SAND74-0140
[redacted]

RECEIVED BY TIC APR 16 1976

DEVELOPMENT OF A LOW-PERMEABILITY GLASS-CERAMIC TO SEAL TO MOLYBDENUM

R. J. Eagan

Sandia Laboratories

SF 2900 Q(7-73)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

~~DISTRIBUTION OF THIS DOCUMENT IS LIMITED~~
~~To Government Agencies and Their Contractors~~

[redacted]

NOTICE
[illegible]

SAND74-0140

DEVELOPMENT OF A LOW-PERMEABILITY GLASS-CERAMIC TO SEAL TO MOLYBDENUM

R. J. Eagan
Ceramics Development Division-5846
Sandia Laboratories, Albuquerque, New Mexico 87115

March 1975

This report describes the development of low-permeability glass-ceramics which can be sealed directly to molybdenum for the purpose of producing long-life vacuum tubes. Low permeability to helium and thermal expansion match to molybdenum are the bases upon which particular glass-ceramic compositions were selected and developed. The fabrication of tube envelopes using glass-ceramics is simplified when compared to conventional ceramic/metal tubes and these melting and sealing techniques are presented.

MASTER

[redacted]
[redacted] PATENTABLE SUBJECT MATTER. THE CONTENTS
MUST NOT BE DIVULGED OUTSIDE OF SANDIA [redacted] THE
[redacted]
NAL RECIPIE[redacted]ST NOT DIVULGE THE INFORMATION TO OTHERS

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

~~DISTRIBUTION OF THIS DOCUMENT IS LIMITED~~
~~To Government Agencies and their Contractors~~

ACKNOWLEDGMENTS

The author wishes to thank R. D. Snidow, R. D. Bland, C. R. Pennington, and K. A. Peters (all 3621-4) for their assistance and suggestions with regard to fabricating seals and test specimens.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

One of the requirements on envelope materials for long-life vacuum tubes is that they have low permeability to gases, particularly He and H_2. An additional requirement is that the materials be refractory enough to permit high-temperature brazing and bakeout of the tubes. To meet these requirements in the past, tube designers have employed coated Kovar or molybdenum with alumina ceramics for insulator parts. However, expansion characteristics of these metals do not match those of the ceramics. As a result, serious constraints have been imposed on tube designs. In addition, because of requirements to machine the fired ceramic and because of the multiple firings involved in making ceramic-to-metal seals, the fabrication of such tubes is difficult and expensive.

In recent years a new class of materials has been developed which combines the ease of fabrication of glass with the strength and high-temperature stability of traditional oxide ceramics.[1] These materials, glass-ceramics, are melted and formed as a glass. Subsequently, they can be sealed to a metal or ceramic part and crystallized in a single operation. The glass-ceramic is mechanically stable at temperatures approaching the sealing temperature. Because the properties are dependent on the type of crystals produced as well as on the nature of the residual glass, physical properties, such as thermal expansion, can be "tailor-made" by appropriate choices of composition and heat treatment.

The first use of a glass-ceramic materials as the insulator in a neutron tube was in the AWRE Type 851 tube. This glass-ceramic,[†] Nexim

---

[†] Developed by Nelson Research Laboratories, English Electric Co.

WX2/2228, seals directly to molybdenum and is sufficiently refractory to permit brazing of molybdenum-Mexim assemblies at 800°C. It does not have a particularly low permeability to He; therefore, it is not suitable for components which must have long-term vacuum integrity.

This report describes the development at SLA of glass-ceramics with substantially lower gas permeabilities than Mexim and with thermal expansions which match the thermal expansion of molybdenum. Brief descriptions of melting and sealing techniques are presented.

BACKGROUND AND SELECTION CRITERIA

Prior Work on Glass-Ceramic to Molybdenum Seals

During the development of the Mexim WX2 2228 glass-ceramic and the associated sealing technology, it was found that compositions which crystallized to give $2ZnO \cdot SiO_2$ (Willimite) were the most successful.[illegible] The characteristics of this glass-ceramic which are of particular importance for successful seal formation are that it expands slightly upon crystallization and that at the sealing temperatures (1000-1050°C) ZnO in the glass can be reduced by molybdenum. The MoO_2 formed by this reaction, which is adherent to the molybdenum, promotes the formation of a strong seal.[5] The expansion during crystallization tends to keep the glass-ceramic in intimate contact with the molybdenum throughout the sealing cycle.

The AWRE found that, by using graphite jigs and appropriately heating the Mexim/molybdenum assembly in an argon atmosphere, hermetic seals could be formed.

Thermal Expansion of Glass-Ceramics

Glass-ceramic materials generally consist of one or more crystalline phases embedded in a matrix of glass. The thermal expansion of this composite structure depends on the expansions and volume fractions of the constituents. The types and volume fractions of crystals formed and the composition of the residual glass are dependent not only on the composition of the original glass but also on the heat treatment used in crystallizing the glass. Therefore, the expansion cannot be accurately predicted from the composition of the original glass. However, when the type and amount of crystalline phase is known, the thermal expansion can be varied in a predictable way by adjusting the composition of the residual glass.

A qualitative basis for predicting the effect of compositional changes on the thermal expansion of a glass can be gained from a knowledge of how particular oxides are incorporated into the glass. For example, the addition of Na_2O breaks Si-O bonds and thus increases the thermal expansion. Quantitative predictions of the effects of oxides on the expansion of glasses are based on empirical data; these predictions are useful over limited ranges of glass compositions. The most comprehensive study of expansion factors was that of Mayer and Havas.[6] Their factors are shown in Table I.

The expansion coefficient ($°C^{-1}$) of a glass is calculated by summing the products of the wt% of each oxide in the glass and the expansion factor for that oxide.

Table I. Thermal Expansion Factors for Glass (Mayer and Havas)

Oxide	Factor x 10^{-7}	Oxide	Factor x 10^{-7}
SiO_2	0.27	PbO	[illegible]
P_2O_5	0.67	ZnO	.7[illegible]
B_2O_3	0.03	CuO	.7[illegible]
Al_2O_3	1.67	CoO	[illegible].47
CaO	1.67	NiO	1.[illegible]
MgO	[illegible]	SnO_2	[illegible]
BaO	1.[illegible]	TiO_2	[illegible]
Na_2O	[illegible]	Cr[illegible]	[illegible]
K_2O	[illegible]	MnO	[illegible]

Permeability of Glass-Ceramics

As with the thermal expansion, the permeability to gas of the glass-ceramic is controlled by the permeabilities of the crystalline phases, the residual glass present, and their relative volume fractions. However, in general, the permeability of the glass phase will dominate because it is the continuous phase. Also, the permeability of the glass is substantially higher than that of the crystalline phases. For this study it has been determined that an adequate estimate of the permeability of the glass-ceramics can be obtained by assuming that only the glass phase contributes to permeability.

The permeabilities of a number of glasses have been related to the concentration of glass-forming oxides (SiO_2, B_2O_3, P_2O_5) by Altemose,[7] as shown in Figure 1. He found that as more modifier oxides, i.e., nonglass-forming oxides, were added to a glass the permeability decreased.

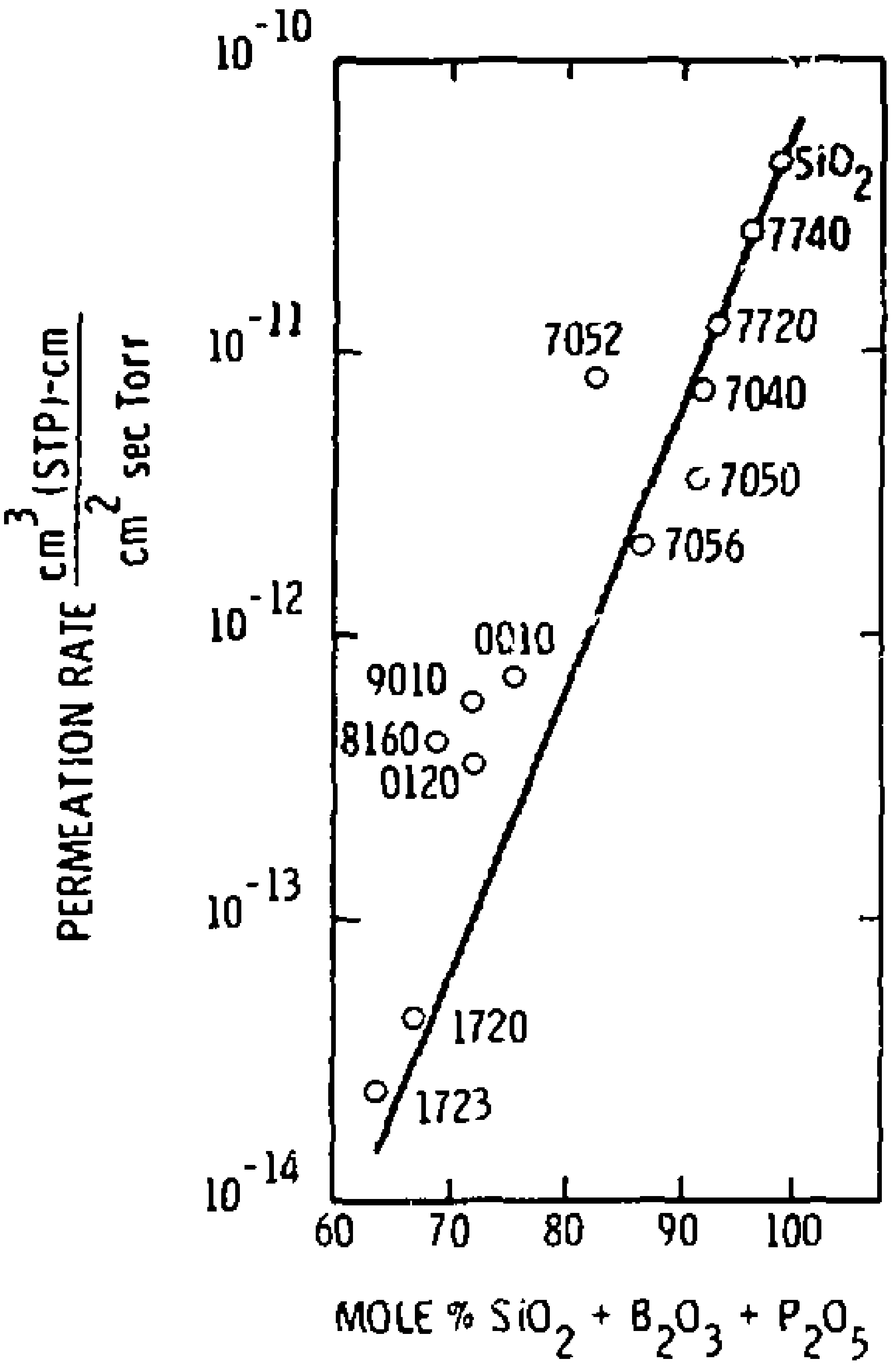

Figure 1. Helium permeability of glasses as a function of glass-former content (Altemose[7]).

The permeability at 300°C can be calculated from the relation in Eq. ([illegible]):

$$K = 1.8 \times 10^{-20} \exp M \left(\frac{cm^3 (STP)\ cm}{cm^2\ sec\ Torr} \right) \qquad (1)$$

where:

K - permeability

M mole % glass-former oxide .

The permeabilities of only a few glass-ceramic materials have been measured. Calculations based on the relationship above are compared in Table II with experimental values. For each glass-ceramic it was assumed that the maximum amount of the crystalline phase was formed. The oxides incorporated in the crystalline phase were subtracted from the original composition to obtain the composition of the residual glass.

Table II. Calculated Permeability of Glass-Ceramic Materials

Glass-Ceramic	Mole % Glass Former in Residual Glass	$K_{300°C}$ Calculated	$K_{300°C}$ Measured
			$\frac{cm^3(STP)\text{-}cm}{cm^2 sec\ Torr}$
CGW8603[a]	89.6	6.8×10^{-12}	2.5×10^{-12}
Re-X[b]	74.8	2.5×10^{-13}	3.8×10^{-13}*
Mexim[c]	77.4	4.4×10^{-13}	4.4×10^{-13}

*Extrapolated from 200°C.

[a] G. L. McVay, Sandia Laboratories, flow through membrane.

[b] G. Lucek, General Electric Co., infusion/outgassing.

[c] J. Gibson, AWRE, Aldermaston, England, flow through membrane.

Formation of Glass-Ceramic to Metal Seals

The requirements which apply to forming acceptable glass to metal seals can be used as a guide for fabricating glass-ceramic to metal seals. Two general requirements which must be met are that the expansion of the glass approximately equals that of the metal and that the glass be saturated with the oxide of the metal at the seal interface.[5] The latter requirement is difficult to fulfill with glass-ceramics because they must be held at high temperatures for a relatively long time to allow crystallization to occur. During this holding period, an oxide layer which had previously been formed on the metal can be completely dissolved and a weak bond will result.

The problem of maintaining the appropriate oxide at the interface is aggravated when sealing glass-ceramics to molybdenum because the molybdenum oxides formed by preoxidation are not stable, adherent oxides. However, an alternative to oxidizing the metal prior to sealing is to produce the oxide during sealing. Osborn[3] noted that ZnO, present in Mexim to form the crystalline phase ($2ZnO \cdot SiO_2$), was reduced by the molybdenum during sealing at temperatures over 940°C. An oxide layer which could then partially dissolve in the glass-ceramic was formed. In this circumstance the interface tends to become saturated with MoO_2, which results in the formation of a strong bond.

The development of a strong bond by reduction of ZnO to form MoO_2 may not work in every instance. Calculations (based on the free energy of formation of the oxides) indicate that the appropriate reduction-oxidation reaction commences at ~ 960°C. Thus, although sufficient oxidation occurs so that a bond can be formed at the temperature used in the AWRE sealing process (1050°C), the reaction may be too slow at lower temperatures.

The sealing temperature is an important consideration for the development of the molybdenum-sealing glass-ceramic. Because recrystallization, which reduces the ductility and strength of molybdenum,[8] is a thermally activated process, it can be minimized by reduction of the sealing temperature. The viscosities of the glass-ceramics described in this report are low enough during sealing so that the appropriate deformation can be obtained at 950°C. But, from the argument above, this reduction of temperature may prevent the necessary MoO_2 from forming. To ensure that sufficient oxide is formed, an oxide with a lower free energy of formation than that of ZnO can be added. For these glass-ceramics, CoO has been selected.

Determination of Heat Treatment Schedule

The formation of a glass-ceramic involves melting the raw materials to form a glass, annealing the glass, then heat treating it to induce nucleation and crystallization.[9] The melting temperature, which must be high enough for the raw materials to fuse and make a fluid glass, is determined by observation of the glass during melting. Specification of the other heat treatment temperatures is more critical.

To obtain a stress-free glass preform the glass must be annealed. This process consists of holding the glass at a specified temperature, then cooling it slowly to avoid imposing thermal gradients which could result in substantial residual stress in the glass at room temperature. It is particularly critical that the annealing temperature be accurately specified and maintained when annealing glass-ceramics because the nucleation temperature may be close to the annealing temperature. In some cases, extensive nucleation as a result of poorly controlled annealing will be a detriment during subsequent processing.

The annealing temperature, approximate nucleating temperature, and crystallization temperature can be determined by differential thermal analysis (DTA). A typical DTA trace for a glass-ceramic composition which forms $2ZnO\cdot SiO_2$ upon crystallization is shown in Figure 2.

The first endotherm (~ 610°C), which is associated with the glass transition,[10] is indicative of the annealing temperature of the glass which corresponds to a viscosity of $10^{13.4}$ poise. Nucleation occurs at a significant rate when the viscosity of the glass is 10^{11}-10^{12} poise, which corresponds to a temperature ~ 50°C higher than the annealing temperature.

The exotherm which starts at 900°C indicates the formation of the crystalline phase, $2ZnO\cdot SiO_2$. Melting of the crystalline phase, which occurs at 1250°C, is denoted by an endotherm.

The glass-ceramic processing information one would derive from this DTA plot includes (1) the glass must be melted at a temperature above 1250°C, (2) the glass can be annealed at ~ 610°C, and (3) crystallization will occur at temperatures greater than 900°C. The precise heating schedule used for the melting, annealing, and crystallization will depend on the fluidity of the glass and the size and application of the particular piece being formed and must, to some extent, be empirically derived. For example, the annealing of these glass-ceramics, which are deformed during sealing to molybdenum, must be carefully controlled to avoid extensive nucleation because this will cause rapid crystallization during sealing.

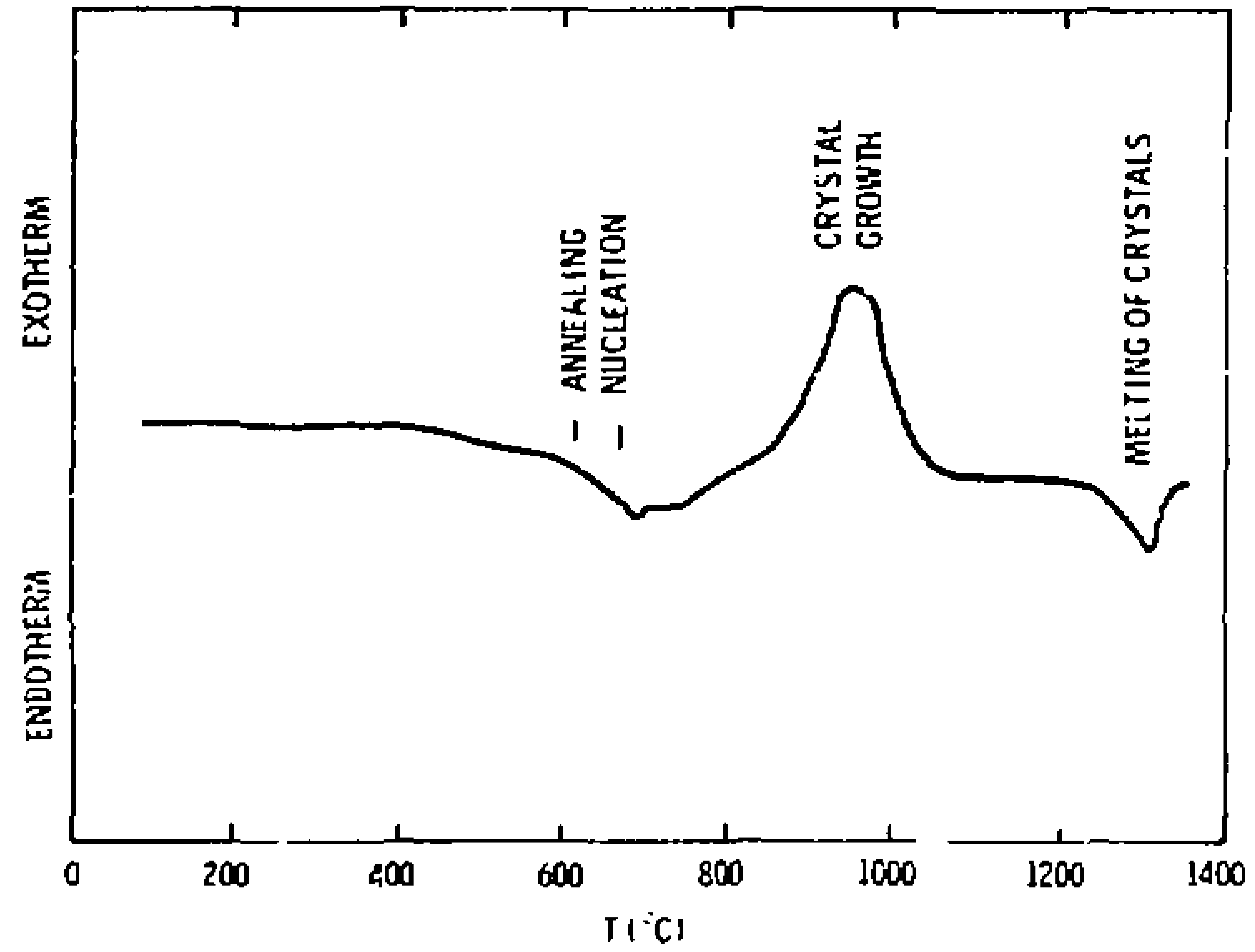

Figure 2. DTA curve of molybdenum-sealing glass-ceramic showing (a) annealing temperature, (b) nucleation temperature, (c) crystal growth range, and (d) the melting temperature of the crystalline phase.

This premature crystallization will rapidly increase the viscosity of the glass-ceramic which will prevent it from flowing and conforming to the shape of the molds.

EXPERIMENTAL PROCEDURE

Development of Glass-Ceramic Compositions

The considerations outlined in the preceding section were used as a basis for developing low-permeability glass-ceramics to seal to molybdenum. Compositions were formulated to yield residual glasses with large concentrations of modifier ions to reduce the permeability of the glass-ceramic. The expansion factors of Mayer and Havas[6] (Table I) were used to estimate the thermal expansion of the residual glass.

Preparation of Glass-Ceramics

Each glass-ceramic used in this program was prepared by fusing reagent-grade chemicals in platinum crucibles. The glasses were melted for ~ 24 hours at 1500-1600°C in electric furnaces. To ensure homogeneity, the glasses were either stirred continuously for ~ 18 hours when prepared in a 500 g batch or stirred several times by hand with a platinum rod when a smaller batch was made.

The molten glass was cast onto a heated steel plate coated with graphite powder. The glass was quickly transferred to an annealing oven preheated to 610°C. The oven was held at that temperature for 5 min and then cooled at a rate of ~ 4°C/min.

Test specimens for the thermal expansion were cut from each plate and crystallized by heating the glass-ceramic at 30°C/min to the sealing temperature, 975°C. Preforms for seal fabrication were formed by diamond core drilling 1.6 in. diameter plates with a 0.6 in. diameter center hole.

Determination of Thermal Expansion

A differential dilatometer[†] with a fused silica reference sample was used to measure the thermal expansion of each crystallized glass-ceramic. The expansion coefficient from 25°C to the set point was determined by considering the set point to be half way between the glass transition temperature and the annealing temperature, both of which were estimated from the thermal expansion curve.[5]

Fabrication of Test Seals

Those compositions which had expansion coefficients of 49-55 x $10^{-7}\,°C^{-1}$ (molybdenum = 53 x $10^{-7}°C^{-1}$) were fabricated into test seals.

The glass preforms, molybdenum, and graphite[‡] jigs were assembled as shown in Figure 3. Proper cleaning procedures and handling of the jigs and piece parts were required to obtain a hermetic, pore-free seal. All molybdenum piece parts were vapor honed and vapor degreased prior to chemical etching. After etching was completed, the parts were passed through a cascade cleaner and then hydrogen fired per specified time and temperature. The glass-ceramic preforms were vapor degreased, lightly etched in an acid bath, rinsed in running tap water, and then passed through a cascade cleaner.

Periodically, the carbon fixtures were vapor honed to produce a matt finish. (Shiny surfaces indicate contamination.) In addition, chipped or

---

[†] Dilatronic IX, Theta Industries, Port Washington, NY

[‡] Poco DFP 1 or TRA1 graphite, Poco Graphite, Inc., Decatur, TX

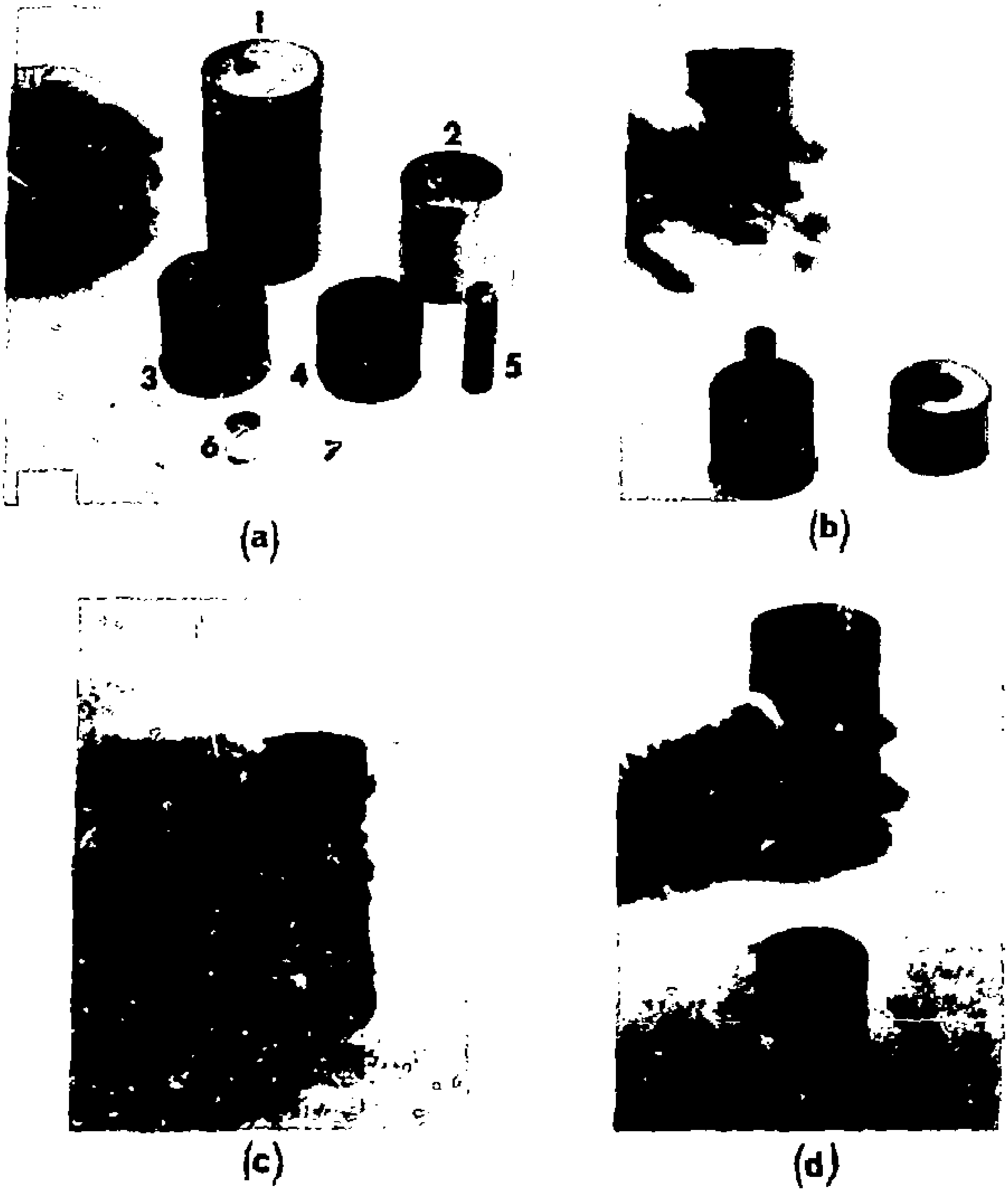

Figure 3. Assembly of parts used to form glass-ceramic/molybdenum seals showing (a) individual parts and (b-d) the assembly sequence. (1) molybdenum weight, (2) molybdenum outer sleeve, (3) graphite base mold, (4) graphite top mold, (5) graphite centering pin, (6) molybdenum inner sleeve, (7) glass-ceramic preform.

scratched surfaces were cause for rejection of the fixtures. After the fixtures were vapor honed, they were cleaned ultrasonically in acetone, placed in a vacuum oven, and baked out at 65°C for 1 hour.

The assembly was weighted with a 2000 g molybdenum weight and fired in a cold wall furnace which had been evacuated and backfilled with argon.

The heating schedule shown in Figure 4 is similar to the one used with Mexim NK2/2228; however, the maximum sealing temperature used in this study was 975°C rather than 1050°C. The mold assembly was heated at ~ 30°C/min to 975°C and held for 45 min to allow oxidation of the molybdenum and crystallization of the glass-ceramic to occur.

RESULTS AND DISCUSSION

The compositions of three glass-ceramics which approximately match the thermal expansion of molybdenum and have low calculated He permeabilities are shown in Table III with Mexim NK2/2228. The MS49 glass-ceramic possesses the best properties for fabricating neutron tube envelopes. This glass-ceramic has an estimated permeability of $1.2 \times 10^{-14} \frac{\text{cm}^3\text{(STP)-cm}}{\text{cm}^2 \text{ sec Torr}}$ at 300°C. At 300°C, Wesgo AL500 Al_2O_3 has a permeability of $2.6 \times 10^{-15} \frac{\text{cm}^3\text{(STP)-cm}}{\text{cm}^2 \text{ sec Torr}}$,[12] and Mexim has a permeability of 4.4×10^{-13} of $\frac{\text{cm}^3\text{(STP)-cm}}{\text{cm}^2 \text{ sec Torr}}$.[13]

The thermal expansion of MS49 from 25°C to the set point ($52.7 \times 10^{-7}\,°C^{-1}$) is close to molybdenum ($53 \times 10^{-7}\,°C^{-1}$), which ensures that residual stresses in the glass-ceramic are small. Concurrent work directed toward fabricating Mexim NK2/2228 into the configurations required for the Sandia-designed long-life tube has shown that the expansion coefficient of the glass-ceramic must be between $49 \times 10^{-7}\,°C^{-1}$ and $55 \times 10^{-7}\,°C^{-1}$.

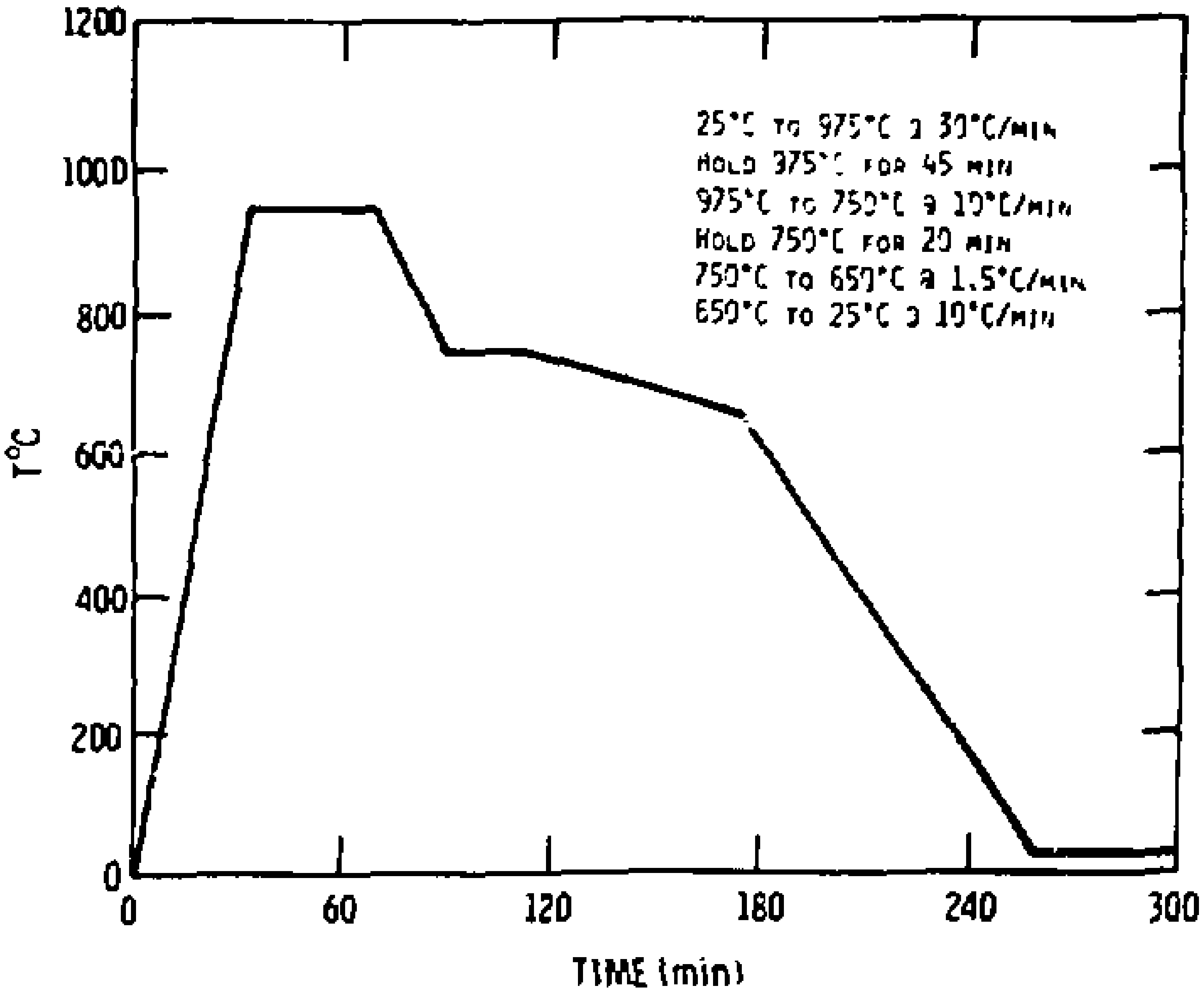

Figure 4. Typical heat treatment schedule used to form molybdenum/glass-ceramic seals.

Table III. Compositions and Expansion Coefficients of Low-Permeability Glass-Ceramics and Mexim

		Glass-Ceramic		
Oxide	Mexim	MS4	MS27	MS49
SiO_2	47.4	40.0	40.5	40.0
P_2O_5	2.1	2.1	3.0	3.0
Al_2O_3	9.5	9.5	9.0	9.0
Na_2O	4.0	1.0	2.5	2.6
MgO	--	5.2	3.0	3.0
CuO	--	5.2	4.0	3.0
BaO	4.8	4.8	4.0	5.2
ZnO	32.2	32.2	33.0	33.0
CoO	--	--	1.0	0.2
TiO_2				1.0
Expansion Coefficient $25 \times 10^{-7} \cdot C^{-1}$ to set point	47.7 (750°C)	48.8 (750°C)	49.8 (750°C)	52.7 (715°C)

CONCLUSIONS

A glass-ceramic of low helium permeability has been developed for fabricating long-life vacuum tubes. The residual stresses in the glass-ceramic are small because the thermal expansion of the glass-ceramic closely matches that of molybdenum. Tube envelopes which utilize this glass-ceramic have been successfully produced using techniques similar to those developed for sealing Mexim NK2/2228 to molybdenum.

REFERENCES

1. P. W. McMillan, Glass Ceramics (Academic Press, New York, 1964).

2. G. Partridge, T. Hales, and O. J. Marsh, "Glass-Ceramic NK2/2226-Molybdenum Seals of AWRE, Aldermaston," English Electric Co., Nelson Research Centre, Stafford, England (1970).

3. C. F. Osborn, "Factors Involved in Making Mexim to Molybdenum Seals in the Unit 851 Base," Report WLE5/CFO/05, AWRE, Aldermaston, England (1970).

4. C. F. Osborn, "Mexim/Molybdenum Sealing: On Varying the Sealing Parameters," Report No. WLE/CFO/03, AWRE, Aldermaston, England (1969).

5. *M. P. Borom, "The Mechanical and Chemical Aspects of Glass Sealing* General Electric Co., Technical Information Series, Report No. 73 CRD 045 (1973).

6. A. I. Andrews, Porcelain Enamels, Data of Mayer and Havas (Garrard Press, Champaign, IL, 1961), p. 54.

7. V. O. Altemose, "Helium Diffusion through Glass," J. Appl. Phys. 32 (7) 1309 (1961).

8. A. K. Hegedus, "The Recrystallization Kinetics of Molybdenum Sheet," Technical Report No. RMTR-1, General Electric Co., Cleveland, OH (1963).

9. D. R. Stewart, "Concepts of Glass-Ceramics," in Introduction to Glass Science, L. D. Pye, H. J. Stevens, and W. C. LaCourse, Eds. (Plenum Press, New York, 1972), pp. 237-273.

10. T. H. Ramsey, "Thermal and X-Ray Analyses of Some Electronic Package Sealing Glasses," Bull. Am. Cer. Soc. 50 (8) 671 (1971).

11. R. J. Eagan, R. D. Bland, and C. R. Pennington, "Glass-Ceramic Neutron Tube Insulators," presented at 8th US/UK Neutron Generator Symposium, Sandia Laboratories, Albuquerque, NM, Oct. 21-25, 1974.

12. A. E. Binder, "Permeation of Alumina Ceramics," Test Report No. 72-63, Sandia Laboratories, Albuquerque, NM (1972).

13. J. E. Gibson, AWRE, Aldermaston, England, personal communication.