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ATOMIC ENERGY OF CANADA LIMITED

CHALK RIVER PROJECT

THE SWELLING OF BERYLLIUM FROM NEUTRON-INDUCED GASES

CRMET-809

BY

C. E. ELLS

CHALK RIVER, ONTARIO

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RESEARCH AND DEVELOPMENT

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ABSTRACT

Specimens of beryllium which had received an irradiation in the Materials Testing Reactor up to an integrated fast flux of 10^{22} nvt have been examined after annealing at various temperatures above 400°C. These annealing treatments have resulted in significant decreases in overall density of the beryllium specimens, the density decrease being 0.8% and 20% after annealing for one hour at 600°C and 995°C respectively.

The quantity of neutron induced gases contained in the beryllium has been determined to be approximately 23 cc of gas per cc of beryllium for an integrated fast flux of 10^{22} nvt. Analysis of the gas shows that it is mainly He^4.

The results of the investigation suggest that the neutron induced gases will not be a serious deterrent to the use of beryllium in reactor applications at temperatures up to 600°C.

THE SWELLING OF BERYLLIUM FROM NEUTRON-INDUCED GASES

I - INTRODUCTION

The properties of beryllium which lead to its projected use as a fuel sheathing material in gas cooled power reactors have been discussed in many publications.[1,2,3,4] Apart from the low capture cross section of beryllium for thermal neutrons it now seems established that, at temperatures up to 600°C, the metal has sufficient strength, the required degree of compatibility with uranium oxide (compatibility with uranium metal is still in doubt [5]) and exhibits satisfactory corrosion resistance to dry carbon dioxide. However, satisfactory methods for producing wrought beryllium with good ductility in three directions have not been developed. There is confidence, however, that the problem of fabrication will be overcome, and intensive development work on beryllium fabrication is proceeding in several laboratories in the United Kingdom and United States. Irradiation of beryllium sheathed fuel elements is now underway in the United Kingdom[6].

It has been recognized for some time that one possible deterrent to the use of beryllium in reactor applications[7] arises from the production of gas, mainly He^4, when beryllium is irradiated with fast neutrons. This gas is formed from the (n,2n) and (n,α) capture reactions on beryllium, the significant parts of the reaction chains being:

(n,2n) $\quad Be^9 + n \longrightarrow Be^8 + 2n$

$\quad Be^8 \longrightarrow 2He^4$

(n,α) $\quad Be^9 + n \longrightarrow He^6 + He^4$

$\quad He^6 \xrightarrow{\beta^-} Li^6$

$\quad Li^6 + n(\text{thermal}) \longrightarrow He^4 + H^3$

The primary reaction in each chain requires neutron threshold energies of 2.70 and 0.71 mev respectively. Sufficient nuclear data is available to permit an estimate of the quantity of gas which will be produced for any given irradiation: details of the calculation are presented in Appendix I. The quantity of gas formed may be as much as 2 cc per cc of metal for an integrated fast flux* irradiation of 10^{21} nvt. No experimental information on the amount of gas produced during irradiation has been published, but beryllium used as a sheathing material can be expected to receive irradiations equivalent to the above figure. When uranium is irradiated it has been found that quantities of fission product gases as high as 2 cc per cc of metal have a serious deleterious effect on the mechanical properties of the metal(8), if the irradiation has been carried out at temperatures of 600°C or higher. Although beryllium is considerably stronger than uranium at these temperatures, it is not possible to make a definite prediction of the effect that this quantity of gas would have on the properties of beryllium. It seemed therefore, at the start of the present investigation, that an initial study of the effect of the neutron-induced gases on beryllium should be undertaken.

Beryllium which had already received a long irradiation at temperatures below 100°C was available at Chalk River, which made it possible to approach the problem through annealing experiments on this type of metal. Although such experiments could not be expected to give a final answer to the technological problem, they would give some idea of its magnitude, and furthermore would give the direction which the high temperature irradiation experiments should take.

* In this report "fast flux" will be taken to cover neutrons having energies above 1.0 mev.

The present report describes the results of these annealing experiments, and the correlation of the observed swelling with the irradiation received by the beryllium.

II EXPERIMENTAL METHODS

(a) Material

Irradiated beryllium available for study came from a shim rod which had been used in the Materials Testing Reactor for an irradiation of 31063 MWD. The beryllium had served as a functional component of the reactor, and there was no prior intent to use this particular component to investigate the irradiation behaviour of beryllium. The beryllium[9] had been fabricated via the powder route, 200 mesh powder being hot pressed at 1050°C in vacuo at 125 psi. The resultant metal had a density in the range 1.84 - 1.85, and a BeO content of approximately 1%. Room temperature mechanical properties of the pre-irradiated metal are reported to be[9]:

Yield Strength (0.2% offset)	23 - 25000 psi
Ultimate Strength	35 - 36000 psi
Elongation in 1"	1.4%

The creep properties of this particular beryllium are not available. The shim rod received the greatest part of its irradiation in the M.T.R. shim rod position L-44; the complete irradiation history is presented in Appendix II. A drawing of the shim rod is shown in Figure 1; the section numbered 5, close to the middle of the rod length, was sent to Chalk River. During irradiation the intensity of thermal neutron flux was quite uniform over any one horizontal plane in the rod, and it is estimated that section 5 received a total thermal neutron irradiation of 2.8×10^{22} nvt.[10]

The intensity of fast neutron flux received at any point in section 5 was affected by intensity gradients in the three mutually perpendicular directions defined by the vertical direction of the reactor and the direction parallel to the long horizontal direction of the reactor core. Of the three gradients, those in the two directions specified above were sufficiently shallow to be unimportant for the purposes of the present experiments[11]. However, the gradient in the third direction was quite steep, mainly due to the moderating properties of beryllium. Evans[12] has estimated that the fast flux intensity dropped by a factor of 5 over the 2.838" thickness of the shim rod in this direction, although the energy spectrum of the fast flux would remain much the same throughout. A detailed drawing of the section is shown in Figure 2. The direction AB is parallel to the vertical direction of the reactor core. AF is the direction of maximum fast flux gradient. Specimens for experimental study were cut from the regions AB, FG, and ADE. The nominal value of integrated fast flux for the side ABCD is 9.5×10^{21} nvt,[13] and the section FG will have received irradiation of one fifth of this value. These flux values, however, are not known to an accuracy of better than ±20%, and they will hereafter be referred to as 10^{22} and 2×10^{21} respectively.

The complete section had a $\beta\gamma$ activity of the order of 3000 r/hr on contact, and therefore experimental specimens were cut in the metallurgy cave. The experimental specimens, each about one gram in weight, exhibited a $\beta\gamma$ contact activity of approximately 2 r/hr, and further experimental work with these specimens could proceed with shielding of less than one inch of lead. The beryllium proved to be

extremely brittle, and most specimens obtained were rather irregular in shape. The ease with which regular rectangular pieces could be cut from unirradiated beryllium in the same cutoff facility confirmed that the material underwent a significant embrittlement during irradiation.

(b) Density Changes

Annealing was carried out in a dynamic vacuum system, at pressures of approximately 10^{-5} mm Hg. The sample tube was made from silica and to overcome any reaction between this and the beryllium sample a molybdenum tube was placed inside and this contained the sample during annealing. The silica and molybdenum tubes were degassed prior to moving the beryllium specimen into the molybdenum tube. This was done without breaking the vacuum, by use of a magnetic pusher. At lower temperature anneals, in the region of 600°C, the cubical specimens of one gram weight exhibited weight gains of the order of 0.0001 grams after several hours annealing. At temperatures around 800°C the specimens lost a similar amount of weight, which could be expected from the high vapor pressure of beryllium and some of the impurities contained in it. Prior to the initial annealing of any one specimen, the beryllium was cleaned with a chemical polish based on chromic acid. It was established that a further cleaning, following each anneal, did not increase the reproducibility of the results. It was also established that the chemical polish did not result in any significant amount of hydrogen pick up by the beryllium.

The density measurements were carried out by the hydrostatic method using a Mettler Grammatic balance with n-octyl alcohol. The alcohol density reported by Mallett[14] was used in calculations, but the measurements were checked with an aluminum alloy of known absolute density. The annealed specimens were placed in the alcohol in the as-annealed condition, no attempt being made to fill in the surface porosity. Because of this porosity, different times were required for the immersed specimens to exhibit an equilibrium weight, from a few hours for specimens which had undergone a density decrease of 5% to several days when the density decrease was of the order of 20%. When the density decrease was below 5%, measurements on individual specimens were reproducible to ±0.1%

(c) Gas Analysis

A determination of the quantity and type of gas contained in the irradiated beryllium was undertaken on specimens from the high and low flux sides of the section. This analysis was divided into two distinct operations. The total gas evolved during vacuum fusion was collected in an apparatus designed for this particular experiment, and the constituent analysis of the gas was carried out in standard experimental systems. A schematic diagram of the gas collection system is shown in Figure 3. The essential operation consisted of melting the beryllium in the furnace tube assembly, with the evolved gases being contained in the previously evacuated pyrex glass system. The beryllium was allowed to resolidify, and the gas pressure measured in the system of known volume. These operations determined the absolute quantity of gas liberated from the beryllium, and specimens of the gas could then be placed in the two transfer flasks attached to the system for transportation to the constituent analysis systems.

In practice, the beryllium specimen was placed in the specimen storage tube, and the system evacuated and partially degassed. The degassing vacuum was provided by an Edwards F203 diffusion pump, which enabled a vacuum of better than 10^{-5} mm Hg to be obtained during degassing procedures. When necessary, pertinent volumes of the vacuum system could then be obtained through use of helium from the calibration flask, the volume of the latter being known from a calibration using distilled water. Following this operation, the degassing was continued. Because comparitively large amounts of gas (several cc at N.T.P.) were eventually removed from individual beryllium specimens, a virtual leak of a few microns per hour could be tolerated; hence greased stopcocks could be used in the system and rather simple degassing procedures were followed for the pyrex portions of the system.

The beryllium was melted by induction heating, using the beryllium as its own susceptor. The furnace tube assembly consisted of two alumina crucibles, one inside the other and separated at their bases by alumina beads, and contained in a silica tube. Beryllium melts at 1284°C and, in the gas removal, temperatures of at least 1350°C were attained. It was not possible therefore to degass the crucible assembly at temperatures as high as those which the inner crucible would eventually reach during melting. The degassing procedure followed was to use an electrical tube furnace over the silica tube, maintaining the temperature at 1050°C for at least one hour at the degassing vacuum. This method obviously provided an effective degass of the silica tube and probably of the outer crucible: subsequent analysis of the gases collected during the melting confirmed that the degassing procedure was effective for the inner crucible as well, at least for the purposes of this experiment.

When degassing was completed, the beryllium specimen was moved with a magnetic pusher from the storage tube into the inner crucible. In melting, the beryllium was brought to the melting point rather slowly (over a period of ten minutes) to avoid any spattering of metal from an explosive disintegration of the specimen. It was observed that the major portion of the gas was given off by the time the specimen had reached the temperature of 1200°C, but small additional amounts of gas were released as the specimen temperature went above 1300°C. On cooling and remelting of the specimen, no further quantities of gas were released.

The problem of determining the quantities of inert gases in metals has been discussed in some detail by Churchman et al[15], and their conclusions suggest that the most likely source of error in the experiments described above would be a failure to remove all the gas from the metal. The gas removal would be facilitated by using as high a temperature as possible: this factor had to be balanced against the desirability of keeping temperatures low to reduce the chances of a spill involving the rather dangerous beryllium vapour. For this latter reason, the molten metal was not taken above 1400°C at any time. As one test of removal efficiency, one specimen was maintained at 1350°C for approximately 10 minutes, during which period a significant amount of the beryllium specimen was evaporated from the crucible and condensed on the silica and attached pyrex. No further gas, however, was given off during this prolonged heating. As an additional expedient, a mercury diffusion pump was built into the system as shown in Figure 3. When the major part of the gas had been placed in a transfer flask, operation of the mercury diffusion pump would reduce the pressure in the furnace tube to 10^{-5} mm Hg. On remelting the beryllium at this

pressure, no significant quantity of gas was obtained.

The total volume of the collection system was approximately 2000 cc. Pressure buildups in the system during gas removal were of the order of 5 mm Hg, and hence pressures were conveniently measured with a dibutyl phthalate manometer. The density value accepted for the dibutyl phthalate was 1.041 gm/cm at 25.7°C, a value recently determined at N.P.L.[16], although on a different batch of liquid. Ambient temperatures in the region of the collection system were measured with a N.B.S. calibrated mercury-in-glass thermometer.

The important part of the constituent analysis was a confirmation that the collected gas was mainly He^4, whereas a second part of the analysis, less important from the point of view of the swelling problem, was a determination of the He^3, H_2^1, and H_2^3 content of the gas. Two analytical methods were available: (1) a mass spectrographic method for He^4, He^3, H_2^1, O_2, N_2, and to a lesser degree of accuracy for H_2^3, CO_2 and CO and (2) a chemical method for CO_2, N_2, O_2, hydrogen isotopes, and helium isotopes. An accurate determination of the H_2^3 content would have required a counting method, but apparatus suitable for the counting of gaseous H_2^3 was not available at Chalk River and this part of the analysis has not been completed. In addition, H_2^2, if present, would not have been detected by the analytical methods used.

In an attempt to obtain a blank value for the gas determination a specimen of Brush reactor grade beryllium was treated in a manner identical to the irradiated specimens. The gas obtained was less than 0.03 cc/cc, an insignificant quantity compared to the gas collected from the irradiated metal.

(d) Metallography

Two specimens of the irradiated beryllium were examined by metallographic techniques. The specimens were mounted and mechanically polished in a shielded dry box, etched in a solution of 1/2% HF in alcohol, and photomicrographs were taken with a Vickers projection microscope.

III RESULTS

(a) Density Changes

Detailed results of the annealing experiments are given in Table I. All anneals were essentially isothermal, but since the specimens were removed from the furnace for density measurements at the times shown in the table the results for the long term anneals represent a certain amount of thermal cycling. Except for the two cases noted in the table, a new specimen was used at each distinct temperature, the same specimen being used for all anneals at any one temperature. A plot of the density decrease observed for the first hour of anneal at each of several temperatures, and for each of the high and low flux sides of the beryllium section, is presented in Figure 4. The ordinates in the plot, as well as the density decreases tabulated in Table I, represent the decrease in density as a percentage of the density determined for the as-cut specimens. The variation of density decrease with time at 595°C is presented in Figure 5.

(b) Gas Analysis

Five different specimens of the as-cut beryllium have been analyzed for neutron induced gases, three of these specimens coming from the high flux side of the specimens. The total gas content obtained from each of the specimens, in cc gas per cc metal, along with

TABLE I

EFFECT OF ANNEALING TREATMENT ON DENSITY OF IRRADIATED BERYLLIUM

Fast Flux Irradiation	Temperature[1] in °C											
	440		595		730		790		890		995	
	Cumulative Annealing Time	Density Decrease	Cumulative Annealing Time	Density Decrease	Cumulative Annealing Time	Density Decrease	Cumulative Annealing Time	Density Decrease	Cumulative Annealing Time	Density Decrease	Cumulative Annealing Time	Density Decrease
nvt	hrs.	%	hrs.	%	hrs.	%	hrs.	%	hrs.	%	hrs.	%
10^{22}	1.0	Nil	1.0 2.5 6.5 13.0 20 44 92 230 570 810 1121 1601	0.76 0.87 0.98 1.09 1.14 1.25 1.31 1.46 1.52 1.64 1.74 1.82	1.0	1.25	1.0 2.5 1.0[3]	5.45 14.2 3.86	1.0[2] 2.5 6.5 13 38 230	15.1 17.6 18.2 18.1 22.1 23.1	1.0	20.1
2×10^{21}			1.0 2.5	0.11 0.12	1.0 2.5	0.50 0.79	1.0	1.30	1.0[4]	9.58		

(1) Temperature given to nearest 5°C.
(2) Specimen used which had previously been annealed at 440°C.
(3) New specimen.
(4) Specimen used which had previously been annealed at 595°C.

the mass spectrographic analysis of the gas, is presented in Table II. The calculated gas contents given in the last column represent the amounts of gas present after irradiation and a storage period of three years. Only four gases, He^4, He^3, H_2^3 and H_1^3 are shown in the analysis; O_2, N_2, CO_2 and CO were not present in significant quantities. The values given for the He^4, He^3 and H_2^1 content are probably accurate, relative to each other, to at least ±10% for individual specimens of collected gas, but the values given for H_2^3 content could, on the basis of the mass spectrometer calibration alone, be in error by a factor of 2. However, for specimens A and B chemical analysis confirmed that the collected gas was of the order of 90% helium isotopes and gave a value for hydrogen isotopes content consistent with the tabulated values. There is some confidence therefore that the H_2^3 analysis may be as good as ±20% for individual specimens of gas. The presence of H_2^3 in the collected gas was confirmed by a counting monitor; any H^1H^2 present would be included in the He^3 content.

(c) Metallography

Two photomicrographs of the irradiated beryllium, for metal in the as received condition and after annealing to a density decrease of 14.2% respectively, are presented in Figure 6. This beryllium was taken from the high flux side of the section. The black particles in the as-received sample are thought to be beryllium oxide and are largely distributed at the grain boundaries. The large black areas at the grain boundaries in the annealed sample are holes and it is worth noting that some grains in this sample were stained and contained very fine black dots. It is possible that these black dots represent very fine holes.

TABLE II

GAS CONTENT OF IRRADIATED BERYLLIUM

	EXPERIMENTAL					THEORETICAL
Irradiation fast flux nvt	2×10^{21}		10^{22}			10^{22}
Specimen No.	A	B	C	D	E	
Total Gas Content cc/cc	5.2	5.5	23.5	24	18.5	23.2
Gas \ MASS SPECTROGRAPHIC ANALYSIS IN %						THEORETICAL ANALYSIS %
He^4	91.3	93.3	91.0	92.8	-	96.7
He^3	1.8	1.8	1.8	1.8	-	0.9
H_2^1	1.1	2.2	0.1	0.3	-	0.2
H_2^3	5.8	2.7	7.1	5.1	-	2.2

IV DISCUSSION

(a) Annealing Results

The important features of the density changes given in Table II are illustrated by the graphs shown in Figures 4 and 5. The plot of the swelling observed in the first hours of anneal, Figure 4, shows that below some temperature, about 500°C, no swelling occurs for amounts of gas up to 20 cc/cc. A similar behaviour is exhibited by uranium after irradiation and subsequent annealing. As would be expected, the beryllium containing the larger amount of gas underwent a significantly greater swelling. The measurements for the high flux material were taken to a temperature at which the expected turnover of the swelling -temperature curve was observed; at some value of density decrease interconnected porosity would permit escape of the bubble forming gas and increasing temperature of anneal would result in very little further decrease in density. In the annealing experiments a detectable amount of gas was released at 800°C.

The failure to obtain a saturation expansion for long annealing times at any temperature below 900°C was a rather unexpected result. From the results of the post-irradiation annealing of uranium it would have been predicted that the swelling of beryllium at temperatures around 600°C should stop after less than 24 hours of annealing. The observed behaviour of beryllium is illustrated in Figure 5; at 595°C the high flux material is still swelling after 1500 hours of annealing.

A preliminary metallographic examination of the irradiated beryllium has indicated some characteristics of the voids causing the swelling. The structure of the as-received irradiated metal, shown in Figure 6, is typical of beryllium containing 1% BeO

fabricated by powder methods. The oxide particles, in general, trace out grain boundaries in the metal. The large black areas in the microstructure of the annealed specimen were, at least when the specimen polishing was completed, holes in the body of the metal. It appears certain that these holes were pockets of gas causing the swelling of the annealed beryllium, and their location at grain boundaries is strongly suggestive that nucleation of gas pockets took place at oxide particles. However, the volume of the large holes shown in Figure 6 accounts for no more than half of the swelling observed for the specimen. It is seen that smaller holes are occurring in the interior volume of some grains and it is assumed that many small voids, not resolved by the optical microscope, give rise to the swelling not accounted for by the larger holes. All of the holes observed are roughly spherical in shape, and no cracks were detected. It seems, therefore, that the beryllium had sufficient isotropic ductility to accommodate the 14% swelling.

The most advanced attempt to correlate the volume change produced by inert gas bubbles in a metal with the mechanical properties is due to Enderby.[17] It is postulated that for the case of annealing following irradiation, the swelling will take place in two stages. The first stage is an immediate expansion against elastic and plastic stresses; thereafter a second stage swelling takes place due to creep. For uranium swelling at 600°C, Enderby has calculated that the initial swelling is by far the greater in short term laboratory tests, i.e., the magnitude of the time-dependent portion over the first few hundred hours is small in comparison. It has already been seen that

this is not an adequate description of the behaviour of M.T.R. beryllium. The expression governing the initial expansion, as developed by Enderby, can be written as:

$$(x - NB) \ln \frac{1}{x} = \frac{3}{2} \frac{NRT}{Y} \qquad \ldots\ldots\ldots\ldots (1)$$

where x is the fractional volume increase, N is the gas content in moles per cc metal, B is the second virial coefficient of the gas in question, R is the gas constant, T is the annealing temperature, and Y is the yield strength of the metal at the annealing temperature. This expression only holds provided that

$$x \geq \frac{3Y}{2E} \qquad \ldots\ldots\ldots\ldots (2)$$

where E is the Young's modulus of the metal at the annealing temperature. Equation (1) does not take into account surface tension forces which would make the calculated volume change smaller. Furthermore, the expression does not predict all of the swelling observed for uranium annealed at 600°C,[18] and at 800°C the surface tension is the determining factor resisting swelling in uranium. One major difficulty in using equation (1) is obtaining the correct value to use for the yield strength. For beryllium, the room temperature value of Y, after an irradiation of 2.6×10^{22} nvt (neutron energy > 100 ev), has been reported to be somewhat greater than 47,800 psi[19]. At 600°C unirradiated beryllium retains about 1/3 of its room temperature yield strength,[20] or Y for the irradiated case might be 16,000 psi at 600°C. For unirradiated beryllium, $E \approx 35 \times 10^6$ psi at 600°C.[21]

$$\therefore \frac{3Y}{2E} \approx 7 \times 10^{-4}$$

or for swellings above 0.07% equation (1) should be valid. Using Y = 16,000 psi, gas content = 20 cc/cc, T = 595°C (868°K) and 9.82 cm^3 /mol as the second virial coefficient for helium[22] equation (1) gives a calculated swelling of 3.5%. From Figure 5 it is seen that this value, although of the right order, is clearly too high for the initial swelling. It appears, therefore, that the Enderby theory contains too many simplifying assumptions to give an accurate representation of the swelling phenomenon.

(b) Gas Analysis

A summary of all experimental results of the gas analysis, and of the results calculated in Appendix I from the irradiation data and nuclear constants, is presented in Table II. The primary object of the gas analysis was to complete the correlation between irradiation and swelling of the irradiated beryllium, confirming that the swelling is due mainly to the He^4 arising from the (n,2n) reaction. In assessing the extent to which this object has been achieved, it is necessary to start with the analysis applicable to the (n,α) reaction.

Although the quantity observed for any one of the gases H_2^1, H_2^3, and He^3 should serve to estimate the validity of the calculation for the (n,α) reaction, it clearly would be desirable to have a check from more than one of the gases. However, only the quantity of He^3 is available for this check. As previously stated, the main uncertainty in the constituent analysis of the collected gases arises from the possible error in the value quoted for the H_2^3 content. This fact alone removes much of the value of the H_2^3 analysis for purposes of drawing quantitative conclusions, but in addition it can be seen from the results in Table II that the values obtained for H_2^3 content

varied quite widely among the specimens used. A wide variation in H_2^1 content was also observed, and although the results indicate that the low flux side had a higher H_2^1 content than the high flux side, the total number of specimens used was too small to establish this pattern with much degree of certainty. In this connection, Barnes[23] has reported that specimens of irradiated beryllium cut from a different section of the same shim rod exhibited a wide variation in H_2^1 content. The amount of H_2^1 contained in the beryllium prior to irradiation is not known, nor is the rate of diffusion of H_2^1 (or H_2^3) in beryllium known, No pertinent conclusions, therefore, can be drawn from the H_2^1 analyses, except to note that the average H_2^1 content of the beryllium specimens examined is much greater than can be accounted for by the (n,α) reaction. For each of the specimens, the content of He^3 was found to be present in the same quantity relative to He^4. Its value of 1.8% indicates that the values calculated from the (n,α) reaction might be low by a factor of 2, in which case the calculated H_2^3 content should be 4.4%.

This latter value is in reasonable agreement with the mass spectrographic analysis and, if accepted, means that about 15 cc of the experimentally determined quantity of He^4 remains to be accounted for by the (n,2n) reaction. The agreement between experimental and theoretical results for the (n,2n) reaction, therefore, is quite satisfactory. From the data now available, it is not possible to account for the apparent discrepancy between claculated and experimental yields of the (n,α) reaction. One source of H_2^3 would be lithium impurity in the fabricated beryllium, but an impossibly high content of 3.7 atomic percent would be required. If the error arises from the

irradiation data, then the method of calculation for the (n,2n) reaction is wrong even though giving the correct result. It would seem more likely that the use of, or the data used for the (n,α) reaction is incorrect.

The total gas quantity obtained from the high flux side was about four times that obtained from the low flux side, as compared to the estimated ratio of five for the integrated irradiation. Both the finite size of the beryllium specimens, and the presence of larger quantities of hydrogen in the gas from the low flux side, would tend to make the experimentally determined ratios lower than the true value and the agreement is, in any event, as good as could be hoped from the irradiation data.

(c) Technological Implications

In attempting to predict the extent of the deleterious effect of the neutron induced helium on beryllium when used as a fuel sheathing material, two main difficulties arise. Firstly, no experimental information is available on the effect of voids on the mechanical properties of the metal; intuitively it might seem that 1% void could be accommodated without serious results. Secondly, it is necessary to consider that, at least in the case of uranium, the amount of swelling which occurs during irradiation at an elevated temperature can be up to ten times as large as the swelling observed for the metal irradiated at some comparatively low temperatures and subsequently given a post irradiation annealing treatment at the same elevated temperature.[8] Within these limitations, and realizing that the irradiation received by the sheath for a given fuel burnup is dependent on the fuel element geometry, some rough predictions are possible.

When a Calder Hall type fuel element is taken to a burnup of 3000 MWD/T, then a portion of the sheath will have received an irradiation of about 1.2×10^{21} nvt integrated neutron flux of virgin fission neutrons.(24) From the point of view of quantity of neutron induced gas, this irradiation is equivalent to one twelfth of the M.T.R. fast flux irradiation of 10^{22} nvt. Or, considering a heavy water moderated gas cooled reactor, with beryllium sheathed uranium oxide fuel elements, taken to a burnup of 10,000 MWD/T, the sheath would receive an integrated fast flux of about 2×10^{21} nvt.(25) This assumes that the fuel elements are numerous enough and closely enough spaced so that fuel, sheathing, coolant and moderator can be considered mixed uniformly within an equivalent fuel cylinder. The swelling behaviour of M.T.R. beryllium at 600°C, as presented in Figure 5, suggests that these irradiations could be completed at 600°C without exceeding the arbitrary limit of 1% swelling.

Since swelling is less if the gas goes into many small voids rather than into fewer larger ones, it has been speculated that swelling could be reduced by providing a large number of nuclei for void formation.(15) On these grounds, it would be advantageous to have beryllium oxide present in a finely dispersed form, rather than as larger particles such as it is in M.T.R. beryllium. However, for some time yet the constitution and structure of the beryllium used for sheathing applications must be determined only by considerations of obtaining maximum ductility of the metal.

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APPENDIX I

PRODUCTION OF NEUTRON INDUCED GASES IN BERYLLIUM

A listing of the nuclear reactions which occur when beryllium is placed in the internal radiation field of a normal reactor has been presented by Evans.(1) Six different reactions are listed in which He^4 is an end product, H^1 and H^3 also resulting from one reaction each. Of these reactions, the (n,2n) and (n,α) are the most important from the viewpoint of total gas production. It can be shown that a third reaction, the (γ,n), is relatively unimportant and that the three other reactions, resulting from recoil protons from the cooling water, produce no significant quantities of gas. Estimates of the quantity of neutron-induced gases to be expected from the (n,2n) and (n,α) reactions have been presented in publications by each of Stehn(2), Evans(1), and Redding and Barnes(3). In the period of time since these above calculations appeared new nuclear data has become available, and it now seems that all estimates of the quantity of He^4 were low. The most comprehensive survey of the neutron-induced gas production is that due to Evans and the re-evaluation given here will, in general, follow that presentation.

The amount of gas produced in a metal by neutron irradiation, for any reaction which forms Q atoms of monoatomic gas per capture, is given by:-

$$\text{gas in cc per cc metal} = 2.24 \; Q \; 10^4 \frac{\rho}{A} F \, \bar{f} \, \bar{\sigma} \qquad \ldots\ldots\ldots \quad (1)$$

where ρ is the density of the metal, A is the atomic weight, F is the integrated flux of all energies, $\bar{f}$ is the fraction of F which lies in the energy range above the threshold energy of the reaction E_T, (if

a charged particle is emitted then E_T is replaced [4] with a higher energy E_{EFF}), and $\bar{\sigma}$ is an average cross section for neutron energies above E_T (or E_{EFF}). The product $\bar{f}\,\bar{\sigma}$ is an approximation to the exact expression

$$\int_0^\infty f(e)\,\sigma(e)\,de \qquad \ldots\ldots\ldots\ldots \quad (2)$$

where f(e) and $\sigma(e)$ are the neutron energy spectrum and reaction cross sections respectively as functions of energy. Although in any arbitrary calculation values for F and f(e) can be assumed, it must be realized that all current measurements of these quantities (in reactors) have errors of the order of 20% associated with them.

In the (n,2n) reaction

$$Be^9 + n \longrightarrow Be^8 + 2n$$

$$Be^8 \longrightarrow 2He^4$$

the half life of Be^8 is insignificantly short, and only the primary reaction needs to be considered in calculation of He^4 produced. The most recent determination[5] of E_T and $\sigma(e)$ for this reaction was obtained using an experimental facility which had considerable improvements over any used in previous measurements of these quantities. This data will be used in the present calculation, and no weight given to previous results. The energy E_T is then clearly defined as 2.70 mev. The choice of $\bar{\sigma}$ is rather an arbitrary operation, but 600 mb seems, from the published data, to be the most reasonable estimate. If F is taken as having the energy spectrum of virgin fission neutrons, but with a low energy cutoff at 1.0 mev, then $\bar{f} = 0.36$[6]. Then for Q = 2 and an integrated fast flux of 10^{22} nvt, equation (1) gives 19.8 cc/cc of He^4.

In the (n,α) reaction

$$Be^9 + n \longrightarrow He^6 + He^4 \quad \ldots\ldots\ldots (A)$$

$$He^6 \xrightarrow{\beta^-} Li^6 \quad \ldots\ldots\ldots (B)$$

$$Li^6 + n \longrightarrow H^3 + He^4 \quad \ldots\ldots\ldots (C)$$

$$H^3 \xrightarrow{\beta^-} He^3 \quad \ldots\ldots\ldots (D)$$

$$He^3 + n \longrightarrow H^1 + H^3 \quad \ldots\ldots\ldots (E)$$

In this chain, reaction (A) requires fast neutrons. The decay of He^6 to Li^6 has a 0.82 sec half life, and hence need not be considered further. Reaction (C) proceeds with thermal neutrons and although Li^6 has a rather high capture cross section of 950 barns the burnup half life of Li^6 must be given some attention. H^3 decays to He^3 with a half life of 12.6 years, but the capture cross section of He^3 to thermal neutrons of 5400 barns means that very little He^3 remains in the beryllium while it is subjected to reactor thermal fluxes. He^3 buildup in the beryllium will only occur, therefore, after the metal has been removed from the reactor.

It is generally accepted that the most reliable determination of E_T and $\sigma(e)$ for the reaction is that of Stelson and Campbell,[7] from which E_T is 0.71 mev. Again, assignment of a value to $\bar{\sigma}$ is somewhat a matter of personal choice; 80 mb has been selected for the present calculation. From Hughes[4], E_{EFF} is 2.41 mev, giving $\bar{f}$ as 0.44. On these assumptions, reaction (A) results in a gas production of 1.5 cc/cc He^4 for the integrated fast flux of 10^{22} nvt. Calculation of the yield from (C) requires a knowledge of both the thermal flux intensity and time of irradiation. Evans[1] states that the burnup half life of Li^6 in the M.T.R. thermal flux is 90 days, and since the beryllium used in the present experimental work had been irradiated

for a period of 1000 days, some 82% of the Li^6 would have been converted to He^4 and H^3. The gas quantities are 1.2 and 0.6 cc/cc respectively.

The results of the previous and present calculations are presented in Table IA. All results taken from other publications have been normalized to common irradiation conditions as well as the assumptions stated in those calculations allow. Evans[8] has since recalculated the gas quantities on the basis of the later nuclear data, and is now essentially in agreement with the present calculation. The differences between the values of Redding and Barnes and the present calculation are due to use of different nuclear data in the case of the (n,2n) reaction, and assignment of a different value of σ for the (n,α) reaction. In addition, Redding and Barnes appear to have assumed complete burnup of Li^6.

At the time of removal from the reactor, the gas from the (n,α) reaction contained in the beryllium irradiated to 10^{22} nvt integrated fast flux has been calculated as 2.7 cc/cc He^4 and 0.6 cc/cc H_2^3. However, in the mass spectrographic analysis of the gas removed from the irradiated beryllium, quantities of He^3 and H_2^1 were detected. The following estimate of the amounts of He^3, H_2^1 and H_2^3 which could be expected is based on the irradiation and nuclear data given earlier.

The beryllium used in the present work was removed from the reactor almost exactly 3 years before the gas analysis was carried out. Over that time, the 0.6 cc of H_2^3 would have decayed to 0.5 cc H_2^3, with the resultant production of 0.2 cc He^3. Of the total calculated quantity of gas, 23 cc, H_2^3 and He^3 form 2.2 and 0.9% respectively.

Production of H^1 results from the reactions (D) and (E) given above. The number of H^1 atoms formed is just the number of He^3 atoms involved in the (n,p) reaction on He^3, and since the burnup of He^3 is effectively complete, the number of H^1 atoms finally resolves into the number of H^3 atoms which decay during the period of irradiation (in the presence of a thermal neutron flux). With the assumption that the neutron fluxes were constant during the irradiation period, and using the approximation that He^3 burnup is instantaneous, the expression for the number of H^3 atoms which have decayed during the irradiation time becomes:

$$\text{No. } H^3 \text{ atoms} = \lambda_H K_L \left[\frac{t^2}{2} - \frac{t}{\lambda_L} + \frac{1}{(\lambda_L)^2} - \frac{1}{(\lambda_L)^2} \exp(-\lambda_L t) \right]$$

where K_L is the rate of production of Li^6 via the reactions (A) and (B), λ_H is the decay constant of H^3, and λ_L is the burnup constant, equivalent to a decay constant, for Li^6. The above expression gives 0.05 cc H_2^1, which is 0.2% of the total gas quantity. This is the maximum quantity of H_2^1 which can appear in the irradiated beryllium, since in fact most H^1 atoms will go to form H^1H^3 molecules. However, the total number of H^1 atoms produced can only reduce the number of H_2^3 molecules formed by 10%. In addition, the quantity of H^1H^3, which will appear in the mass spectrographic analysis as mass 4 along with He^4, is not a significant percentage of the He^4 present.

TABLE IA

NEUTRON INDUCED GAS YIELDS IN BERYLLIUM

Reference	Reaction	Threshold Energy Mev	Effective Energy Mev	Capture Cross Section mb	Gas Produced for 10^{22} nvt Fast Flux		
					Helium Volume cc/cc	Tritium Volume cc/cc	Total gas Production cc/cc
Stehn[2]	(n,2n)	1.85	-	200	-	-	-
	(n,α)	0.71	-	< 50	4.6	1.1	-
Evans[1]	(n,2n)	1.67	-	100	1.2	-	-
	(n,α)	0.71	-	10	0.3	0.2	1.7
Reading and Barnes[3]	(n,2n)	1.84	1.84	200	12.3	-	-
	(n,α)	0.71	2.41	50	1.9	0.4	14.6
Present Work	(n,2n)	2.70	2.70	600	19.8	-	-
	(n,α)	0.71	2.41	80	2.7	0.6	23.1

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APPENDIX II

IRRADIATION HISTORY OF SHIM ROD - 6S

Position	Dates	MWD
L-44	31/3/52 to 19/11/53	12,168
L-22	19/11/53 to 17/1/54	1,548
L-44	17/1/54 to 22/8/55	12,799
L-46	22/8/55 to 27/8/56	4,548
		31,063

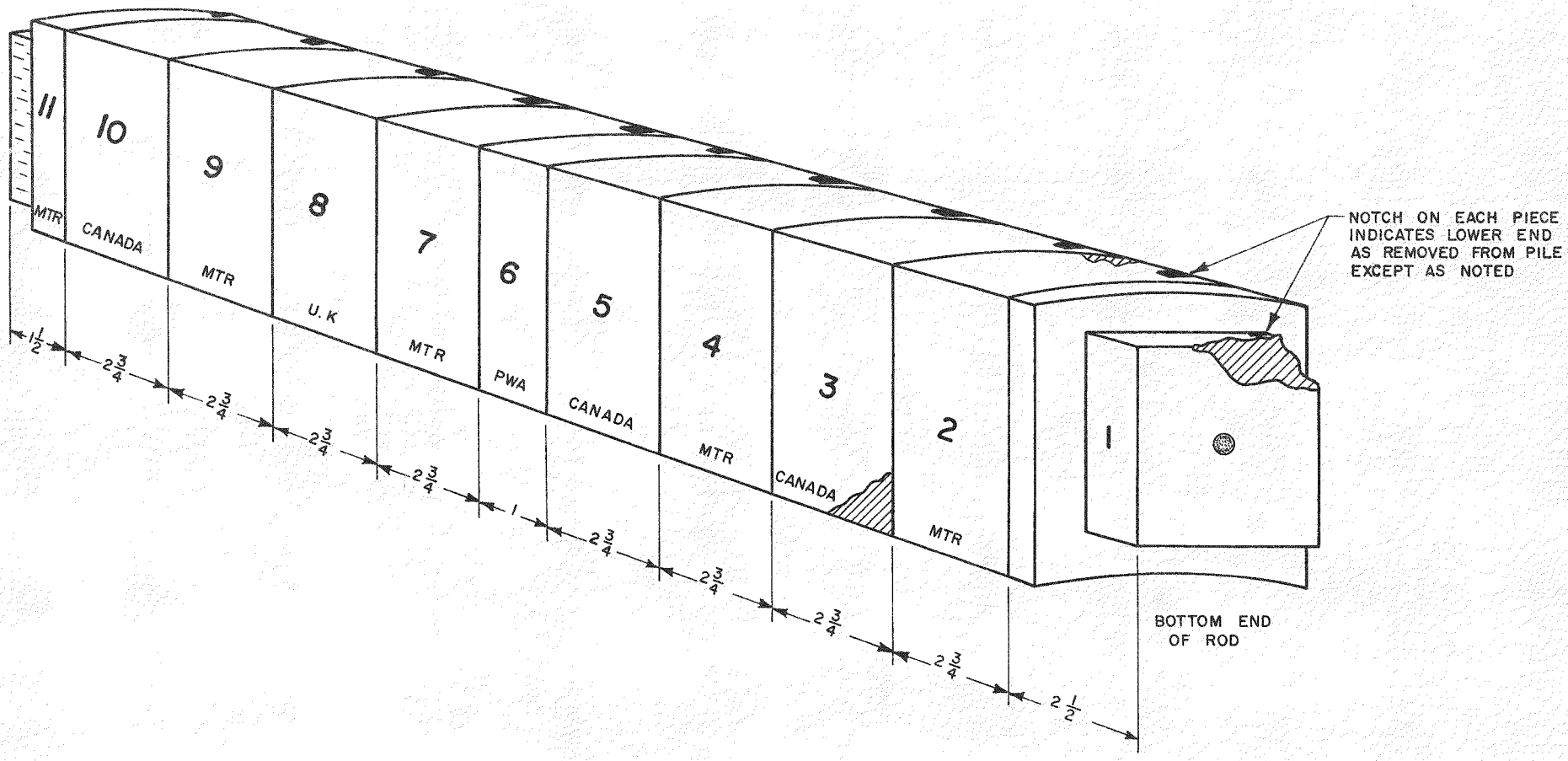

FIGURE I. CUTTING SEQUENCE OF M.T.R. SHIM ROD 6S

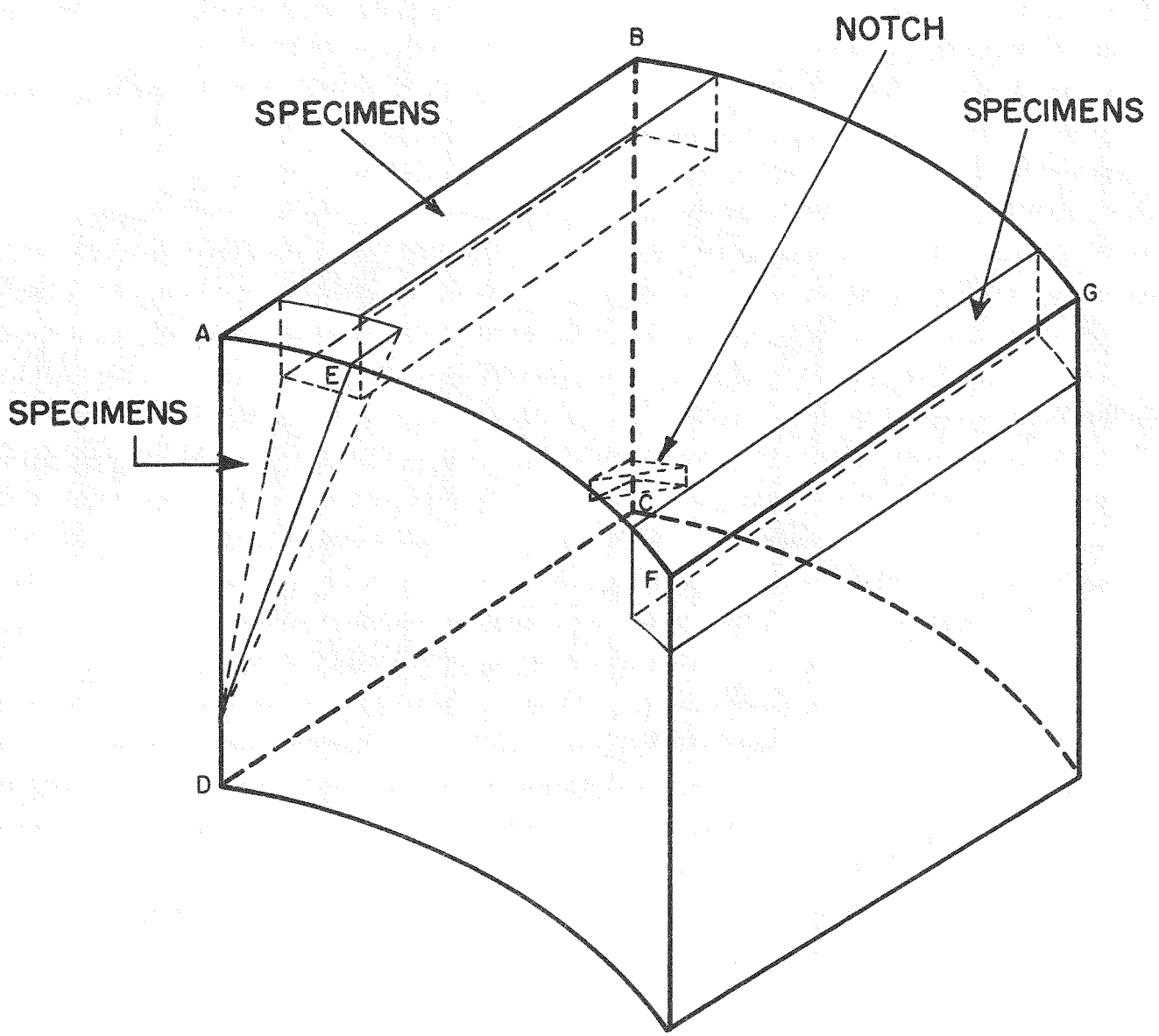

FIGURE 2. LOCATION OF SMALL EXPERIMENTAL SPECIMENS TAKEN FROM SECTION 5 OF SHIM ROD 6S.

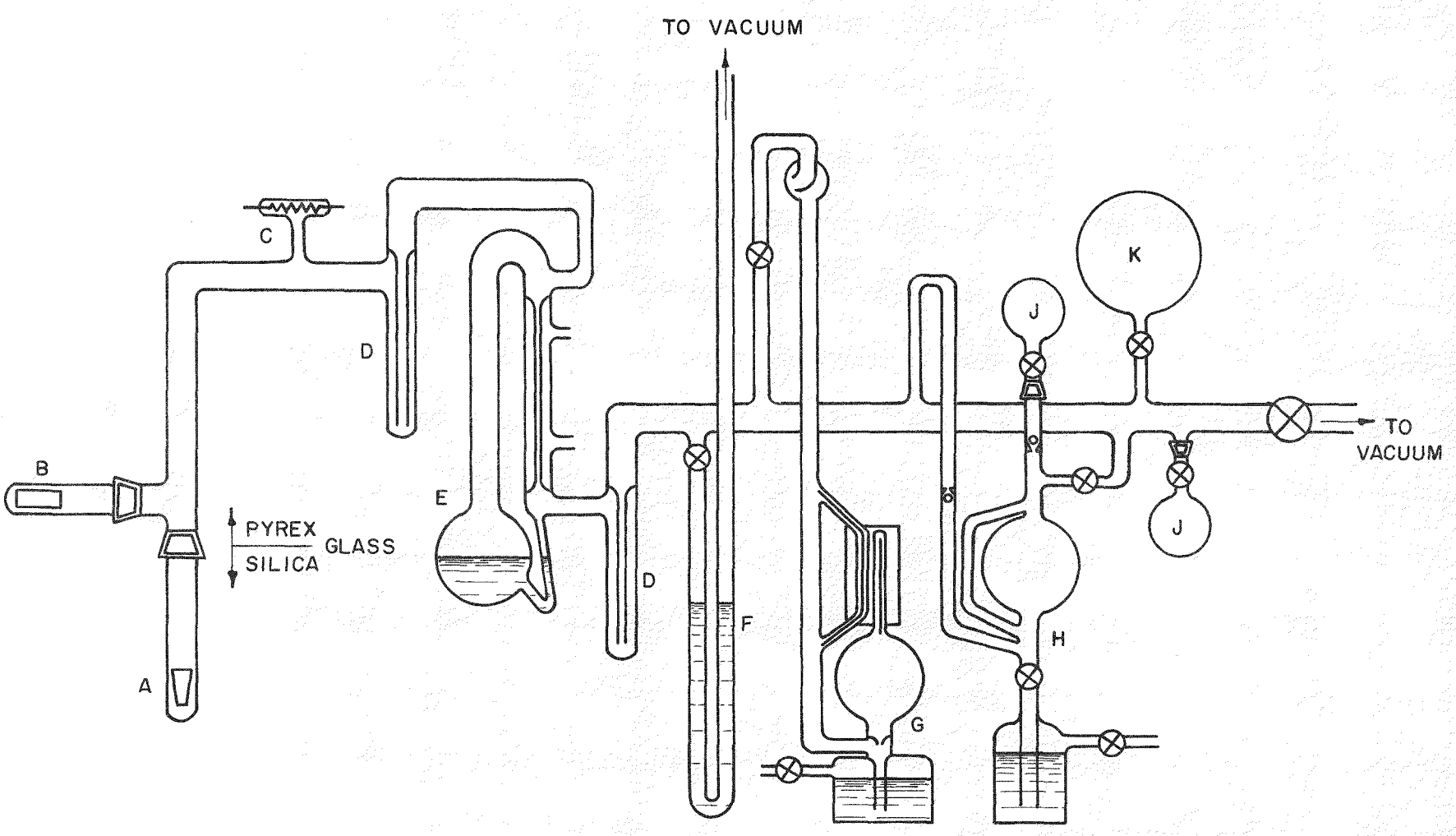

FIGURE 3. SCHEMATIC DIAGRAM OF APPARATUS USED IN THE GAS COLLECTION EXPERIMENTS

KEY

A — FURNACE TUBE ASSEMBLY

B — SPECIMEN STORAGE TUBE

C — PIRANI GAUGE

D — COLD TRAP

E — MERCURY DIFFUSION PUMP

F — DIBUTYL PHTHALATE MANOMETER

G — McLEOD GAUGE

H — TOEPLER PUMP

J — TRANSFER FLASK

K — CALIBRATION FLASK

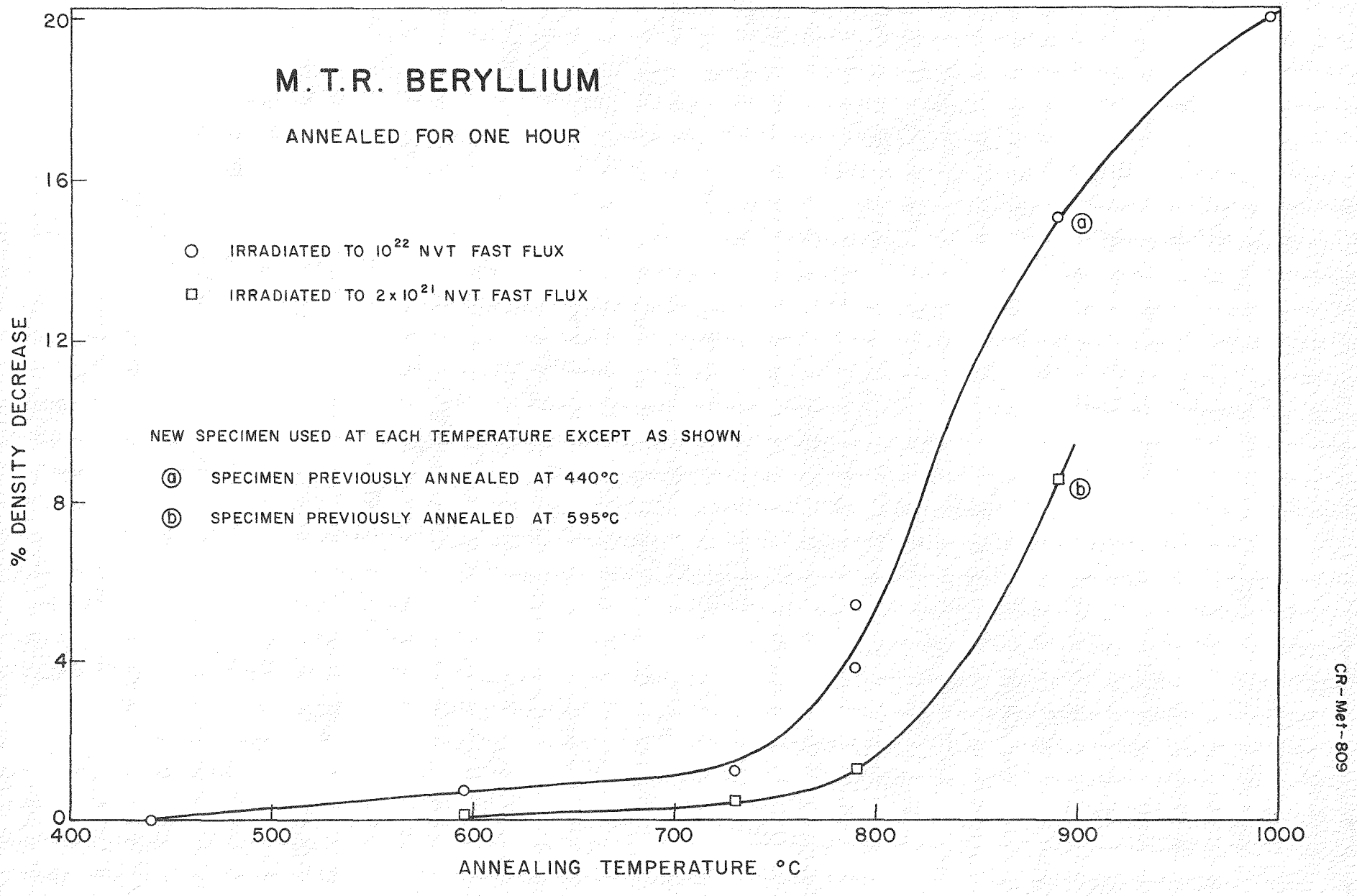

FIGURE 4. DENSITY DECREASES RESULTING FROM ANNEALING SPECIMENS OF M.T.R. IRRADIATED BERYLLIUM FOR PERIODS OF ONE HOUR.

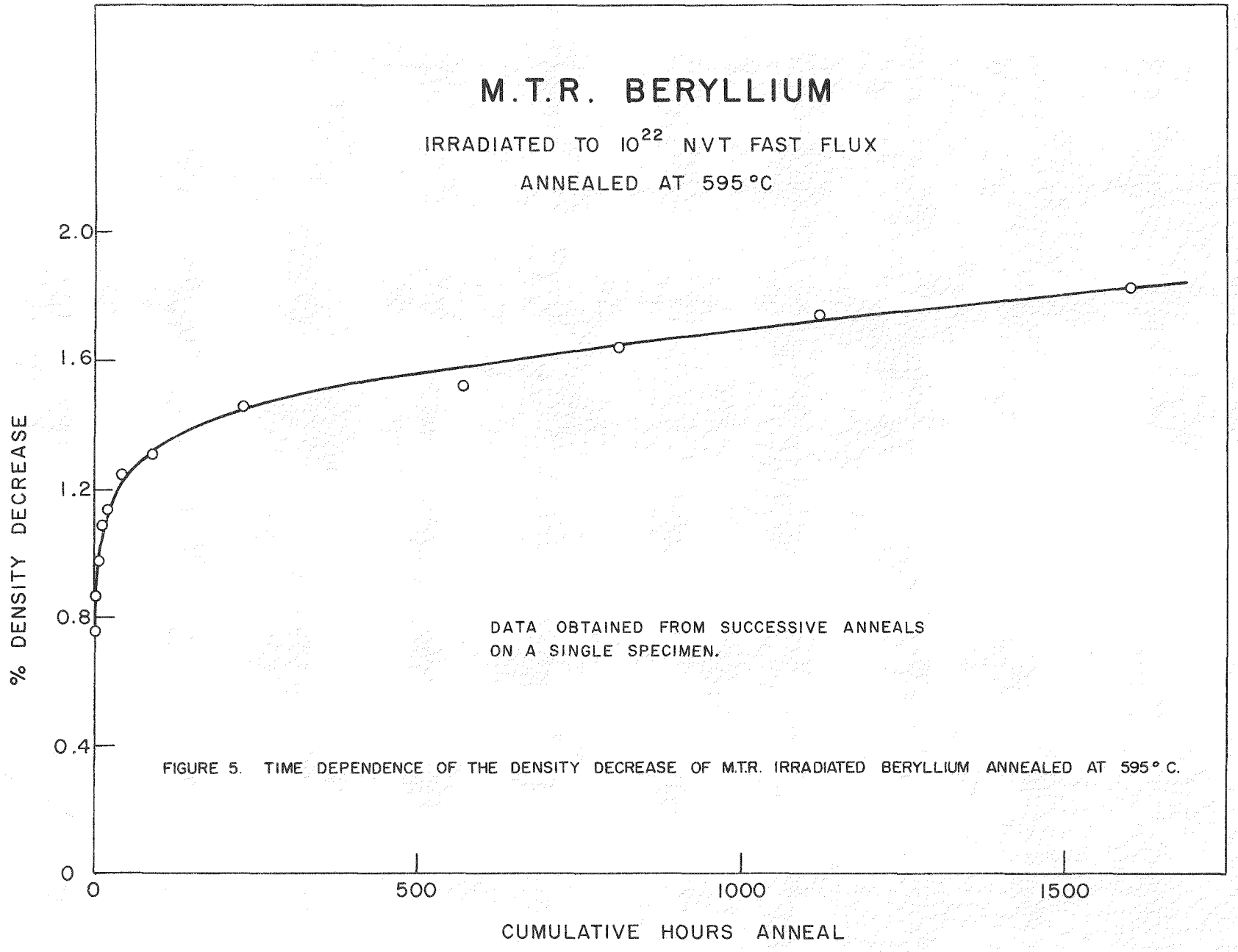

FIGURE 5. TIME DEPENDENCE OF THE DENSITY DECREASE OF M.T.R. IRRADIATED BERYLLIUM ANNEALED AT 595° C.

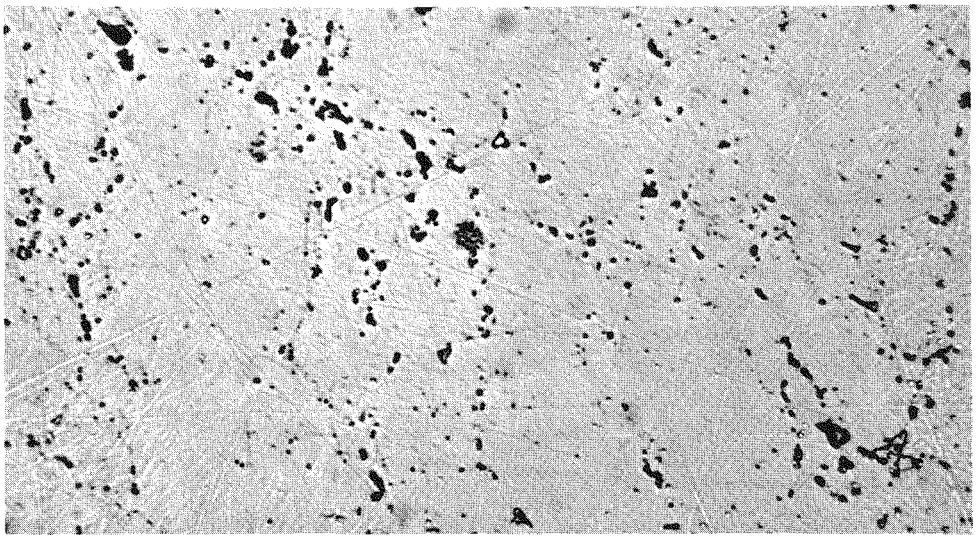

Fig. 6 a 1000 x

As received

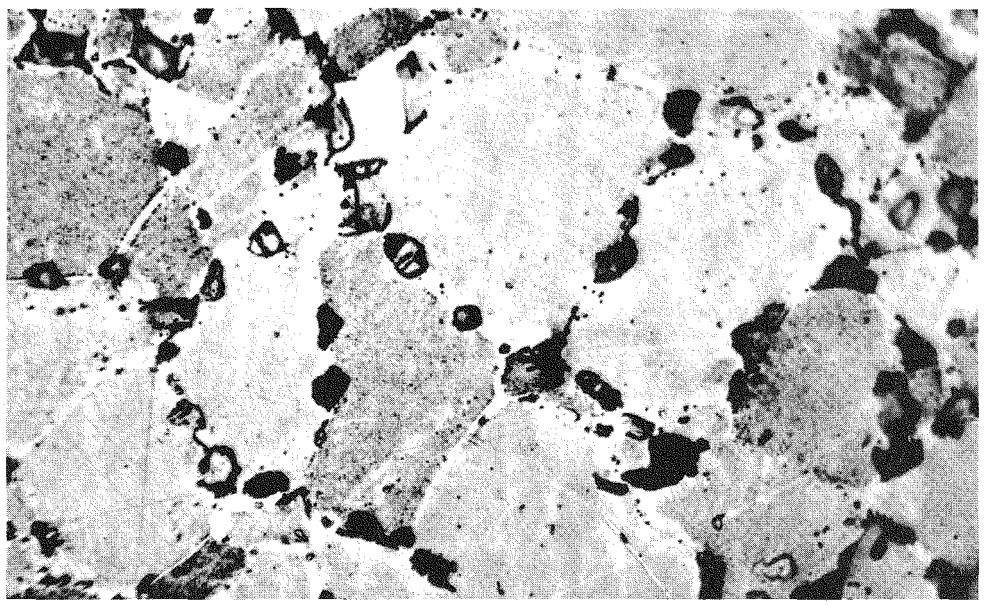

Fig. 6 b 1000 x

Annealed in vacuo for 2.5 hours
at 700° C. Density decrease 14.2%

FIGURE 6. PHOTOMICROGRAPH OF M.T.R. BERYLLIUM IRRADIATED TO 10^{22} NVT FAST FLUX