MULLITE WHISKERS AND MULLITE-WHISKER FELT

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ABSTRACT

Naval Surface Warfare Center has developed processes for the preparation of mullite ($3Al_2O_3 \cdot 2SiO_2$) whiskers and mullite-whisker felt. Three patents on the technology were issued in 1990. The processes are based on chemical reactions between AlF_3, Al_2O_3, and SiO_2. The felt is formed in-situ during processing of shaped powdered precursors. It consists of randomly oriented whiskers which are mutually intergrown forming a rigid structure. The microstructure and properties of the felt and size of the whiskers can be modified by varying the amount of Al_2O_3 in the starting mixture. Loose mullite whiskers can be used as a reinforcement for polymer-, metal-, and ceramic-matrix composites. The felt can be used as preforms for fabricating composite materials as well as for thermal insulation and high temperature chemically stable filters for liquids (melts) and gases.

INTRODUCTION

The current interest in the development of refractory-oxide fibers and whiskers is spurred by the increasing demand for high-temperature structural materials for use in an oxidizing atmosphere. As a reinforcing material, whiskers are preferable to fibers because they are single crystals and their properties are not affected by grain growth and grain boundary-induced creep at high temperatures. The low free energy and high modulus and strength of whiskers compared to polycrystalline materials make it possible to use whiskers to reinforce matrices of the same composition.

Currently, only non-oxide whiskers such as SiC and Si_3N_4 are commercially available. However, they cannot be used in an oxidizing atmosphere at temperatures above 1000° C. Additionally, SiC whiskers are electrically conductive and not suitable for use in dielectric ceramics.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a promising candidate for whiskers because of its excellent chemical stability, low thermal expansion, and good high-temperature strength and creep resistance. Since mullite has a relatively low dielectric constant and loss tangent, the whiskers may be suitable for toughening materials for dielectric applications (such as radomes).

Both loose whiskers (or fibers) and fibrous preforms can be used as reinforcement in the fabrication of composites. The use of fibrous preforms instead of loose whiskers (or fibers) excluded problems of their deagglomeration and uniform distribution in matrix materials. Matrices can be infiltrated into the preforms by vacuum impregnation, sol-gel processing, chemical vapor infiltration and melt infiltration techniques.

PREPARATION OF MULLITE WHISKERS AND FELT

The NAVSWC method for preparation of both mullite whiskers and felt is based on the following two reactions[1-5]:

$$2AlF_3 + 2SiO_2 \text{ -------------> } \underset{\text{Topaz}}{Al_2(SiO_4)F_2} + SiF_4\ (g) \qquad (1)$$

$$6Al_2(SiO_4)F_2 + SiO_2 \text{ ---------> } \underset{\text{Mullite}}{2(3Al_2O_3 \cdot 2SiO_2)} + 3SiF_4\ (g) \qquad (2)$$

In reaction (1), AlF_3 and SiO_2 are heated at 700 - 900° C to form topaz as an intermediate product and in reaction (2), topaz is thermally decomposed at 1250 - 1400° C to yield mullite. The whiskers are grown as a result of a vapor-phase chemical reaction. Heating in a SiF_4 atmosphere is necessary for the preparation of high-quality whisker product. Up to 75% Al_2O_3 can be substituted for AlF_3 in the starting materials. In this case, the mullite whiskers form as a result of chemical interactions involving all of the starting components, as well as the gaseous SiF_4 generated in reactions (1) and (2) - assuming that corresponding portions of AlF_3 required for the process are produced by a reaction between SiF_4 and Al_2O_3.

The whisker preparation process involves mixing the raw powders and firing the loose powders in closed SiF_4-containing system. Mullite whiskers prepared at 1250° C in optimum SiF_4 atmosphere are shown in Figure 1. As produced, they form loose aggregates which are easily separated. The whiskers of rectangular cross section have a narrow size distribution with average aspect ratio of 30.

The felt preparation process involves mixing and shaping (by any conventional method) the powdered precursors (AlF_3, SiO_2 and optional Al_2O_3), followed by firing at 1250 - 1400° C. A significant advantage of this process is that there are no whiskers in the precursor mixture. The whiskers are formed inside the product during firing. Because loose respirable whiskers are not handled at any step of the process, health hazards associated with handling whiskers are eliminated. The final felt product is about 80% porous with low dimensional changes (about 1% expansion) compared to the green shapes which is a valuable feature for the preparation of near-net shape composite preforms. Figure 2 shows the microstructure of the felt consisting of randomly oriented (in 3 dimensions) and uniformly distributed individual mullite whiskers and spherulites which are mutually intergrown or mechanically interlocked. With a bending strength (3 point) of about 3 MPa (427 psi), the felt is rigid and can be used in composite processing utilizing various impregnation techniques.

To decrease the amount of relatively expensive AlF_3 and accordingly decrease the amount of hazardous SiF_4 generated by the reactions, and possibly modify the size of the whiskers, Al_2O_3 (avg. particle size 0.05 μm) was substituted for AlF_3 in amounts up to 75 mole %. The whisker size gradually decreases with increasing Al_2O_3 content up to 75% Al_2O_3 for both loose whiskers and felt (Figure 3). In the felt, the number of spherulites also gradually decrease with increasing Al_2O_3 content. The linear expansion and porosity of the felt slightly decrease but the bending strength significantly increases with more than 25% Al_2O_3 substitution (Table 1.). The almost two-fold increase in strength with 75% Al_2O_3 substitution can be attributed to much smaller whiskers in the felt structure. The felt has pores of 1 to 30 μm depending on the $AlF_3\backslash Al_2O_3$ ratio with very narrow size distribution (Figure 4).

Table 1. - Properties of Mullite-Whisker Felt With Substitutions of Al_2O_3 for AlF_3

Substituted Al_2O_3 (%)	Expansion (%)	Porosity (%)	Bending Strength (MPa/Psi)
0	1.0	78.5	3.1/441
25	1.0	78.1	2.9/412
50	0.5	77.4	5.4/768
75	0.0	76.3	7.0/995

APPLICATIONS OF MULLITE WHISKERS

Mullite whiskers have the potential to be used as reinforcement in a variety of polymer, ceramic and metal matrix composites. Unfortunately, the full potential of these whiskers as a reinforcement has not been completely exploited. Mullite whiskers were successfully used as reinforcement for celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) and fused silica ($SiO_2$) composites[6]. The loose whiskers were uniformly mixed with the ceramic powders and then hot pressed to full density. The fracture toughness of fused silica was doubled by the addition of 20 vol% mullite whiskers with a cross section of 4-12 μm. For the celsian matrix, 20 vol% 12-26 μm whisker additions increased the toughness by 40%. Properties of the composites are shown in Table 2.

Table 2. Properties of Mullite Whisker Composites

Matrix	Mullite Whisker Loading (%)	Relative Density (%)	Fracture Toughness* (MPa$\sqrt{m}$)	Flexural Strength (MPa)
Silica	0	94.5	0.92	67
Silica	20% 4-12 μm	96.2	1.80	49
Celsian	0	99.1	1.56	115
Celsian	20% 12-26 μm	99.4	2.15	115

* Short Chevron Notch Beam Method

APPLICATIONS OF MULLITE-WHISKER FELT

The mullite-whisker felt can be used as a preform for the preparation of polymer-, metal-, and ceramic-matrix composites or by itself as thermal insulation or high temperature filters for liquids or gases. It can be infiltrated with a variety of matrices using various processing techniques such as vacuum impregnation, chemical vapor infiltration (CVI), and melt (glass or metal), sol-gel or pre-ceramic polymer infiltration to produce composites. Polymers with viscosities of up to 10,000 cp have been used to infiltrate the felt. Researchers at Ceramatec have demonstrated that mullite whisker composites can be fabricated using sol-gel techniques[7]. After 8 infiltration cycles, the density of the sample was 2.06 g/cm^3 with 17% porosity. The process is being optimized to yield composites with densities greater than 95% dense.

A forced flow thermal gradient chemical vapor infiltration technique developed at Oak Ridge National Laboratory was used to infiltrate the felt with a SiC matrix. Since the deposition parameters used for the infiltration experiment were optimized for a Nicalon preform,the felt was only infiltrated to about 85% density with variable densities through the thickness of the sample. The properties of the produced composites are given in Table 3.

Fully dense mullite-whisker felt composites were prepared by a vacuum and isostatic pressure-assisted infiltration technique using cast aluminum alloy A356[8]. The alloy was preheated to 680°C and the felt was preheated to 550°C. A 800 psi pressure of nitrogen was required to fully infiltrate the preform. Due to the lack of bonding between A356 Al and mullite, the mechanical properties of the composite did not reflect the reinforcing potential of the whiskers. There was little transfer of the load from the matrix to the mullite whiskers. It will be necessary to increase the affinity of the matrix towards the reinforcement. Many options exist in matrix selection; addition of a small percentage of Li or Mg to the matrix may be sufficient, or contemporary Al-Li alloys such as 2090, 8090, 2091 etc. may be useful in enhancing bonding at the whisker/matrix interface without degrading the strength of mullite.

Table 3. Properties of SiC Infiltrated Mullite-Whisker Felt

Specimen Position	Theoretical Density (%)	Flexural Strength (MPa)	Fracture Toughness* ($MPa\sqrt{m}$)
Top	84.6	79.6	2.18
Middle	86.9	97.2	3.15
Bottom	85.8	105.8	3.35

* Single Edge Notch Beam Method

The felt was also evaluated for possible use as a filter in coal gasification processing. Conversion of coal to a gaseous fuel requires filtering of hazardous impurities from final gases to meet environmental and turbine equipment requirements in advanced coal-fueled power generation systems. The criteria for successful use and operation of porous filters requires not only thermal, chemical, and mechanical stability of the material, but also long-term structural durability and high reliability. Preliminary results indicate that the mullite-whisker felt is a very promising candidate. It showed good chemical stability in the tested gas atmosphere and had very high collection efficiency.

SUMMARY

Processes for the preparation of mullite whiskers and rigid mullite-whisker felt have been developed and patented. The 80% porous felt consists of randomly oriented mullite whiskers mutually intergrown, forming a rigid structure. The felt is formed in-situ during processing shaped powder precursors; thereby eliminating the health hazards associated with handling loose whiskers. Both the mullite whiskers and mullite-whisker felt are promising new reinforcements for polymer-, metal- and ceramic-matrix composites. Additionally, the felt can be used by itself as thermal insulation or high temperature chemically stable filters for liquids (melts) and gases such as for coal gasification.

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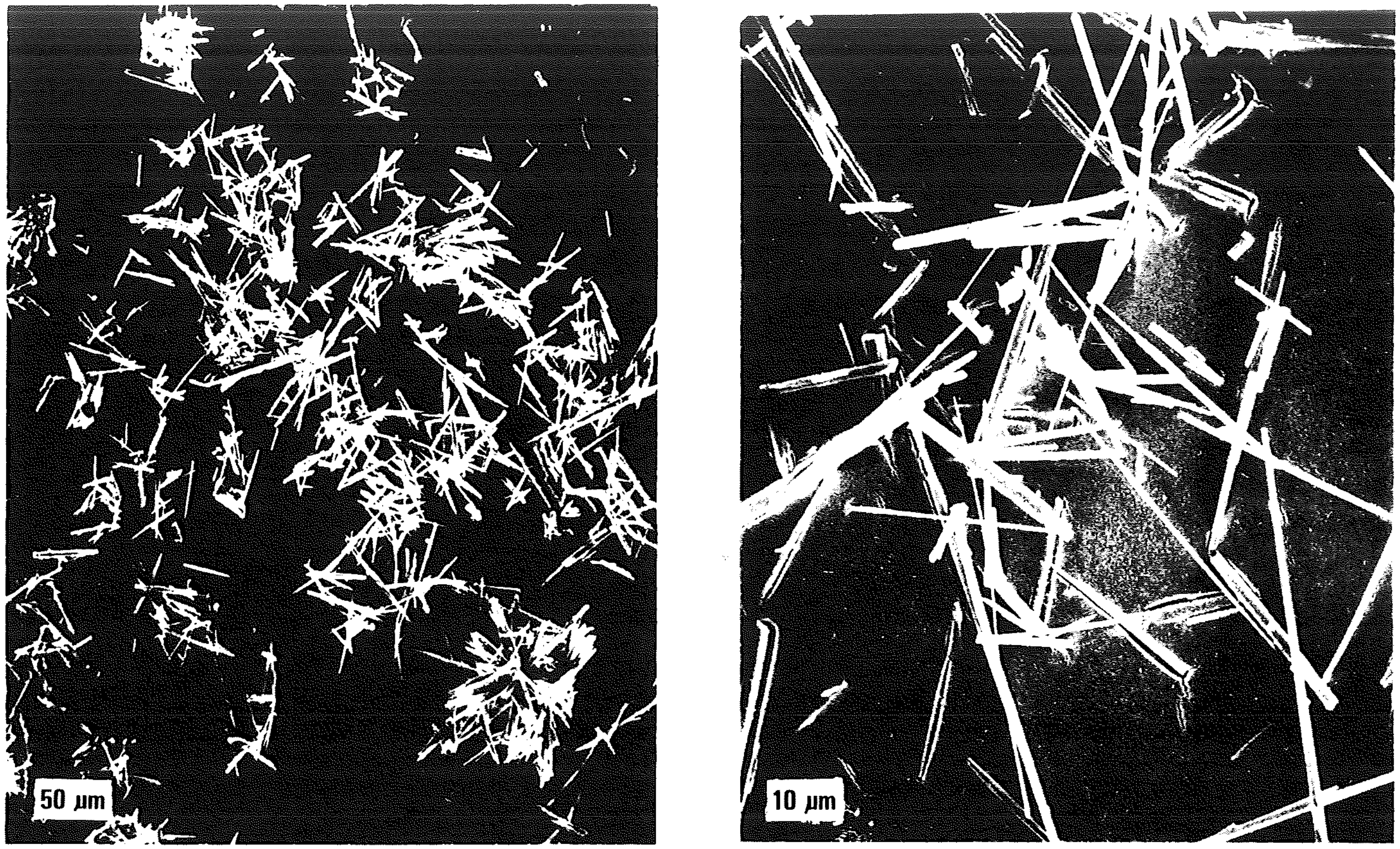

FIGURE 1. SCANNING ELECTRON MICROGRAPHS OF MULLITE WHISKERS

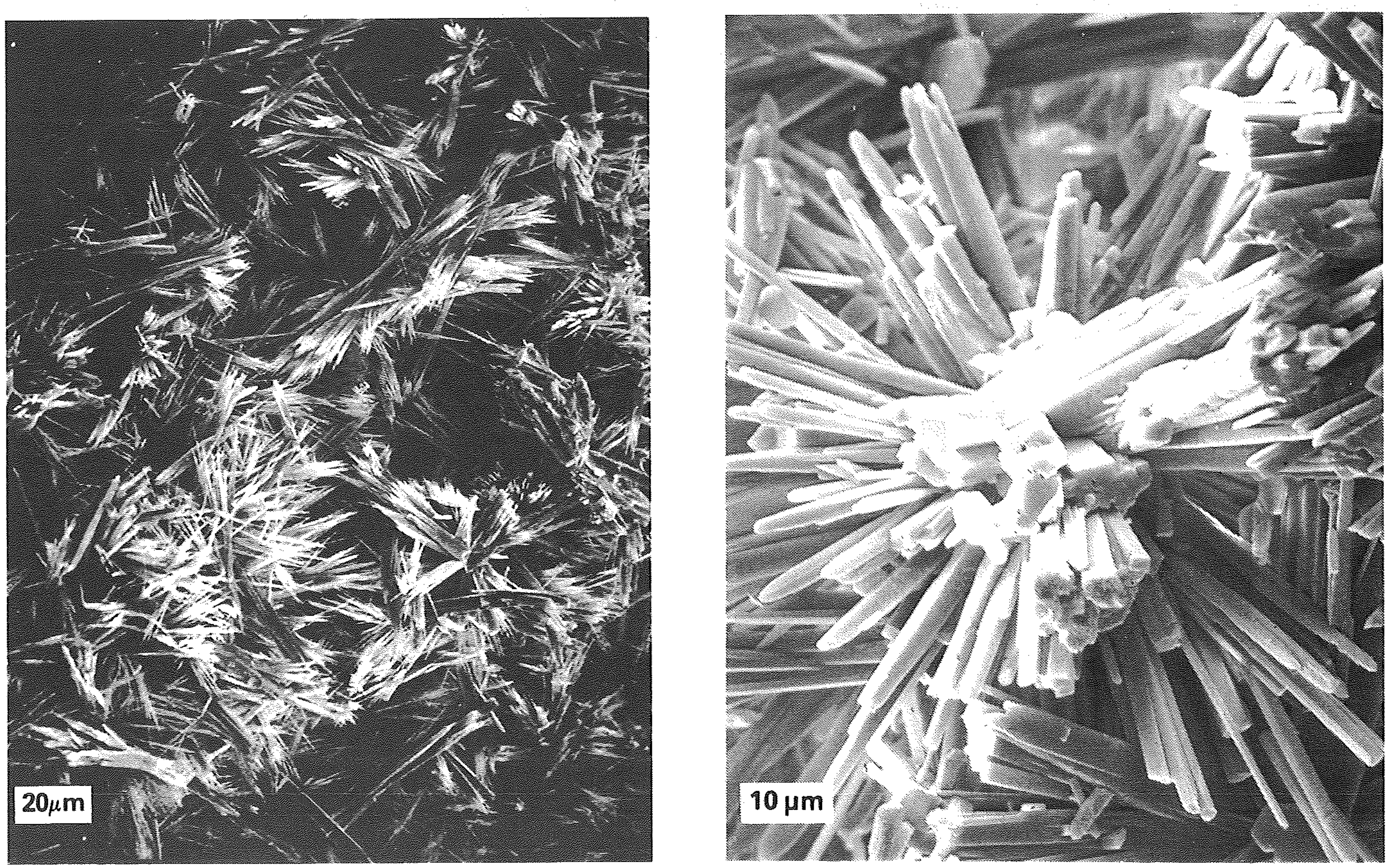

FIGURE 2. SCANNING ELECTRON MICROGRAPHS OF MULLITE WHISKER FELT

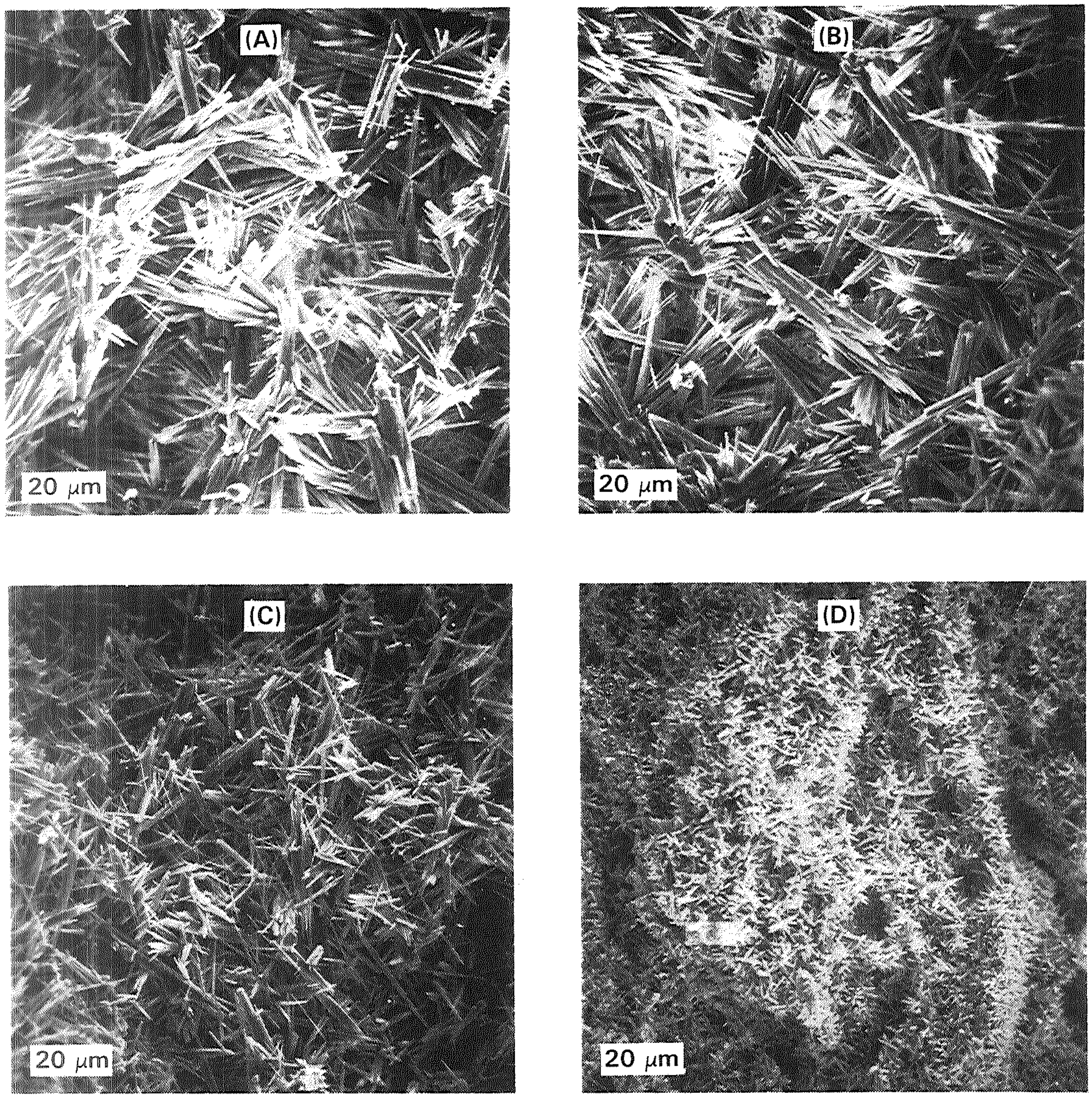

FIGURE 3. SCANNING ELECTRON MICROGRAPHS OF MULLITE WHISKER FELT WITH SUBSTITUTION OF (A) 0%, (B) 25%, (C) 50%, AND (D) 75% Al_2O_3 FOR AlF_3

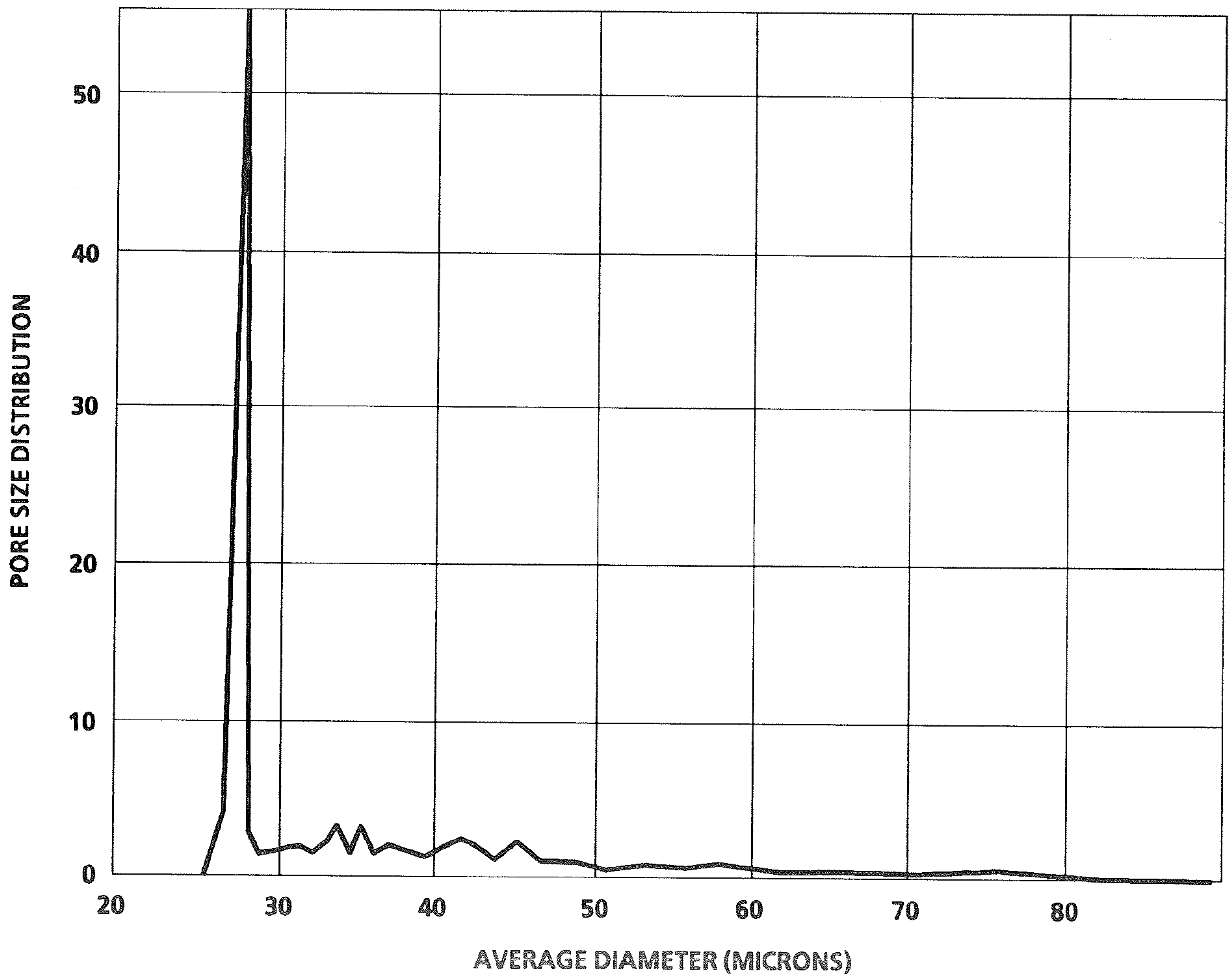

FIGURE 4. PORE SIZE DISTRIBUTION OF MULLITE WHISKER FELT PREPARED FROM AlF_3 AND SiO_2