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Glass-to-Metal Seal Design*

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INTRODUCTION

So far as is known the earliest seals were made in ancient Babylon by the goldsmiths who fused a vitreous glaze or combination of glazes on to gold 'to form enamelled ornaments of noble design in opaque turquoise, cobalt, emerald green and purple'. In the fourth and fifth centuries B.C. the gold drapery of the figure of Zeus in the Temple of Olympia was gorgeously enamelled with figures and flowers. In the days of the Druids Britain exported ornaments decorated with red enamel. Much later, when writing of ancient Britain, Philostratus wrote: 'It is said that the barbarians in the ocean pour these colours into bronze moulds, that the colours become hard as stone preserving the designs.' In the Middle Ages designs were enamelled on foundations of gold, copper or silver.

In 1643 Torricelli enclosed the vacuum in the glass tube of his barometer by a seal of glass to molten mercury. Platinum was discovered about the middle of the eighteenth century. Its ability to seal through some ordinary glasses made it the sealing metal of the nineteenth century. By its aid the first vacuum tubes were made and thus electricity was wedded to high vacuum. The advent of electric discharge tubes and incandescent lamps gave impetus towards the search for cheaper and better sealing metals and hence to the study of glass seals themselves.

The heart of the seal is the junction or seal which bonds the glass to metal. The mechanism of adhesion is relatively obscure, but we do know from experience that some bonds are strong and others weak. Let us examine a small area element. We find that some seals have bright metal apparently united directly to glass, while others have a visible coloured interlayer between the glass and metal. Interlayer seals are often termed oxide seals because the metal surface is oxidized before being wetted by the glass. In practical seal-making in air, proper control of the nature and thickness of such oxide interlayers is very important.

* Based on a paper presented by the author to the Electronics Group of the Institute of Physics in London on 9 June 1945.

THE METAL OXIDE

The reaction of metal with oxygen may be written as follows:

$$\text{Metal} + \text{Oxygen} = \text{Metal oxide} + \text{Heat}.$$

When the oxygen concentration is above the dissociation pressure of the metal oxide, the reaction is towards the right. When it is below, the reaction is to the left. Base metals have low dissociation pressures and noble metals have dissociation pressures exceeding 1 atm., well below their melting-points. The dissociation pressure increases with temperature, and this latter fact is exploited in the case of bright tungsten seals; at red heat in air an oxide seal forms, but in the high temperature of an oxygen/gas flame a bright seal can be made with no visible interlayer.

An oxide with low vapour pressure remains on the metal, but one with high vapour pressure evaporates away almost as it forms so that the thickness remains steady. This is the case with molybdenum.

The oxide may be continuous or discontinuous. Pilling & Bedworth (31) have tabulated for a number of metals the ratio of the volume of oxide to that of the metal replaced by the oxide and called it the 'critical density ratio'. They noted that where this density is less than unity, as in the case of alkali metals, the oxide layer is discontinuous and offers little protection to further access of oxygen. (No sealing metal is of this type.) When the ratio is not less than unity, access of oxygen to the surface is impeded. The first oxide film that forms separates the metal from the air so that further oxidation has to take place through an oxide barrier. One side of the reaction surface continues to be bare metal so that oxygen continues to be used up as it arrives there and causes the oxygen pressure at that point to remain low, probably close to the dissociation pressure of the oxide. Next to the outer surface the oxygen pressure will be either that of maximum solubility of oxygen in the oxide or the partial pressure of oxygen outside, whichever is the lower. More recent work (32) indicates that this simple theory is inadequate; but it does give a picture which is useful for our present purpose.

Practical seal-making conditions are complicated by varying temperatures, flame composition, fracture of the oxide by internal or external mechanical strain, or by undesirable impurities in the sealing flame or the sealing materials.

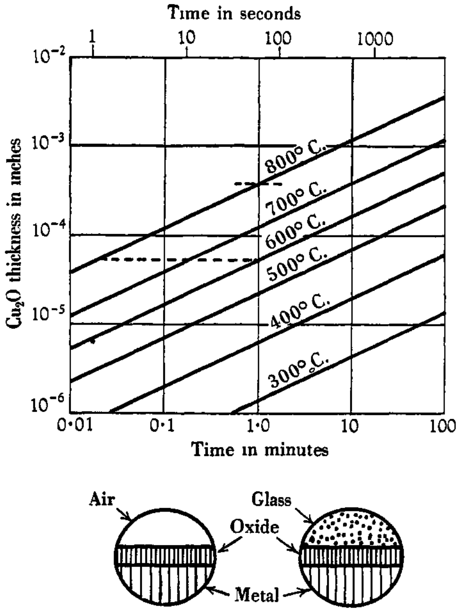

Fig. 1. Oxidation of copper in pure air. *Above:* graph showing rate of oxidation. *Below:* diagram of copper/oxide/air element and of copper/oxide/glass element

Fig. 1 is a graph representing oxide thickness versus heating time for copper at 300, 400, 500, 600, 700 and 800° C. in air. The two dotted lines mark the amount of oxide that forms on heating at 800° C. for 1 min. and at 800° for 1 sec. respectively; the ratio is seven to one. On the other hand, 1 sec. at 800° C. produces as much oxide as 1 min. at 600° C. Furthermore, it has been reported elsewhere (33) that even 0·1 % of sulphur dioxide in the air surrounding a piece of copper may increase the oxidation rate as much as 20-fold at 400° C. From these figures the importance of reasonably close limits of temperature and time and also of adequate flame purity in seal-making will be obvious.

The junction

At the glass/oxide/metal junction (Fig. 1) the heat of sealing may be sufficient to permit chemical reaction between the glass and the metal or its oxide or even to cause some dissociation of the oxide itself. It has been stated elsewhere (30) that in sealing nickel-iron alloy to lead glass the iron replaces lead which is then deposited at the interface. The oxide may, on the other hand, diffuse into or dissolve in the glass either partially or completely, depending upon the heating time and temperature. When this happens, the composition of the glass adjacent to the metal will have changed. While it is conceivable that this can affect adhesion, the modified layer will be thin enough to follow the main glass elastically (34), and so will not directly affect stress in the body of a seal.

Early efforts to make bright seals with base metals and alloys resulted in two techniques: (*a*) to heat an oxide seal so that the oxide dissolves into the glass; (*b*) to seal the glass on to the metal in absence of oxygen.

Carolan (16), in 1903, placed a nickel-iron wire in an evacuated glass tube and fused the glass down on to the wire. Sand (22), in 1913, melted lead into quartz glass also nominally in vacuum. Gabor (27), in 1931, sealed quartz glass on to strips of tantalum or of molybdenum less than 0·0006 in. thick in a high vacuum for current leads of high-pressure mercury-vapour arcs. The reduction of SiO_2 to SiO by certain metals at high temperature suggests that in the latter case chemical reaction of the SiO_2 and molybdenum may produce an oxygen bond. Bright interfaces produced by melting glass on to iron or copper in a hydrogen atmosphere have a very weak bond or no bond at all and cannot be called seals.

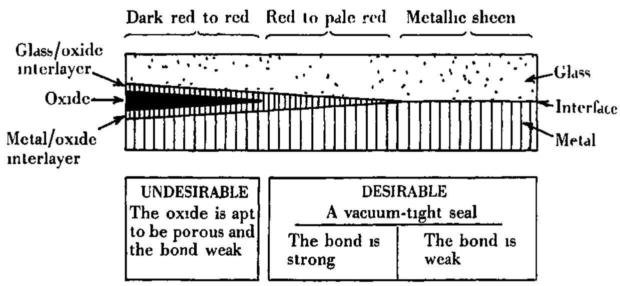

Fig. 2. 'Interlayer' and 'interface' in a copper/glass seal

Fig. 2 is a diagram of a cross-section of a wedge-shaped copper seal containing three types of junctions. At one end glass is united directly to metal forming an interface. In the middle a thin interlayer, of what was originally an oxide of the metal, unites glass and metal; it is assumed that all the layer is engaged in making the bond. If it is thin, its expansion coefficient will not affect the seal. The other end shows a thick interlayer in which only the surface of the oxide has bonded to glass and metal and the centre of the interlayer is the original 'bulk' oxide which may be weak or even porous Different metals give different seal colours. The colour may be changed by heating and by the degree of oxidation. Seals of copper to ordinary glasses may vary from dark red through a greenly irridescent red or a light red, to a seal which has no colour other than that of the copper itself.

Glass composition also can influence colour; for example, ordinary oxide seals of tungsten are yellow, gold, or brown, according to the degree of oxidation and heating, when they are made to glasses which contain sodium and potassium. It has been suggested that the interlayer contains tungstates or tungsten bronzes formed by combination of tungsten oxide with alkali metals in the glass. This view is supported by the fact that the colour changes produced by prolonged heating of such seals and of tungsten bronzes are alike, and in the same sequence. As a further check the author made seals of tungsten through a glass containing lithium instead of sodium and potassium, expecting that as lithium has a blue tungstate the seal would be coloured blue—the seal was blue.

Seal colour is a commonly accepted, but sometimes misleading, criterion of whether a junction is good or bad. For instance, in copper seals it does differentiate between bright seals which have a low adhesion and the stronger red oxide seals, but it does not distinguish between a good interlayer and one which is just a little too thick (see Fig. 2). Again, although good seals to pure copper may have an irridescent sheen which may be lacking in weak seals made with impure copper, some good seals also may lack sheen. Colour is a better guide

Table 1. *Data relating to metal and glass junctions*

Metal	Oxide	Heat of formation k.cal.	Critical density ratio	Colour: Oxide	Colour: Seal
Gold	Au_2O	—	5·5	Grey-violet	Metallic yellow
Silver	Ag_2O	7	1·57	—	Metallic or yellow
Platinum	PtO	17	1·56	Violet-black	Metallic
Copper	Cu_2O	40	1·67	Red	Metallic or red or yellow with green irridescence
	CuO	35	1·7	Black	
Cobalt	CoO	57	1·74	Green-brown	Metallic or grey-brown to dark blue
	CoO_3	—	—	Grey-black	
Nickel	NiO	58	1·51	Green-black	Metallic or grey-green
Iron	FeO	64	1·77	Black	Light grey to black
	Fe_3O_4	266	2·36	Red-black	
	Fe_2O_3	190	2 1	Brown-black	
Tungsten	WO_2	126	1 87	Brown	Metallic or red-brown to pale straw
	WO_3	191	3·4	Yellow	
Molybdenum	MoO_2	131	3·0	Red-brown	Metallic or brown
	MoO_3	174	3·3	Yellow-white	
Chromium	Cr_2O_3	267	1·94	Green	Olive-green
28Cr/72Fe			Complex		Green-brown
29Ni/17Co/54Fe			Complex		Grey to brown
42Ni/6Cr/52Fe			Complex		Brown

when the under-oxidized, correctly oxidized and over-oxidized seals differ in colour, as in the case of iron-nickel-cobalt sealing alloy, where a bright metallic appearance generally indicates a weak bond, a grey to brown colour indicates a good seal, and a black colour a seal which is over-oxidized and therefore may leak.

Interface types of seals are usually colourless (e.g. molybdenum, tungsten, platinum, gold, silver, copper), but seals coloured by metal which has diffused into the glass (e.g. silver) also occur. Little is known of the nature of the bond.

Some facts relating to the junction are embodied in Table 1, in which ten metals are grouped in the order of the heats of formation of their oxides (so far as those are known). Three noble metals, gold, silver and platinum, head the list; all make 'interface' types of seals with a fairly low bond strength. Next comes copper, which is the most widely used metal surface for vacuum seals and normally has a red, strongly adherent, 'oxide' interlayer. Then iron, nickel, and cobalt, which are used extensively in enamel-ware. The two critical density ratios of copper oxide are so nearly equal that the change from one oxide to another during heating should produce little strain. The case is different with iron oxides whose critical density ratios differ widely so that a reduction of Fe_3O_4 to FeO would cause a shrinkage in volume and possible fracturing of the oxide layer if it can be assumed that the ratios hold at sealing temperature and that the oxide is not completely plastic. It is well known that seal-making to iron requires critical control of chemical composition, surface formation, time, temperature and atmosphere, if seals of consistently good quality are to be produced. With due care, tungsten and molybdenum, both of which have high heats of formation, seal easily and well. Chromium by itself (i.e. as an electro-plated layer on nickel-iron alloy) and in alloys gives a strongly protective oxide excellent for sealing.

Cemented seals with deformable interlayers

Glass (or ceramic) can be hermetically sealed to a metal by an interlayer of a solder, a glass, or a cement capable of plastic deformation below normal sealing temperatures. The use of cements such as wax or bitumen (see Fig. 3*a*) is useful for only a small range of temperature. A similar joint can be made with solder; the best-known example is tungsten vacuum soldered into fused silica(22) by pure lead whose

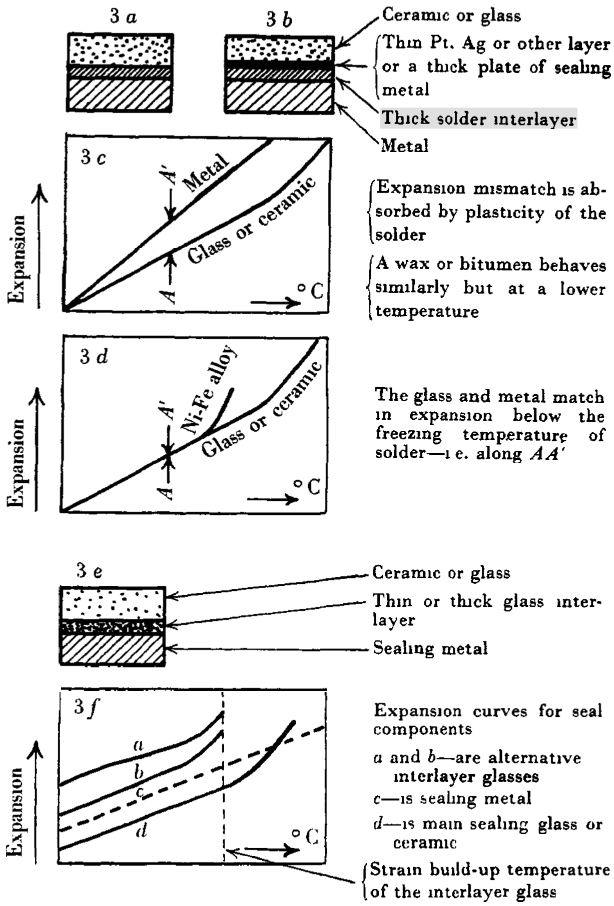

Fig. 3 Cemented seals with fusible interlayers of an organic cement or wax, a solder, or a glass

plastic deformation prevents dangerously high stress building up. In Fig. 3*b* a very thin layer of platinum, silver or other metal is united by fusion or sintering to the glass or ceramic before soldering (13). Soldering may thus be done in air, but requires close control to prevent all the layer diffusing into the solder. When a thick plate of a sealing metal such as silver, platinum or 54/29/17 iron-nickel-cobalt alloy is substituted, the soldering time becomes uncritical. Stress due to mismatch can be relieved by distortion of the interlayer (as in Fig. 3*c*) or by an interlayer which 'freezes' where the glass and metal expansions match (as in Fig. 3*d*). Finally, Fig. 3*e* shows a soft glass bonding a harder glass (or ceramic) to metal. Fig. 3*f* gives expansion curves for a main glass and metal which have equal expansions below the transformation region and which are united by a thin layer of a glass, whose 'strain build-up' point is below the transformation zone of the main glass. When the soft glass is thin enough, the seal stress is determined by the main glass or metal, and a substantially perfect expansion match is obtainable at all temperatures (35).

Physical properties of sealing glasses and metals

The core of a piece of homogeneous solid glass is strong in compression and in tension and remains so indefinitely. The outer surface is strong in compression, but is weak in tension

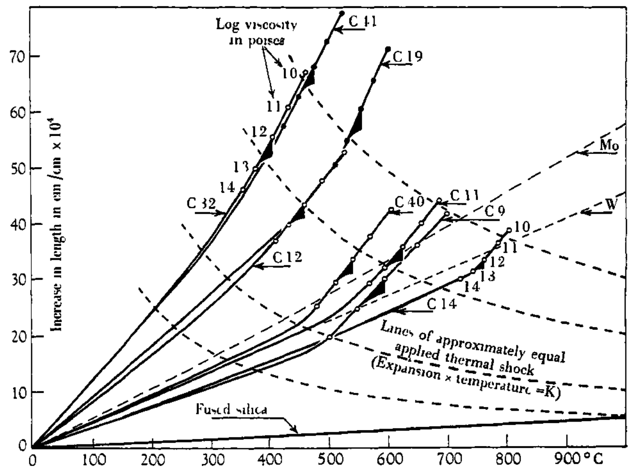

Fig. 4. Linear thermal expansion and viscosity data for nine 'sealing glasses' and expansion curves for tungsten and molybdenum. The dotted curves approximate to lines of equal applied thermal shock

because of the presence of surface flaws which are usually accentuated by weathering. The strength varies but little up to the transformation region (36). In a seal the glass boundary at the junction should not be deemed any stronger than an exposed surface unless the junction is *known* to be as strong or stronger than the glass core itself. Air bubbles in the glass should be looked on merely as surfaces shielded from weathering.

The expansion characteristics of solid glasses are nearly straight up to the transformation region and then curve upwards and continue along another nearly straight line. The contraction characteristic (measured from a temperature at which the glass is not solid) may differ appreciably from the expansion characteristic, and both curves can be modified appreciably by the thermal history of the glass (37). Glass is solid to well above the knee of the expansion curve, and then as the temperature rises the viscosity falls until eventually it becomes molten. The expansion curves for nine sealing glasses, given in Fig. 4, are marked with five viscosities (10^{14}, 10^{13}, 10^{12}, 10^{11} and 10^{10} poises). At 10^{10} poises the glass is still too hard to 'work' in the flame. Between 10^{11} and 10^{12} poises stress can begin to build up in a seal cooling at 5° C / min. (38) At about 10^{12} poises the load imposed on the expansion test specimen usually causes it to buckle, and the 'recorded graph' curves downward from the true value into the shaded area. Finally, at about 10^{13} poises lies the temperature at which glass is usually annealed in practice; here strains will be almost completely relieved in a few minutes.

In Table 2 some experimentally derived figures illustrate the time required for reduction of strain from 1000 to 100 units in one particular seal at various temperatures and viscosities.

Table 2. *Time for reduction of strain*

Temp. (° C.)	470	456	441	433	420
Log viscosity (poises)	12·1	12·7	13 4	13·6	14 3
Time (min.)	3 0	3 4	4·4	9·0	Over 20

Some additional data for sealing glasses are given in Table 3.

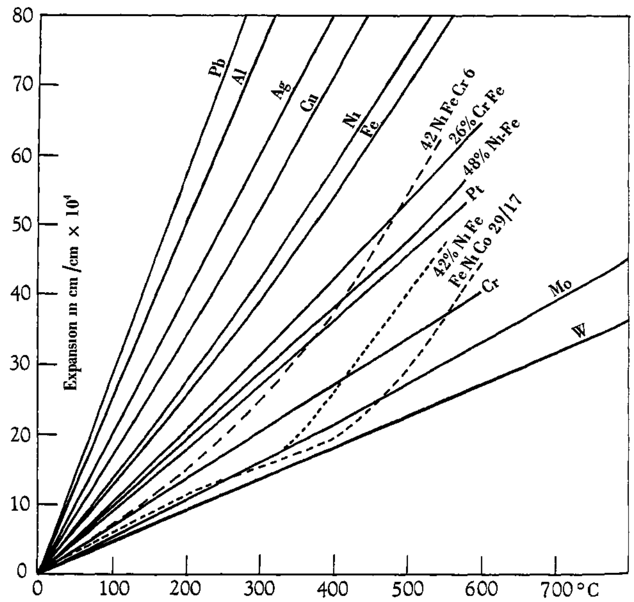

Fig. 5. Linear thermal expansion characteristics of some sealing metals

Table 3. *Data relating to sealing glasses*

Glass	C12	C40	C19	C9	C14
Annealing temp. (° C.)	427	497	524	530	730
Young's modulus (kg./sq.mm. × 10^{-3})	0·62	0·62	0·73	0·63	0 78
Linear expansion per unit length × 10^4 for 0° C. to annealing temperature	40·0	27·5	52 5	22·0	31·0
Mean linear expansion coefficient per 1° C. × 10^7 over the range 0° C. to annealing temperature	94	55	100	42	43
Mean linear expansion coefficient per 1° C. × 10^7 over the range 0–300° C.	90	48	92	36	37
Thermal endurance factor at annealing temperature (arbitrary units)	55	85	35	100	75

Table 4. *Data relating to sealing metals*

Material ...	Copper	Platinum	Tungsten	Molybdenum	Fe/Ni/Co 54/29/17	Ni/Fe 50/50	Cr/Fe 28/62	Iron
Young's modulus (lb./sq.in. × 10^6)	12 (300° C.) 18 (20° C.)	24	20/32	34/46	18/20	22/25	30/33	29
Proportional limit (lb./sq.in.)	3000 to nil	4600–6500	—	30,000–80,000	55,000	25,000	50,000	21,000
Elongation (%)	40/50	—	0/2	2/20	5/33	40	20/30	—
Poissons' ratio	0·33	0·4	0·17	—	—	0·3	—	0·29
Melting-point (° C.)	1083	1773	3370	2620	1460	1450	1450	1510
Calories/c.c./° C.	0·82	0·69	0·64	0·66	—	0·96	—	0·86
Relaxation temperature (° C.)	50/150	—	—	Over 600	450/550	450/550	500/550	500/550
Thermal diffusivity	1·12	0·24	0·59	0·53	—	0·04	—	0·17
Resistivity (Ωcm. × 10^6)	1·7	10·0	5·5	5·7	49	50/60	45/60	10·0
Thermal expansion coeff. (× 10^6)	17·8	9·0	4·5	4·9	6/6·5 (20/500°)	*c.* 9·8	10·8	13·4 (0/450°)
Magnetic inversion temp. (° C.)	—	—	—	—	435	*c.* 500	—	900
Cost in shillings/c.c. (1945)	0·025	102	4·25	1·35	0·18/0·4	0·1	0·17	0·004

Corresponding curves for fourteen metals are plotted in Fig. 5. The expansion characteristics of pure metals are nearly linear; those for nickel-iron, nickel-iron-chromium and nickel-iron-cobalt sealing alloys curve like the glasses to which they are meant to seal. Some further data relevant to seal-making are given in brief for eight sealing metals and alloys in Table 4.

Relative thermal contraction of glass and metal

Perhaps the simplest and most accurate way of comparing the relative contraction of sealing materials is to make a flat sandwich seal and measure photoelastically the strain in the glass at and parallel to the junction under the thermal conditions for which the result is required. The strain can be estimated reasonably accurately from the seal colour as seen in an ordinary strain viewer by using the nomogram or *Abac* of Fig. 6. At the middle of the sandwich, the stress P is given by R/ct, where R is set by the 'strain colour', t is the glass thickness and c is the stress optical constant. For sealing glasses c ranges from 2·5 to 4·0. Values of c for a number of glasses are given in the *Abac* and in Table 5.

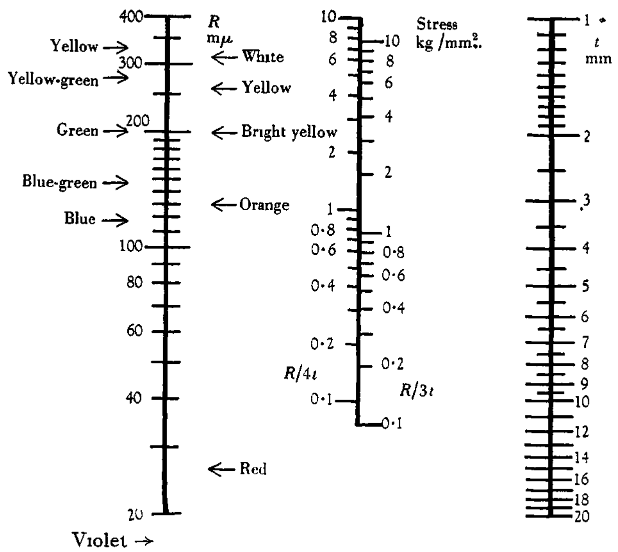

Fig. 6. Nomogram for $P-Q=R/ct$ (colours are for daylight illumination)

Fig. 7 shows curves of stress versus temperature for five pairs of seals subjected to cooling at 5°/min. With C 14 to molybdenum stress begins to build up between 10^{11} and 10^{12} poises which is 50° C. above the nominal annealing point.

Table 5. *Stress optical constant c*

c mμ/cm. / kg./cm.²	Glass (B.T.H.)
4	C 9
3·6	C 11
3	C 12
2·7	C 19
3·6	C 40

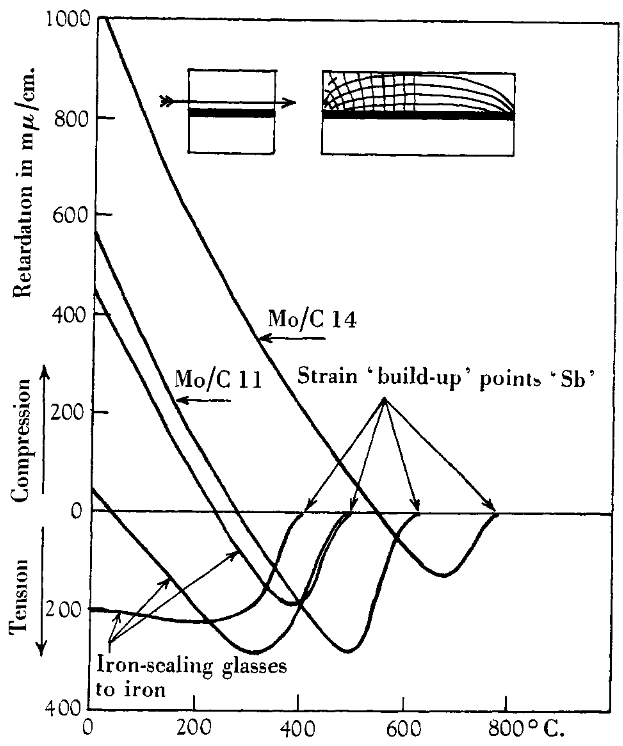

Fig. 7. Relative contractions from 'strain build-up point' (*Sb*) of five pairs of glass and metal, made into sandwich seals and cooled at 5°/min.

During cooling the tension rose, giving 113 mμ/cm. at 670° C., fell to zero retardation at 560° C. and rose to 1000 mμ/cm. compression at room temperature. In the other four cases stress also starts to build up between 10^{11} and 10^{12} poises, but the curves are different. Strain 'build-up' or *Sb* temperature obviously will be high or low, depending on whether the cooling rate is high or low. Rapid cooling in effect 'increases' the contraction of glass whose coefficient of expansion is greater than that of the metal at the 'build-up' point, when the curves cross as indicated.

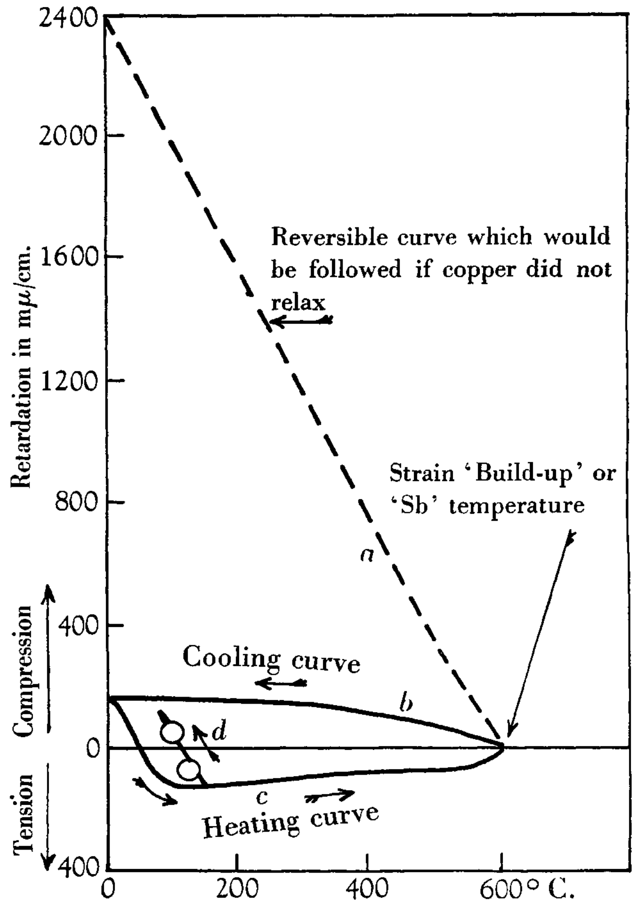

Fig. 8. Metal relaxation in a sandwich seal of copper to B.T.H., C9 glass (after Stanworth and Redston)

Fig. 8 illustrates the relaxation of copper in a sandwich of 'sealing copper' and C9 glass. Stress again builds up between 10^{11} and 10^{12} poises, but does not continue along the steep curve *a* which is computed postulating no relaxation at all. Instead, curve *b* is followed, giving a maximum compression of 160 mμ/cm. On reheating, the curve *c* is at first parallel to *a*, but flattens near 150° C. at 120 mμ/cm. tension. Near 200° C. comparatively rapid annealing of the copper begins, and the stress at 350° C. has fallen to 70 mμ/cm. tension. If the heating is interrupted at 150° C., the cooling curve *d* which is parallel to *a* is followed. Impurities such as silver raise the annealing temperature and also the strength of copper at elevated temperatures, and will increase the stress.

Basic parts and their stress systems

In a good seal the parts not only wet each other, but the stress must be limited to a safe value by proper 'annealing or tempering', by suitable balance of expansion (8, 14, 19, 20, 25, 26, 30), elasticity (18, 21, 27) and plasticity (15, 17, 20, 22, 23, 24, 27) and/or by shaping (10, 11, 12, 15, 17, 18, 21, 23, 24, 27) the seal so that unduly high and dangerous local stresses are prevented. Annealing or tempering, which are necessary for glass by itself, are even more so when metal is present. Now if strained glass or metal has zero thickness, it will exert zero stress. If it has next to no thickness, the stress and strain in the thicker part will be next to nothing, but may be very high in the

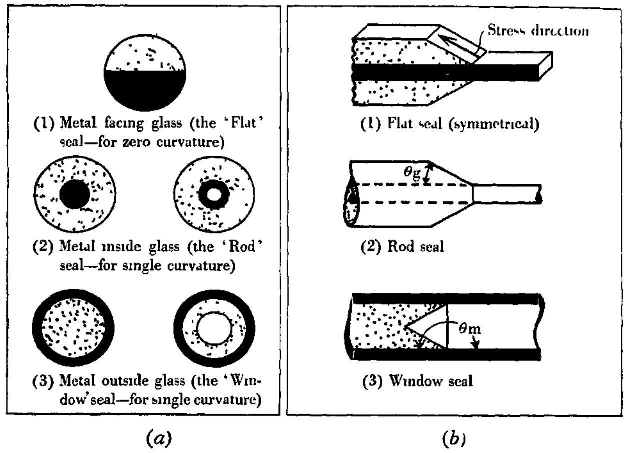

Fig. 9. Construction of elements and stresses. (*a*) Basic glass/metal constructional elements. (*b*) Stress along the glass/air surface nigh and normal to the glass/air/metal junction

thinner part. When the glass is thick, and provided the bond is strong, the elasticity and/or plasticity of a thin metal wire, tube, or sheet may be such as to let the metal distort or relax sufficiently to prevent dangerous stress in the glass even when the mismatch is considerable, as with copper to borosilicate glass and molybdenum to silica glass. When the metal is thick and the glass thin compared with the radius of curvature of the junction, the force normal to the junction will be zero. Fracture will then depend upon the elasticity of the glass (plasticity being zero) and on its strength in compression or tension as the case may be.

Basic glass/metal constructional elements. The three basic seal forms which are illustrated in Fig. 9*a* are: (1) metal facing glass (the 'flat' seal—for zero curvature); (2) metal inside glass (the 'rod' seal—for single curvature); (3) metal outside glass (the 'window' seal—for single curvature).

For an expansion mismatch the stresses at the junction are given in Table 6.

Now, solid glass has never been known to fail in pure compression. It fails due to the *tension* component of stress. Moreover, cracks can only start from a surface (or boundary) either internal or external.

It follows (speaking broadly) that the type 3*M* window

Table 6. *Stress with mismatch*

	Type *M*—*Metal* contracts more than glass. Stress direction relative to junction		Type *G*—*Glass* contracts more than metal. Stress direction relative to junction	
	Perpendicular	Parallel	Perpendicular	Parallel
(1) Flat seal	Zero	Compression	Zero	Tension
(2) Rod seal	Tension	Compression	Compression	Tension
(3) Window seal	Compression	Compression	Tension	Tension

seal and the type $1M$ flat seal are safest, as they alone have no tension component of stress. Rod seals type $2M$ and $2G$ are both safe enough provided the expansion mismatch is small. If the mismatch is great, they will both be unsafe, especially if the bond of glass to metal is very weak. When the bond is so strong that on crushing the seal in a vice the glass cracks off leaving a thin skin of glass adhering to the wire, and the glass shape is also correct, then even quite highly stressed type $2M$ rod seals can be safe. Type $3G$ window seals and type $1G$ flat seals are usually unreliable.

The more complex seal shapes can be analysed into the three basic types as shown in Fig. 10. Such constructions are useful for estimation of stress distribution.

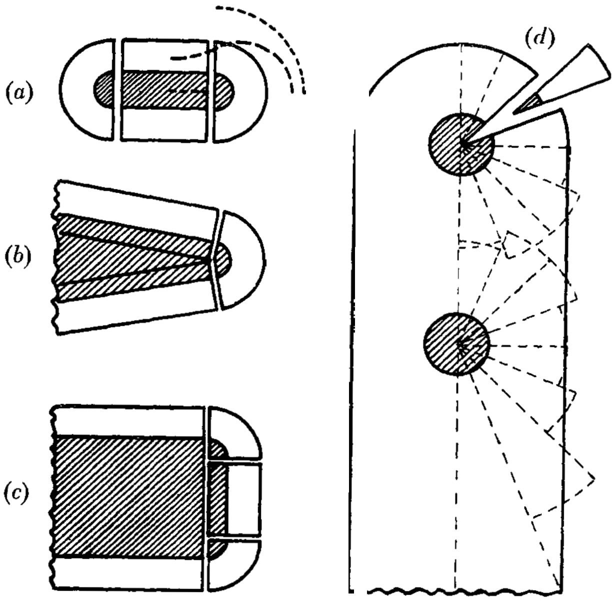

Fig 10. Examples of how complex seal shapes can be built up from the three basic types. The merging of the zero radial stress of a flat seal into the high radial stress in a sector of a rod seal is indicated in Fig. 10*a* by the broken lines

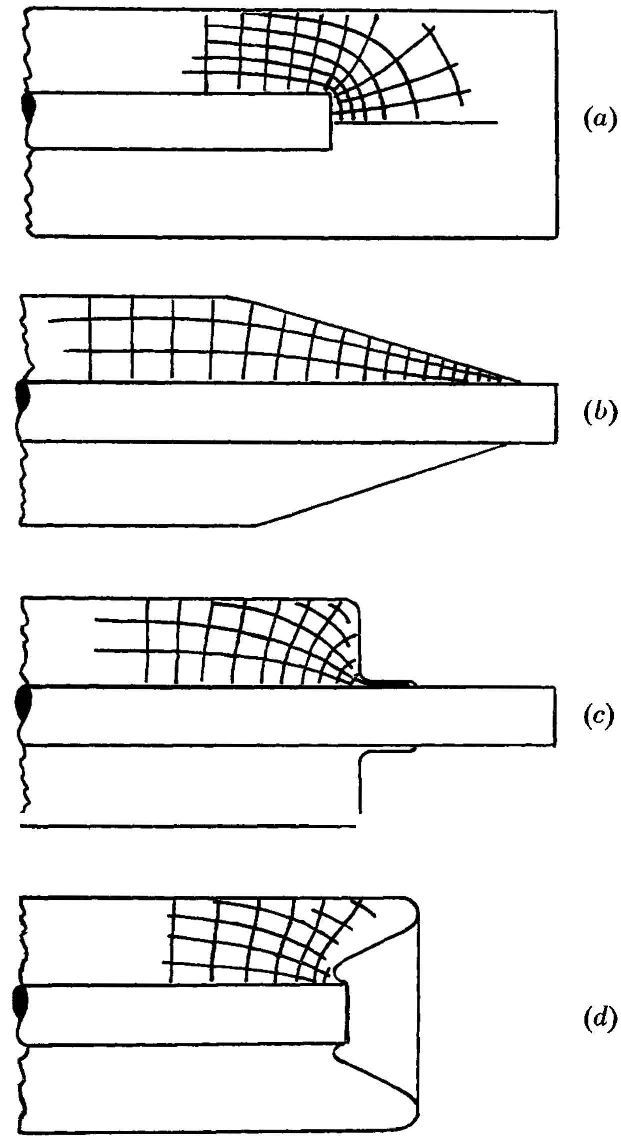

Fig. 11. Lines of principal stress in four rod seals. The pattern is the same for metal contracting more than glass and for glass contracting more than metal

Direction of principal stresses in the glass. The lines of principal stress (derived photoelastically) for four annealed rod seals are shown in Fig. 11. They indicate how high local 'mismatch' stress concentration can be caused by sharp corners. The intensity of stress may vary widely along any line. For example, where a tension line is perpendicular to a glass/air surface the tension falls off to zero at the surface.

Basic air/glass/metal constructional elements. There are two types of basic air/glass/metal constructional elements: (*a*) the interface type as shown in Fig. 12*a*; (*b*) the interlayer type as shown in Fig. 12*b*.

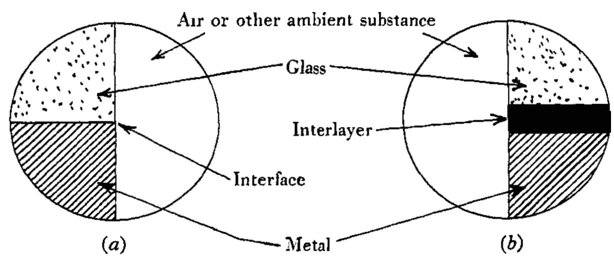

Fig. 12. The two basic air/glass/metal constructional elements

The strength and chemical stability (with the surrounding medium) of glass and metal in both types, and also of the interlayer in the second type, are of high importance because the shape of this triple or quadruple junction often critically affects local stress concentration, and, if chemical action is allowed to modify the physical properties or shape, even slightly, the seal may fracture. For example, in high-pressure mercury-vapour lamps operating at high temperatures in air, and with either glass or fused silica envelopes, molybdenum seals of both types have to be protected from oxygen attack either by an envelope filled with inert gas or by designing the outer end of the seal to operate below oxidation temperature. Any oxide formed occupies some three times the volume of the metal it replaces (see Table 1) and thus tends to cause the glass to 'burst' as in an overstressed type $1G$ seal. Again, in cleaning the metal part of a seal by acid, or by a reducing gas, the process should be such that there is no reaction with the interlayer which could produce a sharp crevice and thereby increase the local stress concentration to a dangerous value.

Stress along the glass/air surface, nigh and normal to the glass/air/metal junction (see Fig. 9*b*) can be either compression or tension according to the type of seal and glass angle, and will be as shown in Table 7.

From Tables 6 and 7, and a knowledge of the nature of the bond and its strength, the fitness of sealing materials for a given seal, or the best general seal shape for a given pair, can be deduced.

but definitely inferior to those with radial tension at the junction (type 2*M*). In window (type 3*M*) seal elements, the glass is enclosed by the metal and therefore (neglecting end cooling) will be at the same temperature throughout except under pulse conditions.

Fig. 13 shows seals with acute, normal and obtuse glass angles, and with radial tension or compression at the junction. The protecting wires are loaded in the direction of the arrow and are assumed to be strong enough to break the glass. In Fig. 13*aT* the weak edge crushes and a crack starts which,

Table 7. *Stress along the glass/air surface, nigh and normal to the glass/air/metal junction*

	Type *M*—*Metal* contracts more than glass			Type *G*—*Glass* contracts more than metal		
Glass angle (θg) ($\theta M = 180°$)	Acute (say 10°)	Normal 90°	Obtuse (say 170°)	Acute (say 10°)	Normal 90°	Obtuse (say 170°)
(1) Flat seal	Compression	Small	Tension	Tension	Small	Compression
(2) Rod seal	Compression	Tension	Tension	Tension	Compression	Compression
(3) Window seal	Compression	Compression	Tension	Tension	Tension	Compression

The effect of glass shape on the mechanical strength of rod seals. Internal strains may either increase or decrease the safety factor by helping or opposing the stresses produced by mechanical or thermal loads applied from without (23). When a seal wire of resistance R carries current I, the I^2R loss causes the wire and the glass sealed to it to become warm.

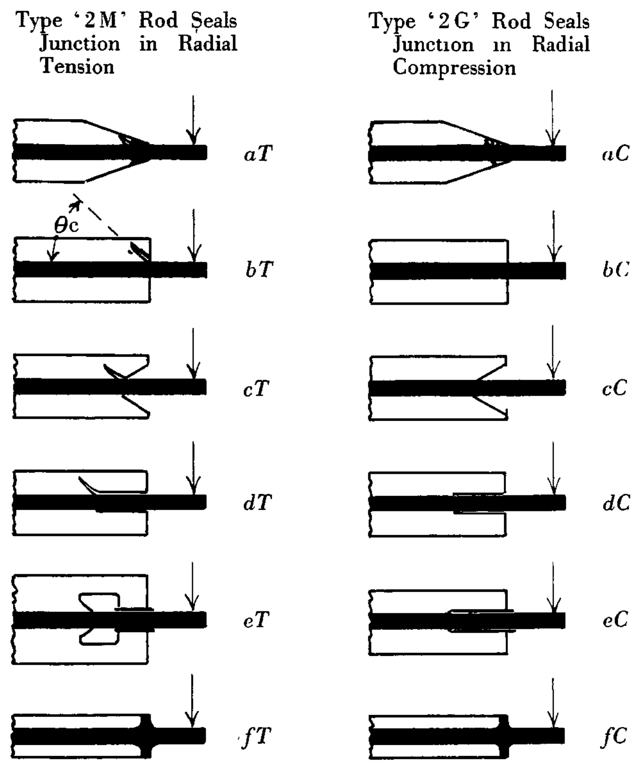

Fig. 13. Crack systems for rod seals loaded mechanically so that the free end is bent downwards

There will be a thermal gradient from the warm core to the cooler exterior. The wire and the inner glass will expand more than the outer glass and add axial and tangential tensions at the outside. When the glass sheath is thin, this stress is small because the temperature difference is small. It follows that in rod seals the current-carrying capacity of unstrained seals is greater than that of seals with radial compression (type 2*G*),

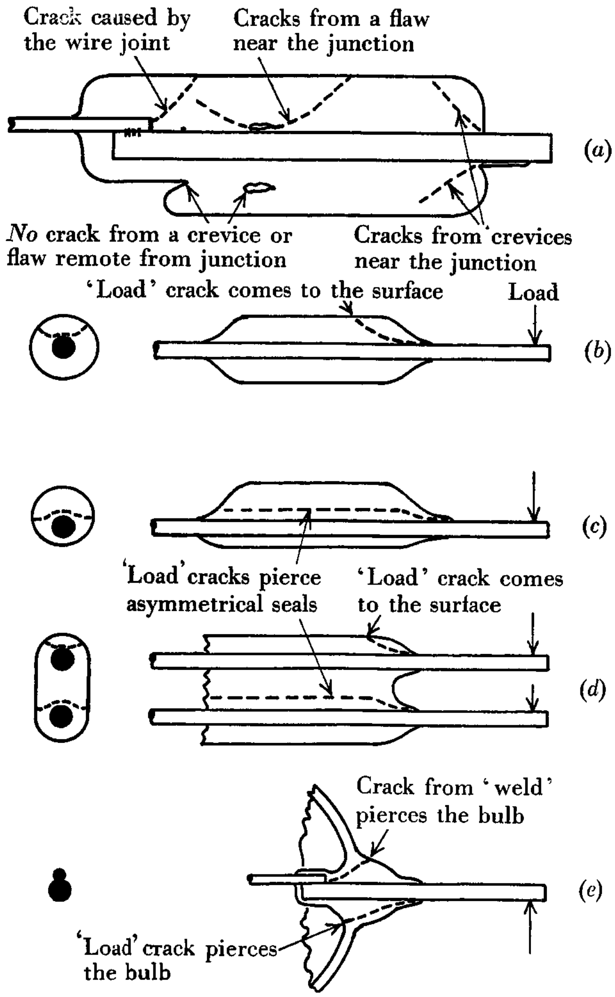

Fig. 14. Typical cracks in rod seals with radial tension and a strong bond, caused by external loading and/or mismatch stress

however, comes to the surface because the crack slopes more than the glass. In Figs. 13*bT*, 13*cT*, and 13*dT*, the crack pierces the glass. In Fig. 13*aC* (where there is radial compression at the junction) the thin glass crushes and cracks.

In Fig. 13*bC* the same happens, but at much greater loads. In Fig. 13*dC* the glass supports the wire and also gives it room enough to bend without causing cracks. Fig. 13*eC* is a variation of 13*dC* in which a thin copper sleeve permits the wire to slide. For seals with radial tension a similar support (Fig. 13*eT*) can be used if the functions of support and sealing are separated, but the method is complex. Figs. 13*fT* and 13*fC* show thin-edged disks radiused out from the wires. They convert the emergence regions from a type (2*M* and 2*G*) to type (1*M* and 1*G*) elements, but once again are complex to make.

Rod seals with radial tension. Fig. 14(*a*) shows a seal of molybdenum to C 14 glass incorporating a number of faults. On the right a steep glass angle (θg) allows the stress at the glass/metal/air junction to become so high that a crack develops. On the lower side a sharp notch rather near the interface allows a similar crack to start, but at the other end a similar notch, which is well away from the interface, fails to initiate a crack because it is in a region of low stress. Similarly, flaws at the junction produce cracks, but those farther out do not. One cause of flaws at the junction is dirt, either on or embedded in the metal or glass. Figs. 14*b*, *c*, *d* and *e* show cracks produced by bending the seal wires. The seal *b* is symmetrical and the crack therefore comes up to the surface. Seal *c* is asymmetrical and the crack travels along parallel with the wire and emerges through the other end. Similarly, in the twin wire seal of Fig. 14*d* a crack on the outside comes to the surface, while one between the wires goes right through. In Fig. 14*e* a wire is shown sealed into the wall of a bulb. A crack, started by bending the outer lead, pierces right through to the inside of the bulb and one started by the weld pierces to the outside.

Rod seal of molybdenum through C 14 *glass*

Rod seal of molybdenum through C 14 glass (Fig. 15*b*) is designed for high radial tension between the C 14 and molybdenum whose bonding is one of the strongest known. The seal has a chocolate brown interlayer. The seal ends are shaped in accordance with the recommendations of Table 6 and the glass is symmetrical. The weld is well back from the glass wall so that the crack, which occurs there inevitably, surfaces harmlessly without piercing the bulb into which the bead is sealed with adequate fillets at the joint. The outer portion projects far enough for any crack caused by bending the projecting wire to surface before reaching the bulb. As the operating temperature is increased, the radial stress gradually falls until it is zero at about 550° C. Seals of this type have high current-carrying capacity.

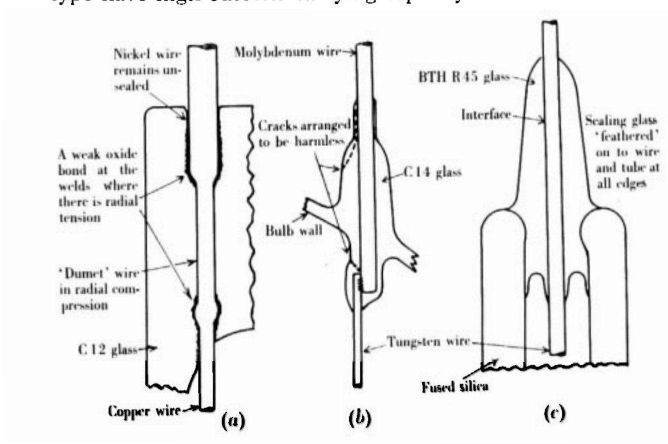

Fig. 15. Rod seals (*a*) copper-Dumet-nickel through C12 glass. (*b*) Molybdenum through C14 glass. (*c*) Tungsten into glass into fused silica

Rod seal of tungsten into glass into fused silica. Fig. 15(*c*) shows a section of a seal which is used in water-cooled silica glass lamps [39]. The bright seal [29] between the glass and tungsten is very strong, and as it is in radial tension the glass angle is made acute to keep the stress within safe limits. The glass into fused silica seal may also be looked on as a type 2*M* rod seal with radial tension, so again the glass angle has to be acute. The glass is tempered to some extent [21]. At the normal high-operating temperature the stresses will be lower than at room temperature.

Rod seal of copper-Dumet-nickel through C 12 *glass.* A Dumet [20] seal widely used in lamps and radio valves is shown in cross-section in Fig. 15*a*. These seals are made on carefully controlled automatic machines, which heat the glass and wire correctly. The soft glass is squeezed on to the wire and then heated for some time longer to cause thorough wetting; a borax film protects the Dumet wire from over-oxidation. However, as the copper and nickel wires are not borated, and are indeed left 'unclean', the copper wire and its weld are covered with a weak oxide layer which forbids a good tension bond. Hence the copper shrinks away from the glass without cracking it. The nickel is kept cool by a metal die in which it is held, and its weld is covered with a weak oxide layer. The result is that the nickel does not bond strongly to the glass and, like the rod in Fig. 13*dC*, is strongly supported.

TWO RECENT DEVELOPMENTS

Glass/metal/terminal seals. Fig. 16 is a photograph of a group of glass/metal terminal seals intended for hermetic sealing of electrical equipment such as condensers, transformers and radio gear. They are made from iron-nickel-cobalt 54/29/17 sealing alloy and B.T.H. C40 low-expansion borosilicate glass and are therefore highly resistant to thermal shock. They are electro-tinned to facilitate soldering and are suitable for use at temperatures ranging from below −50° C. up to well beyond the effective relaxation temperature of the solder used for wiring them in circuit.

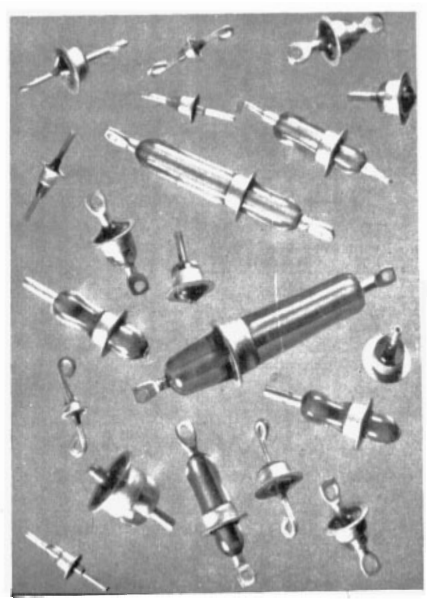

Fig. 16. A photograph of glass/metal terminal seals made for hermetic sealing of electrical equipment (three-quarters full size)

Steel-glass windows. The advent of the new glasses [40] for sealing to iron, which is one of the cheapest of all metals, has led to the introduction of a new product, namely, the steel-glass window [41], which consists, as a rule, of a hollow copper-plated mild steel 'frame' into which a window of iron-sealing glass is cast to form a type $3M$ window seal.

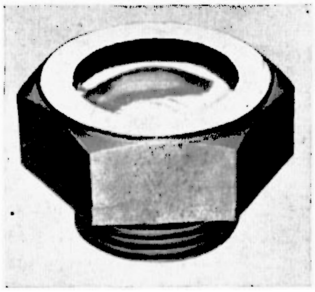

Fig. 17. A photograph of a steel-glass 'Windonut'

The metal body is held at red heat during casting to ensure a sound union of glass and metal. Fig. 17 shows a typical Windonut which was designed primarily for use in an oil-level indicator and has a 1 in. diameter window cast and moulded into a hexagon headed 1 in. B.S.P. screw. The unit is designed to be screwed home with a spanner and withstands hydraulic pressures up to 2 or more tons/in.^{2}.

The co-operation of my colleague Mr J. E. Stanworth, Glass Technologist to the B.T.H. Co. Ltd., and of Mr A. E. Dale and Mr G. D. Redston of his group, who made the measurements of the physical properties of glasses and the stress-temperature curves of seals is much appreciated. The author thanks Mr L. J. Davies, Director of Research, for permission to publish this paper.

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(2) 500 B.C. Greece (enamelled gold).
(3) 50 B.C. Ancient Britain (red enamel on bronze).
(4) 1200 Middle Ages (enamel on gold, silver and copper).
(5) 1600 Mirrors backed with tin amalgam (Venice).
(6) 1643 Torricelli (barometer seal of glass to mercury).
(7) 1744 Platinum discovered.
(8) 1821 Wollaston (platinum sealing wire developed. Used by Davy).
(9) 1879 Edison (incandescent lamp with platinum wire seals).
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