FIG. 1

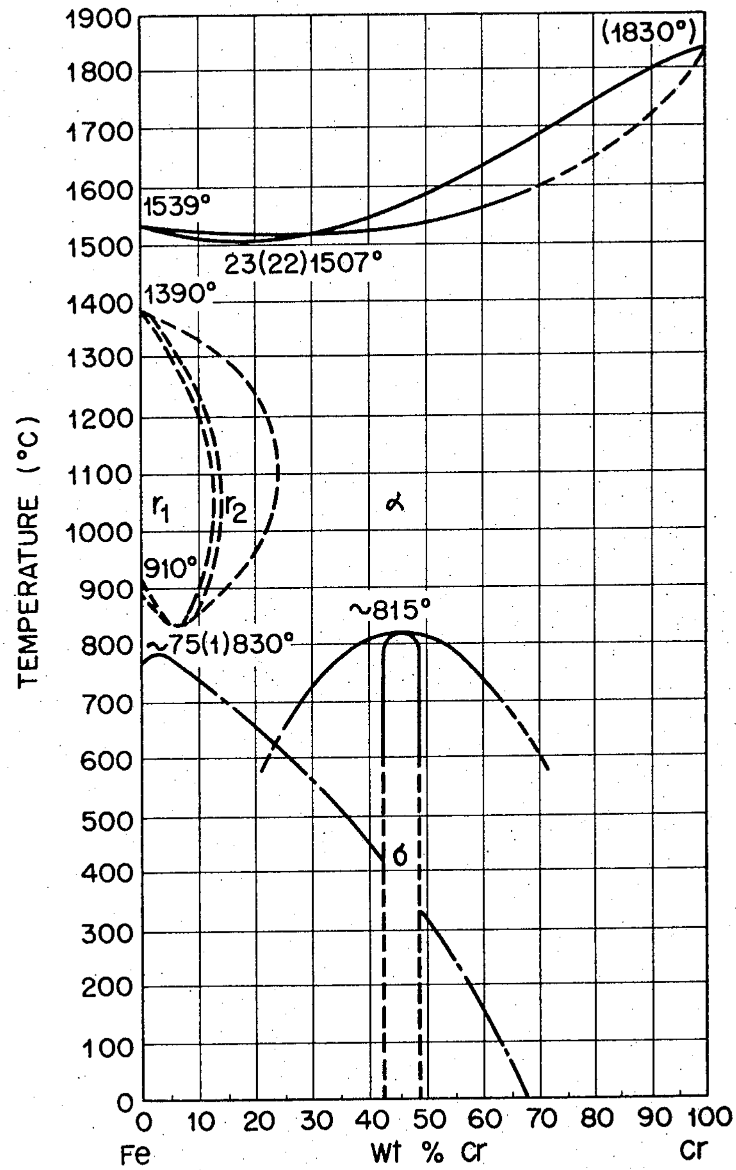

TEMPERATURE (°C)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
(1830°)
1539°
23(22)1507°
1390°
r1
r2
α
910°
~815°
~75(1)830°
σ
0 10 20 30 40 50 60 70 80 90 100
Fe
Wt % Cr
Cr

FIG. 2

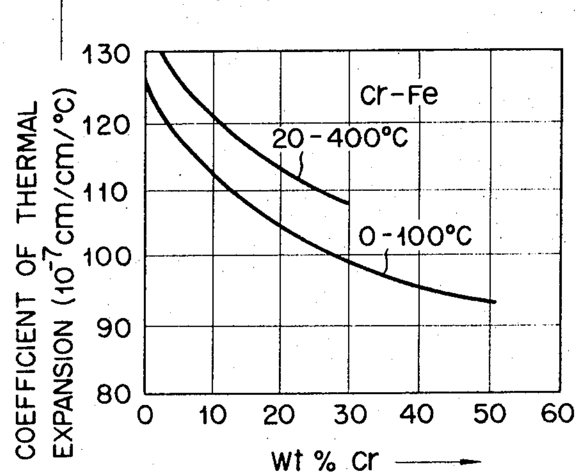
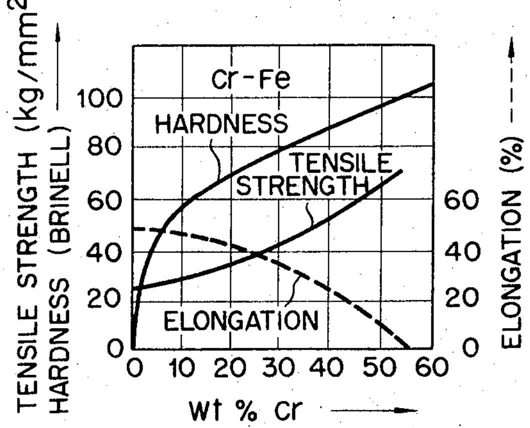

COEFFICIENT OF THERMAL EXPANSION (10^{-7}cm/cm/°C)
130
120
110
100
90
80
0
10
20
30
40
50
60
Cr-Fe
20-400°C
0-100°C
Wt % Cr

FIG. 3


TENSILE STRENGTH (kg/mm²)
HARDNESS (BRINELL)
100
80
60
40
20
0
Cr-Fe
HARDNESS
TENSILE STRENGTH
ELONGATION
ELONGATION (%)
0
10
20
30
40
50
60
Wt % Cr

United States Patent Office

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SEALING ALLOY

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Int. Cl. C22c *39/10, 39/20*
U.S. Cl. 75—124 2 Claims

ABSTRACT OF THE DISCLOSURE

A sealing alloy comprising 15–30% by weight of Cr, 0.001–2.0% by weight of a rare earth metal and balance of Fe is provided. This alloy has excellent corrosion resistance.

This invention relates to an alloy sealable to soft glass and especially suitable for sealing cathode ray tubes.

As the alloy sealable to soft glass, a 18Cr-Fe alloy having a thermal expansion coefficient of 113×10^{-7} cm./cm./° C., which approximates the thermal expansion coefficient of soft glass, is known. This alloy is well known as an α type stainless steel, which is designated as SUS 24 in the Japanese Industrial Standard (JIS). SUS 24 approximately corresponds to AISI–430 in the American Standard of Testing Material (ASTM). The composition thereof is: 16–18% Cr, not more than 0.12% C, not more than 0.75% Si, not more than 1.00% Mn, not more than 0.04% P, not more than 0.03% S (all by weight) and balance Fe. The SUS 24 alloy is, after being formed into a desired shape, subjected to wet hydrogen furnace treatment for 10–90 minutes under the conditions of 900–1200° C. of furnace temperature and 0–40° C. of hydrogen dew point for the purpose of forming oxide film on the surface thereof. The alloy piece thus having the oxide film on the surface thereof is sealable to soft glass.

When the thus surface-treated 18Cr-Fe alloy is sealed to soft glass, the oxide film is firmly bonded to soft glass. However, the 18Cr-Fe alloy is disadvantageous in that it is inferior in corrosion resistance. For instance, the 18Cr-Fe alloy sealed to soft glass is susceptible to intergranular corrosion when the sealed alloy piece is pickled.

In addition to the above, the following problems are left to be solved with respect to the 18Cr-Fe alloy: Bonding strength between the oxide film and the substrate alloy is weak; the electric resistance of the oxide film is so high that establishment of an electric contact through the oxide film is impossible; and the alloy is liable to undergo precipitation of γ phase from the α phase; when it is heat-treated etc.

According to this invention, an alloy comprising 15–30% by weight of Cr, 0.001–2.0% by weight of at least one element selected from a rare earth metal group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and balance of Fe is provided. The alloy of this invention having a composition within the scope of the above-mentioned range possesses very excellent corrosion resistance. Further, the alloy of this invention may contain 0.1–0.9% by weight of Ti, 0.15–1.5% by weight of Al and 0–0.5% by weight of Mo in addition to the rare earth element or elements. Addition of Ti, Al or Mo increases bonding strength between the oxide film and the substrate alloy, decreases electric resistance of the formed oxide film and prevents precipitation of γ phase out of α phase.

The present invention can be more fully understood from the following detailed description when taken in

conjunction with reference to the appended drawings, in which:

FIG. 1 represents a phase diagram of the Cr–Fe binary system;

FIG. 2 is a graph showing the relation between the Cr content and the thermal expansion coefficient of Cr–Fe alloy; and

FIG. 3 is a graph showing the relation between the Cr content and the mechanical properties of Cr–Fe alloy.

It is known that the Cr–Fe alloy becomes brittle as the Cr content thereof increases, since γ phase is precipitated with increase in the Cr content as shown in FIG. 1. So the Cr–Fe alloy the Cr content of which is too high is not suitable as a glass sealable alloy. The relation between the mechanical properties and the Cr content is shown in FIG. 3. As learned from FIG. 3, increase in the Cr content enhances hardness and tensile strength, but abates ductility and thus the alloy becomes brittle. By considering FIG. 3, the Cr content which gives satisfactory mechanical properties to the alloy was experimentally searched for and the results showed that Cr alloys the Cr content of which is in the range of 15–30% by weight are most suitable in this respect. Also the Cr–Fe alloys containing 15–30% by weight Cr have a thermal expansion coefficient approximately the same as that of soft glass (70×10^{-7}–110×10^{-7} cm./cm./° C.) as shown in FIG. 2.

As is well known, the rare earth elements include the lanthanum series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and Sc and Y. The soft glass-sealable alloy of this invention comprises 15–30% by weight Cr, at least one of the above-mentioned rare earth elements in an amount of 0.001–2.0% by weight and balance Fe. An example showing the effect of addition of the rare earth is given in Tables 1 and 2.

TABLE 1.—COMPOSITION

Sample No.	Cr	Mn	Si	Misch Metal	Fe
1	17.8	0.33	0.27	0.02	Balance.
2	17.3	0.21	0.28	--------	Do.
3	17.2	0.25	0.28	--------	Do.
4	18.0	0.4	0.25	--------	Do.

NOTE.—1. Misch Metal is a mixture of rare earth elements mainly comprising Ce. 2. Numerals stand for content in percent by weight.

TABLE 2.—PROPERTIES OF ALLOYS

Sample No.	Bond strength between oxide film and substrate alloy	Electric resistance of oxide film	Corrosion resistance dissolution weight loss
1	Good	Common	Excellent (0.4 mg./cm.²).
2	Poor	High	Common (5.0 mg./cm.²).
3	do	do	Common (14 mg./cm.²).
4	do	do	Common (11 mg./cm.²).

NOTE.—Each sample was subjected to the wet hydrogen furnace treatment for 10 to 90 minutes under the conditions of 900–1,200° C. of furnace temperature and 0–40° C. of hydrogen dew point so as to produce oxide film on the surface of the alloy substrate and thereafter was sealed to soft glass. The sealed specimen was immersed in an acid solution and weight loss thereof was determined after a predetermined period.

It is apparent from Tables 1 and 2 that the alloy of this invention represented by Sample 1 containing 0.02% by weight of Misch Metal the main component of which is Ce is far superior to the controls represented by Samples 2–4 in that the weight loss of the former when immersed in an acid solution is one-tenth or less of that of controls. Also it is learned from Table 2 that bonding strength between the oxide film and the alloy substrate and electric resistance of the oxide film are also improved in the alloy of this invention in comparison with the controls.

The experimental study revealed that the rare earth element content must be more than 0.001% by weight in order that the effect of the addition thereof is achieved and addition of 20% or more of these elements remarkably impairs workability of the alloy.

Now the effect of adding 0.1–0.9% by weight Ti, 0.15–1.5% by weight Al, and 0–0.5% by weight Mo in addition to the rare earth element is explained. As has been described, the SUS 24 alloy is liable to undergo precipitation of γ phase from α phase, that is to say, is susceptible to metallographic transformation when it is heat-treated, when such a metallographic transformation occurs, the thermal expansion coefficient of the alloy is lowered. If the thermal expansion coefficient of the alloy which is sealed to glass decreases, the difference in the coefficient between the alloy and the glass increases, which will result in cracking of the glass.

It is known, too, that occurrence of the metallographic transformation is closely related to the carbon content of the alloy. As seen in FIG. 1, increase in the carbon content has an effect to expand the γ_1 phase domain up to the γ_2 phase domain, which means expansion of the γ phase domain. And such expansion of the γ phase domain means increase in possibility of precipitation of γ phase out of α phase. I have found that the precipitation of γ phase out of α phase is prevented by further adding 0.1–0.9% by weight Ti or 0.1–0.9% by weight Ti and not more than 0.5% by weight Mo to the Cr–Fe alloy containing 15–30% by weight Cr. When the Ti content is less than 0.1% by weight, it is difficult to inhibit the precipitation of γ phase out of α phase, while the Ti content of 0.9% by weight or more adversely affects bonding of the oxide film and the alloy substrate. Molybdenum enhances the effect of addition of Ti. However, addition of Mo of 0.5% by weight or more is undesirable since Mo has an effect to reduce thermal expansion coefficient. Thus addition of Ti or Ti and Mo in combination makes it possible to prevent cracking of glass sealed to the alloy. I have further managed to increase the bonding strength between the oxide film and the alloy substrate and to decrease electric resistance of the oxide film by adding to the alloy 0.15–1.5% by weight of Al in combination with Ti or Ti and Mo. Aluminum does not exhibit the above-mentioned effect thereof until the content thereof reaches 0.15% by weight, over which the effect is remarkably manifested. Increase of the Al content has tendencies to lower the transformation temperature and to increase expansion coefficient. If 1.5% by weight or more Al is incorporated, the alloy will give greater strain to glass to which the alloy is sealed, which constitutes a reason for possible cracking of the glass.

The effect of this invention is best displayed in the following Tables 3 and 4.

TABLE 3.—COMPOSITION

Sample No.	Cr	Mn	Si	Al	Ti	Mo	MM	Sc	Fe
5	17.8	0.33	0.27	0.21	0.49	0.13	0.02	------	Balance.
6	17.8	0.33	0.27	0.21	0.49	0.13	------	0.02	Do.
7	17.3	0.21	0.28	0.15	0.28	0.11	------	------	Do.
8	17.2	0.25	0.28	0.21	0.34	------	------	------	Do.
9	18.0	0.4	0.25	0.1	------	------	------	------	Do.

NOTE.—Numerals stand for content in percent by weight. MM represents Misch Metal which is a mixture of rare earth elements mainly comprising Ce.

TABLE 4.—PROPERTIES OF ALLOYS

Sample No.	Bond strength between oxide film and substrate alloy	Electric resistance of oxide film	Corrosion resistance dissolution weight loss
5	Good	Low (0.7 Ωk.)	Excellent (0.35 mg./cm.^{2}).
6	do	Low (0.7 Ωk.)	Do.
7	do	Low (8.0 Ωk.)	Common (4.0 mg./cm.^{2}).
8	do	Low (0,7 Ωk.)	Common (13 mg./cm.^{2}).
9	do	High (several tens MΩ).	Common (10.1 mg./cm.^{2}).

NOTE.—Corrosion resistance was determined by the same method as in the case of Table 2.

In Tables 3 and 4, Samples 5 and 6 stand for alloys of this invention. Table 4 tells that dissolution weight loss of the alloys of this invention is less than one tenth of that of controls represented by Samples 7–9. In other words, the alloy of this invention has a corrosion resistance oven ten times higher than the controls. Sample 9 which contains 0.1% by weight Al is apparently inferior to the alloys of Samples 5–8 in electric resistance of the oxide film although the former is satisfactory in the bonding strength of the oxide film to the substrate as well as the latter.

Though, in these embodiments, only Sc and Misch Metal were used as the rare earth elements, it should be understood that this is merely of the illustrative purpose and any of the other rare earth elements or combination thereof has the same effect as Misch Metal or Sc. The alloy of this invention may contain Mn and Si. As to the content thereof, it is desirable to follow the SUS 24 alloy, that is, Mn should preferably be not more than 1.0% by weight and Si should preferably be not more than 0.75% by weight. As to P and S, the SUS 24 alloy should preferably be followed, too.

For the convenience of explanation, this invention has been described with respect to a few particular embodiments thereof in which the SUS 24 alloy the Cr content of which falls within the scope of the Cr content of the alloy of this invention is used as the alloy base. It must be understood, however, that it has been established that alloys other than the SUS 24 such as SUS 27 (SUS 24 plus 8–11% by weight Ni) or SUS 29 (plus 9–13% by weight Ni and Ti) can acquire the characteristic properties as illustrated in the above by incorporation of 0.001–2.0% by weight of at least one rare earth element, 0.1–0.9% by weight of Ti, 0.15–1.5% by weight of Al and 0–0.5% by weight of Mo therein. Therefore it will be understood that the alloy of this invention can contain up to 13% by weight of Ni. For reference, SUS 27 and SUS 29 approximately correspond respectively to AISI–304 and AISI–321 in the American Standard of Testing Material (ASTM).

What is claimed is:

1. An alloy for use in sealing to soft glass which consists essentially of the following ingredients in the percentages by weight specified:

	Percent
Chromium	15–30
Rare earth element	0.001–2.0
Titanium	0.1–0.9
Aluminum	0.15–1.5
Molybdenum	0–0.5
Nickel	0–13
Iron	Balance

2. The alloy of claim 1 wherein Misch Metal is the said rare earth element.

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

75—126 D, 126 G