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PREPARATION OF FIBERED CERAMICS BY MECHANICAL DEFORMATION

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16. Abstract

Preparation of ceramic fibers by extrusion of ceramic particles in a metal matrix is described. Various oxides in the form of powder or spheres were used as the starting material. Extrusion was carried out at temperatures of 3600° or 4000° F (1982° or 2204° C). Fibers of zirconium oxide, hafnium oxide, and thorium oxide were produced by single extrusion. Reextrusion of fibers resulted in further reductions in their cross section and a corresponding increase in length. Fibers were removed from the tungsten and examined for grain size and grain orientation by X-ray diffraction. Fiber aspect (length to diameter) ratios were compared to predict values based upon the extrusion ratio.

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SUMMARY

Preparation of ceramic fibers by extrusion of ceramic particles in a metal matrix was investigated. Extrusion was carried out at 3600° or 4000° F (1982° or 2204° C) using nominal extrusion ratios of 20 or 36. Zirconium oxide, hafnium oxide, and thorium oxide were successfully fibered using tungsten as the matrix. Attempts to fiber a magnesia-alumina spinel and aluminum oxide were unsuccessful. Of the successful fibered oxides, best results were obtained with zirconium oxide. Some of the zirconium oxide fibers had average aspect ratios (length to diameter) as high as 77. Reextrusion of zirconium oxide fibers resulted in fibers with aspect ratios as high as 640.

Removal of the fibers from the tungsten matrix was accomplished by electrochemically removing the tungsten and thereby liberating the fibers. After removal from the matrix the fibers were examined for grain size and crystallographic orientation by X-ray diffraction. Fibers were found to have a tenfold decrease in grain size, from the 40- to 100-micrometer size in the starting material to 1 to 5 micrometers in the fiber. Thorium oxide fibers were found to have a preferred orientation to the grains, with the (100) planes parallel to the fiber axis.

INTRODUCTION

One way to make high-strength materials is by using strong fibers to reinforce a relatively weak matrix. The fibers used must have high strength at the application temperature. They should also be lightweight and resistant to reaction with their surroundings. Metal and metalloid fibers which are currently available only partly meet the requirements. Generally, the metal fibers such as tungsten or molybdenum, although strong, are also high in density and reactive. Metalloid fibers such as carbon or boron

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suffer because of their reactivity at elevated temperature. Ceramic fibers offer an attractive alternate. They have high thermal stability and are relatively nonreactive. In addition, they have very high melting temperatures and low weight per unit volume. The major obstacle to increased research on composites using ceramic fibers is the lack of suitable ceramic fibers. Glass and quartz fibers are among the few commonly available, but they do not have the necessary high-temperature strength.

Investigations at NASA (refs. 1 to 3) have shown that high-melting-point ceramic fibers can be produced "in situ" during hot extrusion of a composite of metal and metal-oxide powders. In addition, it was shown that the elevated-temperature mechanical properties of these composites were superior to the base metal in which no oxides were present. These results were obtained for composites of several different oxides in tungsten, columbium, or tantalum. Refractory metals were used as the matrix because fibering of the oxides had to be performed at high temperature. The usable matrix metals were therefore limited to those metals whose melting points were higher than the deformation temperature of the oxide. This limited the number of matrix metals which could be used. For example, nickel and its alloys, which are highly desirable matrix materials for composites, melt at temperatures of 2600° to 2700° F (1427° to 1482° C). This is too low a temperature for the deformation of most oxides to take place. In order to utilize oxide fibers produced by the "in situ" method as reinforcement in lower-melting-point metals they would first have to be produced by deformation in a higher-melting-point metal. After formation, the fibers could then be removed from the high-temperature metal and incorporated into any matrix desired. The high-melting-point matrix could be considered a sacrificial or "carrier" metal.

Oxide fibers produced in past studies (refs. 1 and 3) had aspect ratios (length to diameter, L/D) which were shorter than desirable for use as reinforcing fibers in composites. The objective of the present program was to produce polycrystalline, highly refractory, oxide fibers with aspect ratios suitable for use as reinforcement fibers. Aspect ratios of at least 100 and/or actual lengths of at least 2.5 centimeters were desired, along with high strength at elevated temperature. In addition, the development of a method for the recovery of intact fibers from the matrix for measurement of mechanical and physical properties was important.

Billets of tungsten powder, zirconium oxide, hafnium oxide, thorium oxide, aluminum oxide, magnesia-alumina spinel, or hafnium nitride were prepared and canned in heavy-walled molybdenum extrusion cans. These were extruded at 3600° or 4000° F (1982° or 2204° C). Extrusion ratios were nominally 20 and 36. In some cases, extruded rod was reextruded for a total reduction ratio as high as 1000. The resulting composites were examined metallographically. Fibers were removed from the tungsten by electrochemically dissolving away the metal. The recovered fibers were measured to determine their aspect ratio, and individual fibers were subjected to X-ray diffraction examination, chemical analysis, and determination of room-temperature tensile strength.

MATERIALS, APPARATUS, AND PROCEDURE

Billet Preparation and Extrusion

Extrusion billets of the composition listed in table I were prepared by dry blending mixtures of tungsten powder and metal oxides of known particle size. The particle-size range of the starting materials is listed in table II. Blends were hydrostatically cold pressed at 50 000 psi (349×10^6 N/m^2). Sintering was done in hydrogen for 4 hours at 3200° F (1760° C) for those billets containing aluminum oxide or magnesia-alumina spinel and at 4200° F (2316° C) for the other billets.

Two different billet configurations were used. One configuration, shown in figure 1, consisted of a core of tungsten-hafnium carbide alloy surrounded by an annulus of the blend of tungsten and metal oxide.

The other billet configuration was simply a right cylinder of tungsten and metal oxide without a core. Both types of billet were canned in heavy-wall, 1/4 inch (0.635 cm), molybdenum extrusion cans and welded shut in a vacuum chamber.

The cored billet was used to provide a core of high stiffness along with which the tungsten - metal-oxide mixture could be extruded. Previously (refs. 2 and 3), it had been found that the maximum amount of oxide fibering occurred at the composite-can interface and in those portions of the composite in close proximity to restraining surfaces such as the extrusion tooling. In the cored billets, the annulus of composite was positioned in that portion of the billet where near-maximum deformation would occur.

The billets containing aluminum oxide or magnesia-alumina spinel were extruded at 3600° F (1982° C). All others were extruded at 4000° F (2204° C). Extrusion ratios were nominally 20 or 36, although the actual ratios determined from the finished rod varied (table I). Figure 2 shows samples of extruded rod, some of which were as much as 65 inches (165 cm) long. About 70 percent of the length was usable extruded composite, while the remainder was nose and butt scrap. A more detailed description of the canning and extrusion procedure has been reported in references 3 and 4.

Reextrusion

Reextrusion of tungsten-zirconium oxide fiber composites was done by using the same general procedure. Cut lengths of previously extruded rod were packed in molybdenum cans so that the long axis of the rod was parallel to the extrusion direction. The spaces between the composite rods were filled with molybdenum; the can was welded shut and the canned rods extruded at 4000° F (2204° C) using nominal extrusion ratios of 20 or 36.

Fiber Recovery

Recovery of individual fibers from extruded rod (fig. 3) was done in a two-step process. First, the outer molybdenum case surrounding the composite was removed chemically in a hot solution of 25-percent nitric acid. This exposed the tungsten and oxide fibers. In the second step, the tungsten was removed from around the oxide fibers electrochemically. The composite was suspended in a 10-percent solution of potassium hydroxide. A current density of 3.32 amperes per square inch (0.515 A/cm^2) at 30 volts was used. The cathode and the anode suspension basket were platinum. As the oxide fibers were freed from the tungsten matrix, they dropped to the bottom of the reaction vessel, were collected on filter paper, then were water washed and air dried.

Fiber Evaluation

Fibering, the degree of oxide elongation, was determined by measuring the aspect ratio of the fibers. Individual fibers were also examined under the electron microscope, by X-ray diffraction, by chemical analysis, and their room-temperature tensile strength determined.

Aspect ratio. - The aspect ratio of fibers made from powders was measured from photographs made of the oxide fibers in the tungsten matrix. Three random areas were marked out on each photograph. The length and diameter of each fiber in the area was measured. The area occupied by all fibers smaller than a given aspect ratio was plotted as a function of the total area occupied by all the fibers measured. The aspect ratio at 50 percent was taken as the average aspect ratio of the fibers in a given section. Reference 3 contains a more detailed description of the aspect ratio determination.

The aspect ratio of fibers made from spheres, which were larger than the powders, was determined by measuring discrete fibers after they had been removed from the tungsten matrix. All the fibers from an extruded section of rod 5.08 centimeters long were collected. These fibers were examined under a microscope and those which were obviously pieces of longer fibers were discarded. The remaining fibers were measured by projecting their image on a screen where they were measured with a metric scale, and their aspect ratios were averaged.

Aspect ratios of fibers which had undergone reextrusion were difficult to determine. The fibers were removed from the extruded rod, but because of equipment limitations the longest extruded section from which fibers could be electrochemically dissolved was 5.08 centimeters. Theoretically, the fibers should have been longer than this. Therefore, full-length fibers were not recovered. Because of this, aspect ratios were arrived at by measuring the diameter of the fibers and calculating their length and aspect ratio range from the known size range of the starting particles. Prior to their incor-

poration into the extrusion billets, the ceramic powders and spheres had been separated into fractions of known particle size (table II). It was assumed that the starting particle was a sphere and the resulting fiber a right cylinder having square ends and a circular cross section, and that the volume of the particle remained constant.

Comparison of the actual fiber aspect ratio obtained to that expected from the extrusion ratio used provided a further measure of fibering. The relation between fiber aspect ratio and extrusion ratio was approximated by assuming deformation of a sphere into a right cylindrical fiber and by assuming that both the billet and the metal oxide deform equally using

$$\frac{L}{D} = \frac{2}{3} r^{3/2}$$

where

L/D fiber aspect ratio (i.e., ratio of fiber length to fiber diameter)

r actual extrusion ratio (i.e., ratio of initial cross-sectional area of canned billet to cross-sectional area of extruded rod)

Tensile strength. - Determination of the room-temperature tensile strength was done by using a constant-speed, screw-driven tensile machine. The oxide fibers were tested at a crosshead speed of 0.05 inch per minute (0.127 cm/min). Before testing, the fibers were attached to copper grip tabs with epoxy adhesive. While the epoxy cured, the fiber was held in a special fixture to prevent breakage. The fixture was not removed until after the fiber was mounted in the tensile machine. Once the test had been made, the cross-sectional area of the fiber was calculated from the measured dimensions of the fiber segment in the epoxy. A calibrated, split image eyepiece was used to make the measurement.

RESULTS

Fibering

Thirteen billets of various composition were prepared for single extrusion (table I). Of these, 11 were extruded successfully. The only exceptions were those billets containing 20-volume-percent hafnium nitride. Fibering of the oxides in the billets which were successfully extruded varied. The cored billets containing magnesia-alumina spinel powder in tungsten, and aluminum oxide spheres in tungsten, showed signs of melting and possible reaction between the tungsten and the oxide. Metallographic samples of the extruded rod showed islands of spinel or aluminum oxide in a matrix of tung-

sten. There was no fibering or elongation of the oxides. In some cases, the oxide penetrated between the tungsten particles. Corners of the oxide islands were rounded, indicating that some melting had taken place.

Aluminum oxide. - Aluminum oxide powder (particle size, 105 to 125 μm) in tungsten was extruded at a ratio of 17 at 3600° F (1982° C) to form elongated particles similar in appearance to grains of rice. Their average aspect ratio was 9 (table III(a)). This material, in the form of particles extracted from the matrix, is shown in figure 4(a). Figure 4(b) shows the same particles before they were removed from the tungsten matrix. The particles are irregular in shape and show considerable porosity (fig. 4(c)).

Thorium oxide. - Fibers of thorium oxide were formed from 3- to 5-micrometer powder during extrusion at 4000° F (2204° C). Extracted fibers formed at an extrusion ratio of 16, using a cored billet, are shown in figure 5. The average aspect ratio of these fibers is 16, although there are some fibers which appear to be considerably longer. Figure 5(a) shows some of the longer fibers recovered from this extrusion, while figure 5(b) shows a photomicrograph of these fibers before extraction from the matrix. There are many short fibers present, and it is these that contribute to the low average aspect ratio.

Thorium oxide fibers were also made at an extrusion ratio of 31 at 4000° F (2204 C). The average aspect ratio of these oxides was 5. There were very few long fibers. Because of the poor fibering in this extrusion, no attempt was made to remove the fibers from the matrix for further examination.

Hafnium oxide. - Hafnium oxide fibers produced by extrusion of 3- to 5-micrometers hafnium oxide powder in tungsten are shown in figure 6. The composite was extruded at a reduction ratio of 16 and a temperature of 4000° F (2204° C). Figure 6(a) shows individual loose fibers. Figure 6(b) shows the fibers before their removal from the tungsten matrix. The average aspect ratio of the hafnium oxide fibers, measured while still in the matrix, was 29 (table III).

Zirconium oxide. - Extracted zirconium oxide fibers are shown in figure 7. These fibers were made from calcium-stabilized zirconium oxide powder whose particle size fell in the range from 105 to 125 micrometers. Extrusion of the cored billet was carried out at 4000° F (2204° C) and an extrusion ratio of 17. These fibers had an average aspect ratio of 59. Loose fibers from this extrusion are shown in figure 7(a), while figure 7(b) shows the fibers still embedded in the tungsten matrix. The fibers were 45 to 70 micrometers in diameter and 0.25 to 0.35 centimeter long. The internal structure of these fibers, as well as the zirconium oxide fibers which will be discussed subsequently, consisted of slightly elongated grains oriented more or less parallel to the long axis of the fiber. There were particles of tungsten or tungsten oxide in some of the grain boundaries, but the fibers appeared to be crack free with very little porosity.

Zirconium oxide fibers produced from spheres with an average diameter between

1190 and 1410 micrometers are shown in figure 8. These fibers were formed during extrusion at 4000° F (2204° C) at an extrusion ratio of 17. Their average aspect ratio was 23. Most of the fibers were about 600 micrometers in diameter and some were as much as 2.5 centimeters long, as shown in figure 8(b). Those fibers with untapered ends are probably not full length fibers. They are probably segments of fibers which had been cut or broken during extraction from the matrix.

Fibers of zirconium oxide prepared from similar spheres, but using a higher extrusion ratio (32), are shown in figure 9. These were extruded at 4000° F (2204° C) and had an average aspect ratio of 77. They were about 300 micrometers in diameter and fibers up to 4.45 centimeters long were measured.

Two billets of zirconium oxide spheres in tungsten were prepared without the tungsten alloy core used in the previous billets. The fibers which were produced at an extrusion ratio of 16 had an average aspect ratio of 57. Figure 10 shows fibers made from a similar billet, but extruded at a ratio of 33. These fibers had an average aspect ratio of 50. Both billets had been extruded at 4000° F (2204° C).

Reextruded zirconium oxide fibers are shown in figures 11 to 13. These fibers had been originally produced by the extrusion of powder or spheres at nominal reductions of 20 or 36. Subsequent reextrusion resulted in total reduction ratios from 260 to 1000. The total reduction undergone by each sample and the fiber aspect ratio for each sample are listed in table III(b).

Fibers were produced which had aspect ratios as high as 640. The physical dimensions of the fibers varied depending on the size range of the starting metal oxide and the total amount of reduction. Some fairly long fibers were produced. For example, the fibers which had undergone a total reduction of 520 were about 100 micrometers in diameter (fig. 11). Some of these fibers were as much as 3.8 centimeters long.

X-Ray and Chemical Analysis

A limited number of oxide fibers and the starting materials from which they were made were subjected to examination by X-ray diffraction and chemical analysis. A summary of the results is presented in table IV.

These results show that during extrusion the grain size of the zirconium oxide, as determined by X-ray diffraction, was reduced from 40- to 100-micrometer size range in the starting spheres to 1 to 5 micrometers in the fibers. Final grain size of the fibers made from the powdered oxide were in the same size range.

The starting spheres of zirconium oxide had a mixed monoclinic and cubic crystal structure. After extrusion, the resulting fibers were monoclinic in crystal structure.

Zirconium oxide fibers which were reextruded for a total reduction ratio of as much as 1000 had a grain size in the 1- to 3-micrometer range. Several samples of reex-

truded fibers exhibited mixed cubic and monoclinic crystal structure.

Some portions of both the single- and double-extruded fibers had second-phase materials at the grain boundaries, as detected by examination in the electron microscope. Chemical analysis indicated that the only impurity present in the fiber was tungsten. Some of the tungsten may have been on the surface or it may have been trapped in the fibers during extrusion. This would account for the second phase detected. The zirconium oxide fibers were found to have a random crystallographic orientation.

Thorium oxide fibers produced by extrusion in tungsten were also examined. The interesting fact here is that there was some preferred orientation to crystallographic planes in the fiber. While not detected throughout the fiber, a significant number of grains were found by X-ray diffraction to have their (100) planes parallel to the fiber axis. As in the case of the zirconium oxide fibers, tungsten was found as a second phase in the thorium oxide fibers.

Tensile Strength

A limited number of zirconium oxide fibers produced by single extrusion were tested for room-temperature tensile strength. The fibers were found to have tensile strengths of from 166 to 706 psi (1.14×10^6 to 4.87×10^6 N/m^2). The reason for these low values is not known. The fibers may have been damaged during extraction from the matrix or during the mounting operation before tensile testing.

Tensile tests, at room temperature, on fibers of zirconium oxide which had been produced by reextrusion were somewhat better. These fibers were found to have room-temperature tensile strengths in the range of 4000 to 6600 psi (27.58×10^6 to 45.51×10^6 N/m^2).

DISCUSSION

Fibering

Results of this investigation have shown that ceramic fibers of usable length and high aspect ratio can be made by mechanical deformation of ceramic particles in a metal matrix. Fibers of zirconium oxide, hafnium oxide, and thorium oxide were made from irregularly shaped particles ranging in size from 125 to 3 micrometers. In addition, fibers were made from polycrystalline spheres of zirconium oxide which were from 1190 to 1410 micrometers in diameter. The fibers produced by extrusion of oxides mixed with tungsten varied from irregularly shaped crystallites of hafnium oxide (fig. 6) to long, needle-like fibers of zirconium oxide (figs. 7 to 10).

The ability to fiber the oxides varied. Generally speaking, the zirconium oxide fibered best, while hafnium oxide and thorium oxide followed, in that order. Aluminum oxide and magnesia-alumina spinel did not fiber. The spinel melted during extrusion even though the temperature used, 3600° F (1982° C), was selected to be below the melting point of the oxide, 3875° F (2135° C). Some localized temperature increase due to heat of deformation could have occurred during extrusion. Another possibility is that impurities and/or deviation from stoichiometry in the spinel could have lowered the melting point.

Aluminum oxide, both in the form of high-purity powder and as lower-purity spheres, did not fiber. The spheres melted during extrusion at 3600° F (1982° C). This again could have been due to heat of deformation, but more likely was due to the presence of silicon, as silica, detected as an impurity in the spheres.

High-purity aluminum oxide, when extruded at 3600° F (1982° C), formed porous agglomerates not unlike rice in appearance (fig. 4). The problem of nonfibering of aluminum oxide was encountered previously (ref. 3) when it was extruded using columbium as the matrix. At that time, it was not certain whether the low stiffness of the columbium was the reason for the nonfibering or whether the crystal structure of the oxide, which is hexagonal close packed, was responsible. Since tungsten is so very much stiffer than columbium and fibering still did not occur, it would seem that the limited number of slip systems available in aluminum oxide limit its deformability.

Fibering of zirconium oxide, hafnium oxide, and thorium oxide was successful. The degree of success was evaluated by determining the aspect ratio of the fibers produced. The aspect ratio of the fibers could then be compared to the expected aspect ratio calculated from the known reduction ratio. This is shown in figure 14 and gives some indication of the success of fibering the various oxides. The line is a calculated value of aspect ratio as a function of extrusion ratio mentioned previously in the MATERIALS, APPARATUS, AND PROCEDURE section.

An examination of figure 14 shows that the zirconium oxide fibered best. Single extrusion of zirconium oxide in tungsten at 4000° F (2204° C) and an extrusion ratio of 16 resulted in fibers whose average aspect ratio was 59. The calculated aspect ratio for fibers extruded at an extrusion ratio of 16 is 43.

Fibers produced at an extrusion ratio of 32 were expected to have an aspect ratio of 120. Actually, the highest average aspect ratio of fibers produced at or near this extrusion ratio was 77 for zirconium oxide spheres extruded in a cored billet (WZ-4). The difference between the expected aspect ratio and the observed aspect ratio may be due to several factors. As mentioned previously, it was assumed that the starting particles were fully dense spheres which were deformed into fully dense right cylinders with square ends. It is only in the case of the very long fibers that this shape is approximated. It was also assumed that the metal and the oxide deformed uniformly during extrusion. It has been shown (ref. 2) that this is not necessarily true. Depending upon the

relative stiffness or deformability of the metal and the oxide it is possible to have the metal flow around the particles resulting in less deformation than expected.

The importance of the relative stiffness of metal and oxide can also be seen from figure 14. Zirconium oxide, hafnium oxide, and thorium oxide powder - tungsten composites were all extruded at about 16 at 4000° F (2204° C). Zirconium oxide fibers had an average aspect ratio of 59, as compared to an average aspect ratio of 29 for hafnium oxide and 16 for thorium oxide. The melting points of these oxides, and presumably the optimum deformation temperature, increase in the same order. This would indicate that the zirconium oxide deformability more nearly matched that of the tungsten at the extrusion temperature. The thorium oxide, which fibered least, allowed the tungsten to flow around it and did not fiber as well.

While some of the oxide fibers made by single extrusion had high aspect ratios, none of them exceeded or even approached the desired aspect ratio of 100. In order to accomplish this, it was necessary to reextrude some of the zirconium oxide - tungsten composites. Reextrusion was successful in producing oxide fibers having aspect ratios as high as 640 (RX-1 - WZ-5). The fibers produced by reextrusion were long and uniform in diameter. Intact fibers as much as 4 centimeters long were recovered from rod samples 5.1 centimeters long.

It is also apparent from figure 14 that reextrusion was not as successful as expected. The average aspect ratio of the reextruded fibers was considerably below the expected aspect ratio. The reasons for this are probably the same as for the differences noted in the case of the single extrusions. The effect of mismatch of matrix-oxide deformability is even more pronounced. The samples used for reextrusion were sealed in molybdenum extrusion cans as were the single extrusions. In the reextrusions, however, the space between the composite rods was filled with molybdenum. Since molybdenum is much less stiff than tungsten at 4000° F (2204° C), the pressure to cause extrusion was less. The pressure on the composites in the can was then also less, which could have resulted in less deformation of the oxide than was expected.

The ability to fiber zirconium oxide in cored and uncored billets was also compared in figure 14. Cored billet WZ-4 and uncore billet WZ-7 were extruded at ratios of 32 and 33, respectively. The fibers from these billets had average aspect ratios of 77 and 51. However, cored billet WZ-3 and uncored billet WZ-6, which were extruded at ratios of 17 and 16, showed the reverse order of fibering. The cored billet (WZ-3) contained fibers whose aspect ratio was 23, while the uncored billet (WZ-6) yielded fibers with an average aspect ratio of 57. While the results are not conclusive, it would appear that differences in billet configuration, as used in this investigation, had little effect on fibering of the oxides.

SUMMARY OF RESULTS

Elevated-temperature deformation of zirconium oxide, hafnium oxide, aluminum oxide, magnesia-alumina spinel, thorium oxide, and hafnium nitride powder or spheres in tungsten to produce ceramic fibers was investigated using extrusion as the working method. The results of this investigation may be summarized as follows:

1. Zirconium oxide, hafnium oxide, and thorium oxide particles were mechanically deformed into fibers by extrusion at elevated temperature using a high-stiffness metal (tungsten) as the carrier. Zirconium oxide yielded the best results. Fibers having an actual measured length of 3.8 centimeters and an average aspect ratio of 400 were produced by double extrusion for a total reduction ratio of 1000 at 4000° F (2204° C).

2. Individual oxide fibers were removed and recovered from the tungsten matrix by electrochemically dissolving the tungsten in potassium hydroxide. The fibers were found to have a smaller grain size than was present in the starting material; however, the deformation did not result in fibers of increased tensile strength. The best fibers had room-temperature tensile strengths of less than 7000 psi (48.26×10^6 N/m^2). The zirconium oxide starting material had a grain size of 40 to 100 micrometers. After extrusion at 4000° F (2204° C), the grain size was reduced to 1 to 5 micrometers in the fibers. Fibers of thorium oxide showed some preferred crystallographic orientation to the grains, with their (100) planes parallel to the fiber axis.

3. Differences in billet configuration used in this investigation had little effect on the fibering of oxides. Fibers from zirconium oxide spheres, extruded at ratios of 17 and 32 in special cored billets, had average aspect ratios of 23 and 77, respectively. Fibers from extrusions of uncored billets at extrusion ratios of 16 and 33 had average aspect ratios of 57 and 51.

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TABLE I. - SUMMARY OF EXTRUSION BILLET COMPOSITION

AND EXTRUSION RATIOS

Billet	Nominal billet composition				Extrusion ratio	
	Metal	Vol. % metal	Additive	Vol. % additive	Nominal	Actual
WZ-3[a]	Tungsten	90	ZrO_2	10	20	17
WZ-4[a]	↓	90	↓	10	36	32
WZ-5		80		20	20	17
WZ-6[a]		90		10	20	16
WZ-7[a]		90		10	36	33
WH-1		80	HfO_2	20	20	16
WT-1		↓	ThO_2	↓	20	16
WT-2			ThO_2		36	31
WN-1			HfN		20	(b)
WN-2			HfN		36	(b)
WA-1		↓	Al_2O_3	↓	20	17
WA-2[a]		90	Al_2O_3	10	↓	16
WX-1		80	$MgO \cdot Al_2O_3$	20		16
RX-1		--	ZrO_2 fiber	--		16
RX-2	↓	--	ZrO_2 fiber	--	36	32

[a]Spheres.

[b]Extrusion not complete.

TABLE II. - PARTICLE SIZE OF

STARTING MATERIAL

Material	Particle size, μm
Tungsten powder	5 to 7
ZrO_2 spheres	1190 to 1410
ZrO_2 powder	105 to 125
HfO_2 powder	3 to 5
ThO_2 powder	3 to 5
Al_2O_3 powder	105 to 125
HfN powder	3 to 5
$MgO \cdot Al_2O_3$ powder	105 to 125
Al_2O_3 spheres	1190 to 1410

TABLE III. - ASPECT RATIO OF EXTRUDED CERAMIC FIBERS

(a) Single extrusions

Billet	Ceramic	Actual extrusion ratio	Average aspect ratio, L/D	Measurement method
		Cored billets		
WZ-3	ZrO_2 spheres	17	23	(a)
WZ-4	ZrO_2 spheres	32	77	(a)
WZ-5	ZrO_2 powder	17	59	(b)
WH-1	HfO_2 powder	16	29	↓
WT-1	ThO_2 powder	16	16	↓
WT-2	ThO_2 powder	31	5	↓
WA-1	Al_2O_3 powder	17	9	↓
		Uncored billets		
WZ-6	ZrO_2 spheres	16	57	(a)
WZ-7	ZrO_2 spheres	33	51	(a)

(b) Reextrusions

Billet	Fiber composite	Actual extrusion ratio		Aspect ratio, L/D	Measurement method
		Re-extrusion	Total		
RX-1	WZ-3 fibers	16	270	99 to 165	(c)
	WZ-4 fibers	↓	520	360 to 600	↓
	WZ-5 fibers	↓	270	385 to 640	↓
	WZ-6 fibers	↓	260	260 to 440	↓
RX-2	WZ-3 fibers	32	540	215 to 360	(c)
	WZ-4 fibers	↓	1000	290 to 480	↓
	WZ-5 fibers	↓	540	255 to 425	↓
	WZ-6 fibers	↓	510	125 to 205	↓

[a]Measurement of actual fibers.

[b]Measured from photomicrograph.

[c]Calculated from fiber diameter measurements.

TABLE IV. - EFFECT OF PROCESSING ON CRYSTALLOGRAPHY, GRAIN SIZE, AND IMPURITY LEVEL IN FIBERS AND STARTING MATERIALS

	Sample	Oxide	Condition	Grain size, μm	Preferred orientation	Crystal structure	Impurities	
							Element	Percent by weight
Starting material	AS-1	Al_2O_3	As-received sphere	5 to 10	None	Close-packed hexagonal	Silicon	----
	ZS-1	ZrO_2	As-received sphere	40 to 100	None	Mixed cubic and monoclinic	--------	----
Single extrusion	WZ-3	ZrO_2	Extruded (17:1) from spheres	2 to 4	None	Monoclinic	Tungsten	6.0
	WZ-4		Extruded (32:1) from spheres	1 to 3				4.5
	WZ-5		Extruded (17:1) from powder	1 to 5				4.5
	WZ-6		Extruded (16:1) from spheres	2 to 4				7.3
	WZ-7		Extruded (33:1) from spheres	1 to 3				9.3
	WT-1	ThO_2	Extruded (17:1) from powder	--------	(100) Plane parallel to fiber axis	Face-centered cubic		----
Multiple extrusion	RX-1 - WZ-3	ZrO_2	Reextruded (16:1)	1 to 3	None	Monoclinic	Tungsten	1.04
	WZ-4					Mixed cubic and monoclinic		2.29
	WZ-5					Monoclinic		.47
	WZ-6					Mixed cubic		2.37
	RX-2 - WZ-3		Reextruded (32:1)			Monoclinic		2.16
	WZ-4					Mixed cubic		2.60
	WZ-5					Monoclinic		1.49
	WZ-6					Mixed cubic		3.64

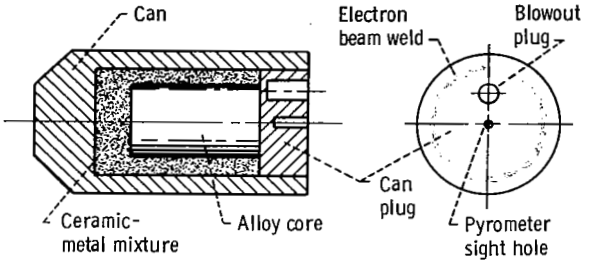

Figure 1. - Extrusion can and cored billet.

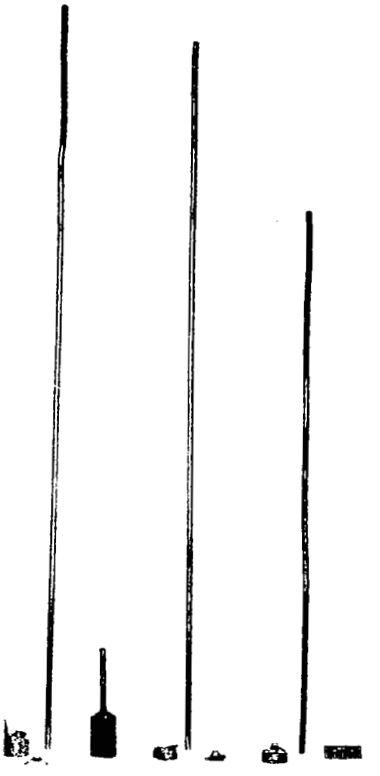

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Figure 2. - As-extruded ceramic-metal composites.

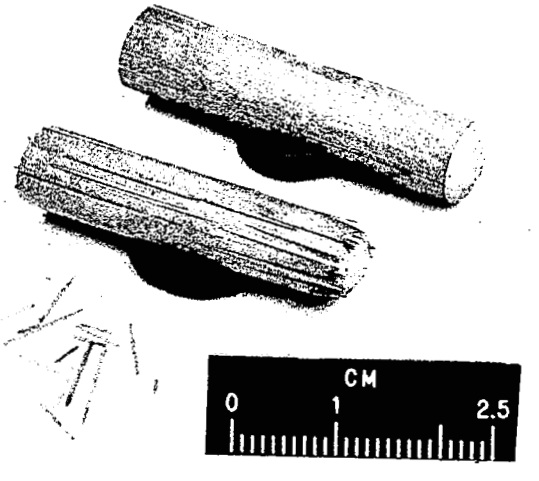

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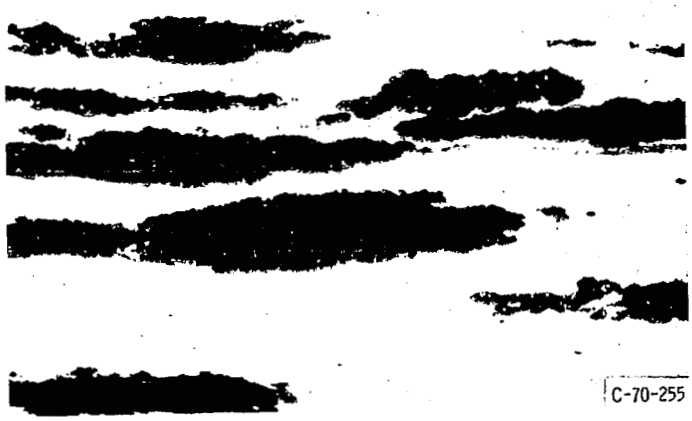
Figure 3. - Extraction of fibers from carrier metal: prior to extraction, fibers partially exposed, recovered fibers.

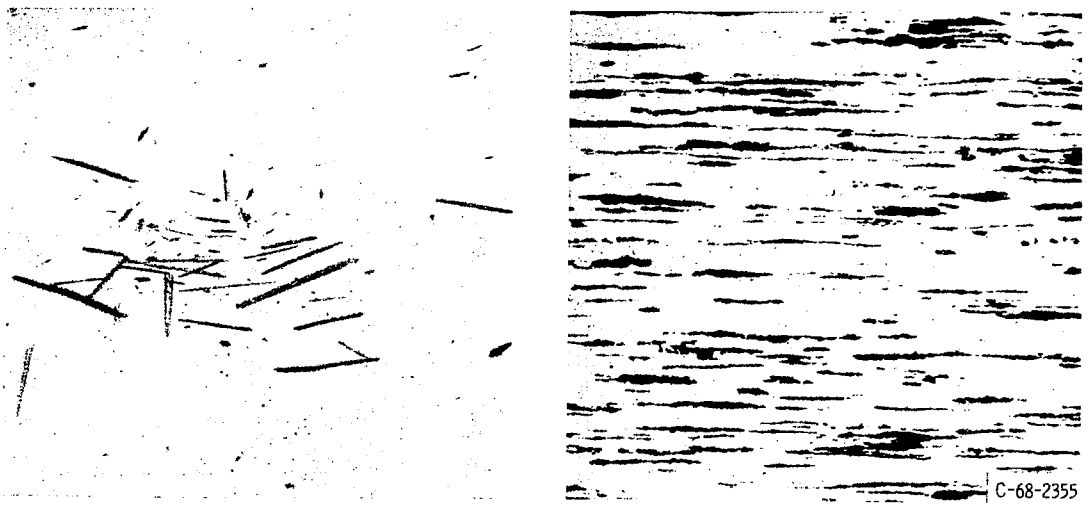
(a) Extracted fibers (X20).

(b) Fibers in matrix (X150).



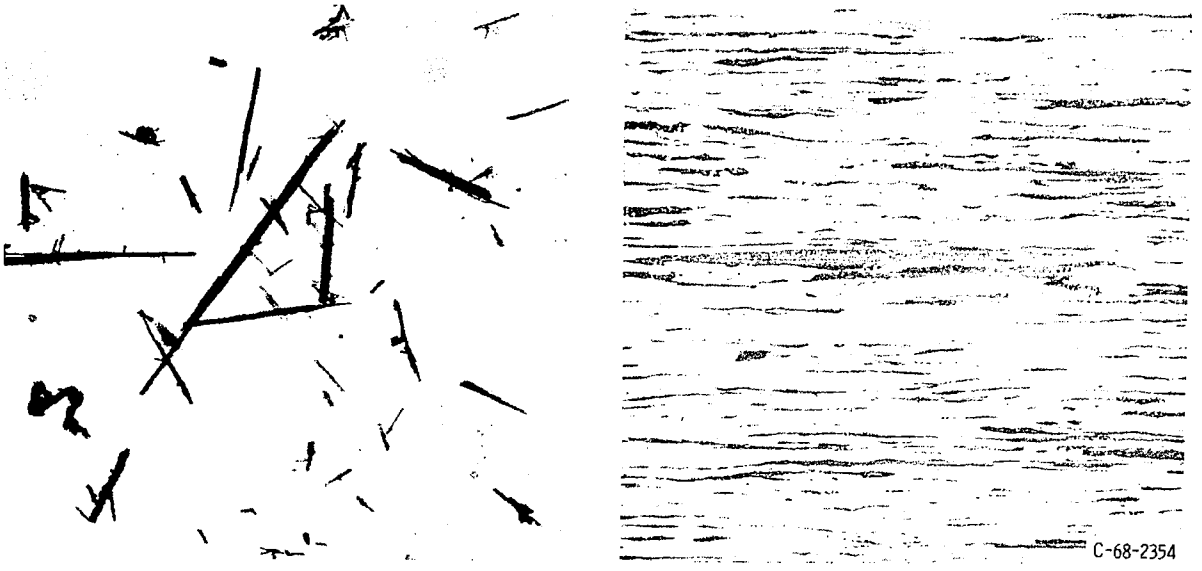
(c) Fibers in matrix (X250).

Figure 4. - Aluminum oxide fibers from 105- to 125-micrometer powder. Extrusion ratio, 17; aspect ratio, 9.



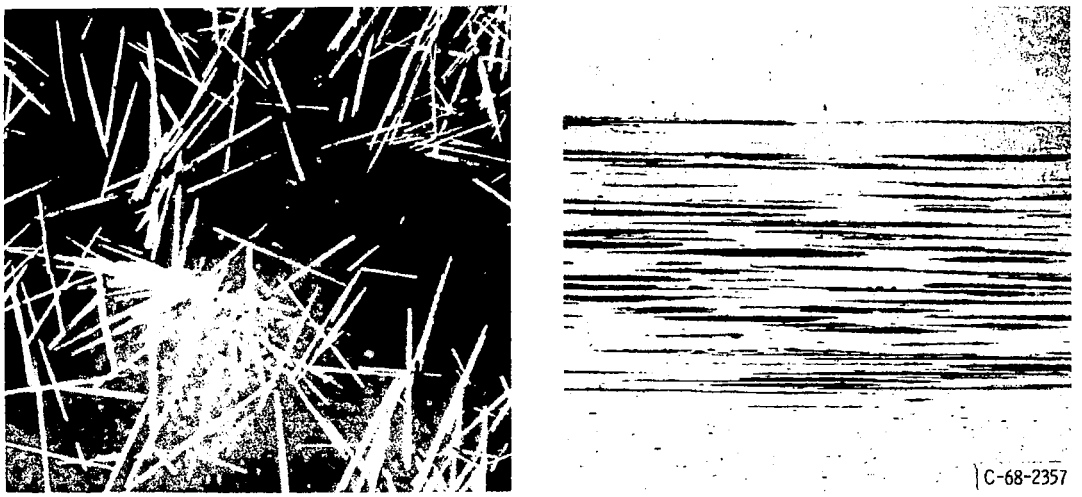
(a) Loose fibers (X2). (b) Fibers in matrix (X250).

Figure 5. - Thorium oxide fibers from 3- to 5-micrometer powder. Extrusion ratio, 16; aspect ratio, 16.



(a) Loose fibers (X100). (b) Fibers in matrix (X250).

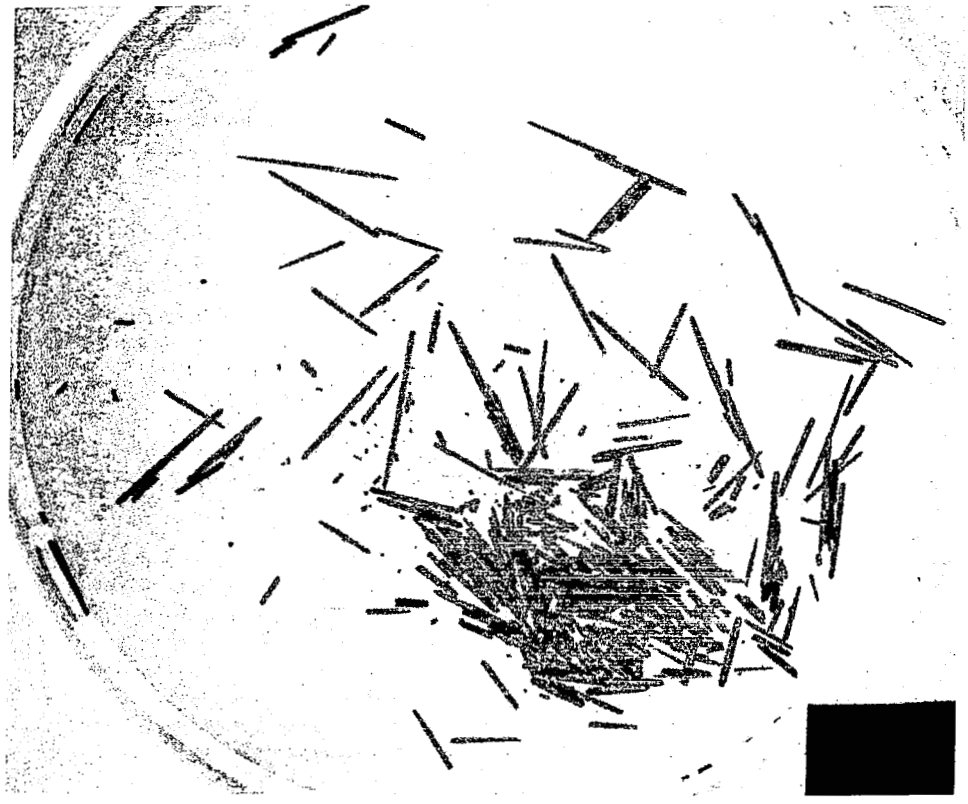
Figure 6. - Hafnium oxide fibers from 3- to 5-micrometer powder. Extrusion ratio, 16; aspect ratio, 29.



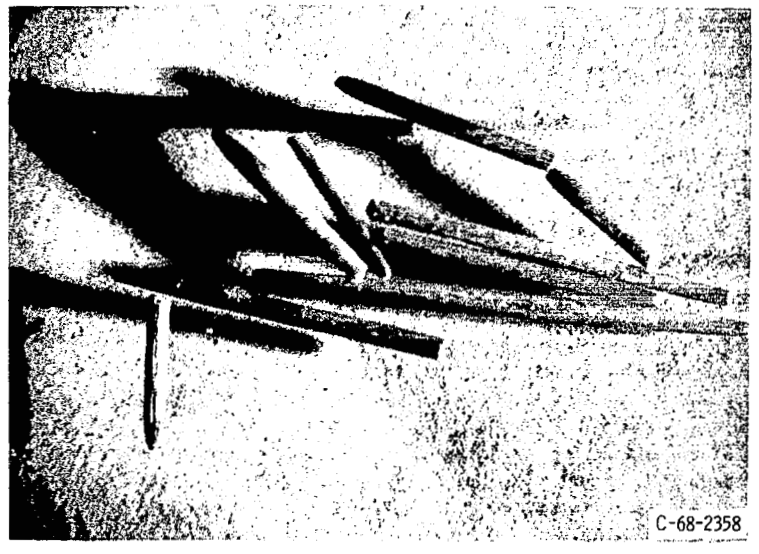
(a) Loose fibers (X10).

(b) Fibers in matrix (X25).

Figure 7. - Zirconium oxide fibers from 105- to 125-micrometer powder. Extrusion ratio, 17; aspect ratio, 59.

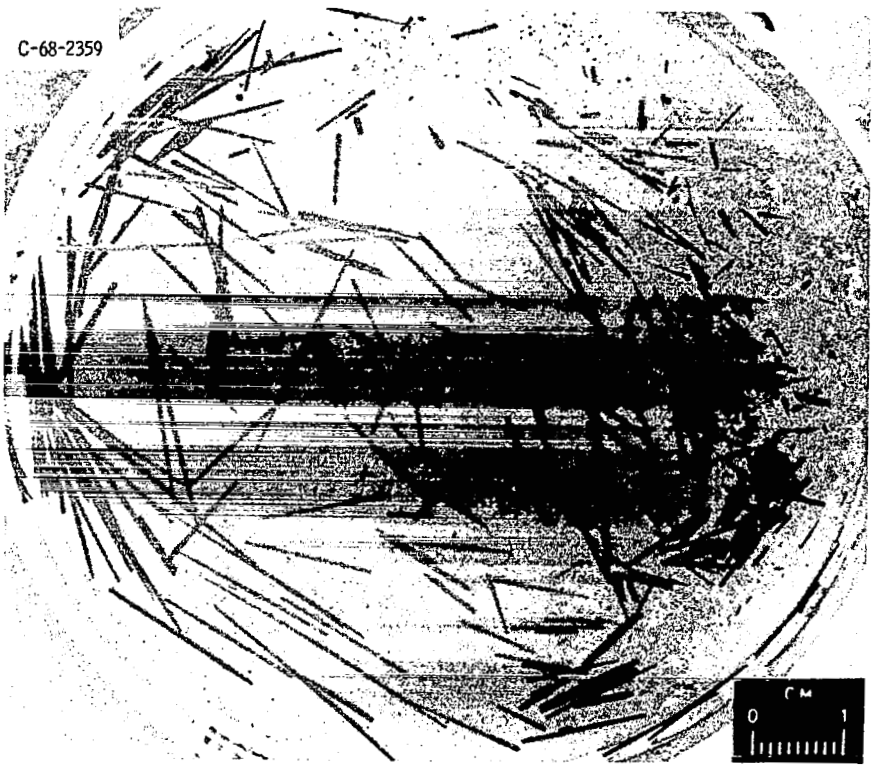


(a) Extracted fibers.

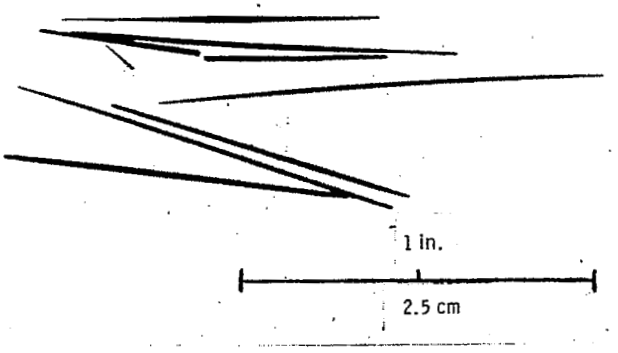


(b) Loose fibers (X5).

Figure 8. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres. Extrusion ratio, 17; aspect ratio, 23.



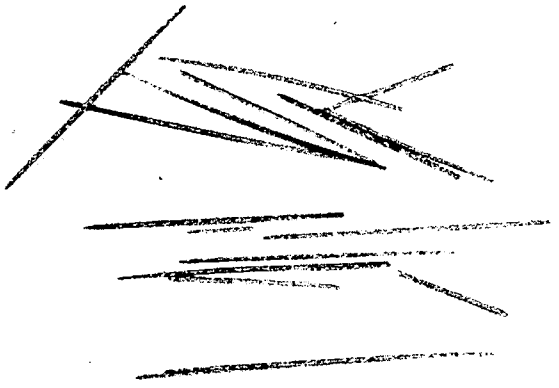
(a) Extracted fibers.



(b) Loose fiber.

Figure 9. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres. Extrusion ratio, 32; aspect ratio, 77.

(a) Extracted fibers.



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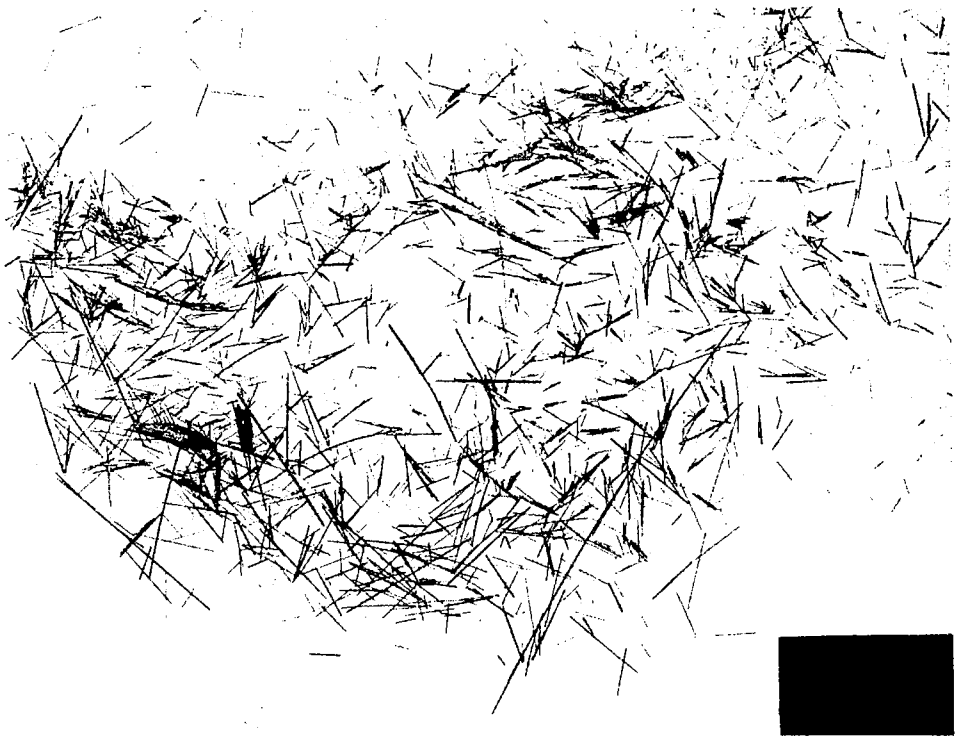
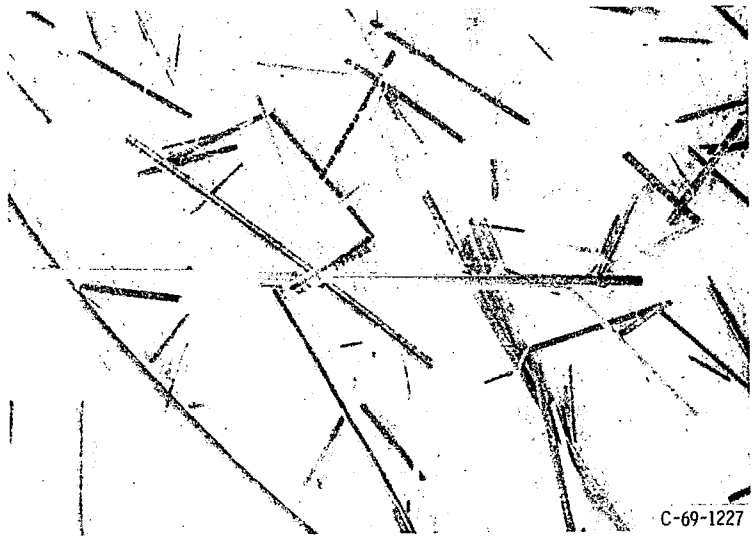
(b) Loose fibers (X2).

Figure 10. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres extruded without core. Extrusion ratio, 33; aspect ratio, 51.

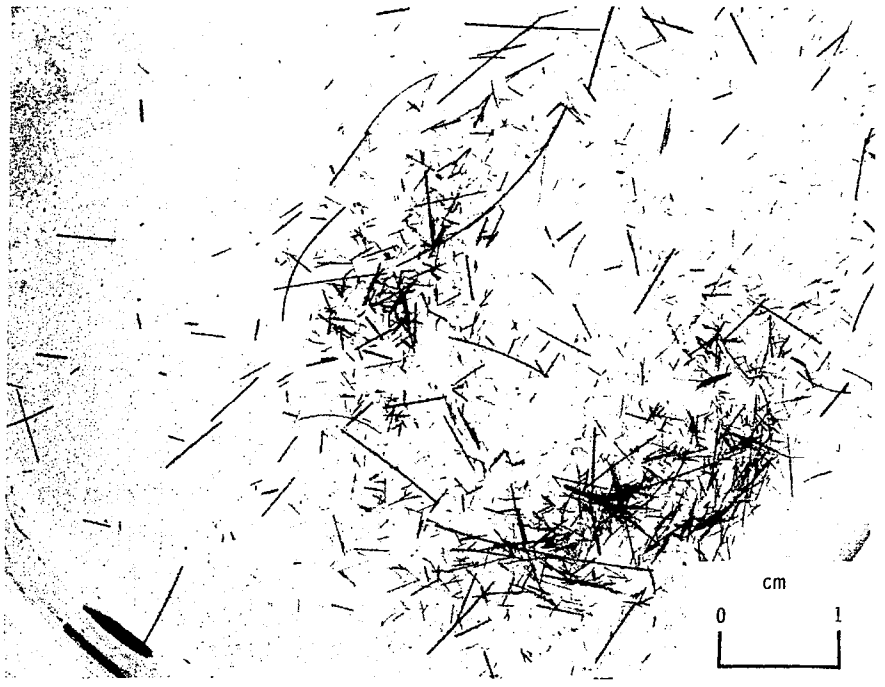


(a) Extracted fibers.



(b) Loose fibers (X10).

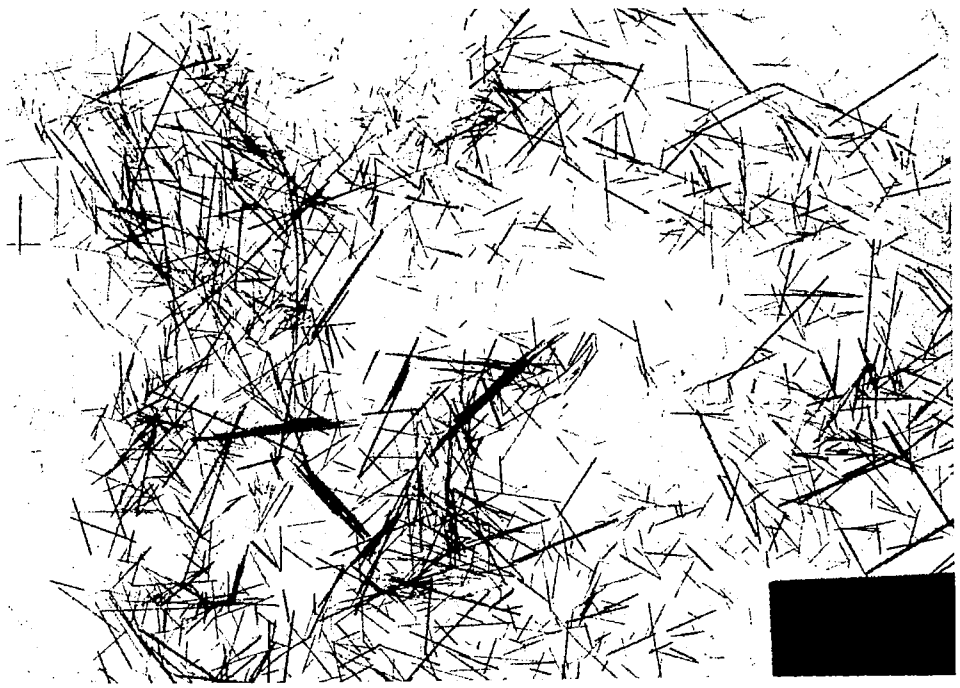
Figure 11. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres double extruded for a total extrusion ratio of 520. Aspect ratio, 360 to 600.



(a) Extracted fibers.

(b) Loose fibers (X10).

Figure 12. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres double extruded for a total extrusion ratio of 1000. Aspect ratio, 290 to 480.



(a) Extracted fibers.

(b) Loose fibers.

Figure 13. - Zirconium oxide fibers from 1190- to 1410-micrometer spheres double extruded without core for a total extrusion ratio of 510. Aspect ratio, 125 to 205.

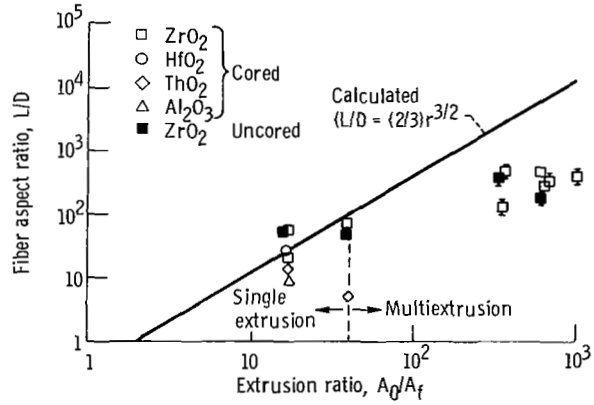


Figure 14. - Fiber aspect ratio of ceramics deformed at various extrusion ratios compared with calculated ratios.

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