

4. ALLOYS CONTAINING IRON, NICKEL AND COBALT.

The inflection temperature of nickel-iron alloys is, as already stated, generally too low to permit them to be fused to the low-expansion normal borosilicate glasses.

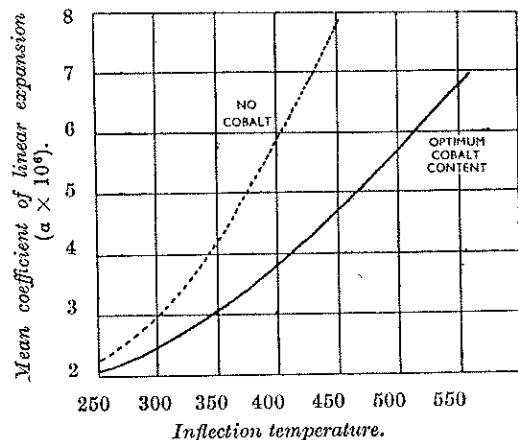


FIG. 32.

Thermal Expansion Characteristics of Iron-Nickel-Cobalt Alloys.

The Effect of Cobalt in Raising the Inflection Temperature for a given Thermal Expansion Coefficient (a).

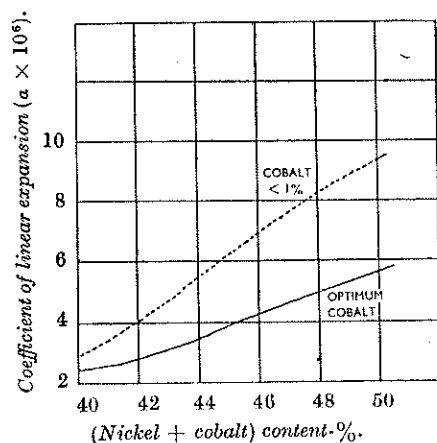


FIG. 33.

The Effect of the Addition of about 18% of Cobalt on the Linear Thermal Expansion Coefficient (a) of Ni-Fe Alloys.

Substitution of cobalt for nickel lowers the thermal expansion coefficient without affecting the inflection temperature, so giving alloys suitable for sealing to hard glasses. In the absence of cobalt, the expansions are considerably higher for a given inflection temperature than those

obtained with the most favourable cobalt content, as shown in Figs. 32 and 33. This lowering of the expansion increases as the proportion of nickel is replaced by cobalt to a limit of about 18 per cent. and the curves showing the relation between (nickel + cobalt) content, expansion and inflection temperature represent substitution to this limit.¹² Consideration of these graphs shows that an alloy containing 46 per cent. (Ni + Co) has the coefficient of linear thermal expansion 4.3×10^{-6} as compared with 7.0×10^{-6} for the corresponding cobalt-free alloy, both alloys possessing the same temperature of inflection of 430° . The inflection temperature of a cobalt-free alloy of expansion coefficient 4.3×10^{-6} is as low as 350° , thus rendering it unsuitable for sealing to low-expansion glasses of the normal borosilicate composition.

The limit to which nickel can be replaced by cobalt is governed by the stability of the alloy. The desired low and reversible thermal expansion of these alloys is characteristic of the face-centred cubic lattice, known as the gamma-phase, which is meta-stable below about 400° , the stable form being the body-centred alpha-phase. The alpha-phase possesses a much higher thermal expansion than the gamma, so that the gamma \rightarrow alpha transformation must be depressed below room temperature in order to ensure the alloy being stable under all conditions of usage. It must not take place in alloys intended for glass-to-metal joints because reversion to the higher-expansion form would cause seals to crack. Increasing the proportion of nickel depresses the transformation temperature, but cobalt raises it. Practical considerations dictate that the gamma \rightarrow alpha transformation should be depressed to about -100° , and so the optimum cobalt content is taken as that which will cause the transformation to occur at this temperature. With fixed proportions of (nickel + cobalt) and of other elements, Howard Scott¹² has shown this to be governed by the relation:—

$$\%Co = 1.55(\%Ni + Co) + 3(\%Mn) + 18(\%C) - 55.$$

By substituting (100%—Fe) for the percentage of (Ni + Co) in the above equation, the proportions of nickel and cobalt for a given iron content are obtained, as shown in Table V, assuming the

TABLE V.

Optimum Proportion of Cobalt in Stable Alloys containing only Iron, Nickel and Cobalt.

(Calculated from Scott's relationship:—

$$\%Co = 1.55(\%Ni + Co) + 3.0(\%Mn) + 18.0(\%C) - 55.)$$

| % Iron. | % Cobalt. | % Nickel. |
|---------|-----------|-----------|
| 40 | 38 | 22 |
| 45 | 30 | 25 |
| 50 | 22.5 | 27.5 |
| 55 | 15 | 30 |
| 60 | 7 | 33 |
| 54 | 16.5 | 29.5 |
| 54 | 18.0 | 27.75 |

Mn 0.2%, C 0.05%

alloys to be free from minor constituents. Taking the iron content of Fernico or of Kovar as 54 per cent., the above relation shows that the optimum proportion of cobalt is about 16.5 per cent. for the pure

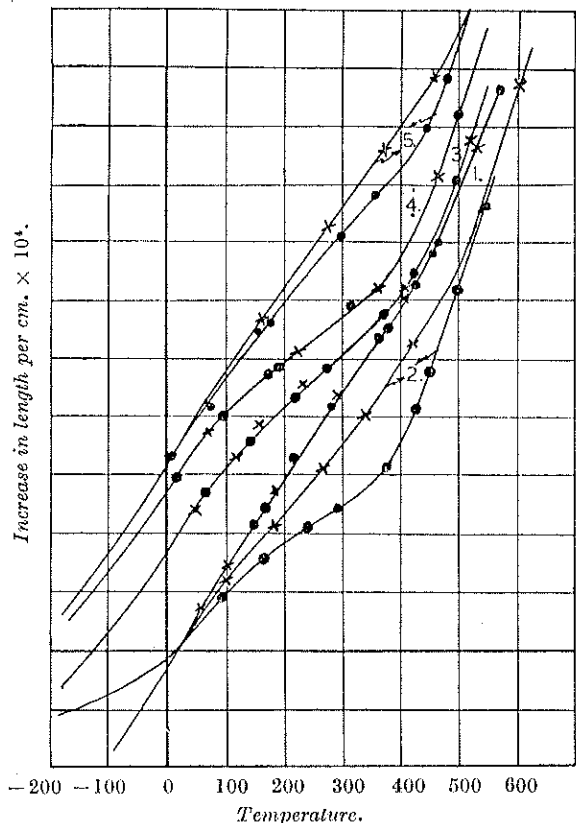


Fig. 34.

Thermal Expansion Curves of Iron-Nickel-Cobalt Alloys.

●—● Initial heating.
 ×—× Heating after immersion in liquid air.

| Curve | Alloy composition | Expansion (20°—350°) | |
|-------|---|---------------------------------------|--|
| | | Initial. ($\alpha \times 10^6$). | After Immersion in Liquid Air. ($\alpha \times 10^6$). |
| 1. | Alloy, 54% Fe, 27% Ni, 19% Co | 7.75 | 7.75 |
| 2. | Unstable commercial alloy | 4.4 | 6.4 |
| 3. | Alloy, 54% Fe, 31% Ni, 15% Co | 5.4 | 5.4 |
| 4. | Stable commercial alloy | 4.8 | 4.8 |
| 5. | Unstable experimental alloy, 55% Fe, 28% Ni, 16.6% Co | 6.5 | 7.3 |

alloy containing no minor constituents, whereas it may be as high as 18 per cent. if the alloy contains 0.2 per cent. manganese and 0.05 per cent. carbon.

As the cobalt approaches the optimum proportion, however, the alloy becomes less stable so far as the gamma \rightarrow alpha transformation is concerned. It has been stated that the alloy containing 54 per cent. Fe, 28 per cent. Ni, 18 per cent. Co possesses the highest transition temperature for stable low-thermal-expansion alloys.¹³ This proportion of cobalt is somewhat higher than that permitted in a pure alloy, according to the values given in Table V. By reducing the proportion of cobalt to 15 per cent., the gamma \rightarrow alpha transformation cannot be induced, even by immersion in liquid air. The contrast in behaviour on heating and cooling between stable and unstable alloys of this type is shown in Fig. 34. These curves show that alloys containing as much as 19 per cent. of cobalt, made from pure materials by powder metallurgy, show reversible expansion characteristics even after immersion in liquid air (-194°). Heat treatment at high temperatures is needed to re-convert the high-expansion alpha form into the lower-expansion gamma form.

The optimum cobalt content is naturally higher the greater the proportion of the elements which lower the transformation temperature; but unfortunately the thermal-expansion coefficient is raised more by the addition of these elements, with the exception of carbon, than it is lowered by the greater cobalt content permitted. They are, therefore, preferably kept to a minimum, although manganese is often added to make preparation and fabrication easier.

Small additions of carbon not only lower the expansion slightly but also permit the use of a higher cobalt content, as shown by the relationship given above. The proportion of carbon should not exceed about 0.3 per cent., an amount which lowers the linear expansion coefficient by 0.4×10^{-6} , because higher proportions may not be retained in solid solution, in which case they do not have the desired effect.

Addition of carbon to these alloys by carburising has been recommended¹⁴ in order to prevent the transformation which is accompanied by an alteration in such physical properties as thermal expansion, hardness, ductility and mechanical strength. In the absence of carbon the change is said to occur between 0° and -50° whereas with 0.05 per cent. or more of carbon it was in the region of -200° . Carburisation is accomplished by heating in graphite in an atmosphere of hydrogen, in hydrogen containing hydrocarbon oils for 30 minutes at 1100° , or by immersion for 10 minutes in sodium cyanide at 800° . Annealing in hydrogen to remove carbon, however, has been suggested to prevent the formation of bubbles at the glass-metal interface,¹⁵ but it has already been shown that stable alloys can be produced by correct proportioning of the major constituents, which is preferable to these carburising methods.

Plastic deformation by cold working, such as by filing, rolling or deep drawing, causes the gamma \rightarrow alpha transformation to occur, so that annealing at 900° to restore the gamma-phase should be carried out after such treatment. The reversible change in expansion in the region of 400° is not fully understood; it has been suggested that the change

is not a true transformation but is somewhat akin to the A2 change in iron.

Freedom from stress in seals can be obtained by agreement of both thermal expansion coefficient and inflection temperatures of metal and glass, so that the non-linear expansion of these nickel-iron-cobalt alloys affords the possibility of realising this close match with hard glass. A. W. Hull, E. E. Burger and L. Navias¹³ have determined the sensitivity of thermal expansion characteristics of the alloy to the small changes in chemical composition which are bound to occur in manufacture, ascertaining their effect on the sealing rather than on the inflection temperature of the alloys. This sealing temperature was determined

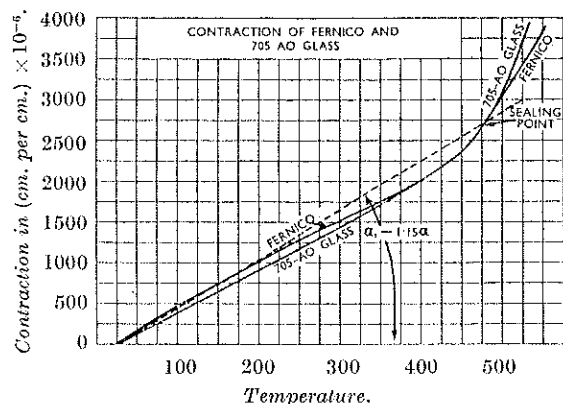


FIG. 35.

(After Hull, Burger and Navias.)

Thermal Contraction Curves of FERNICO and 705-AO Glass, showing determination of sealing temperature from intersection with curve of straight line the slope (α_0) of which equals 1.15 that of average slope (α) of curve between 25° and 300°.

as shown in Fig. 35, by the intersection with the thermal expansion curve of the alloy of a straight line the slope of which with the temperature axis was 15 per cent. greater than the average expansion of the glass between 25° and 300°. The point so determined on the expansion curve of the glass is said to represent the sealing temperature of borosilicate glasses used with these alloys; and hence it also represented the sealing temperature of the metal which matched the glass. The average coefficient of linear thermal expansion between 25° and the sealing temperature was found to be $0.805 (\text{Ni} + 0.75 \text{Co} + 0.5 \text{Mn} + 0.6 \text{Si} + 0.8 \text{Al} - 34.9) \times 10^{-6}$, where the chemical symbols represent the percentage weights present in the alloy.

Taking the upper limit of the tensile stress in the glass component of a glass-to-metal joint as 100 kg. per sq. cm., these authors, from considerations of the changes in length caused by small differences in sealing temperature and expansion coefficient, have calculated the corresponding

changes in chemical composition which would bring about a stress of this magnitude. Such a result would follow if the alloy composition changed by:—

- ± 1.2% nickel
- or ± 2.1% cobalt
- or ± 0.59% manganese
- or ± 0.33% silicon
- or ± 0.34% aluminium.

The sealing temperature might preferably be called the annealing temperature because it coincides with the temperature at which strain would be released rapidly, whereas the temperature at which the glass and metal are sealed to each other is considerably higher. This sealing or annealing temperature can be derived from the relation:—

$$\text{sealing temperature} = 36.0 (\text{Ni} + 0.875 \text{Co} - 0.5 \text{Mn} - 1.4 \text{Si} - 1.0 \text{Al} - 31.0)$$

the chemical symbols representing the percentage of the element present in the alloy.

The presence of minor constituents lowers the sealing temperature, the effect of small changes in composition of the alloy on these characteristics being illustrated in Table VI.

TABLE VI.

The Effect of Minor Constituents on the Sealing Temperatures and Linear Thermal Expansion Coefficients of Nickel-Iron-Cobalt Alloys.

| Change in Chemical Composition. | Effect of Change in Composition. | |
|---------------------------------|----------------------------------|---------------------------|
| | On Sealing Temperature. | On $\alpha \times 10^6$. |
| Addition of 0.1% nickel | + 3.6 | + 0.08 |
| „ 0.1% cobalt | + 3.1 | + 0.06 |
| „ 0.1% manganese | - 1.8 | + 0.04 |
| „ 0.1% silicon | - 5.0 | + 0.048 |
| „ 0.1% aluminium | - 3.6 | + 0.064 |

+ Signifies an increase.

These figures will be of little assistance to the seal maker, since it is preferable to measure the stresses present in a seal rather than to calculate them by comparison with a known batch of alloy. They are a valuable guide, however, to the alloy maker because they enable him to estimate the effect of variability in composition.

These alloys are normally prepared by the customary melting and casting technique and consequently they contain small proportions of manganese, silicon and aluminium which are added to remove sulphur and oxygen from the molten metal thereby assisting in the production of sound wire and strip. They are not necessary if the alloy is produced by vacuum melting or powder metallurgy processes and their effect on the thermal expansion is thereby avoided.

Cobalt lowers the electrical resistivity of nickel-iron alloys, thus reducing the heating effects in the seal when current passes. It also

results in a more fusible oxide when the metal is heated in readiness for coating with glass.

This brief account of the physical properties of the alloys containing iron, nickel and cobalt will enable an estimate to be formed of their suitability for joining to particular glasses. The alloy compositions listed in Table VII have been taken from the patent literature; but, in

TABLE VII.

Composition per cent. of Alloys containing Nickel, Iron and Cobalt.

| As quoted in the Patent Literature. | | | | | | | |
|-------------------------------------|-------|-----------|-------|-------|---------|------|------|
| Iron..... | — | remainder | — | — | 45-54 | 57.4 | 51.5 |
| Nickel..... | 15-32 | 24-30 | 28-34 | 32-38 | 28-30 | 31.9 | 31.8 |
| Cobalt..... | 12-45 | 5-25 | 5-20 | 6 | 18-25 | 9.8 | 16 |
| Manganese..... | 1 | 1 | 1 | 0.5 | — | 0.79 | 0.65 |
| Carbon | — | — | — | — | 0.05 | 0.01 | 0.01 |
| | | | | | minimum | | |

References : U.S. Pat. 2,043,307 Brit. Pat. 491,058 Brit. Pat. 358,934 Brit. Pat. 497,644 U.S. Pat. 2,189,970 U.S. Pat. 2,217,422/3

general, the limits quoted for composition are so wide that it is impossible to express any opinion as to the suitability of the alloys for any given glass.

5. ALLOYS CONTAINING IRON, NICKEL AND CHROMIUM.

In contrast with cobalt, chromium is added to nickel-iron alloys in order to raise their thermal expansion coefficient to suit soft glasses. Its effect can be seen from the results in Table VIII.

TABLE VIII.

The Effect of Chromium on the Linear Thermal Expansion Coefficient (α) of Nickel-Iron Alloys.¹⁶

| Alloy (% Composition). | $\alpha \times 10^6$ | |
|-------------------------------------|----------------------|---------|
| | 20-350° | 20-400° |
| 42 Ni, 58 Fe | 5.3 | 5.9 |
| 42 Ni, 52 Fe, 6 Cr | 8.8 * | 9.4 * |
| 42.2 Ni, 5.5 Cr, Fe remainder | 8.0 | 9.0 |
| 44 Ni, 10.2 Cr, Fe remainder | 11.1 * | 11.0 * |
| 46 Ni, 54 Fe | — | 7.6 |
| 44.3 Ni, 52 Fe, 1.95 Cr..... | 11.6 | 11.7 |

* These values have been derived from the curves in W. E. Kingston's contribution,¹⁶ and are approximate because of the small-scale reproduction.

A range of expansions can be obtained by substituting chromium for iron in the 42 per cent. nickel-iron base alloy, and minor adjustments can be made to the expansion by altering slightly the proportions of nickel and chromium. The expansions are reversible over a wide range of temperature—at least from -75° to 1000°. The alloy containing 8 per cent. of chromium is not nearly so resistant to oxidation as the 26-30 per cent. chrome-iron alloys, and it should be oxidised prior to seal making at 1050°-1250° in an atmosphere of hydrogen which has been saturated with water vapour at 40°. The oxide layer then consists of roughly equal

proportions of Cr_2O_3 and a spinel type oxide— $\text{RO}\cdot\text{R}_2\text{O}_3$ —containing iron, nickel and chromium oxides. Experience with the alloy containing 6 per cent. chromium indicates that care is needed to avoid over-oxidation during seal making. The adherence of the oxide to the base metal is not good, but according to Kingston it is improved by minor additions of compound-forming constituents, of which there were present in his alloys 0.04 - 0.15 per cent. carbon, 0.12 - 0.27 per cent. silicon, and 0.21 - 0.29 per cent. manganese.

Deoxidised and gas-free alloys of this type have been prepared by adding 0.25 per cent. of aluminium and up to 1 per cent. of beryllium to the molten metal. Any compounds formed are converted by suitable fluxes to slag which is removed before casting.¹⁷

The 6 per cent. chromium alloy is soft and ductile in the annealed condition, but can be hardened by the addition of about 0.5 per cent. of carbon. This alloy is used instead of the composite copper-coated nickel-iron alloy for making seals with soft glass.

6. ALLOYS CONTAINING IRON AND CHROMIUM.

The thermal expansion of steels containing about 0.1 per cent. carbon is decreased by adding chromium as shown by the results in Table IX.

TABLE IX.*

The Effect of Chromium on the Linear Thermal Expansion Coefficient (α) of Low Carbon Steels.

| Chromium. | Composition, %. | | | Mean $\alpha \times 10^6$ (20-400°). |
|-----------|-----------------|------|------|---|
| | Mn. | Si. | C. | |
| nil | 0.26 | 0.18 | 0.09 | 14.1 |
| 4.76 | 0.27 | 0.18 | 0.11 | 12.9 |
| 11.96 | 0.25 | 0.19 | 0.12 | 11.7 |
| 17.48 | 0.28 | 0.21 | 0.12 | 11.3 |
| 24.53 | 0.36 | 0.22 | 0.13 | 11.0 |
| 32.27 | 0.36 | 0.26 | 0.12 | 10.8 |

* *J. Iron & Steel Inst.*, 1938, 137, 361-370.

The fall in thermal expansion coefficient is rapid up to 15 per cent. chromium but less marked with the higher proportions. With the exception of the alloy containing 32 per cent. chromium, there is no evidence of sudden volume changes on heating, for the rate of expansion increases but slightly with rising temperature. The lower-expansion alloys are thus suitable for sealing to soft glass, and are used in cases where high sealing-in temperatures would conduce to oxidation of thin Dumet wires too severely.

Alloys containing sufficient chromium are probably the most resistant to oxidation of all metals used for sealing to glass, with the exception of the noble metals. The thin oxide film is rich in chromium oxide, green in colour, and adheres tenaciously to the base metal, which it protects from further oxidation during the seal-making processes. This pro-

TABLE XI.
Processes used for Joining Metals.

| | Tungsten. | Molybdenum. | Platinum. | Iron. | Nickel. | Copper. | Ni-Fe Alloys. | Cr-Fe Alloys. | Kovar. | Dumet. |
|--------------------------|-----------|-------------|-----------|---------|----------------------|---------|---------------|---------------|--------|--------|
| Tungsten | *A-D, H | | | | | | | | | |
| Molybdenum | A-D | A-E | ABC | | | | | | | |
| Platinum | ABC | ABC | — | ABCDEGH | | | | | | |
| Iron | — | — | — | (KL) | ABCFHG ABCFHK | | | | | |
| Nickel | ABCK | ABC | ABC | (KL) | ABCFHG ABCFHK | | | | | |
| Copper | ABK | AB | ABC | (KL) | ABCHK B, HKLM | | | | | |
| Nickel-iron alloys | ABC | ABC | ABC | (KL) | ABC ABC | ABCFH | | | | |
| Chromium-iron | ABCD | ABCD | ABCD | (KL) | ABC ABC | ABC | | | | |
| Kovar or Nicosel | A-D, H | A-E | ABC | A-H | A-D | A-D | ABC | | | |
| Dumet | ABK | AB | ABC | — | F-K ABCHK B, HKLM | H-L | ABC | A-D | F-L | ABCHK |

* The letters refer to the processes described in Table X. Those in brackets are inferior to others.

but sometimes it is necessary to restrict the period to that of a few cycles, when accurate electronic control of the current is essential. Some metals either do not alloy readily or they produce brittle welds. In such cases it is often permissible to use an intermediate metal: for example, nickel is sometimes used to produce stronger welds between tungsten and molybdenum but naturally they will not then withstand so high an operating temperature. Solders, brazes and other fusible metals are also used instead of welding, the choice of method being governed by local conditions. In using these soldering methods it is important to bear in mind the maximum operating temperature in relation to the melting point of the "solder." Further, some metals, notably cadmium and zinc, are volatile when heated *in vacuo* and this may prohibit their use in some circumstances. Diffusion of gold into copper at about 400° has been successfully used for joining copper components together.²⁵ The surfaces to be joined must be scrupulously clean and free from scratches.

It is not possible to deal more fully with this aspect of the subject in this monograph, or to recommend any one method in preference to another because so much depends on the nature of the job. Methods used for joining metals together are listed in Table X.²⁶ Those employed for making joints between metals employed in the more common glass-to-metal seals are given in Table XI.

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