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EFFECT OF CHROMIA DOPING ON THERMAL STABILITY OF SILICA FIBERS

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16. Abstract

Commercial silica fibers of the type being evaluated for reusable surface insulation for reentry vehicles were found to be porous and composed of subfibers. The effect on shrinkage and devitrification of soaking such silica fibers in water, acetic acid, chromium acetate, and chromium nitrate solutions was studied. Felted specimens made of chromia-doped fibers shrunk only about one-half as much as those made of untreated fibers after exposure in air for 4 hours at 1300° C. The devitrification rate of fibers given prolonged soaks in chromium nitrate was as low as that of as-received fibers.

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EFFECT OF CHROMIA DOPING ON THERMAL STABILITY OF SILICA FIBERS

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SUMMARY

This study characterizes certain aspects of the fine silica fibers being used to fabricate reusable surface insulation for reentry vehicles. Its purpose was to improve fiber thermal stability by minimizing both viscous flow, which leads to shrinkage, and devitrification to cristobalite, which leads to disruptive volume changes on thermal cycling. The study revealed that raw silica fibers were porous and were composed of very fine subfibers. By soaking the fibers in aqueous solutions of chromium acetate or nitrate and heat treating in air, a dispersion of Cr_2O_3 was produced in the silica fibers. Such a dispersion decreased the volume shrinkage of felted test specimens from 90 percent for as-received fibers to 50 percent after treatment. Most of the shrinkage in as-received and chromia-containing fibers occurred during the initial stages of heat treatment. It was the result of sintering of the subfibers, accompanied by the elimination of filament porosity. Prolonged soaking in a chromium nitrate solution further reduced the silica devitrification rate to a degree comparable to that of as-received silica fibers.

INTRODUCTION

Fibrous silica insulation is a primary candidate material for the reusable thermal protection system for the Space Shuttle. In this application, the fibers are felted and rigidized to form a low-density tile by use of appropriate binders. During reentry, the external surface of such tiles may be subjected to elevated temperatures as high as 1350° C (ref. 1). The performance of such a thermal protection system will depend on, among other factors, the thermal stability (shrinkage and devitrification) of the fibers used. While the rates of the shrinkage and devitrification processes of the presently fabricated reusable surface insulation (RSI) tiles may satisfy the current reentry requirement, more stable and improved fibers would increase the life and reliability of RSI tiles and allow higher use-temperatures, thus expanding the operational flexibility of a reentry vehicle.

The literature on the nature, physical properties, and devitrification of amorphous silica and the effects of impurities thereon is extensive (refs. 2 to 9). However, most studies have dealt with bulk silica rather than with the ultrafine fibers - approximately 2 to 3 micrometers in diameter - which are used to make RSI. Observations made on bulk silica may not necessarily be applicable to the ultrafine silica fibers, which are characterized by a high surface-volume ratio. Only in a few cases has work on forms other than bulk silica (powder, foamed silica) been reported (refs. 10 and 11).

Recently, as a result of the Space Shuttle thermal protection system effort, silica fiber has become the object of several investigations (refs. 12 to 16). In a previous investigation (ref. 12) the author indicated that silica fibers were porous and thus amenable to treatment leading to their improvement. The present study was conducted to further characterize the as-received silica fibers currently used in the fabrication of RSI tiles and to try to improve fiber thermal stability, that is, to reduce both shrinkage and devitrification rates. The primary approach was based on doping the porous fibers by soaking them in chromium solutions and subsequently heating them to form a dispersion of chromium oxide (Cr_2O_3). The Cr_2O_3 is the only known oxide which does not form any silicates (refs. 17 and 18), and its solubility in solid silica is practically nil (ref. 17 and fig. 1). Therefore, it is reasonable to assume that the presence of Cr_2O_3 could increase the viscosity of silica fibers and thus reduce their shrinkage. One literature source offers hope that chromia might also inhibit devitrification (ref. 10). In this study samples made of as-received and chromia-doped silica fibers were evaluated by shrinkage measurement, X-ray diffraction analysis, transmission electron microscopy, and chemical analysis.

EXPERIMENTAL PROCEDURE

Characterization of Silica Fibers

The Microquartz 108 used in this investigation was the same type of commercial silica fiber which has been used for fabrication of RSI tiles. X-ray diffraction (XRD) analysis of the fibers indicated them to be completely amorphous. Their average diameter was about 2 to 3 micrometers. Multiple spectroscopic analyses for metallic impurities were performed at Lewis and at an independent laboratory. The combined results are shown in table I. A transmission electron micrograph of an oblique thin section of silica fiber (mounted in plastic) is shown in figure 2. This figure reveals that the silica fiber is not a completely dense material but is composed of subfilaments about 0.024 to 0.1 micrometer in diameter. Figure 3 shows a longitudinal section of a fiber at slightly higher magnification. The water content in raw silica fibers as determined at 1000° C was found to be 8.7 percent. This high value is also an indication of porosity in the fibers.

Specimen Preparation

Because it would be extremely difficult to try to observe and measure the shrinkage and devitrification of individual silica fibers, it was necessary to form cylindrical specimens by water casting of the as-received or of the treated fibers. Water-cast cylinders were made from

(1) Fibers in the as-received condition
(2) Fibers washed for 7 days in distilled water
(3) Fibers washed for 7 days in distilled water and then soaked for 5 minutes in a solution of chromium acetate (containing 1.5 g of chromium in 100 cm^3 of solution)
(4) Fibers washed as for type 3 and soaked for 42 hours in the chromium acetate solution
(5) Fibers washed as for type 3 and soaked for 100 hours in the chromium acetate solution
(6) Fibers washed as for type 3 and soaked for 150 hours in a chromium nitrate solution of the same chromium concentration as for type 3
(7) Fibers washed as for type 3 and soaked for 120 hours in a solution of acetic acid with the same acetate ion concentration as in the chromium acetate solution

The specimens of type 1 were prepared by blending 5 grams of silica fibers in 300 cubic centimeters of distilled water for 5 minutes. The suspension thus obtained was filtered through a cylindrically shaped funnel with a large height-diameter ratio. The bottom of the funnel was covered with a fine metallic screen. The filtering process was accelerated by application of vacuum. The settled fibers formed a cylinder. Such cylinders, after removal from the funnel, were dried in an oven at 100° C for 16 hours. The approximate height and diameter of such cylinders were 3.5 and 4.0 centimeters, respectively. Cylinders formed from fibers of types 2 to 6 were prepared by blending the fibers in their soaking solutions. The filtering and drying processes were the same as previously described. All cylinders fabricated in this manner were cut in half, perpendicular to their axes. Each half of the cylinder represented a test specimen and each was labeled after its dimensions were measured with a micrometer. Specimens made of silica fibers treated with the chromium solutions developed a green surface layer about 0.15 centimeter thick which was richer in chromium than the interior. The chromium concentration (as Cr_2O_3) in the surface layer was found to be 7 percent, while in the interior the chromium concentration was only 0.5 percent by weight. The presence of the

Cr_2O_3-rich surface layer had no measurable effect on the specimen shrinkage, therefore this layer was not generally removed prior to thermal exposure.

Thermal Exposure

Cylindrical specimens were thermally exposed in air in a large muffle furnace at 1300° C. In general, the exposure times were 0.25, 0.5, 1, 2, and 4 hours, while in the case of type 6 and 7 specimens, exposure times were as long as 8 hours. After completion of a thermal exposure, the specimens were removed from the furnace and cooled in air. Their diameters and heights were again measured with a micrometer. Each specimen was heat treated only once and thus could provide only one point on the shrinkage-against-time curve. Duplicate runs were made for the specimens of types 3 to 5.

X-Ray Diffraction Analysis

After the dimensions of thermally exposed specimens were measured, all were subjected to X-ray diffraction analysis. For this purpose, they were broken and then ground in a tungsten carbide mortar while wetted with ethyl alcohol. Diffraction patterns were taken on a diffractometer with CuK_α radiation in the 2θ range from 10° to 40°. During pattern taking, the scale factor was such that the α-cristobalite line (200) was always within the range of the chart. The ratio of integrated intensities

$$\frac{I_{\text{amorphous}}}{I_{\alpha\text{-cristobalite}(200)}}$$

or their inverse values were used to determine the relative amount of α-cristobalite (as weight percent) through comparison with a standard curve shown in figure 4.

Transmission Electron Microscopy

Type 2 and 5 specimens, which were heat treated for 2 hours at 1300° C, were investigated by transmission electron microscopy. For this purpose, small samples were cut from their centers and surfaces. After impregnation with an epoxy resin, the samples were microtomed and thin sections thus obtained were examined.

RESULTS

To obtain baseline data, the shrinkage and devitrification behavior of as-received silica fibers was determined. For this material. volume shrinkage (expressed as $(V_0 - V) \cdot 100/V_0$. where V_0 is the initial volume of the specimen and V is its final volume after heat treatment) is plotted as a function of time in figure 5. In the same figure the corresponding curve for specimens washed in distilled water (type 2) is shown. Figures 6 to 8 illustrate the behavior of silica soaked in a solution of chromium acetate (types 3 to 5). Thermal stability of specimens of types 6 and 7 is depicted in figures 9 and 10.

The letters which mark certain points on the curves in figures 4 to 9 indicate the extent of devitrification which accompanied the shrinkage. These letters signify

A	all amorphous
TC	trace of cristobalite (only the strongest line of cristobalite is detected)
DC	several lines of cristobalite are present, but they are not strong enough for quantitative determination
50C	the number preceding C indicates the approximate amount of cristobalite expressed in weight percent
MC	mostly cristobalite, the amount of amorphous phase cannot be determined quantitatively
C	all cristobalite

Because the application of electron microscopy to the study of silica fibers is such a tedious and time-consuming task, only samples of as-received silica and of types 2 and 5 were examined (after a 2-hour treatment at 1300° C). Figures 2, 3, and 11 to 13 are the transmission photographs of thin sections of silica fibers. No Cr_2O_3 particles were observed.

DISCUSSION

The approach taken in this study to improve the thermal stability of silica fibers was based on the idea that an inert dispersion of Cr_2O_3 in amorphous silica fibers would increase their viscosity and thus reduce shrinkage. (While rapid devitrification would also reduce shrinkage, the presence of cristobalite would seriously degrade fiber properties and thermal cycling resistance.) The dispersion was accomplished by impregnating raw fibers with an aqueous solution of chromium salt which was subsequently converted to Cr_2O_3 by heating in air. Figures 2 and 3 show that as-received silica fibers are composed of intertwined subfibers which provide pores for impregnation with chromium acetate or chromium nitrate solutions. During heating at elevated temperatures in air, these chromium salts were converted to oxide. Although direct evidence is lacking, the Cr_2O_3 is believed to be enclosed in the fibers by sintering of the subfibers. Figures 11 and 12 show that during heat treatment at 1300° C the porosity in the fibers was completely eliminated. Although the concentration of Cr_2O_3 in silica fibers was chemically analyzed to be 0.5 weight percent, discrete Cr_2O_3 crystals were not detected by transmission electron microscopy (fig. 12) at this level of doping. The grains near the surface of the fiber are probably cristobalite. This supposition is based on the observation that transmission of electrons through these grains is similar to that of the rest of the silica fiber. On the average, only one in a hundred examined sections showed such cristobalite crystals. The Cr_2O_3 grains, due to the higher atomic number of Cr, would be more opaque to electrons and would appear darker, as shown in figure 13. This figure presents a microtomed section of a silica fiber taken from a specimen (cake) surface layer which contained a much larger amount (7 weight percent) of Cr_2O_3. Here it can be seen that most of the chromia is not contained in the fiber but forms crystals of hexagonal symmetry on fiber surfaces.

Examination of figures 5 to 9 reveals that doping silica fibers with chromium oxide reduced volume shrinkage. The shrinkage was only about 50 percent for the doped fibers compared to 90 percent for the as-received fibers. In all cases, the initial rate of shrinkage is considerable. Apparently the sintering of the subfibers and the elimination of the pores contributed significantly to the rate and amount of shrinkage of the specimens during the initial stage of heat treatment. The same figures also indicate that the extent of devitrification was greater for silica fibers soaked in chromium acetate solutions than for untreated ones. This observation is difficult to reconcile with the idea that Cr_2O_3 is supposed to inhibit the devitrification process. The explanation of this discrepancy may be that Cr_2O_3 in combination with the impurities on the silica fibers initially enhanced devitrification. It appears that prolonged soaking of the fibers in the chromium acetate solution reduces this effect. Figure 14 illustrates the effect of the time that silica fibers were soaked in the solutions of chromium acetate and nitrate on the time necessary to form a detectable amount of cristobalite at 1300° C. Seemingly, prolonged soaking allowed the impurities to be leached away or exchanged. Washing silica fibers with dilute acetic acid alone did not affect shrinkage or devitrification of silica fibers as compared to as-received material (fig. 10). However, washing in distilled water (fig. 4) seemed at least initially to accelerate devitrification and, thus, reduce shrinkage.

The obtained results indicate that the thermal shrinkage of bodies composed of felted silica fibers could be lessened by long-time soaking of fibers in chromium nitrate solutions and subsequent heating in air to form chromia. The chromia probably exists in the fibers as a finely dispersed phase, the particles of which are beyond detection by transmission electron microscopy. Such a dispersion of the chromia reduced the shrinkage of the silica fiber samples at elevated temperatures. The reported inhibiting effect of chromia on the devitrification rate of silica was not observed. But long-time soaking, at least in chromium nitrate, did not accelerate devitrification as did some of the other treatments.

CONCLUDING REMARKS

The present study indicated the feasibility of doping silica fibers with Cr_2O_3 to reduce their shrinkage rate without increasing their devitrification rate. It is possible that other properties of the fibers such as mechanical strength and opacity (optical) may also be improved by such a treatment. If the improvements in thermal stability of such fibers could be translated to RSI tiles, even more reliable thermal protection systems would be possible.

SUMMARY OF RESULTS

This study was conducted to better characterize raw silica fibers and to explore the possibility of improving their thermal stability. These fibers are being considered for use in the manufacture of reusable surface insulation (RSI) for reentry vehicle heat shields. Water- or solution-cast silica fiber specimens as received, as washed in distilled water, as soaked in solutions of acetic acid, and as doped with chromium salts were heat treated in ambient air at 1300° C and were evaluated by shrinkage measurements, X-ray diffraction analysis, transmission electron microscopy, and chemical analysis. The results were as follows:

1. The raw silica fibers were found to be composed of subfibers about 0.024 to 0.1 micrometer in diameter and to contain a significant amount of porosity. The initial rapid shrinkage rate of test specimens was caused by the sintering of the subfibers and the elimination of porosity in the fibers.

2. Volume shrinkage was reduced from 90 percent for specimens made of as-received fibers to about 50 percent for specimens made of silica fibers doped with Cr_2O_3. In addition, in contrast to the other treatments, prolonged soaking in chromium nitrate solution did not increase the fiber devitrification rate when compared to the as-received fibers.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 18, 1973,
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TABLE I. - SPECTROSCOPIC ANALYSIS

OF AS-RECEIVED SILICA FIBERS

Element	Independent laboratory	Lewis			
	Content of element, ppm				
Aluminum	1000	560	405	722	655
Boron	(a)	(b)	(b)	(b)	(b)
Calcium	100	67	35	154	91
Chromium	(a)	4	3	3	3
Copper	(a)	2	2	2	3
Iron	150	150	114	148	130
Lithium	(a)	(b)	(b)	(b)	(b)
Magnesium	30	34	16	18	14
Sodium	600	460	262	618	616
Nickel	(a)	(c)	<1	<1	<1
Lead	500	165	95	128	123
Tin	(a)	(d)	(d)	(c)	(c)
Strontium	(a)	8	5	11	12
Titanium	100	10	119	115	110
Zirconium	50	39	33	32	30
Potassium	70	(c)	(c)	(c)	(c)

[a] Not detected - less than 10 ppm.

[b] Not analyzed.

[c] Not detected.

[d] Trace.

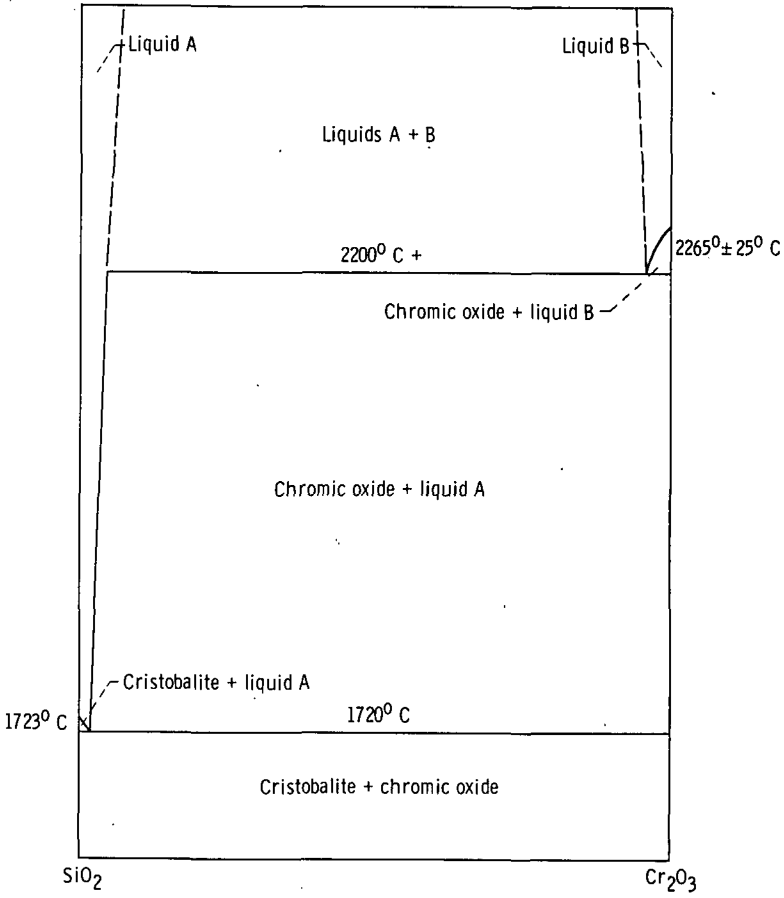

Figure 1. - System Cr_2O_3 - SiO_2 (probable) (ref. 17).

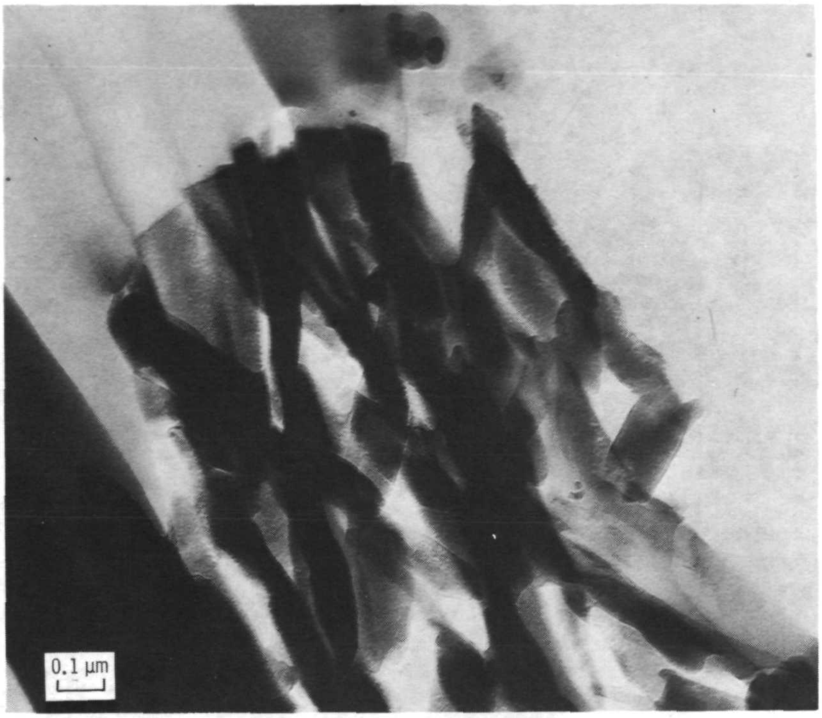

Figure 2. - Oblique section of as-received fibrous silica.

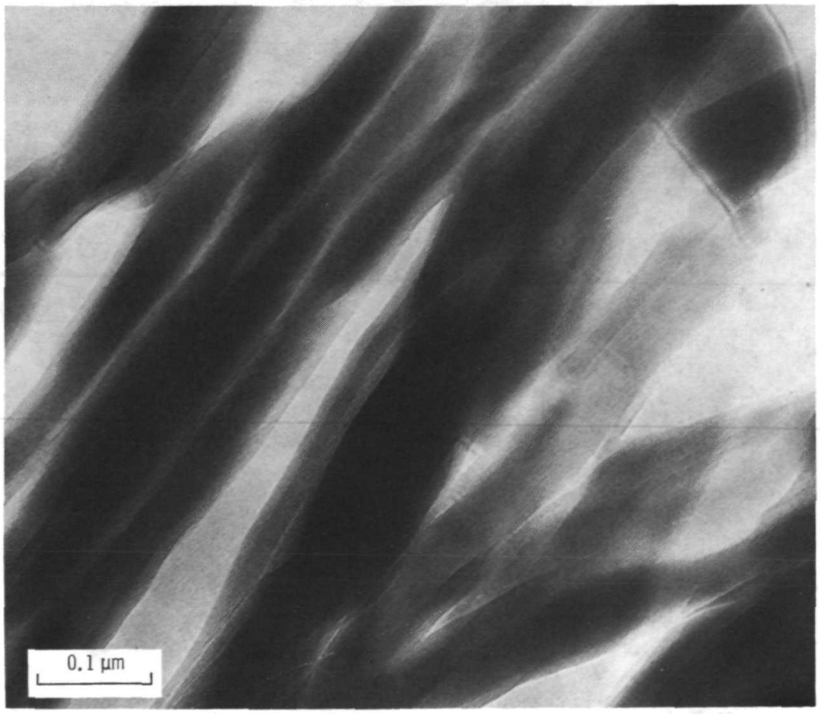

Figure 3. - Longitudinal section of as-received fibrous silica.

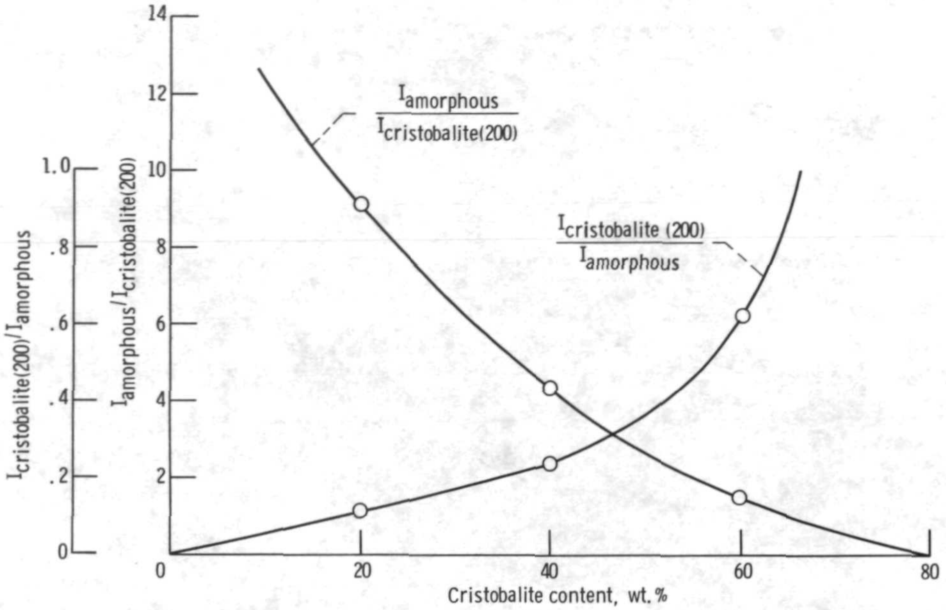

Figure 4. - Standard curve for quantitative determination of cristobalite in cristobalite - amorphous silica mixtures.

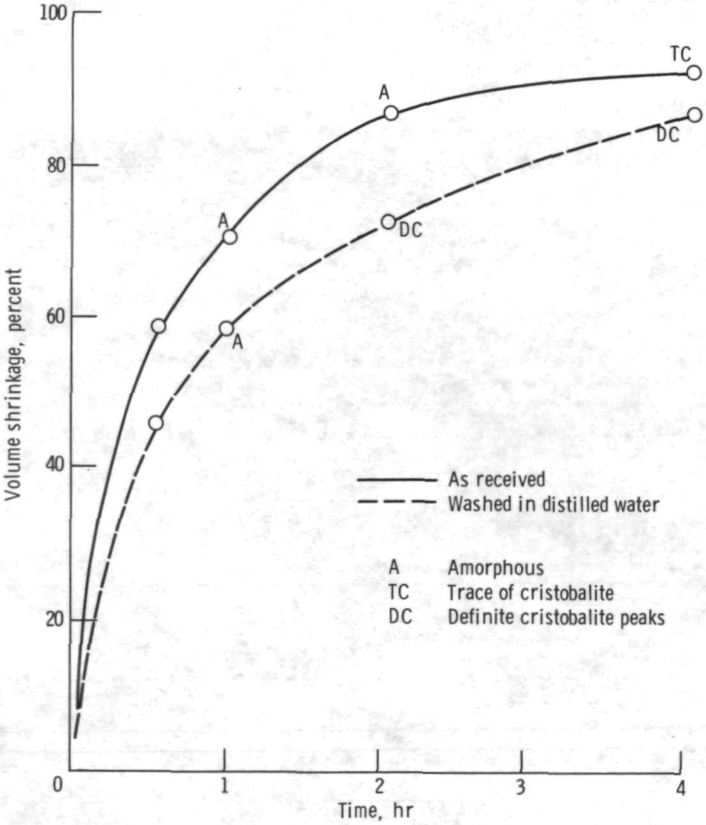

Figure 5. - Shrinkage and devitrification of water-cast silica fiber samples heated at 1300° C in air.

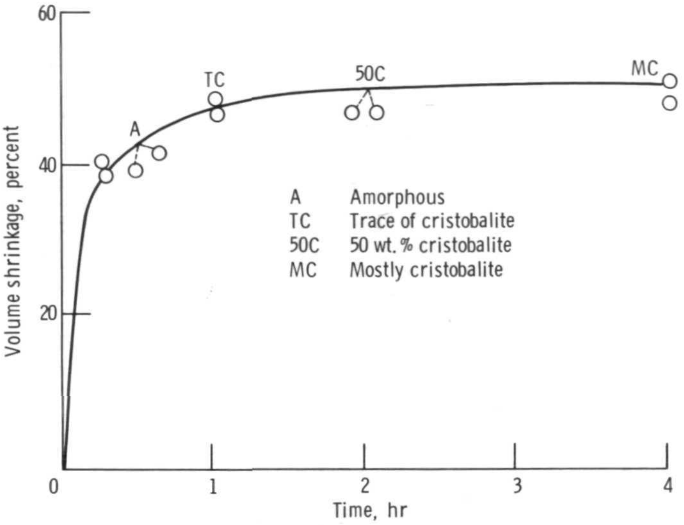

Figure 6. - Shrinkage and devitrification of silica fiber samples purified and treated for 5 minutes in 1.5 percent chromium acetate solution and then heated at 1300° C in air.

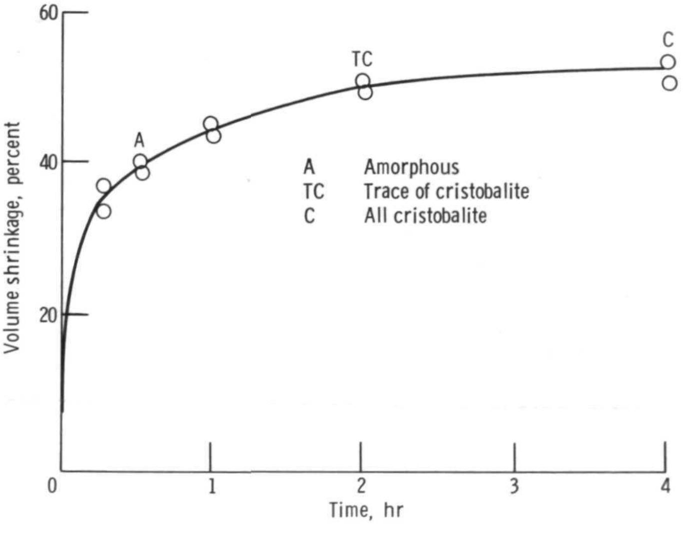

Figure 7. - Shrinkage and devitrification of silica fiber samples purified and treated for 42 hours in 1.5 percent chromium acetate solution and then heated at 1300° C in air.

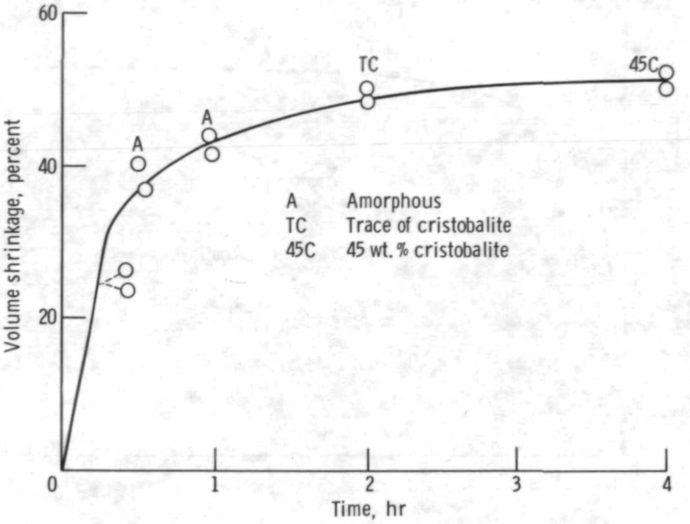

Figure 8. - Shrinkage and devitrification of silica fiber samples purified and treated for 100 hours in 1.5 percent chromium acetate solution and then heated at 1300° C in air.

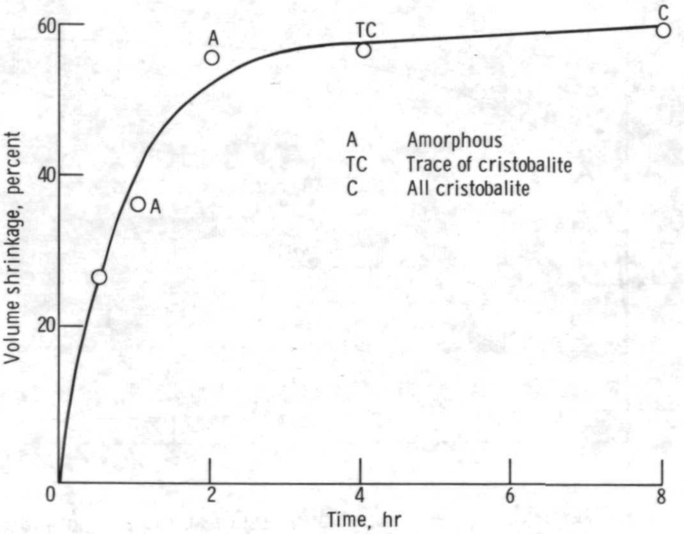

Figure 9. - Shrinkage and devitrification of silica fiber samples purified and treated for 150 hours in 1.5 percent chromium acetate solution and then heated at 1300° C in air.

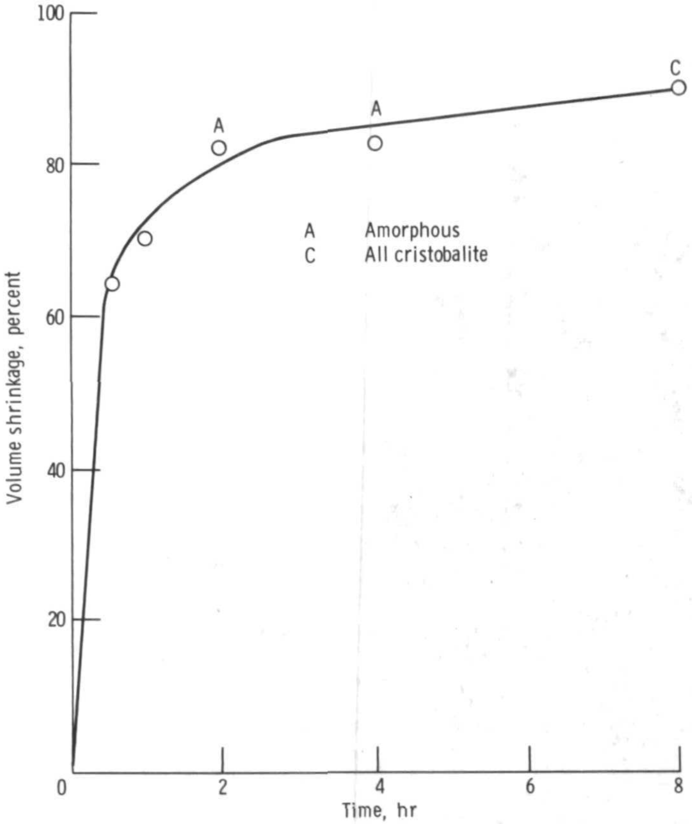

Figure 10. - Shrinkage and devitrification of silica fiber samples purified and treated for 120 hours in a solution of acetic acid and then heated at 1300° C in air.

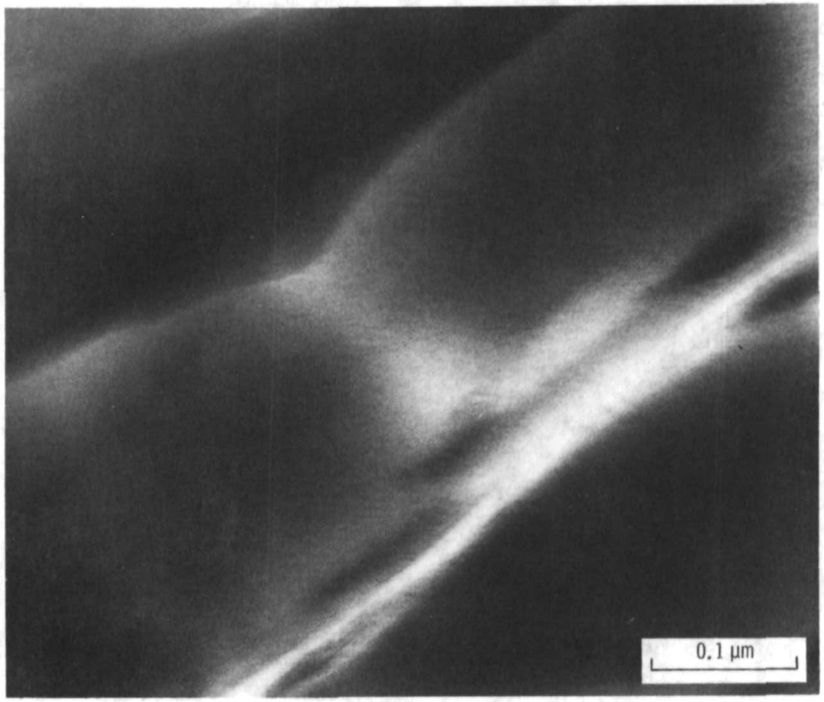

Figure 11. - Thin section of silica fiber purified and heated for 2 hours at 1300° C in air.

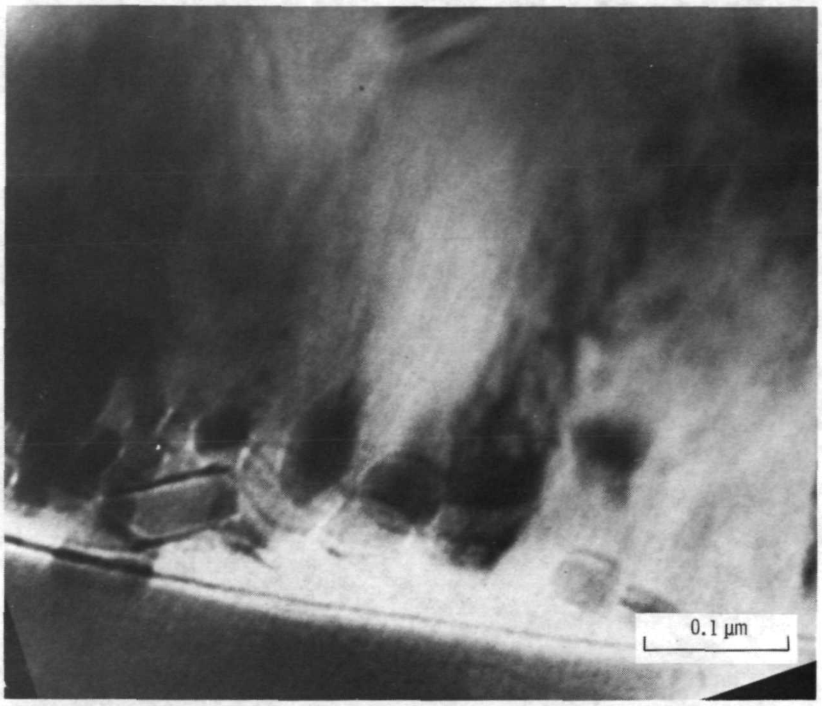

Figure 12. - Thin section of silica fiber (inside the specimen) purified and treated for 100 hours in 1.5 percent chromium acetate solution and then heated for 2 hours at 1300° C in air.

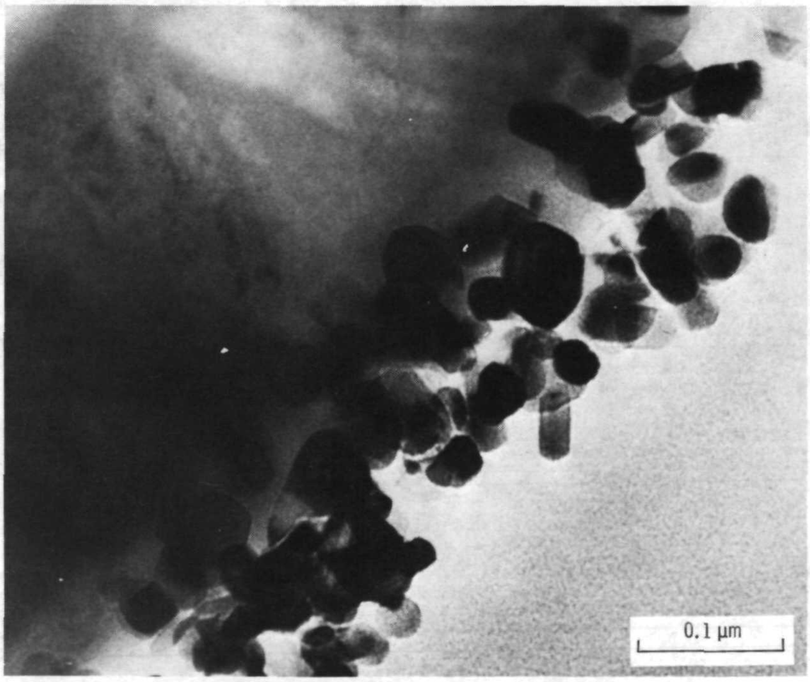

Figure 13. - Thin section of silica fiber (near the surface of the specimen) purified and treated for 100 hours in 1.5 percent chromium acetate solution and then heated for 2 hours at 1300° C in air.

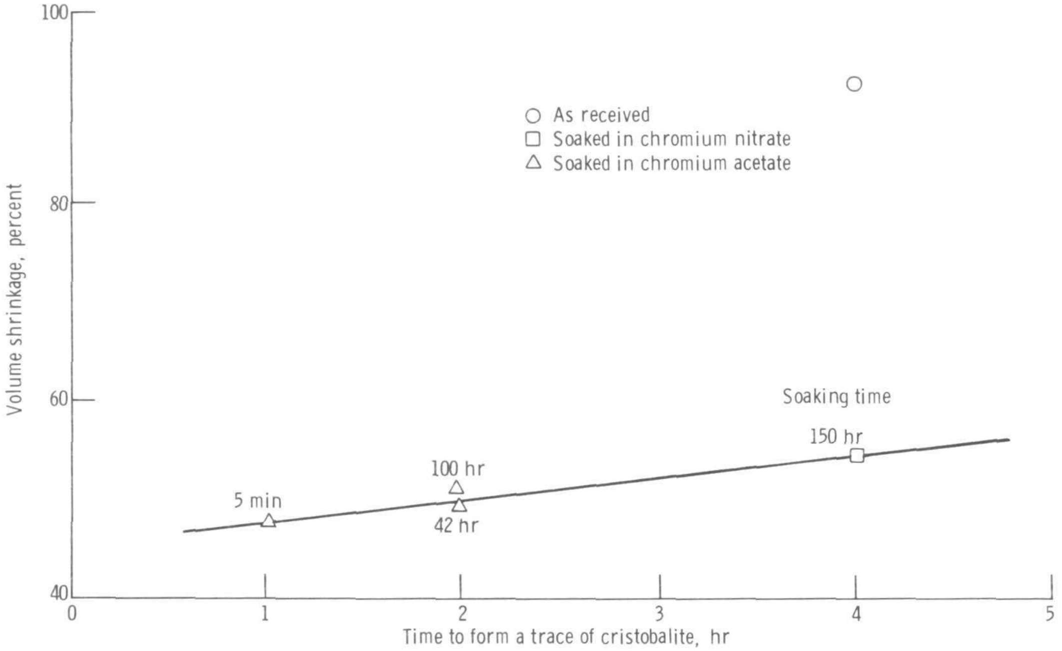

Figure 14. - Effect of soaking time in chromium solutions upon devitrification process. Materials soaked in chromium solution for various times and then heat treated at 1300° C in air.

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