Glass-Sealing Alloys

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To meet the needs of the growing number of applications of glass-to-metal seals, a whole family of special glass-sealing alloys has been developed. Steel industry metallurgists, working with glass experts, have developed a complete series of alloys that can be used for matched or compression seals with most of the glasses normally used for sealing applications. In this article, Mr. Eberly discusses these special alloys and some of the design considerations important to their successful application.

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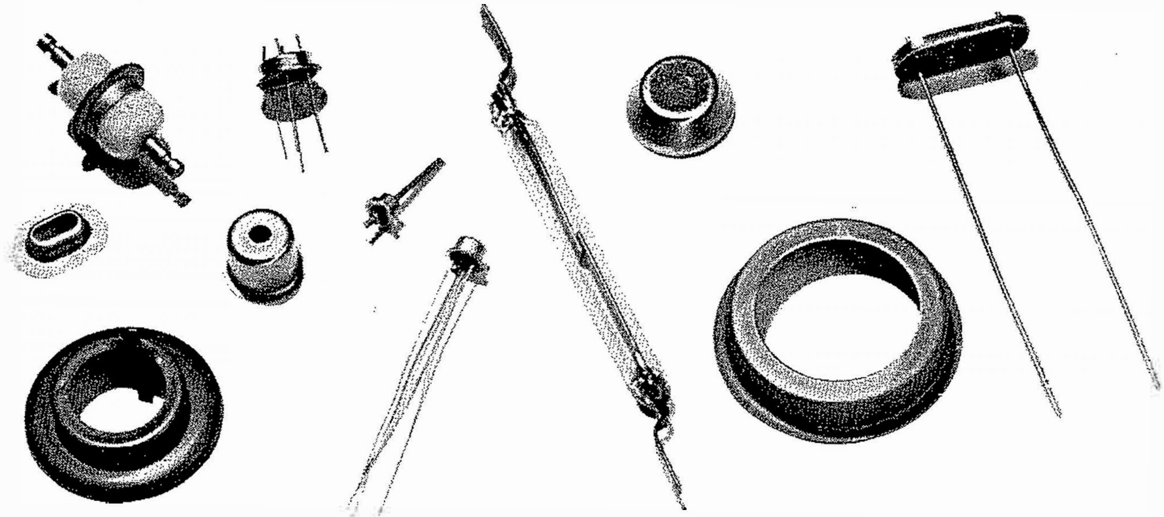

Glass-Sealing Alloys

By Warren S. Eberly, Metallurgist, High Nickel and Special Alloys, The Carpenter Steel Co., Reading, Penna.

There are a growing number of applications where glasses have to form a perfect seal with metals. Air tight glass-to-metal seals are needed for vacuum tubes, transformers, capacitor bushings, resistors, transistors, high-voltage lamps, insulators, mercury switches and similar products. In addition, sealing is important in the manufacture of X-ray, audio, microwave, electron and similar tubes.

GLASSES, like metal, expand when heated and shrink when cooled, but they usually expand less than conventional metals like copper, aluminum and silver over the same temperature range. This difference in expansion makes it difficult to join such metals to glass and keep the glass from cracking when the assembly is heated and cooled in service.

The basic objective in designing a tight seal is to prevent undue strains from setting up in the glass when cooling it after sealing. These strains are minimized by making seals with metal alloys having thermal expansion characteristics (Table I) similar to those of glasses. Ideally, the alloy used for sealing would have exactly the same thermal expansion characteristics as that of the glass. However, exact matching is a rare possibility. If the expansion coefficients of the glass and metal are reasonably close through the anticipated temperature range, there is little danger of undue strain developing in the glass when cooled from the sealing temperature and annealed.

With respect to thermal expansion, there are three types of glasses: hard, with thermal expansion coefficient up to 2.5 x $10^{-6}/°F$; semi-hard, with expansion coefficient of 2.5 to about 5 x $10^{-6}/°F$; and soft, with coefficient above about 5 x $10^{-6}/°F$.

A high wattage lamp (Fig. 1) is a good example of the general problems involved in sealing glass to metal. In this application, two metal conductors must go through the Pyrex glass, leaving a vacuum tight seal. Assuming it were possible to pass a copper wire through the glass and seal it at room temperature, the glass would crack at the seal the first time it was heated because of the high stresses built up by the difference in expansion. If this lamp were heated to 300°F in service, for example, the stress developed in the glass at the seal would be 30,000 psi, which, of course, is much more than glass can take. However, when using the proper glass-sealing alloy, the maximum stress in the glass—even when heated to 900°F—is only about 2000 psi, and this the glass can withstand (Table II) without cracking. The stress can be further reduced by good design, such as the use of thin sections, or feathered edges, where the metal is imbedded in the glass. The thin metal will then distort slightly to prevent excessive strains in the glass. Any strains which result from difference in contraction rate are minimized by the relatively light metal sections, and proper subsequent cooling technique.

In sealing glass to metal, the glass must wet and stick tightly to the metal surface when both materials reach the working temperature of the glass. There should be no sharp change in the metal's expansion rate between the setting temperature of the glass and the lowest temperature expected in final service. The glass must not reboil when heated, nor should the metal produce gases. Standard sealing procedures for glass-to-metal sealing are:

1. Cleaning of the metal.
2. De-gassification of the metal (if necessary).
3. Oxidation of the metal.
4. Application of the glass.
5. Annealing.

The types of seals commonly referred to are as follows:

1. Internal Seal. Metal rod enclosed by glass.
2. External Seal. Glass enclosed by metal cylinder.
3. Tubular Seal. Metal cylinder sealed to a glass cylinder.
4. Butt Seal. Glass cylinder sealed to a flat piece of metal.
5. Window Seal. Flat piece of glass sealed to an opening in a flat piece of metal.
6. Ring Type Seal. Similar to a tubular seal employing a glass and metal having a difference in expansion. Metal part has a feathered edge (Fig. 2) inserted into the glass and the metal is able to absorb the difference in expansion.

Standard Alloys

When designing a seal, the engineer can choose from approximately seven standard glass-to-metal sealing alloys. The expansion (Fig. 3 and 4) characteristics of the selected steel and glass must compare closely to minimize stresses at the seal in application. If design is changed from a small to a larger seal, the resulting stresses may necessitate using still another alloy.

Most commonly used of all sealing alloys (Table III and IV) is a 29 per cent nickel—17 per cent cobalt-iron alloy (ASTM F-15) with thermal expansion properties closely matching those of the harder glasses. This is a low expansion material used for making vacuum-tight seals. The expansion rate remains low up to approximately 815°F, the Curie point* for this alloy.

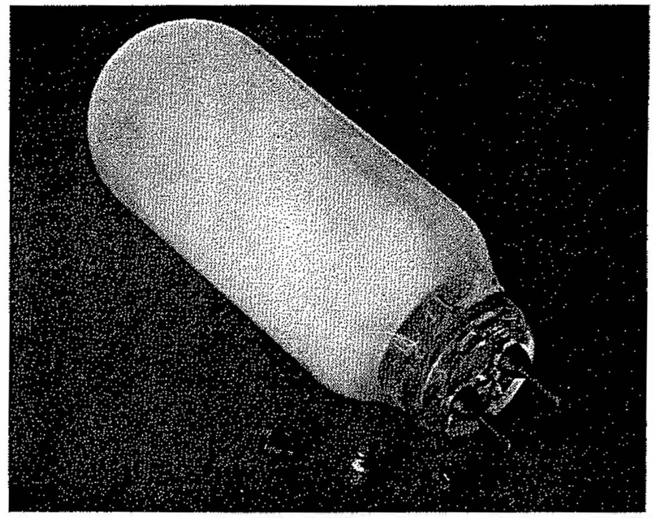

Fig. 1. Metal conductors must be sealed to Pyrex glass in this high-wattage lamp.

Another important glass-to-metal sealing alloy is the 42 per cent nickel-iron alloy (Fig. 5) used for sealing a

*Curie point is the approximate temperature at which a metal loses is magnetism on heating or regains it on cooling. Inflection point is in this same range.

TABLE I—Typical thermal expansion coefficients (as annealed) for the more common glass and ceramic sealing alloys.

Temperature Range	42% Ni-Fe	42% Ni-Fe Gas Free	42% Ni-6% Cr-Fe	45% Ni-6% Cr-Fe	46% Ni-Fe Gas Free	51% Ni-Fe	28% Cr-Fe	29% Ni-17% Co-Fe (ASTM F-15)
				(in./in./°C x 10⁻⁶)				
25°C — 100°C	4.63	4.34	6.55	7.60	7.10	9.95	9.46	5.86
25 — 200	4.76	4.41	7.08	8.17	7.37	10.10	10.05	5.20
25 — 300	4.88	4.61	8.26	8.75	7.50	10.10	10.53	5.13
25 — 350	5.02	5.35	9.04	9.00	7.44	10.02	10.70	4.89
25 — 400	5.65	6.41	10.00	10.00	7.43	10.10	10.78	5.06
25 — 450	6.90	7.53	10.60	10.50	7.91	10.04	10.90	5.25
25 — 500	7.78	8.56	11.50	11.22	8.68	10.21	11.12	6.15
25 — 600	9.90	10.01	12.58	12.23	10.02	11.00	11.26	7.80
25 — 700	11.00	11.15	13.40	13.02	10.99	11.80	11.62	9.12
25 — 800	11.99	12.10	14.15	13.70	11.82	12.50	11.65	10.31
25 — 900	12.78	—	14.70	—	—	13.10	12.78	11.26
				(in./in./°F x 10⁻⁶)				
77°F — 212°F	2.57	2.41	3.64	4.22	3.95	5.53	5.25	3.25
77 — 392	2.64	2.45	3.94	4.54	4.09	5.61	5.60	2.89
77 — 572	2.71	2.56	4.59	4.86	4.16	5.61	5.86	2.85
77 — 662	2.79	2.97	5.02	5.00	4.13	5.57	5.94	2.72
77 — 752	3.14	3.56	5.56	5.56	4.12	5.56	5.98	2.81
77 — 842	3.83	4.17	5.89	5.84	4.40	5.59	6.06	2.92
77 — 932	4.32	4.75	6.39	6.24	4.82	5.68	6.19	3.41
77 — 1112	5.50	5.57	6.99	6.80	5.58	6.11	6.25	4.34
77 — 1292	6.11	6.20	7.45	7.24	6.10	6.56	6.46	5.06
77 — 1472	6.65	6.73	7.87	7.62	6.57	6.97	6.48	5.73
77 — 1652	7.10	—	8.17	—	—	7.28	7.09	6.25

TABLE II—Basic mechanical properties (as annealed) of the more common glass and ceramic sealing alloys.

	42% Ni-Fe	42% Ni-Fe Gas Free	42% Ni-6% Cr-Fe	45% Ni-6% Cr-Fe	46% Ni-Fe Gas Free	51% Ni-Fe	28% Cr-Fe	29% Ni-17% Co-Fe (ASTM) F-15)
Tensile Strength, psi	82,000 120,000*	80,000	80,000	80,000	82,000	80,000	85,000	75,000
Yield Strength, psi	—	34,000	40,000	40,000	34,000	40,000	55,000	50,000
Elongation in 2", %	30 3*	30	30	30	27	35	25	30
Hardness	B-76 B-100*	B-76	B-80	B-80	B-76	B-83	B-85	B-68
Elastic Modulus, psi x 10⁻⁶	21.0 21.0*	21.0	—	—	23	—	—	20

*Values for cold drawn bars and cold rolled strip.

TABLE III—Type analyses of common glass-to-metal sealing alloys.

	42% Ni-Fe	42% Ni-Fe Gas Free	52% Ni-6% Cr-Fe	45% Ni-6% Cr-Fe	46% Ni-Fe Gas Free	51% Ni-Fe	28% Cr-Fe	29% Ni-17% Co-Fe (ASTM F-15)
Carbon	0.10%	0.05%	0.10%	0.10%	0.10%	0.10%	0.15	0.02%
Manganese	0.50	0.50	0.50	0.30	0.50	0.50	0.60	0.30
Silicon	0.25	0.25	0.25	0.30	0.25	0.25	0.40	0.20
Nickel	42.00	42.00	42.50	45.00	46.00	51.00	0.50	29.00
Iron	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Chromium	—	—	5.75	6.00	—	—	28.00	—
Titanium	—	0.40	—	—	—	—	—	—
Cobalt	—	—	—	—	—	—	—	17.00

TABLE IV—Basic physical properties of the more common glass and ceramic sealing alloys.

	42% Ni-Fe	42% Ni-Fe Gas Free	42% Ni-6% Cr-Fe	45 Ni-6% Cr-Fe	46% Ni-Fe Gas Free	51% Ni-Fe	28% Cr-Fe	29% Ni-17% Co-Fe (ASTM F-15)
Specific Gravity	8.12	8.12	8.12	8.14	8.17	8.30	7.6	8.36
Density—lbs. per cu. in.	0.293	0.293	0.294	0.295	0.295	0.30	0.27	0.302
Thermal conductivity								
cal./cm³/sec/°C	0.025	0.025	0.029	0.029	—	0.032	0.054	0.04
BTU/hr./sq. ft./°F/in.	74.5	74.5	87.0	87.0	—	97	158	—
Electrical Resistivity								
microhms/mc³	72	72	95	95	46	43	63	—
ohms per cir. mil. ft.	430	430	570	570	275	258	380	294
Inflection point	650°F	—	650°F	680°F	—	1050°F	—	—
Curie Temperature	715°F	380°C	—	—	460°C	—	—	815°F
Melting Point	2600°F	1425°C	2600°F	2600°F	1425°C	2600°F	2600°F	2640°F
Specific Heat	0.12	0.12	0.12	0.12	0.12	0.12	0.14	—

number of special electronic tubes, transformers and capacitor bushings. It may be used with hard glasses when employing a ring-type or housekeeper-type seal with a feathered edge about 0.002 in. thick.

A slight variation of the 42 per cent nickel-iron alloy is used as the core of Dumet wire for leads in electron tubes, fluorescent and incandescent lamps. The Dumet wire, which is clad with copper amounting to about 20 per cent of the overall cross section, provides good seal with soft glasses when used in diameters of about 0.008 to 0.040 in. Another variety of this alloy has been of service, too, in making ferrules for passing a high current into a vacuum, using Pyrex glass.

A 42 per cent nickel—6 per cent chromium-iron alloy has thermal expansion properties suitable for sealing with soft glasses and the 0010 and 0120 glasses. This metal offers an important advantage in that it produces a dark green chrome oxide when heat treated in a wet hydrogen or wet dissociated ammonia atmosphere. The oxide fluxes with the glass and makes a strong, vacuum-tight seal tightly adhering to the base metal.

Tendency of this nickel-chromium-iron alloy to form a chrome oxide during heat treatment provides advantages in making terminals which must be vacuum tight and withstand twisting and other stresses. A good glass-to-metal seal is possible due to the fact that the chrome oxide is soluble in the glass when the glass-to-metal

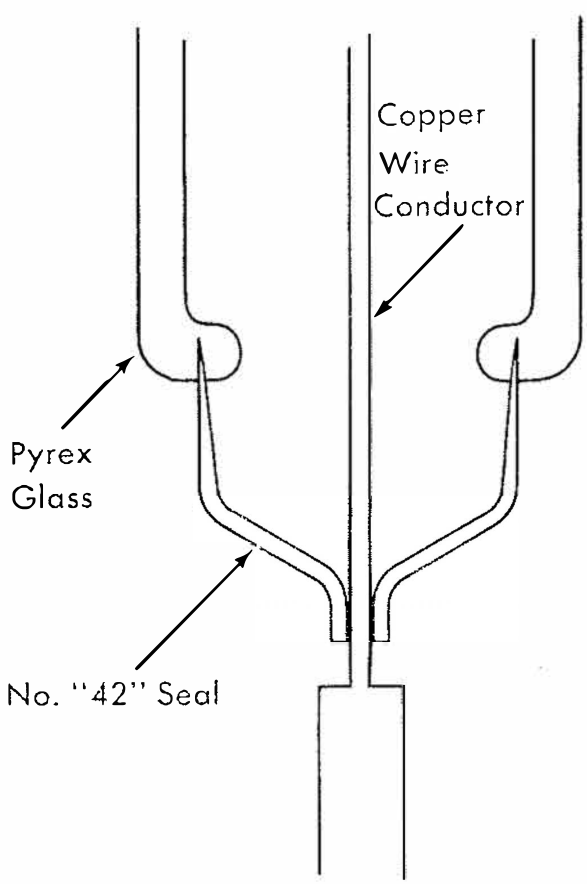

Fig. 2. Stress in glass is minimized by tapering edge of seal so metal will bend elastically.

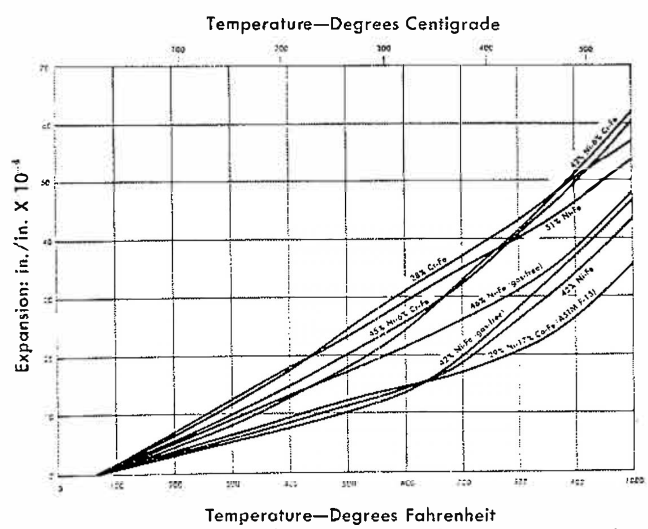

Fig. 3. Expansion rates of common glass and ceramic sealing alloys. All metals are in annealed condition.

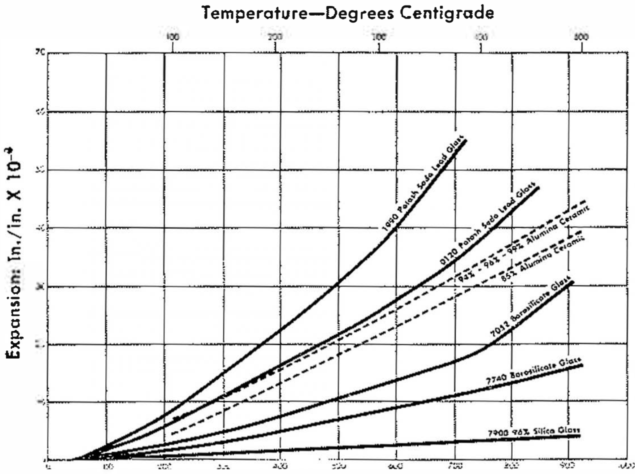

Fig. 4. Expansion rates of common glasses and ceramics.

match is good. For some types of seals, the 42-6 alloy can provide satisfactory service with the 9010 glass.

The 42-6 alloy is also used to make pressure type seals which are soldered onto cans and containers. Terminals generally consist of an SAE 1010 grommet, a soft glass and a 42-6 pin. Due to the high expansion of the 1010 steel, the grommet (Fig. 7) exerts compressive stresses on the glass. The 42-6 pin withstands the resultant strain because the 42-6 alloy has a lower expansion rate than the 1010 steel and also the glass.

There is a 45 per cent nickel—6 per cent chromium-iron alloy which is better suited to the 9010 glass than the 42-6 alloy because their expansion rates match very closely. This 45-6 alloy has about the same expansion coefficient at 752°F as the 42-6 alloy. But in the temperature range of 400°F to 575°F, the expansion characteristics of the 45 per cent nickel alloy are higher than those of the 42-6 material. Like the 42-6 alloy, the 45-6 steel is also suitable for sealing with the 0010 and 0120 glasses. The higher nickel alloy also produces an oxide coating conducive to a good seal when heat treated in a wet hydrogen or wet cracked ammonia atmosphere.

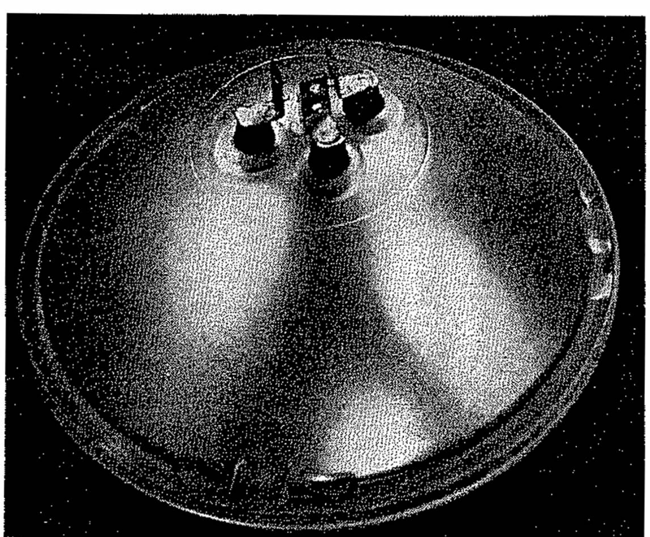
Fig. 5. Hard glass for sealed beam headlight is sealed by ferrule of 42 per cent Ni-Fe alloy. Ferrule is drawn out of very light gage strip and feathered down to thin edge.

A 51 per cent nickel-iron alloy can be used to make many direct glass-to-metal seals with some soft glasses. It is applicable also for terminals using 1010 grommets. These seals, however, are not as strong as the terminal seals using the 42-6 alloy because the 51 per cent nickel alloy is more prone to twist in the glass seal. On the other hand, the 51 per cent nickel grade is easy to acid clean for plating after the glass-to-metal seal is made.

Soft glasses such as lead glass and lime glass can be matched quite well by a 28 per cent chromium-iron alloy. This is a ductile alloy used most commonly in lumiline and Circling lamps. In some cases it can be used to advantage in special electronic devices and vacuum tubes.

There is still another important glass-sealing alloy: a 46 per cent nickel-iron alloy designed for enamel coating, glass-to-metal sealing and ceramic-to-metal sealing.

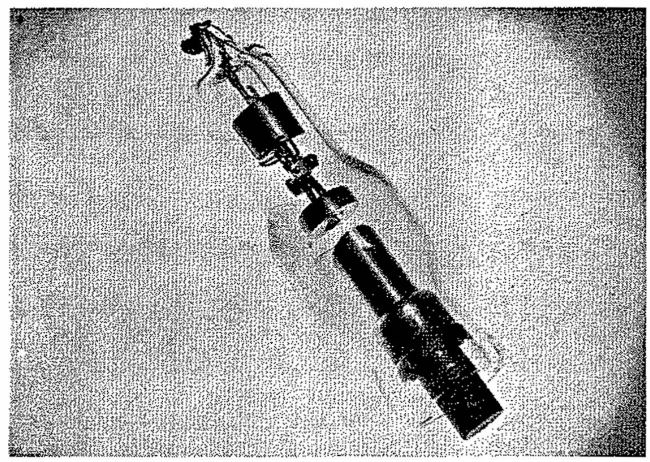
Fig. 6. This high-voltage X-ray tube is typical of the many types of tubes requiring vacuum-tight glass-to-metal seal.

Oxide Film Formation

All sealing alloys form an oxide film during heat treatment (either in special preoxidizing treatment or in the sealing process). The best film for sealing is that of chrome oxide because it is the most tightly adhering to the base metal. Chrome oxide films or coatings are generally produced when annealing the 42 per cent nickel—6 per cent chromium-iron alloy, the 45 per cent nickel—6 per cent chromium-iron alloy, and the 28 per cent chromium-iron alloy. If heat treatment is done properly, the oxide film produced on the surface of the alloy is quite strong and tenacious; in fact, the bond holding the parent metal and glass together at the seal can be stronger than the glass itself. It is possible to break the seal and still leave a shiny film of glass on the surface of the part.

Avoid Gas Pockets

A major problem encountered in making glass-to-metal seals is the tendency for gas pockets to develop between the glass and metal. Subsequent cracking occurs at the seal. Under such conditions, it is impossible to get the air-tight seal required for many applications.

Gas is caused by a chemical reaction in the sealing process. Conventional iron-nickel alloys, containing no chromium, tend to eject carbon monoxide and carbon dioxide from the metallic lattice when heated. This emission can be eliminated by decarburizing the surface of the part with an anneal in wet hydrogen atmosphere, by keeping carbon content low, or by tying up the carbon through formation of a stable carbide.

Users can eliminate gas pockets by hydrogen annealing or degassifying the alloy before sealing. Those who

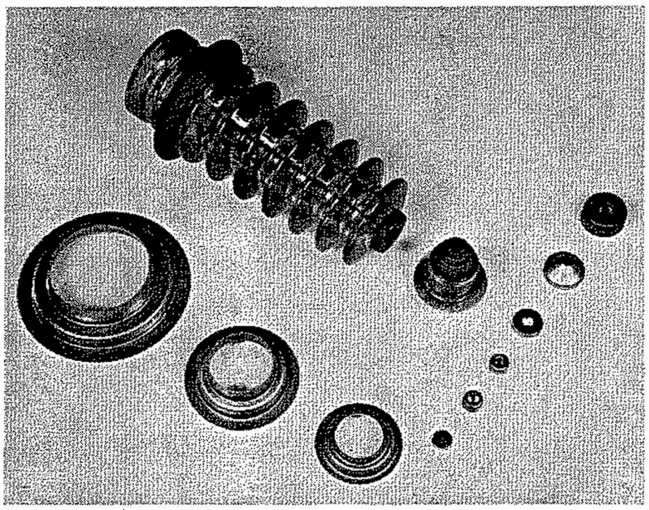

Fig. 7. Grommets for high-voltage bushings must be made from an alloy which, from lot to lot, will stay consistently within narrow range of expansion limits.

are not equipped for hydrogen annealing must depend on a supplier providing a gas-free alloy. Vacuum melting, careful annealing and special alloying elements are means of providing gas-free properties.

Availability of Alloys

All of the basic sealing alloys are available in various forms including cold rolled strip, cold drawn wire, and bars—either hot rolled, cold drawn, or centerless ground. Generally strip is purchased in deep drawn condition with its surface free of any oxides, annealed with either a bright and clean finish, or annealed for deep drawing applications. Several alloys are available in billet form for forgings.

The metals described herein will serve about 90 per cent of all glass-to-metal or ceramic-to-metal sealing applications. If the grades discussed here do not provide the characteristics to produce certain type seals, there is always a possibility that adjustments in analysis can be made to vary the necessary properties.

Production of sealing alloys requires the utmost in steelmaking quality controls because, pound after pound, the alloy must have the same expansion characteristics. Chemical composition must be controlled within narrow limits to assure both consistent and precise expansion properties. Non-metallic inclusions must be kept to a minimum to assure freedom from pinholes which can develop in seals. Processing of every alloy from ingot to finished size must be done under strictest controls to provide uniform physical and mechanical properties and easier deep drawing, stamping and machining. Grain size must be controlled for better forming properties and for the elimination of earing and orange peel in parts drawn from strip.

If you would like more information on special alloys for glass-to-metal and ceramic-to-metal sealing, write for a copy of the Carpenter booklet, Carpenter Electronic, Magnetic and Electrical Alloys.

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Glass - Sealing alloys .. W S Eberly

a exact glass - metal matching is a rare possibility
b. hard glasses COE's up to 2.5×10^{-6} per °F (4.5×10^{-6} per °C)
c. stress can be reduced by good design ie thin sections, feathered edges. (thin metal will distort slightly to prevent excessive strains in the glass)
d. there should be no sharp change in metals contraction rate (?) between setting temp of glass + lowest temp expected in final serve. The glass must not reboil when heated, nor should the metal produce glasses.

NB. steelmaking quality controls

Chemical composition must be controlled within narrow limits to ensure consistent expansion properties

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processing from ingot to finished size must be done under strictest controls to provide uniform physical and mechanical properties and easier deep drawing, stamping, + machining

grain size must be controlled especially for better forming properties to eliminate earing + orange peel in deep drawn parts

surface quality (free from oxides) bright, clean finish