steel ring was placed around the assembly. Pressure was applied by means of heavy set screws to force the nickel into contact with the cross. After heating at 1350F, it was found that the two gold layers had bonded, except in the corners.

A second experiment was made on a six-inch length and gave the same result - good bond except in the corners. At this stage it became apparent that bonding a full-length control rod by the gold-bonding method would require a complicated fixture and much development work. The ideal fixture would be one in which hydraulic pressure could be applied to all surfaces of the cross at 1350F. Such development work did not seem to be justified for an alternate method, so the gold diffusion bonding was not developed further.

4. Spray Coating of Stainless Steel

A heavy deposit (over 1/16 in.) of stainless steel was sprayed onto a 4 in. section of extruded cross. The deposit had a smooth surface, but was porous; adhesion was so poor that the steel cladding broke away from the silver-cadmium alloy when the specimen was dropped.

5. Nickel Plating

Due to the difficulty in applying a uniform pressure to all surfaces of the cross to secure a good bond, it was decided to concentrate effort on electroplated claddings, as a simpler fixture and equipment would be required. The specifications required a cladding 0.030 in. thick which would resist corrosion in 600F oxygenated water. The only metal which seemed practical to plate to a thickness of 0.030 in., and which might resist corrosion, was nickel, so work was concentrated on nickel plating of crosses.

Small sections of extruded crosses were sent to the Plating Engineering Company of Milwaukee, Wisconsin. This company specializes in heavy nickel plating and had little trouble in applying an adherent plate. It quickly became apparent that the geometry of the part made it impossible to apply a uniform coating 0.030 in. thick, and that it would be necessary to apply a much greater thickness to certain areas, followed by machining down to 0.030 in. The major difficulty was that of throwing 0.030 in. of nickel into the corners (1/8 in. radius) between arms of the cross.

The first attempts at plating a full-length control rod made use of nickel anodes in the form of 1/2 in. rounds, 1 in. rounds, and sheet bent into angles. All resulted in a heavy buildup of nickel at the points closest to the anodes, and only a thin coat in the corners.

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The next attempt was with flat nickel anodes, cut from 1/4 in. Nickel "A" sheet, and so located that the anode bisected the angle of the two arms of the cross. The edge of the anode closest to the cross was beveled in an attempt to direct more current into the corner. This method failed in that small slivers of anode material fell into the gap between anode and cross, causing a bridge, or shorting out, between anode and cross.

Several full-size crosses were plated, with much difficulty from tree formation. Anodes of graphite were next attempted to eliminate the tree formation. The nickel was supplied from the bath which was replenished with nickel salts. The wetting agent in the bath deteriorated due to chlorine discharge at the anode, causing a black slime to be deposited in the corners of the cross. This slime acted as an insulating layer, permitting only a thin deposit of nickel.

At the time the project was terminated it was thought that the best chance of success lay in using 1/4 in. lead anodes, a low chloride Watts bath with peroxide but no wetting agent, and a Koroseal-lined steel tank.

6. Nickel-Tin Alloy Plating

Corrosion testing at 600F of the nickel plate described in the preceding section indicated that nickel alone would not resist corrosion in oxygenated water. It was decided to modify specifications to call for a cladding of 0.028 in. of nickel plus 0.002 in. of a more corrosion-resistant material. The nickel-tin alloy (65% tin) developed by the Tin Research Institute was considered to be the most suitable material for the surface cladding. Specimens which had been plated over silver-cadmium were obtained and corrosion tested. Corrosion data are given in the Appendix. It was though that the nickel-tin alloy would be satisfactory for service at 600F, especially after Mark I design was modified to allow hydrogenated cooling water.

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C. Inspection Problems

Inspection of the bare extruded crosses was a simple problem, as etching the surface easily revealed metallurgical defects. After plating with nickel, the problem of inspection was more difficult. Ultrasonic testing was used to search for areas of poor bond. The major problem, which was never completely solved, was measuring the thickness of the nickel plate. As mentioned above, the plating operation produced a cladding which varied from 0.010 in. in the corners to 0.070 in. opposite the anode. The plate was machined down by straddle milling to an over-all arm thickness of 0.182 to 0.187 in. By this method there was no assurance that there was the same amount of nickel on either side. Because no satisfactory non-destructive method existed for measuring the thickness, it was necessary

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to mask off small areas on top, bottom, and center of the cross to use as locating pads in the straddle-milling operation. In a second plating operation the milled surface was masked off and the locating pads filled in with nickel. A second straddle-milling operation then cleaned up the surface. This method would be practical only if facilities were available close by for the plating, straddle milling, and inspection.

D. Procedures Used in Four Attempts to Make Full-Size Control Rods

Each attempted procedure was an improvement over the preceding attempt. The rods were designated by XD numbers, as they were experimental. The four control rods are shown in Fig. 3.

XD-1: The first attempt used an extruded cross of 75% silver-25% cadmium, cold drawn to size. It was plated with nickel using round anodes. The excess nickel was removed by a planing operation at Argonne. The cross was scrapped when the planing cutter dug through the nickel into the silver.

XD-2: The second attempt also used an extruded cross drawn to size, of the same composition as XD-1. Instead of planing, the excess nickel was removed by grinding at the Quality Hardware Company in Chicago. Due to lack of a method for locating the silver-cadmium alloy in the nickel cladding, the nickel was again cut through, exposing the core. It was thought that grinding generated heat enough to warp the arms of the cross, causing them to buckle up against the grinding wheel. Grinding was abandoned.

XD-3: The third attempt was with an alloy of 67% silver-30% cadmium, 3% copper. The alloy was extruded oversize and straddle milled at the Rock Island Arsenal to remove the extrusion defect. The cross was precipitation hardened at 600F, to make it more resistant to distortion in handling, and plated with nickel, using a specially designed fixture and "A" nickel anodes. The nickel formed trees from anode to cathode. The cross was removed from the bath, the trees ground off, and the cross replated. After plating, the nickel plate was straddle milled down to 0.185 in.; however, the milling cut through the nickel on two fins, due to inability to locate the silver-cadmium core.

XD-4: The final attempt was made with the same alloy as in XD-3, straddle milled to give a good bare cross. The nickel plate was applied in two steps, leaving locating

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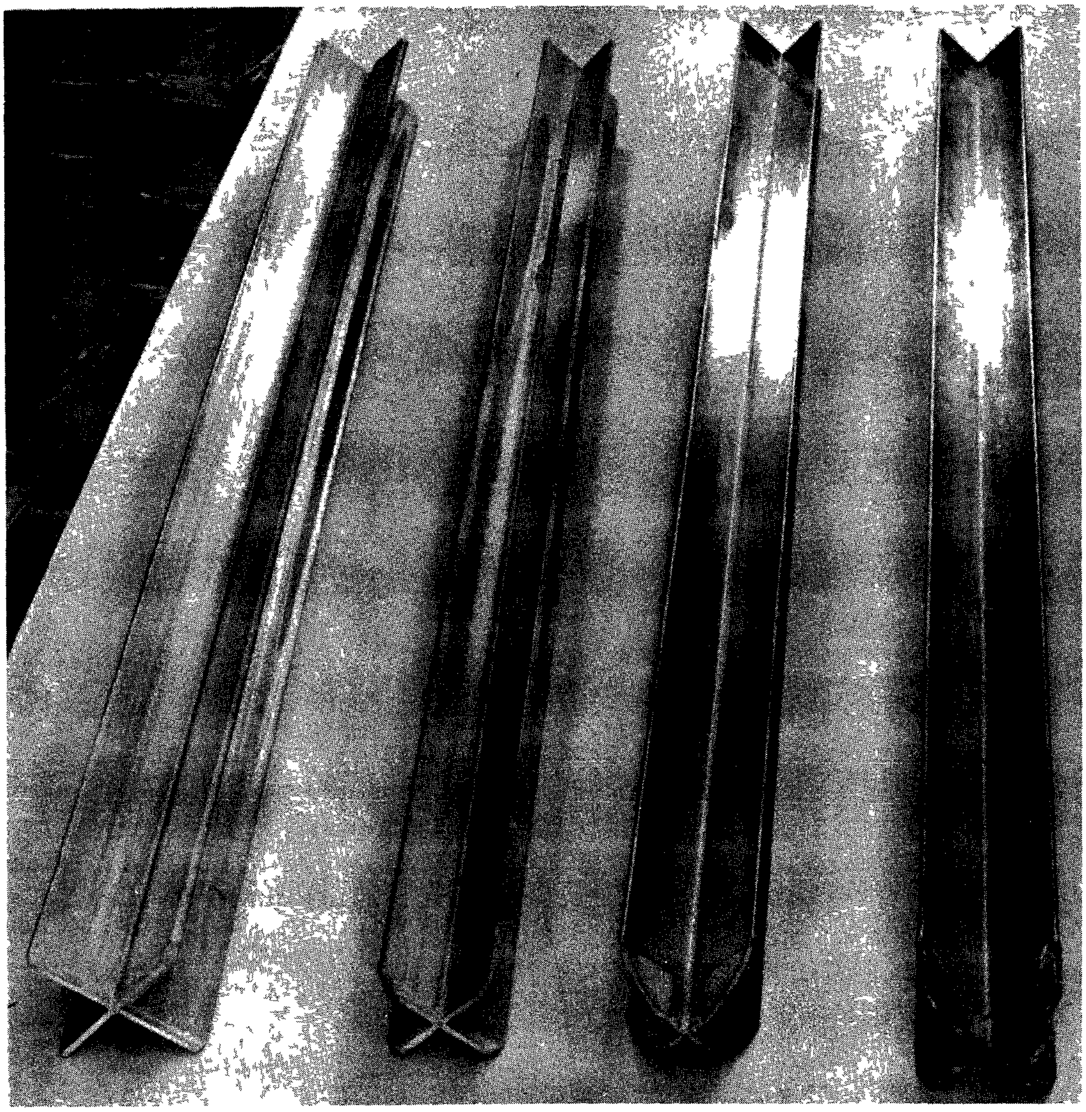

XD-1 XD-2 XD-3 XD-4

FIG. 3
UNCOMPLETED NICKEL-CLAD EXTRUDED
SILVER-CADMIUM CONTROL RODS

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pads at top, center, and bottom after the first step. The nickel cladding was successfully milled to final dimensions. Work was underway to develop a method for attaching a stainless steel shoe on the bottom and an adapter on the top, when the project was terminated.

E. Recommended Procedure for Production

The procedure recommended for production of nickel-clad, extruded, cross-shaped control rods is essentially the same as was attempted on XD-4. The details of material, dimensions, and procedure are given on drawing NR-6506-F. The suggested, but unproved, procedure for attaching the adapter and shoe is to silver solder them to the bare cross, then to nickel plate over the soldered joint, so that only nickel and stainless steel are exposed. The entire cross should then be given a light overplate of the tin-nickel alloy.

IV. PRODUCTION OF ZPR CONTROL RODS

In the Spring of 1952 the need arose for a set of silver-cadmium-copper cross-type control rods to be used in the Zero Power Reactor at Argonne. The extrusion technique was sufficiently well developed so that it was specified for fabrication of the ZPR rods. The alloy composition included nickel and aluminum as hardening agents. The billets were cast by Goldsmith Brothers, scalped at Argonne, and extruded at Revere. The extruded rods were straddle milled at Rock Island Arsenal and equipped with fittings at Argonne. No difficulties were experienced in the production of these control rods. The arms were thicker than those of the Mark I rods, which simplified the extrusion by lowering the extrusion ratio. Full details of dimensions, material, and procedure are given on drawing NR-6705-C.

V. PHYSICAL AND MECHANICAL PROPERTIES OF SILVER-CADMIUM ALLOYS

A. Theory of Alloying and Selection of Solutes

The phase diagram for the silver-cadmium system[3] is shown in Fig. 4 as corrected according to the work of L. Muldawer, et al.[4] The composition of 75% silver-25% cadmium was selected originally as a compromise between the increased neutron absorption and lowered melting point resulting from increased cadmium content. The alloy is excessively soft and weak, and is incapable of being hardened by heat treatment. The only possible method of hardening the alloy is by cold drawing; as mentioned in Section III-A-3, this proved impractical due to warpage of the arms of the cross. Therefore, the binary 75% silver-25% cadmium alloy can only be used in applications where very little structural strength is needed.

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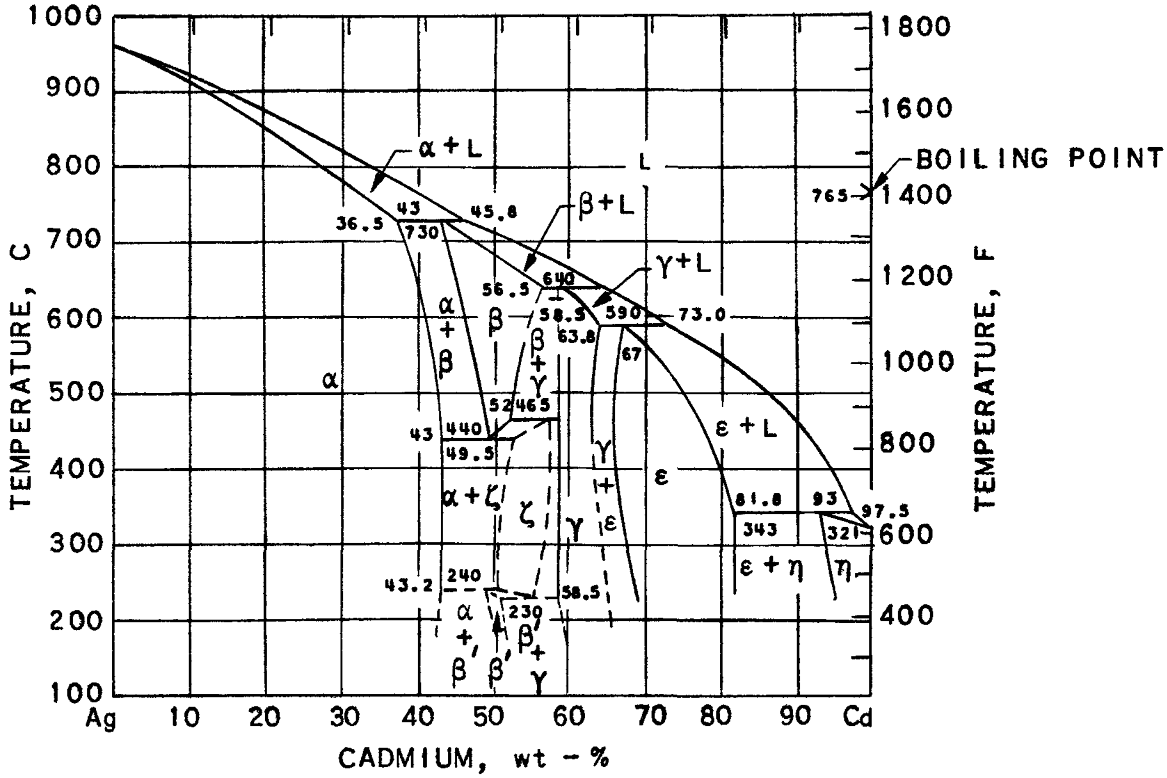

FIG. 4
PHASE DIAGRAM OF THE
SILVER-CADMIUM SYSTEM [3,4]

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A.DWIGHT:F.J.S.,1-25-54

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Alloying additions may be of two classes: one which forms solid solutions having properties superior to the binary solid solution, and the other which forms a second constituent which makes the alloy susceptible to heat treatment.

Palladium and gold each form continuous solid solutions with silver, and these may form a ternary solid solution up to a limiting amount of cadmium. Indium and palladium were added to some alloys to form a quaternary solid solution. The addition of gold, palladium, or indium was primarily for the purpose of improving the corrosion resistance, so that a protective cladding would not be needed. These three elements also strengthened and hardened the silver-cadmium alloy.

Elements which were added primarily to make the alloy susceptible to heat treatment were copper, aluminum, and nickel, with the emphasis on copper. The elements were selected because their binary phase diagrams with silver show limited solubility in silver and a sloping solvus line, indicating a potential age-hardening alloy.

B. Solid Solution Alloys

1. Binary 75% Silver-25% Cadmium Alloys

In designing a control rod it is necessary to consider the thermal expansion of both the core alloy and the cladding material. These data are shown in Fig. 5. The thermal conductivity was determined, but is presented in a Battelle Memorial Institute report[5] and is not reproduced here. The tensile strength and modulus of elasticity are shown in Figs. 6 and 7, respectively. The Rockwell hardness lies in the range 10-22 R_F in the extruded condition and in the range 60-75 R_F after a 12% cold-drawing operation. The microstructure is that of a solid solution very similar to alpha brass; a typical microstructure is shown in Fig. 8.

The response of the binary silver-cadmium alloy to work hardening and annealing is shown in Figs. 9 and 10. These graphs show behavior typical of a solid solution alloy.

2. Ternary Solid Solution Alloys

Alloys shown in the following tabulation were investigated to determine their physical properties and corrosion resistance:

Identification Number	Composition, %		
	Silver-Cadmium	Palladium	Indium
1553	67-30	3	--
1559	65-30	6	--
2550	50-30	20	--
2562	50-20	20	10

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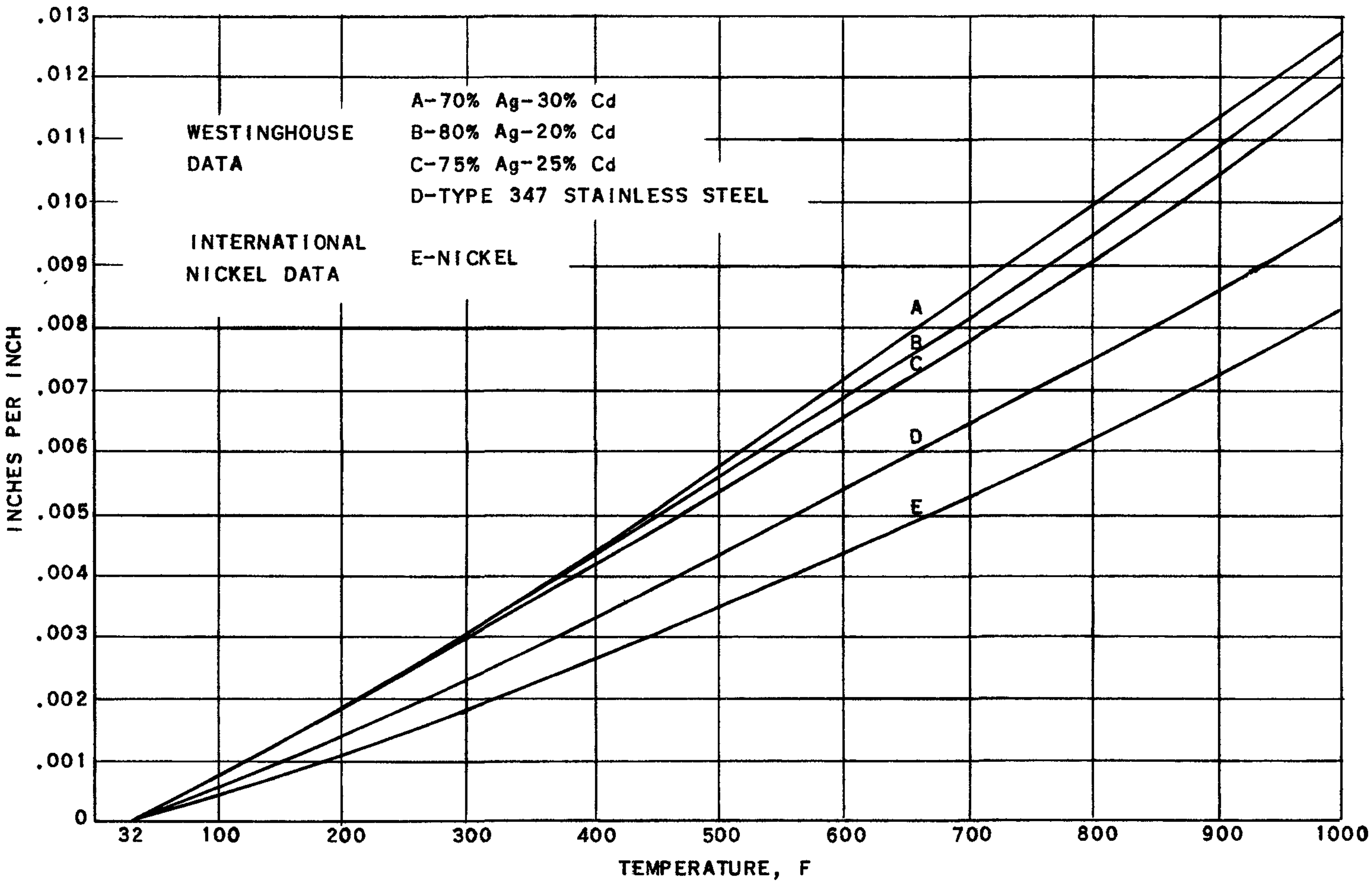

FIG. 5
LINEAR EXPANSION OF SILVER-CADMIUM ALLOYS AND CLADDING MATERIALS

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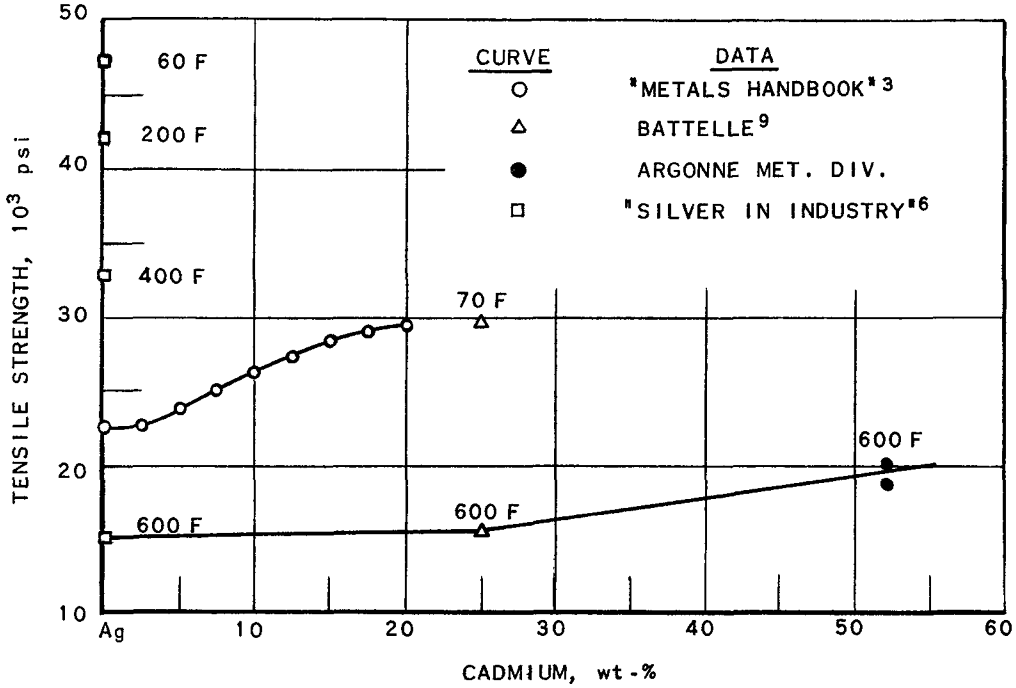

FIG. 6
TENSILE STRENGTH OF
SILVER-CADMIUM ALLOYS

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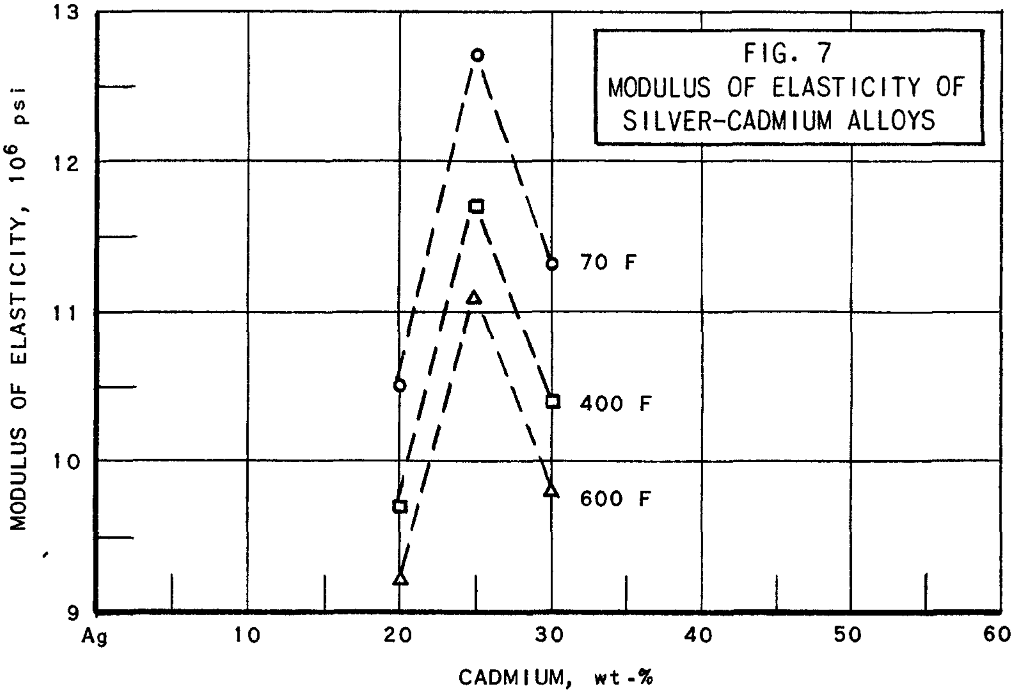

FIG. 7
MODULUS OF ELASTICITY OF
SILVER-CADMIUM ALLOYS

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A.E.DWIGHT:F.J.S.,1-21-54

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FIG. 8
MICROSTRUCTURE OF 75% SILVER-
25% CADMIUM ALLOY ANNEALED 2 HOURS
AT 650 F AFTER 20% REDUCTION
BY COLD ROLLING. 250X

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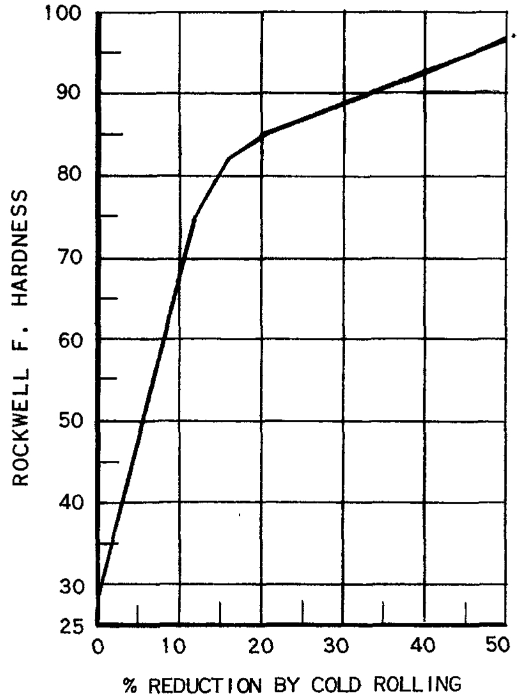

FIG. 9
EFFECT OF COLD ROLLING ON HARDNESS OF
EXTRUDED 75% SILVER-25% CADMIUM ALLOY

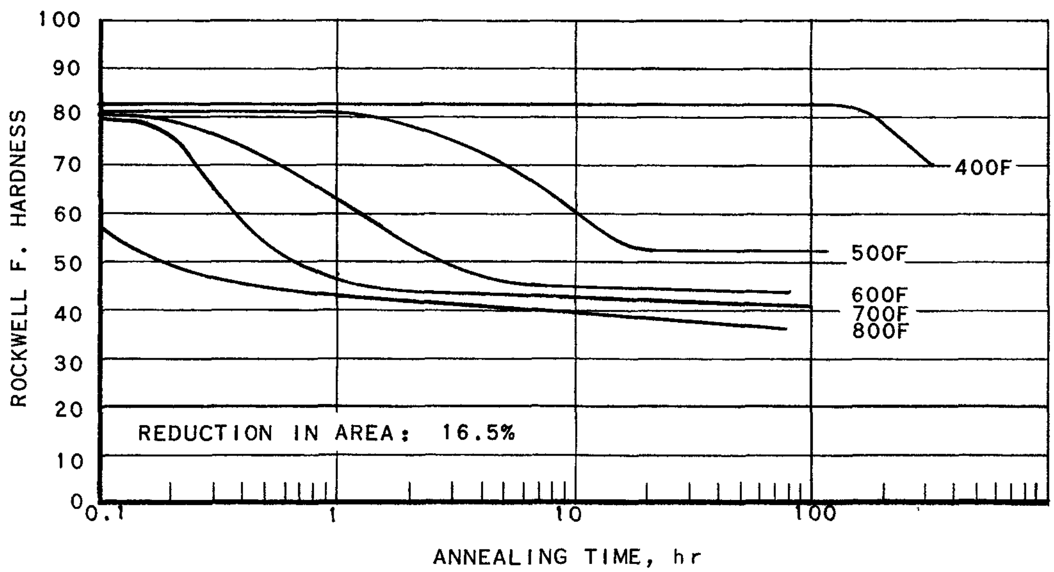

FIG. 10
EFFECT OF ANNEALING ON HARDNESS OF
COLD-DRAWN 75% SILVER-25% CADMIUM ALLOY

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A.DWIGHT:F.J.S.,1-26-54

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It was found that the alloys containing 3 and 6% palladium were of the solid solution type, stronger and more corrosion resistant than the binary alloys, but not sufficiently enough to justify the cost of the palladium. The 20% palladium alloys showed a response to heat treatment which proved they were not of the solid solution type, at least not at all temperatures. Alloy No. 2550, after water quenching from 1500F, had a Rockwell B hardness of 63, which was raised to 90 by aging at 650F for 64 hr.

No extrusion work was attempted on the palladium-bearing alloys, though there is little doubt that extruded shapes could be made.

Elevated temperature tensile tests made at Battelle on the indium-bearing alloy showed a range of ultimate tensile strength from 52,300 psi at room temperature to 25,600 psi at 700F.

The ternary silver-cadmium-palladium phase diagram is not yet determined. Two of the limiting binary systems, silver-cadmium, and silver-palladium, are well known, and the palladium-cadmium system was recently published.[7]

C. Silver-Cadmium Alloys Susceptible to Heat Treatment

1. Silver-Cadmium-Copper Alloys

The phase diagram for this system has been published[8] and a translation is on file at the Argonne National Laboratory library. An investigation of physical and mechanical properties was made because the ternary alloy appeared superior to the binary alloy for use in extruded control rods.

To gain extrusion experience, three ternary alloys containing 3, 6, and 9% copper, with cadmium held at 30%, were extruded into 1-1/16 in. round rod. It was learned that copper lowers markedly the solidus temperature and introduces a hot-short temperature range not found in the binary alloy. The microstructure of the three alloys is shown in Fig. 11. It was found that the copper-bearing alloys were responsive to heat treatment, and this is illustrated by the data in Table I.

The hardness values in the table are an average of at least five measurements. Four conclusions were drawn from the data in the table:

a. All three alloys exhibit a similar response to heat treatment, but vary in degree of response, with so little response in the 6 and 9% copper alloys as to make heat treatment of little value.

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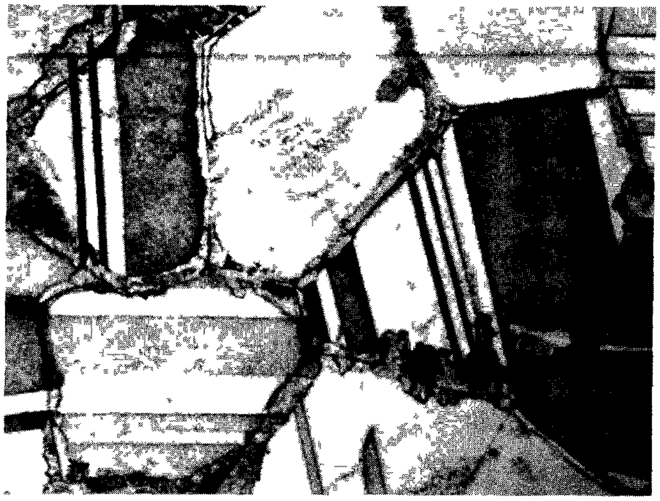
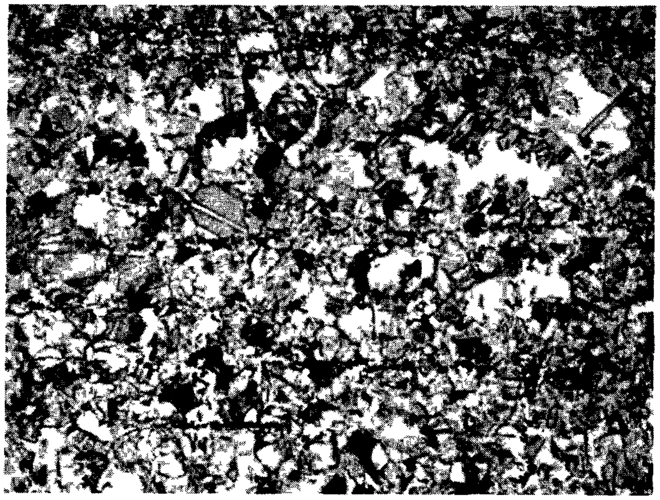


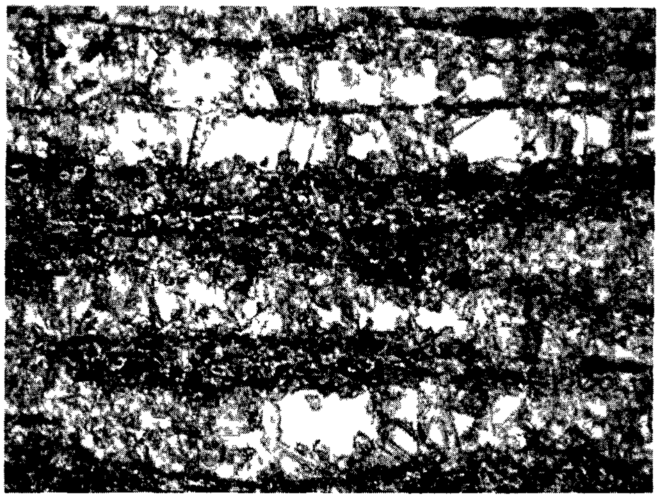
NEG. NO. 11259

(a)
3% COPPER
30% CADMIUM
67% SILVER



NEG. NO. 11260

(b)
6% COPPER
30% CADMIUM
67% SILVER



NEG. NO. 11261

(c)
9% COPPER
30% CADMIUM
61% SILVER

FIG. 11
MICROSTRUCTURE OF SILVER-CADMIUM-COPPER ALLOYS AS EXTRUDED. 250X

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b. The 3% copper alloy can be hardened to nearly as high a Rockwell value as can the 6 and 9% copper alloys. Therefore, work was discontinued on the 6 and 9% copper alloys.

c. A water quench is unnecessary for any of the alloys as adequate hardness can be obtained by aging the extruded material. Quenching a control rod is undesirable because of the danger of distortion.

d. Aging at 600F for 2 hr. is a practical and adequate treatment in fabricating control rods.

Table I

EFFECT OF HEAT TREATMENT ON ROCKWELL HARDNESS OF SILVER-CADMIUM-COPPER ALLOYS

Heat Treatment	Alloy Composition		
	1549 3% Cu 30% Cd	1550 6% Cu 30% Cd	1551 9% Cu 30% Cd
	Rockwell F Hardness		
1. As extruded	64	81	85
2. Water quenched from 1120F	41	66	72
3. No. 2 plus 65 hr. at 510F	88	91	93
4. As extruded plus 18 hr. at 510F	82	86	86
5. Water quenched from 900F	65	78	81
6. No. 2 plus 1 hr. at 610F	63	92	93
7. No. 2 plus 42 hr. at 610F	84	89	90
8. As extruded plus 18 hr. at 600F	87	85	89
9. As extruded plus 6 hr. at 700F	81	83	86
10. As extruded plus 2 hr. at 600F	84	86	89

2. Complex Silver-Cadmium Alloys

It was decided to add small amounts of nickel and aluminum to the alloy containing 3% copper in an attempt to further harden the alloy, and to increase its response to heat treatment. Three 5 in. OD billets were extruded into 1-1/16 in. round rod to investigate the effect of nickel and aluminum on the extrusion characteristics of the alloy. The three billets, whose composition is shown in Table II, extruded quite well. The billet

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with the higher aluminum content showed a greater susceptibility to hot-shortness, indicating that aluminum should be limited to 0.4% maximum. The complex alloys responded to heat treatment essentially the same as did the ternary alloys.

Table II

EFFECT OF HEAT TREATMENT ON ROCKWELL HARDNESS OF COMPLEX SILVER-CADMIUM ALLOYS

Heat Treatment	Alloy Composition		
	A-2054 30% Cd 3% Cu 0.45% Al bal. Ag	A-2055 30% Cd 3% Cu 0.42% Ni bal. Ag	A-2056 30% Cd 3% Cu 0.66% Al bal. Ag
	Rockwell F Hardness		
1. As extruded	74	70	72
2. No. 1 plus 138 hr. at 410F	99	97	97
3. No. 2 plus 72 hr. at 600F	85	92	88
4. No. 3 plus 137 hr. at 700F	83	87	84

From the data in Table II it was concluded that small amounts of nickel and aluminum generally increased the hardness of silver-cadmium-copper alloy, and that nickel tends to resist softening of the alloy after extended periods at temperatures in the range 600 to 700F. Because of the possibility that the temperature of reactor control rods might rise to 600 or 700F due to an accident, nickel is recommended as an alloying addition.

The tensile properties of the complex alloys are given in Table III, as they were reported by Battelle.[9] The specimens were machined from bars in the as-extruded condition. It is apparent that a nickel addition of 0.42% gave the highest yield and tensile strengths, and yet had adequate ductility. The thermal expansion and thermal conductivity of the copper-bearing alloys was not determined.

As the over-all result of the studies on complex silver-cadmium alloys, the specification shown in Table IV was set up as the recommended composition for extruded silver-cadmium shapes. The recommended heat treatment is 2 hr. at 600F. The specification is tentative, as the project was terminated before a Mark I control rod was fabricated to this specification. The probability is great that the above specification is correct since a set of ZPR control rods was successfully produced to a similar specification.

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Table III

TENSILE PROPERTIES OF COMPLEX SILVER-CADMIUM ALLOYS
(Bar Specimens)

Specimen Number	Test Temp., F	0.2% Yield Strength, psi	Ultimate Tensile Strength, psi	Elongation in 2 In., Per Cent	Reduction in Area, Per Cent
A-2054	Room	17,800	43,200	48.2	67
	600	16,100	21,600	30.2	--
A-2055	Room	27,400	45,500	35.8	49
	600	20,400	25,500	35.2	--
A-2056	Room	20,400	44,200	34.9	--
	600	19,600	24,400	56.5	53

Table IV

RECOMMENDED COMPOSITION FOR
EXTRUDED CONTROL RODS

Element	Weight - Per Cent
Cadmium	29 to 31
Copper	3 to 4
Aluminum	0.2 to 0.4
Nickel	0.3 to 0.5
Silver	Balance

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APPENDIX

Corrosion Data

During the course of the materials development program described in this report, a considerable number of corrosion tests were made. These tests were largely at 500F and 600F in oxygenated water and were intended as screening tests to indicate the potential uses of the various materials. The test data were reported in internally distributed corrosion reports, and in monthly and quarterly progress reports. Partial data from internally distributed reports are given in Table V.

Data on the static corrosion testing of nickel plated and bare binary silver-cadmium alloys were published in ANL-4519.[10] Data on the dynamic corrosion testing of silver-cadmium-palladium alloys were published in ANL-4898.[11] From the latter data it may be concluded that silver-cadmium alloys containing 15 and 20% palladium are unsuited for use in 500F oxygenated water but have potential uses in hydrogenated and degassed water.

From the data in Table V, it appears that increasing amounts of copper increase the weight change rate, and that the alloys in the precipitation hardened conditions have higher weight change rates than do those in the extruded condition.

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Table V

CORROSION DATA

Sample No. and Composition	Time Hr	Temp., F	Conditions	pH Before	pH After	Water Resis., ohms Before	Water Resis., ohms After	Weight Change, $mg/cm^2/mo$	Comments
A-1546A. 75% Ag-25% Cd alloy.	552	600	Deaerated, distilled water plus 30 cc/1 O_2 dissolved in water at start of test.	7.2	7.2	71,000	22,000	+0.925	Gray-brown coating. Small, loose, white powder and pitting.
A-1549. 30% Cd-3% Cu-Ag alloy. Age hardened.	402	600	Same as above	6.9	7.1	77,000	24,000	1)+0.246 2)-0.290	Yellowish-gray-powdery coating. Black deposit around area of contact.
A-1550. Same as above but 6% Cu.	402	600	Same as above	7.0	7.0	24,000	10,000	1)+0.615 2)-2.02	Samples covered with loose, pinkish-brown powder. Some silvery crystals on surface.
A-1551. Same as above but 9% Cu.	402	600	Same as above	7.2	7.2	107,000	30,000	1)+1.05 2)+0.815	Powdery, light-purple coating except for dark yellow-brown at area of contact.
A-2055. 66-1/2% Ag; 30% Cd; 3% Cu; 1/2% Ni alloy. Cleaned in 10% HNO_3.	339	600	Same as above	7.7	*	75,000	*	+0.226	Black and gray tarnish on flat face. Cylindrical surface white.
A-2055H. Same as above but precipitation hardened.	339	600	Same as above	7.6	7.6	106,000	40,000	-1.13	Powdery, white coating. Silvery deposit. Black streaks at contact with autoclave.
A-2584B. 66% Sn-34% Ni alloy plated (.001) on 75% Ag-25% Cd sample by Tin Research Institute.	1824	600	Same as above	6.9	6.2	185,000	20,000	-1.26	Dull black coating with white spots on one surface.

*Autoclave dry at end of test.

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