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Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems

Quarterly Status Report No. 6

Contract NASW-1301

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SUMMARY

Research in this quarter brought advances in four phases of the over-all program.

The micro-furnace designed to permit microscopic observations of crystals growing in molten oxides has been used to establish growth curves for cordierite and sapphirine crystals originating in molten $MgO-Al_2O_3-SiO_2$ systems.

A critical survey of the shapes of hand-drawn glass fibers produced in this laboratory and used to measure the properties of various experimental glasses has shown that such fibers customarily have a distorted elliptical shape far from the perfect round shape postulated in calculating their elastic moduli. Consequently, the very high values for elastic moduli of such hand-drawn glass fibers reported both by this and other laboratories and occurring in the existing patent literature are probably nonsensical. Only elastic moduli measured on carefully controlled machine-drawn glass fibers or on samples of the bulk glass should be regarded as valid.

Two of the new experimental glasses prepared in this quarter have shown an additional 10% improvement in elastic modulus as measured on precision ground bulk glass samples.

It has proven possible to replace the massive expensive one-hole platinum bushing customarily used for the research production of mechanically wound glass filaments by a 20 cm^3 platinum crucible with properly shaped nozzle formed by adding platinum foil to the crucible bottom and taper reaming with a hundred-fold subsequent cost saving.

INTRODUCTION

This report is the sixth quarterly status report for Contract NASW-1301, "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems." The sixth quarter of the contract includes that period from December 1, 1966 through February 28, 1967. The primary objective of this program is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the degree of control of this rate which can be achieved by nucleating and anti-nucleating agents for such systems as would tend to form complex three-dimensional structures. Determination of the crystallization rate is carried out by continuously measuring the viscosity and electrical conductivity of the molten system as a function of time and temperature and starting last quarter by direct microscopic observation of such systems. Glass formation in this research program is, therefore, regarded as a rate phenomenon where the probability of such glass formation can be markedly increased by employing chilling rates high enough to defeat the formation of the complex many-atom, three-dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis.

OPTICAL STUDIES OF THE KINETICS OF CRYSTALLIZATION

In this quarter research was concentrated on the direct microscopic observation of the kinetics of crystallization of two crystal species, cordierite and sapphirine, originating in molten MgO-Al_2O_3-SiO_2 systems. Since this is the first application of this technique to the program, we give both the experimental procedures followed and the results obtained in detail.

Experimental Procedures

The microfurnace is nearly the same as that described in the last quarterly report. The principal alteration has been to increase the size of the copper bars between which the platinum-rhodium heater tube is clamped. These bars are now 3/16 in. by 3/4 in. and the contact area has been chrome-plated. This was necessary because of electrical contact problems, which have been alleviated by the modification. The heater tubes are now platinum-20% rhodium instead of platinum-10% rhodium.

When preparing to make a measurement of growth rates, the crucible is filled by first dropping in a fragment of glass so large that it will not fall through the bottom of the crucible. This fragment is melted, and then smaller particles

are added and melted so as to fill the crucible. The temperature is then increased until convection in the crucible completely homogenizes the glass. The thermocouple is lowered into the melt and the temperature is reduced to that at which the measurements are to be made. This large change in temperature can be made in a few seconds, and the sample will come to thermal equilibrium in another few seconds. As soon as the glass comes to a constant temperature and crystals have nucleated and grown to a few tens of microns in length, photographs are made at the desired intervals of time. The shortest interval of time which is convenient is about 30 seconds, but this has been satisfactory in the observations made to date. The measurements of the crystal size are made on the polaroid print by using a scale which was made by photographing a millimeter scale from an optical comparator. These measurements are considered to be no better than $\pm$ 5 microns. During the photography, attention is concentrated on getting the outside edges of the mass of crystals in focus so that the measurements will be more exact. After a set of observations has been made at a certain temperature, the temperature of the sample is increased to melt the crystals and again homogenize the melt, after which another series of observations is made. The number of observations and the time between observations is dependent upon the rate of crystal growth. Even at the highest rates of growth so far measured, it is possible to get two or three pictures of the growing crystals before they fill the crucible. A magnification of 40 diameters has been the most suitable for the systems studied to date.

The measurements from the prints are plotted versus time and a straight line is fitted to the data points. The slope of this line then gives the rate of crystal growth, in microns per minute. This value is then plotted versus temperature, to give the rates of crystal growth at the various temperatures.

Experimental Results

Glass from batch 1 of the summary report was selected for this initial study because many of the glasses which have a high Young's modulus are composed of MgO-Al_2O_3-SiO_2 plus another component. The composition of batch 1 is shown as point A in Fig. 1. This composition was checked by calcining the individual components at 1050° for approximately 17 hours and measuring the weight loss. Only the basic magnesium carbonate lost any appreciable amount of weight. It can be seen that this composition is close to, if not on the boundary between the primary phase areas of cordierite and spinel. Therefore the equilibrium phase obtained upon cooling the glass should be either cordierite or spinel. However, it is well known that the products of devitrification may not be the equilibrium phases. In the case of batch 1, the devitrification product was sapphirine, which has a primary phase area adjoining those of cordierite and spinel. The reason for the appearance of sapphirine is that it is easily nucleated by the platinum crucible or the platinum-rhodium thermocouple. At certain temperatures it would also nucleate throughout the melt, and not in contact with the crucible nor the thermocouple. There may have been very small particles of platinum in the melt, therefore, which acted as nucleation sites. Cordierite will also grow in batch 1 if nucleated, but it is considerably more difficult to nucleate than sapphirine.

The phase identification of sapphirine is somewhat complicated by the fact that batch 1 will not crystallize completely to sapphirine because of its bulk composition. Therefore, X-ray diffraction patterns of samples which were allowed to crystallize for long periods time consisted of a pattern for sapphirine and diffuse bands which indicated the presence of large amounts of glass. Sapphirine was not recognized as an equilibrium phase in the $MgO-Al_2O_3-SiO_2$ system for a long period of time (Ref. 1) and it is surprising to find that it nucleates and grows so readily. For this reason, the X-ray diffraction data are presented in Table I along with those for synthetic sapphirine. The agreement between the data is quite good, even though some of the weaker lines were not detected. Crystals were grown from batch 1 at 1140°, 1272° and 1310°, and despite the fact that there was a change in crystal habit, all had the X-ray diffraction pattern of sapphirine. This change in crystal habit is probably due to the number of crystals which nucleate, as well as the temperature at which they are grown. At the highest rate of growth, there was a great number of needle-like crystals growing on the thermocouple. At higher and lower temperatures there are fewer crystals growing, but all were of dendritic habit.

The growth data for batch 1 are tabulated in Table II and graphically depicted in Fig. 2. It can be seen that the maximum rate of growth of sapphirine is approximately 25 microns per minute at 1250°. This is a fairly slow rate of growth and is of the same order of magnitude as that found by Swift (Ref. 2) for the rate of growth of devitrite in a commercial type glass. Another feature of interest is that the curve is not symmetrical around a vertical line extending downward from the temperature of maximum growth, and that the points on the high temperature side of the curve can be connected by a straight line. No measurements were made of the rate of solution of the sapphirine crystals, because upon increasing the temperature the dendrites drifted away from the thermocouple. It should be possible to nucleate and grow just a few, thicker crystals which would be suitable for solution experiments.

The composition of batch 1-A is that of cordierite, $2MgO-2Al_2O_3-5SiO_2$ (point B in Fig. 1). As can be seen in the diagram, the first equilibrium phase to crystallize from a liquid of this composition is mullite, $3Al_2O_3-2SiO_2$. Upon heating a crucible of glass of this composition, many small crystals form and the glass becomes opaque. With further heating, a low viscosity liquid forms, so that the crucible contains a mixture of this liquid and the fine crystals. The crystalline material in the sample melts at $1530^{\circ} \pm 10^{\circ}$ to a clear liquid of rather low viscosity. Upon cooling 20° to 30°, needle-like crystals nucleate and grow at rates faster than those of sapphirine in batch 1. The crystals are straight-sided, approximately 20 microns in diameter and grow to lengths of 1500 microns. These crystals are apparently mullite, but not enough were grown for an analysis by X-ray diffraction. Because of the high temperature and low viscosity no further experiments were performed with this composition.

The composition of batch 1-B is approximately that of cordierite rich in magnesia and silica, point C in Fig. 1. The rate of growth of cordierite was studied with this composition. Cordierite crystals were not as easy to nucleate

as was sapphirine in this system, and in most cases were nucleated by seeding the melt with a few small crystals of cordierite. Once nucleated, cordierite has a high rate of growth, as seen in Fig. 3. More data were taken for this composition (Table III) than for batch 1, and the high temperature end of the growth curve is more clearly delineated. This portion of the curve shows an asymptotic approach to the liquidus temperature. This is in direct contrast to the data of Swift (Ref. 2) who showed that the rate of crystal solution was continuous with the rate of crystal growth through the liquidus temperature. Further, the data of Morley (Ref. 3) also suggest an asymptotic approach to the liquidus in his measurements on lithium silicate glasses. In Fig. 3, the last three data points, at 1418 $\pm$ 4°, 1433 $\pm$ 4° and 1435 $\pm$ 4°, represent no measureable crystal growth for periods of 4, 4, and 5 minutes, respectively. Another data point, not shown in Fig. 3, which was taken at 1435 $\pm$ 8° had a value of rate of solution of 16 microns per minute. Attempts to measure the rate of solution of the cordierite crystals were frustrated by the fact that the polycrystalline clumps of crystals did not melt only from the outside edges inward, but also melted along grain boundaries, so that the crystals came apart and drifted away from the thermocouple. Even before the polycrystalline masses disintegrate, pressing upon them with the thermocouple will indicate the presence of this intergranular solution.

It is proposed to next measure the rate of growth of cordierite in batch 1 and to relate the growth data to the viscosity and the degree of undercooling. Then the effects of a fourth component will be investigated.

NEW GLASS SYSTEMS AND THEIR CHARACTERIZATION

Eighteen new glasses were formulated, mixed and melted in the sixth quarterly period along with a number of repreparations of older glass formulations to provide additional material for property evaluation. More particularly, these older glass batch remelts were used in developing the mechanization of the glass fiberizing process. Two of the new glass batches yielded values for Young's modulus 10% higher than any of our earlier formulations.

Viscosity Measurements

Viscosity measurements using the Brookfield viscometer, tungsten spindle with elongated shaft, tungsten crucible and tungsten resistance furnace described in earlier reports were carried out on seven of the glass batches. All seven batches were shown to have viscosity-temperature curves suitable for fiberization from orifices in platinum crucibles.

Sonic Determination of Young's Modulus on Precision-Ground Bulk Glass Samples

Precision ground rods were prepared from four of the new glass batches melted in this period. Using sonic methods a total of forty-eight specimens, twelve from each batch, were evaluated.

Average values obtained were 15.14, 11.37, 16.5 and 16.54 million psi respectively with some individual sample values as high as 17.3 million psi. The two batches yielding the 16.5 million psi bulk modulus values are approximately 10% better than any previously prepared in this laboratory.

Modulus Measurements on Hand-Drawn Glass Fibers

In our last quarterly report, the values obtained for Young's modulus on hand-drawn specimens of experimental glass AB were shown plotted against fiber diameter in mils. Unfortunately, almost all of the fiber used for these measurements had been discarded before the thought occurred to us that these unusually high values might be due to a departure from circularity in the cross-section of the glass fiber specimens. All other sources of error in this experiment had been previously checked and ruled out, and the one or two large diameter fibers from this batch found were circular in cross-section. Serious error in the reported values was not, therefore, anticipated but occurred nevertheless.

Experimental glass batch AB has since been remelted and additional hand-drawn glass fibers prepared. Typical cross sections (the best and the worst) of these fibers are shown in Fig. 4. It is evident, therefore, that hand-drawn fibers tend to possess a distorted elliptical cross-section. In view of this fact, the values reported in the last quarterly report for experimental glass batch AB are in serious error. Preliminary measurements on machine-pulled fibers from this batch give an average modulus of 14.9 million psi with some higher individual values such as 15.2, 15.0, 16.4, 15.6, 15.4, 15.3.

Many of the earlier studies reported in our literature survey likewise showed unusually high values for Young's modulus as measured on hand-drawn glass fibers from experimental batches and indeed, such values occur even in the patent literature. These values like our high values of the fifth quarterly report probably reflect the ellipticity of such hand-drawn samples and should not be taken seriously. In fact, any values of strength or modulus reported on hand-drawn fibers without accompanying detailed proof by measurement or microscopic examination that the fiber is circular in cross-section must be considered untrustworthy.

Mechanical Drawing of Glass Fibers from an Orifice

The above problems encountered in attempting to obtain a reliable value for Young's modulus on hand-drawn fibers made it quickly obvious that it was time to switch to mechanical drawing of the experimental glass fibers. Normally this is done by purchasing massive platinum-rhodium bushings of proven design. But in our case several bushings would be necessary since the experimental glass compositions vary so widely that the life-time of such a bushing might be very limited. Several such bushings would represent an expenditure for materials three to four times as great as the program material cost to date. Fortunately, it has proven possible using the platform furnace pictured and described in the last quarterly report to substitute a relatively inexpensive 20 cc platinum crucible for the platinum bushings customarily employed. To make this substitution it was necessary to reinforce the bottom of the platinum crucible in a small central area by welding foil to the crucible until a thickness of 3/16 inch was obtained. This central area was then tapered reamed to form an orifice 0.088 inch at top, 0.063 inch at bottom and 3/16 inch long. In addition, water cooling almost directly beneath the crucible had to be introduced into the furnace as well as a ring orifice arrangement for cooling the fiber as it forms with helium jets. This equipment has now been extensively tested and proven to yield glass fiber that is very close to circular, approximately one mil in diameter when pulling speeds of 800 feet/minute are employed, and suitable for improved modulus determinations.

REFERENCES

1. W. R. Foster, J. Am. Cer. Soc., 33, 73-84, (1950).

2. H. R. Swift, J. Am. Cer. Soc., 30, 165-169, (1947).

3. J. G. Morley, Glass Tech., 6, 69-89, (1965).

TABLE I

X-ray Data

Devitrification Product(1)		Synthetic Sapphirine(2)		Mullite(3)	
d, Å	I	d, Å	I	d, Å	I
5.40	≪10			5.38	70
4.11(4)	10				
4.02	10	4.01	10		
3.38	30	3.58	10	3.39	100
3.26	≪10	3.25	10		
3.07	≪10	3.07	10		
2.98	40	2.98	50		
2.83	40	2.82	40		
2.76	<10	2.76	20		
2.69	10	2.67	20		
		2.62	10		
2.56	20	2.56	40		
2.53	10			2.54	90
2.44	100	2.44	100		
2.38	<10	2.38	20		
2.34	30	2.34	50		
2.21	20	2.23	10		
2.12	10	2.12	10		
2.07	<10	2.06	10		
2.01	80	2.01	90		
		1.94	10		
1.89		1.89	20		
		1.82	10		
		1.754	10		
		1.703	10		
		1.638	10		
		1.571	20		
		1.549	30		
1.54	10	1.542	30		
1.515	10			1.523	90
		1.48	10		
1.435	70	1.435	90		
1.418	40	1.419	70		
1.411	10	1.410	40		

(1) This material was grown from batch 1-B; the material grown from batch 1 did not contain mullite, but the X-ray diffraction patterns were not as good as this one.

(2) W. R. Foster, J. Am. Cer. Soc., 33, 73-84, (1950).

(3) These are only a few of the most intense lines for mullite.

(4) This line may be due to cristobalite

TABLE II

Batch I

Observation No.	Sample	Temperature	Rate of Growth microns/minute
1	A	1251 ± 4	21
2	A	1299 ± 4	14
3	A	1237 ± 5	16
4	A	1150 ± 5	10
5	A	1089 ± 5	3
6	A	1248 ± 5	25
7	A	1242 ± 5	22
8	A	1194 ± 5	20
9	A	1235 ± 5	22
10	A	1295 ± 5	14
11	A	1255 ± 5	31
12	A	1337 ± 4	3
13	A	1209 ± 5	19
14	A	1251 ± 5	15
15	B	1178 ± 5	11
16	B	1280 ± 5	20
17	B	1028 ± 5	2
18	E	1260 ± 5	25
19	E	1342 ± 5	1
20	E	1223 ± 8	21
21	E	1245 ± 6	25
22	F	1237 ± 5	26
23	F	1228 ± 5	24

TABLE III

Batch 1-B

Observation No.	Sample	Temperature	Rate of Growth microns/minute
1	B	1083 ± 5	27
2	B	1372 ± 4	13
3	B	1197 ± 5	235
4	C	1055 ± 5	68
5	C	1405 ± 5	5
6	C	1101 ± 4	109
7	C	1260 ± 4	290
8	C	1418 ± 4	0 in. 4 min.
9	D	1322 ± 4	210
10	D	911 ± 5	0 in. 9 min.
11	D	1088 ± 4	104
12	D	1191 ± 3	290
13	D	1197 ± 4	300
14	D	1141 ± 5	175
15	D	1046 ± 4	34
16	D	1264 ± 4	290
17	D	1210 ± 4	265
18	D	1266 ± 4	295
19	D	1009 ± 5	11
20	E	1361 ± 4	3
21	E	1189 ± 4	270
22	E	1193 ± 5	275
23	E	1280 ± 5	305
24	E	1325 ± 5	200
25	E	1310 ± 4	225
26	E	1435 ± 4	0 in. 5 min.
27	E	1433 ± 4	0 in. 4 min.
28	E	947 ± 5	2
29	E	1318 ± 4	250
30	E	1372 ± 4	45
31	E	966 ± 6	0 in. 4 min.
32	E	1347 ± 4	130
33	E	1364 ± 4	38
34	E	1435 ± 8	-16 (solution)
35	E	1364 ± 4	30
36	E	966 ± 5	5
37	E	1343 ± 4	135

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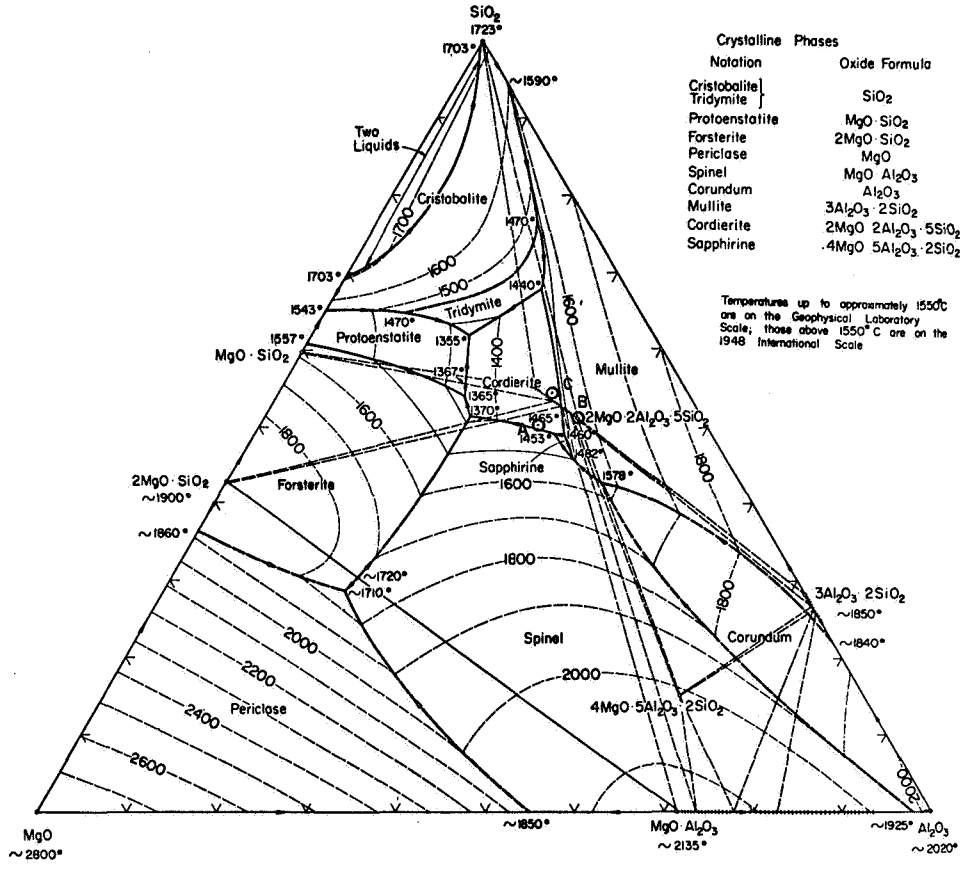
FIG. 1

THE SYSTEM $MgO - Al_2O_3 - SiO_2$

THIS DIAGRAM WAS TAKEN FROM PHASE DIAGRAMS FOR CERAMISTS, PUBLISHED BY THE AMERICAN CERAMIC SOCIETY, COLUMBUS, OHIO

$MgO–Al_2O_3–SiO_2$



Crystalline Phases	
Notation	Oxide Formula
Cristobalite, Tridymite	SiO_2
Protoenstatite	$MgO \cdot SiO_2$
Forsterite	$2MgO \cdot SiO_2$
Periclase	MgO
Spinel	$MgO \cdot Al_2O_3$
Corundum	Al_2O_3
Mullite	$3Al_2O_3 \cdot 2SiO_2$
Cordierite	$2MgO\ 2Al_2O_3 \cdot 5SiO_2$
Sapphirine	$4MgO\ 5Al_2O_3 \cdot 2SiO_2$

Temperatures up to approximately 1550°C are on the Geophysical Laboratory Scale; those above 1550° C are on the 1948 International Scale

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FIG. 2

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH OF SAPPHIRINE

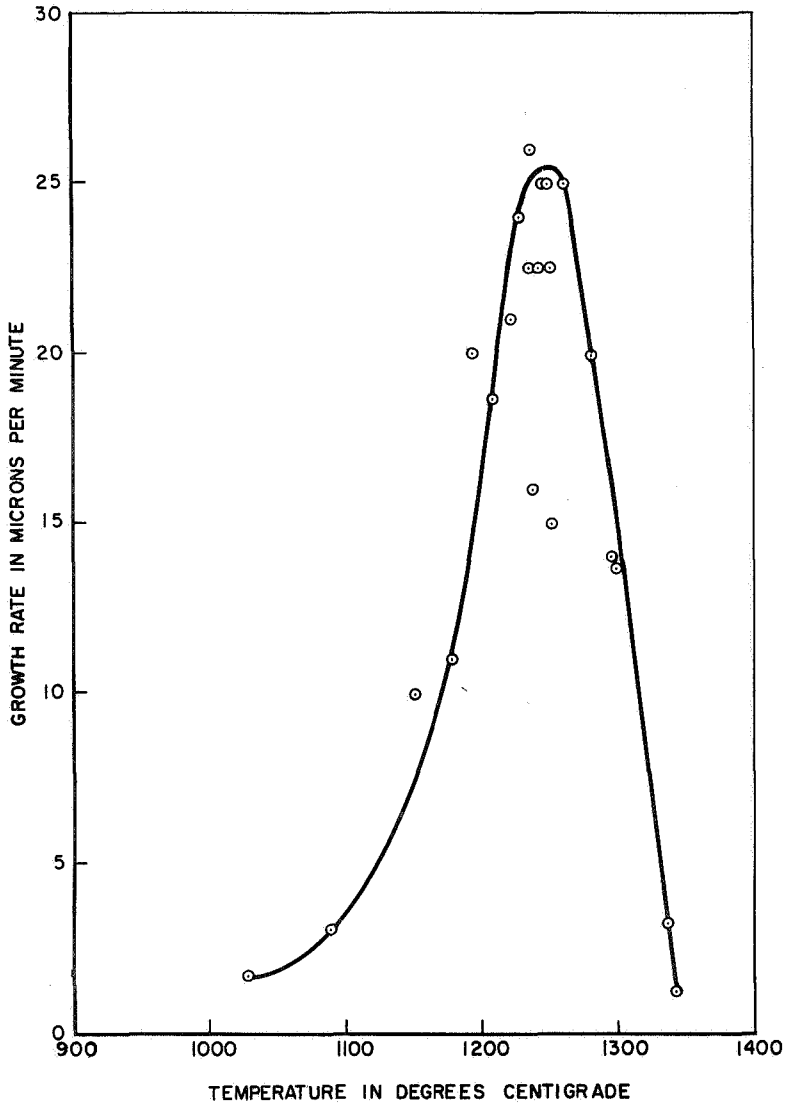

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FIG. 3

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH OF CORDIERITE

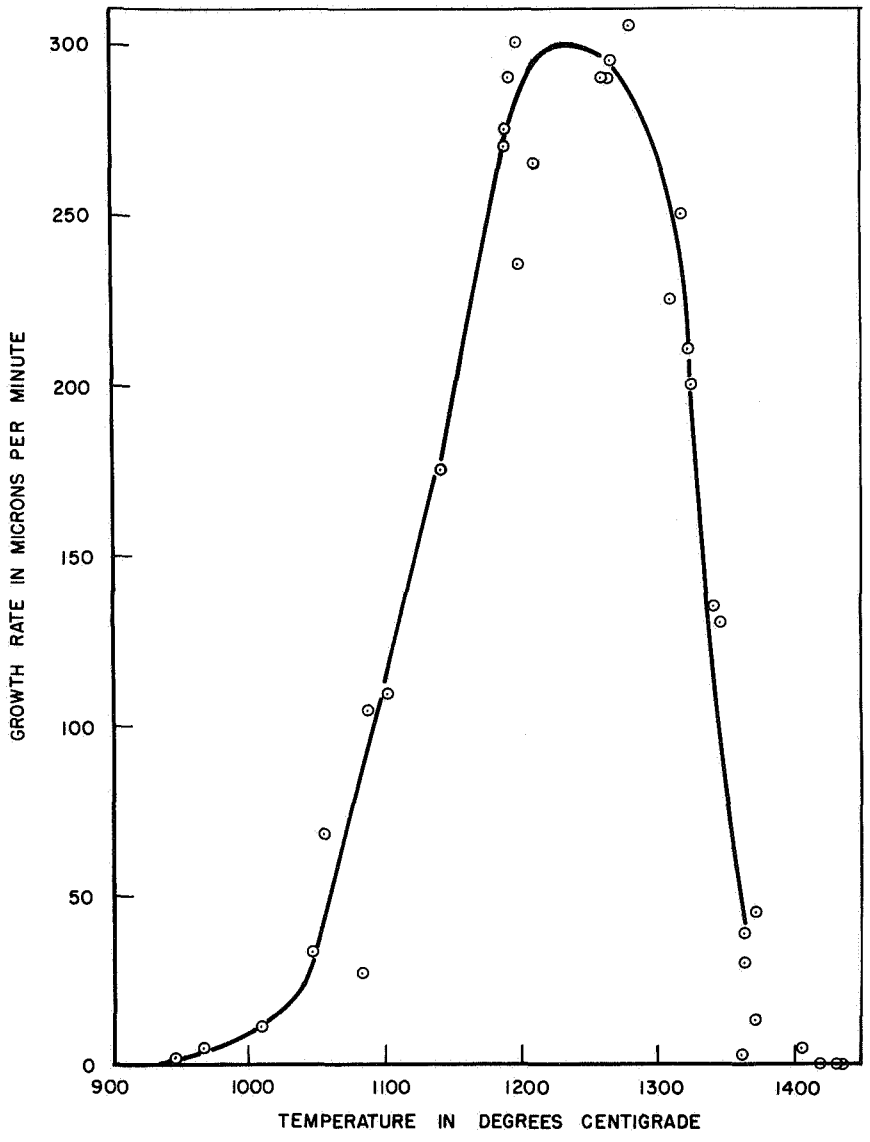

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FIG. 4

CROSS-SECTIONS OF HAND-DRAWN GLASS FIBERS SHOWING THE LEAST AND THE MOST DEPARTURE FROM CIRCULAR CROSS-SECTION COMPARED TO A PLATINUM WIRE (WHITE DOT). 100X IN ORIGINAL PHOTOGRAPH