

FIG. 3. Alloy activated for maximum initial gain.

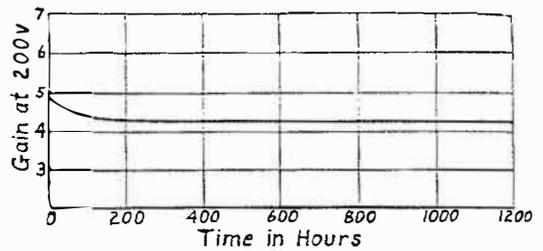


FIG. 4. Alloy activated for maximum stable gain.

multipliers, is its very low dark current,<sup>1</sup> as compared with the commonly used types of emitters employing alkali metals in their formation.

Although evidence upon which to base an explanation of the secondary emission behavior of the alloy is not conclusive, one reasonable hypothesis is that the stable gain of about 4 is due to the silver-magnesium oxide itself, while the higher gains are due to oxygen adsorbed or absorbed in the silver-magnesium surface. The initial rapid decrease in gain with time of operation is due primarily to the surface losing its absorbed oxygen. Thereafter the behavior is a function of ion bombardment, loss of oxygen by

<sup>1</sup> Z. Bay, Rev. Sci. Inst. 12, 127 (1941).

the surface, and rejuvenation by oxygen from other parts of the tube.

Another possible explanation is that the high gain is due to the Ag-MgO and that the decay under bombardment is caused by the decomposition of the MgO with the liberation of oxygen (which is taken up by the getter), and thus the gradual formation of a surface of silver magnesium. Curves of the type shown in Fig. 4 would be explained by the formation of a less decomposable silver-magnesium oxide structure.

Although there are many points of both theoretical and practical interest that still need clarifying, the use of the alloy as a secondary electron emitter in certain types of thermionic tubes is now feasible.

## Glass-to-Metal Seals. II

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(Received June 25, 1941)

This is a continuation of the work reported in 1934. The greater part of the paper is devoted to a discussion of the properties of iron-nickel-cobalt alloys, especially the composition Fe 54 percent, Ni 31 percent, Co 15 percent—called fernico—including sensitiveness to impurities and polymorphism. Three new glass-metal combinations are described, the metals being 42 percent nickel-iron, 26 percent chromium-iron, and pure iron, respectively. The strength of the glass-metal bond is discussed briefly.

### 1. INTRODUCTION

IN a previous article<sup>1</sup> we showed how the stress in wire seals can be calculated from the difference in expansion of wire and glass; and the calculated stresses in test seals were compared with photoelastically observed stresses for a number of common sealing materials. A new alloy of composition Fe 54 percent, Ni 28,

<sup>1</sup> A. W. Hull and E. E. Burger, Physics 5, 384 (1934).

Co 18 was described, whose thermal expansion matched very closely, over the whole range from room temperature to the sealing temperatures, the expansion of a special glass, 705-AO, developed by the Corning Glass Works for this purpose. It was shown that seals made with this alloy and 705-AO glass were practically free from strain.

The present article gives the results of a continuation of these studies. It includes the

properties of iron-nickel-cobalt alloys, especially an alloy of composition Fe 54 percent, Ni 31, Co 15; which will be referred to as fernico. Two new glasses that seal to 42 percent nickel-iron and pure iron, respectively, are described. Some data on the strength of seals are given.

## 2. FERNICO

Iron-nickel-cobalt alloys have two properties which recommend them for sealing purposes: (1) Their thermal expansion in the neighborhood of room temperature is less than that of any other available metals or alloys, with the exception of tungsten and molybdenum. This is important for seals, because it allows the use of low coefficient glasses which are less likely to be broken by sudden changes of temperature than glasses of high expansion. (2) The thermal expansion of these alloys is non-linear like that of glasses, thus affording the possibility of a glass and metal with identical thermal expansion. The non-linear property of Fe-Ni-Co alloys appears to be associated with ferromagnetism; the expansion being low in the temperature range in which the alloy is ferromagnetic, and increasing by a factor of three at the temperature (Curie point) at which ferromagnetism is lost.

The expansion curves of the Fe-Ni-Co alloys which are of interest are shown in Fig. 1, compared to molybdenum, against which they were measured. It will be noted that the temperature of the transition from low to high expansion rises with increasing cobalt content, up to about 18 percent. However, as this percentage is approached, the alloy becomes less and less stable with respect to the  $\gamma \rightarrow \alpha$  transformation (see next section). The composition 54 percent Fe, 28 Ni, 18 Co represents the highest transition temperature for stable low coefficient alloys.

The transition temperature of low expansion glasses, on the other hand, is in general high—higher than that of any of these alloys, or any known low expansion alloys; and the glasses become less stable, especially with respect to water solubility, the lower their transition temperature.

For strain-free seals the transitions of glass and metal should coincide, as well as their average expansions. This requirement could be

satisfied only by choosing a metal alloy having the highest possible transition temperature, and a glass with the lowest possible transition temperature. The combination of 705-AO glass and 54 Fe, 28 Ni, 18 Co, given in our former paper, appeared to be the closest match obtainable.

Since that paper was published, we have succeeded in matching the expansion and transition of 705-AO glass with a still more stable alloy, *viz.*, 54 Fe, 31 Ni, 15 Co. This alloy is a correct match only when free from all impurities, including manganese and silicon, which are considered essential to the ductility of cast nickel alloys. We have found that pure Fe-Ni-Co alloys, without manganese or any other added element, made in hydrogen by the sintering process under proper conditions, are ductile and free from embrittlement under all the conditions of ordinary use. These conditions include heating and annealing in air, hydrogen, or gas; soldering; brazing; and welding. The following Table I gives some of the physical properties of pure 54 Fe, 31 Ni, 15 Co, made in this way. This alloy will be designated as *fernico*.

Figure 2 shows the thermal contraction of

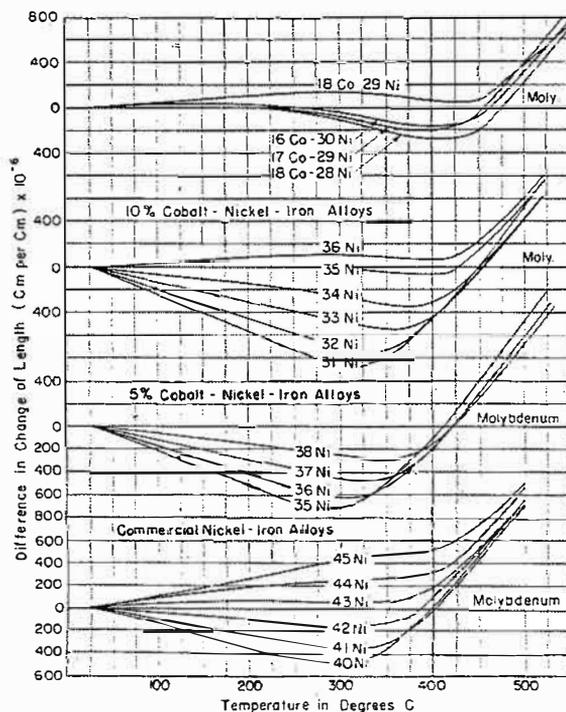


FIG. 1. Thermal expansion of iron-nickel-cobalt alloys, compared to molybdenum.

TABLE I. *Physical properties of fernico: Fe 54, Ni 31, Co 15*

|                                      |   |
|--------------------------------------|---|
| Tensile strength                     | —72,000 to 80,000 lb. per sq. in.         |
| Percent elongation                   | —25 to 33                                 |
| Percent reduction in area            | —62 to 63                                 |
| Elastic modulus                      | — $18 \times 10^6$                        |
| Density                              | —8.24 grams per cc                        |
| Electrical resistivity               | —43.8 microhms per cm cube                |
| Temperature coefficient of expansion | — $4.95 \times 10^{-6}$ from 25° to 300°C |
| Melting point                        | —1460°C                                   |
| Hardness                             | —75 "Rockwell B"                          |
| Yield point                          | —55,000 lb. per sq. in.                   |

fernico and of 705-AO glass. These curves were taken during cooling at the rate of 1 degree/min. from above the annealing temperature of the glass. Hence the close agreement of the curves from the annealing temperature down to room temperature means that glass and metal, if joined together at the annealing temperature, will contract at the same rate as they cool, and be free from strain both during cooling and after reaching room temperature.

The confirmation of this prediction is shown by the insert in Fig. 2, which gives the photoelastic stress pattern<sup>2</sup> of a test seal made with these materials and cooled at the rate of 1 degree/min. In this pattern, stress in the glass is indicated quantitatively by bending of the interference lines where they cross the samples. For the seal here shown, *viz.*, 705-AO glass of diameter 7.5 mm on a fernico wire of 2.5 mm diameter, a deviation of one-tenth the distance between fringes would represent an axial stress of 0.20 kg/mm<sup>2</sup>. The lines in Fig. 2 are straight within one one-hundredth of a fringe, showing that the stress is less than 0.02 kg/mm<sup>2</sup>.

#### Dependence of stress on composition of alloy

The chief criterion for freedom from stress in seals is close agreement of both the expansion coefficients and the transition temperatures of metal and glass. This agreement depends principally upon composition of glass and alloy. The sensitiveness of this agreement to composition of the alloy, and hence the maximum allowable variations in composition, can be calculated easily, if expansion and transition temperature are expressed as functions of composi-

tion.<sup>3</sup> Instead of transition temperature, it is more useful to calculate the "sealing temperature," defined as the temperature of intersection with the expansion curve of a line 15 percent greater in slope than the average expansion coefficient between 0° and 300°C (see Fig. 2). A point so determined on glass curves represents quite accurately the sealing temperature of borosilicate glasses used with these alloys; hence it also represents the sealing temperature of a metal which matches the glass.

Values of sealing temperature of iron-nickel-cobalt alloys as defined above were obtained from thermal expansion curves like those in Figs. 1 and 10, and are plotted in Fig. 3 as a

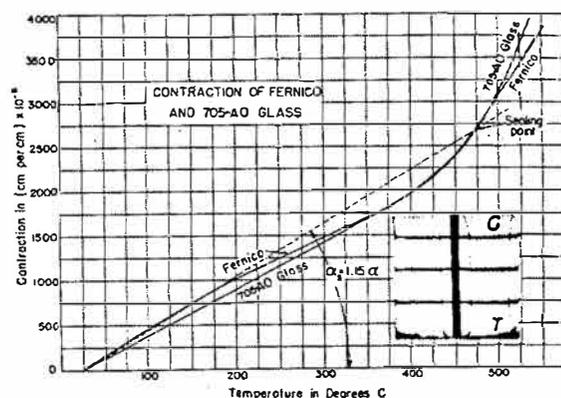


FIG. 2. Thermal contraction of fernico and 705-AO glass. The insert shows the stress pattern of a test seal between these materials.

function of nickel and cobalt content. These data are represented satisfactorily over the complete range of low expansion alloys by a linear relation between sealing temperature and percentage composition:

$$T_s = 36.0 (\text{Ni} + 0.875 \text{Co} - 31.0) \text{ deg. C} \quad (1)$$

when Ni, Co represent percent weights of Ni, Co.

Similarly, the average expansion coefficient between 25°C and the sealing temperature is given by

$$\alpha_s = 0.805 (\text{Ni} + 0.75 \text{Co} - 34.9) \times 10^{-6} \quad (2)$$

These equations can be used to calculate the

<sup>2</sup> A. W. Hull and E. E. Burger, *Rev. Sci. Inst.* 7, 98 (1936).

<sup>3</sup> H. Scott (*Trans. A.I.M.E., Inst. of Metals Div.*, 1930, p. 506) has given approximate equations for these quantities.

changes in length at sealing caused by variations  $\delta T_s$  and  $\delta \alpha_s$  in sealing temperature and expansion coefficient, respectively, of the metal. It can be shown easily (see Fig. 4) that the differences in length at the sealing temperature of the glass between metal and glass (assumed equal in length at room temperature) due to variations  $\delta T_s$  and  $\delta \alpha_s$  are:

$$\delta l_T = -(\tan \alpha' + \tan \alpha_s) \delta T_s, \quad (3)$$

$$\delta l_\alpha = (T_s / \cos^2 \alpha_s) \delta \alpha_s, \quad (4)$$

where  $T_s$  is the sealing temperature,  $\alpha_s$  the average expansion coefficient between room temperature and sealing temperature, and  $\alpha'$  the coefficient (slope) at the sealing temperature.

Since the angles are small, Eqs. (3) and (4) may be written:

$$\delta l_T = -(\alpha' - \alpha_s) \delta T_s, \quad (3')$$

$$\delta l_\alpha = T_s \delta \alpha_s. \quad (4')$$

Insertion of  $\delta T_s$  and  $\delta \alpha_s$  from (1) and (2) in Eqs. (3') and (4') gives:

$$\delta l_T = 36 \alpha_s (\delta \text{Ni} + 0.875 \delta \text{Co}), \quad (5)$$

$$\delta l_\alpha = 0.805 \times 10^{-6} T_s (\delta \text{Ni} + 0.75 \delta \text{Co}). \quad (6)$$

For fernico,

$$\alpha' = 12.3 \times 10^{-6}$$

$$\alpha_s = 5.92 \times 10^{-6}$$

$$T_s = 472^\circ \text{C}.$$

Hence,

$$\delta l_T = -230 \times 10^{-6} (\delta \text{Ni} + 0.875 \delta \text{Co})$$

$$\delta l_\alpha = 380 \times 10^{-6} (\delta \text{Ni} + 0.75 \delta \text{Co}).$$

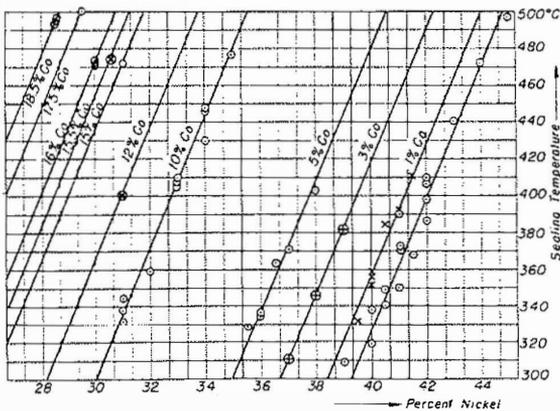


FIG. 3. Sealing temperature of iron-nickel-cobalt alloys as function of nickel and cobalt content.

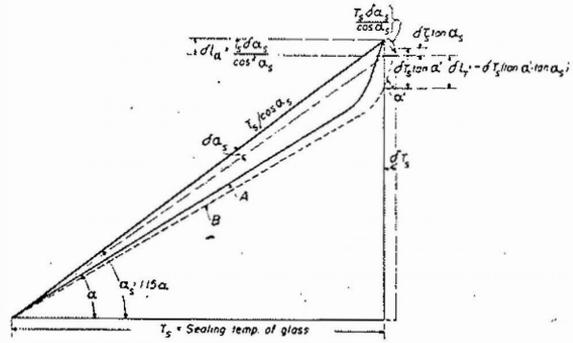


FIG. 4. Plot showing changes in the length of the metal at sealing caused by variations  $\delta T_s$  and  $\delta \alpha_s$  in sealing temperature and average expansion, respectively. Curve A is the thermal expansion curve of a correctly matched metal; Curve B, a mismatched one.

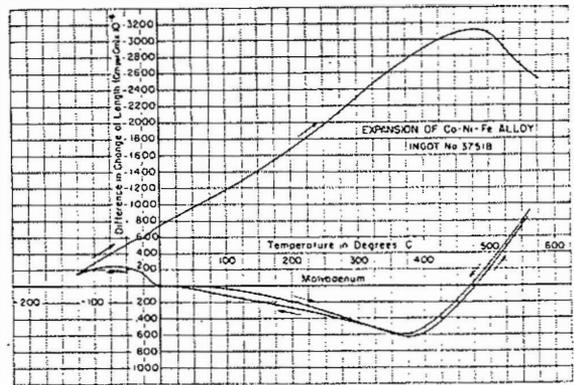


FIG. 5. Thermal expansion cycle of iron-nickel-cobalt alloy with  $\gamma$ - $\alpha$  transformation at  $0^\circ \text{C}$ , compared to molybdenum. Note the difference in expansion of the  $\alpha$  and  $\gamma$  phases.

The total variation in length at sealing is

$$\begin{aligned} \delta l &= \delta l_T + \delta l_\alpha \\ &= 10^{-6} (150 \delta \text{Ni} + 84 \delta \text{Co}). \end{aligned} \quad (7)$$

This difference  $\delta l$  in length at sealing is equal to the difference in contraction during cooling, and is a measure of the resulting stress. It was shown in our former paper,<sup>4</sup> that, for thick glass, a difference in contraction of  $10^{-6}$  cm/cm will cause a tensile stress of  $0.55 \text{ kg/cm}^2$ . Hence the limiting stress of  $100 \text{ kg/cm}^2$ , which was given in our former paper as the "breaking stress," and which represents well our experience with the breakage of seals during the last five years, corresponds to a difference in contraction of  $100 / 0.55 \times 10^{-6} = 180 \times 10^{-6} \text{ cm/cm}$ . Equation (7)

<sup>4</sup> See reference 1, Table I.

shows that this difference in contraction, and hence a breaking stress, can be caused by a variation of 1.2 percent in Ni or 2.1 percent in Co. A seal stressed to the breaking point would not be satisfactory. If we define a satisfactory seal as one which has *not more than one-fourth the breaking stress*, then a total variation in Ni of  $\pm 0.3$  percent, or a total variation in Co of  $\pm 0.5$  percent (assuming no variation in Ni), could be tolerated. This is probably within the reach of good metallurgical practice.

The situation is very different with regard to impurities. Only "desirable" impurities will be considered, *viz.*, Mn, Si, and Al, the first being useful as a de-sulphurizer, the latter two as de-

oxidizers. The equations for sealing temperature and average expansion at the sealing temperature of alloys containing these impurities are:

$$T_s = 36.0(\text{Ni} + 0.875 \text{Co} - 0.5 \text{Mn} - 1.4 \text{Si} - 1.0 \text{Al} - 31.0), \quad (1)$$

$$\alpha_s = 0.805(\text{Ni} + 0.75 \text{Co} + 0.5 \text{Mn} + 0.6 \text{Si} + 0.8 \text{Al} - 34.9) \times 10^{-6} \quad (2')$$

and the changes in length caused by variations are:

$$\delta l_T = -230 \times 10^{-6} (\delta \text{Ni} + 0.875 \delta \text{Co} - 0.5 \delta \text{Mn} - 1.4 \delta \text{Si} - 1.0 \delta \text{Al})$$

$$\delta l_a = 380 \times 10^{-6} (\delta \text{Ni} + 0.75 \delta \text{Co} + 0.5 \delta \text{Mn} + 0.6 \delta \text{Si} + 0.8 \delta \text{Al}).$$

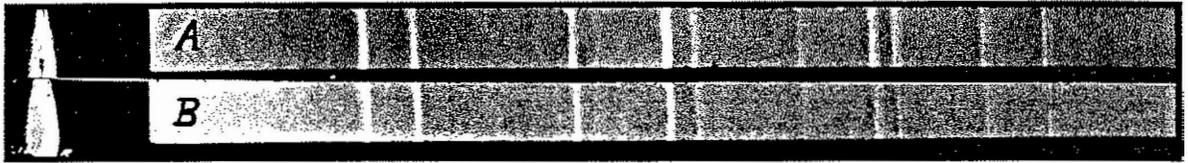


FIG. 6. X-ray diffraction patterns of annealed fernico: (A) before and (B) after 4 hours in liquid air. Both show the face-centered lattice of the  $\gamma$  phase, with no sign of transformation.

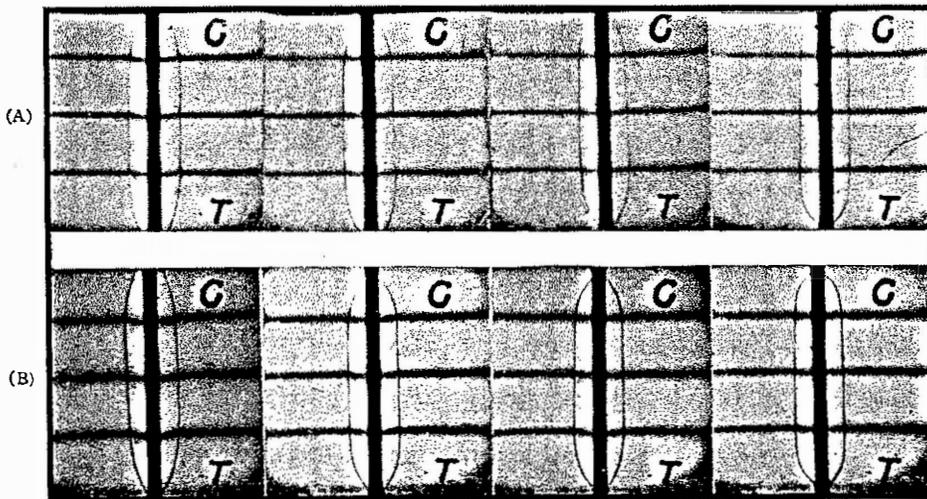


FIG. 7. Photoelastic stress patterns of fernico-705-A seals: (A) before and (B) after 15 hours in liquid air. No strain has been produced by the low temperature treatment.

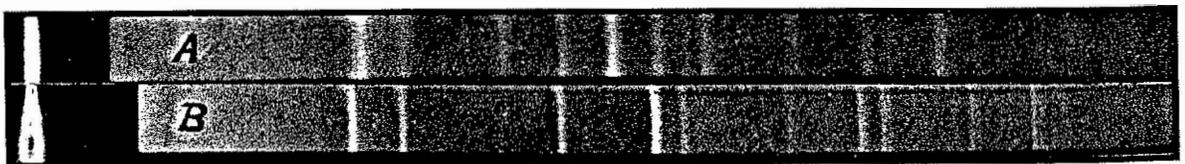


FIG. 8. (A) X-ray diffraction of filings from annealed fernico rod. The body-centered lattice proves transformation to  $\alpha$  phase caused by plastic deformation. (B) Pattern of same filings after 5 min. anneal in  $\text{H}_2$  at  $900^\circ\text{C}$ , showing restoration of  $\gamma$  phase.

The total change,  $\delta l = \delta l_T + \delta l_\alpha$  is:

$$\delta l = 10^{-6}(150\delta \text{ Ni} + 84\delta \text{ Co} + 305\delta \text{ Mn} + 550\delta \text{ Si} + 534\delta \text{ Al}). \quad (7')$$

Since breaking stress will result when  $\delta l = 180 \times 10^{-6}$ , the equation for breaking stress is

$$180 = 150\delta \text{ Ni} + 84\delta \text{ Co} + 305\delta \text{ Mn} + 550\delta \text{ Si} + 534\delta \text{ Al}. \quad (8)$$

This shows that a breaking stress will result if the alloy contains 0.21 percent more or less of Mn and of [Si+Al] than the prescribed amount; while for a "satisfactory" seal ( $< \frac{1}{4}$  breaking stress) the content of Mn and Si must each be accurate to 0.05 percent.

The uncertainty in Mn and Si concentration in commercial alloys is generally much larger than this.

### Polymorphism of fernico

The low thermal expansion of fernico is characteristic of its  $\gamma$  (face-centered cubic) phase. This phase is metastable below about  $400^\circ\text{C}$ , the stable form being the  $\alpha$  (body-centered) phase. The  $\alpha$  phase has a much higher thermal expansion than the  $\gamma$ , as can be seen in Fig. 5, which shows the contraction and expansion, as the temperature is changed from  $+500^\circ\text{C}$  to  $-100^\circ\text{C}$  and back again, of an alloy whose  $\gamma$ - $\alpha$  transformation temperature is  $0^\circ\text{C}$ . The composition of this alloy, by analysis, is:

Composition of Fe-Ni-Co Alloy No. 37518

|    |                                |
|----|--------------------------------|
| Fe | —55.04 (by difference) percent |
| Ni | —27.86                         |
| Co | —16.59                         |
| Si | — 0.23                         |
| Mn | — 0.18                         |
| C  | — .05                          |
| P  | — <.02                         |
| S  | — <.03.                        |

It is evident from Fig. 5 that the presence of even a small amount of the  $\alpha$  phase would cause large stresses, and must be avoided.

In the case of 54 percent Fe, 31 Ni, 15 Co fernico, the stability of the  $\gamma$  phase is so great that the  $\gamma$ - $\alpha$  transformation point, if it exists, is below the temperature of liquid air; i.e., the transformation to the body-centered form cannot be induced by temperature at any temperature down to and including that of liquid air. This is

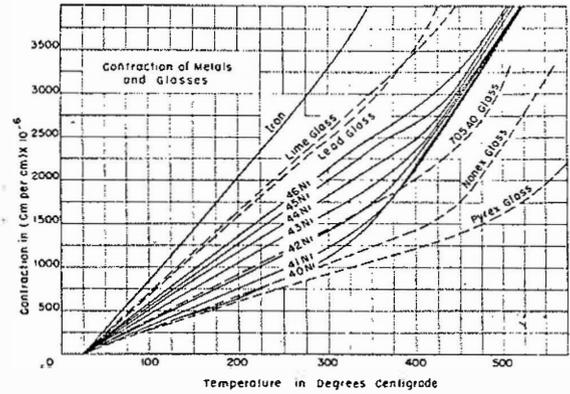


FIG. 9. Thermal expansion of iron-nickel alloys. The expansion curves of the common commercial glasses are shown for comparison.

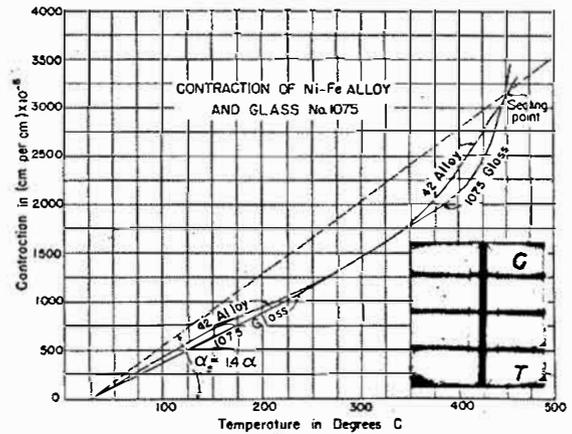


FIG. 10. Thermal expansion curves of 42 alloy and 1075 glass, and photoelastic stress pattern of a seal between them. Absence of stress in the seal is shown by the straightness of the interference lines crossing it.

shown in Fig. 6, in which (A) is the x-ray diffraction pattern of a thin strip of fernico annealed at  $1100^\circ\text{C}$  in hydrogen for one hour, and (B) that of the same strip after four hours at liquid-air temperature. Both show the perfect face-centered lattice of the  $\gamma$  phase.

The immunity to transformation at low temperature is also demonstrated by the strain patterns of a group of fernico-705-AO seals, shown in Fig. 7, (A) before, and (B) after 15 hours in liquid air. Not only are the seals uninjured, but no strains can be detected as a result of the prolonged exposure to liquid air.

While these tests prove that the  $\gamma \rightarrow \alpha$  transformation of fernico (Fe 54, Ni 31, Co 15) cannot be induced by temperature, it may be produced

by plastic deformation, for example, by rolling, drawing, or filing. Fig. 8(A) shows the x-ray diffraction pattern of filings from a fernico rod which had previously been annealed. The filings show a mixture of the face-centered pattern and the body-centered cubic pattern of the  $\alpha$  phase, caused by the plastic deformation of filing. After annealing 5 min. at 900°C, these filings gave the face-centered cubic pattern shown in Fig. 8(B), proving complete restoration of the  $\gamma$  phase. The  $\gamma$  phase can be restored by a brief anneal, e.g., 5 minutes, at any temperature between 900° and 1200°C. But a longer anneal, viz., 4 hours at 900°C or 1 hour at 1100°C in hydrogen, is recommended in order to remove carbon, which causes bubbles in seals by reducing the oxides of the glass.

### 3. NICKEL-IRON ALLOYS

We have made a careful study of the nickel-iron system, in the hope of finding a combination of glass and nickel-iron alloy whose thermal expansions are "matched" in the sense defined in the last section. Figure 9, which gives the thermal expansions of the iron-nickel alloys in the low expansion range that is of interest, shows that

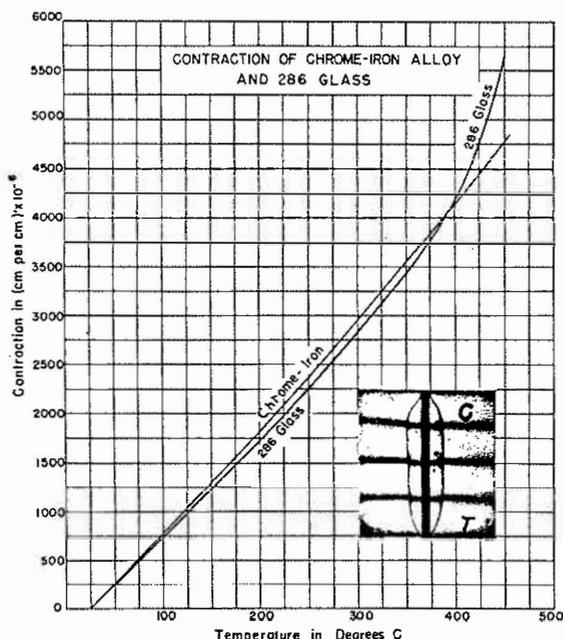


FIG. 11. Thermal expansions of 286 glass and 26 chrome-iron, and photoelastic stress pattern of a seal between them. Absence of stress is shown by the straightness of the dark lines crossing the seal.

the transition temperatures of these alloys are all much lower than those of commercial glasses. Hence a new glass had to be found to meet these conditions. This glass, whose General Electric designation is "1075 glass," is a lead-borosilicate, of the following composition (see Table II):

TABLE II. Composition of 1075 glass.

|                                |             |
|--------------------------------|-------------|
| SiO <sub>2</sub>               | —34 percent |
| B <sub>2</sub> O <sub>3</sub>  | —28 "       |
| PbO                            | —29 "       |
| Al <sub>2</sub> O <sub>3</sub> | —7 "        |
| Na <sub>2</sub> O              | —2 "        |

1075 glass has satisfactory chemical and electrical properties.

The alloy, referred to as 42 alloy, which matches this glass, has the composition:

|           |               |
|-----------|---------------|
| Iron      | —57.8 percent |
| Nickel    | —41.5         |
| Manganese | —0.5          |
| Silicon   | —0.2          |
| Carbon    | —<0.06.       |

The thermal expansions of 42 alloy and 1075 glass are shown in Fig. 10. It will be noted that the expansion in the range 0–300°C is essentially the same as that of fernico and 705-AO glass; but that the sealing point occurs at a lower temperature and much higher up on the curve, i.e., the expansion at the sealing temperature departs more from the low temperature expansion than in the case of 705-AO; the average expansion from room temperature to the sealing temperature being 1.4 times the 0–300°C value, as compared to 1.15 for the fernico—705-AO combination. This difference is characteristic of the two types of glass. As a result of this, the curves of glass and metal depart slightly in the range just below the sealing temperature, to join again at about 350°C. The stresses caused by this departure are not sufficient to cause breakage during cooling, and the seal is free from stress at all temperatures below 350°C. The photoelastic stress pattern of a seal between 1075 glass and 42 alloy, at room temperature, is shown in the insert in Fig. 10.

A special problem encountered in making seals with 1075 glass is the appearance of lead at the interface between glass and metal, lead

oxide being reducible by ferrous metals. This can be avoided by coating the iron-nickel alloy with copper or platinum, which do not reduce lead oxide; or with a lead-free glass, for example, a pure borosilicate. We have obtained excellent results by "precoating" the metal with a thin layer of 705-AO glass.

#### 4. CHROME-IRON SEALS

Seals between 26 percent chromium-iron alloy and Corning B-12 glass are highly strained. We have obtained satisfactory seals with this alloy and a glass of the following composition:

Composition of Laboratory Glass No. 286

SiO<sub>2</sub>—54 percent  
PbO—29  
K<sub>2</sub>O— 8  
Na<sub>2</sub>O— 5  
BaO— 4

Figure 11 shows the relative thermal expansion of 26 chrome-iron and 286 glass. The insert shows the stress pattern of a seal between them.

#### 5. IRON SEALS

Although the art of enameling is old, the glasses used as enamels are generally of lower expansion than the metal. This is desirable for an enamel, since it gives tangential compression of the glass, which prevents cracking, while the radial stress, which is tension, is small so long as the thickness of the enamel is small compared to the radius of curvature. But it is not desirable for a thick glass seal. The standard commercial glasses, also, are all much lower in expansion than iron, as can be seen from Fig. 9.

For thick seals, as contrasted with thin enamels, a glass is needed whose average expansion between room temperature and the sealing point matches iron as closely as possible. A perfect match, such as that between fernico and 705-AO glass, cannot be had, since the expansion of iron is nearly linear. In addition to having the correct expansion, the glass must satisfy the usual requirements, for electrical applications, of high electric resistance and of chemical stability, especially with respect to water and acids. These requirements, as well as the expansion match, have been found to be satisfied by a glass of the

following composition:

Composition of 542 Glass

SiO<sub>2</sub>—45 percent  
K<sub>2</sub>O—14  
Na<sub>2</sub>O— 6  
PbO—30  
CaF<sub>2</sub>— 5

Figure 12 shows the thermal expansion of this glass compared to iron; and the insert shows the stress pattern of a seal, annealed to 1°/min. It is seen that the seal is practically stress-free.

Direct application of 542 glass to iron results in a layer of lead at the interface, as already noted in the case of 1075 glass and 42 alloy. This can be avoided by copper plating, or by

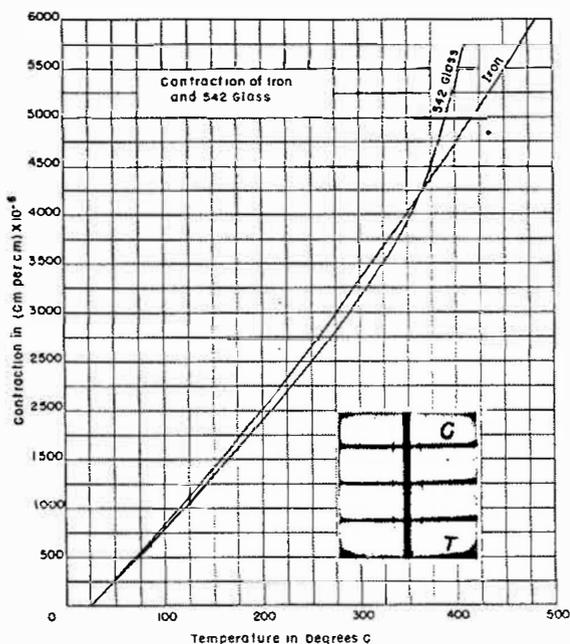


FIG. 12. Thermal expansions of 542 glass and iron, and photoelastic stress pattern of a seal between them.

precoating with a leadless glass. We have had good results from precoating with standard soda-lime lamp glass.

#### 6. THE STRENGTH OF SEALS

It is obvious that a seal which is entirely free from stress may be worthless, unless the glass adheres to the metal. This second half of the problem of sealing, *viz.*, the question of adhesion, must be dismissed with only a brief discussion;

not because it is less important, but because it has not yet been studied. A few rough measurements and some general observations are all that can be given at present.

For the purpose of discussion, several techniques will be described:

### (1) Thin oxide bond

The thickness of the oxide formed by heating the metal is carefully controlled: if too thin, it is dissolved by the glass; if too thick, it flakes off.

An example is a combination of tungsten with Corning Nonex Glass. The tungsten wire is carefully oxidized in the flame. A thin tube of "wetting glass" is then slipped over it and quickly sealed, thus preventing further oxidation. The coated wire may now be incorporated in any desired seal, care being taken not to injure the oxide layer by overheating. A certain "straw" color is a reliable index of correct oxide thickness.

This may be termed the Ideal Sealing Technique, since tungsten oxide dissolves in glass sufficiently to form a firm bond, but not so rapidly as to be completely absorbed; and the thin oxide layer may be expected to adhere firmly to the metal. The strength of the bond is not easily measured directly, since this sealing technique has been applied only to wires. But two indirect observations place upper and lower limits to the strength: (a) The bond is weaker than the glass, since tungsten-Nonex seals which are crushed in a vice break at the oxide-metal interface. (b) Tungsten-Pyrex seals, in which the radial tensile stress at the glass-metal surface is  $4.8 \text{ kg/mm}^2$ ,<sup>5</sup> frequently do not break during the first few hours, but invariably break in less than a week. Hence the bond initially is stronger than  $4.8 \text{ kg/mm}^2$ .

### (2) Thick oxide bond

The thick oxide layer behaves like a mismatched enamel coat, which breaks loose from the metal during heating and cooling, because of the difference between its thermal expansion and that of the metal. Typical examples are seals to iron and copper, which over-oxidize easily. The danger may be minimized by careful sealing

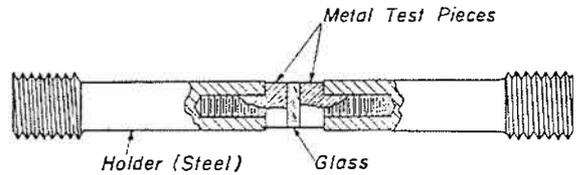


FIG. 13. Form of seal used for testing the strength of bond between metal and glass. The studs, with the glass between them, are screwed into the jaws of a steel-testing machine.

technique, such as is employed in machine-made Dumet seals. Here two necessary conditions are fulfilled: (a) The wire is kept hot until covered with glass, so that cracking of the oxide layer, which is irreparable, does not occur before sealing. (b) The glass contracts more than the metal during cooling, and thus holds the oxide layer tightly to the metal, both during and after cooling. The strength of the bond is unimportant in this case, since the radial stress is compression.

### (3) Anchored oxide

An example is 26 percent chromium-iron alloy, deeply etched by chemical pickling or by heating in wet hydrogen. The pores of the honeycomb-like surface support the oxide, which bonds firmly to the glass. Both lead glasses and lime glasses seal strongly to such a surface, and break in the glass rather than at the interface when crushed in a vice. Two direct measurements of the strength of bond between flat surfaces of 26 chrome-iron and 286 glass gave tensile strengths of  $4.4$  and  $6.8 \text{ kg/mm}^2$ . In contrast to this, unetched 26 chrome-iron gives a very weak bond.

### (4) Oxide-free seals

Large seals usually require such a long heating time that the oxide layer is completely dissolved in the glass when the seal is finished. This is usually true of fernico-705-AO seals. Measurement of the strength of such seals will therefore be a test of the bond between glass and clean metal.

We have made rough tests of the strength of bond in this and a few other sealing combinations by joining the heads of two tension bolts with a layer of glass, as shown in Fig. 13. The glass was kept smaller in diameter than the studs, or was

<sup>5</sup> Reference 1, p. 407, Table VII.

ground off flush with the metal if it protruded, so that the tension was purely normal. All seals were annealed and were essentially free from strain when tested.

The strength was measured in a standard steel-testing machine. Tests of 28 seals between fernico and 705-AO glass, of  $\frac{1}{2}$ -inch diameter, gave values ranging from 1.14 to 3.36 kg/mm<sup>2</sup>, the average being 1.48 kg/mm<sup>2</sup>. All but 7 of these broke in the glass at the center, midway between the seals; in these cases the values obtained are those of the strength of the glass;

they are not the bond strength, but only lower limits. For the 7 which broke, wholly or partially, at the glass-metal interface, the average strength was 2.23 kg/mm<sup>2</sup>.

A few seals of this same type were made between 42 alloy, which had been precoated with 705-AO glass, and 1075 glass. Tensile tests of 8 of these seals gave strengths varying from 1.56 to 3.05, the average being 2.27 kg/mm<sup>2</sup>. This is somewhat higher than the value found for the fernico-705-AO seals, and may indicate a certain advantage in precoating.

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# Glass to Metal Seals

A. W. Hull

## a. Fe-Ni-Co alloys

i thermal exp is less than that of any other available metals or alloys, exception ~~is~~ W + Mo

ii thermal exp w non-linear - provides design capability to match to glasses

b exp above Curie pt is 3X greater

c Mn + S are considered essential to ductility of cast metal alloys

d slow data for  $\chi$  formed alloy

e  $\chi \rightarrow \alpha$   $\chi$  formation may be produced by plastic deformation (e.g. rolling, drawing)

f thickness of the oxide formed by heating the metal must be carefully controlled - if it is too thin, it is dissolved by the glass, if too thick, it flakes off