United States Patent [19]
Merrick
[11] 3,922,182
[45] Nov. 25, 1975

[54] ALLOY ADAPTED FOR FURNACE COMPONENTS

[75] Inventor: Howard Francis Merrick, Suffern, N.Y.
[73] Assignee: The International Nickel Company, Inc., New York, N.Y.

[22] Filed: Jan. 22, 1973
[21] Appl. No.: 325,887

[52] U.S. Cl. .... 148/32; 29/182.5; 75/171; 75/206; 139/425; 148/11.5 F; 148/126
[51] Int. Cl.² C22C 19/05
[58] Field of Search ...... 75/171, 170, .5 AC, .5 BA, 75/.5 BC, 205; 148/32, 32.5, 11.5 F, 126; 29/182.5; 139/425

[56] References Cited

UNITED STATES PATENTS

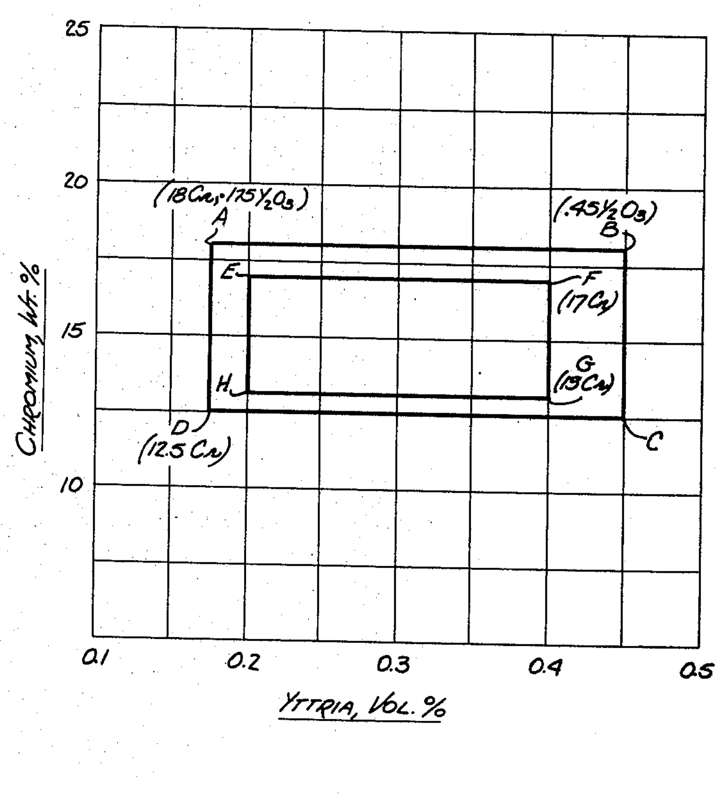
1,609,849	12/1926	Wagner	34/208
2,152,939	4/1939	Wentworth	156/3
3,368,883	2/1968	Barnett et al.	29/182.5
3,388,010	6/1968	Stuart et al.	148/11.5 F
3,393,067	7/1968	Alexander et al.	75/171
3,556,769	1/1971	Lambert et al.	75/.5 AC
3,749,612	7/1973	Benjamin et al.	148/11.5 F

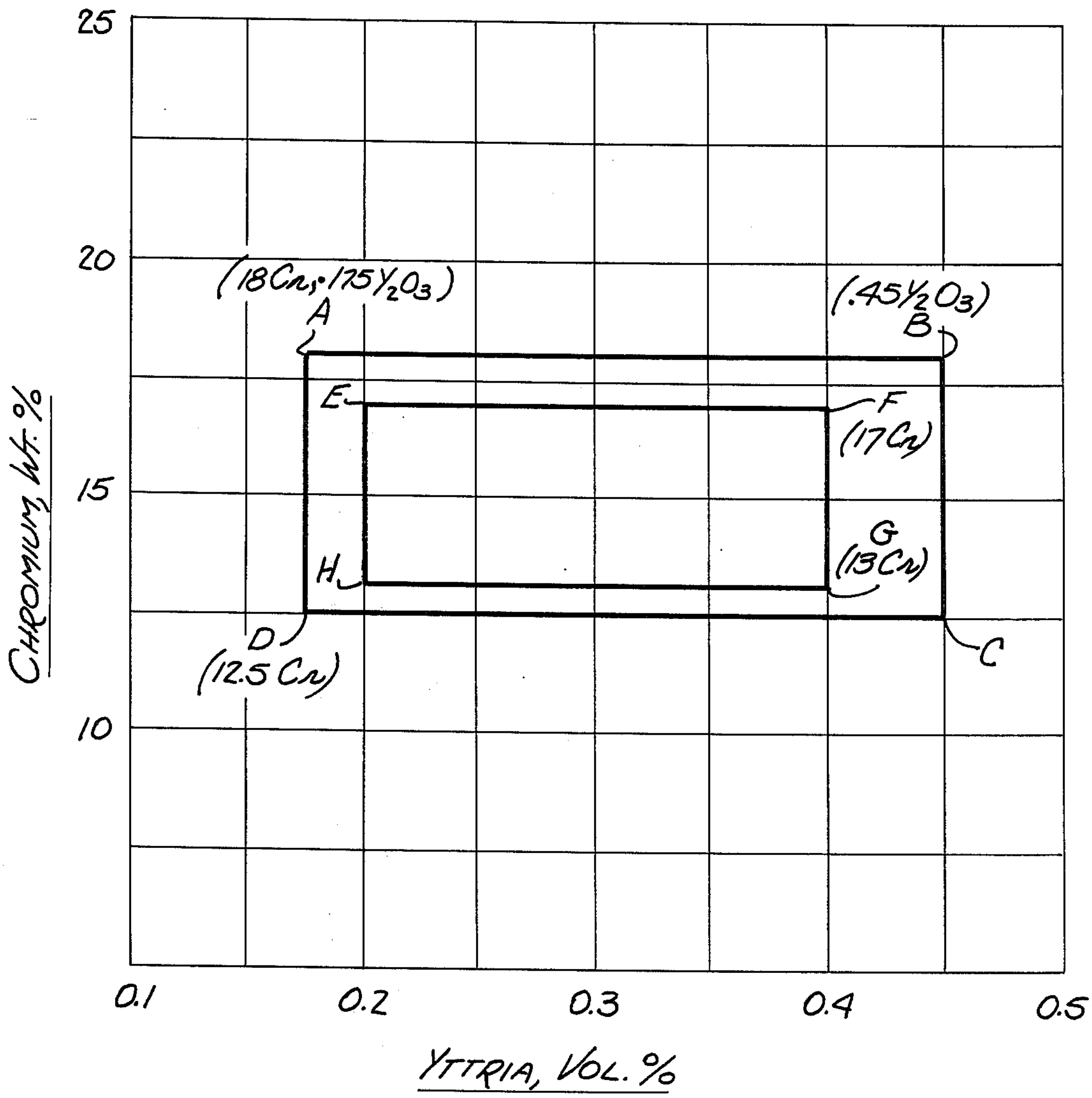
Primary Examiner—R. Dean
Attorney, Agent, or Firm—Raymond J. Kenny; Ewan C. MacQueen

[57] ABSTRACT

A dispersion strengthened nickel-base alloy containing correlated percentages of chromium, yttria, aluminum, titanium and carbon, the alloy being adapted for use in the fabrication of components for high temperature furnaces.

4 Claims, 1 Drawing Figure




25
20
15
10
(18Cr, .175 Y2O3)
A
(.45 Y2O3)
B
E
F
(17Cr)
G
(13Cr)
H
D
(12.5 Cr)
C
CHROMIUM, WT. %
0.1
0.2
0.3
0.4
0.5
YTTRIA, VOL. %

ALLOY ADAPTED FOR FURNACE COMPONENTS

The subject invention is addressed to high temperature alloys, and particularly to novel cold workable, dispersion-strengthened nickel-chromium alloys capable of being fabricated into structural components for use in high temperature furnaces.

As is known, nickel and nickel-base alloys have found extensive use in combatting the destructive effects occasioned by high temperature. For example, in respect of furnaces of the heat treating and sintering types, wire mesh conveyor belts are fabricated from such alloys by virtue of the fact that the alloys offer reasonably good strength characteristics and resistance to oxidation at elevated temperature. Such attributes notwithstanding, it is considered that the wire mesh belt industry would respond favorably to a material of increased temperature capability. This is not to say the present invention is intended to be restricted to wire mesh belt fabrication.

During the course of my investigation, some consideration was given to TD Ni and also to TD NiCr, alloys of the dispersion strengthening type. TD Ni does possess good high temperature strength and is relatively cold workable; however, it suffers from lack of oxidation resistance. On the other hand, while the resistance to oxidation of TD NiCr is acceptable, its strength characteristics leave something to be desired, this by reason of difficulties encountered in respect of using practical, conventional cold working procedures while retaining a fibrous grain structure, particularly one in which the aspect ratio exceeds about 5 or 7 to 1. And good cold working characteristics are rather indispensable if such products as wire and sheet are to be produced for subsequent fabrication.

In any case and in accordance with the present invention, it has been found that highly oxidation resistant, cold workable alloys can be produced and which are capable of delivering high strength at elevated temperature, provided a special correlation is maintained among a combination of certain constituents, including nickel, chromium, yttria and other elements as discussed below, and provided further that the alloys are characterized by a microstructure as also described below.

Generally speaking, alloys in accordance herewith contain from about 12.5 to 20% by weight of chromium, a small but effective amount of yttria (by volume) sufficient to impart improved strength to the alloys, the upper level preferably being not greater than about 0.45%, up to 0.5 or 1% each of aluminum and titanium, up to 0.1% carbon and the balance essentially nickel. As will be understood by those skilled in the art, in referring to nickel as constituting the balance or "balance essentially" of the alloys, other elements may be present which do not adversely affect the basic characteristics of the alloys.

In carrying the invention into practice, the chromium level should not fall below about 12.5%, less oxidation resistance be impaired. Chromium percentages much above 20% tend to introduce other problems, notably undesirable limitations with regard to cold working procedures in combination with grain structure defects as will be discussed in greater detail herein. A chromium range of about 13 to 18% is deemed particularly beneficial.

Careful control should be exercised in respect of the yttria content, particularly in relation to chromium. Though a yttria level of up to possibly 0.5% (volume) might be tolerated, if yttria is present to the excess, cold working problems can be introduced. Although in accordance herewith the yttria content is quite low, nonetheless, tensile strength at room temperature and tensile and stress rupture strengths at elevated temperatures, circa 2000° to 2100°F., are quite adequate. In seeking the best combination of strength and cold workability, the alloys should contain about 0.2 or 0.25 to about 0.4 or 0.45% by volume of yttria.

In addition to the foregoing, the chromium and yttria percentages should be correlated such as to represent a point falling within the area encompassed by the rectangle ABCD of the accompanying drawing. In this regard, it is considered that if the upper yttria levels are used concurrently with the higher chromium contents, a lesser amount of cold work can be imparted to the alloys than otherwise would be the case. Thus, to cold draw an alloy containing about 0.45 to 0.5% yttria (volume) and 20% chromium, results in a situation in which not much more than about the cold reduction of 10% can be obtained while retaining the necessary elongated grain structure upon high temperature exposure essential to strength. This places a heavy burden on fabricability. It is of benefit that the yttria and chromium be proportioned to give a point within area EFGH of the drawing.

In seeking optimum results in terms of cold working, aluminum and titanium should not exceed about 0.5%, respectively, a range of about 0.1 to 0.5% being satisfactory for each. Carbon should not exceed about 0.075%. As to other elements, iron is unnecessary although amounts up to say 5 or 10% can be present. Oxygen and nitrogen should preferably not exceed about 0.5% and 0.2%, respectively.

In order to obtain a fine, uniform yttria dispersion throughout the alloy matrix, the alloys should be prepared by the "mechanical alloying" technique as described in U.S. Pat. No. 3,591,362. This is a process in which a charge of constituent powders is subjected to dry, intensive high energy milling in a machine such as an attritor whereby the initial constituents become intimately interdispersed to form dense and exceptionally homogeneous composite alloy powder particles, the composition of which correspond to the respective percentages of the constituents found in the original charge. For purposes of illustration and using a 4 gallon attritor, a ball-to-powder ratio of 10:1 to 30:1 (volume) can be used at an impeller speed of about 250 to 300 rpm for a period of 15 to 25 hours under a nitrogen-oxygen atmosphere. In using 52100, through hardened balls, it should be borne in mind that iron will be likely introduced into the final composite particles. If iron is undesired, nickel carbonyl balls might be preferred.

It is important that the alloys ultimately be characterized by a microstructure of coarse, elongated grains as opposed to, for example, a fine grain structure. In the latter case, stress rupture strength at the temperatures under consideration is virtually nil. To explain—in the normal course of processing, the composite product particles are hot consolidated, as by hot extrusion, temperatures of 1800° to 2100°F. being used together with extrusion ratios of 10:1 to 25:1. Subsequent to further hot working, if any, the alloys are subjected to a germinative grain growth heat treatment over the range of about 2350° to about 2500°F. for about ½ to 1 hour.

Should the temperature be too low, the fine grain structure of the hot consolidation treatment will persist with attendant inferior properties. Incipient liquation difficulties will ensue should the grain growth treatment be too high.

In order to give those a better appreciation of the present invention, the following data are given:

A series of Alloys 1, 2 and A (outside the invention) Table I, was prepared by the mechanical alloying process, 123 carbonyl nickel powder of minus 325 mesh, 99.99% chromium powder minus 100 plus 200 mesh, 300M iron powder minus 100 mesh, a nickel-aluminum master alloy minus 100 mesh and fine yttria, were blended into a charge and placed in a 4-gallon attritor. The impeller speed was maintained at about 250 rpm, the milling being conducted for a period of about 20 hours. A ball-to-powder ratio (volume) of about 25:1 was used with a nitrogen-air atmosphere being maintained during processing.

The composite alloy powders so produced were then sealed in a cylindrical mild steel can and extruded to three-fourths inch bar at a temperature of 2000°F., an extrusion ratio of 22:1 being used.

TABLE I

Alloy	Chemical Composition Cr %	Y_2O_3* %	Al %	Fe %	N %	O %	C %	Ni %
1	13.1	0.22	0.24	—	0.034	0.48	0.056	Bal.
2	17.8	0.21	0.27	—	0.034	1.1	0.053	Bal.
A**	18.8	0.26	0.35	46.0	0.049	1.13	0.029	Bal.

*weight %
**contained 0.25% titanium

Upon extrusion, bar stock specimens were annealed for 1 hour at temperatures of 2300°F., 2400°F. and 2500°F. to ascertain the temperatures at which germinative grain growth would occur. At 2300°F., none of the alloys manifested any appreciable evidence of grain growth. When annealed at 2400° and 2500°F., however, both Alloys 1 and 2 were characterized by a desired coarse microstructure. In the case of Alloy 1, the structure was more of a stubby grain type, whereas the grains were elongated in respect of Alloy 2. In contrast, Alloy A was incapable of responding to treatment and exhibited an undesired fine-grain, equiaxed structure.

Reported in Table II below are the tensile properties determined at both room temperature and 2050°F. for each of the three alloys as extruded and annealed for 1 hour at 2400°F.

TABLE II

Alloy	70°F. .2 Y.S. ksi	70°F. U.T.S. ksi	70°F. El. %	70°F. R.A. %	2050°F. .2 Y.S. ksi	2050°F. U.T.S. ksi	2050°F. El. %	2050°F. R.A. %
1	57.1	94.6	28	47.5	13.1	13.5	14	34.5
2	71.6	127.9	18	28	17	17.8	8	15
A	76.7	102.2	13	17.5	1.6	2.8	27	29

It will be observed that both alloys 1 and 2 exhibited excellent tensile characteristics including both strength and ductility not only at room temperature, but more importantly, at elevated temperature. Quite apart from the fact that Alloy A was characterized by an undesirable fine, equiaxed microstructure, it greatly suffered in respect of tensile strength, notably at 2050°F. This occurred notwithstanding the relatively higher yttria level. It is also considered that the lower ductility level of Alloy 2 vs. Alloy 1, particularly room temperature ductility, was in large part due to the much higher oxygen content.

Stress rupture properties were also determined in respect of Alloys 1 and 2 and the results are given in Table III. (Tests were not conducted on Alloy A owing to the inherently low tensile strength thereof). In the course of the stress rupture evaluation, specimens were first tested at a selected stress level for approximately 100 hours. If failure did not occur within this given time period, the stress was increased and allowed to creep a further 100 hours. This procedure was repeated until a stress level was obtained leading to rupture in less than 100 hours.

TABLE III

Alloy	Test Temp. °F.	Stress ksi	Life hrs.	Elong. %	R.A. %
1	2050	8	115	Unbroken	
		10*	99	Unbroken	
		11*	34.3	4	9.8
2	2050	12	121.5	Unbroken	
		13*	37.8	7	24

*stress on specimen raised to shown value

Both Alloys 1 and 2 responded very well in this test. In this connection, an acceptable wire belt alloy should afford a 100 hour rupture strength at a temperature of 2050°F. at a minimum stress level of 6,000 psi. This was far surpassed by each of the alloys in question.

Alloys 1, 2 and A were tested for response to cold working. Specimens were first extruded, annealed at 2400°F. and then subjected to various percentages of cold reduction. As a result, it was determined, for example, that Alloy 1 could be cold reduced by a factor of 86% without recourse to re-annealing. Notwithstanding that Alloy 1 was susceptible to such a high degree of cold deformation, a fibrous grain structure did not develop upon subsequent annealing at 2400°F. Further attempts to develop the desired grain structure by annealing at various temperatures were unsuccessful. However, it was found that with lower percentages of cold reduction, an acceptable and satisfactory grain structure could be produced, the alloy being amenable to recrystallization. In this connection, it was determined that Alloy 1 could be cold reduced by approximately 40 to 45% while maintaining a uniform fibrous grain structure. It should be mentioned that fine grains were developing at the boundaries of the coarse fibrous grains at a cold reduction of approximately 44%. This does permit regions of inhomogeneity to develop.

With regard to Alloy 2, it was not receptive to cold working to the extent of Alloy 1. It was determined that a maximum cold reduction of approximately 36% was obtainable in the absence of re-annealing. Recrystallization to a fine equiaxed grain structure occurred upon annealing after a cold reduction of less than 20%. This alloy contained a higher chromium-yttria level than did Alloy 1. As above indicated, the chromium-yttria corelation should most advantageously fall within the area EFGH of the drawing.

Tabulated in Table IV are the tensile and stress rupture results obtained for Alloys 1 and 2 as a consequence of cold reduction (CR) and then annealing at 2400°F.

TABLE IV

		Tensile Properties				Stress-Rupture Properties			
Alloy	Condition	.2% YS ksi	UTS ksi	El. %	RA %	Stress ksi	Life hrs.	El. %	R.A. %
1	24% CR+1 hr/2400°F (coarse,	15.5	20.5	7.5	23	9	114	Unbroken	
	fibrous grains)					11*	12	3.8	8.7
	44% CR+1	12.3	16.1	2.0	8.5	8	115	Unbroken	
	hr/2400°F					10*	9.6	—	—
1	(coarse, fibrous grains) some fine grains					9	nil	1.2	1.4
2	36% CR+1 hr/2400°F (fine equiaxed grains)	4.9	10	5.5	4.5	9	nil	5	4.4
						6	nil	7.5	7.0

*Stress on specimen raised

With regard to the data immediately above, the tensile tests for Alloy 1 show an increased strength level over that determined in the extruded and annealed condition (Table II). Material cold drawn 24% and then annealed at 2400°F. also exhibited excellent creep rupture strength at 2050°F. The tensile properties of the material cold drawn 44% and annealed are somewhat lower, with the stress rupture results being somewhat mixed. It is thought that this behavior is attributable to the fact that upon annealing after the 44% cold work, some fine grains developed. This in turn would subvert stress rupture characteristics. The fine grain structure was responsible for the poor stress rupture and tensile properties of Alloy 2.

Cyclic oxidation tests were also performed on prepared examples of Alloys 1 and 2, the tests being conducted at 2012°F. for 168 hours in an air-5% H_2O atmosphere, the specimens being cooled to room temperature each 24 hours. Oxidation was measured by weight loss in both the undescaled and descaled conditions. Alloy 1 underwent a loss of 2.92 mg/cm^2 in the undescaled condition and 8.14 mg/cm^2 descaled. The corresponding losses for Alloy 2 were 2.88 and 7.75 mg/cm^2, respectively. These results are considered quite attractive in comparison with currently used alloys (Fe-35-Ni-19 Cr and Fe-35-Ni-19 Cr(Cb stabilized). In a carburization test at 2012°F. in H_2-2% CH_4 for a period of 5 hours, Alloys 1 and 2 were not as good in comparison with the same alloys.

It will be understood that modifications and variations of the invention may be resorted to without departing from the spirit and scope thereof as those skilled in the art will readily understand. Such are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A cold worked dispersion strengthened mechanically alloyed composition suitable for use in the fabrication of components for high temperature furnaces and consisting essentially of from about 12.5 to 20% chromium, a small but effective amount of yttria sufficient to enhance the strength characteristics of the alloy, the upper level being up to 0.45% by volume, up to 1% aluminum, up to 1% titanium, up to 0.1% carbon, and the balance essentially nickel.

2. A cold worked, dispersion strengthened mechanically alloyed composition suitable for use in the fabrication of components for high temperature furnaces, said alloy being characterized by a microstructure (i) substantially devoid of fine grains, (ii) in which the grains are coarse and elongated, and (iii) in which the aspect ratio of the grains is at least 5:1, said alloy consisting essentially of about 12.5 to 18% chromium, about 0.175 to about 0.45% yttria, the chromium and yttria being correlated so as to represent a point falling within the area ABCD of the accompanying drawing, up to 1% aluminum, up to 1% titanium, up to 0.1% carbon and the balance essentially nickel.

3. An alloy in accordance with claim **2** in which the chromium and yttria are correlated so as to represent a point falling within the area EFGH of the accompanying drawing.

4. As a new article of manufacture wire mesh belts for use in high temperature furnaces are formed from an alloy having a composition as set forth in claim **1.**

* * * * *