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ELECTRON MICROSCOPE STUDIES OF IRRADIATED BERYLLIUM METAL

by

J. H. CHUTE

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ABSTRACT

When beryllium is irradiated by fast neutrons, helium is produced by the (n, 2n) and (n, α) transmutation reactions. Electron microscopy techniques have been used to study the nucleation and distribution of helium bubbles in several different grades of beryllium, after irradiation at temperatures in the range 75 – 700 °C. The effect of post–irradiation annealing is also reported. It is shown that for similar neutron doses and irradiation temperatures, there were wide variations in helium bubble size and distribution in specimens of beryllium fabricated by different methods. The most satisfactory material was that fabricated from Pechiney powder by direct hot extrusion followed by annealing for one hour at 800 °C and air cooling. It is suggested that the helium bubbles nucleate on second phase precipitates and that the distribution of this phase is strongly affected by fabrication and heat treatment.

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1. INTRODUCTION

One of the problems associated with the use of beryllium in a reactor system arises from the formation of atoms of helium and tritium in the metal when it is irradiated by fast neutrons. At first these gas atoms are in solid solution but at sufficiently high temperatures and doses they can precipitate to form gas bubbles. These bubbles have a marked effect on the physical and mechanical properties of the metal.

This problem has been investigated at Lucas Heights and some preliminary results have been reported (Hickman 1961). A summary report presenting and discussing all the results obtained to date particularly on mechanical properties, density changes and optical metallography is being prepared. (Hickman and Stevens 1963).

The present report summarizes and discusses the electron-microscopy observations on the nucleation and growth of the gas bubbles in beryllium fabricated at Lucas Heights by various routes. The A.A.E.C. has also been investigating this problem under contract to the U.K.A.E.A. on material fabricated in the United Kingdom. A report has been issued on this work (Hickman et al. 1962) but some of the electron microscopy observations made on these specimens will be discussed again for comparison purposes. In addition some further work is presented on post irradiation annealing of these specimens.

2. EXPERIMENTAL METHODS

All A.A.E.C. beryllium for these tests was made from electrolytically reduced, ground and leached Pechiney powder. The five materials examined were assigned the code letters A, B, C, D, and E. Table 1 lists the different fabrication routes employed.

With the exception of E all were extruded without pre-compaction. For material E, hot extruded beryllium was cut into small pieces, vacuum cast, and again hot extruded. Material D was hot extruded from Pechiney powder which had been partially oxidized at 800 °C in oxygen. This material was of interest as Smith et al. (1961) found that pre-oxidation gave increased resistance to corrosion in moist CO_2 at high temperatures.

The impurity levels given in Table 1 for materials A and B were average values for a number of samples. For nitrogen the values quoted are only approximate as there was a considerable variation along the extrusions.

Fabrication of the U.K.A.E.A. materials (code letters B.1.1 to B.1.6) was described by Hickman et al. (1962) and is summarized in Table 2.

Specimens were irradiated at pile temperatures (75 – 100 °C) and elevated temperatures to doses of up to 6×10^{20} nvt. Full details of the irradiation technique, dose monitoring, etc. are given by Hickman et al. (1962) and Hickman and Stevens (1963). The neutron doses quoted in this report are the doses integrated over the fission neutron spectrum. In addition to the irradiated specimens, several control specimens which had been subjected to the same heat treatment as the irradiated specimens were examined in order to differentiate between irradiation-produced effects and those caused by heat treatment. Some specimens were post-irradiation annealed by heating in vacuum for periods up to 100 hours at temperatures ranging from 650 to 1000 °C.

Replica techniques were used for most examinations. The specimen to be examined was fractured at room temperature by a sharp blow. The surface was then replicated with Bexfilm (cellulose acetate) moistened with acetone, and, after dry stripping, the replica was shadowed at 45° with platinum-palladium alloy, and a thin carbon support film deposited at normal incidence. The replica was then cut into 2 mm squares, immersed in acetone to dissolve the Bexfilm, and caught on 200 mesh copper grids suitable for insertion in the Siemens Elmiskop I microscope. Since the replica is a negative of the fracture surface, depressions and holes in the original surface appear as protuberances on the replica and appear to cast shadows. In some instances thin flakes of metal were torn off with the replica and these could be examined by direct transmission.

3. RESULTS

3.1 Irradiation at Elevated Temperature

A summary is given in Table 3 of the helium bubble distribution observed by electron microscopy in samples of materials A, C, D, and E, which were fabricated at Lucas Heights and irradiated at high temperatures. The significant observations are as follows:

1. No bubbles could be observed in material irradiated to 1.5×10^{20} nvt at any temperature up to 660 °C.

2. With the exception of material E, no bubbles were observed in material irradiated at 560 °C to 4.0×10^{20} nvt. However on many grain boundaries large pores $3 - 5\mu$ in diameter were present; they were usually associated with small inclusions and were also plentiful in the control specimens. It is believed that they were formed during extrusion. In the discussion and in the Tables they will be referred to as fabrication pores.

3. After irradiation to 5.5×10^{20} nvt at 650 °C, extensive bubble formation was observed on many intergranular surfaces in all materials (Figure 1). At 6.0×10^{20} nvt and 700 °C the bubble density had increased although the average bubble size was little different from that observed at 650 °C. In general, materials A, C, and D showed similar behaviour at both temperatures. In these materials the largest bubbles were at grain corners or triple points. None showed any significant amount of bubble formation on cleavage surfaces, that is, within the grains. The coarse-grained cast and extruded material E however, showed somewhat different behaviour. Extensive bubble formation on cleavage surfaces was observed for both irradiation temperatures, the density and size of bubbles being greater for the higher irradiation temperature. The bubble formation at grain boundaries was also different in this material, a considerable number of very large bubbles being observed. These bubbles ranged up to 3μ in diameter (Figure 1 d), had well developed negative crystal faces and were quite different to the fabrication pores noted previously. Zones adjacent to these voids were relatively free of bubbles. Presumably most of the helium originally present in the depleted zone had migrated by boundary diffusion to the large bubbles.

4. In the small cleavage flakes of beryllium which were occasionally torn off the fracture surface when stripping the replica, bubbles were detected to any extent only in material E and occasionally in material A, in agreement with the above observations.

5. It is informative to compare the above results with those reported previously for materials fabricated in the U.K.A.E.A. (Hickman et al. 1962) when material was examined after irradiation to similar doses ($3.5 - 5.5 \times 10^{20}$) at 450 °C, 550 °C, and 650 °C. All the materials fabricated in the United Kingdom showed extensive grain boundary bubble precipitation after irradiation at 550 °C, and one material showed significant effects after irradiation at 450 °C, whereas for the above A.A.E.C. fabricated materials, with the exception of E, no significant bubble formation could be observed at 560 °C. Comparison of the two sets of materials after irradiation at 650 °C shows in general that the grain boundary bubbles were larger and more numerous in the United Kingdom fabricated material than in A.A.E.C. fabricated materials A, C, and D although the bubble distribution was somewhat similar to A.A.E.C. material E. These observations were supported by the amount of cleavage compared with grain boundary fracture in the fracture surfaces examined. The work on the United Kingdom material showed that the ratio of cleavage to grain boundary fracture could be correlated with bubble distribution; a larger number of coarse bubbles caused a higher degree of grain boundary fracture. The A.A.E.C. fabricated materials generally showed a higher proportion of cleavage fracture than the United Kingdom fabricated materials (see Table 3).

3.2 Irradiation at Pile Temperatures Followed by Annealing

Specimens of A.A.E.C. fabricated materials A and B irradiated in the range 4×10^{19} to 5×10^{20} nvt at 75 – 100 °C were examined after annealing at temperatures of 650, 800, and 1000 °C for periods up to 100 hours, in an attempt to gain further information on the various stages of nucleation and growth of the gas bubbles. The results of this examination are summarized in Table 4. Specimens

of the six different United Kingdom fabricated materials which had been irradiated at 400 °C to 5.5 x 10^{20} nvt were examined after annealing for 10 hours at 800 °C and 1000 °C. The results of this examination are summarized in Table 5. These materials with the exception of material B.1.5 showed no microscopic evidence for bubble formation in the as-irradiated condition.

The significant observations in these experiments were as follows:

3.2.1 A.A.E.C. fabricated material

(i) In material irradiated to 4 x 10^{19} nvt bubble formation was only observed after annealing for 100 hours at 1000 °C.

(ii) With material A irradiated to higher doses (3 x 10^{20} nvt) bubbles were first observed on some grain boundaries after 100 hours at 650 °C or after 1 hour at 800 °C. Annealing times of 10 hours and 100 hours at 800 °C (Figures 2a, 2b) increased the bubble density and there was also a slight increase in the average bubble size. The larger bubbles were concentrated at the grain corners and triple points; however there were still many grain boundary surfaces which showed no bubbles at all. After the 100 hour anneal at 800 °C many of the fabrication pores had become elongated and occasionally had linked together. Bubbles first appeared on cleavage surfaces after 1 hour at 1000 °C, at which stage the grain boundary bubbles were larger and more uniformly distributed than for the 800 °C anneal. Annealing for ten hours at 1000 °C (Figure 2c) caused a marked change in the distribution of intergranular bubbles. There was a large increase in size together with a reduction in the number per unit area. Little further change was observed after 100 hours (Figure 2d) except for an increase in the size of the bubbles on the grain boundaries.

(iii) In material A irradiated to 5 x 10^{20}nvt the behaviour was somewhat different to that described above for the nominally identical material irradiated to 3 x 10^{20}nvt. The only difference between these materials was that the samples irradiated to 5 x 10^{20}nvt had been heat treated at 800 °C for one hour before irradiation whereas the samples irradiated to 3 x 10^{20} nvt were not heat treated. Bubbles started to appear on grain boundary surfaces only after 10 hours at 800 °C and even after a similar time at 1000 °C the mean bubble diameter was less than 0.1μ (compare 0.2 – 0.5μ for material irradiated to 3 x 10^{20}nvt).

(iv) In general the bubble growth in the warm extruded material B was more pronounced than in the hot extruded specimens after comparable post-irradiation heat treatment. After only 1 hour at 650 °C a few bubbles appeared on some grain boundary surfaces and after 100 hours at 1000 °C (Figure 3), voids up to 4μ in diameter were common, (compare a maximum of 1μ in the hot extruded material A). As with the hot extruded material the marked bubble growth at 1000 °C was accompanied by a sharp decrease in number per unit area of grain boundary.

(v) It has been suggested that moving dislocations could sweep up helium and cause a change in bubble size and distribution. To check this point some samples of material A irradiated to 5 x 10^{20} nvt were annealed at 800 °C while being subjected to a compressive load of about 550 p.s.i. which should be sufficient to cause creep. There was no marked change in the bubble formation compared with identical specimens heated in the absence of stress although there was perhaps a slight increase in numbers. Some sub-grain boundary formation was evident.

3.2.2 U.K.A.E.A. fabricated material

(i) With the exception of material B.1.5 the intergranular bubble formation in U.K.A.E.A. materials was similar to that observed in the A.A.E.C. warm extruded material B (compare material B.1.4, Figure 4c, with A.A.E.C. material B, Figure 3c) the bubble size being generally greater than in A.A.E.C. hot extruded material A. This difference was particularly marked in the 1000 °C anneal. Material B.1.5, Figures 4b and 4d, showed a greater number of much larger bubbles than any of the other materials; this material also showed a larger number of coarser bubbles than the other materials after irradiation at 550 and 650 °C (Hickman et al. 1962).

(ii) The incidence of bubbles on cleavage surfaces in U.K.A.E.A. materials was markedly different to that of the A.A.E.C. specimens. After the 800 °C anneal all the United Kingdom materials showed extensive bubble formation in the cleavage surfaces, the bubble density varying from 5 x 10^{7} to 10^{8} bubbles per sq. cm. of cleavage surface. Annealing at 1000 °C caused an increase in bubble size and possibly a slight reduction in numbers (Figure 5); the A.A.E.C. materials showed only limited bubble formation on cleavage surfaces after annealing at 1000 °C.

Bubbles were also observed in cleavage flakes in all United Kingdom materials and these were of comparable size to those observed on cleavage surfaces. Some of the larger bubbles were hexagonal in shape (Figure 6). When some of these flakes were heated in the electron microscope by increasing the beam current from the normal value of 10 to 40 microamps, some bubbles grew rapidly, reaching a maximum size of approximately 0.3μ within a few seconds. Coincident with the bubble growth it was observed that the flakes started to evaporate, depositing small Be crystallites on the adjacent carbon support film. Holland (1958) gives 1246 °C as the temperature at which the vapour pressure of Be equals 10 microns of Hg. Since the flakes did not appear to melt they probably reached a temperature somewhere between this value and the melting point, that is, in the range 1246 – 1284 °C. The maximum observed bubble size was probably limited by the thickness of the flake.

3.3 Relation Between Second Phases and Bubble Nucleation Sites

To explain the large difference in bubble size and distribution between the various United Kingdom fabricated materials, Hickman et al. (1962) suggested that bubble nucleation might occur at second phases (possibly Fe–Be compounds) and that differences in the distribution of these precipitates would then explain the differences in behaviour. If the precipitates were present within the grains on a suitably fine scale then helium bubble formation could occur at these precipitates and prevent a significant fraction of the helium from reaching the grain boundary. Throughout the investigation reported in this document a careful watch was kept for any relationship between helium gas bubbles and precipitates. However the only case in which any correlation was observed was in A.A.E.C. material E after irradiation at 650 – 700 °C. In this material many intergranular surfaces showed precipitates of a second phase about 1μ in diameter. At the interface between the precipitates and the metal matrix many bubbles had nucleated (Figure 7). Although grain boundary precipitates were generally observed in most materials this was the only case in which they were related to helium bubbles.

A thin cleavage flake of United Kingdom material B.1.4 showed the presence of a very fine precipitate about 30 – 60 Å in diameter (Figure 8). Assuming a flake thickness of 500 – 1000 Å the density of these precipitates was about 1.5 – 3.0 x 10^{15}/cm^3. However these precipitates were not generally observed and no evidence could be seen for helium precipitation at the precipitates.

4. DISCUSSION

The work described emphasises the fact that material history plays a predominant role in determining the size and distribution of bubbles and that variations occur not only between materials fabricated by different routes but even between materials fabricated by the same route and subjected to different heat treatments before irradiation. It has been shown previously (Hickman et al. 1962) that large decreases in high temperature ductility result from the growth of grain boundary bubbles and that these decreases are greater in material with a large amount of grain boundary bubble formation. One would predict, therefore, that the A.A.E.C. hot extruded material A should show superior high temperature ductility to the United Kingdom fabricated materials and this has been found to be the case (Hickman and Stevens 1963).

Unfortunately the experiments described in this report do not provide much further definite information on the factors governing the nucleation and growth of gas bubbles and the reasons for the variations between materials. However, it is thought that the suggestions made previously (Hickman et al. 1962) that nucleation was occurring on dispersed second phase, possibly an iron rich phase, and that variations in behaviour are due to variations in the dispersion of this phase, are supported by the present results. In particular the following observations are relevant:

(i) The fact that nucleation of bubbles can occur on certain types of precipitates; this was observed in A.A.E.C. material E (see Section 3.3).

(ii) The presence of a very fine precipitate in some materials. It is interesting to note that the concentration of these precipitates (1.5 – 3.0 x 10^{15}/cm^3 is about the same as the bubble density within the grains of similar material, observed by Rhodes and Summerling (1961).

(iii) The significantly different bubble distribution found in the post irradiation annealing of A.A.E.C. material A after irradiation to 3 x 10^{20}nvt compared with the same material irradiated to 5 x 10^{20}nvt. As mentioned earlier the higher dose material showed less bubble formation than the lower dose material and the only difference between the materials was the heat treatment which the higher dose material had received.

(iv) It does not appear that BeO inclusions have any marked effect on the bubble formation because A.A.E.C. fabricated materials A, C, and D, which had widely varying oxide contents present in different forms, all behaved in a similar manner. A similar conclusion was reached by Ells (1961) using α-particle bombardment techniques. Also one would not expect the distribution of oxide to change with heat treatment which would be necessary if the results were to be satisfactorily explained.

A limitation in these investigations which may have prevented confirmatory observations of the bubble formation at a second phase is the resolution attainable in the techniques used. It is thought that the minimum size of bubble which could be observed using the replica techniques was of the order of 100 – 150 Å. The cleavage flakes which were sometimes extracted with the replica were generally of the order of 1000 – 3000 Å thick. Bubbles would be observed in these flakes in transmission, only because of the contrast provided by the decreased inelastic scattering due to the bubble and it is thought unlikely that in the thicker flakes bubbles less than 100 Å in diameter could be observed. If the pressure in the bubbles was in equilibrium with the surface tension and assuming a surface tension of about 1600 erg/cm^2 (Taylor 1954) then all the gas in material irradiated to about 5×10^{20}nvt (about 0.6 cm^3) could be present in bubbles say 20 Å diameter at a spacing of about 600 Å. (Note: this is about the spacing of the finely dispersed second phase observed in some materials). Bubbles of this size would not have been observed in the present investigation. If sufficient helium had precipitated in this fine distribution then only limited quantities would be available for precipitation at grain boundaries. Work on thin films of controlled thickness prepared by polishing bulk specimens may help to resolve these points.

It has been suggested that the superior behaviour of the A.A.E.C. material was due to its lower density, the fabrication pores acting as sinks for the helium. This mechanism would not provide an explanation for all the observations because the fabrication pores were not present on all boundaries, and the bubble distribution appeared similar on all boundaries whether near fabrication pores or not; also from a count of fabrication pores it was estimated that less than 10 per cent. of the total helium content could be in these pores if the gas pressure was in equilibrium with the surface tension.

A comparison of the post-irradiation annealing results with results from specimens irradiated at elevated temperatures can be made by assuming that the diffusion process governing the nucleation and growth of gas bubbles was the same in both cases. The ratio of times required to reach the same state at two different temperatures is then given to a first approximation by:

$$D_1 t_1 = D_2 t_2 \quad ,$$

where D_1 and D_2 are the diffusion coefficients at temperatures T_1 and T_2. Assuming $D = D_o \cdot \exp(-Q/kT)$, this reduces to:

$$\frac{t_1}{t_2} = \frac{\exp(-Q/kT_2)}{\exp(-Q/kT_1)}$$

$$= \exp \frac{Q}{k} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad .$$

Assuming an activation energy Q equal to 2 eV (that is, about the activation energy for self diffusion in beryllium) the post-irradiation annealing times equivalent to the 650 °C irradiation (which took approximately 1.5×10^7 sec) are 125 hours at 800 °C and 4 hours at 1000 °C.

For A.A.E.C. fabricated material the only direct comparison that can be made is for material A. In this case the bubble distribution in specimens irradiated at 650 °C (Figure 9 b) was very similar to that in material irradiated at 75 – 100 °C and annealed for ten hours at 1000 °C (Figure 9 a).

A comparison can be made for all the United Kingdom materials between irradiation at 650 °C and irradiation at 400 °C followed by annealing at 1000 °C for ten hours. In all these specimens the bubble distribution was quite different; the specimens annealed after irradiation showed a smaller number of much larger bubbles on the grain boundaries than the specimens irradiated hot (Figure 10 compares corresponding samples of material B.1.4) and the former showed extensive bubble formation on cleavage faces whereas the latter showed little, if any.

A probable explanation of the difference between the United Kingdom and A.A.E.C. materials in this respect is that bubble nucleation had already occurred during the irradiation at 400 °C in the United Kingdom material. Other work showed that the helium was mobile at about these temperatures (Hickman and Stevens 1963) and indeed bubble nucleation was observed in one of these materials (B.1.5) before annealing. These persisting nuclei therefore probably influenced the behaviour on further heating. In the A.A.E.C. material, on the other hand, the helium was still in random solid solution after irradiation at 75 – 100 °C and the nucleation and growth processes would not be influenced by any pre-existing bubble structure. It would appear therefore, that post-irradiation annealing results cannot generally be related to in-pile results although in some cases a good correlation is observed.

One conclusion which can be made from the post-irradiation annealing results with some confidence is that larger bubbles can grow at the expense of smaller bubbles. At the higher annealing temperatures the number of bubbles generally decreased, while the bubbles increased in size both with increasing annealing temperature or with increased time at the same temperature. This effect was observed in all materials for bubbles on grain boundaries with the possible exception of material A annealed before irradiation. In some cases where there was a considerable range of bubble sizes present the larger bubbles often were surrounded by zones relatively free of bubbles. The mechanism for this process, which has been observed by other workers, is rather obscure. Owing to its inert nature one would not expect re-solution of helium to occur once it had precipitated into bubbles. Before re-solution could occur, adsorption must take place and an inert gas such as helium would not be expected to be adsorbed on the bubble surface. Diffusion along grain boundaries could occur more easily but the effect is occasionally observed within grains as well as in boundaries. It has been suggested that moving dislocations can sweep bubbles along with them but the experiments described in which the beryllium was heated under stress would not support this. Also one would only expect this mechanism to be operative for very small bubble sizes. It would appear that re-solution would be the only possible mechanism and that the driving force for the process is the higher gas pressure in the smaller bubbles compared with the larger bubbles.

5. CONCLUSIONS

1. The nucleation and growth of helium bubbles in irradiated beryllium metal depends to a large extent on the material history as well as on temperature and dose. Wide variations in the number and size of bubbles were observed between materials fabricated by different routes and between materials fabricated by the same route but subjected to heat treatment before irradiation.

2. Direct hot extruded Pechiney powder annealed for one hour at 800 °C and air cooled before irradiation showed significantly less bubble formation than any other material for the same temperature and dose. This resulted in superior high temperature mechanical properties. Addition of oxide by pre-oxidizing the powder before extrusion, which markedly improves the corrosion resistance of this material, did not appear to affect the bubble distribution.

3. The only satisfactory explanation of this wide variation in behaviour is thought to be that nucleation of bubbles occurs at second phase precipitates and that the distribution of this phase (possibly an iron-beryllium compound) is markedly affected by material history. Although no direct confirmatory evidence for this was obtained in the present investigations, several observations supported this hypothesis and none contradicted it.

4. Post-irradiation annealing studies showed that growth of large bubbles can occur at the expense of small bubbles and re-solution of helium appears to be the only satisfactory explanation of the phenomenon.

5. There were limitations in the resolution of the techniques used in these experiments and it is hoped that additional work on thin films prepared from bulk material will further explain the phenomena.

6. Care must be exercised in taking quantitative measurements on bubble distribution in cleavage flakes extracted with replicas because the poor thermal conductivity of the replica may result in electron beam heating of the area under examination, causing growth and coalescense of small bubbles.

6. ACKNOWLEDGMENTS

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7. REFERENCES

Ells, C.E. (1961). – C.R.G.M. – 1022, A.E.C.L. – 1253.

Hickman, B.S. (1961). – Conference on the Metallurgy of Beryllium – The Effects of Neutron Irradiation on Beryllium Metal. Institute of Metals, London.

Hickman, B.S., Bell, J.C., Bannister, G., Chute, J.H., McCracken, J.G., and Smith, R. (1962). – T.R.G. 540(S).

Hickman, B.S., and Stevens, G. (1963). – Report in preparation.

Holland, L. (1958). – Vacuum Deposition of Thin Films.

Rhodes, D., and Summerling, R. (1961). – UKAEA (Reactor Group) Risley T.R.G. Memorandum 467 W.

Smith, R., Stuart, W.I., Van Peer, W.J., and Price, G. (1961). – Conference on Metallurgy of Beryllium – Inhibition of Breakaway Oxidation of Beryllium in Carbon Dioxide. Institute of Metals, London.

Taylor, J.W. (1954). – Metallurgia 50 : 161.

TABLE 1

FABRICATION OF A.A.E.C. BERYLLIUM

MATERIAL	FABRICATION	EXTRUSION NUMBERS	IRRADIATION RIG NO.	TYPICAL IMPURITY LEVELS (p.p.m.)					
				Fe	Al	Si	N	Cl	O
A	Hot extruded (h/x) at 1050 °C from powder	28, 35	X75/1, X–73* X–5*, X–39*	300	400	400	1800	100	0.45%
B	Warm extruded (w/x) at 750 °C from powder	96, 97	X75/1	1300	1300	500	300	–	0.7%
C	2% BeO powder added, then hot extruded (h/x + 2% BeO)	125	X–73*	Not Available					
D	Hot extruded at 1050 °C from pre–oxidized powder (P/o, h/x)	124	X–73*	Not Available					
E	Vacuum cast and hot extruded (v/c, h/x)	123	X–73*	Not Available					

* All specimens for rigs X–5, X–73, and X–39 were vacuum annealed at 800 °C for one hour prior to irradiation.

TABLE 2

DETAILS OF MATERIALS USED

Material No.	Source	Fabrication Route	Heat Treatment
B.1.1	Pechiney	V/C, L/S, H/X	None
B.1.2	Pechiney	L/S, W/X	None
B.1.3	Pechiney	L/S, H/X	None
B.1.4	Brush	L/S, H/X	None
B.1.5	Pechiney	V/C, H/X, W/X	Annealed at 850 °C slow cooled at 1–3 °C/hour
B.1.6	Brush	L/S, H/X, W/X	Standard anneal

V/C – Vacuum cast – induction melted in BeO crucible

L/S – Loose sintered – Powder of –200 mesh at maximum tap density heated to 1220 °C

H/X – Extruded at 1050 °C (extrusion ratio 12:1)

W/X – Extruded at 850 °C (extrusion ratio 8:1)

TABLE 3

FRACTOGRAPHY OF A.A.E.C. BERYLLIUM IRRADIATED AT HIGH TEMPERATURE

MATERIAL	SAMPLE NO.	FABRICATION	DOSE	IRRAD. TEMP. °C	% CLEAVAGE FOR COLD FRACTURE	HELIUM BUBBLE DISTRIBUTION			FIGURE
						CLEAVAGE SURFACES	INTERGRANULAR SURFACES	CLEAVAGE FLAKES	
A	451	h/x	1.5×10^{20}	640–660	–	None	None	None	1(a) 9(b)
	843		4.0×10^{20}	530–580	~ 90	No bubbles	No bubbles. Some pores 3–4μ (from fabrication)	No bubbles	
	848		5.5×10^{20}	640–660	> 90	One or two bubbles on some surfaces	Some bubbles on boundaries. Definite preference for grain corners. Mean dia. 0.05μ Max. 0.1μ	No bubbles detected	
	853		6.0×10^{20}	680–720	~ 80	Occasional bubbles up to 0.1μ	Many bubbles. Large size range. i.e. <0.02μ to ~0.3μ. Some preference for grain corners	One or two bubbles located in some flakes	
C	867	h/x + 2% BeO	4.0×10^{20}	530–580	~ 90	No bubbles	No bubbles. Many small inclusions (BeO added in fabrication)	No bubbles	
	872		5.5×10^{20}	640–660	70–80	Rarely observed	Many bubbles, from <0.02μ to 0.3μ. Some preference for grain corners	None observed	1(b)
	876		6.0×10^{20}	680–720	80–90	Rare	Largest bubbles on corners. Size range similar to 650 °C. Bubble density appears to have increased. Max bubble dia. ~0.4μ	None observed	
D	885	h/x oxidized powder	4.0×10^{20}	530–580	~ 30	None. Grains are very elongated	No bubbles. Grain surfaces often rough, probably from trapped oxide	None	
	889		5.5×10^{20}	640–660	~ 80	Rare	Bubbles ~0.03 to 0.1μ dia. Larger on grain corners	None observed	1(c)
	893		6.0×10^{20}	680–720	> 90	Rare	Similar to 650 °C specimen. Some bubbles up to 0.3μ	None observed	
E	903	Cast and h/x (very large grain size)	4.0×10^{20}	530–580	80–90	None	Precipitates on some boundaries together with some very small bubbles <0.02μ	None	
	907		5.5×10^{20}	640–660	80–90	Bubbles up to ~0.1μ on all cleavage surfaces	Many bubbles 0.05–0.5μ. Large faceted voids up to 3μ. Zones adjacent to these depleted of bubbles. Many ppts. ~1μ, usually with many bubbles at edges	None observed; few suitable flakes	1(d) 7
	911		6.0×10^{20}	680–720	60–70	Bubble density increased compared to 650 °C spec. Up to ~0.2μ dia.	Many bubbles ~0.1–0.8μ. Inclusions as for 650 °C spec. Larger voids not as prominent as in 650 °C spec.	Bubbles up to 0.1μ in some flakes	

TABLE 4

FRACTOGRAPHY OF A.A.E.C. BERYLLIUM IRRADIATED AT PILE TEMPERATURE AND ANNEALED

MATERIAL	FABRICATION	RIG NO.	DOSE (fission neutrons)	POST IRRADIATION ANNEAL		% CLEAVAGE (Cold Fracture)	VOID DISTRIBUTION	VOID SIZE (Intergranular Surfaces)		FIGURE
				TEMP °C	TIME (hrs)			MEAN	MAX.	
A	h/x		4×10^{19}	800	100	–	No bubbles	–	–	
	”		”	1000	100	–	A few bubbles on some intergranular surfaces	0.02–0.03μ	0.1μ	
	h/x (1050 °C)	X75/1	3×10^{20}	650	1	80–90	No bubbles	–	–	
	”	”	”	650	10	–	No bubbles	–	–	
	”	”	”	650	100	~50	Small bubbles on some grain surfaces and at grain corners. Some large fabrication pores, 2–3μ on intergranular surfaces	~0.04μ	0.1μ	
	h/x (1050 °C)	X75/1	3×10^{20}	800	1	50–70	Bubbles on some intergranular surfaces. Larger bubbles at grain corners. Some fabrication pores 1–4μ	<0.03μ	0.1μ	
A	”	”	”	800	10	80–90	Many bubbles on most intergranular surfaces. Larger at grain corners	0.03–0.06μ	0.15μ	2(a)
	”	”	”	800	100	–	Bubbles on most grain surfaces. Fabrication pores increased in size, 6–8μ and commencing to link up	0.05–0.1μ	0.2μ	2(b)
	h/x (1050 °C)	X75/1	3×10^{20}	1000	1	50–70	Bubbles on all intergranular surfaces and occasionally on cleavage surfaces (<0.03μ). Large fabrication pores 6–8μ, usually associated with small inclusions	0.05–0.2μ	0.6μ	
	”	”	”	1000	10	~70	Bubbles coarser, and less/unit area of boundary than after 1 hour at 800 °C. Fabrication pores elongated. Some bubbles on cleavage surfaces	0.2–0.5μ	1μ	2(c)
	”	”	”	1000	100	~60	Little change from 10 hour anneal. Bubbles show some preference for grain corners. Some bubbles in cleavage surfaces up to 0.2μ dia.	0.1–0.5μ	1μ	2(d)
	h/x	X39*	5×10^{20}	600	100	–	No bubbles	–	–	
	”	”	”	800	1	~20	No bubbles. Many fabrication pores up to 20μ long usually associated with small inclusions 0.3–0.5μ	–	–	
	”	”	”	800	10	~10	Small bubbles on most grain surfaces. Largest bubbles at grain corners	~0.02μ	0.05μ	
	”	”	”	800	100	–	Many small bubbles on grain boundaries	0.02–0.03μ	0.05μ	

A	"	"	"	1000	10	20–30	Many bubbles on intergranular surfaces. Some bubbles on cleavage surfaces, 0.03–0.05μ dia. Occasional large elongated fabrication pores ~ 15 x 2–3μ	0.05–0.1μ	0.2μ	9(a)
	h/x	X39	5 x 10^{20}	800 †	1	40–50	No bubbles. Fabrication pores >20μ long. Apparently some sub–grain boundary formation	–	–	
	"	"	"	800 **	1	30–40	As for previous specimen, except that occasional grain corners had a few small bubbles, 0.02–0.03μ	–	–	
	"	"	"	800 **	10	40–50	Bubbles on most grain surfaces. Fabrication pores again > 20μ long, 2–4μ wide	0.03–0.05μ	0.1μ	
	w/x (No. 96, 750 °C)	X75/1	2 x 10^{20}	650	1	70–80	A few small bubbles on some grain surfaces	~0.02μ	0.05μ	
	"	"	"	650	10	50–70	As for 1 hour anneal	~0.02μ	0.04μ	
	"	"	"	650	100	~70	Bubbles on most intergranular surfaces	0.03–0.05μ	0.07μ	
	w/x (No. 96)	X75/1	2 x 10^{20}	800	1	60–80	Bubbles on all intergranular surfaces. Some preference for grain corners	0.02–0.05μ	0.08μ	
	w/x (No. 97)	"	"	800	10	~95	Many bubbles on intergranular surfaces	0.05–0.1μ	0.3μ	3(a)
B	"	"	"	800	100	60	Very uneven distribution of bubbles on grain surfaces. Largest bubbles have strong preference for grain corners	0.03–0.06μ	0.5μ	3(b)
	w/x (No. 97)	X75/1	2 x 10^{20}	1000	1	90–95	Grain boundary bubbles have coarsened considerably with a consequent reduction in number on many boundaries. Many have well developed facets. Largest bubbles are at grain corners. Small bubbles, maximum diameter 0.1μ are present on cleavage surfaces	0.1–0.4μ	2.5μ	3(c)
	"	"	"	1000	10	–	As for 1 hour anneal	0.1–0.4μ	2μ	
	"	"	"	1000	100	~30	Grain boundary bubbles coarser and fewer than for 1 and 10 hour anneals	0.2–0.5μ	4μ	3(d)

* Rig X39 specimens were annealed for 1 hour at 800 °C prior to irradiation.

† After heating to 800 °C this specimen was loaded to 540 p.s.i. Load was maintained during 1 hour anneal.

** These specimens were loaded to 540 p.s.i. before heating to 800 °C. Load was maintained during the annealing period.

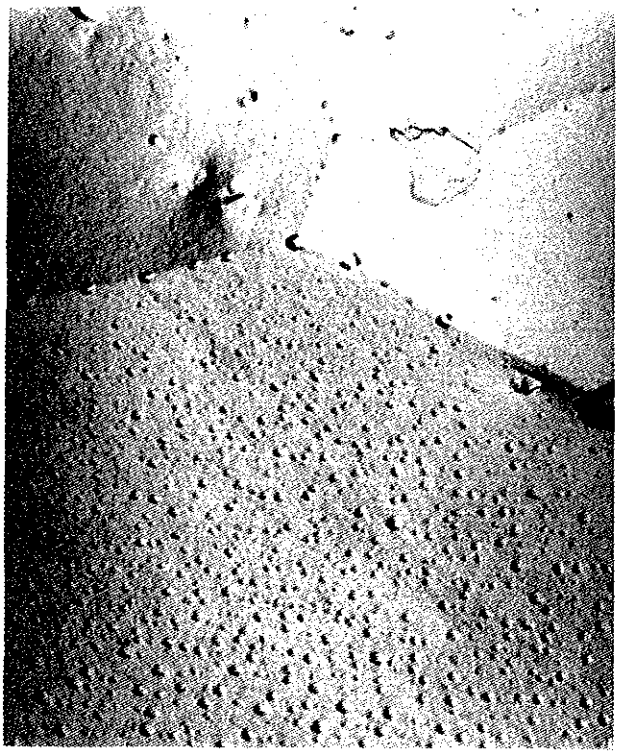
TABLE 5

FRACTOGRAPHY OF U.K.A.E.A. BERYLLIUM AFTER POST–IRRADIATION ANNEALING

MATERIAL	ANNEALING TEMPERATURE	BUBBLE DISTRIBUTION			FIGURE
		INTERGRANULAR SURFACES	CLEAVAGE SURFACES	CLEAVAGE FLAKES	
B.1.1	800 °C *	Many bubbles 0.05 – 0.1μ. Maximum 0.2μ. Tendency towards alignment	Approximately 10^8 bubbles/sq.cm. of cleavage surface. ~0.05μ diameter. Maximum 0.1μ	Bubbles 0.02–0.06μ observed in several flakes. The larger bubbles have a rounded hexagonal shape	5(a) 6(a)
	1000 °C	Great range in bubble sizes from <0.02μ to a maximum of 12–15μ. No obvious preference for grain corners. Most big bubbles have facets	~ 10^8 bubbles/sq.cm. Maximum 0.25μ. Some of the larger bubbles have hexagonal shape		5(b)
B.1.2	800 °C	Bubbles range from <0.02 to 0.3μ diameter. Many large shallow pores, 5- 25μ, with terraced surfaces. These pores have many rounded inclusions, probably type II, 0.5–1μ associated with them †	Some bubbles seen on cleavage surfaces. Usually 0.05μ diameter. Maximum 0.1μ	No suitable flakes	
	1000 °C	Bubbles from <0.03 to 2μ. Larger bubbles have crystallographic facets and a slight preference for grain corners. Large pores and inclusions are also present	Bubbles have increased in number compared with 800 °C specimen. Mean diameter now ~0.1μ	A few bubbles in some flakes. Maximum diameter ~0.1μ. Can increase to ~0.4μ by heating in electron beam	
B.1.3	800 °C	Bubble distribution very irregular. Some alignment. Size 0.02 – 0.2μ. Maximum 0.3μ. Precipitates, probably type P2 and inclusions type I and II on many boundary surfaces	Fairly uniform distribution of bubbles. Maximum ~0.08μ	Bubbles aligned in rows. Maximum diameter ~0.05μ	
	1000 °C	Most bubbles 0.2 – 0.8μ. Maximum 2μ. Large pores 8 – 10μ apparently nucleated on type I or II inclusions	Numerous bubbles. Maximum ~0.1μ	Small bubbles in most flakes	
B.1.4	800 °C	Most bubbles aligned in near parallel rows. Majority 0.05 – 0.4μ diameter	Few detected in grains. Maximum 0.15μ	Few suitable flakes. Many bubbles in these. Maximum 0.05μ	4(a)
	1000 °C	Bubbles increased to maximum of 2μ. Larger bubbles prefer grain corners. Weak facet development on most	Again ~ 10^8 bubbles/sq.cm. ranging from <0.03μ to 0.5μ. Distribution rather uneven	Bubbles up to 0.1μ in some flakes	4(c) 5(c) 10(b)
B.1.5	800 °C	Greatest bubble concentration yet observed. Three distinct size ranges, < 0.1μ – 0.5μ; 1 – 2μ, 5 – 20μ. The facets on the largest bubbles tend to smooth out and fine terrace markings appear	~5 x 10^7 bubbles/sq.cm. Majority < 0.1μ. Fairly uniform distribution	Few good flakes. Bubbles up to 0.2μ in some	4(b)
	1000 °C	Bubbles have increased in size and reduced in number. Many have linked to form extended voids > 100μ in length. Majority in range 3 – 12μ	~2.5 x 10^7 bubbles/sq.cm. Range < 0.1μ – 1μ. Largest bubbles have hexagonal shape, probably see these because of basal cleavage	No good flakes	4(d) 5(d)
B.1.6	800 °C	Bubbles range from <0.02μ to a maximum size of ~0.6μ. They usually tend to be aligned. Inclusions are present on most surfaces. Probably type I		Bubbles occasionally seen in some flakes. Sizes range from <0.03μ to maximum of 0.2μ. Larger bubbles are hexagonal	6(b)
	1000 °C	Bubbles have coarsened and decreased in number on most surfaces. Range from <0.05μ to 3μ. A few large pores 6 – 8μ associated with inclusions	~5 x 10^7 bubbles/sq.cm. Range ~0.05 – 0.5μ. Largest bubbles have rounded hexagonal shape	Many bubbles seen. <0.05μ to maximum size of 0.25μ. Heating in electron beam caused growth of some bubbles	

* All specimens irradiated at 400 °C. Annealed 10 hours at temperatures shown.

† Inclusions and precipitates classified by system of Rhodes and Summerling (1961).



x 15,000

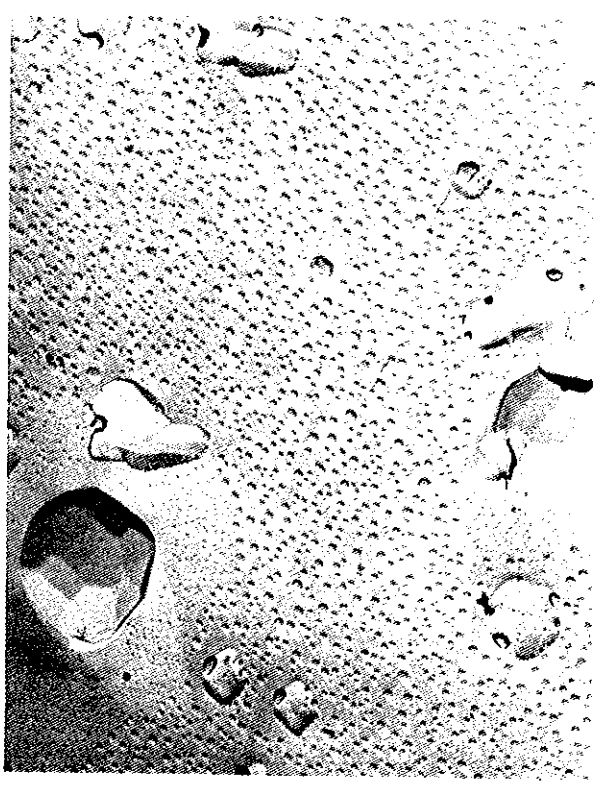
(a) A.A.E.C. Material A

x 15,000

(b) A.A.E.C. Material C

x 15,000

(c) A.A.E.C. Material D



x 7,500

(d) A.A.E.C. Material E

FIGURE 1 A.A.E.C. BERYLLIUM IRRADIATED TO 5.5 x 10^{20} nvt AT 650 °C.
Intergranular fracture surfaces.

x 15,000

(a) 10 hours at 800 °C

x 15,000

(b) 100 hours at 800 °C

x 6,000

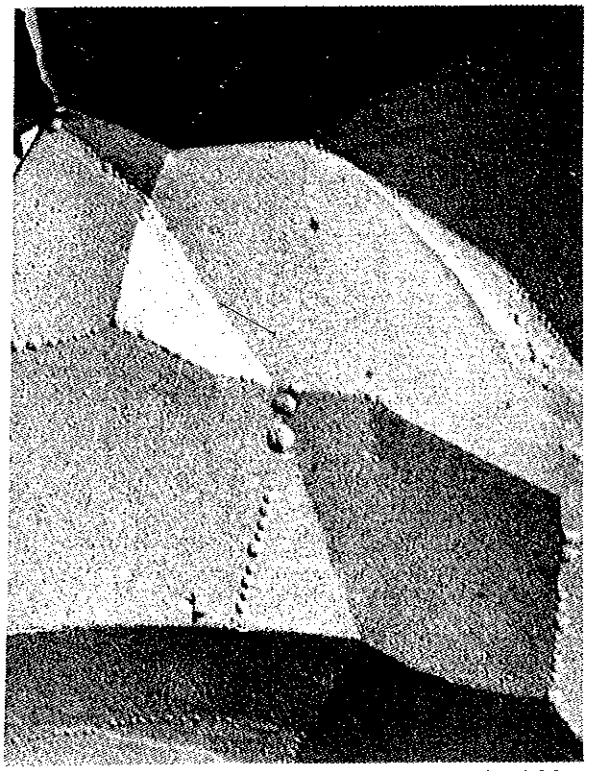
(c) 10 hours at 1000 °C

x 7,500

(d) 100 hours at 1000 °C

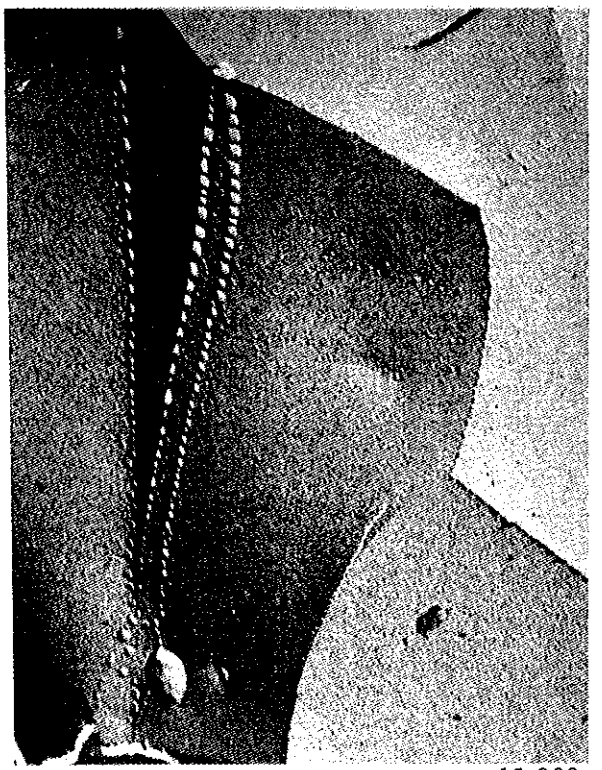
FIGURE 2 FRACTURE SURFACES OF SOME HOT EXTRUDED A.A.E.C. BERYLLIUM AFTER POST-IRRADIATION ANNEALING. RIG X-75 3 x 10^{20} nvt.

NOTE: Sample not annealed in vacuum prior to irradiation.



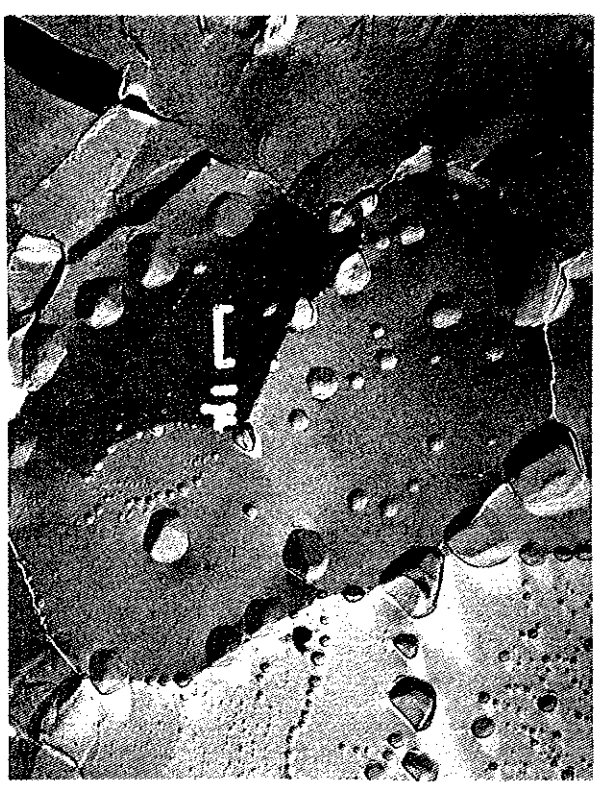
x 15,000

(a) 10 hours at 800 °C



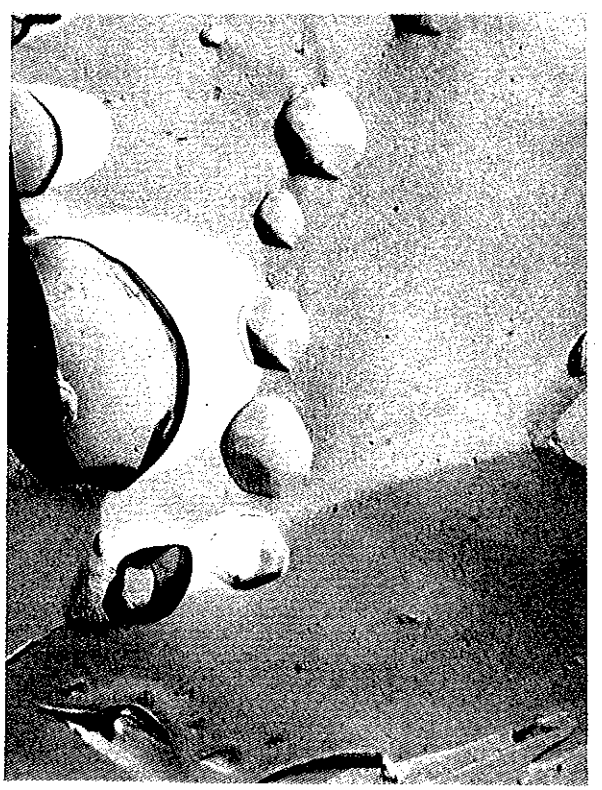
x 15,000

(b) 100 hours at 800 °C



x 7,500

(c) 1 hour at 1000 °C



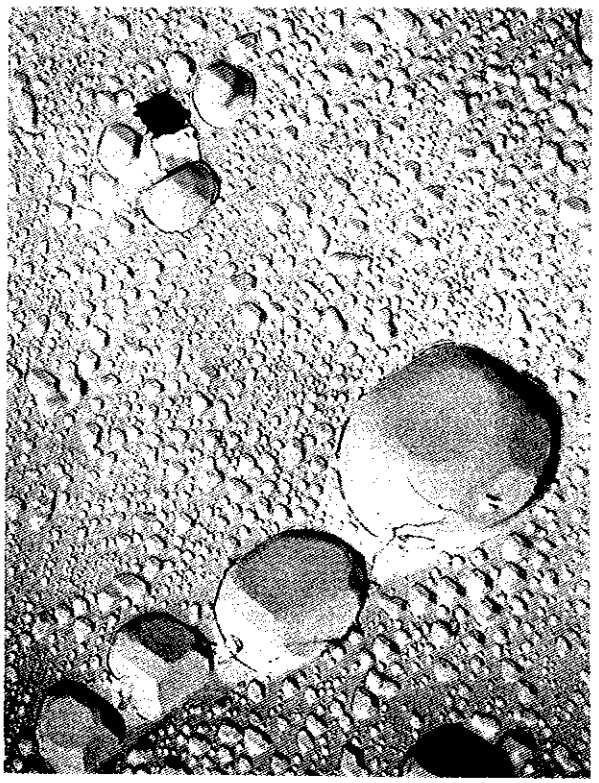
x 7,500

(d) 100 hours at 1000 °C

FIGURE 3 FRACTURE SURFACES OF SOME WARM-EXTRUDED A.A.E.C. BERYLLIUM AFTER POST-IRRADIATION ANNEALING.

x 7,500

(a) B.1.4 10 hours at 800 °C

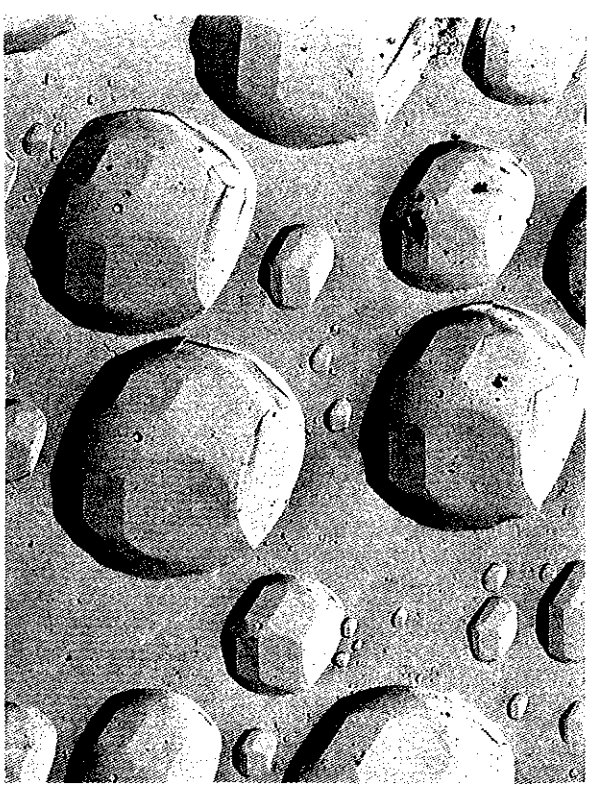


x 3,000

(b) B.1.5 10 hours at 800 °C

x 7,500

(c) B.1.4 10 hours at 1000 °C



x 6,000

(d) B.1.5 10 hours at 1000 °C

FIGURE 4 INTERGRANULAR FRACTURE SURFACES OF U.K.A.E.A. BERYLLIUM AFTER POST-IRRADIATION ANNEALING AT 800 °C FOR 10 HOURS, (a) AND (b), AND 1000 °C FOR 10 HOURS, (c) AND (d).

x 9,000

(a) B.1.1 10 hours at 800 °C

x 6,000

(b) B.1.1 10 hours at 1000 °C

x 9,000

(c) B.1.4 10 hours at 1000 °C

x 4,500

(d) B.1.5 10 hours at 1000 °C

FIGURE 5 CLEAVAGE FRACTURE SURFACES OF U.K.A.E.A. BERYLLIUM AFTER POST–IRRADIATION ANNEALING AT 800 °C FOR 10 HOURS, (a), AND 1000 °C FOR 10 HOURS, (b), (c), AND (d).

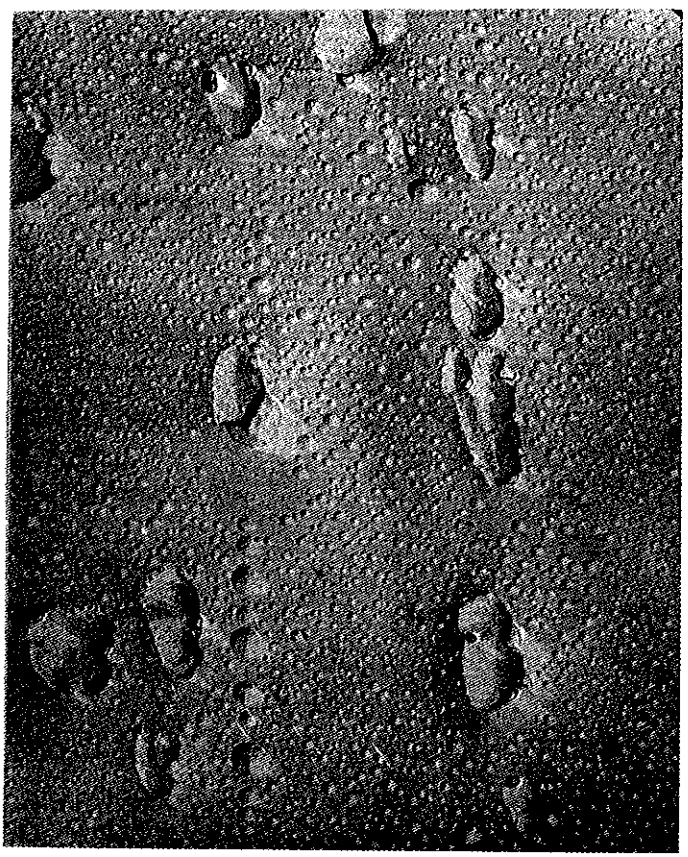
x 100,000

(a) B.1.1 annealed for 10 hours at 800 °C

x 30,000

(b) B.1.6 annealed for 10 hours at 800 °C

FIGURE 6 HELIUM BUBBLES IN CLEAVAGE FLAKES OF SOME U.K.A.E.A. BERYLLIUM AFTER ANNEALING FOR 10 HOURS AT 800 °C.



x 7,500

FIGURE 7 A.A.E.C. MATERIAL E AFTER IRRADIATION TO 5.5×10^{20} nvt AT 650 °C.

Helium bubbles have nucleated on a coarse intergranular precipitate.

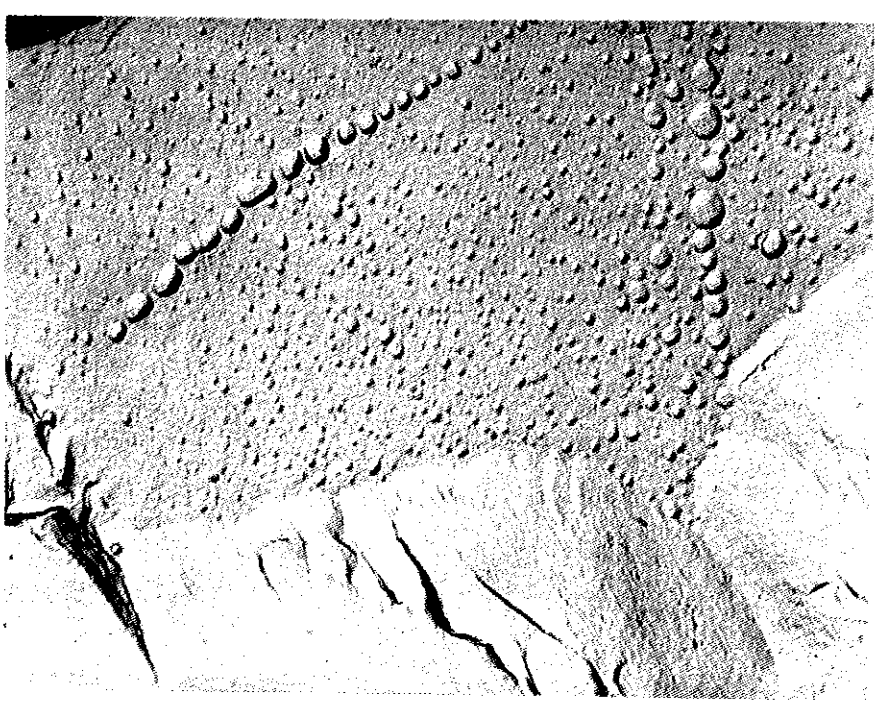
x 280,000

Material B.1.4

FIGURE 8 POSSIBLE FINE SCALE PRECIPITATES IN U.K.A.E.A. BERYLLIUM

x 15,000

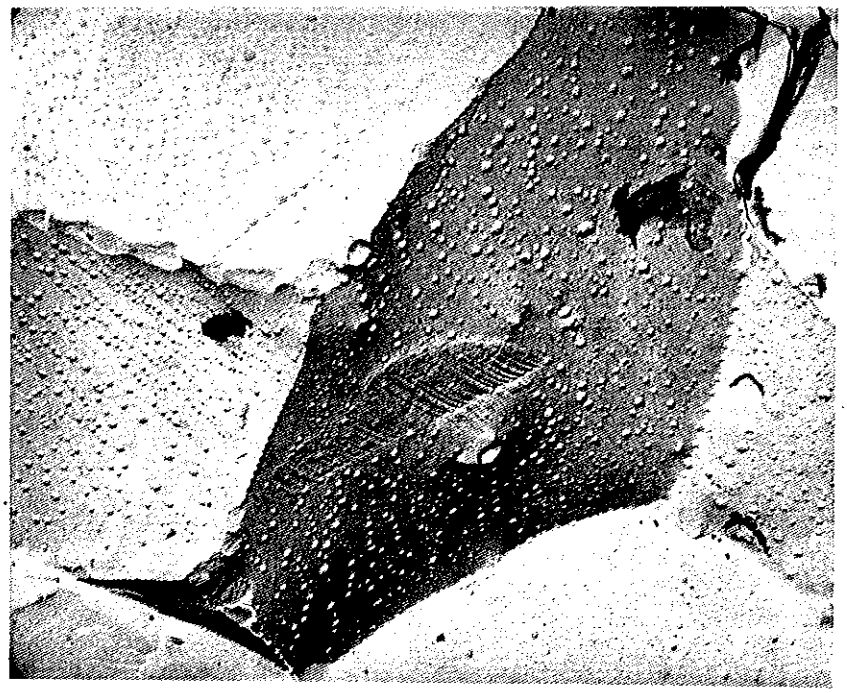
(a) Irradiated at pile temperature and annealed



x 15,000

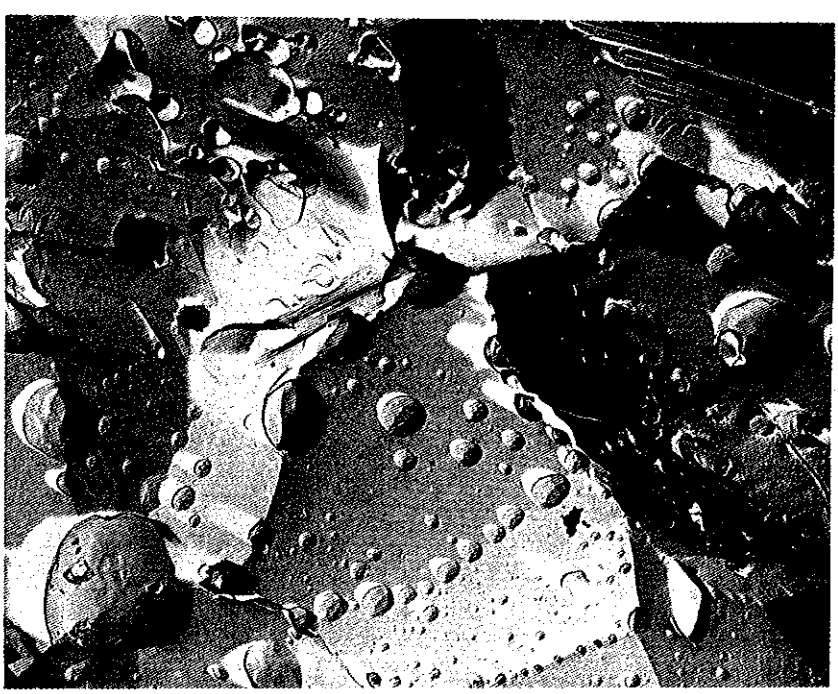
(b) Irradiated at 650 °C

FIGURE 9 COMPARISON OF INTERGRANULAR HELIUM BUBBLE FORMATION IN A.A.E.C. MATERIAL A AFTER (a) IRRADIATION AT PILE TEMPERATURE TO 5 x 10^{20} nvt FOLLOWED BY VACUUM ANNEALING AT 1000 °C FOR 10 HOURS, AND (b) IRRADIATION TO 5.5 x 10^{20} nvt AT 650 °C.



x 12,000

(a) B.1.4 irradiated at 650 °C



x 6,000

(b) B.1.4 annealed 10 hours at 1000 °C

FIGURE 10 COMPARISON OF HELIUM BUBBLE FORMATION ON INTERGRANULAR SURFACES OF U.K.A.E.A. BERYLLIUM (a) AFTER IRRADIATION AT 650 °C, AND (b) IRRADIATION AT 400 °C FOLLOWED BY ANNEALING FOR 10 HOURS AT 1000 °C.