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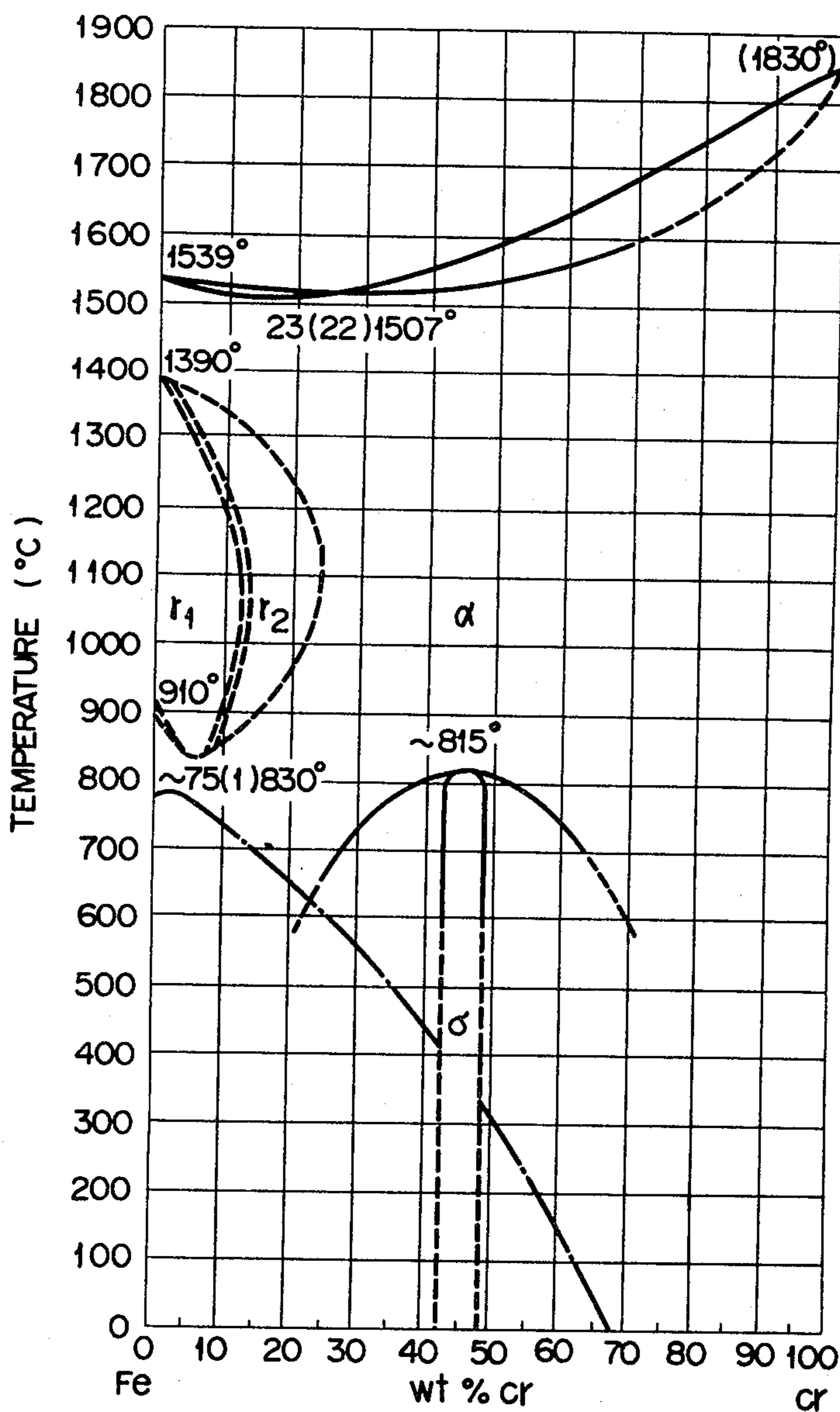
3,737,308

CHROMIUM-IRON ALLOY

Filed July 26, 1971

2 Sheets-Sheet 1

FIG. 1



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FIG. 2

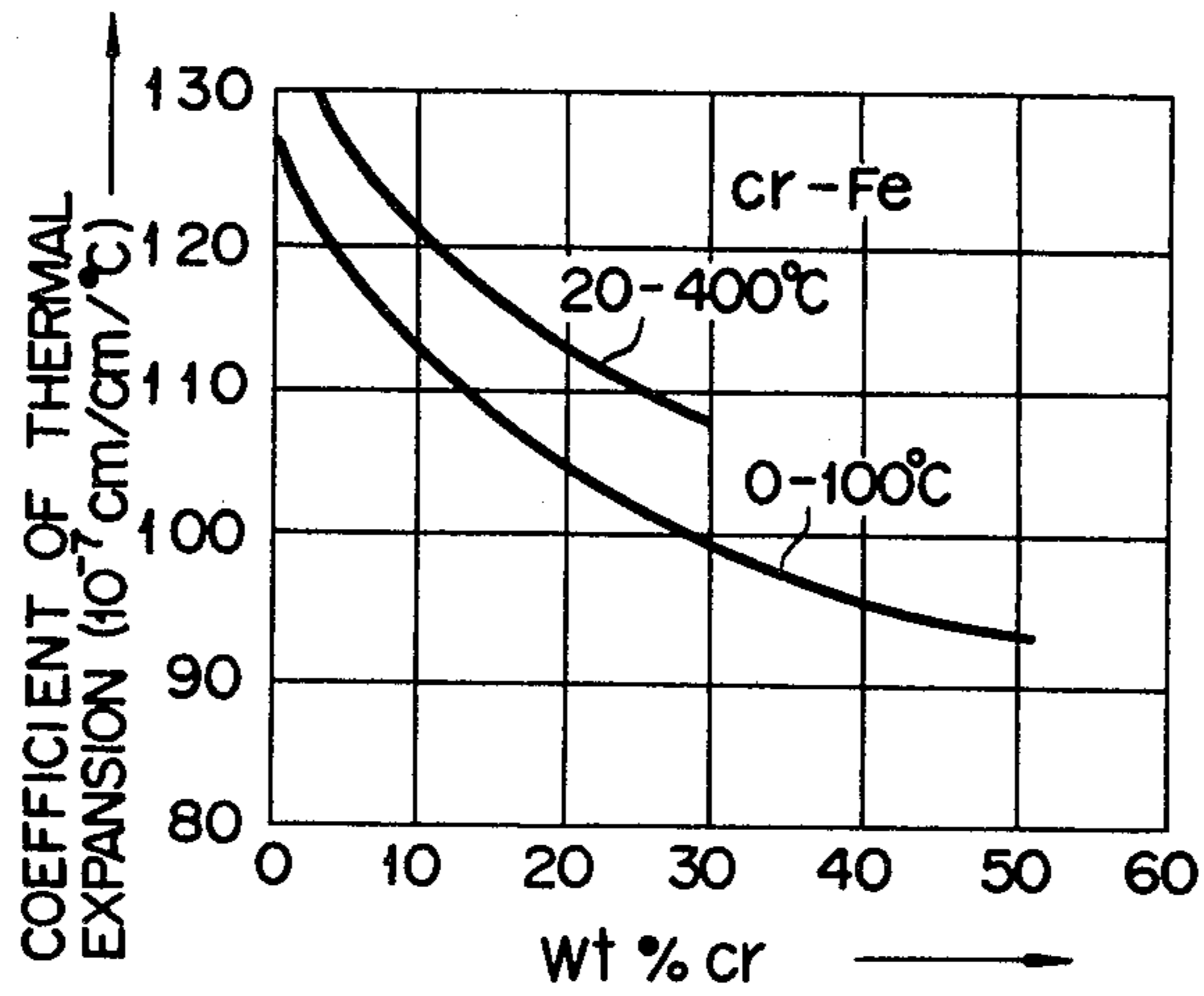
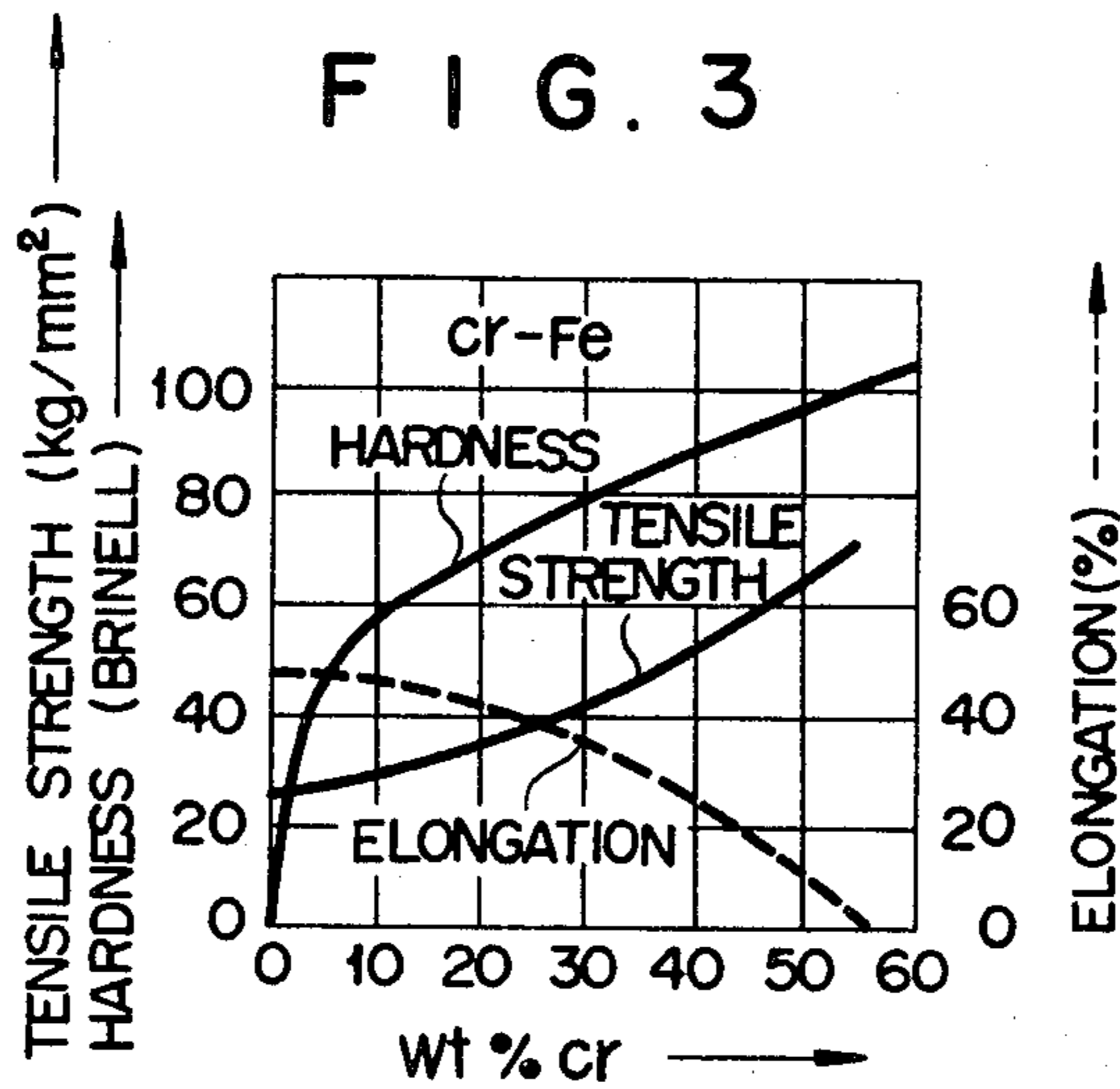


FIG. 3



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CHROMIUM-IRON ALLOY

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1 Claim

ABSTRACT OF THE DISCLOSURE

A sealing alloy comprising 15-30% by weight Cr, 0.1-0.9% by weight Ti, 0.15-1.5% by weight Al, 0-0.5% by weight Mo and balance Fe is provided. The oxide film formed on the surface of this alloy has very low electric resistance and therefore electric contact can be established through the oxide film.

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

As the alloy for sealing soft glass, an 18 Cr-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 Standards (JIS). And 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, after being formed into a desired shape, is 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 having the oxide film on the surface thereof is sealable to soft glass.

When the thus surface-treated 18 Cr-Fe alloy piece is sealed to soft glass, the oxide film is firmly bonded to soft glass. However, the following problems are left to further improvement: (1) Bonding strength between the oxide film and the substrate alloy is weak; (2) The electric resistance of the oxide film is so high that establishment of an electric contact through the oxide film is impossible; (3) The 18 Cr-Fe alloy is, when heat is applied to, liable to undergo metallographic transformation, that is, γ phase is easily precipitated from α phase; etc.

The alloy of this invention is characterized by comprising 15-30% by weight Cr, 0.1-0.9% by weight Al, 0-0.5% by weight Mo and balance Fe. The alloy of this invention having such a composition not only overcomes the above-mentioned defects of the prior art alloy but provides a strong bond between the oxide film formed on the surface of the alloy and soft glass.

This invention can be more fully understood from the following detailed description when taken in connection with the reference to the accompanying drawings, in which:

FIG. 1 is a phase diagram of the Fe-Cr system;

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

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

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As shown in FIG. 2, the thermal expansion coefficient of the Cr-Fe alloys decreases as the Cr content increases. It is learned from FIG. 2 that the Cr-Fe alloy the thermal expansion coefficient of which approximates the thermal expansion coefficient of soft glass (70×10^{-7} - 110×10^{-7} cm./cm./° C.) contains 15-30% by weight of Cr. It will be noted that if the Cr content is increased as shown in FIG. 1, for example, to 42-48% by weight, then a σ phase will be precipitated from α phase, resulting in the Cr-Fe alloy being brittle. Therefore, a Cr-Fe alloy the Cr content of which is too high is not glass-sealable. The relation between the Cr content and the mechanical properties of the alloy is shown in detail 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-Fe alloys the Cr content of which is in the range of 15-30% by weight are most suitable in this respect. Fortunately the Cr-Fe alloys containing 15-30% by weight Cr have a thermal expansion coefficient approximately the same as that of glass as mentioned above with respect to FIG. 2.

The SUS 24 alloy is disadvantageous in that precipitation of γ phase out of α phase easily occurs when heat is applied thereto as referred to in the above. It is known that such precipitation lowers thermal expansion coefficient. That is, if such precipitation takes place in the alloy, the difference of the thermal expansion coefficients between the alloy and the glass increases leading to cracking of the glass.

It is known, too, that occurrence of the phase transformation in which γ phase is precipitated out of α phase is closely related with the carbon content of the alloy. Increase in the carbon content expands the γ_1 phase domain toward the γ_2 phase domain. Such expansion of the γ phase domain means increase of precipitation of γ phase out of α phase. It is also established that such precipitation can be prevented by adding Ti in an amount 5 times that of carbon because the added titanium fixes carbon by carbide formation and thus inhibits expansion of the γ phase domain.

With respect to an alloy the composition of which is similar to the SUS 24 alloy, that is, an alloy containing 15-30% by weight Cr, we could inhibit precipitation of λ phase from α phase by 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 alloy. According to the results of our experiments, the Ti content more than 0.1% by weight is unable to inhibit the precipitation of λ phase from α phase, while the Ti content not less than 0.9% by weight adversely influences bonding of oxide film and the substrate metal. Molybdenum generally enhances effect of Ti, although addition thereof greater than 0.5% by weight is undesirable because it lowers the thermal expansion coefficient.

Though the addition of Ti or Ti and Mo is effective for preventing cracking of glass which is caused by change of expansion coefficient of the alloy due to metallographic transformation thereof, weakness of the bonding between the oxide film and the substrate metal and high electric resistance of the oxide film still remain as the defects. We have managed to overcome these defects with satisfactory results by adding 0.15-1.5% by weight of Al to the alloy in addition to Ti or Ti and Mo. The Al content must be 0.15% by weight or more in order that the effect of the Al addition may be remarkably exhibited. Increase in the Al content lowers the phase transformation temperature and exhibits a tendency of increasing thermal expansion coefficient, and the Al content

greater than 1.5% increases stress in glass when sealed to glass, and may cause cracking of glass.

The effects of this invention will be better understood by referring to the following table.

TABLE

Sample No.	Composition	Bond between oxide film and metal substrate	Electric resistance of oxide film	Phase transformation
1	18 Cr-Fe	Weak	High	Yes.
2	18 Cr-Fe-0.1-0.9 Ti	do	do	No.
3	18 Cr-Fe-0.15 Al	Good	do	
4	18 Cr-Fe-0.1-0.9 Ti-0.15-1.5 Al	do	Low	No.

The alloy of this invention as represented by Sample No. 4 overcomes the defects of the alloy of Sample 1 with respect to all of (1) bonding between the oxide film and the metal substrate, (2) electric resistance of the oxide film and (3) phase transformation. The alloy of Sample 2 is a SUS 24 to which 0.1-0.9% by weight titanium is added. The addition of Ti eliminates phase transformation, but does not improve two other defects. The alloy of Sample 3 which is a SUS 24 alloy containing Al shows remarkable improvement in the bonding between the oxide film and the metal substrate, but shows still high electric resistance of the oxide film.

The alloy of this invention may further contain Mn and Si. But these elements should preferably be not more than 1.00% by weight for Mn and not more than 0.75% by weight for Si in content as well as in the case of the SUS 24 alloy. The carbon content should be as low as possible, preferably not more than 0.1% by weight. As to the contents of P and S, the standards for the SUS 24 alloy are followed.

This invention has been illustrated with respect to the SUS 24 alloy which is a known alloy, the Cr content

of which is within the scope of this invention, for the convenience of easier understanding. However, it has been established that the purpose of this invention can also be achieved by an alloy which is a SUS 27 alloy (SUS 24 plus 8-11% by weight Ni) or a SUS 29 (SUS 24 plus 9-13% by weight Ni and Ti) to which 0.1-0.9% by weight Ti and 0.15-1.5% by weight Al and 0-0.5% by weight Mo, which characterize this invention, are added. For reference, SUS 27 and SUS 29 approximately correspond respectively to AISI 304 and AISI 321 in the American Standard of Testing Material (ASTM). Therefore, it will be understood that the alloy of this invention may contain up to 13% by weight of Ni.

As has been explained, the electric resistance of the oxide film of the alloy of this invention for sealing soft glass is extremely low. When this alloy is used as the material for supporters of a shadow mask of a colour cathode ray tube, a remarkable advantage that the shadow mask and the fluorescent film on the inside surface of the face plate can be made equipotential is achieved.

What we claim is:

1. An alloy sealable to glass consisting essentially of 15-30% by weight Cr, 0.1-0.9% by weight Ti, 0.15-1.5% by weight Al, up to 0.5% by weight Mo and the balance Fe.

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