crystals pulled from a quartz container. Optical absorption measurements at 9μ are suitable for a quantitative oxygen analysis in silicon. Oxygen-free silicon has a weak lattice absorption at 9μ.

A corresponding absorption at 11.6μ in germanium, due to Ge—O stretching oscillations, was found to be superimposed above a weak lattice band.

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Radiation Damage in Vitreous Silica: Annealing of the Density Changes[*]

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The kinetics of annealing of the nuclear reactor radiation-induced change in density of a sample of irradiated vitreous silica was studied by means of a series of isothermal annealings performed at various temperatures. The property change was found to anneal gradually over a broad range of temperatures suggesting a range of activation energies for annealing.

INTRODUCTION

A CHANGE in the properties of a vitreous silica sample exposed in a nuclear reactor was found by Primak, Fuchs, and Day.[1] They found that the original properties were restored when the irradiated vitreous silica was heated.[2,3] In these preliminary experiments, the heating was performed at randomly chosen temperatures for arbitrary periods of time, and no attempt was made to study the kinetics. The kinetics of the annealing of nuclear reactor radiation-damaged substances was first investigated by Neubert,[4] who concluded that the data were best explained by assuming that the annealing processes were distributed in activation energy.[5] The theory of the annealing of processes distributed in activation energy was investigated by Vand[6] and was extended by Primak.[7] Such kinetics seems typical of disordered solids, microscopically inhomogeneous but macroscopically homogeneous. It was thought that an excellent example of this kind of kinetics would be found in the annealing of radiation-damaged vitreous silica for it is a disordered solid to begin with. The density was the property chosen for study because it could be determined precisely with the samples available, 40–80 mesh grains of irradiated vitreous silica.

EXPERIMENTAL

Samples

The samples had been prepared by Fuchs and Primak. Commercial vitreous silica was crushed in a steel mortar, graded by sifting, and then washed successively with hydrochloric acid and water. The irradiated sample was exposed in a nuclear reactor for 59 units. (This unit is described by Primak, Fuchs, and Day[3] and Primak,[8] and is approximately 10^{18} neutrons/cm^2 having energies in excess of 10^4 ev.) After irradiation, the grains were found to be coated with a brown organic tar probably formed by the polymerization of traces of organic compounds present in the irradiation can. The tar was removed by treating the grains successively with liquid bromine, alcoholic potash, and chromic acid—sulfuric acid cleaning solution. The grains were then washed successively with water and acetone and dried. Samples used for the annealing studies were individual grains selected for transparency and regular shape under a binocular microscope. Individual grains were transferred to Pyrex glass or vitreous silica capillary flotation tubes (like the ones described by Primak and Day[9] in their Fig. 1*A*) in which they remained throughout the course of density determinations and annealings.

Density Determinations

The densities were determined by the flotation techniques described by Primak and Day.[9] The flotation liquid was a mixture of methylene bromide and

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[*] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[1] Primak, Fuchs, and Day, Phys. Rev. **92**, 1064 (1953).

[2] Primak, Fuchs, and Day, Bull. Am. Ceram. Soc. **33**, program p. 25, following p. 130 (1954).

[3] Primak, Fuchs, and Day, J. Am. Ceram. Soc. **38**, No. 4, 135 (1955).

[4] T. J. Neubert (unpublished report, March, 1944); post-deadline paper presented at the American Physical Society Meeting, Baltimore, March 17, 1955 (to be published).

[5] Work done at the Metallurgical Laboratory of the University of Chicago in 1944. (Private communication from M. Burton.)

[6] V. Vand, Proc. Phys. Soc. (London) **55**, 222 (1943).

[7] W. Primak, Phys. Rev. **100**, 1677 (1955).

[8] W. Primak, Phys. Rev. **95**, 837 (1954).

[9] W. Primak and P. Day, Anal. Chem. **26**, 1515 (1954).

n-propyl alcohol. (Barium oxide was used as a desiccant, for with other desiccants the density of the solution changed rapidly presumably because of selective removal of propyl alcohol from the vapor.) The flotation temperature of the annealed grain was compared with the flotation temperature of one of several grains which were chosen for comparison standards, and the density change was computed from the difference in flotation temperatures and the temperature coefficient of the density of the flotation liquid. The flotation temperatures used were in the range 12 to 48°C. The coefficient of expansion of vitreous silica is so small that no correction had to be made for the temperature at which the grain was floated. The flotation temperature was determined with a 0.1°C mercury thermometer located in the thermostat. The flotation temperature was taken as the thermostat temperature adjusted so that no motion of the fragment relative to the cross hairs of the observing telescope could be detected over a five-minute period. The temperature coefficient of the flotation liquid was determined from the weights of a bob suspended in the liquid and in water at several temperatures over the range. In order to avoid a surface tension correction, the weight of the suspending wire at the same liquid level was determined in each case and subtracted from the weight of the bob and wire. All weighings were corrected for atmospheric bouyancy. The weights which were used were class *S* weights which had been calibrated against a National Bureau of Standards calibrated class *M* weight. It was found that even though the composition of the flotation liquid was altered enough to change the flotation temperature of a grain by 2.5°C, the temperature coefficient of density of the liquid did not change noticeably. The flotation liquid was discarded when its density changed by more than 2.5 times its temperature coefficient (per degree). Absolute densities of the grains chosen as comparison standards were determined by weighing the bob in the liquid at the temperatures of flotation of the respective comparison standards. The absolute densities were determined to about 1/2000. The densities of the sample grains relative to the comparison standards were determined to about 1/5000.

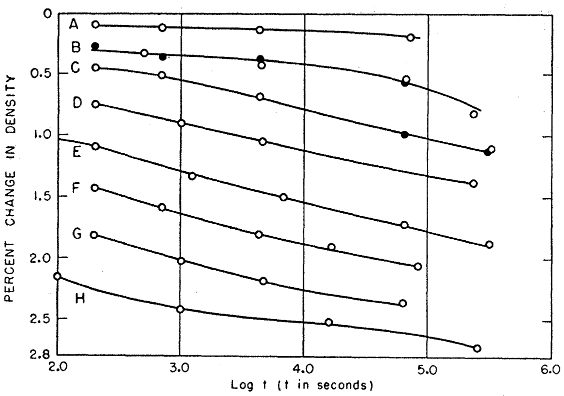

Fig. 1. Annealing of the radiation-induced changes in the density of an irradiated vitreous silica sample. *A*–300°C, *B*–450°C, *C*–550°C, *D*–650°C, *E*–725°C, *F*–800°C, *G*–900°C, *H*–1000°C.

Annealing Procedure

The annealings were performed in long electrically heated horizontal tube furnaces whose windings were arranged to minimize inducing currents in the measuring thermocouples. The lower end of a capillary (where the sample rested) was inserted quickly into a $\frac{1}{4}$-in. diameter blind hole drilled somewhat past center of a $1\frac{1}{4}$-in. diameter×5 in. long aluminum or nickel cylinder resting in the center of the furnace tube so that the capillary was in direct contact with the metal. The aluminum cylinder possessed an additional $\frac{1}{4}$ in. diameter blind hole, placed symmetrically with the sample hole, for insertion of the measuring thermocouple; and a platinum resistance thermometer was wrapped about the exterior of the block to serve as a controlling element. The nickel cylinder possessed two additional blind holes: one for the measuring thermocouple placed symmetrically with respect to the sample hole, and one for the control thermocouple placed near the periphery of the block. The aluminum cylinder was used for annealings up to 550°C, and the furnace temperature was controlled to ±2°C by supplying the furnace current through a thyratron tube connected across a resistance-capacitance ac bridge of which the resistance thermometer was one leg. The nickel cylinder was used for the annealings above 550°C, and the temperature was controlled by an arrangement involving Gouy modulation[10] of the control thermocouple connected to a Brown Electronik recorder-controller operating a mercury switch which lowered the furnace current by a desired fraction when the temperature rose. This arrangement controlled one furnace to ±1°C and controlled a second furnace, which was used only at the highest temperature, to ±3 to 5°C. The temperatures during the shorter annealings were checked at frequent intervals with a platinum 10% rhodium-platinum thermocouple whose emf was read with a Leeds and Northrup type *K*-2 potentiometer. The thermocouple emf was converted to temperatures by using a handbook table since it was found that the temperatures obtained in this manner and with a National Bureau of Standards calibrated platinum resistance thermometer over its permissible temperature range corresponded (with irregular deviations) to ±1.5°C, not much greater than the observed variation of the furnace temperature at one of the thermometers. For much of the work, thermocouple cold junctions were placed into crushed ice; but for the longer annealings, an oil bath regulated to about 0.1°C was used. The temperatures during the longer annealings were recorded on a second Brown

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[10] For the principle see *Temperature: Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1941), p. 611. However, a different electrical circuit was used here.

TABLE I. Isothermal annealing of vitreous silica exposed in a nuclear reactor for 59 arbitrary units.

Sample (Reference No.)	Temperature (°C)	Total time (sec)	Density (g cm^{-3})
456	300	0	2.2606
		2.00×10^2	2.2584
		7.00×10^2	2.2579
		4.30×10^3	2.2576
		7.18×10^4	2.2564
457	450	0	2.2781
		5.00×10^2	2.2705
		4.50×10^3	2.2685
		6.66×10^4	2.2661
		2.35×10^5	2.2599
458	450	0	2.2631
		2.00×10^2	2.2570
		7.00×10^2	2.2550
		4.30×10^3	2.2547
		6.58×10^4	2.2503
459	550	0	2.2613
		2.00×10^2	2.2512
		7.00×10^2	2.2498
		4.30×10^3	2.2461
		3.28×10^5	2.2367
460	550	0	2.2603
		6.54×10^4	2.2382
		3.07×10^5	2.2352
461	650	0	2.2599
		2.00×10^2	2.2429
		1.00×10^3	2.2398
		4.60×10^3	2.2363
		2.37×10^5	2.2287
462	725	0	2.2606
		2.00×10^2	2.2358
		1.22×10^3	2.2306
		6.80×10^3	2.2267
		6.44×10^4	2.2218
		3.18×10^5	2.2183
463	725	0	2.2612
		60	2.2384
464	800	0	2.2606
		2.00×10^2	2.2282
		7.00×10^2	2.2247
		4.30×10^3	2.2200
		1.65×10^4	2.2176
		8.17×10^4	2.2142
465	900	0	2.2596
		2.00×10^2	2.2186
		1.00×10^3	2.2139
		4.78×10^3	2.2105
		6.33×10^4	2.2065
466	1000	0	2.2611
		1.00×10^2	2.2119
		1.00×10^3	2.2065
		1.54×10^4	2.2043
		2.50×10^5	2.1998

Electronik recorder. The shorter annealings were timed with a manually operated stop watch. The watch was checked against electric clocks running on laboratory ac power lines. The longer annealings were timed with these laboratory electric clocks.

Data

The results obtained in a series of isothermal annealings are given in Table I. To check the effect of heating and cooling the fragments, an unirradiated grain (Reference No. 467) was heated at about 900°C and at about 1050°C for periods of time. To find the effect of a prolonged heating at high temperature, the irradiated grain Reference No. 463 which had been annealed at 725°C for 60 sec was annealed at about 1050°C. These results are given in Table II.

DISCUSSION

It is seen in Table I that the densities of the irradiated vitreous silica samples before annealing were not the same. It was therefore necessary to reduce the data to some common unit before analyzing the kinetics. It was shown by Neubert[11] in his investigations of the changes in the electrical resistance of artificial graphite irradiated in nuclear reactors, that although the resistivities of different specimens from the same sample differed, the percent change in resistivity caused by simultaneous irradiation of the different specimens was nearly the same. It was also found by Primak and Day[12] that for irradiated silicon carbide grains of differing densities which had been irradiated simultaneously, the percent changes in density which occurred on annealing were nearly the same. This was not checked for the vitreous silica used in the present studies, but even if reducing the data in this manner were not justified, the error introduced could not be great because the densities of the grains did not differ greatly from each other. The percent changes in density resulting from the annealing of the grains are plotted in Fig. 1 against the logarithm of the length of time of annealing.

It is seen that an acceptable straight line could be passed through the points in Fig. 1 associated with a particular temperature. If it is assumed that the kinetics is to be explained by processes distributed in activation energy, the approximate initial distribution p_0 (the resolution is several times τ) for the percent changes in density is given by[7]

$$p_0(\epsilon_0) = -\frac{dp}{dx}\frac{1}{2.303\tau},$$

$$\epsilon_0 = 2.303\tau \log(Bt),$$

where ϵ_0 is the activation energy (in ev), p is the percent change in density due to annealing, x is $\log t$, t is the time, B is a constant having the dimensions of frequency, τ (in ev) is the product of Boltzman's constant and temperature, and Briggsian logarithms are used throughout to concide with the customary rulings on semilogarithmic paper. If dp/dx were constant for an isothermal

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[11] T. J. Neubert (private communication).

[12] W. Primak and P. Day (unpublished progress report, July, 1952).

TABLE II. Effect of heating irradiated and unirradiated vitreous silica for a prolonged period at high temperature.

Sample (Reference No.)	Approximate temperature (°C)	Approximate annealing period (sec)	Density (g cm^{-3})
467 (unirradiated)	not heated	···	2.2027
	900	4.3×10^{3}	2.2033
	1050	1.7×10^{5}	2.1991
463 (irradiated)[a]	725	60	2.2384
	1050	5.8×10^{5}	2.2000

[a] See Table I.

annealing, the portion of the initial distribution revealed by that annealing would be constant. If the initial distributions calculated for straight lines fitted to the points of Fig. 1 are plotted, it is found that a peak formed of disconnected segments is revealed as is shown by the dotted lines in Fig. 2. It was shown by Primak[7] that such a result could be interpreted as indicating a distribution of both activation energies and frequency factors. However, if instead of fitting straight lines through the points of Fig. 1, they are connected with the curves which are shown, the initial distributions shown by the solid lines in Fig. 2 are obtained. Thus, it is the very small deviations of the data from linearity that reveal the true structure of the initial distribution. The value of the frequency factor 10^9 was chosen to achieve a reasonably good coincidence of the overlapping sections of the distributions obtained at different temperatures. The coincidence which has been achieved is well within the error of the results. At the low temperatures, the slopes dp/dx were small; and departure from a straight line was not great. The solid lines in Fig. 2 therefore do not necessarily represent a more satisfactory "fit" to the data than the dotted lines, and the correct distribution could thus be anywhere between. Even at the higher temperatures, the slopes were not easily judged; and with prior knowledge of the result, one could very reasonably have chosen slopes which would have made the distributions plotted in Fig. 2 coincide completely except for the final point in the 450°C and the final point in the 1000°C annealing. These are considered to be faulty data; perhaps the temperature drifted during these annealings.

Thus the annealing data can be interpreted as revealing an initial distribution of percent changes in density which is a peak over an activation energy range of about 2 ev, about 20 to 40 times τ at which the annealings were conducted. The remainder of this discussion is based on an analysis by Primak[7] of the kinetic behavior of such systems. To explain these results with a discrete activation energy and a high order of reaction, an order ~10 would have to be chosen, and the shape of the peak beyond the maximum could not be well fitted because the region beyond the maximum of the peak is too broad. If it is assumed that the order of reaction can be taken to be near unity, the rising portion of the peak is much like the form of the characteristic annealing curve, and the falling portion is much like an exponential decline. The equations which are obtained in fitting the peak depend on the relation chosen between the exponential functions. Two examples of satisfactory fits are

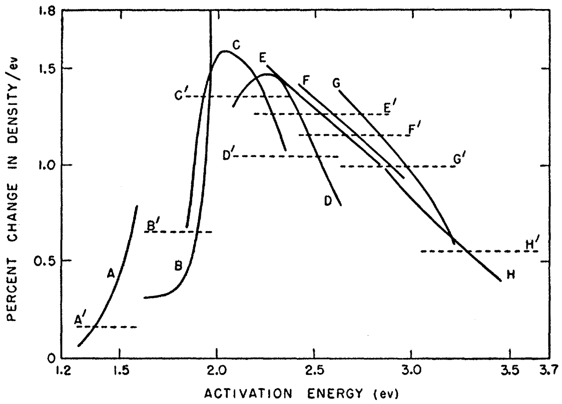

FIG. 2. The initial distribution of density changes over activation energy from the annealing data of Fig. 1. *A*, *A'*–300°C; *B*,*B'*–450°C; *C*,*C'*–550°C; *D*,*D'*–650°C; *E*,*E'*–725°C; *F*,*F'*–800°C; *G*,*G'*–900°C; *H*,*H'*–1000°C.

$$p_0 = \exp(-40.1e^{-\epsilon} - 3.82\epsilon),$$
$$p_0 = a\exp(-119.1e^{-2.035\epsilon} - 2.035\epsilon).$$

Since the coefficient of ϵ appearing in the exponential-exponential is related to the reciprocal τ of annealing, it is evident that these equations are for annealings which have taken place at very high temperatures, about 6000°C for the second equation, and 12 000°C for the first one. The 40.1 and the 119.1 appearing in these equations are the product of the length of annealing and the frequency factor, and therefore indicate annealings whose length is of the order of magnitude $10^2/B$ seconds. The approximations of the equations used to obtain the initial distribution yield a distribution which is slightly broader than the actual one; and since further there may be broadening from the contributions of regions in the solid which have not undergone annealing of the sort described here, the distribution which was found may have arisen from annealing for a somewhat longer time at a lower temperature. The extrapolation of the kinetic laws into this temperature range may be unjustified. However, it may be pointed out that these observations can have little significance if B is as small as $\sim10^9$. If B is $\sim(10^{12}$ to $10^{14})$, the annealing times are $\sim(10^{-10}$ to $10^{-12})$, and the annealing processes could correspond to the thermal spikes in radiation damage.[13]

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[13] W. Primak, Phys. Rev. 98, 1854 (1955).