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DEVITRIFICATION AND SHRINKAGE BEHAVIOR OF SILICA FIBERS

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16. Abstract

Devitrification and shrinkage of three batches of silica fibers were investigated in the temperature range of 1200° to 1350° C. Fibers with high water and impurity content devitrified rapidly to cristobalite and quartz and exhibited rapid, but the least amount of, shrinkage. A batch with low water and impurity content devitrified more slowly to cristobalite only and underwent severe shrinkage by the mechanism of viscous flow. A third batch of intermediate purity level and low water content devitrified at a moderate rate mainly to cristobalite but shrunk very rapidly. Completely devitrified silica fibers did not exhibit any further shrinkage.

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SUMMARY

The water content and the amount of impurities were determined in three batches of amorphous silica fibers, which were produced at various stages of refinement of the manufacturing process. These three batches of fibers were formed into cylindrical specimens by a water casting technique and subjected to thermal exposures at 1200°, 1300°, and 1350° C in order to study their thermal stability in terms of devitrification and shrinkage behavior. The amount of devitrification and the products of devitrification were determined by X-ray diffraction techniques. The extent of shrinkage was evaluated from density measurements. Results indicated that shrinkage was controlled by two simultaneously occurring processes: viscous flow and devitrification. Once the devitrification process was completed, no further shrinkage was observed. Generally, oxide impurities and high water content promote devitrification and lead to minimal shrinkage. Conversely, high purity fibers tend to resist devitrification but shrink excessively. It appears that, as a result of the fabrication process, silica fibers contain large numbers of very small pores which present a large surface area for chemical bonding and physical adsorption of water.

INTRODUCTION

Fibrous silica insulation is being considered as one of the materials for the reusable thermal protection system for the space shuttle. In this application, the fibers are rigidified to a low-density tile by the use of appropriate binders. During reentry, the surface of such tiles will be subjected to supersonic velocities at temperatures as high as 1350° C and pressures from 0.1 to 30 torr (ref. 1). The performance of such a thermal protection system will depend on, among other factors, the thermal stability of fibers used. In the past, considerable variability has been observed in the performance of silica fibers regarding their devitrification and shrinkage behavior. The purpose of this study was to evaluate three batches of silica fibers in terms of thermal stability with particular attention given to the effects of purity and water content on devitrification and shrinkage behavior. The production dates of the three batches of fibers span a time period in which process changes and controls were introduced which resulted in considerable improvements in fiber purity and stability. A knowledge of the behavior of these fibers of varying purity can provide base-line data to which improved fibers of the future and finished tiles might be compared.

The literature on the properties and transformations of silica is very extensive, but it is concerned mainly with the bulk material rather than ultrafine fibers. Several investigators (refs. 2 to 6) studied the effects of water content on the properties and devitrification of vitreous silica. In their considerations, they assumed that water reacted with the Si-O-Si bond to give two Si-O-H bonds. As a result, the three-dimensional bonding might be expected to become weaker as the water content (in the form of hydroxyl radical) increased. Such an assumption is in agreement with the accepted views of the structure of silica glass (refs. 7 to 10).

Some authors (refs. 11 and 12) addressed themselves to the problem of physically adsorbed water and its removal. They found that removal of this water from the small pores (such as in silica gel) was not easy and required temperatures of several hundred degrees Celsius. An infrared study of water adsorbed on silica powders (ref. 13) provided information regarding the nature of surface bonds between silica and water.

Oxides of monovalent and divalent metals were reported (refs. 5, 9, 10, 14, and 15) to affect silica glass in a manner similar to the way water affects it, whereas trivalent metal oxides seemed to inhibit devitrification. An exception regarding the effect of Al_2O_3 was indicated in reference 16.

In this study, three batches of silica fibers representing three purity levels were investigated. The amount and nature of water contained in these fibers and their shrinkage and devitrification behavior were determined, and a relation between shrinkage and devitrification is proposed.

MATERIALS

In this study, three batches of silica fibers were investigated. They were made by converting a low-melting glass to fibers and then leaching them to remove the impurities and obtain high-purity silica. These three batches are designated silicas A, B, and C. Silica A was of recent production (1971); silica B was also made in 1971, but earlier than silica A; and silica C was made in 1969. Thus, they represent the products of a process at various stages of refinement.

By X-ray diffraction (XRD) techniques, all three silica fiber batches were found to be amorphous. Scanning electron microscopy (SEM) revealed that the fiber diameter distribution in the three batches was similar. A typical SEM photograph of silica C is shown in figure 1. The average diameter of the fibers was about 2 to 3 micrometers.

The result of spectroscopic analysis of the fibers for metallic impurities is summarized in table I. Because the impurities in the fibers are in the form of oxides, the analytical data are expressed as oxide weight percent. The impurities are arranged in groups according to their valence.

EXPERIMENTAL PROCEDURE

Determination of Water Content in Silica Fibers

Water content of the silica fibers was determined by measuring their weight loss (TGA) during isothermal heating in air at 1 atmosphere. For this purpose, a 1.3-gram sample of loose fibers was packed in a fused silica basket and suspended in a vertical tube furnace from an automatic analytical balance. The weight change was continuously recorded for a period of 7 hours. Duplicate determinations of water content for each silica batch were made at 500°, 900°, and 1100° C.

Water Casting of Cylinders

Cylinders were prepared by blending 10 grams of silica fibers in 600 cubic centimeters of distilled water. This suspension was filtered through a cylindrically shaped funnel with a large height-to-diameter ratio and having its lower end covered with a fine metallic screen. The process of filtering was accelerated by application of a vacuum. The settled fibers formed a cylinder which after removal from the funnel was dried in an oven at 100° C for about 16 hours. The approximate height and diameter of such water-cast cylinders were 4.5 and 4.6 centimeters, respectively. Their texture is shown in figure 2. All cylinders fabricated in this manner were cut in half, perpendicular to their axes. Each half representing a specimen was marked and its dimensions were determined with a micrometer. At this stage, all the specimens contained unknown amounts of water which could not be removed by drying at 100° C. Therefore, their initial density had to be calculated on the basis of the initial dimensions and the final weight values obtained after subsequent thermal exposure. The values of initial density varied from specimen to specimen within the range of 0.12 to 0.14 gram per cubic centimeter.

Thermal Exposure

Cylindrical specimens were exposed to temperatures of 1200°, 1300°, and 1350° C in a large muffle furnace. The exposure times were 1, 2, 4, 8, 16, and 24 hours at 1200° C; 1/2, 1, 2, 4, 8, and 16 hours at 1300° C; and 1/4, 1/2, 1, and 4 hours at 1350° C. Three specimens representing the three batches of silica fibers were simultaneously exposed (on a platinum tray) to a thermal treatment. After completion of a treatment, the specimens were removed from the furnace, cooled in air for 2 minutes, and rapidly weighed on an automatic analytical balance. When the specimens retained their cylindrical shapes, their diameter and height were measured with a micrometer. In most cases, however, they became slightly distorted. In order to facilitate density determinations, these distorted specimens had to be ground to a regular shape, vacuum cleaned, dried at 900° C for 1 hour weighed, and measured. It will be shown that 900° C is a sufficiently high temperature to remove any adsorbed water.

Because of the necessity of grinding some specimens to cylindrical shape, a shrinkage comparison based on absolute volumes is impossible. For this reason, the percentage of volume shrinkage was calculated from the density values by using the following expression:

$$\text{Percent volume shrinkage} = \frac{d - d_o}{d} 100$$

where d_o is initial density, and d is final density.

X-Ray Diffraction Analysis

After the density determinations were made, most of the specimens were subjected to X-ray diffraction analysis. For this purpose, they were broken into pieces which were ground in a tungsten carbide mortar while wetted with ethyl alcohol. Diffraction patterns were taken on a diffractometer with monochromatic CuKα radiation in the 2θ (theta) range from 10° to 35°.

While taking patterns, the scale factor was such as to ensure that the (101) α-quartz and the (101) α-cristobalite lines were within the range of the chart. Integrated intensities of both lines were used to determine the relative amounts (by weight) of α-quartz and α-cristobalite by comparing them with those of standard mixtures.

Scanning Electron Microscopy

The textures of water-cast silica specimens and the effects of thermal exposure upon these textures were studied by scanning electron microscopy. Small pieces of selected specimens were mounted on aluminum disks and ultrasonically cleaned in alcohol of debris produced by cutting. They were then coated with gold-platinum alloy by vapor deposition. The photographs of the specimens after thermal exposures were taken at 1000 magnification.

Infrared Absorption

The infrared absorption spectra of silica B and C fibers were recorded in the frequency range from 4000 to 1500 cm^{-1}. To accomplish this, a small quantity of as-received silica fibers was ground in a tungsten carbide mortar containing acetone in order to obtain a slurry. This slurry was then cast on two sodium chloride plates (single crystals) in order to obtain thin and uniform layers of silica on one of their faces. After evaporation of the acetone, the sodium chloride plates were clamped together with the coated faces inside. The absorption spectra were recorded at room temperature and atmospheric pressure. Silica A was not tested because it was obvious that it would have produced an absorption pattern similar to that of the other two silicas.

RESULTS

Water Content

The amounts of water that the silica fibers lost during heating at 500^{o}, 900^{o}, and 1100^{o} C are shown in figures 3 to 5. The losses are expressed as percentages of the original weights of the samples and are plotted as a function of time. Figure 3 shows that at 500^{o} C most of the water is lost during the first few minutes of the experiment. Then, the rate of loss decreases, and after 1 hour it becomes nearly constant. After 7 hours, the silica C fibers lost 9 percent, while silica A and B fibers lost 7.4 to 7.7 percent. In view of the data obtained at higher temperatures, these values obviously do not represent the total water content. At 900^{o} and 1100^{o} C (figs. 3 and 4), nearly all the water was lost in the first few minutes, and the rest was driven off in less than 1 hour. At these temperatures, silica C fibers lost approximately 11 percent, and silica A and B fibers lost about 8.4 to 9.2 percent. In view of the zero loss rates observed after less than 1 hour at 900^{o} and 1100^{o} C and the reasonable agreement among the 7-hour weight losses observed at these temperatures, it is believed that these values represent the total water content in the fibers.

The infrared absorption spectra determination (fig. 6) corroborated the presence of multilayered physically adsorbed water. This water produces a very broad band centered at about 3450 cm^{-1} which conceals the presence of chemically bound water at 3743, 3640, and 3500 cm^{-1} (ref. 13).

Shrinkage

The texture of water-cast silica specimens is shown in figure 2. It is apparent that the void space represents the bulk of the volume. Assuming that the density of the fibers is about 2.2 grams per cubic centimeter (the density of vitreous silica), the volume they occupy amounts to only about 5 percent. The textures of the three silica specimens appear to be quite similar.

When exposed to elevated temperatures, the specimens underwent shrinkage and devitrification. Figure 7 shows on a macroscopic scale the shrinkage behavior of the silica specimens at 1300° C. It is apparent that the three silicas behaved differently. These differences are illustrated quantitatively in figures 8 to 10. At each of three test temperatures, silica A specimens shrunk initially less than the specimens of the other two silicas. Also, silica A specimens continued to shrink long after silicas B and C reached their final density. Silicas B and C shrunk rapidly to their final size, and continued heating did not cause any further shrinkage. Silica C specimens exhibited the least amount of total shrinkage at all temperatures. Figures 11 to 13 reveal the textures of selected specimens after exposures at the three test temperatures. Comparison with the photographs in figure 2 reveals that the amount of the void space in the specimens substantially decreased. Silica B shows strong evidence of viscous flow, as suggested by the deformation occurring at the fiber joints.

The shrinkage behavior of the silica fiber specimens and the simultaneously occurring devitrification process are summarized in tables II to IV. They reveal that silica specimens shrunk as long as the amorphous phase was present; and once devitrification was generally complete, no further shrinkage took place. The general review of the results is presented in table V.

DISCUSSION

In an attempt to explain the differences in shrinkage and devitrification behavior of three batches of silica fibers, let us compare their relative impurity contents. Table I shows that silica C contained 0.7 weight percent of metallic oxides, silica B contained 0.57 percent, and the purest was silica A, with about 0.38 percent. And indeed, the results of thermal exposure experiments revealed that silica C devitrified at the fastest rate and that silica A was quite resistant to devitrification. However, the differences in the behavior of silicas B and C are too large to be explained in terms of impurity content alone. Since it has been reported that water has a very significant effect on the devitrification and physical properties of amorphous silica (refs. 2 to 6 and 9), it is reasonable to suspect that different water contents might account for the above-mentioned differences in devitrification behavior of silicas B and C. In the thermogravimetric analyses of this investigation, it was observed that water represented a significant part of the total weight of all three as-received silica fibers (figs. 2, 4, and 5). At this point, it is necessary to distinguish the following four types of water which can be associated with silica:

(1) Physically adsorbed water on external fiber surfaces and in large pores. This water represents the bulk of the total water content and can be easily driven off in the first few minutes of heating at 500° C. This water should not play any role in the devitrification process.

(2) A small amount of physically adsorbed water contained in the pores of the fibers. According to references 15 and 16, removal of this water requires temperatures of 500° C or above, depending on the size of the pore. Part of this water could affect the devitrification of silica.

(3) Water in the form of hydroxyl radicals (OH) bound to the surface of the silica. This water should affect the devitrification of silica because it breaks the Si-O-Si bonds at the surface. Perhaps there is a relation between this and the observed fact that during devitrification the crystalline phase always nucleates on the surface (ref. 2).

(4) Water in the form of hydroxyl radicals in the silica lattice. Its content is very low (ref. 3) and usually is expressed in ppm. Nevertheless, this water affects the physical properties of silica (refs. 3 to 5) and its devitrification behavior.

Figures 3 to 5 indicate that the silica fibers gave off part of their water content only at temperatures above 500° C. This suggests, in accord with references 11 and 12, that they must contain a large quantity of minute pores (the result of leaching) which hold water of types 2 and 3. Further examination of figures 3 to 5 suggests that silica C contained larger amounts of type 2 and 3 water than did silicas A and B. Therefore, it is reasonable to assume that the devitrification behavior of silica C is influenced not only by its metallic impurity content, but also to a large degree by water contained in the pores.

Since silicas A and B contain nearly equal amounts of water, their differences in devitrification and shrinkage behavior must be due to different contents of oxide impurities. The obvious evidence of viscous flow in silica B (figs. 11 to 13) and its rapid shrinkage (figs. 8 to 10) are believed to be due to high content of total impurities, particularly of valence 1+. The slower but continuing shrinkage and delayed devitrification of silica A reflect its lower impurity level.

It is evident that during thermal exposure of the water-cast silica specimens, two processes affect their shrinkage behavior. They are the viscous flow of the amorphous phase under influence of surface tension, and the devitrification process. Devitrification of the silica C specimens was so rapid that they did not shrink to the degree of the other two silicas, which devitrified at a slower rate. The silica A devitrified always to cristobalite, whereas silica C devitrified to cristobalite and quartz. Silica B devitrified to cristobalite and quartz at 1200° C, and only to cristobalite at higher temperatures. When the devitrification process was completed, the shrinkage of the silica fibers stopped.

SUMMARY OF RESULTS

Three batches of silica fibers were characterized by spectroscopic analysis, thermogravimetric analysis, scanning electron microscopy, X-ray diffraction, and infrared absorption. The shrinkage and devitrification behavior of water-cast specimens were studied at 1200°, 1300°, and 1350° C and were related to the impurity and water content of the specimens. The following were the major results obtained:

1. The fibers were shown to contain water in amounts ranging from 8.5 to 11 percent. The bulk of this water was physically adsorbed on the surface and was easily driven off by heating at low temperatures. A portion of the remaining water was physically adsorbed water in the micropores of the fibers. The observation that a part of physically adsorbed water could not be removed by heating the silica fibers at 500° C indicates that the fibers contained large numbers of very small pores. These pores were the result of the fabrication process. They affect the behavior of silica fibers by contributing to the total surface area for adsorption and chemical bonding of impurities (oxides and/or water).

2. The content of metallic oxide impurities appeared to affect the thermal stability of silica fibers by promoting devitrification. In addition, the alkaline oxides seemed to decrease the viscosity of silica.

3. Silica fibers when exposed to elevated temperatures are subjected to viscous flow and devitrification. Viscous flow results in shrinkage of the specimens, while devitrification reduces the amount of amorphous phase and thus leads to smaller amounts of shrinkage. Pure silica fibers, since they are more resistant to devitrification, can undergo considerable shrinkage, whereas silica fibers containing impurities (oxides and/or water) will devitrify rapidly, thus limiting the amount of shrinkage. The silica

fibers with high impurity content divitrified to cristobalite and a variable amount of quartz, whereas silica fibers with lower impurity content devitrified to cristobalite only. Once devitrification had occurred, no further shrinkage could take place.

CONCLUDING REMARKS

The thermal stability, in terms of shrinkage and devitrification, of three batches of silica fibers was studied to temperatures as high as 1350° C. It is apparent that manufacturing-process changes have resulted in fibers of increased purity and lower water content. These changes have resulted in fibers that are more resistant to devitrification. However, in the absence of devitrification, fibers are prone to viscous flow which results in considerable shrinkage.

It must be remembered that these observations refer to as-manufactured fibers and do not necessarily indicate the behavior of reusable surface insulation tiles made from these fibers. The finished tiles are of higher density, contain a rigidifying binder, and may exhibit a high degree of fiber orientation. All of these factors could alter the devitrification and/or shrinkage behavior. The investigation reported herein is part of a larger effort to characterize the behavior of silica fibers. The data from this investigation should be of value as base-line data for evaluating improved fibers of the future and finished tiles.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 16, 1972,
114-03.

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TABLE I. - IMPURITIES IN AS-RECEIVED

SILICA FIBERS AS DETERMINED BY

SPECTROSCOPIC ANALYSIS

Silica	Impurity				
	Cation valence	Oxide	Quantity, wt. %		
A	1+	K_2O	0.008	0.021	0.3833
		Na_2O	.013		
	2+	CaO	0.070	0.1623	
		CuO	[a]<.0012		
		MgO	.005		
		NiO	.0013		
		PbO	.086		
		SrO	[a]<.0012		
	3+	Al_2O_3	0.150	0.179	
		B_2O_3	[a]<.009		
		Fe_2O_3	.029		
	4+	SnO_2	[a]<0.0013	0.021	
		TiO_2	.017		
		ZrO_2	.004		
B	1+	K_2O	0.0097	0.0597	0.5972
		Na_2O	.050		
	2+	CaO	0.084	0.1905	
		CuO	[a]<.0012		
		MgO	.033		
		NiO	.0025		
		PbO	.042		
		SrO	.029		
	3+	Al_2O_3	0.300	0.329	
		B_2O_3	[a]<.009		
		Fe_2O_3	.029		
	4+	SnO_2	[a]<0.0013	0.0018	
		TiO_2	.014		
		ZrO_2	.004		
C	1+	K_2O	0.0036	0.0396	0.7039
		Na_2O	.036		
	2+	CaO	0.25	0.4246	
		CuO	[a]<.0012		
		MgO	.15		
		NiO	.0012		
		PbO	.0210		
		SrO	.0024		
	3+	Al_2O_3	0.200	0.229	
		B_2O_3	[a]<.009		
		Fe_2O_3	.029		
	4+	SnO_2	[a]<0.0013	0.0107	
		TiO_2	.008		
		ZrO_2	.0027		

[a] Detection limit omitted from subtotals.

TABLE II. - DEVITRIFICATION AND SHRINKAGE BEHAVIOR OF WATER-CAST SILICA FIBER SPECIMENS AT 1200° C

Silica	Exposure time, hr	Phases present	Shrinkage, vol. % (a)
A	2	(b)	25
	4	(b)	35
	8	(b)	43
	16	(b)	55
	24	Amorphous, with approx. 10 percent cristobalite	62
B	2	(b)	53
	4	Amorphous	66
	8	80 Percent cristobalite and 20 percent quartz	75
	16	(b)	75
	24	90 Percent cristobalite and 10 percent quartz	75
C	2	Amorphous, with trace of cristobalite	37
	4	Cristobalite, with small amount of amorphous	42
	8	Cristobalite, with trace of quartz	44
	16	(b)	44
	24	Cristobalite, with trace of quartz	44

[a] Values read from curves of fig. 8.

[b] Not analyzed.

TABLE III. - DEVITRIFICATION AND SHRINKAGE BEHAVIOR OF WATER-CAST SILICA FIBER SPECIMENS AT 1300° C

Silica	Exposure time, hr	Phases present	Shrinkage, vol. % (a)
A	0.5	(b)	37
	1	(b)	53
	2	(b)	72
	4	Amorphous	83
	8	Amorphous, with approx. 10 percent cristobalite	89
	16	Cristobalite	(b)
B	0.5	Amorphous, with approx. 45 percent cristobalite	90
	1	(b)	(b)
	2	Cristobalite	91
	4	(b)	(b)
	8	Cristobalite	91
	16	(b)	(b)
C	0.5	60 Percent cristobalite and 40 percent quartz	44
	1	(b)	50
	2	87 Percent cristobalite and 13 percent quartz	53
	4	(b)	54
	8	90 Percent cristobalite and 10 percent quartz	54
	16	92.5 Percent cristobalite and 7.5 percent quartz	55

[a] Values read from curves of fig. 9.

[b] Not analyzed.

TABLE IV. - DEVITRIFICATION AND SHRINKAGE BEHAVIOR

OF WATER-CAST SILICA FIBER SPECIMENS AT 1350° C

Silica	Exposure time, hr	Phases present	Shrinkage, vol. % (a)
A	0.25	Amorphous	47
	.5	(b)	63
	1.0	Amorphous	77
	4.0	Amorphous, with approx. 20 percent cristobalite	91
B	0.25	Amorphous, with approx. 10 percent cristobalite	87
	.5	(b)	(b)
	1.0	Cristobalite	(b)
	4.0	Cristobalite	87
C	0.25	Amorphous, with traces of quartz and cristobalite	72
	.5	Approx. 30 percent amorphous, approx. 49 percent cristobalite, and approx. 21 percent quartz	(b)
	1.0	(b)	(b)
	4.0	Cristobalite	81.5

[a] Values read from curves of fig. 10.
[b] Not analyzed.

TABLE V. - GENERAL REVIEW OF RESULTS

Silica	Water content	Impurities					Shrinkage rate	Final shrinkage	Devitrification rate	Product of devitrification
		Valence				Total				
		1+	2+	3+	4+					
A	Low[a]	Low	Low	Low	High	Low	Slow[a]	High	Slow	Cristobalite
B	Low	High	Low	High	Medium	Medium	Fast	High	Intermediate	Cristobalite and quartz at 1200° C Only cristobalite at 1300° and 1350° C
C	High	Medium	High	Medium	Low	High	Fast	Low	Fast	Cristobalite and quartz

[a] Relative value.

Figure 1. - SEM photograph of silica C as received. X600.

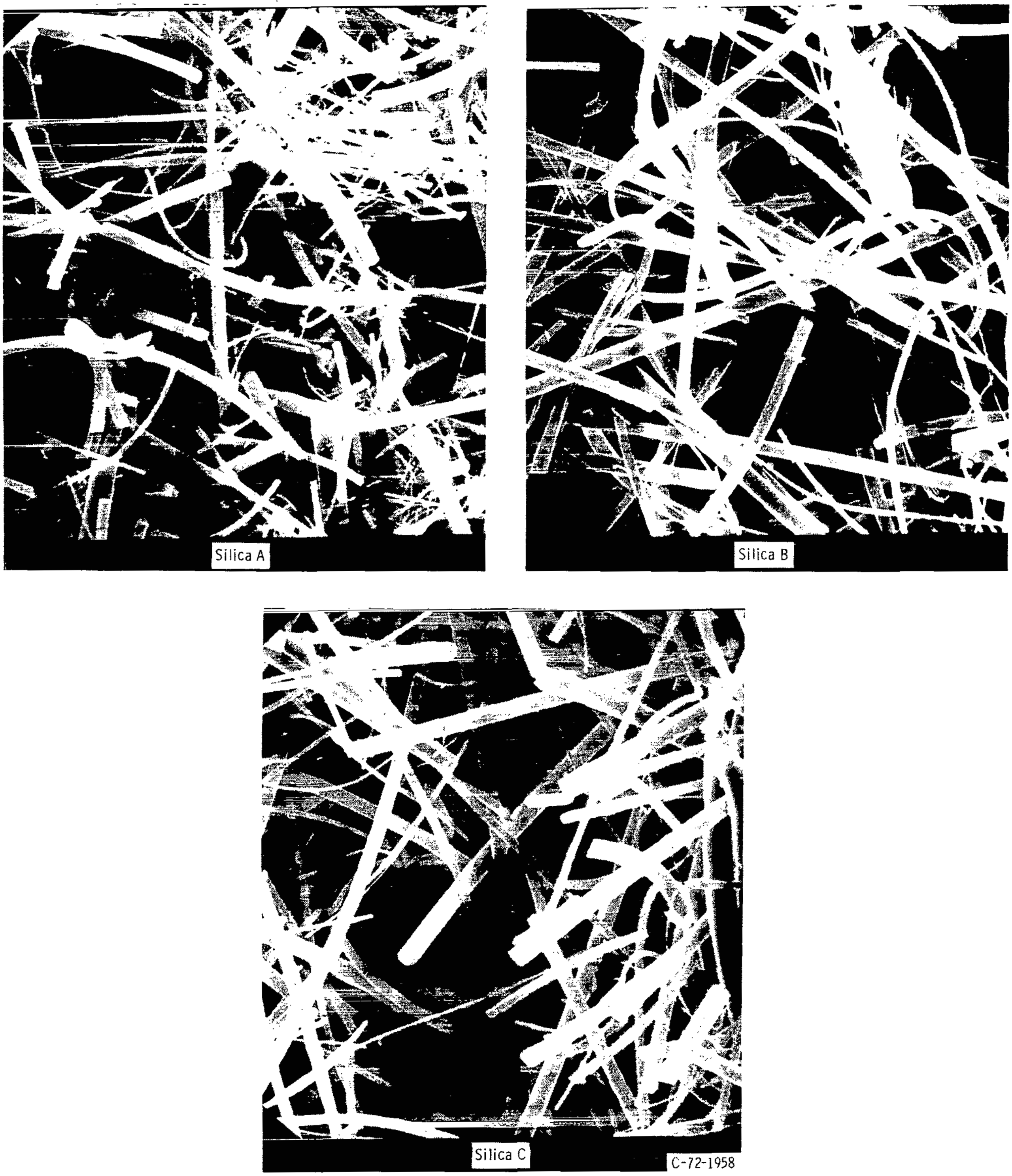

Figure 2. - SEM photographs of water-cast silica specimens. X1000. (Reduced 8 percent in printing.)

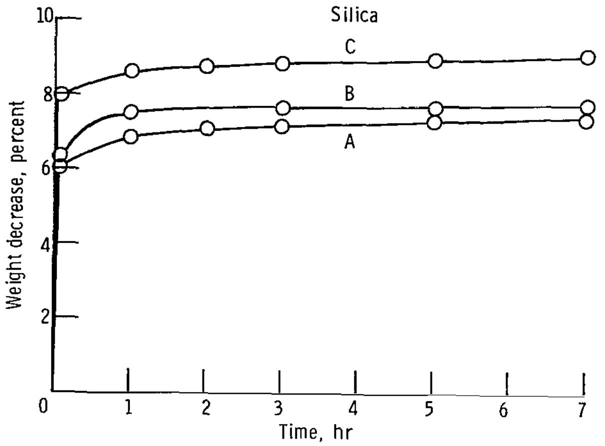

Figure 3. - Water loss during isothermal heating of silica fibers at 500° C.

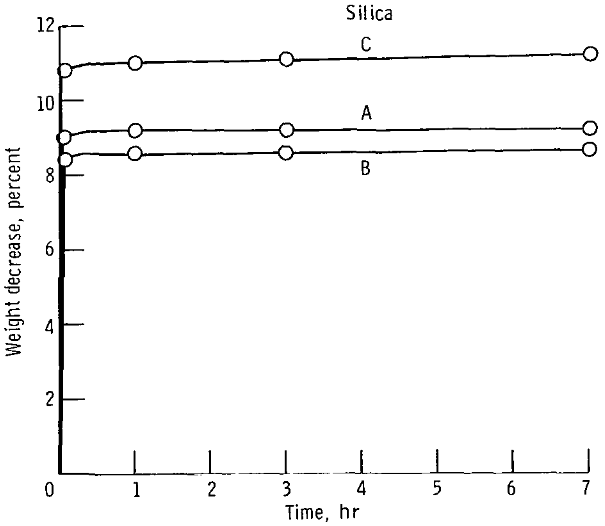

Figure 4. - Water loss during isothermal heating of silica fibers at 900° C.

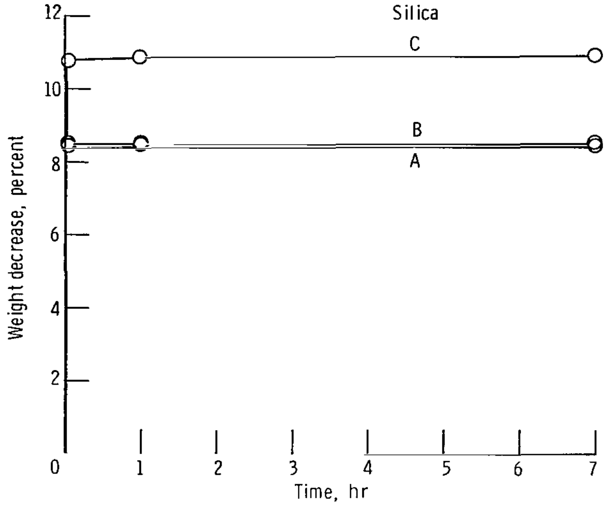

Figure 5. - Water loss during isothermal heating of silica fibers at 1100^0 C.

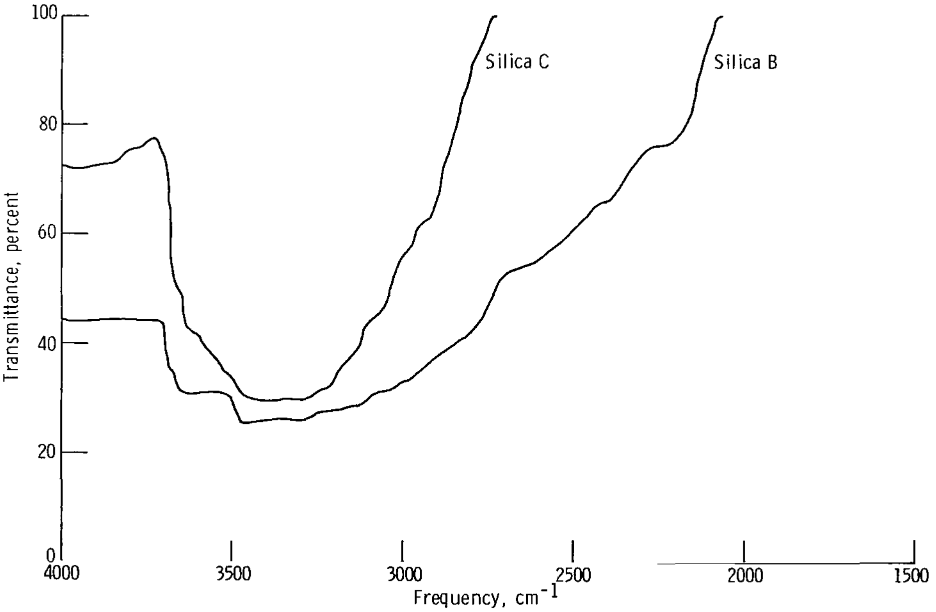

Figure 6. - Infrared spectra of as-received silica fibers at atmospheric pressure and room temperature.

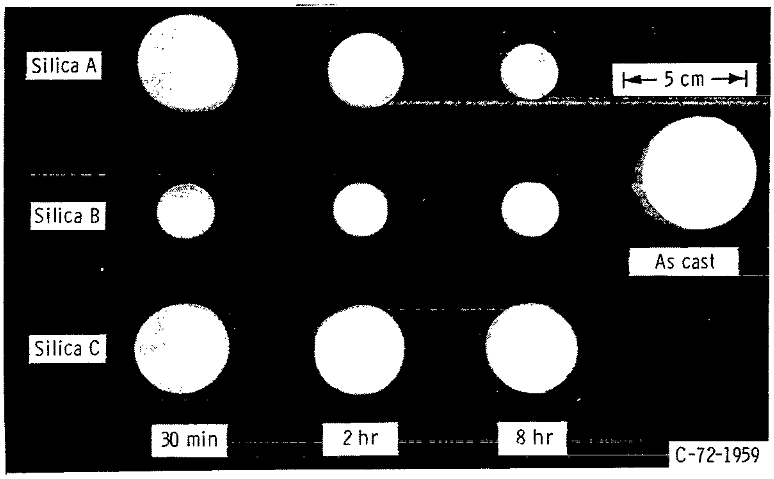

Figure 7. - Shrinkage of water-cast silica cylinders at 1300° C.

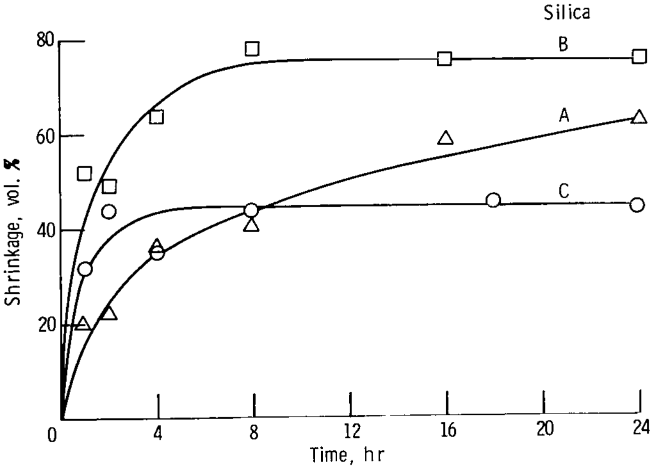

Figure 8. - Shrinkage of water-cast silica specimens heated at 1200° C.

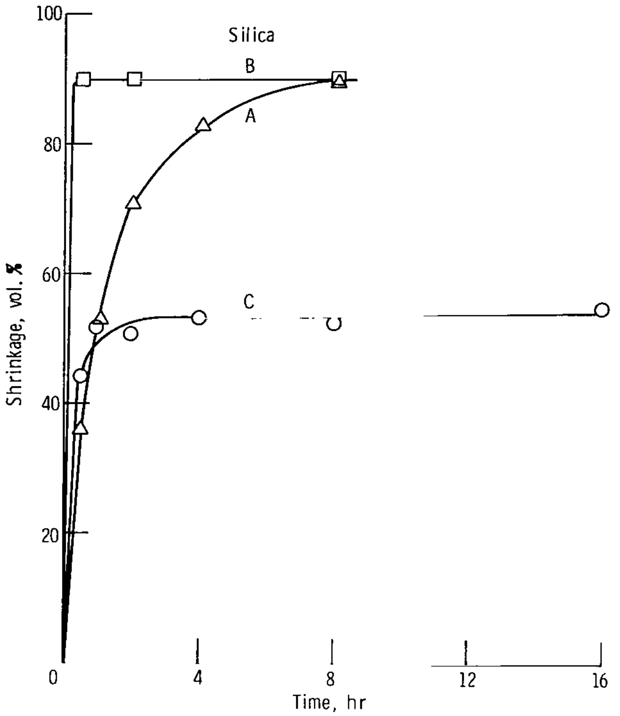

Figure 9. - Shrinkage of water-cast silica specimens heated at 1300° C.

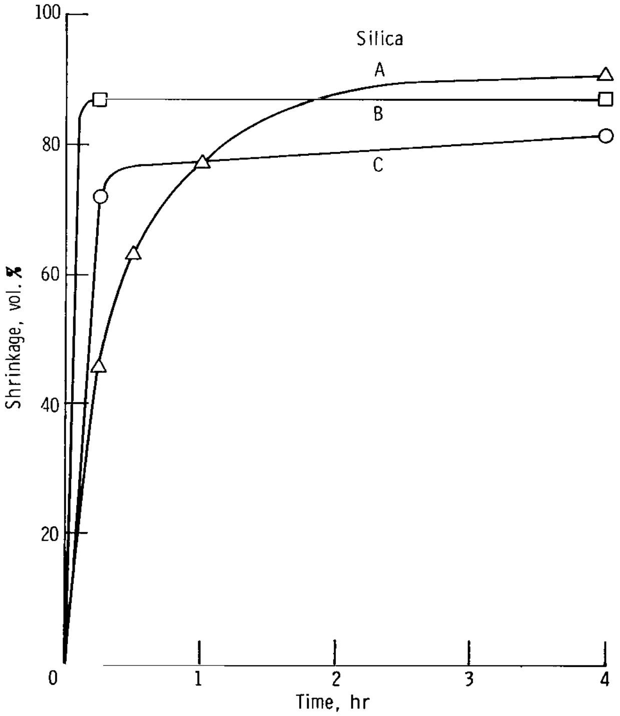

Figure 10. - Shrinkage of water-cast silica specimens heated at 1350° C.

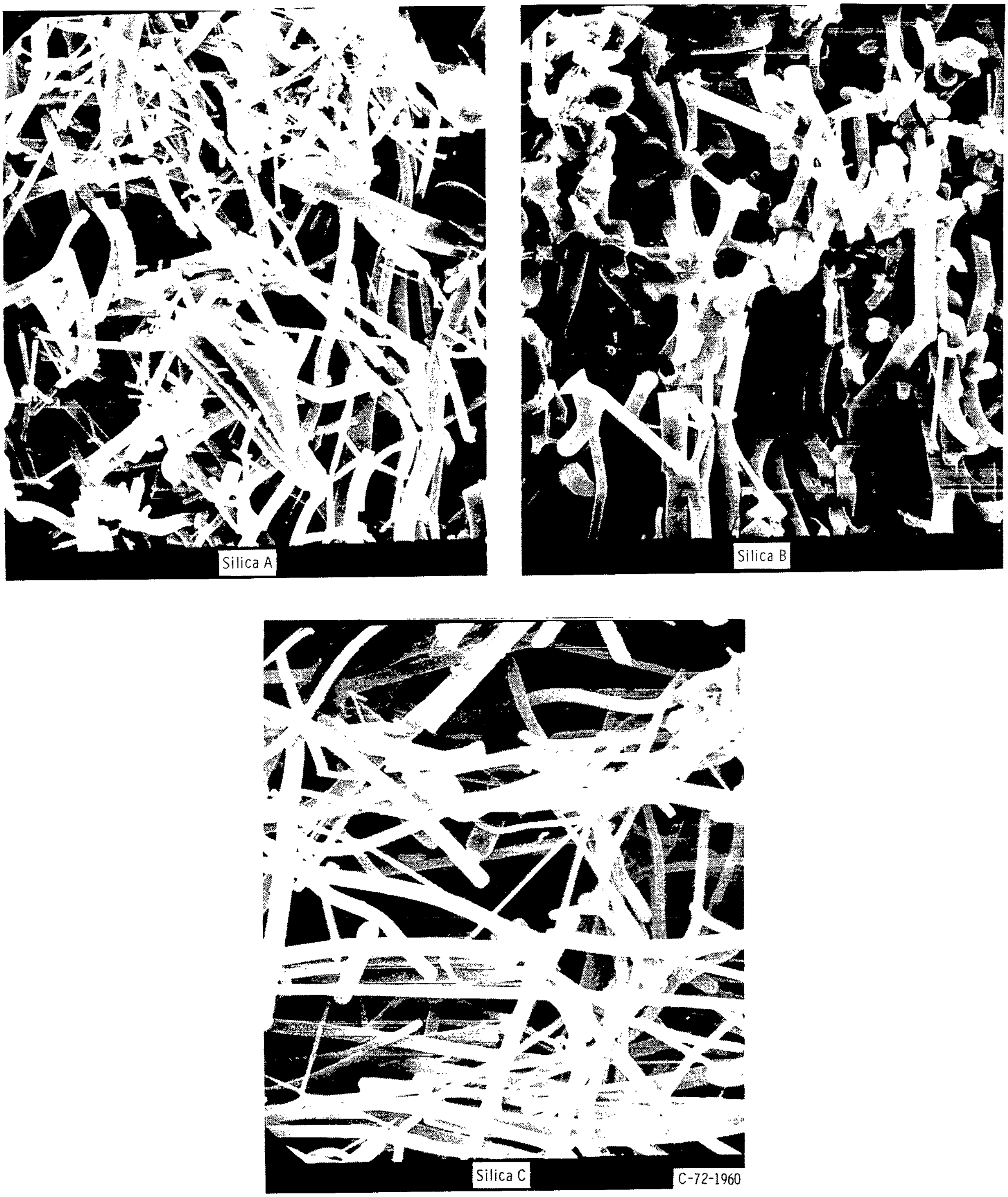

Figure 11. - SEM photographs of water-cast silica specimens heated at 1200^0 C for 24 hours. X1000. (Reduced 8 percent in printing.)

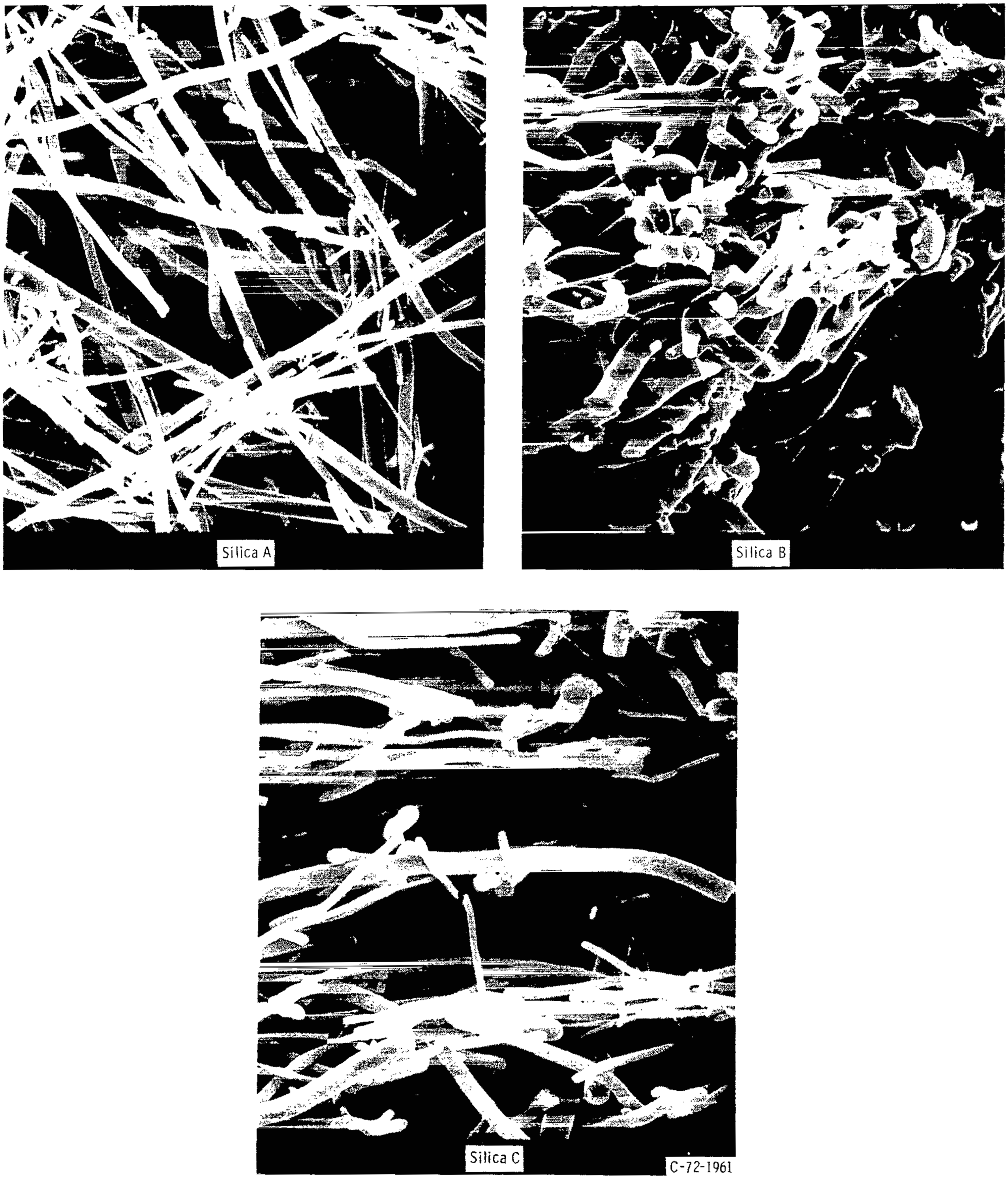

Figure 12. - SEM photographs of water-cast silica specimens heated at 1300° C for 1/2 hour. X1000. (Reduced 8 percent in printing.)

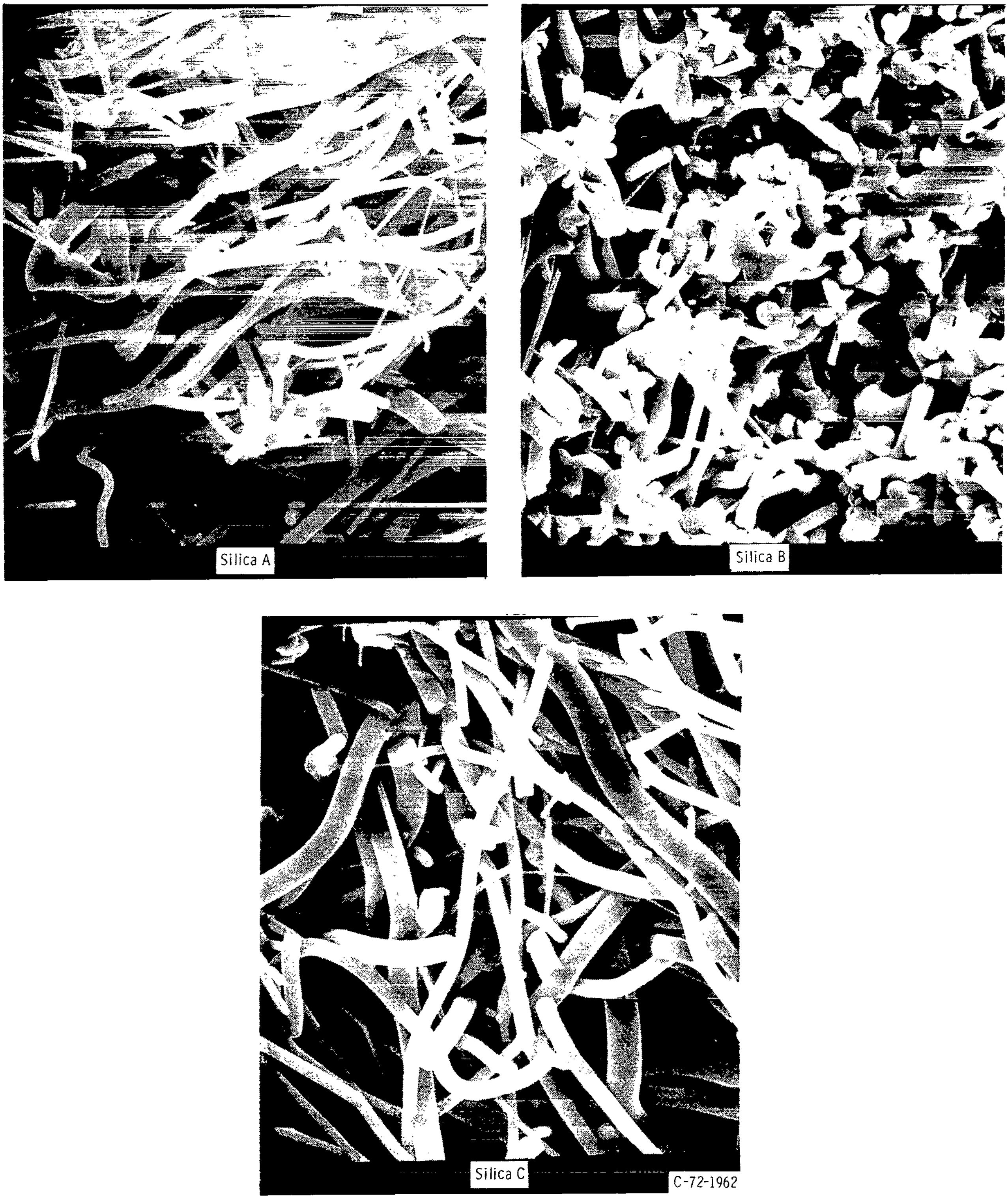

Figure 13. - SEM photographs of water-cast silica specimens heated at 1350° C for 15 minutes. X1000. (Reduced 8 percent in printing.)

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