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INVESTIGATIONS OF RADIOACTIVE
FUEL-BEARING GLASSES

JAN 21 1962
Contract AT-(30-1)-2489
April 1, 1961 - March 31, 1962

P. A. Lockwood

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TECHNICAL REPORT

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SUMMARY AND CONCLUSIONS

A series of high urania-content glasses were fiberized and examined for high temperature strength properties. One glass, RX360 containing 60 per cent U_3O_8 by weight, had better high temperature tensile properties than any glass previously reported. It was observed that many of the glasses studied separated into immiscible phases and that the fiberizable glass phase had lower U_3O_8 content than the base compositions.

A physical analysis of crystal structures of the devitrification products from the nuclear fuel glasses indicated that most of the crystals consisted of uranium oxide in a reduced state. By adding oxygen to molten glass, it was possible to eliminate most of this devitrification. By elimination of crystals, the fiberizing of the glass was more uniform and the glasses produced had more consistent physical properties.

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AEC Research and Development Report

OWENS - CORNING FIBERGLAS CORPORATION

INVESTIGATIONS OF RADIOACTIVE FUEL-BEARING GLASSES

April 1, 1961 - March 31, 1962

by

P. A. Lockwood

Contract AT-(30-1)-2489

U. S. ATOMIC ENERGY COMMISSION

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INVESTIGATIONS OF RADIOACTIVE FUEL-BEARING GLASSES

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INVESTIGATIONS OF RADIOACTIVE FUEL-BEARING GLASSES

by

P. A. Lockwood

Abstract

A series of high urania-content glasses were fiberized and examined for high temperature strength properties. One glass, RX360 containing 60 per cent U_3O_8 by weight, had better high temperature tensile properties than any glass previously reported. It was observed that many of the glasses studied separated into immiscible phases and that the fiberizable glass phase had lower U_3O_8 content than the base compositions.

A physical analysis of crystal structures of the devitrification products from the nuclear fuel glasses indicated that most of the crystals consisted of uranium oxide in a reduced state. By adding oxygen to molten glass, it was possible to eliminate most of this devitrification. By elimination of crystals, the fiberizing of the glass was more uniform and the glasses produced had more consistent physical properties.

INVESTIGATIONS OF RADIOACTIVE FUEL-BEARING GLASSES

INTRODUCTION

The investigations of radioactive fuel-bearing glasses during the period of April 1, 1961, through March 31, 1962, have followed the basic pattern developed during the subcontract work under the Rensselaer Polytechnic Contract AT-(30-3)-321 started in 1958. The basic concepts of this work have been to study a series of glasses containing varying amounts of radioactive fuel materials and to make fiberization trials of these glasses using standard glass fiber technology. When suitable combinations of compositions and fiber-forming techniques have produced materials with properties of interest to the Atomic Energy Commission, samples of these materials have been supplied to the AEC and interested AEC contractors.

The work during this report period was divided into four sections:

1. Basic and applied research to study high temperature, high urania content glasses and the application of standard glass fiber-forming systems to these glasses.
2. Crystallization studies of silicate glasses containing urania.
3. Studies of the effect of the oxidation state of uranium on urania solubility in silicate glass systems.
4. Supplying samples to various AEC contractors.

SUMMARY

Seven high urania-content glasses showing promise in preliminary trials were fiberized but none of them yielded any improvement in high temperature strength properties over RX308 glass previously reported.¹ Six variants of RX308 were fiberized, and one of these--RX360, containing 60 weight per cent U_3O_8 --had approximately 20 per cent better high temperature tensile strength than RX308.

Crystalline phases have been noted in many of the glasses containing high percentages of urania. In particular, RX70 glass containing 50 weight per cent U_3O_8 varied widely in physical properties apparently related to the degree of crystallization in the fibers. X-ray diffraction, optical microscopy, and electron microscopic studies indicated that the crystals were mainly an oxide of uranium in an oxidation state corresponding to the formula $UO_{2.3 - 2.4}$, i.e. part way between UO_2 and $UO_{2.67}$ (U_3O_8).

The study of the crystalline material in the glass stemmed from difficulties encountered in the production of fine fiber mat for various sample requirements. The ability to form mats below five micron fiber diameter was exceedingly erratic and dependent upon the kind and extent of crystallization in the glass cullet. In attempts to eliminate the crystals, it was found that bubbling wet oxygen through the molten glass reduced the crystals to submicroscopic size or eliminated them.

¹AEC Research and Development Report NYO 9735. "Investigations of Radioactive Fuel-Bearing Glasses," Contract AT-(30-1)-2489, May 1, 1960 - March 31, 1961, P. A. Lockwood, Owens-Corning Fiberglas Corporation.

During the course of the year samples were sent to four outside AEC contractors under the contract, and two other AEC contractors were supplied through direct purchase orders.

DISCUSSIONHigh Temperature, High Urania Content Glass
Composition Fiberizability Trials

One of the dominant themes of the research work through the entire project to date has been the attempt to produce glass compositions containing large amounts of fuel-bearing materials and having high temperature properties. In particular, urania glasses have been studied as the most fruitful area of this search. With the high temperature fiberizing equipment of the Owens-Corning Fiberglas Corporation, studies of glass compositions with melting and forming temperatures of up to 4000°F are possible. A long series of high urania glasses with high temperature characteristics were given preliminary tests as reported in the First Annual Report², but all of the glasses which had been determined as possibly suitable for fiberization had not been tried due to failure of the high temperature equipment toward the end of the contract period.

Two glasses were tried at the end of that period which showed erratic results due possibly to impending failure of the equipment. These glasses, RX350 and RX356 (Table I), were restudied with the refurbished high temperature forming equipment and found to be unsuitable for continuous fiber production. Five other glasses (Table I) which had also shown some promise in preliminary testing were tried in the high temperature fiberizing equipment. Only one of these glasses--RX337, 65 per cent U₃O₈ by weight--showed high temperature potential as indicated by moderate tensile strengths at

²Ibid.

TABLE I
 POTENTIAL HIGH TEMPERATURE, HIGH URANIA GLASS COMPOSITIONS
 FIBERIZABILITY TRIALS

Glass No. →	RX309	RX330	RX334	RX337	RX348	RX350	RX356
Composition - % By Weight							
SiO ₂	29.98	31.98	29.98	27.48	37.47	22.49	24.96
Al ₂ O ₃	10.00	2.00	5.00	7.50	2.50	2.50	0.10
U ₃ O ₈	59.97	59.96	64.97	64.97	55.96	74.97	74.89
Fe ₂ O ₃	0.05	0.06	0.05	0.05	0.06	0.04	0.05
BeO	--	6.00	--	--	--	--	--
Melting Temp. - °F	2950	3560	3270	3300	3520	3600	3660
Fiberizing Temp. - °F	3350	3400	3700	3550	3700*	4100*	4100*
Tensile Strength - psi							
Room Temperature	134,000	38,000	138,000	117,000	--	--	--
1600°F	42,000	44,000	Broke on Loading in Tester	Yield - 87,000 Ulti. - 129,000	--	--	--
1800°F	--	--	Badly Devitrified	--	--	--	--
Analysis of Glass Fibers**							
SiO ₂		38.26	49.88	49.34			
Al ₂ O ₃		5.28	8.51	8.17			
U ₃ O ₈		51.12	41.51	42.52			
BeO		5.28	--	--			

*These glasses would not form fibers continuously.

**If more than one phase occurred in glass, analysis was made of the fibers of the stronger phase.

1600°F. RX337 glass failed at 1800°F due to serious yielding or plastic flow of the fibers under low tensile loads. It was noted during this series of fiberizing runs that all the high temperature glasses had a tendency to form immiscible phases during the fiberizing trials. As many as three separate phases have been observed during fiberizing, starting with a non-fiberizable non-glassy phase which changed to a semi-glassy phase and finally to a fiberizable glass phase. Chemical analysis was made of several of these phases. The glass fiber phase is shown in Table I along with the other operating properties of the glasses. Again, considerable difficulty was experienced in maintaining the high temperature equipment in good working order and finally the equipment had to be shut down for repairs.

Rather than start a new series of ternary glass compositions, it was decided to study compositions that were modifications of the best glass reported to date. The data indicated that RX308, containing 60 per cent U_3O_8 by weight, had the best fiber-forming and strength properties. Six glasses starting with RX360 through RX365, Table II, were then studied which were slight modifications of RX308 glass. The data obtained from these trials indicate that RX360 glass has better high temperature tensile strength than RX308. The main problem is that RX360 glass separates into two distinct phases of which the fiberizable glassy phase is of a much lower urania content than the starting composition. Earlier records of trials on RX308 glass did not show a similar separation although due to the erratic fiber-forming behavior of these glasses, these phase separations might not have been observed prior to this reporting period. RX308

TABLE II
HIGH TEMPERATURE, HIGH URANIA GLASS COMPOSITIONS
VARIATIONS ON RX308 GLASS

Glass No. →	RX308*	RX360	RX361	RX362	RX363	RX364	RX365
Composition - % By Weight							
SiO ₂	34.98	35.97	35.97	34.98	33.98	33.98	34.98
Al ₂ O ₃	5.00	4.00	5.00	6.00	6.00	5.00	4.00
U ₃ O ₈	59.96	59.96	58.96	58.96	59.96	60.96	60.96
Fe ₂ O ₃	0.06	0.07	0.07	0.06	0.06	0.06	0.06
Fiberizing Temp. - °F							
	3450	3550	3900	3300	3500	3600	3450
Tensile Strength - psi							
Room Temperature	141,000	73,000	Devit.	34,000	71,500	Devit.	Devit.
1600°F	Yield - 91,000 Max. - 118,000	141,000		45,000	14,000		
1800°F	Yield - 53,000 Max. - 69,000	Yield - 77,000 Ulti. - 94,000					
Analysis of Glass Fibers** - % By Weight							
SiO ₂		53.20					
Al ₂ O ₃		9.20					
U ₃ O ₈		37.45					
Fe ₂ O ₃		0.15					

*Reported in First Annual Report, "Investigations of Radioactive Fuel-Bearing Glasses," Contract AT-(30-1)-2489, May 1, 1960 - March 31, 1961, P. A. Lockwood.

**Analysis was made of the fibers. Glasses normally separated into more than one phase.

glass was restudied and showed a two-phase immiscible system with the fiberizable glass being the second phase. The analysis of this phase shows that the urania content is similar to that of the RX360 glassy phase. Additional analysis of the fiberizable phases of RX308 and RX360 shows that the fiberizable phase can vary through a range of compositions.

Studies of Crystallization in Fuel-Bearing Glasses

From studies of fuel-bearing glass systems by Owens-Corning and by Dr. D. R. Wilder of the Ames Laboratory at Iowa State University, it was apparent that the primary factor in the crystallization of fuel-bearing glasses was the oxidation state of the fuel material. This was particularly true of urania glasses due to the ease with which uranium changes valence states. That behavior has also been noted in plutonia glasses and may be a factor in thoria glasses. The initial studies were carried out with urania glasses to determine what the crystalline material was and the oxidation state of the uranium in the crystalline and glass phases. The first glass examined was RX70 because it contained 50 per cent urania which appeared to be very close to the solubility limit of urania in the U_3O_8 form in the ternary system silica-soda-urania. RX70 glass behaved very erratically during fiberizing trials and this erratic behavior correlated with the amount of crystalline material found in the glass cullet being used. Glass cullet containing very few crystals fiberized readily whereas cullet with even a few per cent crystals was difficult to fiberize. The tensile strength averages decreased with increasing crystal content in the fibers.

The first trials to determine the oxidation state of the uranium consisted of infrared and ultraviolet transmissions through powdered glass to determine absorption peaks which varied with changes in the valence state of the uranium. Due to the mass of the material involved and the presence of crystalline material, scattering was too great to obtain reliable results by this method. An alternate attempt was made to determine the nature of the crystalline material in the glass. This was done by X-ray diffraction techniques and by optical microscopic methods of mineralogy. Both methods showed that the predominant crystalline material was UO_2 crystallized in the tetragonal system. Accurate X-ray diffraction measurements showed that the tetragonal system observed is characteristic of UO_2 crystals which have a surplus of oxygen in the lattice.

Electron microscope studies of the various crystallized glasses then indicated that there seemed to be two types of crystalline materials involved. The first type was a relatively large crystal often UO_2 , but sometimes a siliceous material with indications from its surrounding matrix system that it was probably unmelted batch material. The second type of crystal was much smaller and from its shape and dispersion would seem to be a solid state precipitation of very fine--almost colloidal sizes-- UO_2 coming out of the glassy matrix. The larger urania particles all had an oxygen ratio of about 2.45 per uranium atom whereas the smaller particles varied from about 2.29 through 2.45 in oxygen to uranium atoms. Other investigators have assigned the formula U_3O_7 to this material.³

³See Appendix A for a more detailed explanation of these studies.

It was also determined during this series of studies that the RX70 glass was apparently able to devitrify at room temperature. This is exceedingly unusual in glass systems. It was determined that the devitrification took place most readily when the glass was in large, massive pieces but could still occur when the glass was in relatively small beads weighing one to two grams each. There is also some indication that this devitrification may take place in exceedingly large fibers but that in fibers in the range of 1.5 mils in diameter and less, no devitrification was found in a period of six months. It is believed that this crystal growth takes place at room temperature due to growth of colloidal UO_2 material, utilizing energy released by the natural decay of the uranium.

Fine Fiber Studies

As was noted in the above section, one of the major problems with the production of fibrous samples with the urania glasses--in particular the RX70 glass--was due to its non-uniformity between various experimental runs. In order to eliminate this heterogeneity between the batches and alleviate these fiberization problems, efforts were made to study the effects of small compositional changes and various fiberizational experimentation techniques known to the trade. All efforts to produce a better glass by variations in experimentation and equipment techniques only temporarily reduced the heterogeneity, but they permitted the production of many of the samples which are described later in this report. In order to produce more homogeneous material, a series of composition changes were made. After some deliberation, it was decided that boron would be used in

the RX70 glass to replace some of the soda or some of the silica. It was realized that boron 10 has a neutron capture cross section too large for use in atomic reactor work, but it was thought that in view of the cost of enriched uranium and other processing costs to produce these glasses that the addition of a small amount of boron 11 would not add prohibitively to the cost. Table III shows a series of six glasses containing various amounts of boron added to RX70 glass. None of these glasses showed any improvement over RX70 in fiber-forming characteristics and tendency to crystallize. Also the best of these glasses had lower tensile strengths than RX70 glass and not quite as good high temperature resistance. But during the series of trials with boron glasses, it was observed that when the glasses were cooked for long periods of time at high temperatures that the last of the fibers formed from the cooked portions had considerably better fiber-forming properties and fewer observable crystals. It was concluded that this was due to oxidization by the air of some of the glass in the top of the bushing. It was therefore decided to bubble oxygen gas through the molten glass prior to fiberizing.

The initial trial at bubbling wet oxygen gas through RX70 glass produced a glass material of exceptionally fine fiber-forming properties with no observable crystalline material. The first trials were made by bubbling the wet oxygen through the glass for approximately two and one-half hours. In later trials, depending on the original glass cullet, it required from one to two and one-half hours to produce an equivalent result. One of the notable changes in the glass was that the relatively dark brown color of the fibers was now changed to a fairly pale blondish yellow color somewhat

TABLE III
 COMPOSITION OF GLASSES CONTAINING BORON
 AS A MODIFICATION OF RX70 GLASS

Glass No. →	RX70	RX366	RX367	RX368	RX369	RX370	RX371
Composition - % By Weight							
SiO ₂	39.81	39.81	39.81	39.87	34.84	37.42	32.44
Na ₂ O	7.99	7.49	5.00	7.49	9.99	7.48	9.98
B ₂ O ₃	--	2.50	5.00	2.50	5.00	5.00	7.49
U ₃ O ₈	49.97	49.97	49.97	49.97	49.97	47.89	49.91
Fe ₂ O ₃	0.07	0.07	0.07	0.07	0.06	0.07	0.06
Al ₂ O ₃	0.16	0.16	0.16	2.00	0.15	0.15	0.13

lighter than the colors observed in the boron glasses that had been cooked for long periods of time. This would indicate that oxidization also was the probable reason for the change in colors of these glasses.

Although RX70 glass, before the oxidization trials, had been difficult to run at 2450°F and often had to be formed at temperatures above 2500°F, it was now possible with the oxidized glass to form continuous fibers of good quality as low as 2150°F. A series of trials using various temperatures was made in an attempt to devitrify the oxidized glass. The results indicated that when the glass was returned to standard forming conditions any devitrification of the glass had disappeared.

The next step in the program was to determine if the oxygen was producing this change. The trials consisted of bubbling the following gases through molten RX70 glass: wet and dry oxygen, wet nitrogen, wet and dry argon, wet air. Wet oxygen was also placed over the top of the glass. Table IV shows the results of these trials. In all instances the bubbling action tended to eliminate the devitrification, but the rate at which this elimination of crystals took place varied widely. The question was: Why should argon or nitrogen when bubbled through the glass give the same results as oxygen or air? It should be remembered, though, that the glass in these cases had access to air at the top of the melt and, as the bubbles of inert gases rose to the top where they burst, the glass then fell back on itself probably entrapping some air into the glass. It was therefore believed that the entrapment of the air and the further mixing of the glass by continued bubbling of argon or nitrogen rising through the glass tended to thoroughly mix oxygen into the glass. To eliminate this possibility,

TABLE IV
 BUBBLING OF GASES THROUGH RX70 GLASS

Gas Bubbled Through the RX70	Time to Eliminate 95 ⁺ % of Crystals hours	Index of Refraction
Untreated Glass	--	1.622
Wet Oxygen	2 - 4	1.605
Wet Air	12 - 16	1.607 - 1.617
Dry Oxygen	16 - 20	1.607
Wet Argon	18 - 20	1.609
Wet Nitrogen	18 - 20	1.608 - 1.616
Dry Argon	48 - 60	--
Wet Oxygen Over Top of Glass	72*	1.588 - 1.596
<p>* Cleared Top Half of Melt</p> <p>Note: Wet gases were bubbled through water before entering the molten glass and the dry gases were predried with Drierite.</p>		

nitrogen was bubbled through the glass while the forming apparatus was in an atmosphere containing less than 5 per cent oxygen. The results of these trials indicated that although the crystalline material could be eliminated for short periods of time due to homogenization of the glass by the bubbling action that this elimination of devitrification was not permanent. It was, therefore, concluded that the primary change is due to oxidation of one or more of the glass constituents and that the bubbling action plus the addition of water to the glass enhances the rate at which the glass is homogenized.

The question now was: Why did the addition of oxygen change the fiber-forming characteristics of the glass? A set of theoretical calculations of the number of non-bridging oxygens was made for the RX70 glasses. If the urania was considered to be in the U_3O_8 state and acting as a glass modifier, the number of non-bridging oxygens was calculated to be 1.92 per silica tetrahedron. If the glass was in the UO_2 state and considered to be in the non-bridging or modifying condition, the number of non-bridging oxygens would be 1.60 per silica tetrahedron as an average. Now both of the above figures represent exceedingly high numbers of non-bridging oxygens and often indicate glasses that are easy to devitrify. These figures were based on the assumption that the urania acted as a modifier in the glass. The behavior of an oxide material in a glass is usually indicated by the bond strength. This bond strength is the dissociation energy per gram atom of the cation divided by the cation coordination number (in accordance with the K. H. Sun formula for determination of probable behavior of

oxide systems in a glass⁴). Some assumptions were made for these calculations of bond strengths using variations of the Sun formula (See Appendix B). On the basis of these calculations, UO_2 would seemingly have to act as a modifier in the glass system, but the same calculations indicate that UO_3 would have enough bond strength that the uranium atoms could become part of the glass network. If this were true, it would explain the wide variation in glass properties between the urania at the lower oxidation state and the urania at the higher oxidation state. In fact, the number of non-bridging oxygens per silica tetrahedron now calculates at 0.82 or 0.37 depending on what coordination factor is used for the urania in the structure.

Samples for AEC Contractors

In our discussions with Dr. D. R. Wilder of the Ames Laboratory at Iowa State University, Ames, Iowa, it was determined that his glass compositions using UO_2 in the batch contained considerably more UO_2 than we had found it possible to dissolve in our glass systems. As recorded in the First Annual Report, though, we found that his method of melting the glass could very conceivably produce a higher oxidation state of the uranium than would be obtained under our system of melting. Therefore, two of his high uranium-containing glasses were produced in our laboratory and sent to Dr. Wilder. These compositions are as follows:

⁴W. D. Kingery. Introduction to Ceramics. New York: John Wiley & Sons, Inc., 1960, p. 149.

Glass No. →	RX358	RX359
Composition		
SiO ₂	44.88%	44.88%
Al ₂ O ₃	0.18	0.18
Na ₂ O	9.98	11.97
UO ₂	40.90	40.90
TiO ₂	3.99	--
CaO	--	2.00
Fe ₂ O ₃	0.07	0.07

Only small quantities of these materials were made in our laboratory, but it appeared that they were fairly severely devitrified as opposed to the same glasses produced by Dr. Wilder's techniques which were crystal free.

The largest samples prepared were for the Clevite Research Corporation of Cleveland, Ohio. This work was in conjunction with their efforts to produce an aluminum-glass composite fuel material containing high amounts of enriched uranium in the glass system. The following materials were shipped for the purposes of fuel element construction experiments, construction of irradiation experimental elements, and for the production of an MTR fuel element: approximately 20 pounds of aluminum-coated boron and fuel-free glass fibers, 8 pounds of aluminum-coated RX70 glass containing 50 per cent by weight depleted U₃O₈, and 4 pounds of enriched RX70E glass coated with aluminum. During our sample runs of this material, efforts were made to produce a smoother aluminum coating that would simplify the sampling and analysis of these glasses. While efforts to produce a smoother aluminum coating were successful as such, the technique

could not be used because the percentage of aluminum on the fiber was reduced below the amount desired by the Clevite Corporation.

Rensselaer Polytechnic Institute requested a series of samples for their chemo-nuclear processing studies and 3-micron glass fibers were shipped to them made from RX78E glass containing 35 per cent enriched U_3O_8 by weight, RX70E glass containing 50 per cent enriched U_3O_8 by weight, and X638EE glass containing 10 per cent enriched U_3O_8 by weight. Attempts were also made to produce a glass cloth from a 5-fiber strand of five micron diameter fibers of RX70 glass. Efforts to do this on modified mechanical equipment were not successful.

Assistance has been given to the Mound Laboratory at Miamisburg, Ohio, in the production of the plutonium-bearing glasses. Seven glasses (listed in Table V) to be used as base glasses were sent to Mound Laboratory in October.

These glasses were made up in an effort to increase solubility of plutonium oxide in the glass system. Of interest are X1309 and X638A which contain approximately 10 per cent uranium and X1310 which contains approximately 9 per cent thorium.

In addition to these samples, fuel-bearing materials have been sent to the Aerojet General Nucleonics Corporation and the Brookhaven National Laboratories for use in the study of chemo-nuclear fuel reactor systems on a direct purchase order basis.

TABLE V

BASE GLASS PREPARED FOR THE ADDITION OF PLUTONIUM
FOR FIBERIZING TRIALS AT MOUND LABORATORY

	X-1307	X-1308	X-1309	X-1310	X-1311	X-1312	X-638A
SiO ₂	66.60	66.60	60.53	60.53	66.59	63.41	44.98
Al ₂ O ₃	5.55	5.55	5.05	5.05	5.55	5.29	8.98
CaO	5.55	5.55	5.05	5.05	5.55	5.29	--
Na ₂ O	11.10	5.55	15.13	15.13	11.65	11.09	17.96
K ₂ O	5.55	5.55	5.05	5.05	5.55	5.29	--
Fe ₂ O ₃	0.12	0.12	0.09	0.09	0.12	0.11	0.26
PbO	5.55	11.10	--	--	--	--	--
U ₃ O ₈	--	--	9.09	--	--	--	9.87
ThO ₂	--	--	--	9.09	--	--	--
B ₂ O ₃	--	--	--	--	5.00	9.52	--
TiO ₂	--	--	--	--	--	--	13.46
ZnO ₂	--	--	--	--	--	--	4.49

Glass compositions are listed by % by weight.

A P P E N D I X A

PHYSICAL ANALYSIS OF U_3O_8 -BEARING TERNARY GLASS

C. I. Cohen
E. B. Cohen

Microscopy Laboratory
Physics Research Laboratory
Owens-Corning FIBERGLAS Corporation

PHYSICAL ANALYSIS OF U_3O_8 -BEARING TERNARY GLASS

SUMMARY

Light and electron microscope investigation of RX70 cullet indicates the presence of a crystalline phase. This phase has been identified as U_3O_7 , a tetragonal oxide of uranium. An immiscible phase exists in glasses produced under standard conditions and in those produced under oxidizing conditions. The size of the immiscible regions has been reduced from 2.5μ or larger in the standard glass to 0.02μ or smaller in the glass produced under oxidizing conditions. The size of the individual immiscible regions will determine whether or not RX70 will devitrify.

Immiscibility in this system is due to the competition for available oxygen by both the Si^{+4} and the U^{+6} ion. Owing to similar bond strengths both the Si^{+4} and the U^{+6} occupy network-forming positions. Index of refraction determinations reveal a trend toward lower indices as the O_2 is added to the glass. Fluorescent analysis points to the fact that the uranium is coordinated as uranate groups in RX70 glass.

INTRODUCTION

This study was undertaken to determine the physical properties of RX70 glass, the composition of which is 49.97% U_3O_8 , 39.81% SiO_2 , 7.99% Na_2O , 0.16% Al_2O_3 , and 0.07% Fe_2O_3 . Emphasis was placed on determining the cause of inhomogeneities within the glass and the reason for the rapid devitrification of the glass, both of which served to hinder fiber-forming operations in a glass of this system.

To accomplish this various samples of RX70 glass were investigated utilizing both light and electron microscopy. Crystalline material was identified through X-ray diffraction procedures. Fluorescent analysis was utilized as a means of determining the oxidation state of the uranium ion present in the glass.

DISCUSSION

Preparation of Samples for Microscopic Investigation

Standard surface replicas were prepared for electron microscopic study. The glasses were lightly etched before replication to enhance any inhomogeneities that might be present. Samples were also etched for reflected light studies. Bulk samples were used with no further treatment for transmitted light studies.

Microscopic Study - RX70 Cullet

Reflected and transmitted light investigations of cullet used as the starting material in the production of RX70 fibers indicate the presence of a crystalline phase. The crystalline phase is not uniformly distributed throughout the many portions of cullet investigated, but is present either in layers or in pod-like formations (Figure 1). Some portions of cullet have been found to be entirely crystal-free. In addition to crystalline material there are areas of glass of roughly spherical outlines with differing chemical properties than their surrounding matrix (Figure 2).

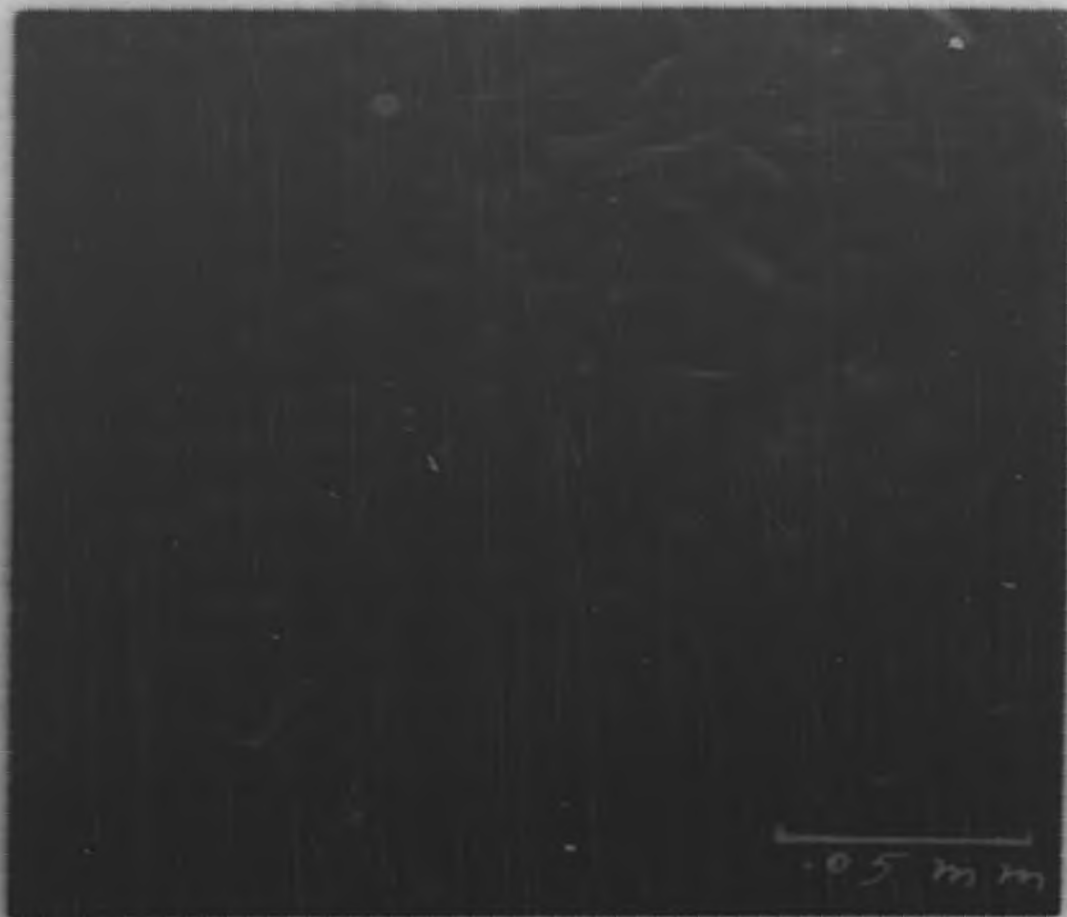


Figure 1. Reflected light photomicrograph of etched surface of RX70 cullet. This photograph was taken along a plane parallel to a macroscopically visible highly crystalline plane.



Figure 2. Reflected light photomicrograph of etched surface of RX70 cullet. This is similar to Figure 1. Note circular area at upper left of photo which represents a large immiscible phase.

The crystals observed in the cullet have decidedly unequal dimensions in the plane observed. The photographs accompanying this report have been taken along a plane parallel to a macroscopically visible plane along which a high degree of crystallinity was noted. Observations have been made perpendicular to this plane and the crystals are seen to have square cross sections. The crystals vary in size from 0.05 mm to below the limit of resolution of the light microscope. The spherical areas vary in size from 0.08 mm to below the limit of resolution of the light microscope. This same plane was replicated for viewing in the electron microscope and the presence of this same crystalline phase was noted (Figure 3).

Electron Microscopic Study of RK70 Beads

A series of electron microscopic studies was undertaken utilizing beads drawn from the bushing in the same manner as a single fiber. These beads whose dimensions were about 0.3 cm x 1 cm were fractured in a direction perpendicular to the long dimension; their surfaces lightly etched, then replicated and viewed in the electron microscope. Beads were chosen which represented various conditions of formation. Those conditions chosen are as follows:

1. Formed directly from cullet with standard cook-out procedure.
2. Formed directly from cullet, cooked out for 100 hours at 2600°F.
3. Formed directly from cullet, cooked out at 2450°F with O₂ bubbling through molten glass.
4. Formed from cullet, cooked out at 2500°F with O₂ bubbling through molten glass.



Figure 3. Electron photomicrograph of same etched surface as Figures 1 and 2 showing the presence of crystalline material on a submicroscopic level.

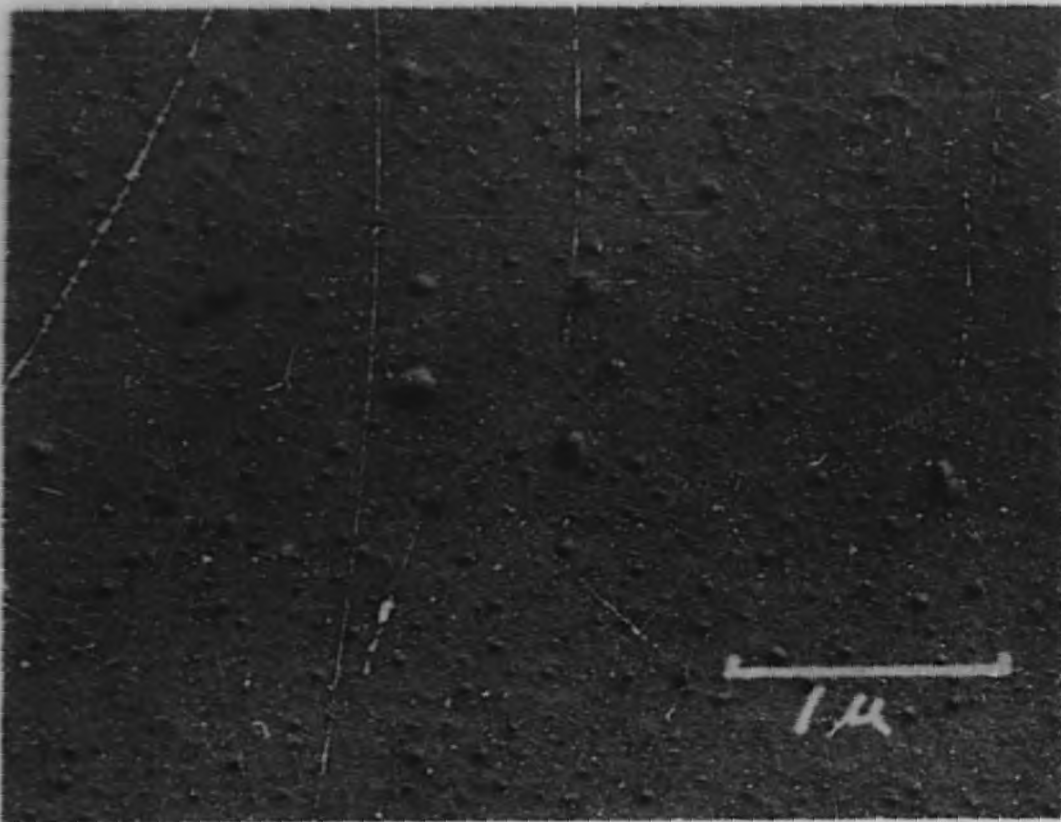


Figure 4. Electron photomicrograph of RX70 bead formed under standard conditions. Irregular to circular areas, which are about 0.25μ in diameter, are urania-rich immiscible regions.

Those glasses formed from cullet under standard conditions show the presence of areas having a different resistance to the etchants utilized. These areas are irregular to spherical in shape, from 2.5μ in diameter to below the limit of resolution of the electron microscope (Figures 4, 5, and 6). It is apparent that these inhomogeneities in the glass formed under standard conditions represent the formation of an immiscible phase. Noticeable throughout the glasses formed under standard conditions is a structure having dendritic outlines (Figure 7). The larger immiscible regions in the 2.5μ range exhibit a high degree of devitrification whereas the smaller areas lack any signs of visible crystal growth (Figure 6).

Glasses prepared under specialized conditions indicate several major differences. Those cooked out at 2650°F for 100 hours no longer exhibit large scale immiscible areas (Figure 8). There is now a predominance of a microphase lying in the 0.04μ size range, but there are still larger immiscible areas present. No crystalline material was noted in these preparations.

Those glasses through which O_2 was bubbled once again show the presence of an immiscible microphase, but the microphase has been reduced in size to less than 0.02μ . Especially noticeable is the uniformity in size of this microphase on both a small and large scale basis. Due to difficulty in controlling the degree of etching, the photomicrograph (Figure 9) showing the structure of the bead drawn at 2450°F greatly enhances the presence of the microphase. This intense etching does not cause an increase in size of the microphase, but only enhances its presence. The degree of uniformity is substantiated by this photograph. Structure of the



Figure 5. Electron photomicrograph of several immiscible regions in RX70 bead formed under standard conditions.

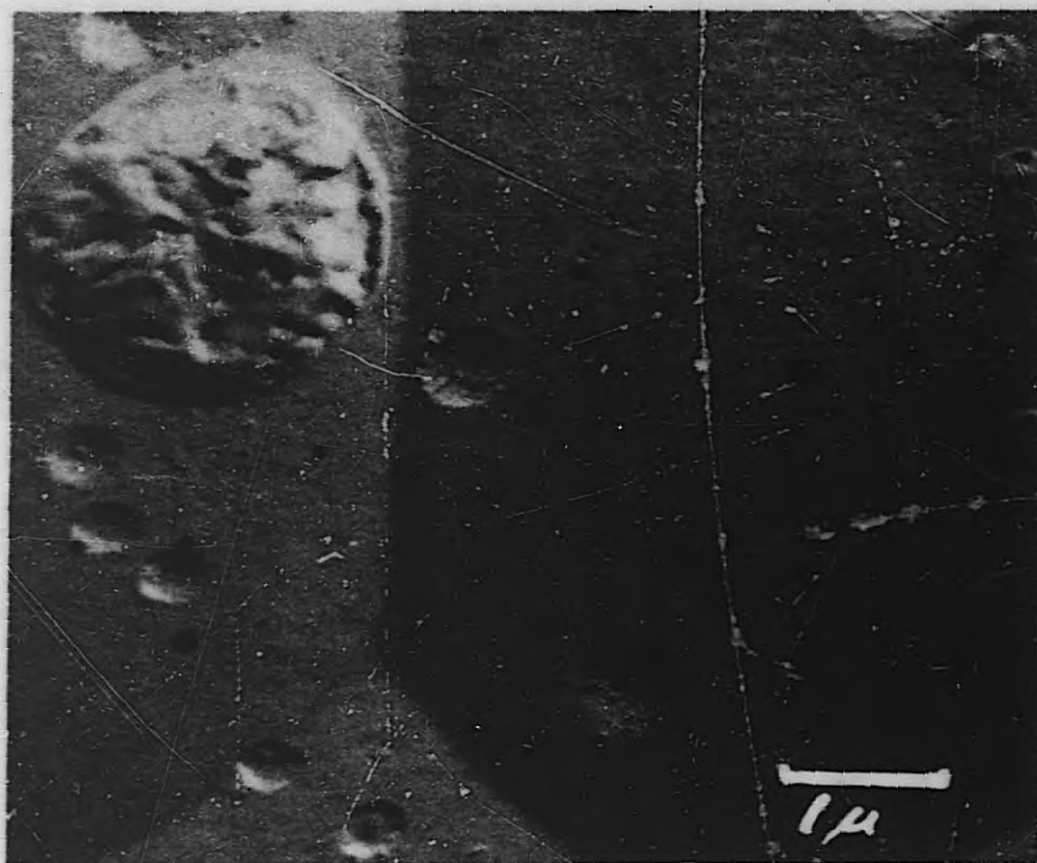


Figure 6. Electron photomicrograph of immiscible regions in RX70 bead formed under standard conditions. Note that the larger of the immiscible regions has almost completely devitrified.



Figure 7. Electron photomicrograph of an immiscible region in RX70 bead formed under standard conditions. Note shape of this area and compare it to skeletal crystal in Figure 11.



Figure 8. Electron photomicrograph of bead prepared in 100 hour cook-out. In this instance the immiscible regions have been reduced in size to about 0.04μ .



Figure 9. Electron photomicrograph of glass formed at 2450°F through which O₂ has been bubbled. Etching in this preparation has been too intense and has led to the extreme enhancement of the immiscible phase.

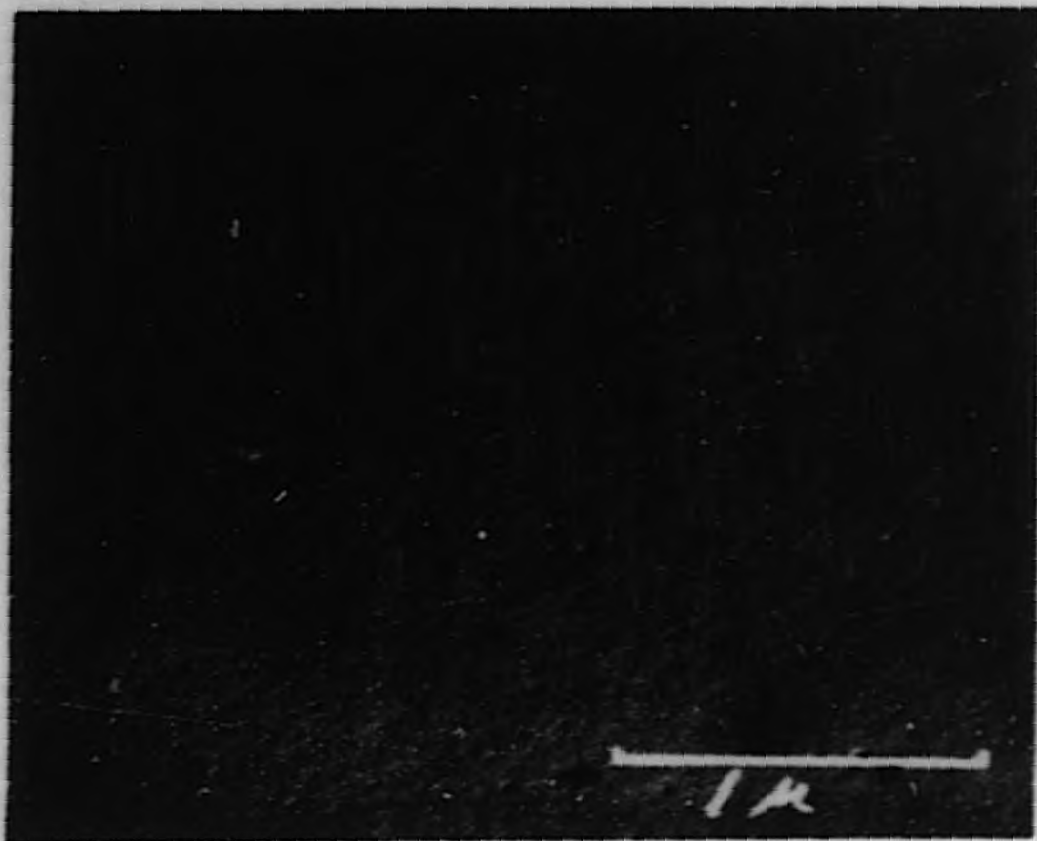


Figure 10. Electron photomicrograph of RX70 bead formed at 2500°F through which O₂ has been bubbled. Note small size and uniformity of distribution of microphase.

glass is well exhibited by the photomicrograph of the specimen formed at 2500°F (Figure 10). Once again no crystalline material is noted.

Light Microscope Study of RX70 Fibers

In addition to an electron microscope examination, fibers were also investigated with the light microscope. Those fibers formed under standard conditions exhibited crystalline material and dusty areas. Morphologically, the crystals assumed square cross sections with one long dimension. Several fibers exhibited what appeared to be skeletal crystals having dendritic outlines (Figure 11).

Index of Refraction Determination

The index of refraction of RX70 glass beads, prepared under various conditions, was determined microscopically by the Becke line method using crushed fragments and sodium light ($\lambda = 5890 \text{ \AA}$) is shown in Table 1. All values are ± 0.001 .

X-Ray Diffraction Analysis

To identify the devitrified material present in many fibers, the crystalline material was concentrated and X-ray diffraction photographs were taken. The crystalline phase is identified as U_3O_7 , a tetragonal oxide of uranium. This phase is considered identical with that synthesized



Figure 11. RX70 fiber formed under standard conditions with typical skeletal crystal.

TABLE 1
 INDICES OF REFRACTION
 OF VARIOUS RX70 GLASS BEADS

Conditions of Formation	Index of Refraction (n_d)
Standard glass - no cook-out	1.622
100-hour cook-out	1.614
Oxygen feed at 2350°F	1.607
Oxygen feed at 2450°F	1.607
Oxygen feed at 2500°F	1.607
Oxygen feed at 2550°F	1.607 - 1.609
Wet oxygen bubbled over top	1.588 - 1.596
Argon feed	1.607 - 1.611
Wet nitrogen - 18-hour cook-out	1.608 - 1.617
Dry oxygen bubbled 20 hours	1.607
Wet oxygen 3 hours	1.605

by DeMarco, Heller, Abbot, and Burkhardt.¹ It has the following cell constants $A_o = 5.38 \text{ \AA}$ $C_o = 5.54 \text{ \AA}$ and $C_o/A_o = 1.02$.

Discussion of Data

The data presented substantiate the conclusion that an immiscible field exists in the ternary glass of composition RX70. It is not implied that standard glasses of RX70 composition will result in a homogeneous phase separation on a large scale. The phase separation is highly inhomogeneous and is a function of local component concentration and oxygen availability. One can visualize this localized component concentration by considering the nature of the cullet utilized for the production of RX70 fibers. Each crystal present will represent a localized area of urania concentration. During melting, due to the viscosity of the mass on one hand and the competition for the available oxygen by the uranium and the silicon ions on the other, diffusion of material from the urania-rich areas to the glassy matrix will be slow. Uniform attenuation of the glass in fiber formation then will be difficult owing to the presence of phases with differing mechanical properties.

The size of the immiscible phase as found in standard RX70 glass before fiber attenuation will definitely determine whether or not crystals will be present in the final fiber. Note the 2μ areas in Figure 6. These show signs of almost complete devitrification whereas those smaller than 2μ show little

¹R. E. DeMarco, H. A. Heller, R. C. Abbot, and W. Burkhardt. "Oxidation of UO_2 to U_3O_8 ," Bulletin of the American Ceramic Society, Volume 38, No. 7 (1959).

or no crystal growth (Figures 4 and 5). The question of crystal formation in standard RX70 glass can then be directly related to the size of the immiscible regions, as those regions having a diameter greater than 1μ usually show devitrification to some degree.

Immiscible phase shape as well can be related to crystal formation in this glass. A common phenomenon in RX70 glass produced under standard conditions is the occurrence of irregularly shaped areas varying from 2μ to much larger (Figure 7). These appear to have formed through the coalescence of several nearby immiscible phases. When a critical phase size and critical temperature are attained, devitrification occurs. Devitrification in these areas can very well take the form of the skeletal crystal (Figure 11). This crystal and many like it are found along the length of many filaments of RX70 glass prepared under standard conditions.

The effect of variations in conditions under which the RX70 fibers are produced from cullet is reflected in the submicroscopic structure of the glass. The most pronounced effect is the reduction in size of the immiscible microphase, from 2μ and larger in the glass produced under standard conditions to less than 0.02μ in the glass through which O_2 was bubbled. Long period of cook-out and the bubbling of a gas through the glass has a twofold effect. It apparently has a homogenizing effect, i.e. it causes a physical breakdown in the size of the immiscible areas. More important, possibly, is the effect that the addition of quantities of oxygen has on the ultimate structure of the glass. An inert gas also increases the oxygen content indirectly by bringing new glass in contact with air at the top of the glass reservoir.

Interpretation of Results

Data given for index of refraction of the glasses studied indicate that there is a trend toward a structurally less dense material as O_2 is bubbled through the glass. Consideration of immiscibility mechanism according to Levin and Black² further substantiates the conclusion that the addition of excess oxygen will lead to a more open structure which will in turn permit more of the uranium ions to enter into the structure of the glass. A comparison of the bond strengths, $Z/C.N.$ where Z = charge on cation and $C.N.$ = coordination number of cation, between Si^{+4} and the three possible ionic states of uranium which might occur in glass (Table 2) indicates that strong competition for the available oxygen will result.

Ability to compete for available oxygen is reflected in the magnitude of $Z/C.N.$ for the introduced cation with respect to $Z/C.N.$ for Si^{+4} . For example, in a simple system such as SiO_2-Na_2O no immiscibility is present. The value of $Z/C.N.$ for Na^+ is $1/6$. Ordinarily, the oxygen introduced along with the foreign cation serves to fulfill the coordination needs of the Si^{+4} and the cation fits into the structure so as to maintain electrical neutrality. Such is the case in the system SiO_2-Na_2O . Where the foreign cation also possesses a high bond strength, the oxygen introduced will not readily be contributed to the formation of the glassy network

¹Stanley Black and Ernest Levin. "Structural Interpretation of Immiscibility in Oxide Systems II. Coordination Principles Applied to Immiscibility," Journal of the American Ceramic Society, Volume 40, No. 4 (1961).

and separation will result. This separation occurs in RX70 glass produced under standard conditions. Vogel and Gerth³ have experimentally demonstrated this mechanism in their electron microscopic studies of model glasses. It is obvious then that an oxide possessing a high value of $Z/C.N.$ will tend toward immiscibility in a silicate system. The values of $Z/C.N.$ for the possible ionic states of uranium in glass are listed in Table 2. It should be kept in mind that the addition of excess oxygen will nullify the trend toward immiscibility.

Oxidation State of the Uranium

The utilization of fluorescent spectra offers a convenient means of determining the oxidation state of the uranium ion in RX70 glass. The findings of Kröger, Stevels, and Botden⁴ indicate that in uranium glass prepared under oxidizing conditions the uranium exists in the hexavalent state. According to Rodriguez, Parmelee, and Badger,⁵ the excess oxygen offers a protective sheath to the hexavalent ion thus allowing it to fluoresce with greater intensity when stimulated by the proper spectra. Weyl⁶ finds that

³Von Werner Vogel und Klaus Gerth. "Über Modellsilikatgläser und ihre Konstitution Die Glassysteme $LiF - BeF_2$, $NaF - BeF_2$ und $RbF - BeF_2$ " Glastechnische Berichte, Volume 31, No. 1 (1958).

⁴F. A. Kröger, J. M. Stevels and P. J. Botden. "The Fluorescence of Hexavalent Uranium in Glass," Phillips Research Reports, Vol. 3, No. 1 (1948).

⁵A. R. Rodriguez, C. W. Parmelee and A. E. Badger. "Study of Photoluminescence in Glass," The Journal of the American Ceramic Society, Vol. 26, No. 5 (1943).

⁶"The Fluorescence and the Solarization of Glass," Journal of the Society of Glass Technology, Volume 30 (1948).

TABLE 2
 ELECTROSTATIC BONDING ENERGY
 (Z/C.N.) OF SOME CATIONS WITH OXYGEN

Ion	Radius (Å)	Radius Ratio $R_{\text{ion}}/R_{\text{O}^{2-}}$	C.N.	Z/C.N.
Na ⁺	.95	.68	6	1/6
U ⁺⁶	.80	.57	6	1
U ⁺⁴	1.01	.72	8	1/2
U ⁺⁴	.97	.69	6	2/3
Si ⁺⁴	.41	.29	4	1

the hexavalent ion will fluoresce at room temperature when coordinated in uranyl grouping, but when coordinated as the uranate group no fluorescence is noted at room temperature. According to Kröger, Stevels, and Botden⁷ fluorescence takes place in the uranyl group in a band between 5000 and 6500 Å, whereas the uranate groups fluoresce in the same region but at -180°C.

To determine the oxidation state of uranium in RX70 glass, crystal-free glass fibers prepared under standard conditions and fibers prepared under strongly oxidizing conditions were powdered and impressed into K Br discs. The region between 5600 and 6500 Å was scanned and no fluorescent spectra were observed. From this one might conclude that the uranium exists in the uranate group as the hexavalent ion. In previous work involving fluorescent uranium glass, the amount of uranium oxide included in the glass has ranged from 1 to 12 weight per cent. Kröger, Stevels and Botden⁸ have found that an increase in the urania content causes the uranium to occupy positions in the network of the glass as the uranate ion.

A Model of RX70 Glass

On the basis of experimental evidence a model of RX70 glass can now be postulated. The Si^{+4} is present in its normal tetrahedral coordination while the uranium is present as a hexavalent ion in sixfold coordination.

⁷ Kröger, Stevels, and Botden, op. cit.

⁸ Ibid.

Since the values for bond strengths of U^{+6} and Si^{+4} are almost identical, it would be difficult to assign a network forming position to one and a network modifying position to the other. Therefore a continuous network of Si^{+4} and U^{+6} is present while the Na^+ occupies interstitial positions to maintain electrical neutrality.

Uniformity of structure is not constant throughout a given body of the glass, as illustrated by the electron photomicrographs. In the glass produced under oxidizing conditions small areas are still present in which the ratio of urania to silica is high as compared to the surrounding matrix. These areas of urania concentration are more prominent in the glass produced under standard conditions. In the glasses produced under oxidizing conditions a greater quantity of U^{+6} is incorporated into the structure of the glass and this quantity of U^{+6} is drawn from the immiscible areas. One would conclude then that the uranium ion enters into the glass network as the hexavalent ion in both the standard glass as well as the glass formed under oxidizing conditions. The degree to which the hexavalent ion enters the network of the glass is greater, of course, in the glass produced under oxidizing conditions.

Suggestions for Further Research

In order to definitely establish the valence state of the uranium present in both the fibers produced under standard conditions and those produced under oxidizing conditions, a further series of studies is suggested. A program of fluorescent analysis is recommended to carry out this investigation. It would be necessary to vary the amounts of urania

added to the ternary glass of RX70 to determine if an increased amount of urania nullifies the fluorescent effect. At the same time these studies should be carried out under varied temperature conditions especially in the -180°C region to positively determine the grouping of O^{\ominus} about the uranium ion.

CONCLUSIONS

Immiscible regions and a crystalline phase are the inhomogeneities of this glass. These immiscible regions, depending upon their size, may or may not lead to devitrification. The crystalline phase formed has been identified as U_3O_7 , a tetragonal oxide of uranium. Addition of O_2 to RX70 glass serves to remove uranium ions from the immiscible regions and aid in their incorporation into the glassy network. Because of the similarity in bond strengths both the U^{+6} ion and the Si^{+4} ion occupy network forming positions in RX70 glass.

APPENDIX B

BEHAVIOR OF U^{+4} AND U^{+6} IN SILICA GLASS SYSTEMS

Paul A. Lockwood

Physics Research Laboratory
Owens-Corning FIBERGLAS Corporation

BEHAVIOR OF U⁺⁴ AND U⁺⁶ IN SILICA GLASS SYSTEMS

Using RX70 glass consisting of a nominal composition of 50% by weight U₃O₈, 40% by weight SiO₂ and 10% by weight Na₂O, the following calculations for uranium oxides in various U to O ratios were made.

The number of non-bridging oxygens per silica tetrahedron can be calculated by the following formula¹

$$N_M = \frac{\frac{m}{MfM}}{\sum \frac{n}{W_M}}$$

N_M = Non-bridging oxygens/silica tetrahedron
 m = Number of atoms of a cation in molecular formula of oxide
 f_M = Weight fraction of oxide
 W_M = Molecular weight
 n = Number of oxygen atoms in molecular formula

The results of this formula indicate that if the uranium oxide and sodium oxide are calculated as glass modifiers the following numbers of non-bridging oxygens are found with

UO ₂	-	1.60
U ₃ O ₈	-	1.92
UO ₃	-	2.08

Using the Huggins-Sun formula, the bond strengths of uranium oxide are calculated as follows:

U ⁺⁴	53 k cal/mole	CN 6
U ⁺⁴	40 k cal/mole	CN 8
U ⁺⁶	62.5 k cal/mole	CN 6

CN - Coordination Number

¹Henry H. Blau. "The Relations of Thermal Expansion, Composition and Structure of Glasses. I. The Sodium Oxide-Silica Glasses," Transactions of the Society of Glass Technology, 1951, Volume 35, pp. 304 - 317.

From the H. K. Sun studies, U^{+6} could act as a network former in the presence of another network former such as SiO_2 . If in the fully oxidized state uranium oxide is considered as a network former, the number of non-bridging oxygens in the network is as follows

UO_3 - 6 coordination number - 0.37 non-bridging oxygens
 UO_3 - 4 coordination number - 0.82 non-bridging oxygens

This is based on non-bridging oxygens per average unit structure with UO_3 and SiO_2 as the unit network and Na_2O as the modifier.

This theory varies in viewpoint slightly from that shown in Appendix A, but in essence produces the same final result.

END