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CHROMIUM-NICKEL ALLOY

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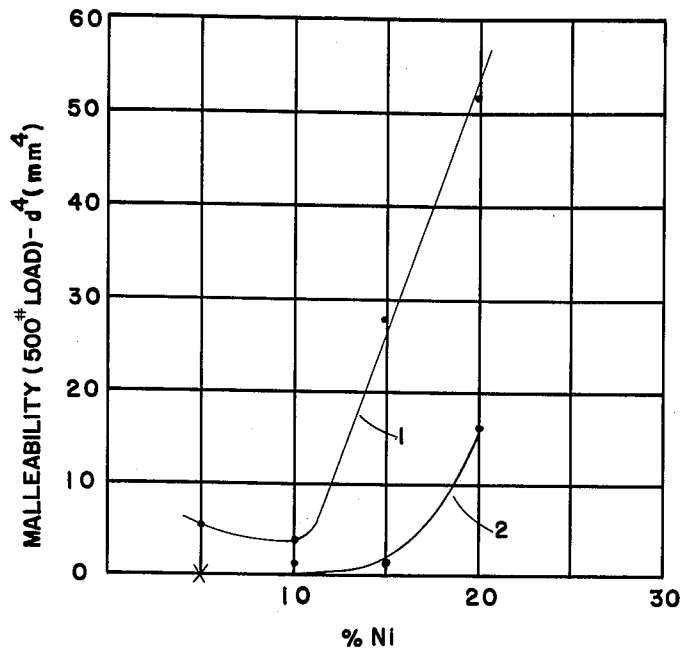


FIG. 1

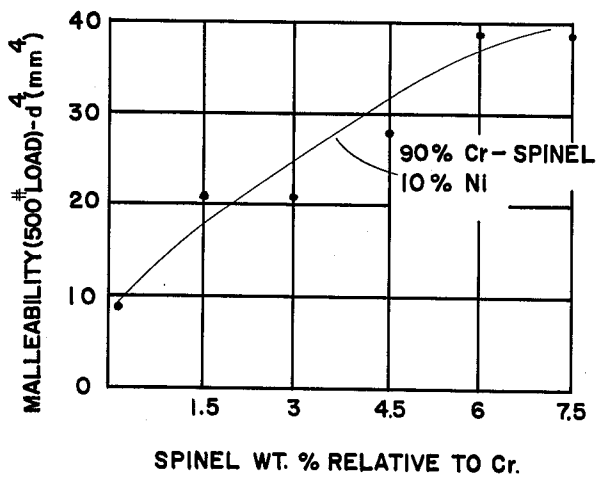


FIG. 2

CHROMIUM - NICKEL

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3,235,380

CHROMIUM-NICKEL ALLOY

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3 Claims. (Cl. 75-176)

The present invention is a continuation-in-part of my co-pending commonly-assigned patent application Serial Number 182,074, filed March 23, 1962, now U.S. Patent No. 3,175,279, granted March 30, 1965, entitled "Ductile Chromium Composition" which, in turn, is a continuation-in-part of my prior application Serial Number 88,302, filed February 10, 1961, and now abandoned.

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

In the present state of the art, nickel-chromium alloys commonly are not available in the wrought condition when containing more than 30% chromium, and cast alloys containing more than 40% chromium are not available.

I have discovered that when spinels or spinel-like oxide formations in finally-divided form are distributed throughout a chromium rich nickel 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.

Spinel is 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 $\frac{1}{8}$ of the tetrahedral vacancy positions and trivalent cations in $\frac{1}{2}$ the octahedral vacancy 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-nickel 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.

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

Alloys containing various quantities of chromium and nickel, both with and without spinel for comparison purposes, were fabricated into pellets $\frac{1}{8}$ " thick by $\frac{1}{2}$ " 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 four examples of spinel containing chromium-nickel 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 Examples 1 through 4 of 6% by weight spinel relative to the chromium content.

Table I

Example	Nickel (wt. percent)	Chromium-Spinel (combined wt. percent)	Sintering Temperature, °C.	d^4	Load on Indenter (lbs.)
1g-----	5	95	1,500	5	500
2g-----	10	90	1,500	4	500
3-----	15	85	1,470	28	500
4-----	20	80	1,350	53	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, four similar pellets were prepared of chromium-nickel alloys excluding the spinel and fabricated and tested identically with Examples 1 through 4, giving the malleability or deformation data recorded in Table II below.

Table II

Example	Controls (wt. percent)	Chromium (wt. percent)	Sintering Temp., °C.	d^4	Load on Indenter (lbs.)
5-----	5	95	1,500	0	500
6-----	10	90	1,500	1.0	500
7-----	15	85	1,470	1.0	500
8-----	20	80	1,350	16	500

The data recorded in Tables I and II are plotted on the graph of the drawings. The graph is a plot of malleability (d^4), versus chromium or combined chromium-spinel content of the chromium-nickel alloy. Curve 1 is a plot of spinel containing Examples 1 through 4 whereas curve 2 is a plot of the control Examples 5 through 8.

The curves show increased malleability for all spinel containing chromium-nickel alloys. The trend is for increased malleability for alloys departing in either direction from the 10% nickel-90% chromium point. Alloys having less than 60% chromium (spinel containing) tend to form two phases which can not be readily worked. Thus, in the chromium-nickel system, the advantages of spinel addition discussed herein can be best achieved with chromium contents of greater than 60% related to the continuous phase of the alloy if other metal additions are present.

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	Nickel (wt. per- cent)	Spinel (wt. percent compared to Cr)	Cr-Spinel (combined wt. percent)	Sintering Temp., °C.	d^4	Load on Indenter (lbs.)
9-----	10	1.5	90	1,500	2.1	500
10-----	10	3	90	1,500	2.1	500
11-----	10	4.5	90	1,500	2.8	500
12-----	10	6	90	1,500	3.8	500
13-----	10	7.5	90	1,500	3.8	500

Examples 9 through 13 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 less than 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 be either 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. 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

5 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

10 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-nickel 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-nickel alloy described herein for special purposes as desired and the malleability improvement described herein will be obtained as long as the spinel containing chromium-nickel 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-nickel alloy having a continuous phase consisting of chromium, nickel, 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 60% by weight of the continuous phase.

2. A chromium-nickel alloy having a continuous phase consisting of chromium, nickel 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 from 60% to 90% by weight of the continuous phase.

3. A chromium-nickel alloy having a continuous phase consisting of chromium, nickel and a spinel-like oxide dispersed therein; said spinel-like oxides selected from the groups consisting of chromate spinels, aluminate spinels, and mixtures of chromate and aluminate spinels; 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 60% by weight of the continuous phase.

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DAVID L. RECK, Primary Examiner.