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CHROMIUM-IRON ALLOY

Filed March 26, 1965

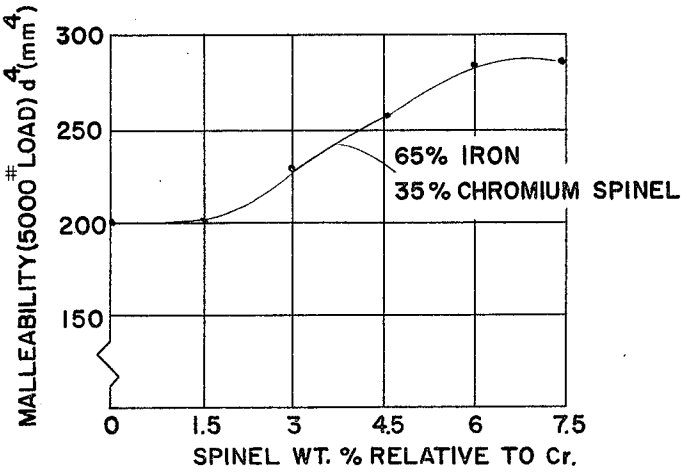


FIG. 2

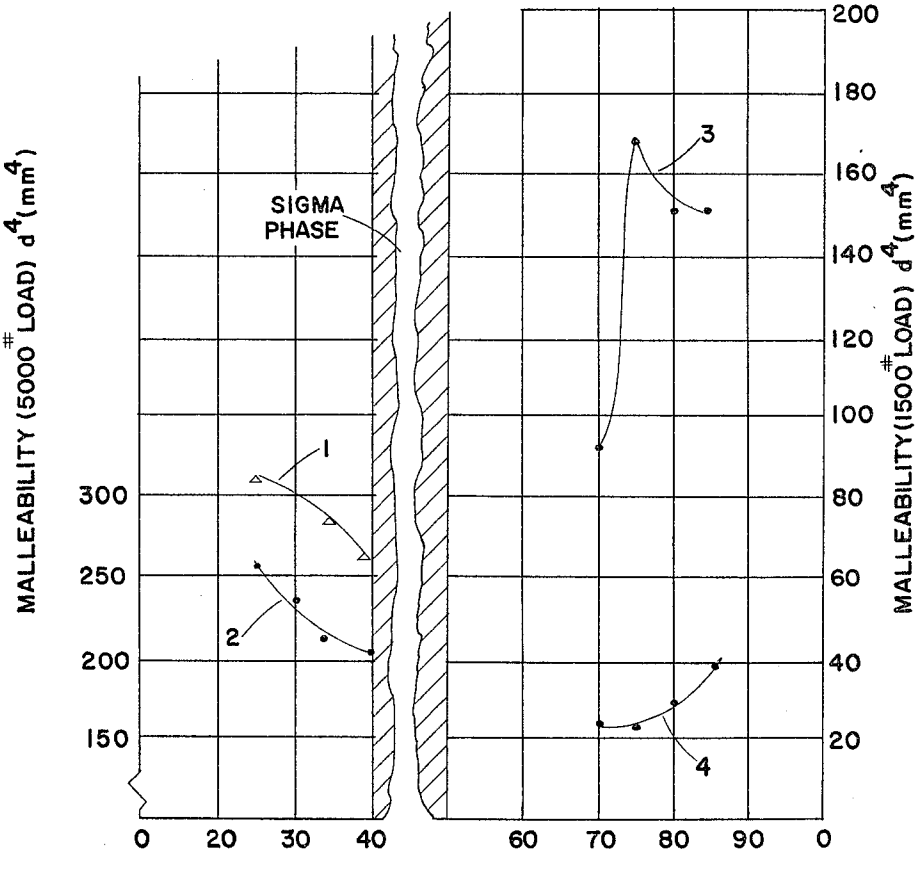


FIG. 1

CHROMIUM - IRON

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CHROMIUM-IRON ALLOY

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5 Claims. (Cl. 75—126)

The present invention is a continuation-in-part of my co-pending commonly-assigned patent application Ser. No. 182,074, filed March 23, 1962, now U.S. Patent No. 3,175,279, entitled Ductile Chromium Composition, which, in turn, is a continuation-in-part of my prior application Serial No. 88,302, filed Feb. 10, 1961, now abandoned.

The present invention relates to a new and improved alloy of chromium and iron having improved malleability and ductility, particularly at low or room temperatures compared to alloys of present commercial grades.

In the iron-chromium alloy system, alloys containing more than 25 to 26% chromium are virtually unused in the present state of the art since they have heretofore been extremely brittle and non-workable at normal temperatures, thus seriously limiting the use of high chromium alloys.

I have discovered that when spinels or spinel-like oxide formations in finally-divided form are distributed throughout a chromium rich iron alloy and said alloy is held at elevated temperatures for a period of time, the spinel acts as repositories for minute amounts of embrittling impurities such as nitrogen, oxygen, carbon, and sulphur and thereby purify the alloy, increasing the room temperature and elevated temperature malleability to a degree not heretofore obtainable, except by prohibitively expensive laboratory techniques.

Spinels are a mixture of metal monoxide and metal sesquioxide which combine according to the general formula $MO \cdot M_2O_3$ (or $M \cdot M_2O_4$), where the M's may be the same or dissimilar metals of the appropriate valence. Monoxide and sesquioxide unite in a complex cubic crystalline structure; however, the cubic crystalline form is not critical to the practice of the present invention and certain metal oxides which combine according to the spinel formula but have tetragonal symmetry or distorted cubic symmetry rather than a perfect cubic symmetry can be used. The term "spinel-like oxide" used herein refers to the broader category including true spinels, inverse spinels, and those compositions corresponding to the spinel formula but having a distorted type of structure, usually tetragonal.

The true spinel structure is essentially a close packed face centered cubic array of oxygen ions with divalent cations in ⅛ of the tetrahedral vacancy positions and trivalent cations in ½ the octahedral vacany positions. Inverse spinels exchange positions of the divalent ions with the trivalent ions. The same coordination may be held

while distorted by larger divalent ions as in calcium chromate, $CaCr_2O_4$ forming a distorted quasi-spinel structure which no longer has cubic symmetry but is tetragonal and remains functional as an electronic isomorph.

It is an object of my invention to provide a chromium-iron alloy having a high chromium content and which includes a small percentage of spinel or spinel-like metal oxide distributed throughout to significantly increase low and elevated temperature malleability of the alloy body even though the alloy constituents are formed of relatively impure commercial grade materials which are readily available.

Other objects and advantages of the present invention will become apparent with reference to the accompanying description and drawings.

The several test and control examples described herein were uniformly processed and tested as described below.

Alloys containing various quantities of chromium and iron, both with and without spinel for comparison purposes, were fabricated into pellets ⅛" thick by ½" diameter by die pressing minus 325 mesh powder at 20,000 p.s.i. These pellets were then sintered in a dry hydrogen, palladium purified atmosphere in a silicon carbide resistor muffle furnace at the temperatures listed in accompanying tables for one hour. The pellets were then ground to a flat finish on one side with emery paper and tested for hardness and malleability.

The hardness test consisted of placing the pellet in a conventional hardness test machine with a ten millimeter Brinell indenting ball in place. The load was applied in increments and the diameter of the impression made by the indenter at each increment was measured and recorded. The load was then increased to 10,000 lbs. or until the pellets cracked. The volume of metal displaced by the indenter is a function of the malleability or ductility of the material; thus, by geometrical considerations the fourth power of the indentation diameter is a deformation number which is directly related to the volume of metal displaced. This can be used to compare the amount of metal displaced at a given load, which, in turn, is related to the malleability or deformability of the particular specimen. The indentation test, briefly described above, was developed by W. H. Lenz, associated with the Los Alamos Scientific Laboratories and is more fully set forth in Los Alamos Scientific Laboratory Report LAMS 2906 entitled, "A New Brittleness Test for Powder Metallurgy Materials," which can be obtained through the Office of Technical Services, United States Department of Commerce.

In Table I below, there are listed eight examples of spinel containing chromium-iron alloys in accordance with the teachings of the present invention fabricated and tested in the above-described manner. A uniform proportion of spinel relative to chromium was maintained in Example 1 through 8 of 6% by weight spinel relative to the chormium content.

TABLE I

Example	Iron (wt. (percent)	Chromium-Spinel (combined wt. percent)	Sintering Temperature, ° C.	d^4	Load on Indenter (lbs.)
1	60	40	1,470	255	5,000
2	65	35	1,470	283	5,000
3	70	30	1,470	310	5,000
4	75	25	1,470	310	5,000
5	40	60	1,500	92	1,500
6	35	65	1,500	168	1,500
7	30	70	1,500	148	1,500
8	25	75	1,500	148	1,500

In the above table, d^4 represents the fourth power of the diameter of the impression made by the Brinell indenter at the load indicated in the adjacent column and is proportional to malleability.

For comparison, eight similar pellets were prepared of chromium-iron alloys excluding the spinel and fabricated and tested identically with Examples 1 through 8, giving the malleability or deformation data recorded in Table II below.

TABLE II

Example	Iron (wt. percent)	Chromium (wt. percent)	Sintering Temperature ° C.	d^4	Load on Indenter (lbs.)
9	60	40	1,470	208	5,000
10	65	35	1,470	208	5,000
11	70	30	1,470	230	5,000
12	75	25	1,470	255	5,000
13	40	60	1,500	24	1,500
14	35	65	1,500	24	1,500
15	30	70	1,500	28	1,500
16	25	75	1,500	38	1,500

The data recorded in Tables I and II are plotted on the graph of FIGURE 1. The graph is a plot of malleability (d^4) versus chromium or combined chromium-spinel content of the chromium-iron alloy. Curve **1** is a plot of spinel containing Examples 1 through 4, whereas curve **2** is a plot of the control Examples 9 through 12. Since acceptable ductility or malleability can be obtained with conventional non-spinel containing chromium-iron alloys having chromium contents of less than 25%, the curves have not been extended below 25% chromium. At slightly greater than 40% chromium content, a sigma phase is produced which is unusable because of intermetallic formation of the constituents causes the alloy to be very brittle and hard.

The right-hand portion of FIGURE 1 is a plot above the sigma phase region wherein curve **3** is a plot of spinel containing Examples 5 through 8 and curve **4** of the control Examples 13 through 16. It will be observed that all spinel containing chromium-iron alloys have increased malleability compared to the controls with a general trend indicated of a greater proportionate increase with higher chromium content. This trend will continue to the 100% chromium-0% iron point as more fully explained in my co-pending previously-referenced patent application Serial Number 182,074, now Patent No. 3,175,279.

The effect of different spinel proportions relative to the chromium content is recorded in Table III wherein the test pellets were fabricated and tested in the previously-described manner.

TABLE III

Example	Iron (wt. percent)	Spinel (wt. percent compared to Cr)	Cr-Spinel combined wt. percent	Sintering Temp., ° C.	d^4	Load on Indenter, lbs.
17	65	1.5	35	1,470	208	5,000
18	65	3	35	1,470	230	5,000
19	65	4.5	35	1,470	255	5,000
20	65	6	35	1,470	283	5,000
21	65	7.5	35	1,470	283	5,000

Examples 17 through 21 are plotted on the curve of FIGURE 2 which plots spinel content versus malleability. As can be observed, malleability increases with spinel content up to a peak at 6 to 7.5% by weight. A desirable malleability improvement is obtained up to approximately 10% by weight spinel. Beyond this point the dispersion hardening effect of the ceramic spinel becomes a negative factor, reducing the effectiveness of further additions. Thus, compared to the chromium content, a maximum of 10% spinel is recommended with a preferred range from 1.5 to 7.5%.

Generally, I have found that chromate and aluminate spinel-like oxides are the most effective and provide the least deleterious effect on the high temperature capability of the metal alloy. The spinels may either be added direct as spinel powder or in the case of chromate spinels, a metal oxide formed from a metal in Group II of the atomic table may be added and will form a chromate spinel during the sintering process with a somewhat impure commercial grade chromium metal as more fully described in my prior application Serial Number 182,074, now Patent No. 3,175,279. From a cost standpoint, chemical inertness, high temperature capability and overall general applicability, the spinel-like oxides or mixtures thereof listed below are preferred:

(Group II oxide) Cr_2O_3—Group II metal oxide-chromate spinels
$CaCr_2O_4$—calcium chromate (distorted spinel)
$MgAl_2O_4$—magnesium aluminate
$ZnAl_2O_4$—zinc aluminate
$MgCr_2O_4$—magnesium chromate
$NiAl_2O_4$—nickel aluminate
$NiCr_2O_4$—nickel chromate

It can be appreciated that spinels are readily available, low cost, and in the percentages employed, provide minimum dilution of the alloy material. This invention provides a low cost practical means to achieve ductility in chromium-iron alloys not now available in wrought or cast form. The described material is readily adaptable for large scale production needs and causes a minimum effect on properties other than malleability or ductility of the base metal property.

Other metals and additives may be added to the chromium-iron alloy described herein for special purposes as desired and the malleability improvement described herein will be obtained as long as the spinel containing chromium-iron alloy is the continuous phase of the end material and such additives are in solution or form a discontinuous phase.

I claim:

1. A chromium-iron alloy having a continuous phase consisting of chromium, iron, and a spinel-like oxide dispersed therein; said spinel-like oxide comprising less than about 10% by weight relative to the chromium content; and the combined chromium and spinel-like oxide content comprising greater than 25% by weight of the continuous phase.

2. A chromium-iron alloy having a continuous phase persed of chromium, iron, and a spinel-like oxide dispersed therein; said spinel-like oxide comprisng from 1.5%

to 7.5% by weight relative to the chromium content; and the combined chromium and spinel-like oxide content comprising greater than 25% by weight of the continuous phase.

3. A chromium-iron alloy having a continuous phase persed of chromium, iron, and a spinel-like oxide dispersed therein; said spinel-like oxide comprising from 1.5% to 7.5% by weight relative to the chromium content; and the combined chromium and spinel-like oxide content comprising from 25% to 40% by weight of the continuous phase.

4. A chromium-iron alloy having a continuous phase consisting of chromium, iron, and a spinel-like oxide dispersing therein; said spinel-like oxide comprising from 1.5% to 7.5% by weight relative to the chromium content; and the combined chromium and spinel-like oxide content comprising greater than 60% by weight of the continuous phase.

5. A chromium-iron alloy having a continuous phase consisting of chromium, iron, and a spinel-like oxide dispersed therein; said spinel-like oxide selected from the groups consisting of chromate spinels, aluminate spinels,

and mixtures of chromate and aluminate spinels; said spinel-like oxide comprising from 1.5 to 7.5% by weight relative to the chromium content; and the combined chromium and spinel-like oxide content comprising greater than 25% by weight of the continuous phase.

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