May 18, 1971 SATORU MITO ET AL 3,579,329

OXIDATION RESISTANT IRON-CHROMIUM-ALUMINUM ALLOYS

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FIG. 1

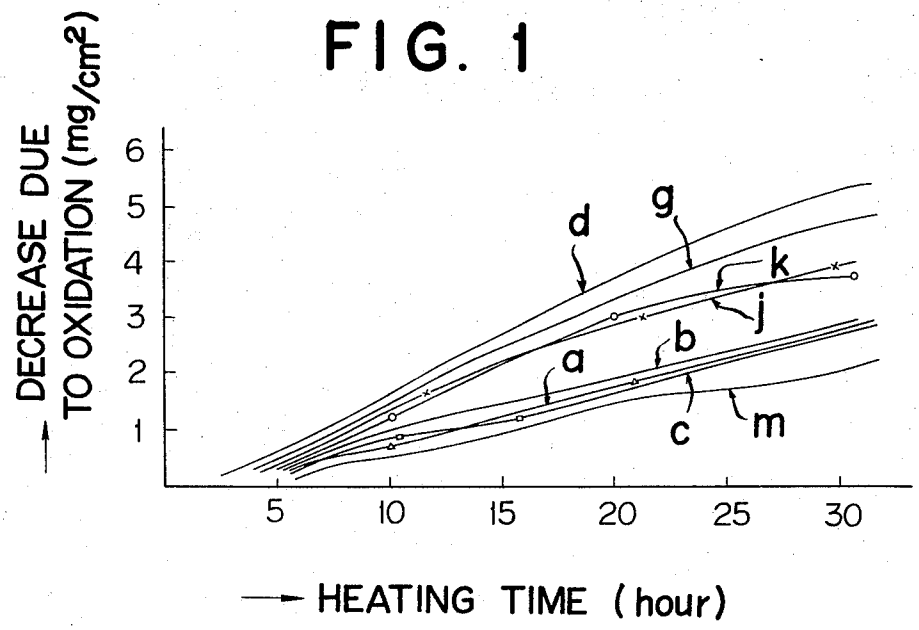
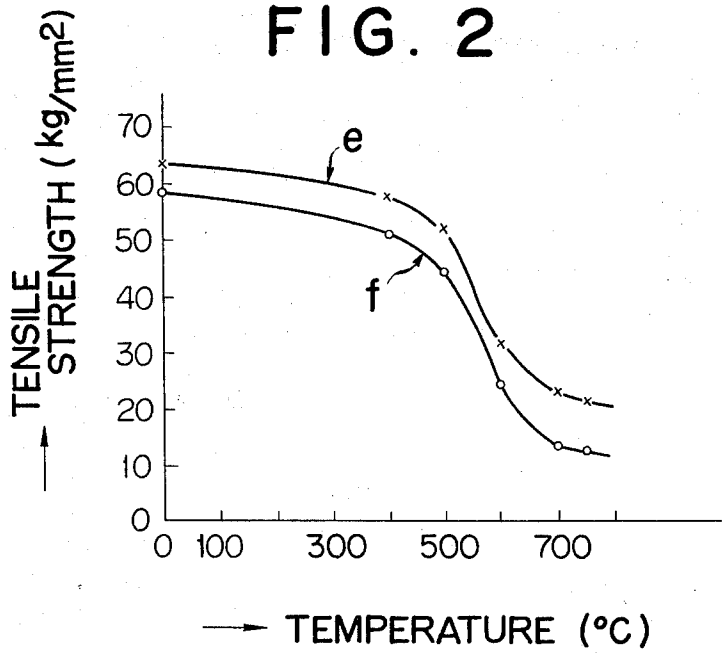


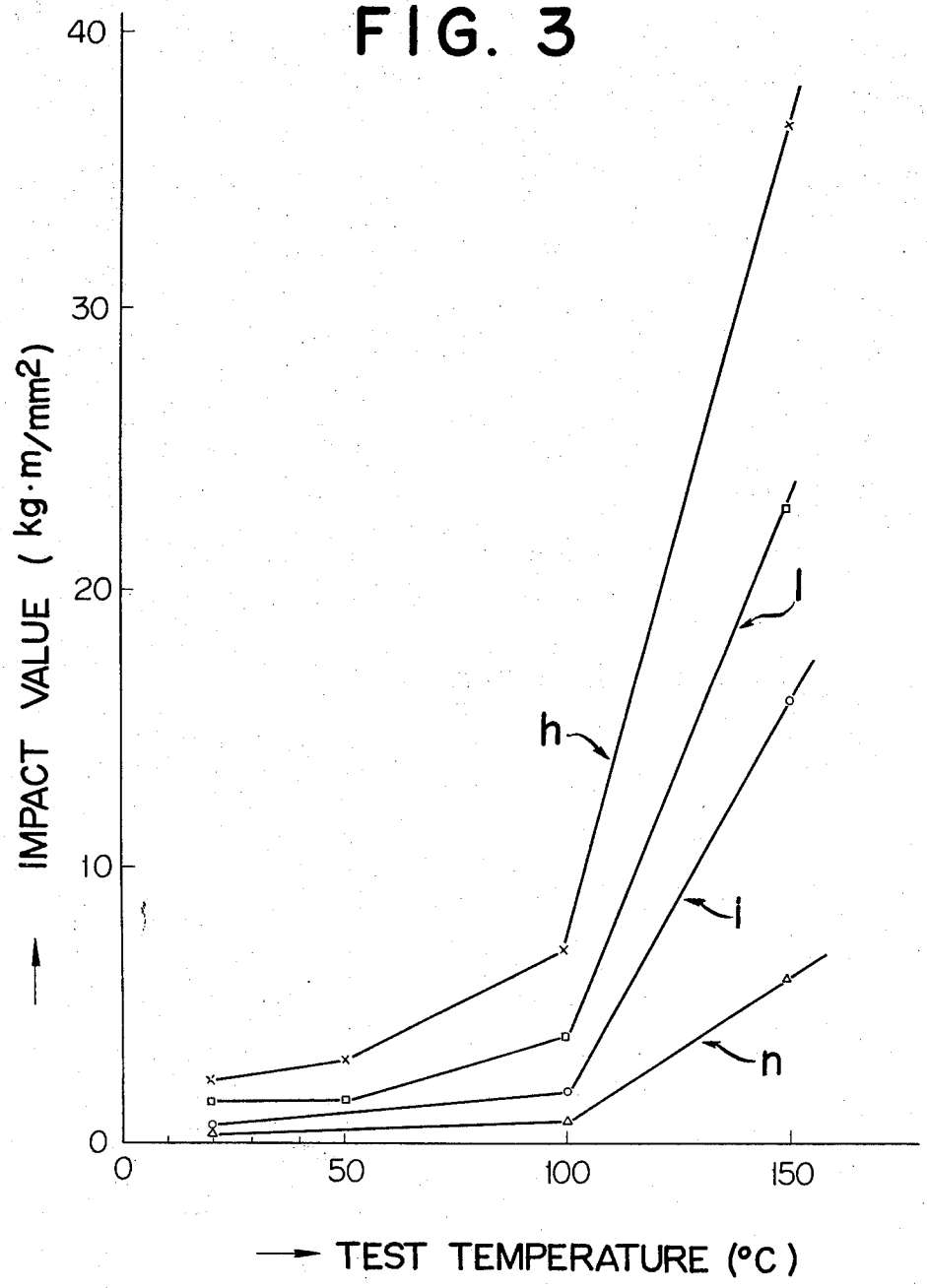
FIG. 2



OXIDATION RESISTANT IRON-CHROMIUM-ALUMINUM ALLOYS

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FIG. 3



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OXIDATION RESISTANT IRON-CHROMIUM-ALUMINUM ALLOYS

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ABSTRACT OF THE DISCLOSURE

Heat resistant and oxidation resistant iron-chromium-alumiunm alloys consisting of 15 to 30 percent by weight of chromium, 3 to 7 percent by weight of aluminum, 0.001 to 0.5 percent by weight of one or more of beryllium, magnesium and barium, remainder iron and incidental impurities.

BACKGROUND OF THE INVENTION

The present invention relates to iron-chromium-aluminum alloys having good mechanical strength and oxidation resistance at elevated temperature.

Heretofore, iron-chromium-aluminum alloys have been employed as materials adapted for electrical and heat resistance due to their excellent anti-oxidation properties at elevated temperature. However, the prior art iron-chromium-aluminum alloys did not display sufficient resistance to oxidation and heat at an elevated temperature of more than about 1300° C.

SUMMARY OF THE INVENTION

The present invention has been accomplished to eliminate the aforementioned shortcomings encountered with the prior art product and provide iron-chromium-aluminum alloys having great high temperature mechanical strength, permitting easy cold rolling and drawing into wires, and particularly possessing excellent oxidation resistance at an elevated temperature of more than 1300° C. and strong resistance to corrosion by sulphur, phosphur, vanadium and lead oxide. Namely, the iron-chromium-aluminum alloys of the present invention are characterized in that they consist of 15 to 30 percent by weight of chromium, 3 to 7 percent by weight of aluminum, 0.001 to 0.5 percent by weight of one or more of beryllium, magnesium and barium, remainder iron and incidental impurities.

BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a curve diagram comparing the depletion due to high temperature oxidation of the alloys of the present invention with that of the prior art alloys;

FIG. 2 is a curve diagram comparing the high temperature tensile strength of the alloys of the invention with that of the prior art alloys; and

FIG. 3 is a curve diagram comparing the impact strength of the alloys of the invention with that of the prior art alloys.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

There will now be described the limits on the composition of the alloys of the present invention.

(1) Chromium imparts anti-oxidation properties to these alloys. If the chromium content falls to below 15 percent by weight there will not be obtained full oxidation resistance. If said content exceeds 30 percent by weight it will reduce the workability of the alloy as a whole. Accordingly, the range of application is set at between 15 and 30 percent by weight.

(2) Aluminum renders the alloys resistant to oxidation at elevated temperature. If the proportions of aluminum decrease from 3 percent by weight the alloy will not have sufficient resistance to oxidation at a temperature of more than 1100° C. If said proportions increase over 7 percent by weight, then not only the workability of the resultant alloy will be harmfully affected, but also its depletion due to oxidation will become more prominent. Thus the proportions of aluminum should fall within the range of 3 to 7 percent by weight.

(3) Beryllium, magnesium and barium may be incorporated singly or in combination of two or more. These materials form in the alloy oxides having a stable melting point and have the effect of improving the high temperature oxidation resistance and workability of the alloy. If one or more of these materials are used in amounts of less than 0.001 percent by weight, the aforesaid effect will not be fully displayed. Conversely, if the addition rises beyond 0.5 percent by weight it will lead to the poor workability of the resultant alloy. Therefore, the preferable range of application is specified at between 0.001 and 0.5 percent by weight.

The alloys having various compositions defined within the aforesaid limits will have the following properties at normal temperature:

Electrical resistance—130 to 140 μΩcm.
Density—77.1 to 7.6
Elongation—30 to 40%
Yield point—35 to 45 kg./mm.²
Tensile strength—65 to 70 kg./mm.²

There will now be described the method of preparing the alloys of the present invention having the aforesaid range of composition. There are first weighed out prescribed amounts of iron and chromium into a crucible made of, for example, alumina. They are thermally melted in the open air, or preferably in vacuum, followed by deoxidation. There are added a prescribed proportion of aluminum and a prescribed amount of one or more of beryllium, magnesium and barium. Finally, the mixture is cast into any desired mold to form an alloy.

As compared with the known Fe-Cr-Al alloys, those of the present invention have a greater resistance to oxidation and are markedly improved in resistance to high temperature oxidation. This may be for the following reason that there are formed on the alloy surface high melting stable oxides such as BeO, MgO or BaO, which will effectively protect the alloy surface with the aid of Al_2O_3 and Cr_2O_3. Accordingly, the alloys of the present invention are fully resistant to a temperature of more than 1300° C. and display, as shown in FIG. 2, far greater high temperature mechanical strength than the same type of alloys of the prior art. Where an alloy of 25 wt. percent chromium-5 wt. percent aluminum-iron as the remainder, an example of the prior art alloys of such type, was melted and cast in the open air, and cold rolled or drawn into wires, it presented cracks at the time of casting at 1050 to 1100° C., obstructing the cold rolling or drawing into wires. With the alloys of the present invention, however, one or more of beryllium, magnesium and barium added seem to carry out forced oxidation, preventing the occurrence of cracks in casting and consequently facilitating cold rolling and drawing into wires. Further, the alloys of the present invention have a greater impact strength and more improved cold working properties than the same type of alloys according to the prior art.

The alloys of the present invention are strongly resistant to corrosion by sulphur, phosphorus or vanadium.

Accordingly, when said alloys are used in the combustion cylinder of a gas turbine, they are prevented from being easily corroded by combustion gases containing the aforementioned elements. Further, the present alloys have a great resistance to corrosion by lead oxide, so that they are well adapted for use in an exhaust gas combustion apparatus for an automobile.

The present invention will be more fully appreciated from the examples which follow. It will be understood, however, that they are only offered by way of illustration and should not be construed to restrict the scope and breadth of the invention or limit the scope of the present claims appended hereto.

EXAMPLE 1

There were weighed out into an alumina crucible 1400 g. of iron and 500 g. of chromium (24.8 percent by weight). The mixture was melted by high frequency heating in an evacuated furnace. To the molten mass was added 0.74 g. of carbon to remove the oxygen contained therein. Then there was added 105 g. (5.2 percent by weight) of aluminum and 8 g. (0.4 percent by weight) of magnesium. The mass was cast into a metal mold to form an alloy. 17.4 g. of the alloy thus prepared was heated to a temperature of 1350° C. in a fully aerated Elemer furnace and kept at this temperature for a certain length of time to measure its depletion per hour due to oxidation. The results are presented as the curve *a* in FIG. 1.

EXAMPLE 2

There was prepared an alloy in the same manner as in Example 1 excepting that the magnesium used in Example 1 was replaced by 10 g. (0.5 percent by weight) of barium. The depletion due to oxidation of this alloy is indicated by the curve *b* of FIG. 1.

EXAMPLE 3

There was prepared an alloy in the same manner as in Example 1 excepting that the magnesium used in Example 1 was replaced by 6 g. (0.3 percent by weight) of beryllium. The depletion due to oxidation of this alloy is indicated by the curve *c* of FIG. 1.

Further by way of comparison, there was formed another alloy in the same manner as in Example 1 excepting that there was not added magnesium. The depletion due to oxidation of this reference alloy is shown by the curve *d* of FIG. 1. Thus it is disclosed that addition of barium, magnesium or beryllium according to the present invention reduced the depletion due to oxidation of the resultant alloy.

EXAMPLE 4

There was obtained an alloy in the same manner as in Example 1 excepting that the addition of magnesium was decreased to 6 g. (0.3 percent by weight). The tensile strength of this alloy from normal temperature to about 800° C. was determined, the results being given by the curve *e* of FIG. 2.

By way of comparison there was prepared another alloy in the same manner as in Example 1 excepting that there was not added magnesium. The tensile strength of this reference alloy is indicated by the curve *f* of FIG. 2. As apparent from this graph, the alloys of the present invention were confirmed to have a more excellent high temperature strength than the same type of alloys of the prior art.

EXAMPLE 5

There were weighed out 1400 g. of iron and 500 g. (24.8 percent by weight) of chromium into an alumina crucible. The mixture was melted by high frequency heating in the open air and deoxidized by adding one gram of silicon. Then there were added 105 g. (5.2 percent by weight) of aluminum and 2 g. (0.1 percent by weight)

of magnesium. After being stirred, the mass was cast into a metal mold to form an alloy. There was conducted an oxidation test on this alloy in accordance with the process used in Example 1, the results being given by the curve *g* of FIG. 1. The alloy was also measured for its impact strength as a means of finding its workability, the results being indicated by the curve *h* of FIG. 3.

By way of comparison, there was formed another alloy in the same manner as in this Example 5 excepting that there was not added magnesium. The alloy displayed an impact strength as shown by the curve *i* of FIG. 3. Comparison of these curves *h* and *i* clearly shows that the presence of minute amounts of magnesium in an alloy substantially improved its workability.

There was cast an alloy in the same manner as in Example 5 excepting that the magnesium was replaced by 2 g. (0.1 percent by weight) of beryllium. The depletion due to oxidation of this alloy is indicated by the curve *j* of FIG. 1.

EXAMPLE 7

There was cast an alloy in the same manner as in Example 1 excepting that the magnesium was replaced by 2 g. (0.1 percent by weight) of barium. The depletion due to oxidation of this alloy is shown by the curve *k* of FIG. 1 and its impact strength by the curve *l* of FIG. 3. These curves *k* and *l* disclose that the alloys of the present invention displayed smaller depletion due to oxidation and more improved impact strength than the prior art Fe-Cr-Al alloys.

This example represents the case where there was used magnesium, a component of the alloys according to the present invention, in amounts exceeding the specified range. There was cast an alloy in the same manner as in Example 1 excepting that there was added 16 g. (0.8 percent by weight) of magnesium. The depletion due to oxidation of the alloy is indicated by the curve *m* of FIG. 1 and its impact strength by the curve *n* of FIG. 3. As apparent from these figures, it is disclosed that any excess addition of magnesium reduced the workability of the resultant alloy due to its low impact strength, though it did not raise any problem in that it decreased the depletion due to oxidation of said alloy.

What is claimed is:

1. Oxidation resistant iron-chromium-aluminum alloys consisting of 15 to 30 percent by weight of chromium, 3 to 7 percent by weight of aluminum, 0.001 to 0.5 percent by weight of at least one metal selected from the groups of beryllium, magnesium and barium, remainder iron and incidental impurities.

2. Oxidation resistant iron-chromium-aluminum alloys consisting of 24.8 percent by weight of chromium, 5.2 percent by weight of aluminum, 0.4 percent by weight of magnesium, remainder iron and incidental impurities.

3. Oxidation resistant iron-chromium-aluminum alloys consisting of 24.8 percent by weight of chromium, 5.2 percent by weight of aluminum, 0.5 percent by weight of barium, remainder iron and incidental impurities.

4. Oxidation resistant iron-chromium-aluminum alloys consisting of 24.8 percent by weight of chromium, 5.2 percent by weight of aluminum, 0.3 percent by weight of beryllium, remainder iron and incidental impurities.

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