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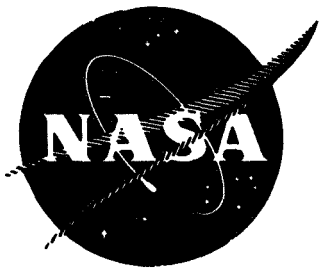

INVESTIGATION TO DEVELOP A PROCESS FOR PRODUCTION OF OXIDE FIBERS BY MELT DRAW TECHNIQUE

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Henry E. Otto and Dwight G. Moore

Prepared for

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UNIVERSITY OF DENVER • DENVER RESEARCH INSTITUTE

FINAL REPORT

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NASA Lewis Research Center
Cleveland, Ohio
Albert Anglin, Project Manager
Materials and Structures Division

FOREWORD

The research described herein, which was conducted by the Denver Research Institute, University of Denver, was performed under NASA Contract NAS3-13201 over the period June 1969 to June 1970. The work was done under the management of the NASA Project Manager, Mr. Albert Anglin, Materials and Structures Division, NASA Lewis Research Center.

Henry E. Otto served as Program Director with Dwight G. Moore acting in a consulting capacity. James W. Sartin performed most of the melt-drawing experiments.

ABSTRACT

A melt-drawing process was investigated as a possible technique for preparing high-strength, high-modulus fibers of polycrystalline alumina. Fibers were formed by drawing small-diameter thoriated tungsten wires through a bath of molten oxide.

Variables investigated included wire size, immersion time, oxidation state, and melt composition. It was found that oxidizing conditions were required to achieve wetting; also, that fast drawing speeds were necessary to prevent the molten oxide from coalescing into a series of small beads on the tungsten filaments.

Tensile strengths of prepared fibers were as high as 134, 800 psi (95 Kg/mm^2) at room temperature and 75, 500 psi (53 Kg/mm^2) at 2000 °F (1372 °K). The alumina sheath contributed little or nothing to the strength of fibers formed on a 5-mil tungsten core; however, the oxide sheath on a 1-mil tungsten core increased the load bearing capacity of the fiber by as much as a factor of five.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Current demand for increased power from gas turbines and compressors has resulted in the need for higher working temperatures. Unfortunately, the limits for stress and temperature are already closely approached for the current types of high-temperature alloys and it is necessary to look to completely new kinds of materials.

One such material is a fiber-reinforced metal or alloy. At temperatures at which creep assumes a major role, fiber reinforcement has been shown to offer high-strength bonuses over, for example, dispersion hardening (Ref. 1). For these benefits to be realized, however, it is first necessary to have suitable fibers available at reasonable cost.

A refractory metal fiber such as tungsten has the required high strength and high modulus of elasticity at temperatures in the range 2000-2500°F; and, fiber composites have been produced with excellent rupture strength at 2000-2200°F (Refs. 2 and 3). However, ceramic oxide fibers have the potential for even higher strength and are less susceptible to property degradation resulting from reaction with the matrix.

Because of their excellent high strengths, most of the research on oxide reinforcements has been concentrated on single-crystal whiskers, and more particularly on sapphire whiskers. However, according to a recent report (Ref. 4), such whiskers (laboratory produced) sell, at the present time, for $7,500.00 a pound. This price would be reduced by mass production techniques, but the nature of the method for growing the whiskers is such as to suggest that the price would always be high. In addition, whiskers do not lend themselves to the type of composite production techniques that have been used so successfully in the fiber glass-resin industry. Recently, single crystal continuous filaments have been grown from the melt (Ref. 5). Although the resulting filaments show high strength and high modulus of elasticity, the process is inherently slow and expensive as compared to various processes that might be used for forming polycrystalline fibers.

Polycrystalline ceramic oxides are known to give lower strengths than their single crystal counterparts. Experience has shown, however, that if grain size can be kept in the submicron range, high strengths can be achieved in polycrystalline material. This can be accomplished in oxide fibers by, (a) rapid cooling from the melt, (b) controlled sintering, and (c) the use of grain-growth inhibitors.

The investigation as described in this report was concerned with the forming of "core-sheath" fibers of polycrystalline alumina on a small-diameter tungsten filament. In concept, the filament would be drawn through a bath of molten oxide and, hopefully, by a suitable adjustment of temperature, atmosphere, and bath composition, the tungsten wire could be made to pick up a continuous coating or sheath of aluminum oxide. Such a process, if successful, would be capable of providing relatively low cost, nonreactive fibers for the reinforcement of heat-resistant alloys. Also, even though the strength and modulus of a fiber was not enhanced significantly by the presence of the Al_2O_3 sheath, the fibers, because of the high strength and high modulus of tungsten (Ref. 6) might still be useful for reinforcement. The alumina layer under these conditions would be functioning solely as a diffusion barrier to prevent reaction between the tungsten and the matrix alloy.

II. EXPERIMENTAL

2.1 MATERIALS

Core materials for the fibers consisted of thoriated tungsten wire, mullite tows and glass fibers. The tungsten wire was obtained as a standard stock item from the General Electric Company. Sizes ranged from 0.0005 to 0.005 inches (0.0127 to 0.127 mm.) in diameter. Mullite fibers were obtained from the Research Laboratories of the Babcock and Wilcox Company. These fibers were in the form of a tow with individual fibers ranging from about 7 to 10 microns in diameter. Fiberglass yarn was obtained locally in which individual fibers were of the same size range as the mullite.

The primary sheath constitutent was aluminum oxide. Three forms were used as melting stock: high purity powder (< 300 ppm impurity), Norton RR Alundum grain, (-60 mesh), and 1/8-in. diam. sapphire rod. Additions to the bath included CaO, SiO_2, Gd_2O_3, MgO, NiO and TiO_2. All of the oxides added to the alumina were at least 99.5+ in purity.

2.2 EQUIPMENT AND MELTING PROCEDURE

A modified filament furnace was used for preparing the oxide melts. Figure 1 shows the arrangement that was used for the single-pass and multiple-pass melt drawing tests (Sects. 2.4 and 2.5). The dipping tests (Sect. 2.3) were made with this same equipment except that the boat-type crucible did not contain a hole at the bottom.

The material found most satisfactory as a container for the molten oxide was a double thickness of tungsten foil 0.001 in. thick. The boat, which was approximately 1-1/2 in. long by 3/8 in. deep, was heated by internal resistance. The power required for melting was of the order of 1000 watts (6v, 180A). A new boat was used for each test. Molybdenum and tantalum were not satisfactory boat stock. Thicker gage tungsten boats would burn out as the result of buckling.

Temperatures were measured using a Pyromicro-pyrometer. Observations of the melting temperatures of high-purity oxides were used to construct a calibration graph for true temperatures.

Melting of the alumina was conducted in a vacuum and after melting, gettered argon was admitted to the furnace. A positive pressure of 6 lbs./in.^{2} gage of argon was used to prevent air from entering the furnace and oxidizing

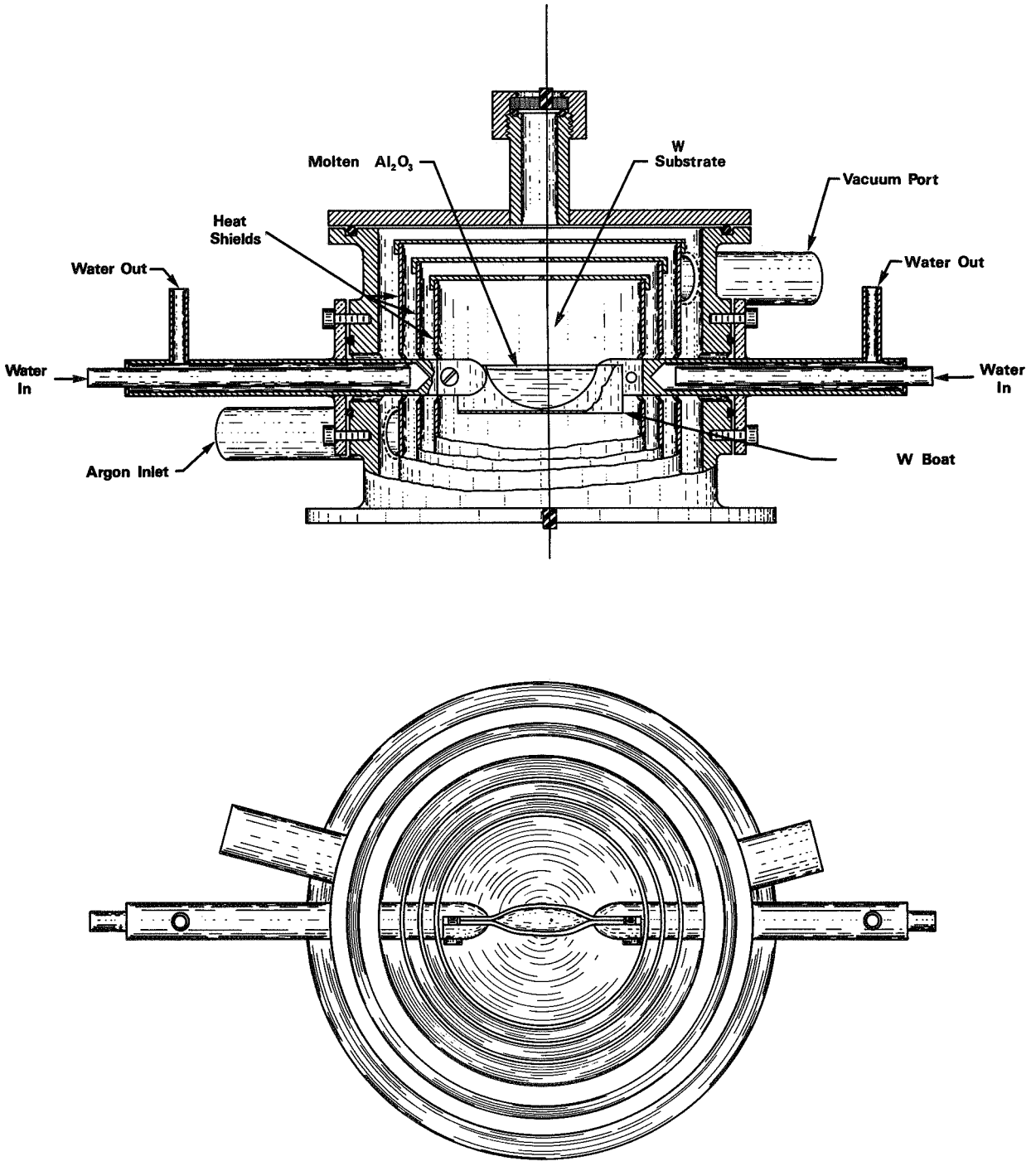


Figure 1. Schematic Sketch of Melting Furnace

the boat and metallic cores. By gettering the argon, a dew point of -50 to -55°F (227 to 225°K) was attained. Later it was found desirable to obtain some oxidation of the tungsten core, and conventional tank argon was used without the gettering operation.

High-purity aluminum oxide powder (-325 mesh) was not a satisfactory melting stock even when compressed into pellets. The pellets would melt where they were in contact with the boat and then bridge over across the boat without melting the major portion of the pellet. Broken sapphire rod (1/8 in. diam.) and Norton RR Alundum (60 mesh) were both found to be quite satisfactory for melting. Oxide additions were made by placing the desired oxide in the bottom of the boat, putting the alumina on top and then heating. After the mixture had melted, it was stirred with a 0.02 inch (0.51 mm.) tungsten wire before any testing was conducted. The CaO was added as calcined $CaCO_3$. The MgO additions also required a pretreatment to remove moisture.

Two of the additions, SiO_2 and NiO, caused a reaction with the tungsten boats. However, it was found that SiO_2 could be tolerated in the melt if the temperature was kept lower than that used with pure alumina. Amounts of NiO had to be reduced to 0.5 w/o to minimize the reaction of this oxide with the boat.

Even with high-purity alumina, a minor reaction occurred between the tungsten boats and the molten oxide. This reaction first became noticeable after the argon was admitted to the furnace, with the melt developing a metallic luster on the surface. Metallographic examinations of the boat showed no appreciable loss in metal thickness; however, some metallic particles were present in the alumina along the W-Al_2O_3 interface and on the surface. Several melts after cooling were examined by X-ray diffraction. Lines for both α-Al_2O_3 and pure tungsten were present as well as other diffraction lines which were not identified. Although tungsten oxide or tungsten aluminate were suspected, these compounds were not present. Another contaminate may have been a thorium compound formed from a reaction between the Al_2O_3 and the ThO_2 present in the wire. However, the existence of this type of compound is speculative, since no data are available in the literature on the ThO_2-Al_2O_3 system.

2.3 PRELIMINARY DIPPING TESTS

The initial studies consisted of dipping the substrate material in molten oxide and observing the degree and type of wetting as a function of immersion

time, composition of bath and bath temperature. In the case of the tungsten-wire substrates, the fine filament wire was twisted around one end of a 0.02 inch (0.51 mm.) tungsten support wire so as to give a short protruding length of filament wire for immersion into the metal. The wire was dipped in a vertical position to simulate the position of a wire during a drawing operation.

Attachment of the ceramic substrates for the dipping tests was accomplished by making a single loop at the end of a tungsten wire, sliding the ceramic filaments through this loop, and using the point of loop closure as a pressure point to hold the fibers. This gave an unsupported end that could be dipped into the melt. Dipping experiments were made using this arrangement. Both glass and mullite dissolved immediately upon contact. Twisting the mullite fibers to give a yarn with a larger cross-section did not alleviate the problem. Glass yarns also melted upon contact with the bath. Because of these solution difficulties all work with ceramic substrates was discontinued and full attention was directed to a study of variables associated with the dipping of tungsten substrates. In one set of tests different diameters of tungsten wire were dipped to evaluate the effect on coating continuity and thickness. The minimum contact time in the bath was on the order of one second. Even this short time allowed considerable heating of the small-diameter tungsten wire. Results of the dipping experiments are presented in Table 1.

In most instances the short length of wire dipped did not coat uniformly, or the coating balled, particularly at the ends of the wire. Varying immersion times, bath temperatures, or wire diameters had little effect on the resulting coating. Also, adding SiO_2 and CaO to the Al_2O_3 had little noticeable effect upon the coatings although the melting temperatures were lowered by the additions. One observation of interest was that beads formed on the wire more readily with the baths that contained SiO_2 or CaO. Decreasing the temperature of the bath with 10 w/o CaO from 2100 to 2050° C improved the coating, but lowering it further to 2000° C was found to have an adverse effect.

2.4 SINGLE-PASS MELT DRAWING EXPERIMENTS

The dipping tests indicated that the tungsten wire could be wet even though the coatings were inconsistent. However, the dipping technique did not allow a true assessment of the type of conditions that would be encountered in a drawing operation, in which a unidirectional draw would be made with a regulated drawing speed. Therefore, the procedures and approach were modified to allow the wire to be drawn through the bath. In the first attempts, a tungsten wire with a diameter of 0.02 in. (0.51 mm.) was fastened across the

two sides of the boat-type crucible and the filament to be coated was passed through under this guide wire. This approach failed as the filament fused to the guide wire.

An arrangement as illustrated in Fig. 1 was employed for the next series of tests. Tungsten wire with a diameter of 0.005 in. (0.13 mm.) was threaded through the hole in the bottom stopper, up through the tungsten boat and then out through the rubber stopper in the sighting port. The hole in the bottom of the tungsten boat had a diameter of approximately 0.03 in. (0.8 mm.). This was found to be sufficiently small to prevent leakage of the molten alumina which as a surface tension almost 10 times that of water (Ref. 7).

The wire was drawn by hand up through the melt in most of the tests. In a few cases the wire was drawn in the opposite direction; however, the results were about the same with respect to wetting.

In several of the tests the wire became welded to the boat where it passed through the bottom hole and this resulted in breakage of the wire. In other tests failure of the boat occurred.

The test results are presented in Table 2. Unless otherwise stated, all of the tests were conducted in an argon atmosphere which appeared to give better results, both in the prior dipping tests and in the single draw tests.

Several bath compositions were evaluated using the single draw techniques. One bath composition containing 10 w/o NiO reacted severely with the tungsten boat ultimately leading to holes and failure of the boat. No particular advantage was noted by using Gd_2O_3 or Y_2O_3 additions. The most uniform coatings were obtained using CaO additions to the bath.

A few tests were conducted in which the tungsten wire was pretreated in an effort to improve the wettability of the filament. In the first treatment, the wire was immersed in a 10 w/o NaOH solution at 90° C (363° K) for 10 minutes, rinsed in distilled water, air dried and then tested for wettability. In another test, the wire was etched in a solution containing 10 grams $K_3Fe(CN)_6$ and 10 grams NaOH in 100 milliliters of water. This solution removed about 10 percent of the cross section of the wire before it was tested. After etching the wire was rinsed in distilled water and dried in air. Again, no improvement in wettability was noted.

In another series of tests, the tungsten wire was precoated by (1) drawing the wire through a slurry of 3-micron Al_2O_3 and distilled water

followed by baking in air at 900° C, (2) drawing a hot wire through the same slurry and baking at 1400° C, and (3) drawing the wire through the slurry two times. Subsequent drawing tests with the precoated wires showed no improvement in wettability. Also, altering the composition of the slurry to $15SiO_2$ - $85Al_2O_3$ and $10CaO$ - $90Al_2O_3$ failed to improve wettability.

2.5 MULTIPLE-PASS MELT DRAWING EXPERIMENTS

The single-pass melt drawing tests were encouraging in that they showed that a filament could be coated with alumina even though the resulting coatings were thin, rough, and in many instances discontinuous. Since the wire pretreatments that were tried did not improve coating continuity, it was decided to try passing the wire up and down through the bath to build up the coating and to coat areas of the wire that were not coated in a single pass. This particular approach proved to be quite successful inasmuch as it gave wire that was completely coated in lengths as long as 20 in. (50.8 cm).

However, a good deal of dexterity was required to prevent breakage of the wire during drawing. Tension on the wire was required to minimize rubbing against the sides of the boat and the holes in the furnace. Any hang-up of the wire usually resulted in wire breakage.

The smallest wire that could be continuously coated consistently over lengths of 5 to 6 inches had a diameter of 0.005 in. (0.13 mm.). It was found impossible to coat wire having a diameter of 0.0005 in. (0.013 mm.) using the multiple drawing technique. This was attributed to the low load bearing capacity of the wire which at room temperature would sustain a load of less than 0.1 lb. (46 grams). Any bending or friction resulted in immediate failure of this fine diameter wire. It was possible to draw the wire with a diameter of 0.001 in. (0.025 mm.) back and forth through the bath if extreme care was taken in handling the wire. In using a wire of this size, relatively large holes were required in the boat to prevent any friction or hang-up of the wire.

Drawing rates were varied with a rate of about 2 ft./sec. being used in most tests. In a few tests a rate of 6 ft./sec. was used with the wire having a diameter of 0.005 in. (0.13 mm.). Wire breakage was a problem at the fast rates although a more continuous coating was achieved.

Most of the coatings with high-purity alumina had a rough surface as shown in Fig. 2. Although wires with diameters of 0.001 in. (0.025 mm.) and 0.003 in. (0.075 mm.) were coated with alumina, the coatings on these smaller wires were not nearly as continuous as was the case with the larger

wire. However, in one case (Melt 158) a continuous coating was realized over a length of the 0.001 in. (0.025 mm.) wire that was sufficient to permit mechanically testing. Two areas of approximately 0.5 in. (1.27 cm) were coated. Results of multiple draw experiments with high purity alumina are given in Table 3.

One of the most successful coating baths was one containing $95Al_2O_3$ - 5CaO (weight percent). This gave relatively smooth coatings (Table 4.) The number of passes or draws through the melt was varied in an effort to determine an optimum for this particular coating. In most instances, a maximum fiber diameter of 0.02 in. (0.51 mm.) was approached after five passes through the molten bath. However, five passes through the melt did not in all cases insure an acceptable coating. Many of the fibers had a nonuniform diameter which was probably the result of short sections of the wire not being coated during the first few passes through the bath. Small beads that adhered to the wire during the first few phases resulted in a rough coating after the wire had been completely coated. Therefore, with almost all wires coated with the $95Al_2O_3$ - 5CaO, there would be areas with a relatively smooth coating and other areas that were rough. Increasing the CaO content to 10 w/o did not improve the smoothness since the higher time contact appeared to increase the tendency for the coating to bead.

A few tests were conducted with baths containing 5 and 10 w/o additions of MgO (Table 5). These coatings were not continuous although heavy coating was obtained in some areas. Coated lengths were not adequate for mechanical testing.

Two tests were conducted with a bath of alumina containing 2.5 w/o CaO and 2.5 w/o of MgO. This bath was more fluid than the baths with CaO alone. The coatings obtained were very thin although they were relatively smooth. Tests with 10 weight percent Gd_2O_3 additions gave erratic coatings that had a tendency to bead. One test was conducted with an addition of 5 w/o TiO_2 which resulted in a heavy uneven coating.

2.6 MICROSTRUCTURE

Microscopic examination at low power showed that the great majority of the melt-drawn fibers were lacking in uniformity over the entire coated length. Three examples of this nonuniformity are shown in Fig. 2. The surface of the upper fiber is fairly rough with some evidence of notches in the coating near the right side of the micrograph. The center fiber illustrates a region of nonuniform diameter where wetting was substandard during one or

more of the multiple drawing operations. The bottom fiber contains a short length in which the tungsten is completely free of coating. This was undoubtedly caused by poor wetting.

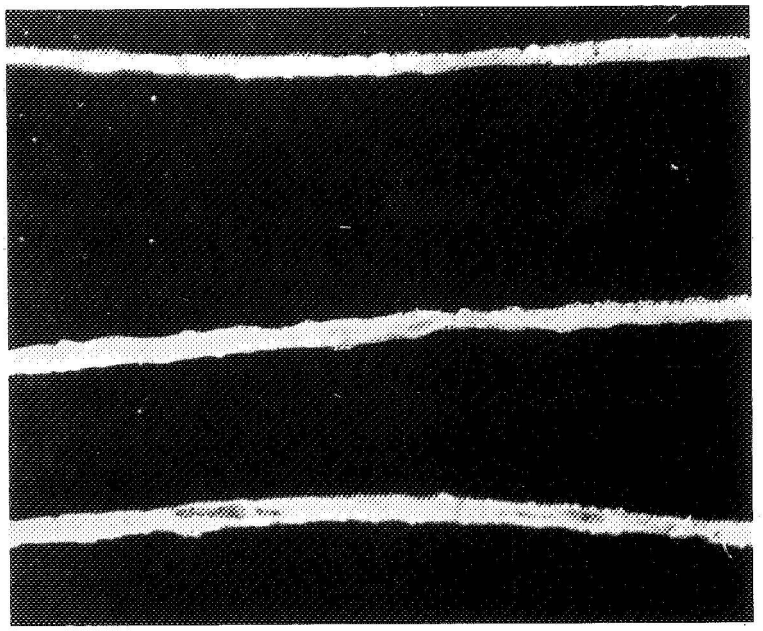
All three fibers have a grainy appearance in Fig. 2. The surface of the fibers, however, are not grainy in nature; rather the grainy appearance is due to localized areas of the coating being tilted with respect to the fiber axis, thus causing variations in the amount of reflected light. The mere fact that this occurs, though, is strong evidence of the irregularity of the alumina surface.

Figure 3 shows a typical cross section of a fiber that has been formed by multiple drawing through an Al_2O_3 bath. A layered structure is present in which little or no fusion has occurred between successive layers. The amount of alumina deposited during each pass through the bath is not too uniform, which can be attributed in part to the manual operation.

Figure 4 shows a longitudinal cross section of a $95Al_2O_3$ - 5CaO fiber that has been drawn through the bath five times. The lack of fusion between subsequent passes is again evident in this fiber. Each layer, with the exception of the last, is approximately 0.002 to 0.003 in. (0.051 to 0.076 mm.) thick.

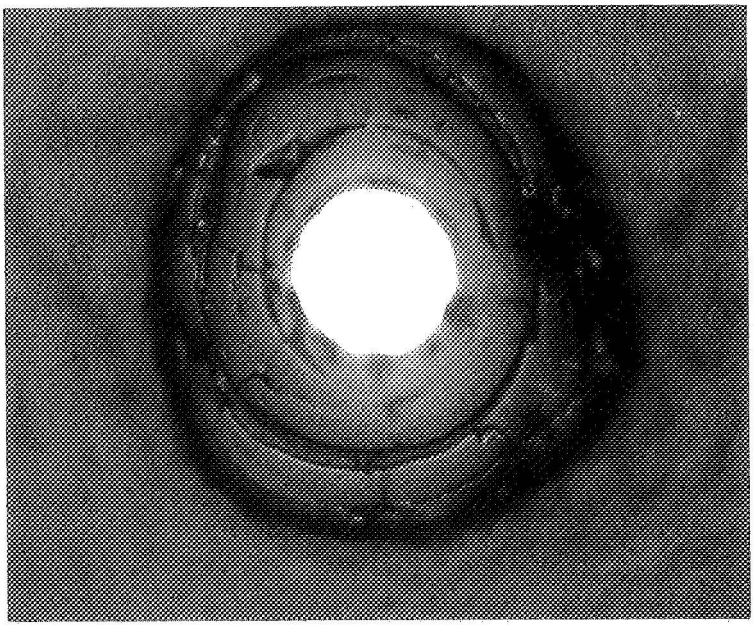
There is a definite tendency in solidification of the oxide to form a dendrite structure with the dendrites oriented radially outwards from the core as is shown in Fig. 5. The grain size is small though, which is a desirable feature. In Fig. 5, in which the sheath is $95Al_2O_3$ - 5CaO, the grains are α-Al_2O_3 and the interdendritic material is β-$CaO \cdot 6Al_2O_3$. Porosity is present in the sheath, the degree of which is hard to distinguish since the oxide is friable and some "plucking" may have occurred during metallographic preparation.

Actual bonding of the core to the sheath is not apparent in Figs. 4 and 5 except in a few spots. In several of the fibers a reaction zone was present at the interface, with small amounts of tungsten being present in the ceramic. Even when these zones were present, separation of the core and ceramic could occur during metallographic preparation of a longitudinal cross section, indicating that the bond needs to be improved.



15X

Figure 2. Coated 5-mil Tungsten Wire



200X

Figure 3. Micrograph of Coated Tungsten Wire Showing Layered Structure of Al_2O_3 Formed by Multiple Drawing

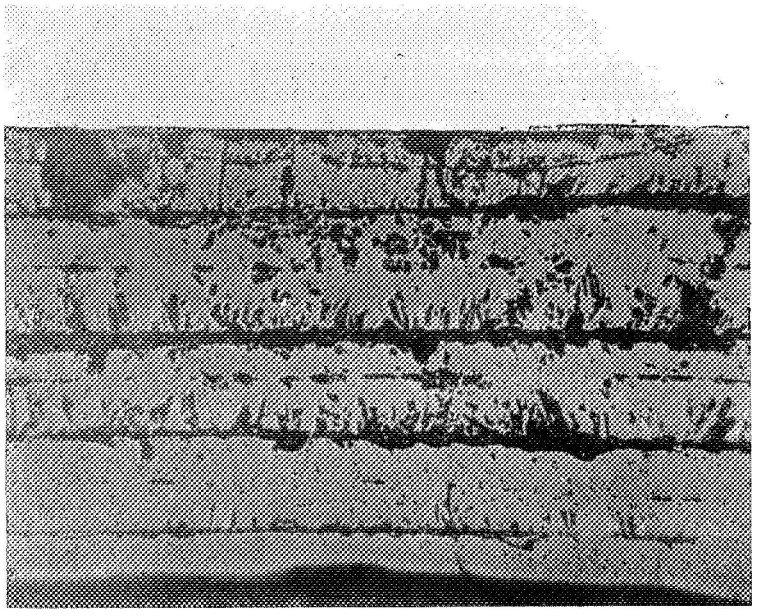


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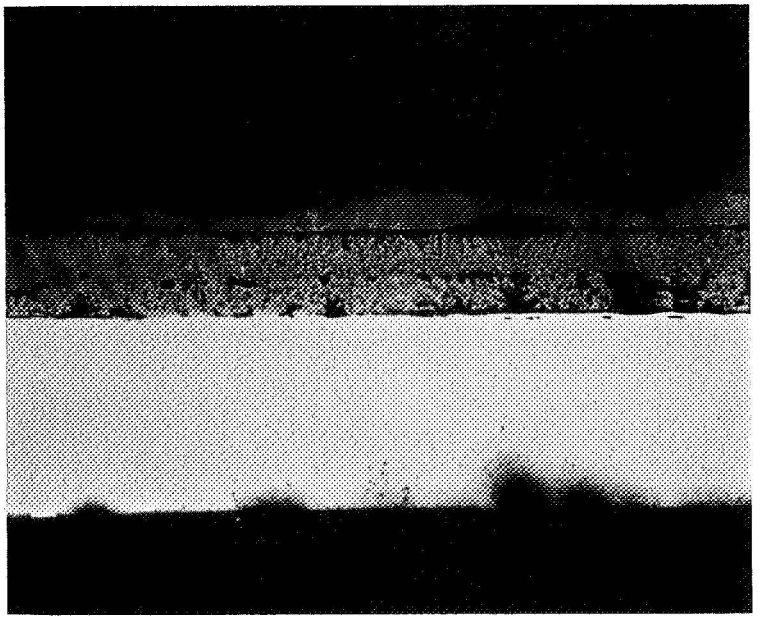
Figure 4. Longitudinal Cross Section of a 95 Al_2O_3 Fiber Drawn Through the Bath Five Times



200X

Figure 5. Cross Section of a 95 Al_2O_3 - 5 CaO Showing Dendrite Coating

2.7 TENSILE TESTS

An Instron Model TT Universal Testing Machine was used to conduct the tensile tests of fibers. The fibers to be tested were first inspected for continuity of coating and cracks using a light microscope at a magnification of 100x. The minimum cross section that would be within the gage length of the inspected fiber was then measured using a filar microscope. Gage lengths of 1/2 and 3 in. (1.27 and 7.62 cm) were used for room temperature and 2000°F (1366°K) tests, respectively. A strain rate of 0.02 in./in./minute was used at room temperature, while that used in the 2000°F tests was 0.05 in./in./minute. The machine was calibrated prior to each test.

The fiber was glued to a grooved brass tab with Hysol Epoxy, being sure that alignment was maintained. Holes in the ends of the tabs allowed the whole assembly to be attached to hooks that were held in the machine with screw-action grips.

Tests at 2000°F (1366°K) required a small slotted furnace to heat the fibers. The height of the furnace was 1-1/2 in. Fiberfrax wool was glued to the tabs and moistened with water to prevent softening of the epoxy during testing. A preload was used in the high-temperature tests so the position of the fiber could be maintained while the furnace was slid into position. The fiber was held in position for 15 seconds prior to testing so it could reach the testing temperature. All tests were conducted in air.

The results of the tensile testing are listed in Table 6. The room-temperature strength of the uncoated tungsten wires are in the neighborhood of a half million psi and there are only minor changes in strength with changing diameter.

Most of the strength tests were conducted on fibers having 5 mil tungsten substrates. The strength of this substrate with no coating fell from an average of 410,000 psi at room temperature to only 5800 psi at 2000°F. The tests were made in air, however, and much of this reduction undoubtedly occurred because of reduction of wire cross section from oxidation

Placing a sheath of either Al_2O_3 or $95Al_2O_3$ - 5CaO around the 5 mil wire substrates by melt drawing resulted in a fiber that was approximately 60% stronger than the uncoated tungsten wire that had been subjected to the same drawing conditions. This was, however, only when the stress for failure was computed on the tungsten cross-sectional area. When the total area

of the fiber was used for the computation, the core-sheath fiber had an appreciably lower tensile strength than the tungsten core.

The strength of wires with coating was considerably higher in the high-temperature tests than the uncoated wires. Again this was believed due to oxidation effects with the oxide sheaths acting as protective coatings to inhibit oxidation of the tungsten.

The number of passes through the melt had little or no effect on the resulting fiber strengths of the multiple-draw fibers. This is shown by the data for the $95Al_2O_3$- 5CaO compositions. In general, the thickness of oxide increased with each pass through the melt. The 5-pass fibers had oxide thicknesses of as much as 0.006 to 0.008 in. (0.15 to 0.20 mm.). The data indicate, however, that even these thick applications failed to contribute to fiber strength.

Some of the $95Al_2O_3$ - 5CaO fibers on a 5 mil substrate were heat treated in vacuum at 1600° C (1873°K) for 24 hours, in an effort to sinter the subsequent layers. No apparent increase in load capacity, either at room temperature or 2000° F was noted.

The last column in Table 6 shows tensile strengths based on the tungsten core carrying the entire load at failure. These values are remarkably consistent. This observation together with the much lower and less consistent tensile values when the strengths are computed for the cross-sectional area of the fiber (tungsten core plus oxide) strongly suggests that the oxide sheath is contributing little, if anything, to the fiber strength. This is not the case, however, for the fibers formed from a core of 1-mil tungsten. The oxide thickness on these specimens was 1.4 and 3.0 mils, respectively. The high loads to failure for these specimens are an indication that the Al_2O_3 sheath, in this case at least, is making an important contribution to the strength of the fiber.

III. DISCUSSION OF RESULTS

Wetting of the tungsten filament by the molten oxide remained a problem throughout the investigation. The best wetting was achieved when the atmosphere in the furnace enclosure was slightly oxidizing. However, complete and consistent coverage of the wire was still not achieved in most trials unless the wire was passed back and forth through the molten oxide bath at least two to three times.

Even when the furnace conditions were such as to promote wetting of the tungsten, the coating was oftentimes beaded. Decreasing the wire diameter from 0.005 to 0.001 inches (0.127 to 0.025 mm.) increased the tendency to form a beaded structure. This can be explained by considering what would happen if a small stream of molten alumina were allowed to flow through an orifice. Surface tension forces pull the stream into small spheres. If a fine filament is placed in the stream, the sphere-forming forces are still present but the spheres would form on the wire with the tendency to form spheres being a function of the size of the filament.

This beading tendency was greatly reduced by passing the wire through the bath at a rapid rate. In so doing a quenching or freezing action resulted in which a layer of oxide froze on the filament. A layered-type structure was readily observed in fibers formed by multiple drawing (see Figs. 3 and 4). The interface between layers is probably a zone of weakness, since the mere presence of the interface shows that complete fusion had not occurred between the layers. Before fibers formed in this way could be used as a matrix reinforcement, it would first be necessary to demonstrate that the required shear stresses could be transmitted across these interfaces. This could probably best be studied by incorporating fibers into actual composites.

Experiments with the 0.005 inch (0.127 mm.) diameter wire indicated a relatively smooth coating could be achieved although several passes were required to build up the sheath. A drawing rate of 2 ft./sec. (0.61m./sec.) gave fairly uniform bead-free coatings on a 0.005 inch (0.127 mm.) wire.

The 0.005 inch (0.127 mm.) wire probably did not reach a temperature higher than about 1500°C (1773°K) during the first pass through the bath. On subsequent passes, the temperature of the tungsten would probably be even less since the thermal conductivity of the alumina is lower than that of tungsten.

To achieve a smooth coating on smaller diameter wires, a faster rate would be required. Using the 2 ft./sec. rate that gave a relatively smooth coating with the 0.005 inch (0.127 mm.) wire, the coating rates for smaller wires would be as follows:

Wire Diameter (inches)	Drawing Rate to Achieve Smooth Coating		Total Time in 1/8" Deep Bath
	ft./sec.	ft./min.	millisec.
0.005	2	120	5.2
0.003	5.6	336	1.4
0.001	25	1500	0.4
0.0005	100	6000	0.1

Although wires as small as 0.001 in. (0.025 mm.) in diameter were coated, the coating on the small-diameter wire was rough and irregular. Mechanical drawing would have been needed to achieve the high speeds required for the very fine diameter, 0.0005 inch (0.013 mm.), wire that was originally proposed as a core material. Mechanization of the process was beyond the scope of this program.

The tensile tests indicated that the strength of the fibers produced with a 5-mil tungsten core was the same as that of the core material. In other words, the oxide sheath did not contribute to the strength which can be ascribed at least in part to the manner in which the coating was obtained and its structure. In the first pass through the bath, a completely continuous coating on the core was not always obtained. Uncoated areas after the first pass were coated in subsequent passes. The fact that fusion was not continuous between each subsequent layer gave rise to discontinuities that ran the length of the fiber. Also, freezing of the alumina was such as to orient the grain structure in the wrong direction for maximum strength; i.e., perpendicular rather than parallel to the fiber axis.

Differences in thermal expansion between alumina and tungsten may be the greatest single factor responsible for the low strengths of the fibers formed on the 5-mil tungsten filaments. The expansion coefficient of alumina is some 40% higher than tungsten. This means that the alumina contracts more than the tungsten during cooling, a condition that would be expected to generate transverse microcracks in the alumina coating or sheath. If the alumina sheath was massive with respect to the tungsten core, as was the case with the fibers formed on 1-mil substrates, the Al_2O_3 sheath should be capable of absorbing the strain from the differential contraction, and no

cracking should be present. Under these conditions the alumina should contribute strength to the fiber which, as indicated in Table 6, is exactly what occurred.

Melt drawing of Al_2O_3 on the small 1/2-mil and 1-mil diameter tungsten wires was found to be extremely difficult by a hand-drawing operation. Mechanization of the process with close control of variables would be essential if satisfactory fibers were to be produced. Even with mechanization, many problems could be anticipated not the least of which is the low breaking loads of these small wires at temperatures in the 1500-2000°C range. In view of these difficulties, it might be preferable to concentrate future efforts on the larger substrates (3 and 5 mil). A 1-mil thick Al_2O_3 coating on filaments of this type should be an excellent diffusion barrier, thereby permitting high-strength, high-density tungsten wire to be used as a reinforcement in heat-resistant alloys. The presence of microcracks and other strength-reducing defects would not be nearly as important in a diffusion-barrier coating as they would be in an alumina layer that was intended to impart high strength.

IV. SUMMARY AND CONCLUSIONS

This investigation was conducted to determine the feasibility of producing a core-sheath fiber of aluminum oxide on a suitable substrate by using a melt-drawing technique. The following conclusions are made based upon the observations made during the course of this study.

1. The presence of an aluminum oxide sheath on a 1-mil tungsten wire increased the load bearing capacity of the wire by as much as a factor of five. On a 5-mil wire an alumina sheath contributed little or nothing to the strength of the wire at room temperature. However, at a temperature of 2000°F, the strength of the 5-mil coated wire was as much as 30 times as strong due to the oxidation protection provided by the coating. The contribution of the alumina to the strength of the 1-mil wire is probably the result of less microcracking resulting from differential thermal contraction on the smaller wire since the oxide to metal ratio was greater than for the 5-mil wire.

2. Available ceramic fibers (mullite and glass) are not suitable substrates for the drawing speeds used, since they melt on contact with the molten oxide.

3. Thoriated tungsten wires serve as satisfactory substrates if they are drawn rapidly through the molten bath in such a way as to freeze a layer of oxide on the wire.

4. Slightly oxidizing conditions are essential in the furnace chamber; otherwise wetting of the tungsten wire does not occur.

5. The speed of drawing must be increased as the wire diameter is decreased. If slow speeds are used, the oxide forms a series of beads on the tungsten wire rather than a continuous sheath.

6. Thickness of the oxide sheath can be increased by repeatedly passing the fiber through the molten oxide bath. However, this procedure gives a layered-type structure with a possibility of weak bonding between layers.

7. Smooth, uniform coatings or sheaths are difficult to achieve on tungsten wires by hand-drawing techniques due to erratic pulling pressures, contact with the melting boat, and centering the wire for an even draw through the boat; production of any substantial quantity of acceptable fibers would

require mechanization to overcome the difficulties mentioned above. A motor-drawn, constant speed drawing system coupled with pulleys for precision alignment would be required for the drawing operation. A multiple bath system would eliminate drawing the wire through the system more than one time.

8. Even with mechanization, tungsten wires with diameters of 0.001 in. (0.025 mm.) or less would probably be unsuitable substrates for melt-drawing operations because of (a) the high drawing speeds required, and (b) the low load-bearing capability of the small wires at the drawing temperatures.

9. The aluminum oxide in the melt-drawn fibers crystallized as dendrites. These dendrites, which grew at right angles to the fiber axis, were less than 5μ in thickness.

10. Addition of CaO, MgO, NiO, Gd_2O_3, Y_2O_3, TiO_2, or SiO_2 to the Al_2O_3 in amounts up to 10 w/o did not improve the fiber-forming properties. However, one composition (95 Al_2O_3 - 5 CaO) gave fibers with a somewhat smoother surface finish.

11. The strongest core-sheath fiber produced during the course of the investigation had a room-temperature strength of 134, 800 psi (95 Kg/mm^2) and a strength of 75, 500 psi (53 Kg/mm^2) at 2000 °F (1367 °K).

V. RECOMMENDATIONS

The exploratory study has demonstrated that the forming of core-sheath fibers of alumina on tungsten is possible by a melt-drawing process. Additional work is needed, however, before the full potential of the process can be realized.

More specifically, the process needs to be mechanized so as to achieve better control of variables and permit longer fibers to be produced. Mechanization should consist of a constant speed drive system, and alignment pulleys for drawing the wire through the molten bath. A multiple bath system would eliminate the necessity of drawing the wire through the system more than one time.

Initial work after mechanization should emphasize alumina-coated tungsten filaments rather than core-sheath fibers. The tungsten filaments, when incorporated into a heat-resistant alloy, would provide the high-temperature reinforcement; the sole purpose of the alumina would be to prevent diffusion of the tungsten into the alloy matrix.

A core-sheath fiber consisting almost entirely of alumina has excellent long-range potential; however, difficult problems are involved in achieving flaw-free structures, and it is quite probable that these problems would require an extensive research effort for their solution.

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TABLE 1. RESULTS OF DIPPING TESTS

Melt No.	Bath Comp.	Batch Mtls. [a]	Bath Temp. °C	Core Mtl. [b]	Core Diam. Mils	Immer. Time Sec	Test Results
8	Al_2O_3	A	2140	W	5	< 1	Uneven wetting
9	Al_2O_3	A	2100	W	5	10	Uneven wetting
					5	20	Discontinuous ctg.
					5	30	Discontinuous ctg.
					20	10	Discontinuous ctg.
					20	20	Discontinuous ctg.
					20	30	Discontinuous ctg.
10	Al_2O_3	B	<2000	W	3	60	Some wetting
					5	60	Some wetting
					20	60	Froze in boat
15	Al_2O_3	C	2200	W	1/2	1	Some wetting
19	Al_2O_3	C	2180	W	1/2	1	Uneven ctg.
20	Al_2O_3	C	2240	W	5	1	Partial ctg.
21	Al_2O_3	C	2200	W	5	1	Ctg. flaked
					20	1	Good wetting
22	Al_2O_3	C	2220	W[c]	1/2	1	Ctg. discontinuous
					10	1	Ctg. discontinuous
					20	1	Ctg. discontinuous
			2200	W[c]	10	5	Ctg. discontinuous
					10	10	Ctg. discontinuous
					10	20	Ctg. discontinuous
23	Al_2O_3	C	2200	W[c]	20	5	Good wetting
					20	10	Discontinuous ctg.
					20	20	Discontinuous ctg.
25	Al_2O_3	C	2150	W	1/2	1	Wire came off
				W	5	1	Some wetting
				W	10	1	Some wetting
				W	20	1	Some wetting
				Mullite	1/2	1	Melted in bath
				Glass	1	1	Melted in bath
27	Al_2O_3	C	2050	W	1/2	1	Discontinuous ctg.
				W	1/2	5	Discontinuous ctg.
				W	1/2	15	Discontinuous ctg.
				W	5	1	Discontinuous ctg.
				W	5	5	Discontinuous ctg.
				W	5	15	Discontinuous ctg.
				Mul. Yarn	1/2	< 1	Melted in bath
				Glass Yarn	1/2	< 1	Melted in bath

TABLE 1 (Continued)

Melt No.	Bath Comp.	Batch Mtls. [a]	Bath Temp. °C	Core Mtl. [b]	Core Diam. Mils	Immer. Time Sec	Test Results
28	Al_2O_3	C	2150	W	1/2	1	Ball at end
					1/2	5	No wetting
					1/2	15	No wetting
					5	1	Good wetting
29	90 Al_2O_3	C	2100	W	1/2	1	No wetting
	10 SiO_2						
32	90 Al_2O_3	C	2050	W	1/2	1	Ctg. beaded
	10 SiO_2	D					
34	95 Al_2O_3	C	2150	W	1/2	1	No wetting
	5 CaO	E			1/2	5	No wetting
					1/2	15	No wetting
					5	1	No wetting
					5	5	No wetting
					5	15	No wetting
35	90 Al_2O_3	C	2200	W	1/2	1	Some wetting
	10 CaO	E					
37	85 Al_2O_3	C	1950	W	1/2	1	Some wetting
	15 CaO	F	1900	W	1/2	1	Some wetting
			1850	W	1/2	1	Some wetting
38	90 Al_2O_3	C	2100	W	1/2	1	Coating balled
	10 CaO	F			1/2	5	Coating balled
					1/2	15	Coating balled
					5	1	Coating balled
					5	5	Fair coating
					5	15	Discontinuous ctg.
			2050	W	5	5	Fair coating
			2000	W	5	5	No coating

[a] A refers to 1/8-in. diam. sapphire rods, B to -325 mesh high-purity alumina powder pressed into pellets, C to Norton 60 mesh RR Alundum, D to -200 mesh silica powder, E to CP calcium carbonate, F the same as E except precalcined at 1200°C.

[b] W signifies thoriated tungsten

[c] Oxidized prior to dipping

TABLE 2. RESULTS OF SINGLE-PASS MELT-DRAWING EXPERIMENTS WITH 5-MIL TUNGSTEN WIRES

Melt No.	Bath[a] Comp.	Bath Temp. °C	Pretreatment	Furnace[b] Atmosphere	Test Results
43	95 Al_2O_3 5 CaO	2100	None	Vac.	No coating
44	95 Al_2O_3 5 CaO	2100	None	Ar	Con't but uneven ctg.
45	95 Al_2O_3 5 Gd_2O_3	2200	None	Ar	Some areas coated
46	95 Al_2O_3 5 Y_2O_3	2200	None	Ar	Fast pull: continuous ctg. Slow Pull: beaded ctg.
49	95 Al_2O_3 5 CaO	2100	None	Ar	Uneven ctg.
50	95 Al_2O_3 5 CaO	2100	Hot NaOH	Ar	Partly coated
52	95 Al_2O_3 5 CaO	2100	Etched	Ar	No coating
63	90 Al_2O_3 10 NiO	2050	None	Ar	Reacted with boat
65	99.5 Al_2O_3 0.5 NiO	2200	None	Ar	No wetting
67	90 Al_2O_3 10 SiO_2	2200	Al_2O_3-SiO_2 baked on	Ar	Partly coated
68	90 Al_2O_3 10 CaO	2200	Al_2O_3-CaO baked on	Ar	Partly coated
69	90 Al_2O_3 10 CaO	2150	Al_2O_3-CaO baked on	Ar	Coating beaded
70	90 Al_2O_3 10 CaO	2200	None	Ar	Partly coated

[a] Al_2O_3 added as 60 mesh RR Alundum, CaO as calcined CP $CaCO_3$, others as >99.5% powders.

[b] Vacuum 10^{-3} torr; Ar is tank argon, unpurified.

TABLE 3. RESULTS OF MULTIPLE-PASS MELT-DRAWING EXPERIMENTS WITH HIGH-PURITY ALUMINA

Melt No.	Bath Temp. °C	Wire Diam. mils	No. of Passes	Test Results
74	2200	5	11	Heavy, rough but continuous ctg.
75	2200	1/2	0	Wire broke
76	2250	1/2[a]	1	Wire broke on second pass, ctg. formed beads on wire
77	2200	1/2[b]	0	Wire broke
79	2200	5	20	Discontinuous ctg.
84	2200	1	0	Wire broke
89	2200	5	25	Ctg. continuous, uneven thick.
91	2200	5	20	Heavy, rough ctg.
92	2200	5	10	Fairly uniform ctg.
93	2200	5	5	Heavy, rough ctg.
94	2200	5	20	Fairly smooth ctg.
96	2200	1	1	Wire broke, ctg. in spots
143	2200	3	5	Ctg. on certain areas
146	2200	3	5	Ctg. form beads on wire
158	2200	1	5	Ctg. on certain areas
159	2200	1	10	Fairly uniform ctg.
160	2200	1	5	Coating beaded
161	2200	1	5	Coating beaded

[a] Supported by 5 mil W wire. Both wires went through boat.

[b] Supported by 20 mil W wire. Both wires went through boat.

TABLE 4. RESULTS OF MULTIPLE-PASS MELT-DRAWING EXPERIMENTS WITH 95 Al_2O_3 - 5 CaO

Melt No.	Bath Temp. °C	Wire Diam. mils	No. of Passes	Test Results
99	2200	5	4	Fairly uniform ctg.
102	2200	5	20	Fairly smooth ctg; no increase in diam. after 5 passes
103	2200	1	0	Wire broke
108	2200	1	10	Coating beaded
109	2200	1	10	Coating beaded
110	2200	1	10	Coating beaded
111	2200	5	5	Fairly smooth ctg.
123	2200	5	5	Smooth regions, beaded regions
124	2200	5	10	Smooth coating
125	2200	5	5	Smooth and rough regions
131	2200	3	3	Coated on one area only
132	2200	3	10	Wire broke
153	2200	1	5	Coated in spots only
158	2200	1	5	Heavy ctg. in some areas
162	2200	5	5	Fairly smooth ctg.
163	2200	5	5	Uneven ctg.
164	2200	5	5	Fairly smooth ctg.
165	2200	5	5	Good coating
166	2200	5	5	Discontinuous coating
167	2200	5	5	Good coating on some areas
169	2200	5	2[a]	Heavy, uneven coating
170	2200	5	5	Heavy coating, some areas beaded

[a]Fast drawing speed

TABLE 5. RESULTS OF MULTIPLE-PASS MELT-DRAWING EXPERIMENTS WITH BATH COMPOSITIONS OTHER THAN Al_2O_3 or 95 Al_2O_3-5CaO

Melt No.	Bath Comp.	Bath Temp.	Wire Diam.	No. of Passes	Test Results
73	90 Al_2O_3 10 CaO	2200	5	4	Both smooth and beaded areas
144	90 Al_2O_3 10 CaO	2200	3	15	Coating beaded
126	95 Al_2O_3 5 MgO	2200	5	5	Smooth ctg. on some areas
133	95 Al_2O_3 5 MgO	2200	3	5	Heavy ctg. on some areas
141	95 Al_2O_3 5 MgO	2200	3	3	Ctg. on some areas only
134	90 Al_2O_3 10 MgO	2200	3	5	Ctg. on some areas only
135	90 Al_2O_3 10 MgO	2200	3	5	Heavy ctg. in some areas
129	95 Al_2O_3 2.5 MgO 2.5 CaO	2150	5	5	Thin, even coating
130	95 Al_2O_3 2.5 MgO 2.5 CaO	2100	5	10	Smooth thin coating
115	90 Al_2O_3 10 Gd_2O_3	2200	5	5	Ctg. on some areas only
117	90 Al_2O_3 10 Gd_2O_3	2200	5	3	Ctg. on some areas only
121	95 Al_2O_3 10 TiO_2	2200	5	10	Heavy uneven ctg.

TABLE 6. RESULTS OF TENSILE TESTS ON COATED AND UNCOATED WIRES

Type of Specimen	Test Temp. °F	Load at Failure Lbs.	Stress in Fiber at Failure psi	Stress in Tungsten Wire at Failure psi[a]
1/2 mil wire, as rec'd	70	0.09	--	470,000
	70	0.09	--	470,000
1 mil wire, as rec'd	70	0.375	--	477,000
	70	0.375	--	477,000
3 mil wire, as rec'd	70	2.48	--	359,000
	70	2.48	--	359,000
5 mil wire, as rec'd	70	7.30	--	370,000
	70	8.85	--	450,000
	2000	0.86	--	4,400
	2000	1.42	--	7,250
5 mil wire, exposed to drawing conditions	70	2.60	--	115,000
	70	5.80	--	270,000
5 mil wire, coated with Al_2O_3	70	5.40	33,500	274,000
	70	5.22	20,300	265,000
	2000	2.90	37,700	147,000
	2000	2.45	26,400	125,000
5 mil wire, coated with 95 Al_2O_3 - 5 CaO	70	6.78[b]	130,450	344,000
	70	6.60[b]	54,300	335,000
	70	6.37[c]	75,100	323,000
	70	6.40[c]	63,900	325,000
	70	6.10[d]	48,000	310,000
	70	6.00[d]	134,800	304,000
	70	6.20[e]	60,000	315,000
	70	6.52[e]	96,500	331,000
	2000	2.55[b]	16,200	130,000
	2000	2.64[b]	17,000	134,000
	2000	2.60[e]	75,500	132,000
1 mil wire, coated with Al_2O_3	70	0.80	72,000	1,015,000
	70	2.00	49,800	2,540,000

[a] Based on tungsten carrying entire load at time of failure

[b] Coated by 5 passes through melt

[c] Coated by 4 passes through melt

[d] Coated by 3 passes through melt

[e] Heat-treated after coating for 24 hours at 1600 °C in vacuum

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