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STUDIES FOR THE PREPARATION OF ZIRCONIUM-CLAD URANIUM-10 w/o MOLYBDENUM FUEL PINS

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to

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Production methods for producing an homogeneous uranium-10 w/o molybdenum fuel-alloy pin with a uniform zirconium cladding have been studied. The effect of various impurities has been investigated and the nature of and methods for eliminating cracking in swaged fuel pins have been examined.

A major portion of the results is based on the study of material produced from 25-lb ingot castings. Small experimental-scale ingots were also employed in impurity, heat-treatment, and cracking studies.

On the basis of the data obtained recommendations concerning casting, fabrication, and heat-treatment techniques necessary to produce a fuel pin of satisfactory integrity are presented. Specifications as to allowable carbon, chromium, iron, nickel, oxygen, and zirconium content are recommended.

INTRODUCTION

The uranium-10 w/o molybdenum fuel alloy, which is intended for insertion as the first core loading in the Enrico Fermi Fast Breeder Reactor, has been the subject of considerable study over a period of years. However, no concerted effort during this time has been devoted to determining fabrication and impurity specifications for the preparation of fuel pins for the reactor core. The need for such a determination became apparent as a result of a number of observations made on fuel pins which lead to questions concerning their integrity. Specific observations are given below:

(1) Upon metallographic examination of zirconium-clad uranium-10 w/o molybdenum fuel pins which were prepared by coextrusion and swaging of cast ingots, a swirled or distorted microstructure was observed. Study revealed that the pattern reflected inhomogeneity of the fuel alloy, the inhomogeneity originating during casting. Electron-microbeam analysis showed variations in compositions between grains of from at least 3 to 12 w/o molybdenum. This coring-type segregation is produced as a consequence of the difference in liquidus and solidus temperatures of the alloy. Coextrusion and swaging produce a flow pattern in cross section in which these areas are swirled, and also produce stringers of high and low alloy content along the length of the pin. The resultant pin has variable properties and, during irradiation, variable burnup throughout its volume due to the nonuniform uranium content. Stringers of low strength and high burnup can be expected to present areas of potential fuel-element failure. Therefore, to optimize performance and irradiation life, a homogeneous fuel alloy is desirable.

(2) The preparation of irradiation specimens of the 10 w/o molybdenum alloy using enriched uranium has presented problems, enriched-uranium alloys being considerably more difficult to fabricate than those prepared from natural uranium. The impurity content of the enriched uranium, in particular, carbon, chromium, iron, nickel, nitrogen, and oxygen, has always been found to be considerably higher than encountered in natural uranium, and was, therefore, suspect. Enriched uranium is prepared by a batch-type process and the chromium, iron, and nickel are undoubtedly picked up in the system employed. Small biscuits of the enriched uranium are prepared having a high surface-to-volume ratio; oxygen and nitrogen are concentrated at the surface, and, consequently, a higher average content of these impurities results. The carbon is introduced during melting of the biscuit in a carbon crucible, and, again, the average carbon content is higher since small melts are involved. In addition to the difficulties encountered in the fabrication of enriched-uranium alloys, during the examination of irradiated specimens cracks were found at times to be associated with impurity phases in the fuel alloy. Thus, the need for controlling impurity content both from the viewpoint of fabricability and irradiation stability was indicated.

(3) During the examination of coextruded and swaged specimens cracks were at times found to be present. These apparently developed during storage at room temperature. In addition, cracks were often found to be associated with the failure of irradiation specimens which, in some cases, it is felt may have been present or initiated prior to irradiation. The necessity of finding and eliminating the cause of these cracks is evident.

On the basis of these observations and the need to determine methods for the production of fuel pins of insured integrity this program was undertaken. Its objectives were: the determination of production procedures required to produce a homogeneous fuel alloy with a uniform cladding; to define impurity specifications with respect to homogeneity, fabricability, and radiation stability; and to determine the cause and methods for eliminating cracking of fabricated fuel pins.

EXPERIMENTAL TECHNIQUES

In order to provide the data required for specifying production procedures in the preparation of homogeneous clad fuel pins, procedures consistent with APDA Reference Specification 30-8 and with subsequent revisions to this specification were employed. In addition, small 1/2-in.-diameter ingots were prepared for supplemental impurity and cracking studies.

Production Processes

For the determination of techniques required to produce a clad homogeneous uranium-10 w/o molybdenum alloy, 25-lb ingots 2 in. in diameter were cast. Casting temperatures and mold-wall thicknesses were varied initially to determine their effect on homogeneity of the alloy casting. Subsequent alloy castings were prepared by the method found to yield maximum and minimum alloy ingot homogeneity. For this purpose the alloys were poured at 2850 F from zirconia crucibles into 2-in.-wall and 5/8-in.-wall graphite molds, respectively. Melting was accomplished under a vacuum of 1 μ of mercury and with an alloying time of 1 min.

During melting, thermocouples in protection tubes were placed in all melts to a depth of 1 in. The temperature reported above is for the thermocouple. Optical-pyrometer readings taken at the same time on the melt surfaces were found to range from 2550 to 2660 F.

Castings prepared initially in studying the effect of casting variables were subsequently forged and rolled and then remelted, leaving all scale on the surface. An addition of 1.27 w/o zirconium was made to these melts. Initial starting stock was reactor-grade uranium, which contained 700 ppm carbon, and sintered molybdenum pellets from the Cleveland Wire Works Division of General Electric Company. The final remelt ingots were intended to represent the extreme in ingot impurity and zirconium pickup likely to result from recycling scrap.

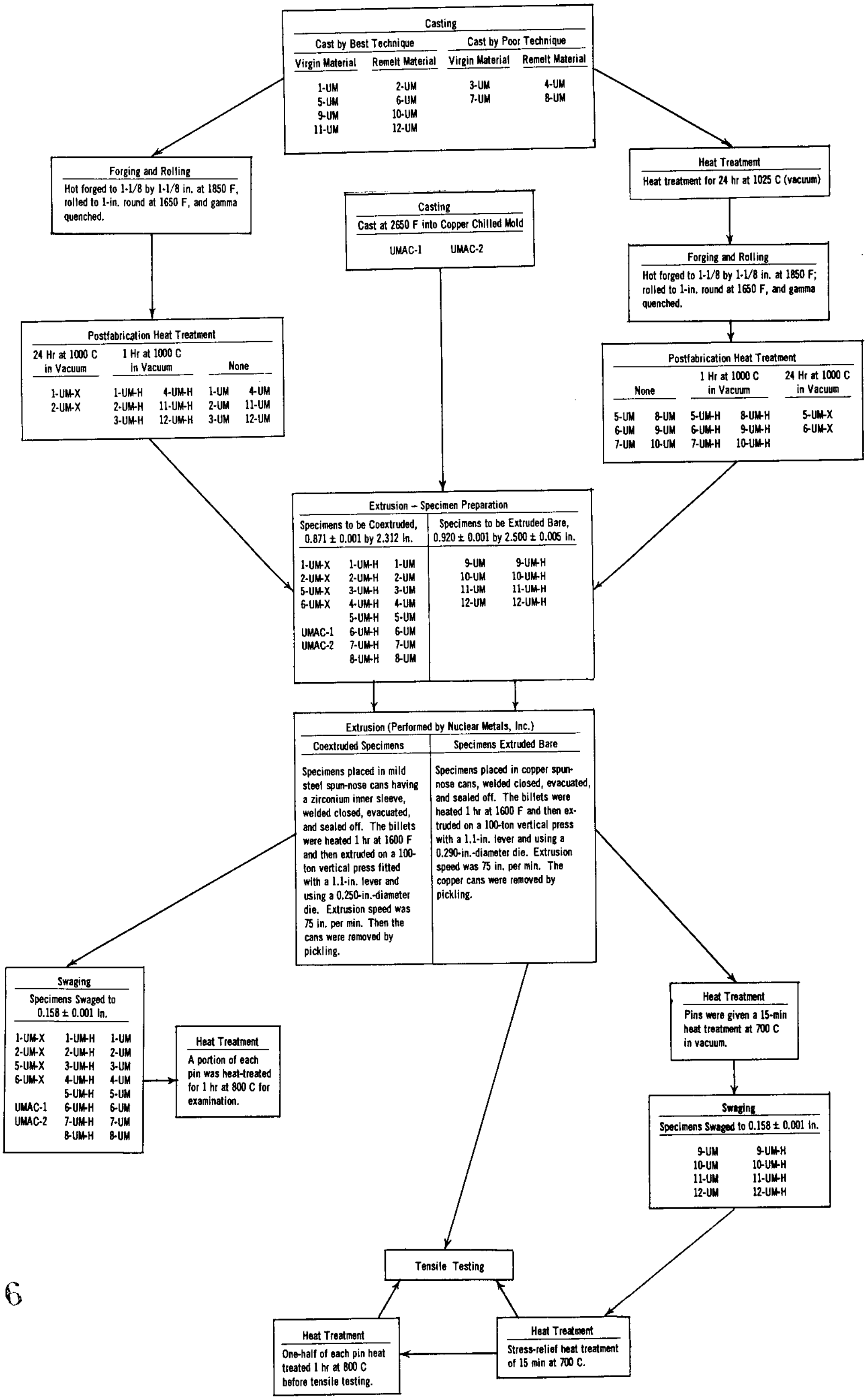
Ingots were also prepared from virgin metal. For this purpose ingots were prepared from center-cut derby uranium, containing approximately 100 ppm carbon, and sintered molybdenum pellets as above.

Billets for coextrusion were prepared from the ingots by the following procedure: The ingots were presoaked for 30 min at 1850 F in a helium-atmosphere furnace obtained by a constant helium purge and then fabricated bare by forging from the furnace to 1-1/8-in.-square billets. These billets were then placed in a helium-atmosphere furnace at 1650 F from which they were rolled to 1-in.-diameter rod and then water quenched. The combined reduction by forging and rolling represents a 75 per cent reduction.

Various heat treatments, designed to determine the stage in the production cycle where it could be best introduced to provide a homogeneous fuel-alloy pin, were employed on the cast ingots and fabricated rod. Heat treatments were performed in furnaces under a vacuum of less than 1 μ of mercury. Details as to the stages at which the various heat treatments were introduced are shown in Figure 1, which is a flow chart of the treatment of the complete series of ingots.

Billets for extrusion and coextrusion with zirconium were machined to size and shipped to Nuclear Metals, Inc. Billet size for coextrusion was $0.871 \frac{+0.000}{-0.001}$ in. in diameter by 2.312 ± 0.005 in. long. Billet size for extrusion was 0.920 ± 0.002 in. in diameter by 2.500 ± 0.005 in. long.

Each billet provided two pins approximately 36 in. long. The bare extruded specimens were prepared specifically to study the effect of various production procedures on mechanical properties.



287 006

FIGURE 1. FLOW CHART DETAILING INGOT PREPARATION, HEAT TREATMENT, AND FABRICATION HISTORY OF REFERENCE-SIZE FUEL PINS

The extrusion billets were shipped to Nuclear Metals where they were degreased and fitted into spun-nose copper cans which were welded shut, evacuated, and sealed off. The billets for coextrusion were degreased and fitted with clean zirconium sleeves. After assembly, the outside surfaces of the sleeves were coated with Alundum and the assemblies placed in oxidized spun-nose mild-steel cans along with cupronickel nose plugs and cutoffs. The assemblies were welded closed, evacuated, and sealed off. They were then heated at 1600 F for 1 hr in a muffle furnace and were coextruded on a 100-ton vertical press fitted with a 1.1-in. liner which was maintained at 900 F. The die was 0.250 in. in diameter and was inserted cold. The extrusion speed was 75 in. per min, with pressures of approximately 65,750 psi at the start and finish and 75,730 psi during the actual extrusion.

The extruded and coextruded pins were returned to Battelle where they were cold swaged. The clad coextruded pins were swaged to 0.158 ± 0.001 in.

The effect of various postswaging heat treatments on the fuel pins was examined. Heat treatments were conducted in vacuum furnaces under a vacuum of less than 1 μ of pressure.

Experimental-Scale Melts

Small 1/2-in.-diameter ingots were cast from biscuit uranium and sintered molybdenum stock. One series of ingots was employed for study of the effect of fabrication and various heat treatments on cracking of the 10 w/o molybdenum alloy. A second series was prepared with varying amounts of different impurity additions. These ingots were reduced 75 per cent by hot rolling at 1800 F after a homogenization treatment of 24 hr at 1025 C. The resulting rod was then cold swaged to 0.150 in. in diameter.

Metallography

Metallography played a major role in evaluation of the fuel alloy. In the preparation of metallographic specimens of the uranium-10 w/o molybdenum alloy, standard procedures used were as follows:

(1) Grind on 240-, 400-, and 600-grit SiC papers using water as a coolant.

(2) Polish for 5 to 10 sec with 1-μ alumina on Forstmann's cloth on a fast polishing wheel to remove any imbedded grinding grit and to rough polish the surface.

(3) Polish 2 to 5 min on a 246-rpm polishing wheel using 1-μ diamond paste on Forstmann's cloth with kerosene as a lubricant.

(4) Employ, if necessary, further mechanical polishing. Either of two methods is satisfactory:

   (a) Same as Step (3) except with 1/2-μ diamond paste.

   (b) Linde "B" alumina on Microcloth with a fast wheel (10 to 20 sec is required).

(5) Electropolish 5 sec at 20 v dc on the open circuit in a solution of 5 parts orthophosphoric acid, 4 parts ethylene glycol, and 4 parts ethyl alcohol. The specimen is the anode and a stainless steel cathode is used.

(6) Electroetch 1 to 2 min in a solution of 1 part stock solution chromic acid (1 g CrO_3-1 cm^3 H_2O) to 18 parts glacial acetic acid. Open-circuit voltage to 10 v dc is used. If samples are transformed, a much shorter time (5 to 10 sec) is needed.

(7) Swab the specimen, if the structure of the zirconium cladding is desired, with either:

   (a) 60 cm^3 H_2O_2, 30 cm^3 HNO_3, 20 cm^3 C_2H_5OH, and 2 drops HF

   (b) 50 cm^3 HNO_3, 50 cm^3 lactic acid, and 5 drops HF.

(8) Immerse the specimen, if it is desired to delineate UC inclusions, in a solution of 50 per cent nitric acid in water for 5 to 30 sec, depending on surface condition. The carbides are darkened, while other inclusions are not affected other than a slight pickling effect on the edges after prolonged immersion.

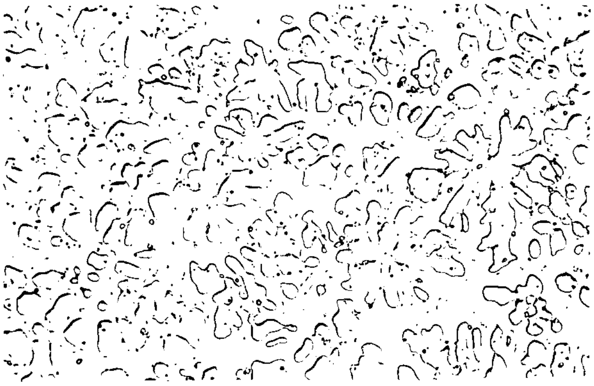
In preparing metallographic samples of unalloyed uranium the above procedures may be followed. However, better surface preparation of uranium can be achieved by employing slightly different electropolishing and electroetching methods. These are:

(1) Electropolish 2 to 10 sec at 2-sec intervals at 40 v dc on the open circuit in a solution composed of 1 part stock solution of chromic acid (118 g CrO_3-100 cm^3 H_2O) to 4 parts glacial acetic acid. If polarized-light technique is to be applied it is usually advisable to prolong the polishing time.

(2) Electroetch as listed in Step (6) above using an applied potential of 20 v dc.

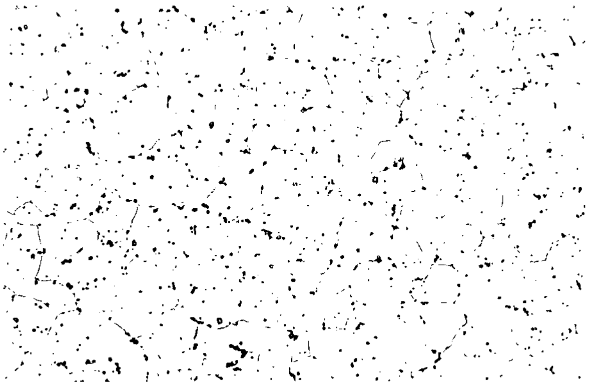
Metallographic preparation of molybdenum follows the same mechanical polishing procedure as listed above. Murakami's etchant, which is composed of 10 g $K_3Fe(CN)_6$, 10 g KOH, and 100 cm^3 H_2O, was employed.

207 008



100X Electroetched RM11150

FIGURE 2. STRUCTURE PRODUCED IN 2-IN. -WALL MOLD AT CENTER OF INGOT 11-UM



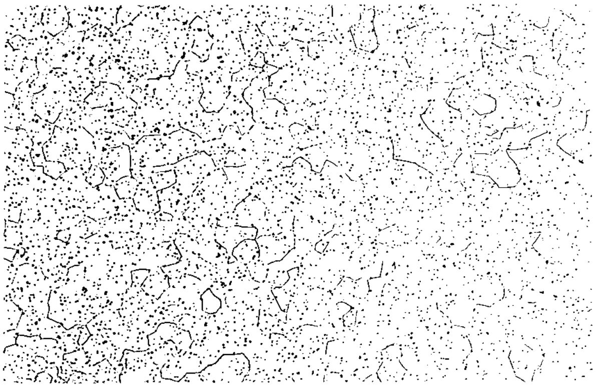
100X Electroetched RM9864

FIGURE 3. STRUCTURE PRODUCED IN 2-IN. - WALL MOLD AT EDGE OF INGOT 11-UM

100X Electroetched RM11151

FIGURE 4. CENTER OF INGOT CAST INTO 5/8-IN. - WALL MOLD

Ingot 3-UM.



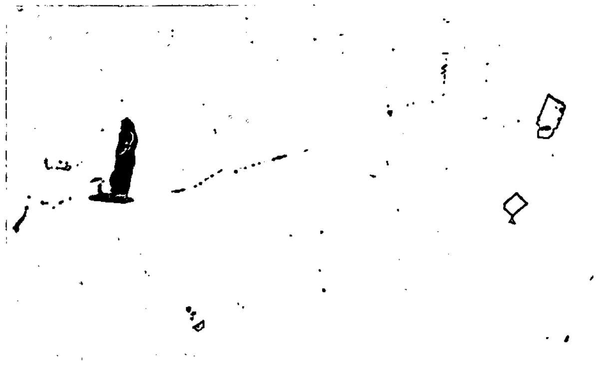
100X Electroetched RM9868

FIGURE 5. STRUCTURE NEAR THE EDGE OF INGOT CAST INTO 5/8-IN. -WALL MOLD

Ingot 3-UM.

500X 1:1 $HNO_3 \cdot H_2O$ Etchant RM9705

FIGURE 6. REACTOR-GRADE URANIUM AS USED IN REMELT INGOTS



500X As electropolished RM9839

FIGURE 7. DERBY URANIUM USED IN VIRGIN-MELT SERIES

EXPERIMENTAL RESULTS

Results of the program which provide a basis for various recommended specifications for the preparation of uranium-10 w/o molybdenum fuel pins are presented in this section.

Production-Scale Ingot Studies

Results obtained on production-scale ingots are discussed below.

Casting Variables

In the study of production casting techniques, six 25-lb ingots 2 in. in diameter were cast using variable mold and temperature conditions. Casting temperatures ranging from 2550 to 3050 F were used. Metallographic examination of sections from each ingot showed that varying the pouring temperature over the above range produced no appreciable difference in the resulting structure of the ingots.

Split graphite molds 1/2, 5/8, and 2 in. in wall thickness were employed as a means of varying effective cooling rate of the ingots; the cooling rate increases with mold-wall thickness. It was found that a 2-in.-wall mold produced a relatively uniform dendritic structure from the center to the edge of the ingot, as illustrated in Figures 2 and 3. The 5/8-in.-wall mold produced a less uniform structure since there was an appreciable difference in grain size and dendrite distribution from edge to center (Figures 4 and 5). The 1/4-in.-wall mold was found to be structurally unsound and leaked.

On the basis of the above experiments, it was apparent that 2-in.-wall molds produce a more homogeneous structure and these were used subsequently as part of the optimum technique of casting. Since the structure found in 5/8-in.-wall molds was less homogeneous, such molds were employed to provide samples of material representative of a poorer casting technique.

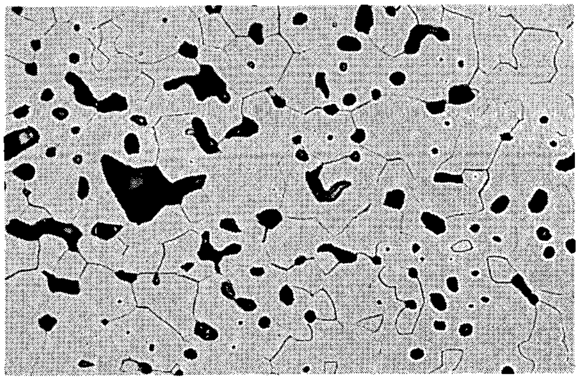
While differences in homogeneity do result from variations in casting techniques, these differences are not marked. After the initial 75 per cent reduction no effect of variation in casting history, within the limits outlined, was detected.

Zirconia crucibles were used throughout these studies since melting uranium in graphite results in extremely high carbon pickup. While a wash can be employed to protect the melt from graphite pickup the integrity of a wash cannot be assured.

Effect of Starting Materials

The two types of uranium used in this study were reactor grade and center-cut derby uranium. Photomicrographs showing the typical inclusion distributions for these materials are shown in Figures 6 and 7. The reactor-grade uranium contained 760 ppm carbon and was used as a basis for the "remelt" series to obtain poor-quality metal such as would be found when recycling fuel elements. Note that the photomicrograph (Figure 7) of the derby uranium used in the "virgin melts" shows several large UH_3 inclusions. A metallographic estimation placed the hydrogen content of this material at 5 ppm. However, the finished ingots contained less than 1 ppm as a result of degassing during vacuum melting. The carbon content of this material was estimated to be approximately 100 ppm.

A typical structure of the molybdenum used in all ingots is shown in Figure 8. A batch analysis of the molybdenum sintered pellets provided by the supplier at the time of purchase gave a gas analysis for carbon, hydrogen, and oxygen as a total of 400 ppm. When metallographic and chemical analyses showed that the virgin melt stock contained 250 to 300 ppm carbon, an analysis was performed on the molybdenum stock. The carbon content was analyzed to be 1200 ppm, and accounts for the excess of carbon found in the good ingots. It is suggested that the carbon content of molybdenum melting stock be specified closely when it is purchased, and that the stock be analyzed in order to prevent this problem during production.



500X Murakami's Etch RM10050

FIGURE 8. MOLYBDENUM MELTING STOCK

The high-carbon alloy ingots were fabricated and remelted with the addition of 1.27 w/o zirconium and without removal of the oxide and scale produced during the hot fabrication. Large inclusions and agglomerates which were identified by X-ray diffraction as zirconium carbide were quite prevalent in the resulting remelt ingots. Figures 9 through 12 show the inclusion size and distribution in these remelt and virgin-melt ingots. UO_2, resulting from the inclusion of scale in the remelt ingots, was found to be associated with the zirconium carbide stringers.

Metal quality had little effect on fabrication of the alloy. The large agglomerates of zirconium carbide and UO_2 formed large stringers in the remelt rod. This had a pronounced effect on the surface quality of extrusion billets produced. Large striations which have the appearance of cracks were apparent. The difference between virgin-material and remelt extrusion-billet surfaces is shown in Figure 13.

257 011

500X Electropolished RM9851

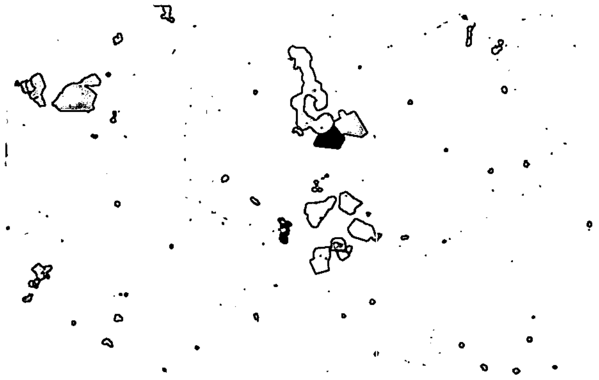
FIGURE 9. VIRGIN-MELT INGOT PRODUCED BY BEST CASTING TECHNIQUE

Ingot 1-UM.

500X 1:1 HNO_3-H_2O Etchant RM9848

FIGURE 10. VIRGIN-MELT INGOT PRODUCED BY THE POOR CASTING TECHNIQUE

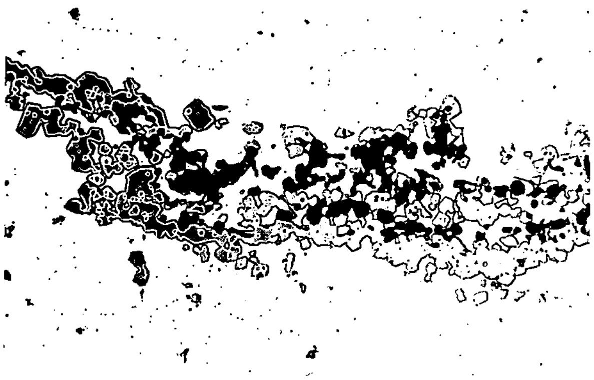
Ingot 7-UM.



500X 1:1 HNO_3-H_2O Etchant RM9846

FIGURE 11. ZrC AND UO_2 INCLUSIONS IN REMELT INGOT PRODUCED BY BEST CASTING TECHNIQUE

Ingot 10-UM.



250X Electropolished RM9844

FIGURE 12. TYPICAL STRINGER OF ZrC AND UO_2 FOUND IN REMELT INGOTS

This sample found in Ingot 10-UM.

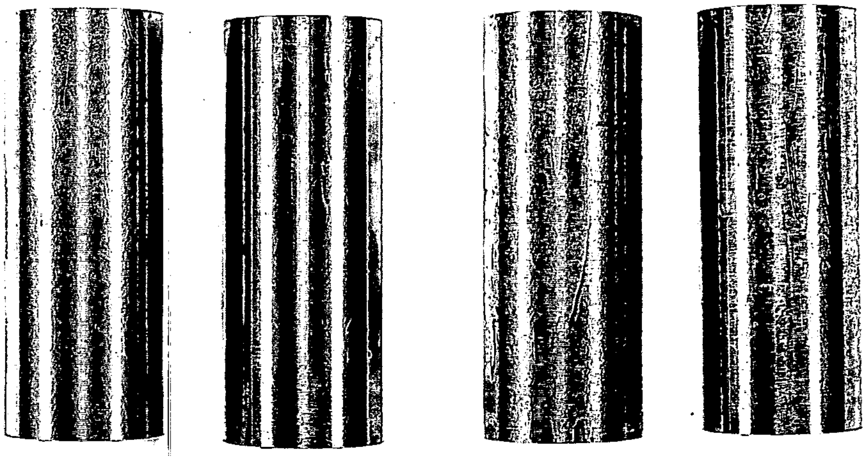
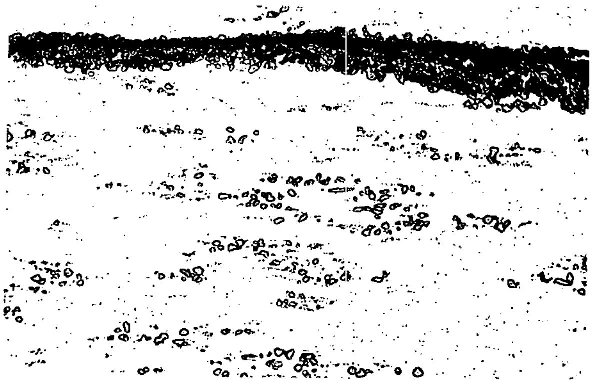


FIGURE 13. A PHOTOMACROGRAPH SHOWING TYPICAL COMPLETED EXTRUSION BILLETS

Those on the left were made from center-cut virgin biscuit; the two on the right were fabricated from remelt stock with the addition of zirconium. Note striations on remelt stock due to stringering of ZrC and UO_2.

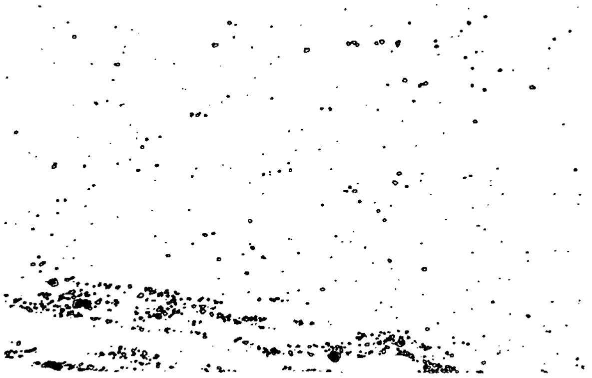
287 013



100X Electropolished RM9973

FIGURE 14. ZrC AND UO_2 STRINGERS PRODUCED IN ROLLING OF A REMELT INGOT

Ingot 4-UM.



100X Electropolished RM10000

FIGURE 15. UC STRINGERS IN ROLLED ROD OF VIRGIN MELT

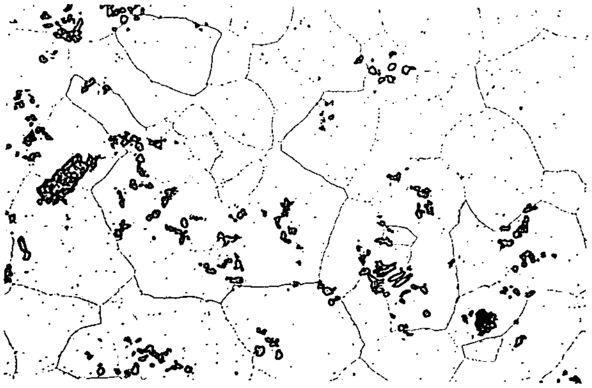
Small particles of UO_2 are also visible.

Ingot 2-UM.

100X Electroetched RM10178

FIGURE 16. STRUCTURE NEAR CENTER OF VIRGIN-MELT INGOT AFTER 24 HR AT 1025 C

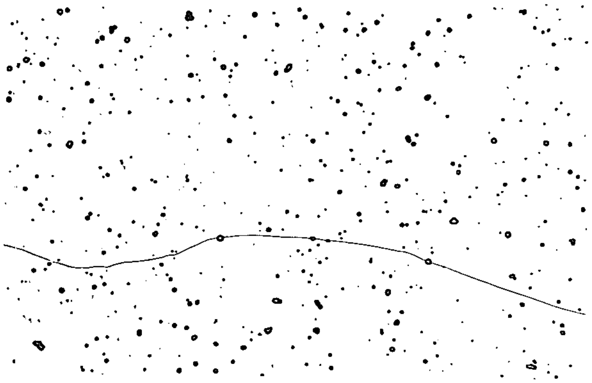
Ingot 7-UM.



100X Electroetched RM10175

FIGURE 17. STRUCTURE NEAR CENTER OF REMELT INGOT AFTER 24 HR AT 1025 C

Ingot 6-UM.



100X Electroetched RM10177

FIGURE 18. TYPICAL EDGE STRUCTURE OF INGOTS AFTER 24 HR AT 1025 C

Ingot 7-UM.

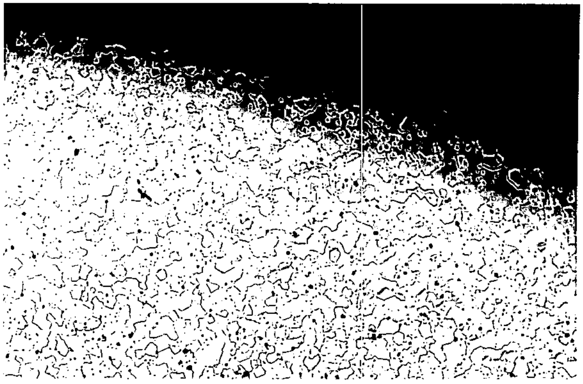


FIGURE 19. BARE EXTRUDED ROD FROM VIRGIN MELT

Note relatively smooth surface and equiaxed grains.

Ingot 11-UM.

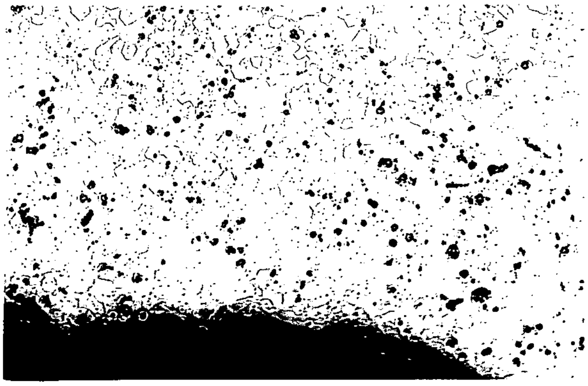


FIGURE 20. TYPICAL ROUGH SURFACE ON BARE EXTRUDED REMELT STOCK

Ingot 12-UM.

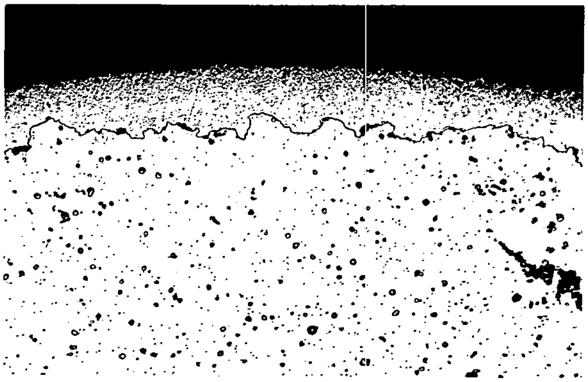


FIGURE 21. CLADDING ON SWAGED PIN OF REMELT STOCK

Heated 24 hr at 1000 C prior to extrusion. Etched with HNO_3-HF-H_2O_2-C_2H_5OH mixture after electropolishing.

Ingot 2-UM.

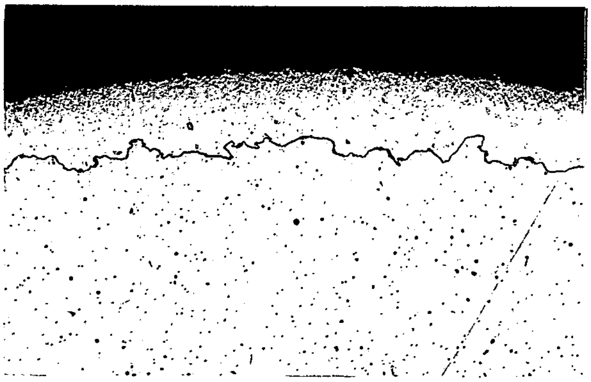


FIGURE 22. CLADDING ON SWAGED PIN OF VIRGIN-MELT MATERIAL

Heated 1 hr at 1000 C prior to extrusion. Etched with HNO_3-HF-H_2O_2-C_2H_5OH mixture after electropolishing.

Ingot 1-UM.

The stringers from which the surface striations result in the remelt billets are typified by the one shown in Figure 14. Stringers were also found in the virgin-material billets (Figure 15). However, stringers when found in the latter billets were rather small, and subsequent extrusion and swaging further reduced their size.

Neither zirconium nor carbon exhibited any pronounced effect on the response of the alloy to heat treatment. Microscopic examination of ingot sections after a homogenization heat treatment of 24 hr at 1025 C showed that all ingots, regardless of casting or impurity conditions, had the same structures and similar grain sizes. Figures 16 and 17 show typical structures near the center virgin-melt and remelt ingots, respectively. Near the periphery of the ingots an extremely large grain size is produced as shown in Figure 18.

An additional difference in the behavior of the virgin-melt and the remelt materials was noted in the bare extruded rods. The virgin-melt surface was much smoother and more uniform than the surface of remelt stock after extrusion (Figures 19 and 20). This was not evident in the coextruded pins, where the cladding-core surface was approximately the same for all samples.

Figures 21 and 22 show the cladding on pins of remelt and virgin stock. It is felt that the quality of the zirconium used for cladding contributes more to the evenness of the cladding than does the quality of the fuel alloy or its previous history.

Homogenization Heat Treatment

Details of the stages at which various heat treatments were applied to the uranium-10 w/o molybdenum alloy prior to extrusion or coextrusion are presented in Figure 1. The heat treatments employed were 24 hr at 1025 C for the cast ingot and 1 or 24 hr at 1000 C for the rod produced by fabrication of the ingot.

Extrusion billets were prepared having either no heat treatment or one or two of the above heat treatments. In addition, an as-cast ingot, produced by casting the 10 w/o molybdenum alloy into a 1-in.-diameter chilled copper mold, was included in the program in order to provide a comparison of material which was worked prior to extrusion with material which had received no pre-extrusion working.

Metallographic studies of the extent of inhomogeneity were conducted at all stages in the production of fuel pins. Examinations were made of the as-cast ingots, and after fabrication, after the various heat treatments, after coextrusion, after swaging, and after a postswaging heat treatment of 1 hr at 800 C.

As mentioned earlier, the effect of variations in casting techniques was investigated. In this work, the cooling rate, as influenced by wall-mold thickness, produced an effect on the ingot homogeneity. However, microscopic examinations of ingot sections after a homogenization heat treatment of 24 hr at 1025 C showed that all ingots so treated had the same structure.

The effects of homogenization are exhibited first in the microstructures of the rolled rods. The rods from ingots which had been homogenized by the 1025 C treatment for 24 hr generally had a more uniform grain size than those which had not been heat treated prior to fabrication. Figures 23 and 24 show edge and center structures of a rod which had no homogenization while Figures 25 and 26 are from rods which were given the 24 hr at 1025 C treatment. It will be noticed that the difference in grain size from edge to center is not nearly so great in the latter two micrographs.

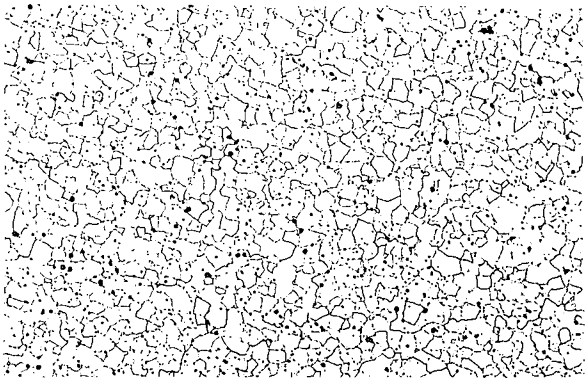
Here, too, microsegregation remaining from the ingot stage can also be noticed. This is best seen in the longitudinal sections, as shown in Figure 27, in which shaded streaks in the rolling direction are seen. Figure 28, on the other hand, is from a rod rolled after the homogenization heat treatment. It can be seen that there is no background compositional shading or staining in this sample. The remelt specimens require much more than normal etching to show the staining clearly.

After coextrusion, evidence of microsegregation was quite apparent in all specimens which had received no homogenization heat treatment either in the as-cast condition or after hot forging and rolling. Also, specimens from rod which had received only the 1-hr heat treatment at 1000 C after forging and rolling showed little effect of this heat treatment, exhibiting swirled areas similar to those appearing in material which had received no heat treatment. All specimens from ingots which had been heat treated for 24 hr at 1025 C or which had been heat treated for 24 hr at 1000 C after hot forging and rolling appeared to be homogeneous. These specimens had clean equiaxed structures. Microstructures illustrating the coextruded structures are shown in Figures 29 through 34.

After swaging the coextruded rods, swirl patterns were detected in the same specimens in which inhomogeneity was detected directly after coextrusion. Initially, employing normal metallographic etching techniques, the remaining specimens which had received a 24-hr heat treatment, either at 1025 C in ingot form or at 1000 C after forging and rolling, appeared homogeneous. However, faint swirl patterns (Figure 35) were developed in those specimens which had received only the 24-hr heat treatment at 1000 C by employing an extremely heavy etching and staining technique. A postswaging treatment of 1 hr at 800 C removed this evidence of microsegregation (Figure 36) and also produced grain growth. Heavy etching as above showed no swirl patterns in these samples. All specimens which did not receive a 24-hr homogenization treatment either before or after forging exhibited extremely pronounced segregation patterns at their centers, as illustrated by Figures 37, 38, and 39.

On the basis of these results, it was concluded that the 24-hr treatment at 1025 C in the ingot stage produces a homogeneous alloy, and no additional treatment after forging and rolling is required.

Examination of the as-coextruded pins revealed a herringbone pattern on the surface of the clad specimens. This pattern appeared on all coextruded pins with the exception of pins prepared from virgin melts which were heat treated for 24 hr at 1025 C prior to forging and rolling, and pins prepared from either virgin or remelt stock which were heat treated for 24 hr at 1000 C after forging and rolling. On remelt stock which was heat treated prior to forging and rolling the pattern was also found. Swaging, however, removed all evidence of this pattern.

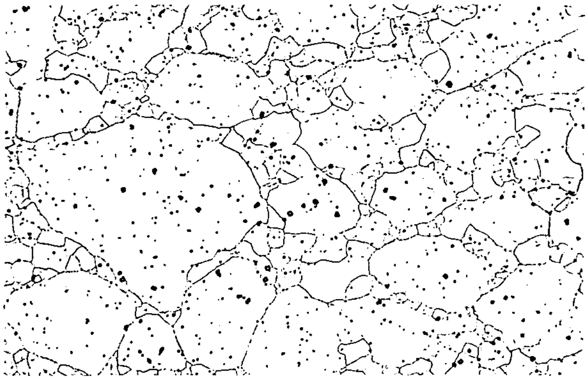


100X Electroetched RM9990

FIGURE 23. EDGE STRUCTURE IN ROD ROLLED AT 1650 F WITHOUT PRIOR HEAT TREATMENT

Transverse section.

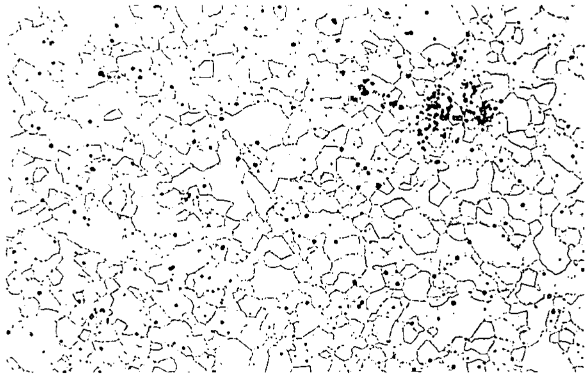
Ingot 1-UM.



100X Electroetched RM9991

FIGURE 24. CENTER STRUCTURE IN SAME SAMPLE AS SHOWN IN FIGURE 23

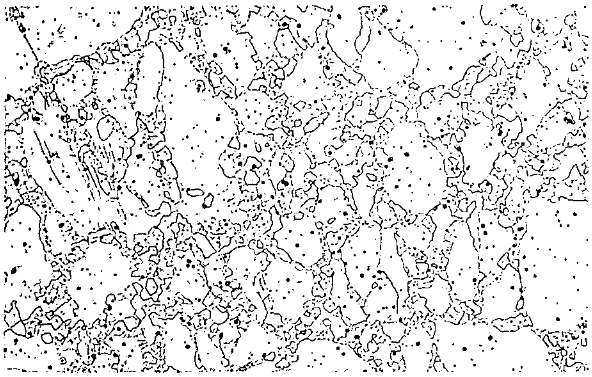
Transverse section.



100X Electroetched RM9951

FIGURE 25. EDGE STRUCTURE IN INGOT HEAT TREATED 24 HR AT 1025 C PRIOR TO ROLLING AT 1650 F

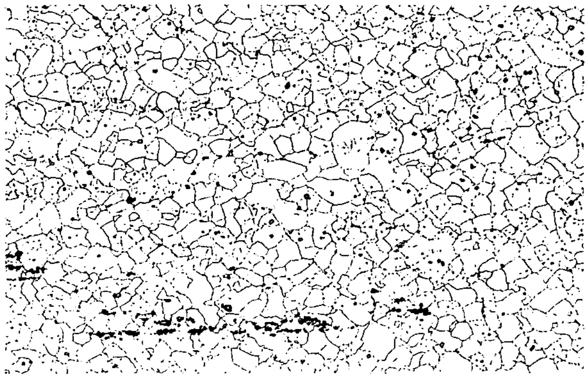
Transverse section of rod from Ingot 7-UM.



100X Electroetched RM9996

FIGURE 26. NEAR CENTER OF TRANSVERSE SECTION OF ROD ROLLED AT 1650 F FROM INGOT HEAT TREATED 24 HR AT 1025 C BEFORE FORGING AND ROLLING

Ingot 9-UM.

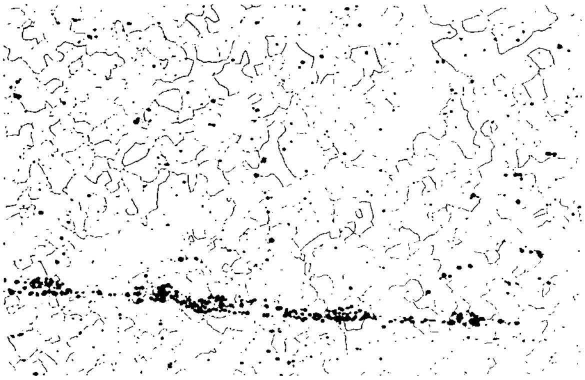


100X Electroetched RM9950

FIGURE 27. LONGITUDINAL SECTION OF ROD ROLLED FROM INGOT WITHOUT HEAT TREATMENT

Inhomogeneity is indicated by streaks in background parallel to stringered inclusions

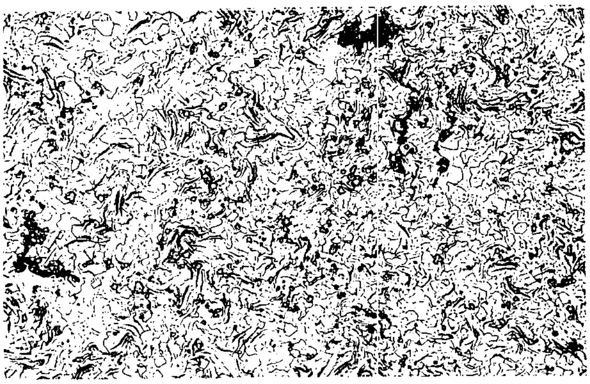
Ingot 3-UM.



100X Electroetched RM10001

FIGURE 28. LONGITUDINAL SECTION OF ROD ROLLED FROM INGOT HEAT TREATED 24 HR AT 1025 C

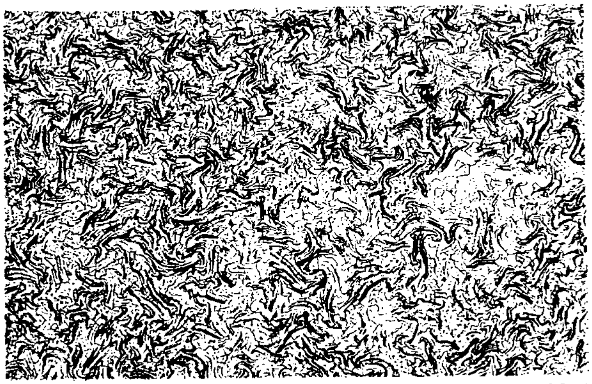
Ingot 7-UM.



100X Electroetched RM10618

FIGURE 29. REMELT STOCK COEXTRUDED WITHOUT PRIOR HEAT TREATMENT

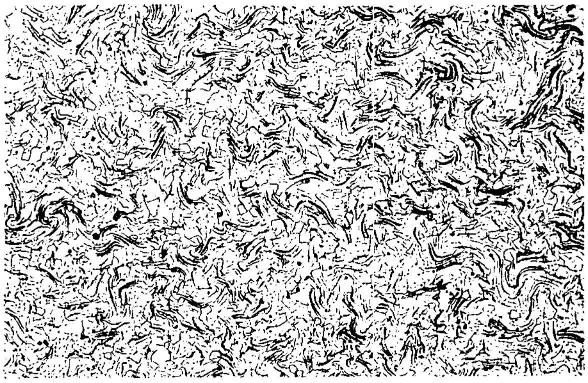
Ingot 4-UM.



100X Electroetched RM10631

FIGURE 30. VIRGIN-MELT MATERIAL COEXTRUDED WITHOUT PRIOR HEAT TREATMENT

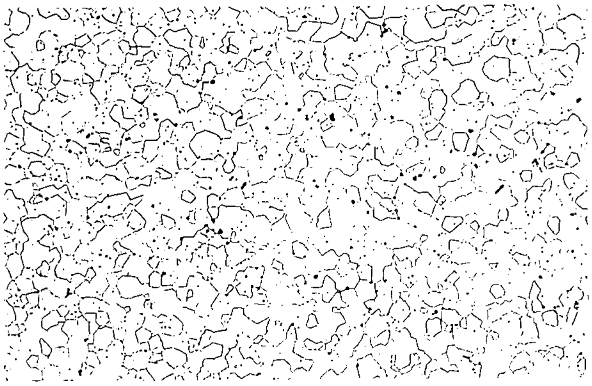
Ingot 3-UM.



100X Electroetched RM10632

FIGURE 31. VIRGIN-MELT MATERIAL HEATED 1 HR AT 1000 C BEFORE COEXTRUSION

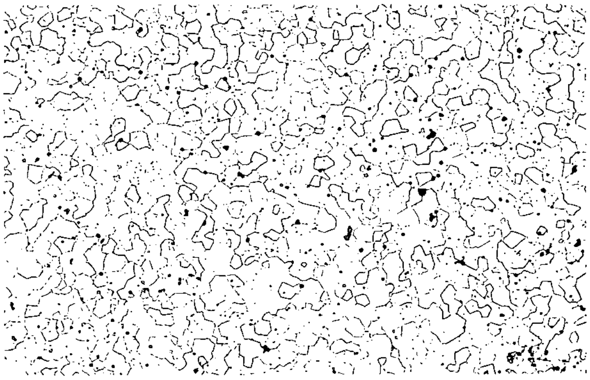
Ingot 3-UM.



100X Electroetched RM10629

FIGURE 32. VIRGIN-MELT MATERIAL HEATED 24 HR AT 1000 C BEFORE COEXTRUSION

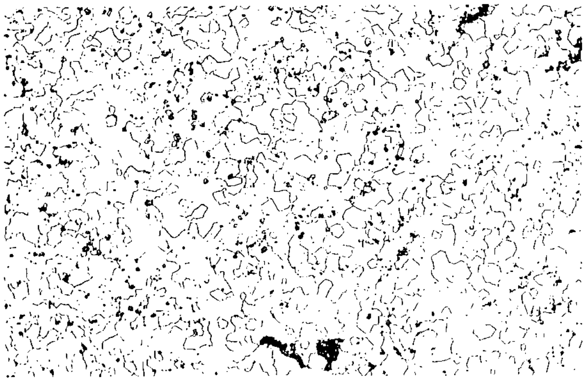
Ingot 1-UM.



100X Electroetched RM10633

FIGURE 33. VIRGIN-MELT MATERIAL HEATED 24 HR AT 1025 C PRIOR TO FORGING, ROLLING, AND COEXTRUSION

Ingot 7-UM.



100X Electroetched RM10624

FIGURE 34. REMELT STOCK HEATED 24 HR AT 1025 C PRIOR TO FORGING, ROLLING, AND COEXTRUSION

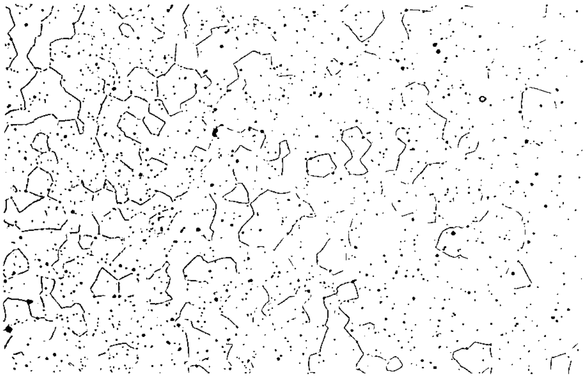
Ingot 6-UM.

100X RM10368

FIGURE 35. SWIRL PATTERNS DETECTED IN SWAGED PIN HEAT TREATED 24 HR AT 1000 C PRIOR TO COEXTRUSION

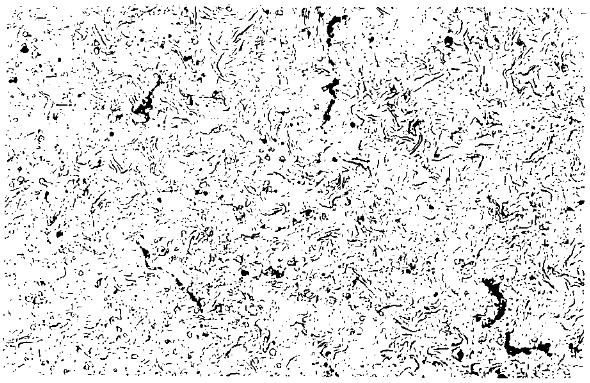
Heavily etched with HNO_3-HF-H_2O_2-C_2H_5OH solution after electro-polishing and etching in order to show swirl patterns clearly.

Ingot 1-UM.



100X Electroetched RM10369

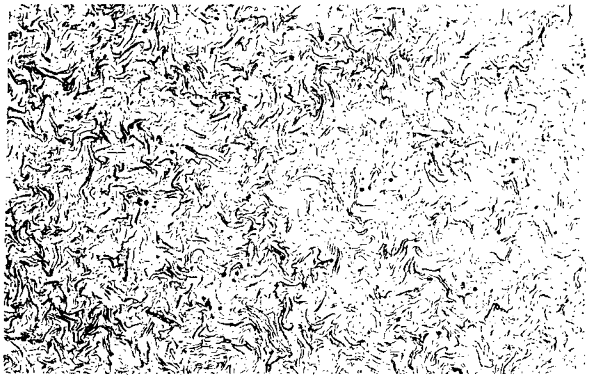
FIGURE 36. SAME SPECIMEN AS SHOWN IN FIGURE 35 BUT WITH POST-SWAGING TREATMENT OF 1 HR AT 800 C



100X Electroetched RM10637

FIGURE 37. REMELT STOCK FORGED, ROLLED, COEXTRUDED, AND SWAGED WITHOUT HEAT TREATMENT

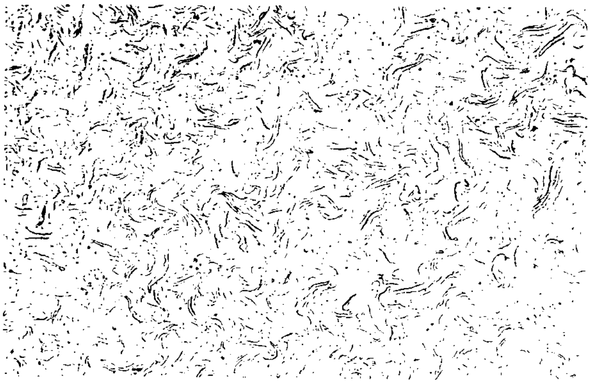
Ingot 4-UM.



100X Electroetched RM10649

FIGURE 38. VIRGIN-MELT MATERIAL FORGED, ROLLED, COEXTRUDED, AND SWAGED WITHOUT HEAT TREATMENT

Ingot 3-UM.



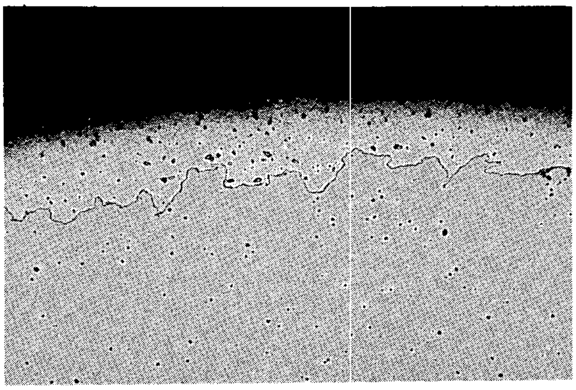
100X Electroetched RM10646

FIGURE 39. VIRGIN-MELT MATERIAL FORGED, ROLLED, ANNEALED 1 HR AT 1000 C, EXTRUDED, AND SWAGED

Ingot 1-UM.

Additional observations were made on the coextruded pins. Those pins which had received a 24-hr anneal at 1000 or 1025 C either before or after forging and rolling and prior to coextrusion exhibited a much more uniform diameter over their length than did specimens which received either no heat treatment or a shorter heat treatment of 1 hr at 1000 C after forging and rolling. Variations in the diameter of the pins of approximately ±3 mils and ±20 mils for these materials, respectively, were measured.

No effect of heat treatment or fabrication on quality or uniformity of the cladding was noted. Measurements of the cladding thickness were made on all of the swaged pins as tabulated in Table 1. The measurements were made to obtain maximum and minimum thicknesses as well as a few additional randomly selected thicknesses. Variations from a minimum of 2.57 to a maximum of 5.96 mils were recorded. The variations were random with no effect attributable to prior history being evident. The pins produced by coextrusion of as-cast material, UMAC-1 and UMAC-2, show variations similar to those for forged and rolled material. However, a portion of the variations are attributable, in the as-cast coextruded material, to the poor surface quality of the as-cast ingot, which contained numerous voids. Typical cladding variations are shown in Figures 40 and 41 as well as Figures 21 and 22.

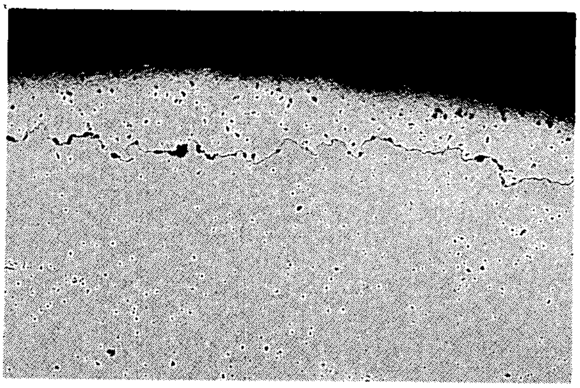


100X RM10344

HNO_3-HF-H_2O_2-C_2H_5OH Etchant

FIGURE 40. VIRGIN-MELT MATERIAL, AS SWAGED, GIVEN NO HEAT TREATMENT AT ANY STAGE

Ingot 1-UM.



100X RM10338

HNO_3-HF-H_2O_2-C_2H_5OH Etchant

FIGURE 41. SAMPLE EXTRUDED IN AS-CAST CONDITION

Ingot UM-AC-1.

It should be pointed out that the alloy pins prepared in this study were coextruded in accordance with original specifications to achieve a 4-mil cladding with a minimum thickness of 2 mils permissible. The revised specifications call for a 5 ± 0.5-mil cladding with minimum and maximum cladding thicknesses of 3 and 7 mils, respectively. The measurements given in Table 1 show that no problems in meeting these limits need be anticipated.

TABLE 1. CLADDING MEASUREMENTS ON SWAGED PINS

Material	Melt	Heat Treatment[a]	Cladding-Thickness Measurements, mils Random	Average
Remelt stock	4-UM	B	4.14, 4.92, 3.13, 4.4, 4.66, 4.92	4.45
Remelt stock	4-UM	A	3.37, 4.66, 4.18, 4.14, 3.88, 4.40	4.27
Remelt stock	8-UM	A	4.40, 4.92, 4.66, 4.92, 4.66, 4.40	4.66
Remelt stock	8-UM	A and B	2.85, 4.66, 4.4, 5.18, 5.44, 3.63	4.36
Remelt stock	2-UM	C	3.88, 5.44, 4.4, 4.92, 4.14, 4.66	4.57
Remelt stock	6-UM	A	3.10, 5.70, 5.96, 3.63, 4.66, 4.14	4.53
Remelt stock	6-UM	A and B	5.18, 3.63, 4.66, 4.14, 4.40, 4.66	4.46
Remelt stock	6-UM	A and C	5.18, 4.4, 5.44, 3.10, 4.14, 3.37	4.27
Virgin-melt stock	1-UM	B	4.66, 5.18, 3.88, 5.18, 4.14, 3.37	4.40
Virgin-melt stock	1-UM	C	3.37, 5.18, 5.44, 3.88, 4.4, 4.92	4.53
Virgin-melt stock	5-UM	A and C	5.18, 2.85, 4.92, 4.40, 4.14, 3.88	4.23
Virgin-melt stock	3-UM	None	3.10, 5.18, 4.40, 4.40, 4.92, 3.88	4.31
Virgin-melt stock	3-UM	B	3.37, 4.40, 5.44, 4.66, 5.18, 3.63	4.45
Virgin-melt stock	7-UM	A	3.37, 4.66, 5.70, 4.66, 4.92	4.83
Virgin-melt stock	7-UM	A and B	2.57, 4.92, 4.66, 4.14, 5.44, 5.18	4.49
Virgin-melt stock	UMAC-1	None--coextruded As-cast	3.37, 2.85, 4.66, 4.92, 5.18	4.20
Virgin-melt stock	UMAC-2	None--coextruded As-cast	3.37, 5.70, 3.37, 4.92, 5.18, 4.4	4.49

(a) Heat treatments:

A. 24 hr at 1025 C, furnace cooled in the ingot stage
B. 1 hr at 1000 C, furnace cooled after initial fabrication.
C. 24 hr at 1000 C, furnace cooled after initial fabrication.

Postswaging Heat Treatment

The value of a postswaging heat treatment of 1 hr at 800 C in promoting additional homogenization has been demonstrated in the previous section. The advisability of such a heat treatment is further demonstrated in a later section where the results of fuel-pin-cracking studies are reported. Further studies of the effect of postswaging treatment on the thermal stability of the gamma phase and on the cladding and core alloy are reported here.

Examination of clad pins which received a postswaging treatment of 1 hr at 800 C showed that a marked increase in core-cladding diffusion accompanied the treatment. In the as-swaged specimens this band measured 0.065 mil, while measurements made on heat-treated samples ranged from 0.512 to 0.905 mil, the major number of specimens having diffusion-zone thicknesses of 0.755 mil. Accompanying the increase in diffusion-zone width was a marked increase in grain size of the zirconium cladding (Figures 42, 43, and 44).

The effect of various postswaging heat treatments on thermal stability of the gamma phase is illustrated in Figure 45. The hardness of the uranium-10 w/o molybdenum alloy is observed to increase after approximately 5 per cent transformation product appears in the microstructure, while the time at which maximum hardness is attained coincides with about 95 per cent transformation. Thus, hardness measurements have been employed to provide a measure of the degree and rate of alloy

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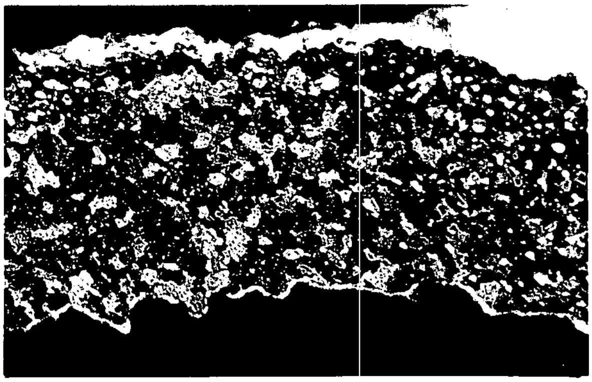


250X HNO_3-HF-H_2O_2-C_2H_5OH Etchant RM10363

FIGURE 42. ZIRCONIUM CLADDING, AS EXTRUDED

Polarized light.

250X HNO_3-HF-H_2O_2-C_2H_5OH Etchant RM10364

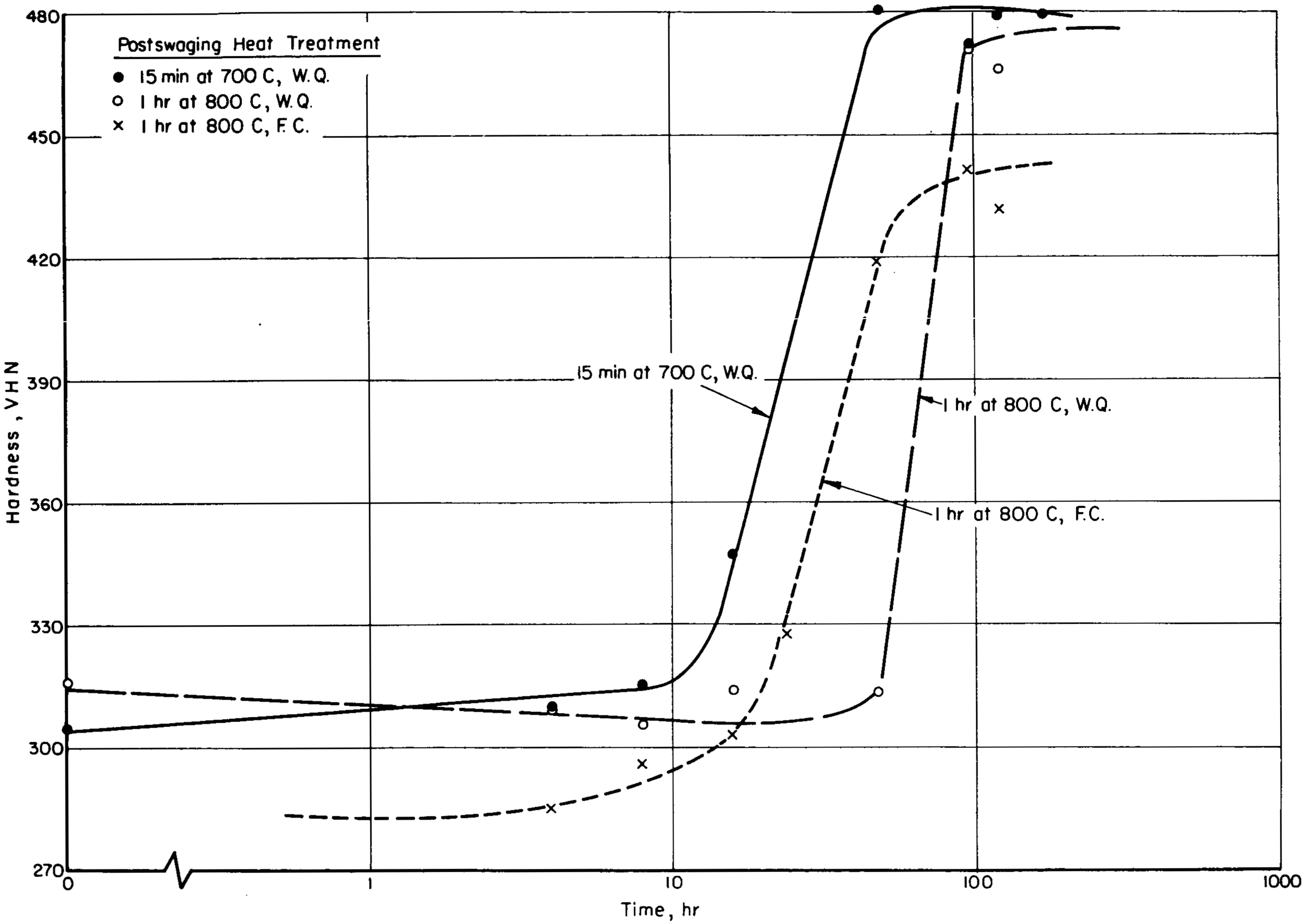
FIGURE 43. ZIRCONIUM CLADDING, AS SWAGED

Polarized light.

250X HNO_3-HF-H_2O_2-C_2H_5OH Etchant RM10365

FIGURE 44. ZIRCONIUM CLADDING ON FUEL PIN HEATED 1 HR AT 800 C AFTER SWAGING

Polarized light.



A-29331

FIGURE 45. HARDNESS CHANGES IN URANIUM-10 w/o MOLYBDENUM ALLOY PINS AS A FUNCTION OF HEAT TREATMENT DURING TRANSFORMATION AT 500 C

transformation. Specimens given a stress-relief heat treatment at 700 C transform most quickly. A 1-hr anneal at 800 C which promotes additional stress relief and grain growth produces a marked increase in the time at which the hardness increase accompanying transformation is noted. However, furnace cooling from 800 C, which permits nucleation of the gamma-phase decomposition products, is responsible for an increased rate of transformation as compared with the rate obtained on water quenching from 800 C. For comparison, times of about 16 and 50 hr for the start of the hardness increase accompanying transformation at 500 C are observed for 800 C furnace-cooled and water-quenched specimens. Heat treatments of 1 hr at 800 C followed by furnace cooling to 375 C in 2 hr and air cooling, and 1 hr at 800 C followed by quenching into a furnace at 350 C and furnace cooling, produced results similar to those shown for the simple furnace cool from 800 C. However, the quench into a 350 C furnace, which corresponds to the treatment accorded fuel pins irradiated in the CP-5 Reactor, resulted in a slightly lower transformation rate for the alloy than the other two heat treatments, the hardness increase beginning after about 20 hr.

The importance of these results lies in the requirement that a stable gamma phase be produced for radiation stability. Thus, while a neutron flux tends to keep the alloy in the disordered gamma-phase condition, there is an opposing tendency for thermal decomposition of the phase. It is desirable to prevent transformation during irradiation since it appears that transformation is accompanied by swelling.

It should be pointed out that the as-swaged alloy begins to transform after very short periods of time, less than 2 hr at 500 C being sufficient to produce noticeable precipitation of alpha uranium at the grain boundaries of the cold-worked gamma matrix. Consequently, a postswaging heat treatment is indicated, and a 1-hr anneal at 800 C followed by as rapid a cool as possible is recommended.

Mechanical Properties

Tensile tests of the as-extruded uranium-10 w/o molybdenum alloy were conducted. These tests were performed on bare extruded material received as 0.25-in.-rounds and machined into standard 1/8-in.-diameter ASTM threaded tensile specimens. Results for specimens of varying history, prepared as shown in Figure 1, are given in Table 2.

In general, no effect of degree of homogeneity, as affected by heat treatment, or of metal quality on properties is noticeable. The total elongation or ductility was affected slightly by heat treatment after forging in that there was less variation between values of individual specimens with the same history.

Average values for the ultimate strength, 0.2 per cent offset yield strength, and elastic modulus are 150,000 psi, 148,000 psi, and 14.7 x 10^6 psi, respectively.

The effect of a postswaging heat treatment at 800 C was investigated on these same alloys. The tests were conducted on swaged wire specimens given an initial stress-relief heat treatment which was required to prevent cracking. Results are given in Table 3.

TABLE 2. THE TENSILE PROPERTIES OF URANIUM-10 w/o MOLYBDENUM EXTRUDED ALLOYS AT ROOM TEMPERATURE

	Heat Treatment								
	Before Forging		After Forging						
Specimen(a)	Time, hr	Temperature, C	Time, hr	Temperature, C	Ultimate Tensile Strength, psi	0.2 Per Cent Offset Yield Strength, psi	Elastic Modulus, 10^6 psi	Reduction in Area, per cent	Total Elongation, per cent in 1-1/2 in.
9-UM-1	24	1025	None		151,600	149,000	14.42	19.6	4.5
9-UM-2	24	1025	None		148,100	147,500	14.55	33.0	6.8
9-UM-3	24	1025	None		152,300	149,600	14.37	49.0	8.0
11-UM-1	None		None		152,500	149,800	15.7	41.7	8.0
11-UM-2	None		None		153,100	150,300	14.05	46.0	9.1
11-UM-3	None		None		149,900	148,500	15.3	43.0	6.8
9-UM-1	24	1025	1	1000	149,000	145,200	14.2	52.0	6.8
9-UM-2	24	1025	1	1000	150,000	148,500	15.45	52.0	6.2
9-UM-3	24	1025	1	1000	150,200	–	–	52.0	6.8
11-UM-1	None		1	1000	150,700	150,500	15.1	48.0	6.28
11-UM-2	None		1	1000	149,600	145,300	14.0	48.0	5.7
11-UM-3	None		1	1000	151,500	150,900	14.5	47.0	6.8
10-UM-1(b)	24	1025	None		153,000	149,600	15.47	36.0	6.28
10-UM-2(b)	24	1025	None		149,500	148,000	14.65	38.4	6.28
10-UM-3(b)	24	1025	None		155,500	149,500	15.7	12.0	3.4
12-UM-1(b)	None		None		152,700	150,000	14.95	15.5	4.0
12-UM-2(b)	None		None		151,900	149,000	14.16	36.8	6.2
12-UM-3(b)	None		None		151,400	149,000	14.2	38.5	8.0
10-UM-1(b)	24	1025	1	1000	147,200	142,500	14.7	36.0	6.28
10-UM-2(b)	24	1025	1	1000	149,500	148,000	15.6	36.0	6.8
10-UM-3(b)	24	1025	1	1000	149,300	147,500	14.62	41.7	7.42
12-UM-1(b)	None		1	1000	153,100	150,000	14.36	39.2	8.5
12-UM-2(b)	None		1	1000	153,000	149,800	15.6	36.0	8.0
12-UM-3(b)	None		1	1000	149,700	148,400	14.0	18.8	6.28

(a) Specimens 9 and 11 were prepared from virgin stock, center-cut biscuit uranium, and General Electric Lamp Wire Division molybdenum. Good melting and casting techniques used. Specimens 10 and 12 were prepared from remelted stock, Reactor Grade uranium, and General Electric Lamp Wire Division molybdenum. Good melting and casting techniques. Fabrication history: hot forged and hot extruded, no heat treatment after extrusion.

(b) 1.27 w/o zirconium added.

TABLE 3. THE TENSILE PROPERTIES OF SWAGED URANIUM-10 w/o MOLYBDENUM ALLOYS AT ROOM TEMPERATURE

Specimen	Fabrication	Heat Treatment[(a)] Time, hr	Heat Treatment[(a)] Temperature, C	Zirconium Addition, w/o	Ultimate Tensile Strength, psi	0.2 Per Cent Offset Yield Strength, psi	Elastic Modulus, 10^6 psi	Reduction in Area, per cent	Total Elongation, per cent in 2 in.
9-UM-S	Cold swaged after extrusion	None		None	151,300	143,700	13.2	49.0	9.0
9-UM-SHT	Cold swaged after extrusion	1	800	None	127,700	126,800	13.1	57.0	15.0
11-UM-S	Cold swaged after extrusion	None		None	146,700	145,800	13.3	32.6	5.5
11-UM-SHT	Cold swaged after extrusion	1	800	None	128,500	126,800	13.4	54.0	13.0
10-UM-S	Cold swaged after extrusion	None		1.27	149,100	149,100	13.2	37.0	6.0
10-UM-SHT	Cold swaged after extrusion	1	800	1.27	133,500	132,200	12.9	37.0	12.0
12-UM-S	Cold swaged after extrusion	None		1.27	152,700	152,200	13.1	23.6	6.5
12-UM-SHT	Cold swaged after extrusion	1	800	1.27	132,900	132,900	13.2	40.5	10.0

(a) All specimens given stress relief heat treatment of 15 min at 700 C. Treatment of 1 hr at 800 C represents additional heat treatment.

In the as-swaged condition following a 15-min treatment at 700 C, the alloy exhibited properties similar to those recorded for the as-extruded alloy. The heat treatment at 800 C for 1 hr reduced the tensile and 0.2 per cent offset yield strengths by approximately 15 per cent, while ductility increased by a factor of 2. Thus, the net effect is an increase in toughness of the alloy.

The remelt alloys containing 1.27 w/o zirconium appeared to be slightly stronger and less ductile after the swaging operation for either condition of heat treatment than the virgin-melt alloy specimens.

Chemical and Spectrographic Analyses

Analyses of the starting materials and of the alloys prepared were obtained at various stages of the production cycle.

Chemical and spectrographic analyses of the dingot uranium used in the preparation of virgin-melt ingots, of Reactor Grade uranium used in the preparation of the remelt ingots, and of the sintered molybdenum pellets are given in Table 4. Of particular interest are the carbon analyses, 100 ppm, 760 ppm, and 1200 ppm, respectively, for these materials.

Oxygen vacuum-fusion analyses of the virgin-melt material from Ingot 8-UM were also obtained at various stages in the production process. While there was some fluctuation in the data, a gradual increase in oxygen content from about 45 ppm in the cast condition to about 70 ppm for the finished and heat-treated pin was indicated. The remelt Ingot 7-UM analyzed approximately 500 ppm oxygen throughout the process.

Impurity Studies

Studies directed toward determining specifications on allowable limits of zirconium, carbon, oxygen, iron, nickel, and chromium were performed. On the basis of these studies, limits are recommended in the sections following.

Zirconium

The investigation of allowable limits of zirconium was one of the more important of this series. The amount of scrap which can be recycled and the amount of care taken in removing zirconium cladding from scrap will be highly dependent on the amount of zirconium which can be tolerated in the alloy.

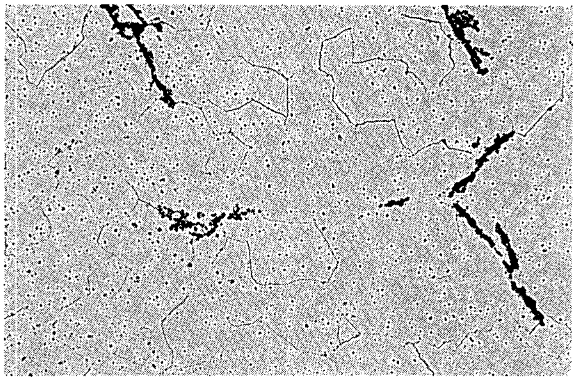
Additions of 2,700, 7,300, and 12,700 ppm zirconium were made to the base alloy. The 2700-ppm zirconium alloy had nearly the same microstructure as the base uranium-10 w/o molybdenum alloy. However, there were occasional groups of small inclusions that appeared to be ZrC. The photomicrograph shown in Figure 46 was taken from the section of a rolled rod which would have been near the top of the cast ingot. Thus, there was a marked tendency for the zirconium carbide to concentrate at

TABLE 4. CHEMICAL AND SPECTROGRAPHIC ANALYSES OF STARTING MATERIALS AND ALLOY INGOTS

	Chemical Analysis, w/o				Spectrographic Analysis, ppm																			
Material	C	Mo	Zr	N	Al	B	Be	Cd	Cu	Co	Cr	Fe	Mg	Mn	Mo	Ni	Pb	V	W	Si	Zn	Ca	Sn	Zr
Dingot uranium	0.010	–	–	0.004	40	2	<0.2(a)	<0.6(a)	10	40	10	60	10	5	60	20	6	<6	200	<15	8	8	<1	<200
Reactor Grade uranium	0.076	–	–	0.003																				
Molybdenum	0.12	–	–	–	30	<100(a)	<20(a)	<100(a)	<10	<50(a)	30	200	<10	<10	–	350	20	<30	<3000(a)	<30	<500(a)	20	<30	<50(a)
Virgin melt of ingot prepared from Reactor Grade uranium used for remelt ingot, top and bottom analyses	0.07	9.8	–	0.008		<0.4(a)	<1	<0.5	10	10	30	220	2	12	–	60	<2	<15	<400(a)	20	–	–	<5	–
	0.06	9.9	–	0.008		<0.4(a)	<1	<0.5	10	5	120	140	<0.2	8	–	80	<2	<15	<400(a)	20	–	–	<5	–
Remelt, Ingot 8-UM	0.07	10.2	1.2	–																				
Virgin melt, Ingot 7-UM, top and bottom analyses	0.026	9.7	<0.05(a)	0.004	<100	0.6	<0.5	<0.6	20	35	20	100	<10	6	–	60	<4	<6	<400(a)	70	<500(a)	<100	10	<200
	0.030	9.8	<0.05(a)	0.004																				

(a) Not detected.

the top of the ingot. The concentration at the top also appeared to increase with zirconium content. Such concentrations were associated with cracks and voids in the casting which would necessitate considerable cropping of the ingot with the probability that the cropping would not be recoverable. Consequently, a limitation to the zirconium addition is indicated.



100X Electroetched RM9909

FIGURE 46. STRUCTURE OF URANIUM-10 w/o MOLYBDENUM ALLOY CONTAINING 0.27 w/o ZIRCONIUM AS ROLLED AT 1650 F

In addition to the effects noted above, zirconium was found to exhibit a deleterious effect on gamma-phase stability. This is illustrated in Figure 47 by hardness measurements made on specimens transformed at 500 C. A marked change in behavior is apparent with increasing zirconium content. By comparison with the base alloy in which the hardness change accompanying transformation begins after 40 hr and is complete after 175 hr, the alloy with a 12,700-ppm zirconium addition begins to increase in hardness after about 4 hr with the hardness change complete after 24 hr. The alloys with 2700-ppm and 7300-ppm additions begin and complete their hardness changes after about 15 and 50 hr. Figures 48 through 51 present microstructures of these alloys after the same time of transformation to show comparative degrees of transformation. The desirability of limiting zirconium additions from the viewpoint of gamma stability is apparent.

In order to further determine a limit to the zirconium addition, alloys containing 500, 1000, and 2000 ppm of zirconium were prepared. These showed a gradual change in rate of transformation with decreasing zirconium content. The most pronounced effect was on the time required to complete transformation. Thus, while the alloy containing 2000 ppm zirconium had completed its hardness change within about 50 hr, both alloys containing 500 and 1000 ppm zirconium required about 100 hr. Little effect on the time for start of transformation was noted. On the basis of these results the indications are that at some concentration between 1000 and 2000 ppm the gamma-destabilizing effect of zirconium begins to increase. Consequently, it is recommended that specifications permit a maximum of 2000 ppm zirconium.

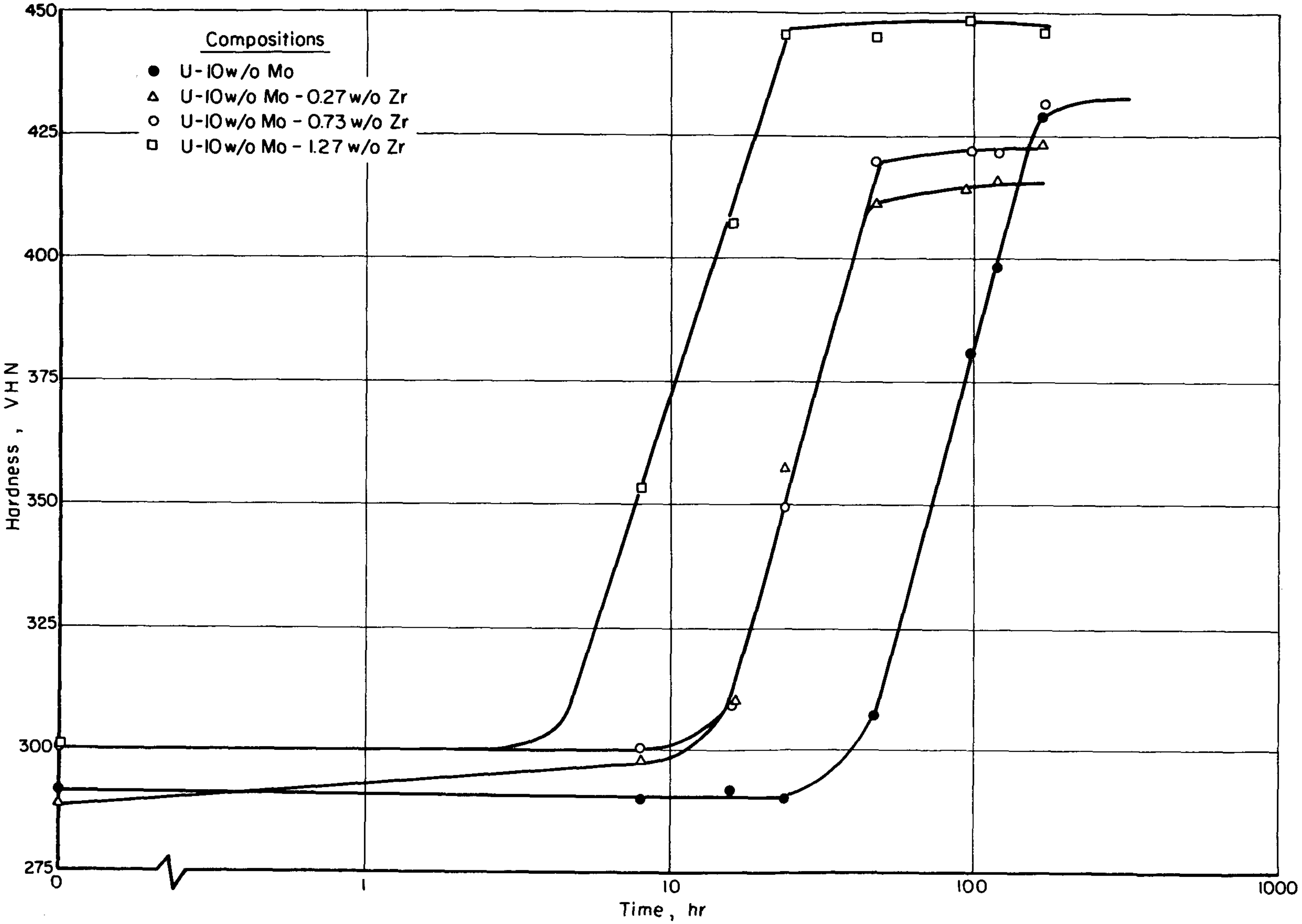
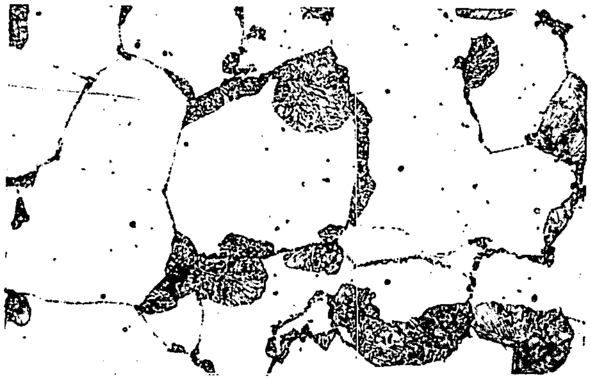


FIGURE 47. EFFECT OF ZIRCONIUM ON TRANSFORMATION OF URANIUM-10 w/o MOLYBDENUM ALLOY AT 500 C



500X Electroetched RM10189

FIGURE 48. STRUCTURE OF URANIUM-10 w/o MOLYBDENUM ALLOY HEATED 1 HR AT 800 C AND WATER QUENCHED AND 48 HR AT 500 C AND WATER QUENCHED

500X Electroetched RM10196

FIGURE 49. STRUCTURE OF URANIUM-10 w/o MOLYBDENUM ALLOY CONTAINING 0.27 w/o ZIRCONIUM HEATED 1 HR AT 800 C AND WATER QUENCHED AND 48 HR AT 500 C AND WATER QUENCHED

500X Electroetched RM10192

FIGURE 50. STRUCTURE OF URANIUM-10 w/o MOLYBDENUM ALLOY CONTAINING 0.73 w/o ZIRCONIUM HEATED 1 HR AT 800 C AND WATER QUENCHED AND 48 HR AT 500 C AND WATER QUENCHED

500X Electroetched RM10200

FIGURE 51. URANIUM-10 w/o MOLYBDENUM ALLOY CONTAINING 1.27 w/o ZIRCONIUM HEATED 1 HR AT 800 C AND WATER QUENCHED AND 48 HR AT 500 C AND WATER QUENCHED

Carbon

A specification limit of 300 ppm carbon is recommended for the uranium-10 w/o molybdenum fuel alloy. This specification is based on the satisfactory preparation of the alloy containing approximately 300 ppm by production processes. The necessity of this limit is based on the requirement that carbide stringers be minimized in the alloy since such stringers are associated with cracks in both as-fabricated and irradiated alloy specimens. While even an alloy containing 300 ppm will contain some stringers, these are generally small and are not expected to present a problem. By comparison, the alloys containing 700 ppm contained numerous large stringers. The surface striations which appeared on the extrusion-billet surfaces of these alloys are one apparent result of the high carbon content. In addition, stringering can be expected to be more pronounced if high oxygen contents are associated with high carbon contents. Carbide and UO_2 tend to agglomerate in the same areas.

Oxygen

Several attempts to introduce oxygen in the form of UO_2 into experimental melts were made. These attempts were not too successful since the UO_2 tends to segregate in the melt so that some areas contain large amounts of UO_2 inclusions while others will have none. Figure 52 shows the as-cast structure of an ingot to which a nominal 225-ppm oxygen addition was made. The particular surface from which this photograph was taken had very large stringers of UO_2 in and around cracks. Other sections had little or no UO_2 showing. However, the photomicrograph provides a good illustration of how UO_2 in high concentrations is usually associated with cracks.

The importance of limiting oxygen content is further illustrated by the microstructure of a swaged specimen in which cracks developed (Figure 53). Oxide inclusions are seen to be associated with the cracks. It is felt that these inclusions are excellent stress raisers and provide a source of cracking in the fuel alloy.

On the basis of examination of the sample containing the 225-ppm oxygen addition and past experience with uranium, an oxygen limit of 225 ppm is recommended. It is felt that at this level stringering and agglomeration of oxides will be minimized.

Iron and Nickel

Iron and nickel have been combined in the recommended specification since both elements can be expected to form low-melting compounds, U_6Fe and U_6Ni, when added to a high-uranium alloy. These compounds tend to form at grain boundaries and then melt during fabrication at elevated temperatures, thereby rendering the alloy "hot short" in fabrication as a result of grain-boundary parting.

Iron was added to the base alloy in amounts of 500, 800, and 1200 ppm. Microstructures of the first two alloys in the as-cast condition appear in Figures 54 and 55. A precipitate is seen in the alloy containing 800 ppm iron; this alloy was hot short and not fabricable.

The alloy containing 500 ppm iron was fabricated, but the final surface was found to be extremely rough, indicating parting at the grain boundaries. Subsequent metallographic examination showed that precipitation at the grain boundaries had occurred, apparently either during the homogenization treatment or during hot rolling. In order to prevent such precipitation a limit of 400 ppm iron is suggested.

Combinations of 400 ppm iron and 100 ppm nickel and 400 ppm nickel and 100 ppm iron were also investigated. Alloys with these additions fabricated satisfactorily, indicating that the nickel specification can be combined with the iron specification without creating additional problems. This combined limit is 400 ppm.

Chromium

Chromium was also checked since chromium forms a low-melting eutectic with uranium and therefore might affect fabricability. An alloy containing 400 ppm chromium was prepared, and its as-cast structure is shown in Figure 56. No evidence of chromium precipitate is evident and the alloy fabricated satisfactorily. Therefore, 400 ppm chromium is established as a permissible limit.

Other Impurities

While no specific study of either hydrogen or copper was performed, some discussion of them can be offered.

Hydrogen is not regarded as presenting any problem in the alloy. While the starting uranium may contain hydrogen, this boils off quite rapidly during melting at reduced pressures. Hydrogen contents of uranium metal melted at pressures as high as 500 μ run less than 1 ppm. The hydrogen evolves immediately on melting of the uranium, and consequently most of the hydrogen will have boiled off during melting of the alloy before the alloying temperature is reached.

Copper as a contaminant was not encountered directly in the study, although a source of copper pickup was indicated when a specimen for chemical analysis was inadvertently cut in a manner to contain a portion of the copper-nickel end plug from the coextrusion process. These end plugs extend to a considerable depth into the fuel-pin core. Nickel contamination from this source is regarded as being more serious than the resultant copper contamination from the viewpoint of fabricability of the alloy. Liquid forms in uranium-copper alloys at temperatures above 1920 F, which is above the fabrication temperature for the alloy.

Cracking Studies

During the swaging of pins in the study of production processes, difficulty was encountered in swaging material which had been extruded bare. While the clad coextruded pins swaged satisfactorily, all the bare pins regardless of prior history or preparation cracked severely after one or two swaging passes. Examination of the cracks indicated a highly worked, brittle skin on the surface of the pin. Apparently

500X Electropolished RM9881

FIGURE 52. LARGE CRACK AND UO_2 STRINGER IN A NOMINAL 225-PPM OXYGEN MELT

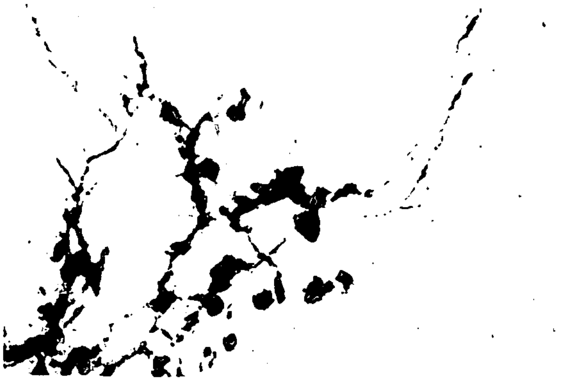


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FIGURE 53. OXIDE INCLUSIONS IN CRACKS OF SWAGED URANIUM-10 w/o MOLYBDENUM SPECIMEN

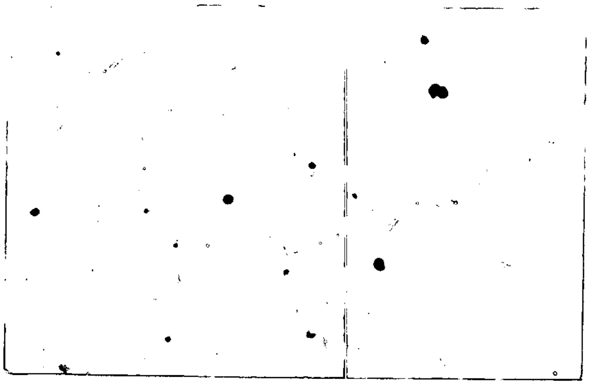

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FIGURE 54. AS-CAST STRUCTURE OF INGOT CONTAINING 500 PPM IRON

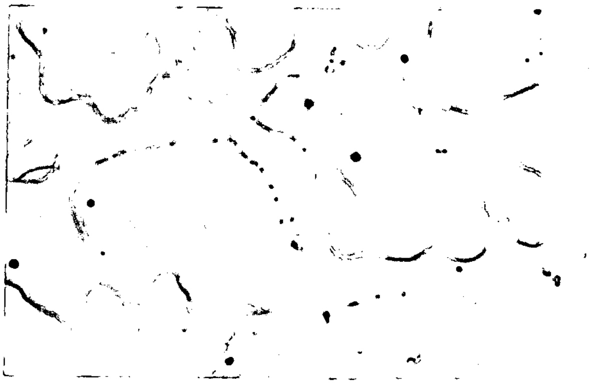

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FIGURE 55. AS-CAST STRUCTURE OF INGOT CONTAINING 800 PPM IRON

Note grain-boundary precipitate.

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FIGURE 56. AS-CAST STRUCTURE OF INGOT CONTAINING 400 PPM CHROMIUM

surface stresses remaining from the extrusion process prevent subsequent center penetration by working, with the result that all of the cold work is absorbed in the surface of the bare pin. The stress distribution in the clad pin is probably slightly different and in addition the cladding is available to absorb the surface impacts during swaging and thereby prevent the formation of a highly stressed brittle layer at the fuel-alloy surface.

Subsequently two sets of bare extruded specimens were annealed for 15 min at 800 C and cold swaged satisfactorily. One set was given a stress-relief heat treatment of 15 min at 700 C after swaging, the other set no additional heat treatment. The latter set cracked on standing overnight while the set given a postswaging heat treatment did not crack at any time. The appearance of a typical cracked specimen which had been extruded bare and then swaged is shown in Figure 57.

1X RM10337

FIGURE 57. TYPICAL APPEARANCE OF A BARE EXTRUDED SPECIMEN WHICH CRACKED AFTER SWAGING

The cracking in swaged specimens appears to be connected with areas of high UO_2 or inclusion content, as appear in Figure 53. Examination of a crack in one specimen revealed a nonmetallic inclusion stringer at the base of the crack. The stringer was removed and X-ray diffraction examination resulted in the identification of UO_2, UC, and a faint trace of UN_2. While the stringer itself may not be directly responsible for cracking, it is likely that such stringers act as stress raisers to promote cracking.

The only observations of cracking in the clad coextruded specimens were made in the region of the extrusion end plugs. Small cracks were observed in this region but not throughout the length of the pins.

No evidence has been obtained in this study to show that inhomogeneity leads to cracking. One series of specimens was prepared and swaged in various conditions – as cast, as hot rolled at 1850 F, and as homogenized at 1025 C for 24 hr and hot rolled. Of these specimens, the as-cast cracked during swaging. However, this represents an extreme case. The specimens which were extruded bare and swaged had been subjected to a variety of heat treatments and represented a complete range of degrees of homogenization, yet all of these cracked in the absence of postextrusion and postswaging heat treatments.

Cracking was also observed in cold-swaged specimens taken from rod prepared by casting 1/2-in.-diameter ingots. The ingots were initially homogenized 24 hr at 1025 C, hot rolled at 1850 F to a 75 per cent reduction, and cold swaged. Samples taken at different steps in the reduction were allowed to age at room temperature. After 2 weeks, small cracks appeared in some of the samples which had received cold reductions between 15 and 41 per cent but with no particular relationship to the amount of reduction. However, none of the rods reduced to a final size of 0.150 in. for a total cold reduction of 64 per cent showed any evidence of cracking.

Two possible explanations are offered for the above observations. Either may supplement the other as a cause of cracking.

It may be that a critical stress distribution is required before cracking occurs in the pins. Thus, an initial surface-stress buildup is required before cracking can occur. Extrusion and swaging both produce more severe working of the surface than the interior and consequently surface stresses and properties are quite different from the stresses and properties of the interior. Under these conditions a critical region may exist where a crack is initiated. However, as the amount of cold reduction is increased, the degree of cold work imparted to the interior increases, thereby eliminating the condition required for the initiation of a crack.

Inclusions may play a role in the initiation of cracks. Inclusions, particularly when present in stringers, can be expected to act as stress raisers. Thus, the cracking observed above may occur at some intermediate stage where the stringer size produces a sufficient discontinuity in the stress pattern across the cold-worked specimen to initiate crack formation. As cold reduction is increased, the inclusions become strung out to such a degree that their effectiveness as stress raisers is lost.

In general, the time delay observed in the initiation of cracking suggests a time-dependent stress relaxation. Reduction of stress by relaxation in one area results in an increase in stress in another area. If the latter stress is sufficiently high that the fracture stress is exceeded, a crack will result.

While cracking has not been observed in any of the clad coextruded pins, cracking has been found to be of an extremely variable nature which is incompletely understood. Consequently, in order to be certain that cracks will not develop during the production of fuel-alloy pins a postswaging stress-relief heat treatment is regarded as essential. Furthermore, since cracks develop on standing overnight at room temperature, it is recommended that this stress-relief heat treatment be applied within 8 hr after the pins are swaged.

SUMMARY AND RECOMMENDATIONS

The following procedures are recommended for the production of zirconium-clad uranium-10 w/o molybdenum fuel alloy pins: Induction melt the uranium and molybdenum charge in a zirconium crucible. Pour from 2850 F, after an alloying time of 1 min, into a 2-in.-wall graphite mold. Heat treat the ingot in a vacuum furnace under a vacuum of 1 μ or less at 1050 ± 25 C for 24 hr and furnace cool. Reduce ingot 75 per cent; forging and rolling temperatures of 1850 and 1650 F, respectively, are suggested. Coextrude billets and cold swage to final size. Cut pins to required length, anneal pins 1 hr at 800 C, and cool as rapidly as possible.

The above recommendations are based on results obtained by fabricating fuel pins from 25-lb ingots. Employing these techniques, a homogeneous fuel pin with a zirconium cladding of satisfactory uniformity was produced. The final heat treatment of 1 hr at 800 C is recommended in order to prevent the possibility of cracking. Furthermore, in order to prevent this possibility, the heat treatment must be performed within 8 hr after swaging. The heat treatment followed by a fast cool also produces a gamma-phase alloy of optimum thermal stability.

Two other effects of the postswaging heat treatment must be considered, the effect on cladding-core diffusion-zone growth and the effect on grain growth of the zirconium cladding. In general it is desirable to minimize both. A limitation to the permissible amount of uranium diffusion into the cladding is introduced since it is desirable to prevent the introduction of fission products into the coolant by recoil through the cladding. Since the 1 hr heat treatment at 800 C produces a diffusion zone less than 1 mil wide, the unaffected cladding will be greater than 2 mils thick, which exceeds the fission-fragment range in zirconium. Therefore the 800 C treatment is permissible on this basis. However, no specific limit to the permissible amount of grain growth in the cladding can be set, although strength decreases with increases in grain size, and grain boundaries may present a source of surface cracking in the cladding. Consequently, a fine grain size is desirable and on this basis a minimum stress-relief heat treatment is indicated. But while grain growth is undesirable, this effect must be balanced against the requirement that a thermally stable core alloy be obtained. While the latter requirement has been emphasized in selecting the 800 C heat treatment, the grain size of the zirconium cladding produced by this heat treatment is regarded as being satisfactory (Figure 44), there being sufficient grains in the cladding to act as barriers to crack propagation.

The following specifications on impurity limits have been determined:

	Maximum, ppm
Zirconium	2000
Carbon	300
Oxygen	225
Iron and nickel combined	400
Chromium	400

A limit to the permissible amount of zirconium is required on the basis of its gamma-destabilizing effect. At some point between 1000 and 2000 ppm zirconium this effect becomes pronounced. Since the satisfactory irradiation performance of the 10 w/o molybdenum alloy is based on ability to retain the gamma phase, a limitation is required.

Both carbon and oxygen limits are required in order to prevent carbide and oxide agglomeration and stringering. If the above limits are exceeded, pronounced agglomeration and stringering, with which cracks in the alloy are associated, can be expected.

The iron and nickel limit is required for fabricability. Higher amounts lead to an alloy which is hot short with tearing and parting in grain boundaries.

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In recovering and recycling scrap material, all clad fuel material should be thoroughly stripped of zirconium in order to keep the zirconium content below 2000 ppm. Care must be taken with the ends of coextruded rods; the copper-nickel end plugs extend to a considerable depth in the fuel alloy. The end plugs must be pickled out completely in order to prevent copper pickup and also nickel pickup, which renders the alloy hot short. All scrap from the initial ingot breakdown should be descaled either mechanically or chemically in order to prevent oxygen pickup. The starting molybdenum stock represents a source of carbon contamination, and an analysis to check the carbon content of this stock is suggested.

During the course of various programs involving the preparation of clad fuel pins, zirconium cladding containing numerous carbide inclusions has been encountered. Nonuniformity of cladding on fuel pins may be associated with quality of the zirconium. Consequently, analysis of the zirconium stock is suggested; metallography is a satisfactory technique.

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