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Schultz et al.

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[45] **Oct. 14, 1975**

[54] **OXIDATION RESISTANT DISPERSION STRENGTHENED ALLOY**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 254,106, May 17, 1972, abandoned.

[52] **U.S. Cl.** .... **148/31;** 29/182.5; 75/.5 BA; 75/.5 BC; 75/122; 75/124; 75/134 F; 75/171; 75/206; 148/32; 148/32.5; 148/126

[51] **Int. Cl.** **C22c 19/00**

[58] **Field of Search** .... 75/171, 170, .5 BA, .5 BC, 75/206, 122, 134 F, 124; 148/32, 32.5, 126, 31; 29/182.5

[56] **References Cited**

UNITED STATES PATENTS

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Primary Examiner—R. Dean
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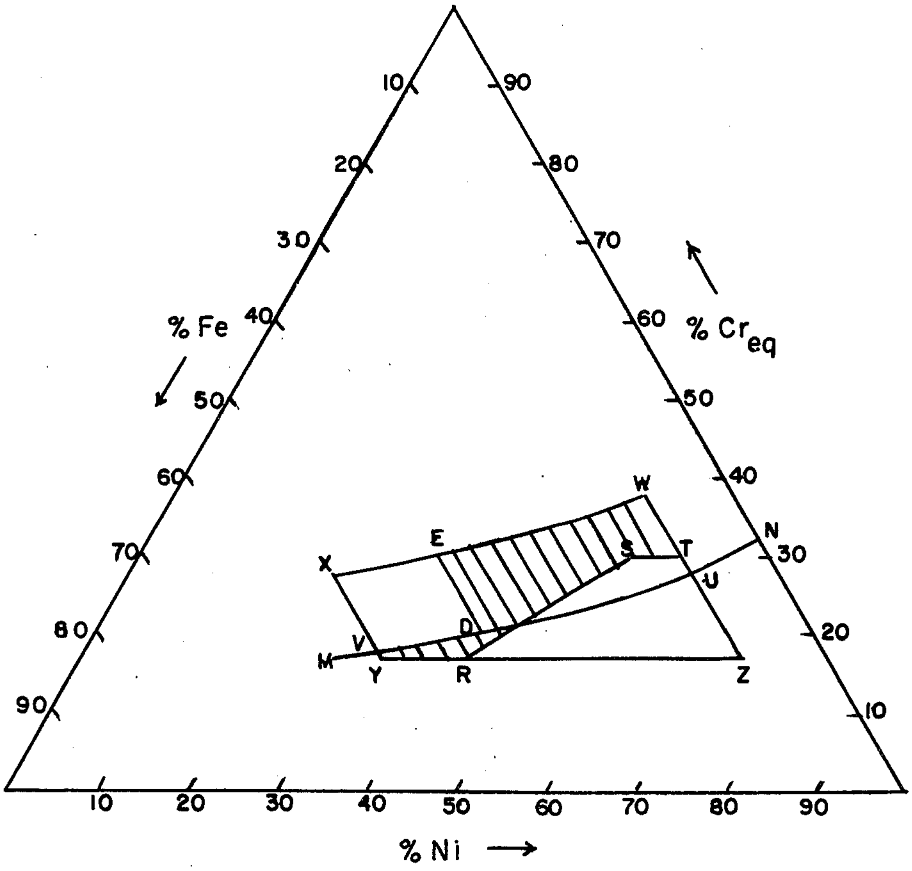
[57] **ABSTRACT**

A dispersion-strengthened nickel-base alloy comprising correlated amounts of iron, chromium, and aluminum. The alloy exhibits superior oxidation and sulfidation resistance and high temperature strength.

21 Claims, 5 Drawing Figures



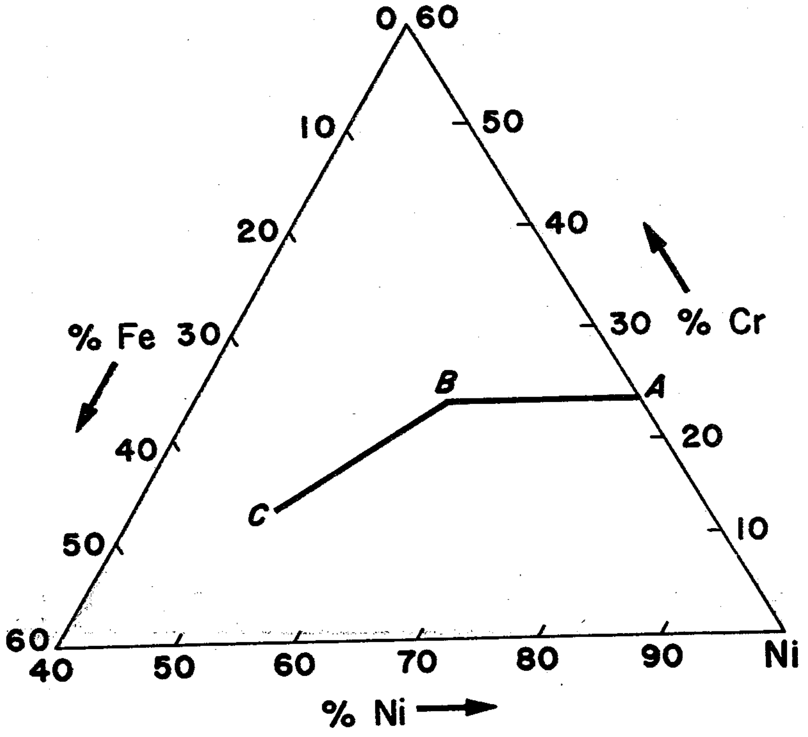


FIGURE I. SULFIDATION RESISTANCE

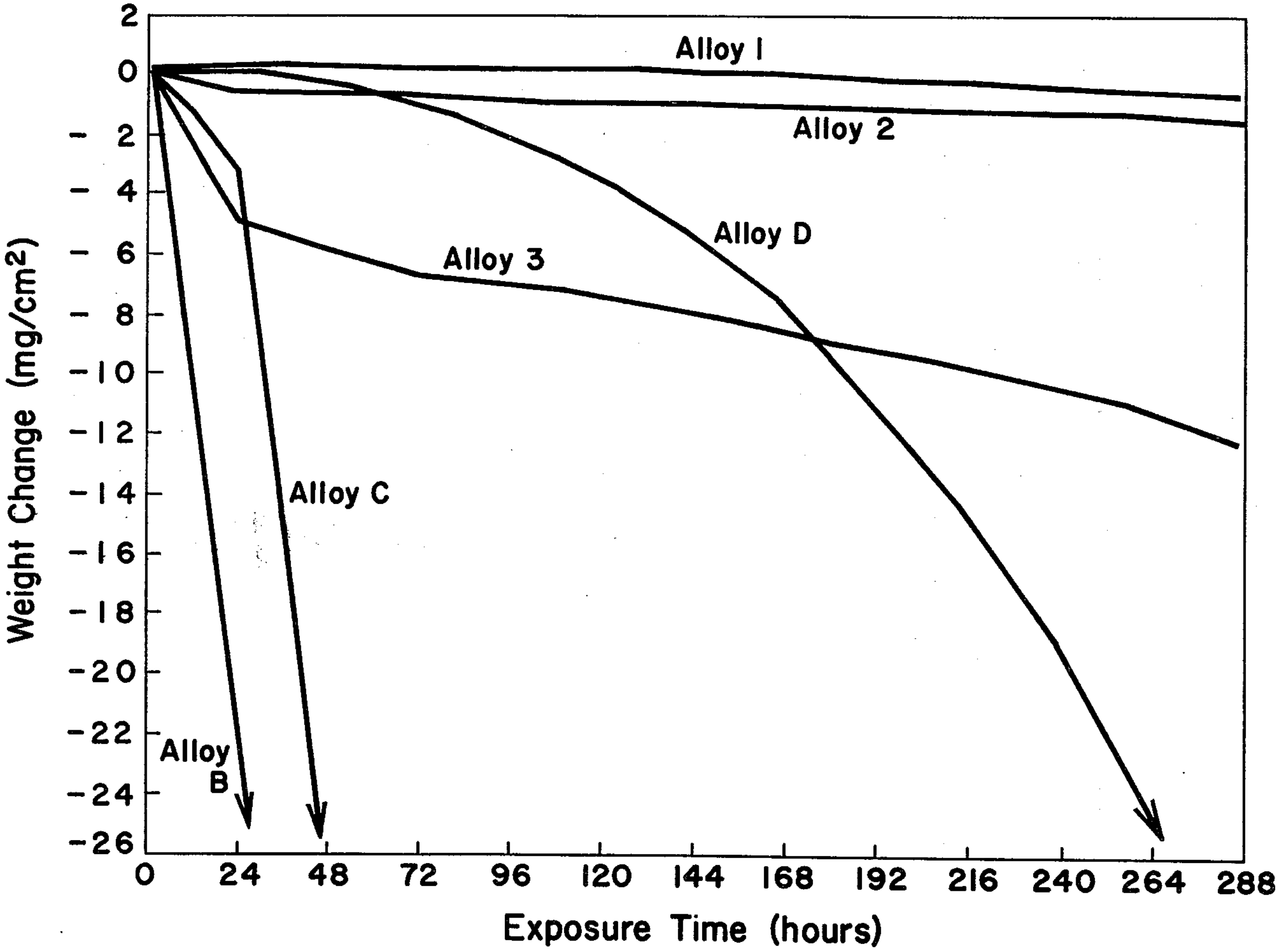


FIGURE 2. SCALING RESISTANCE DURING CYCLIC OXIDATION

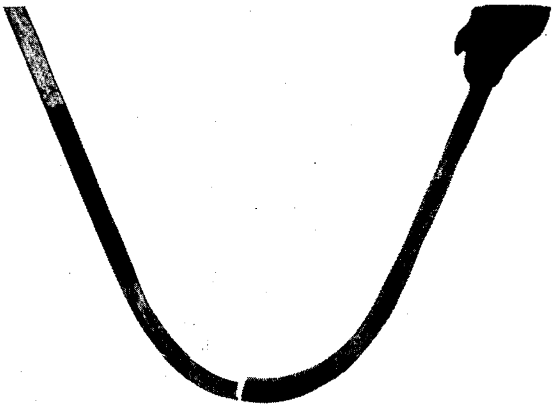


FIGURE 3A

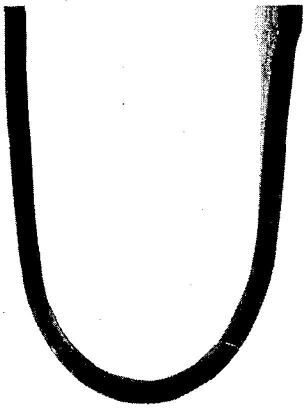
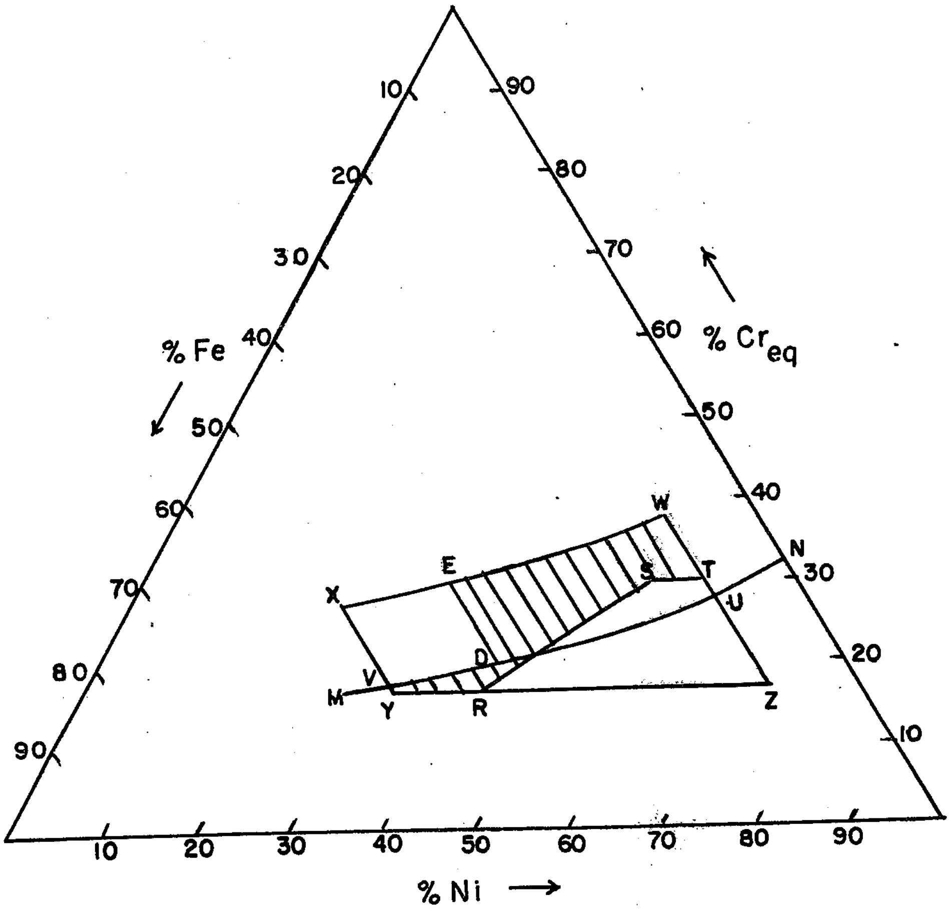


FIGURE 3B



10
20
30
40
50
60
70
80
90
% Fe
90
80
70
60
50
40
30
20
10
% Cr_{eq}
10
20
30
40
50
60
70
80
90
% Ni
W
E
S
T
N
X
U
D
V
M
Y
R
Z

Figure 4

OXIDATION RESISTANT DISPERSION STRENGTHENED ALLOY

This application is a continuation-in-part of application Ser. No. 254,106, filed May 17, 1972 and now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a nickel-base alloy, particularly to one dispersion-strengthened.

Materials exhibiting good corrosion resistance are often sought in various forms, such as sheet, strip, wire, etc., for use at elevated temperature so that a material having a combination of good corrosion resistance, notably to oxidation, and high temperature stress-rupture strength, and which is relatively readily fabricable would meet a substantial commercial need.

In the prior art, it has been proposed to obtain desired high temperature strength properties by incorporating a dispersoid material, e.g., thoria, in both metals and alloys. Extensive research investigations have been made in respect of nickel-chromium alloys and the literature reflects that dispersion hardening and strengthening has been achieved. However, the prior art has, to the best of our knowledge, been unable to produce on a significant commercial basis, highly oxidation-resistant sheet material from dispersion-strengthened nickel-chromium alloys.

SUMMARY OF THE INVENTION

It has been found that a dispersion-strengthened nickel-base alloy characterized by outstanding oxidation resistance and high temperature strength can be produced in sheet form and the like, and fabricated into various forms, provided the alloy contains, in addition to a controlled amount of dispersoid correlated percentages of chromium, aluminum, iron, titanium, etc. Moreover, it has been found that particular compositions within the present invention further provide excellent sulfidation resistance. Indeed, this overall combination of characteristics is not only superior to dispersion treated prior art alloys, but is achieved at reduced cost and with an amount of dispersoid less than half that normally recommended heretofore in connection with other nickel chromium alloys.

Generally speaking, the present invention comprises an age-hardenable, austenitic nickel-base alloy containing, by weight, about 10 to about 30% chromium, about 10 to about 40 or 50% iron, with the chromium and iron percentages being advantageously interrelated such that they represent a point on or above the line A-B-C of FIG. 1 of the drawings, aluminum in an amount of at least about 4%, at least one refractory dispersoid in small but effective amount, e.g., 0.2 or 0.3% by volume, sufficient to impart improved stress-rupture strength at temperatures on the order of 1900° or 2000°F., the dispersoid having an average particle size of about 50 angstroms to about 5000 angstroms, and up to about 1% titanium. It is most advantageous that the alloy be produced by mechanical alloying, after which it is processed such that it is comprised of relatively coarse grains, elongated in one or two working directions. Preferably the grains have aspect ratios of about 3:1 to about 100:1 with average widths of about 15 to about 2000 microns, and average lengths of about 150 to about 12,000 microns, the grain thickness being less than the smaller of the width and length dimensions. Grains elongated in two dimensions (i.e., generally elliptical) can be produced by working the alloy in two directions, e.g., cross-rolling at an elevated temperature, the two major axes of the grains being disposed longitudinally and transversely in the rolling plane, while grains elongated in a single direction, i.e., fibrous grains, can be produced by working in one direction.

The alloy combines precipitation and dispersion hardening and provides what we believe to be a most superior combination of high strength and sulfidation and oxidation resistance at temperatures up to at least 2000°F. while affording comparatively high ductility which contributes to the ready fabrication thereof.

DESCRIPTION OF THE DRAWING

FIG. 1 is a diagram depicting an interrelationship of the constituents iron, chromium, and nickel in terms of sulfidation resistance.

FIG. 2 is a graph depicting the oxidation resistance of alloy compositions of the present invention as compared with that of prior art alloys.

FIG. 3A and 3B are photomacrographs taken at 3 times magnification respectively demonstrating the difference in fabricability of iron-free and iron-containing alloys.

FIG. 4 is a diagram depicting an interrelationship of the chromium, nickel, and iron components of the alloy of this invention, wherein the chromium concentration is adjusted to allow for the aluminum and titanium content of the alloys. In the diagram, the adjusted chromium level, calculated as $Cr + 6 + (Al-3) + Ti$, takes into account the effects of aluminum and titanium on the phase relationships in the Fe-Ni-Cr system. The adjusted chromium is referred to as chromium equivalents or Cr_{eq}.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In carrying the invention into practice, care must be exercised in respect of the respective amount of the required constituents described above.

The aluminum generally serves to impart oxidation resistance to the alloy, this resulting from formation of a strongly adherent layer of Al_2O_3-based oxide at the alloy surface on exposure to an oxidizing environment. The oxide layer inhibits oxidation of the sub-surface regions and is extremely stable. In general, good oxidation resistance is achieved with aluminum contents of at least about 4.1 to 4.3% and above, with outstanding resistance being achieved at about 5% or more, this being reflected in FIG. 2 by Alloys 1, 2 and 3 which are described below. It can be less than about 4%, e.g., 3.9%, but at a sacrifice in oxidation resistance. The aluminum level should not fall below 3.75%. Also, alloys produced according to the invention exhibit high composition uniformity, i.e., homogeneity, even with the substantial amounts of aluminum that are present.

Where the initial powder charge is mechanically alloyed under conditions allowing oxidation of some aluminum, the aluminum should be adjusted to compensate for such dilution so that the metallic aluminum is not below the minimum aluminum level desired.

It is desirable, however, to limit the percentage of metallic aluminum to less than about 6% in order to minimize the possibility of precipitating large amounts of aluminum-rich phases that can cause embrittlement.

An overall highly satisfactory range is from about 4.5 to about 5.5%.

Chromium and iron are best considered together. The former is important because it lends sulfidation resistance to the alloy, resistance to attack being more or less a function of chromium content. To achieve the level of sulfidation resistance contemplated herein the chromium level in prior alloys would have to be excessively high. As will be explained below, for all the virtues of chromium, it can work as a drawback to the subject invention unless controlled. However, in accordance with this invention the chromium level can be suitably controlled. By way of explanation, reference is made to FIG. 1. It will be observed that nickel-chromium alloys below the curve A-B-C exhibit relatively low sulfidation resistance. Thus, in a low iron content alloy, e.g., an alloy containing less than about 15% iron, upwards of about 25% chromium should be present for high resistance to sulfidation. In an alloy containing more than about 15% iron, the chromium content must be correlated to the iron content. For example, at an iron content of about 35 or 37% the chromium content may be as low as about 12 or 13% and the alloy will still have good sulfidation resistance.

Although the explanation may not be completely understood, it has been found that controlled amounts of iron in our dispersion-strengthened alloy unexpectedly provide the significant advantages of markedly improved sulfidation resistance, this in turn permitting the use of much lower chromium, and enhance workability of the alloy. The presence of iron in the amount specified also imparts fabricability, i.e., bendability, formability, drawability, etc., to the alloy, thereby permitting the cold shaping of the alloy into various forms. Moreover, the presence of iron in controlled amounts retards or reduces the overall hardening response of the alloy. An iron content of at least about 15% e.g., about 20 or 25% and up to about 33 or 35% is particularly advantageous. Also, it is advantageous to have a chromium content of about 10 to 20%. However, for sulfidation resistance, as above indicated, the iron and chromium should be correlated to give a point above the curve A-B-C of FIG. 1.

It is known at intermediate temperatures, i.e., in the range of about 1200°–1500°F. and at certain levels of concentration in a Ni-Fe-Cr alloy system chromium can induce the formation of the chromium-rich phases alpha prime (body centered cubic) and sigma (tetragonal). These two phases are very hard and can severely embrittle alloys of the type within the contemplation of the present invention. For this reason traditionally compositions in which these two phases — particularly the sigma phase — can form have been considered undesirable. It has been found that it is possible to minimize the formation of alpha prime and sigma phases in the alloys of this invention by suitable adjustment of the iron, chromium, aluminum and titanium levels. It has also been found that in alloys of this invention alpha prime and/or sigma phase can be tolerated to some extent so long as they are not excessive. These alloys are defined with reference to FIG. 4.

FIG. 4 is a pseudo-ternary phase diagram at 1300°F. for Ni-Cr-Fe alloys containing 4–6% aluminum and 0.5% titanium. The chromium, as noted above, is given in chromium equivalents and is equal to the weight % chromium + 6 + (weight % of aluminum −3) + weight % titanium. Implicit in this equation is the assumption that the first 3% Al has twice the effect of 3% Cr, hence the value 6 in the equation. At above 3% Al, the Al appears to be equivalent to Cr in affecting phase stability, hence the (Al−3) term. Ti appears to be equivalent to Cr in affecting phase stability.

With reference to FIG. 4, the alloys of this invention have a nickel, iron and chromium equivalents composition falling within the boundaries of W-X-Y-Z-W. Such alloys, which as noted above are further comprised of an effective amount of refractory dispersoid, have suitable oxidation resistance and high temperature strength.

As noted above, the sigma and alpha prime phases can be tolerated to some extent, and these phases will be formed in some of the alloys having an Fe-Cr_{eq}-Ni composition within the given area bounded by W-X-Y-Z-W. In various preferred embodiments of this invention the possibility of forming sigma and/or alpha prime phases is minimized by suitable adjustment of the metallic components.

Thus the boundary M-V-D-U-N separates alloys, in terms of metallic components, in which the tendency to form alpha prime and sigma is minimized or possibly nonexistent (i.e., below M-V-D-U-N) from alloys in which some alpha prime or sigma may be formed, albeit in tolerable limits. Thus in the area within the boundary V-D-U-Z-Y-V the tendency to form either alpha prime or sigma phases is minimized. To minimize the possibility of forming sigma phase, the iron content must not exceed the boundary D-E (about 37% Fe) when the chromium equivalents exceed M-V-D-U-N. The metallic components of the alloys falling within the latter system are bounded by D-E-W-U-D. Such alloys may form a tolerable amount of alpha prime, but the tendency to form sigma is limited or nonexistent. In general, in alloys falling within the boundary D-E-W-Z-Y-V-D the tendency to form sigma phase is inhibited or nonexistent.

Put in another way, it will be noted that the iron content of the alloys of this invention can be as high as 40 or 50%, provided the chromium equivalents level is adjusted accordingly. Furthermore, where the chromium and aluminum content exceed about 15% and 4%, respectively, to inhibit sigma formation on exposure to high temperatures the percentage of iron should not exceed about 35 to 37%. Higher amounts of aluminum and chromium are employed with lower iron content, e.g., as much as about 38% Cr_{eq} when the iron content is about 10%.

The boundary R-S-T on FIG. 4 is comparable to the boundary A-B-C shown in FIG. 1, suitably adjusted for chromium equivalents. Accordingly in FIG. 4 compositions falling above R-S-T will be more resistant to sulfidation than those falling below it. Thus, in a preferred embodiment of this invention the composition of the metallic components of the alloy system falls within the boundary E-W-T-S-R-Y-V-D-E. This area is shown as a cross-hatched section of the diagram. Such alloys are characterized by oxidation and sulfidation resistance and a minimized tendency to form sigma phase.

An alloy otherwise within the invention but free of or low in iron tends to undergo rapid and strong aging reactions with the formation of Ni_3Al, the gamma prime phase. The addition of iron in the required amounts apparently somewhat neutralizes or suppresses the strengthening effect of this precipitation reaction and possibly the degree of the reaction, thereby enhancing workability.

In any case, specimens cut from ⅛-inch thick sheet produced according to the invention and comprised of a substantially iron-free alloy containing 14.8% chromium, 4.6% aluminum, 0.41% titanium, 0.22% yttria, balance essentially nickel, are quite stiff and exceedingly difficult to bend after being solution treated at, for example 2000°F. to 2400°F. for 15 or 30 minutes or longer, and air cooled, whereas similar specimens from an iron-containing alloy containing 31.9% iron, 17.9% chromium, 4.9% aluminum, 0.45% titanium, 0.25% yttria, balance nickel, were readily bent over on themselves after a similar solution treatment and air cool. The iron-free and iron-containing specimens are shown as FIGS. 3A and 3B, respectively, the 3A specimen showing a fracture that resulted from the attempt to bend it.

As referred to above herein, it has been further determined that very good high temperature strength properties are achieved with low dispersoid contents, e.g., about 0.5% by volume. This was fortunate, for at higher levels of at least certain dispersoids, fabricability, though acceptable, was a little on the low side. In any event, improved fabricability is obtained with the reduced percentages of dispersoid but without substantially detracting from stress-rupture life at very high temperatures, e.g., 1900° to 2000°F. Higher dispersoid levels can be employed including up to 2 or 3% by volume or more, e.g., possibly 5 or 10%, but at the expense of workability. For example, sheets or plates including coarse grains that were elongated in two directions (i.e., generally elliptical) and containing, on the average, 35% iron, 18.5% chromium, 4.2% aluminum, 0.45% titanium, and 0.65 weight % (1 volume %) yttria dispersoid, exhibited high 2000°F. stress-rupture strengths, viz. 100-hour lives at stresses on the order of 10,500 psi, but were somewhat difficulty fabricable.

A reduced dispersoid content enhanced the fabricability and, surprisingly, provided excellent stress-rupture strengths as well. Specifically, plates having nominal alloy composition of 33% iron, 18% chromium, 5% aluminum, 0.45% titanium, and 0.25% by weight (about 0.5 volume %) yttria dispersoid and having generally elliptical grains (viewed two-dimensionally) were fabricable with relative ease and exhibited 2000°F. stress-rupture lives of 100 hours at loads of between 6000 and 7000 psi. Indeed, the high order of elevated temperature strength achievable with compositions within the present invention is further demonstrated by a similarly grain-coarsened alloy nominally containing 33% iron, 18% chromium, 5% aluminum, 0.4% titanium, 0.35% (about 0.5 volume %) lanthana dispersoid material, balance essentially nickel, the alloy having a 100-hour stress-rupture life at 2000°F. and a load of 8500 psi, this composition also being fabricable with relative ease.

It is quite beneficial that the dispersoid have an average particle size of about 50 angstrom to about 5000 angstroms, preferably about 100 angstroms to about 1000 or 1500 angstroms. Generally, higher percentages of iron, e.g., about 35%, are preferred with relatively high dispersoid contents, e.g., about 2 volume %, to alleviate the workability problems arising from the high dispersoid levels. Satisfactory dispersoid materials include those with melting points of at least 2500°F. and free energies of formation of minus 120 kcal. per gram atom of oxygen or more negative, at 1000°C, e.g., rare earth oxides, such as lanthana, yttria and ceria, thoria, alumina and magnesia. Lanthana and yttria are considered to be superior dispersoid materials as each appears to enhance corrosion resistance and other properties of the alloy.

Where the alloy contains substantial amounts of nitrogen, e.g., about 0.004 weight % or more, it is advantageous to include at least an amount of titanium sufficient to combine with substantially all of the nitrogen, thereby minimizing the adverse effects of the nitrogen on cold ductility of the alloy. In general, the titanium content need not exceed about 1%, about 0.1 to about 0.6% being satisfactory for most situations. For example, mechanical alloying under nitrogen-0.7% oxygen atmosphere for about 20 hours results in a nitrogen content of about 0.1 to 0.15% so that 0.4 to 0.6% titanium would be desirable to neutralize effectively the nitrogen by forming a stable nitride, e.g., TiN. In addition to titanium, other stable nitride-forming materials that can be added to the alloy are up to about 0.3% zirconium, up to about 1% niobium, and up to about 0.5% silicon. Where a minimal nitrogen content is sought, the powder can be mechanically alloyed under an argon-oxygen atmosphere.

For special effects, the alloy can also include up to about 10% manganese, up to about 10% cobalt, up to about 5% molybdenum, up to about 5% tungsten, and up to about 5% tantalum. Other elements or impurities can be present, e.g., up to about 0.03% each of sulfur and phosphorus and up to about 0.5% copper.

Production of the present alloy is advantageously carried out by mechanically alloying, i.e., high energy milling, a powder charge of the desired composition such that the initial powder constituents are interdispersed, comminuted and welded together to provide composite particles. The powder charge can comprise elemental and/or alloyed powders, generally of fine size not exceeding minus 10 mesh. Mechanical alloying is described generally in Benjamin U.S. Pat. No. 3,591,862 and in co-pending U.S. application Ser. No. 850,861, filed by Benjamin. The mechanical alloying process is conducted so as to produce composite powder particles characterized by a cohesive internal structure in which the constituents, including the initial dispersoid material, are intimately united to provide a homogeneous inter-dispersion of comminuted fragments of the starting constituents, the composition of the individual composite powder particles corresponding to the final alloy product. Mechanical alloying is beneficially carried out such that the composite powders exhibit substantially saturation hardness. Such composite powders have substantial compositional homogeneity, the dispersion particle being distributed substantially uniformly throughout the various composite powder particles at average spacings not exceeding 1 micron.

Mechanical alloying can be conducted under dry conditions in a high energy mill such as the Szegvari attritor, for example. The preferred milling conditions with a 4-gallon Szegvari attritor are about 16 to 24 hours with an impeller speed of about 250 to 350, e.g., 290 rpm, using a nitrogen-0.7% oxygen atmosphere and ⅜-inch diameter steel balls present in an amount sufficient to provide a ball-to-powder weight ratio of about 15:1 to 20:1.

The mechanically alloyed powder can then be hot consolidated, e.g., by hot extrusion or hot compaction.

Generally, powder consolidation can be conducted by extrusion of powder held in a metal, e.g., steel container, at a temperature in the range of about 1800° to 2200°F., e.g., 1950°F., with an extrusion ratio of about 5:1 to 20:1, e.g., 10:1. The consolidated material may be extensively hot worked, e.g., hot rolled over a temperature range of about 1800°F. or 1900°F. to about 2200°F. or 2300°F. to provide hot reductions of up to about 75% or 90% or higher. The hot workability of the consolidated material readily leads to the production of sheet, strip and other hot reduced mill forms. The hot worked product is then grain coarsened by heating to a sufficiently high secondary recrystallization temperature, e.g., on the order of about 2200°F. or 2400°F. and below the incipient melting point of the alloy to coarsen the grains. It is important that the consolidated product be sufficiently worked to impart to it energy that is adequate to provide secondary recrystalization on subsequent heat treatment. If the product is worked too much, coarse, substantially equiaxed grains will result, whereas too little work results in a relatively fine equiaxed grain structure.

The grain-coarsened product can later be subjected to other hot working and heat treatment operations within the above limits without foregoing the secondarily recrystallized grain structure that confers good high temperature properties upon the alloy.

To illustrate the invention the following examples and data are given:

EXAMPLE I

Various alloys having the composition shown in Table I were produced by mechanically alloying respective 4.25 kg dry powder charges in a 4-gallon capacity Szegvari attritor operated at an impeller speed of 250 rpm, with an 85 kg charge of ⅜-inch diameter steel balls under an atmosphere of nitrogen-0.7% oxygen, for 20 hours. The powder charge for Alloy 1 contained 1430 grams of carbonyl nickel powder of minus 325 mesh, 1095 grams of minus 200 mesh low carbon ferrochrome containing 74% chromium, 78 grams of a minus 200 mesh nickel-16.5% aluminum-28% titanium master alloy, 1200 grams of minus 100 mesh high purity iron powder, 435 grams of a minus 200 mesh nickel-46% aluminum master alloy, and 10.6 grams of yttria having an average size or about 250A. The powder charge for Alloy 2 contained 1431 grams of the carbonyl nickel, 1095 grams of the low carbon ferrochrome, 73 grams of the nickel-16.5% aluminum-28% titanium master alloy, 1200 grams of the high purity iron, 435 grams of the nickel-46% aluminum master alloy, and 15 grams of lanthana having an average size of about 400 angstroms. The nitrogen-oxygen atmosphere served to retard welding of the powders and yet allow adequate processing to obtain composite powders that were homogeneous in composition and structure at 200 times magnification, including a relatively uniform distribution of the dispersoid particles. The Alloy 1 composite powder had a total oxygen content of about 0.63%.

The mechanically alloyed powders were then individually canned in 3-inch diameter mild steel cans, sealed, and extruded at 1950°F. with a 10:1 extrusion ratio, and pieces of the extrusions were subsequently hot rolled at 1950°F. to ⅜-inch thick plates, the total reduction being equivalent to extrusion with a ratio of about 22:1. The plates were then grain coarsened by heating at about 2400°F. for about one hour. Pieces cut from each plate, Alloys 1 and 2 in Table 1, as well as commercial Alloy A, were tested at 1700°F. for sulfidation resistance in a molten solution of 99% Na_2SO_4–1% NaCl. This medium, albeit severe, was used to simulate corrosion seen in gas turbine engines as a result of the conversion of ingested sea salt. Under such service conditions, Na_2SO_4 is condensed on turbine parts and causes a catastrophic form of corrosion, labeled sulfidation.

TABLE I

SULFIDATION TEST

Alloy No.	Composition (Wt %)	Total Penetration (Mils) 16-H4. Exposure	Total Penetration (Mils) 100-Hr. Exposure
1	31.9Fe—17.9Cr—4.9Al—0.45Ti—0.25Y_2O_3—Bal Ni	1.0	<1
2	32.3Fe—18Cr—4.9Al—0.38Ti—0.29La_2O_3—Bal Ni	<1	<1
A(1)	21Cr—1.5Co—9Mo—0.6W—19Fe—0.1C—Bal Ni	<1	>150

(1)Nominal Compositiion

It can be seen from Table I that Alloys 1 and 2 of the present invention are vastly superior to the commercial alloy under the above long-term sulfidizing conditions.

EXAMPLE II

A powder charge of substantially the same composition as that for Alloy 1 in Example 1, was mechanically alloyed and extruded in the manner described in Example 1, the extrusion comprising material that is within the present invention and designated as Alloy 3 in Table II below. The Alloy 3 composite powder had a total oxygen content of about 0.62%. Other pieces from the extrusions of Alloys 1 and 2 as well as pieces from the Alloy 3 extrusion were hot rolled at 1950°F. to ⅛-inch thick sheets and grain coarsened by heating at 2400°F. for 1 hour. Pieces cut from these ⅛-inch thick sheets and pieces of commercial Alloys B, C, and D shown in Table II, were tested for oxidation resistance by temperature cycling at 24-hour intervals for a period of 288 hours at 2300°F. in air-5% H_2O, the results being depicted in FIG. 2 and shown in Table II. Alloys B, C, and D, outside the invention, are included in Table II for comparison. The 24-hour temperature cycling comprised 23-hour exposure to elevated temperature, i.e., 2300°F., followed by a 1-hour cool in still air. The descaling of the various pieces was carried out with an abrasive cleaning unit using carbon dioxide-propelled 50 micron particle size alumina, the descaling being carried out until all oxide was removed and bare metal exposed.

TABLE II

OXIDATION TEST

Alloy No.	Composition (Wt T)	Weight Change (mg/cm^2 Undescaled	Descaled
1	31.9Fe—17.9Cr—4.9Al—0.45Ti—0.25Y_2O_3—Bal Ni	−0.6	−1.4
2	32.3Fe—18Cr—4.9Al—0.38Ti—0.29La_2O_3—Bal Ni	−1.5	−2.4
3	33.1Fe—17.2Cr—5.1Al—0.43Ti—0.25Y_2O_3—*Bal Ni*	−12.4	−14.5
B(1)	22Ni—22Cr—14W—1.5Fe—0.75Mn—Bal Co	+100.2(2)	—
C(1)	25Cr—10Mo—Bal Ni	−153.2(2)	—
D(1)	20Cr—2ThO_2—Bal Ni	−31.1(3)	−37.3

(1)Nominal Composition.
(2)120-hour test result-withdrawn from test due to heavy scaling.
(3)Very heavy edge erosion.

It can be seen from FIG. 2 and Table II that Alloys 1, 2 and 3 exhibited very good oxidation resistance compared with Alloys B, C and D. The exceptional oxidation resistance of Alloys 1, 2 and 3 is particularly significant since oxidation-resistance testing of materials in sheet form is considered to be a particularly severe test due to edge effects.

Alloys 1 and 2 formed an adherent scale with little weight change, even after 288 hours, while Alloy 3 showed some loss of scale initially but then formed an adherent scale with little weight change, none of these alloys demonstrating any tendency toward catastrophic oxidation during the test period. In comparison, Alloys B and C (FIG. 2) exhibited catastrophic oxidation after a period of less than 96 hours and Alloy D exhibited a continually increasing weight loss between 120 and 288 hours.

A cylindrical piece of a 3/16-inch diameter and ¾-inch length of another nickel-base alloy containing, by weight, 36.0% iron, 18.4% chromium, 0.49% titanium, 0.64% yttria but only 3.9% aluminum, was tested for oxidation resistance in the same manner, i.e., 24-hour cycles in air-5% water at 1250°C. This alloy exhibited after 288 hours a weight change of about minus 50 mg/cm^2 undescaled (despite the fact that an oxidation resistance test of a cylindrical specimen is less severe than that of a sheet specimen). This reflects the effect of aluminum content. As indicated above herein, it is most beneficial that the aluminum level be at least 4 or 4.1%.

EXAMPLE III

A grain coarsened ⅛-inch thick sheet of material designated as Alloy 4 in Table III was produced in the same manner as the grain coarsened ⅛-inch thick sheets of Alloys 1 and 2 described in Examples I and II. The initial powder charge that was mechanically alloyed in producing the Alloy 4 sheet contained 1555 grams of minus 325 mesh carbonyl nickel powder, 1155 grams of minus 200 mesh low carbon ferrochrome containing 74% chromium, 74 grams of minus 200 mesh nickel-16.5% aluminum-28% titanium master alloy, 1275 grams of minus 100 mesh high purity iron powder, 412 grams of minus 200 mesh nickel-46% aluminum master alloy, and 27 grams of yttria of about 250 angstroms average size.

Other portions of the grain coarsened ⅛-inch thick sheets of Alloys 1 and 2 described in Example II and portions of the grain-coarsened Alloy 4 sheet were tested, with the commercial Alloys A, B, and D, for 2000°F. stress-rupture properties, the test results being set out in Table III. As to Alloy 1, it contained grains generally ranging in size from 500 to 1200 microns in length and about 30 to 100 microns in width, while Alloy 2 contained grains generally ranging from 150 to 3000 microns in length and 15 to 100 microns in width. Alloy 4 contained grains that ranged generally from 400 to 2000 microns in length and 80 to 200 microns in width.

TABLE III

Alloy No.	Composition (Wt %)	Av. 100-Hr. Stress-Rupture Strength (psi) at 2000°F.
1	31.9Fe—17.9Cr—4.9Al—0.45Ti—.25Y_2O_3—Bal Ni	6,500
2	32.3Fe—18.0Cr—4.9Al—0.38Ti—0.29La_2O_3—Bal Ni	8,500
4	34.8Fe—18.5Cr—4.4Al—0.43Ti—0.67Y_2O_3—Bal Ni	10,500
A(1)	21.Cr—1.5Co—9Mo—0.6W—19Fe—0.1C—Bal Ni	<2,000
B(1)	22Ni—22Cr—14W—15Fe—0.75Mn—Bal Co	<3,000
D(1)	20Cr—2Tho_2—Bal Ni	8,000

It can be seen from Table III that the 2000°F. stress-rupture strengths for Alloys 1, 2 and 4 are quite good, all of them far surpassing such strengths for commercial alloys A and B. It is especially noteworthy that Alloy 2 is somewhat superior to Alloy D despite the fact that its dispersoid content is only about one-eighth, of that present in Alloy D on a weight basis, Alloy 2 provided the additional benefit of tremendously greater oxidation resistance than Alloy D.

EXAMPLE IV

Additional alloys in accordance with this invention are listed in TABLE IV. These alloys are suitably prepared using the method described in Example I. The column "Cr_{eq}" is calculated based on the formula. $Cr_{eq.} = Cr + 6 + (Al–3) + Ti +$ elements similar to Cr, e.g., Nb, W and the like.

TABLE IV

Alloy	COMPOSITION (Wt %)							
No.	Fe	Cr	Al	Ti	C.	La_2O_3	Ni	Cr_{eq}
5	10.0	29.5	5.0	.5	—	.35	bal.	38.0
6	20.0	26.3	5.0	.5	—	.35	bal.	34.8
7	28.1	17.1	4.8	.46	.06	.35	bal.	25.4
8	28.2	22.9	5.0	.49	.07	.35	bal.	31.4
9	29.2	18.5	4.6	.48	.08	.35	bal.	26.6
10	30.0	21.0	4.8	.48	.17	.35	bal.	29.3
11	30.0	17.3	4.7	.48	.09	.35	bal.	25.5
12	30.0	13.3	5.0	.5	—	.35	bal.	21.8
13	30.0	18.4	5.0	.5	—	.25	bal.	26.9
14	30.0	23.5	5.0	.5	—	.35	bal.	32.0
15	30.1	23.1	5.2	.46	.07	.35	bal.	31.8
16	30.3	19.0	4.6	.47	.07	.35	bal.	27.1
17	30.7	18.9	4.7	.47	.16	.35	bal.	27.1
18	34.2	19.0	4.6	.45	.08	.35	bal.	27.1
19	34.8	19.2	4.4	.48	.12	.35	bal.	27.1
20	34.9	17.9	4.1	.49	.08	.35	bal.	25.5
21	35.0	18.9	4.7	.52	.07	.35	bal.	27.1
22	40.0	21.1	5.0	.5	—	.35	bal.	29.6
23	50.0	19.1	5.0	.5	—	.35	bal.	27.5

Alloys of the present invention find use in a broad range of applications, among which are those involving exposure to oxidizing or sulfiding conditions and/or high temperatures. Some specific uses are turbine engine applications, including combustion cans and afterburners; the skin for space shuttle craft and hypersonic aircraft; and specialized furnace applications and chemical processing equipment.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

What is claimed is:

1. An age-hardenable dispersion-strengthened alloy consisting essentially of, by weight, about 15 to about 50% iron, about 4 to about 6% metallic aluminum, about 10 to about 30% chromium, up to about 1% titanium and the balance essentially nickel, the weight percents of said nickel and said iron and the chromium equivalent, calculated as the weight percent of chromium plus 6 plus the weight percent of aluminum minus 3, plus the weight percent of titanium, being so correlated as to fall within the area equivalent to that defined by E-W-T-S-R-Y-V-D-E in FIG. 4, and further comprising a refractory dispersoid in a small but effective amount for improved strength, said dispersoid having a fine particle size.

2. An age-hardenable dispersion-strengthened alloy consisting essentially of, by weight, about 15 to about 40% iron, about 4 to about 6% metallic aluminum, about 10 to about 30% chromium, up to about 1% titanium, and the balance essentially nickel, the weight percents of said nickel and said iron and the chromium equivalent, calculated as the weight percent of chromium plus 6 plus the weight percent of aluminum minus 3, plus the weight percent of titanium, being so correlated as to fall within the area equivalent to that defined by E-W-T-S-R-Y-V-D-E in FIG. 4, and further comprising a refractory dispersoid in a small but effective amount for improved strength, said dispersoid having an average particle size of about 50 to about 5000 Angstroms, with the proviso that said iron content be about 35% or less where said chromium content exceeds about 15%.

3. An alloy according to claim **2**, wherein said dispersoid is selected from the group consisting of rare oxide, thoria, alumina and magnesia.

4. An alloy according to claim **3**, wherein the dispersoid is lanthana or yttria.

5. An alloy according to claim **1** comprising, by weight, about 15 to about 35% iron, about 10 to about 20% chromium, about 4.3 to about 5.5% aluminum, up to about 0.6% titanium and about 0.2 volume % to about 1 volume % of said refractory dispersoid.

6. An alloy according to claim **1**, comprising at least about 4.5 to about 5.5% aluminum.

7. an alloy according to claim **1**, comprising at least about 12% chromium.

8. An alloy according to claim **1**, comprising about 25 to about 35% iron.

9. An alloy according to claim **1**, comprising about 0.5 to about 1% by volume refractory dispersoid.

10. An alloy according to claim **1**, comprising a refractory dispersoid in an amount up to about 3% by volume.

11. An alloy according to claim **1**, comprising a refractory dispersoid in an amount up to about 2% by volume.

12. An alloy according to claim **1**, comprising a refractory dispersoid in an amount up to about 10% by volume.

13. An alloy according to claim **1**, further comprising relatively coarse, elongated grains having an average aspect ratio of about 3:1 to about 100:1 with an average width of about 15 microns to 2000 microns and an average length of about 150 microns to 12,000 microns, said grains having a thickness dimension less than said width and said length.

14. A mechanically alloyed metal powder comprising individual particles of substantial saturation hardness, said powder consisting essentially of by weight, about 10 to about 50% iron, about 4 to about 6% metallic aluminum, about 10 to about 30% chromium, up to about 1% titanium, and the balance essentially nickel, the weight percents of said nickel and said iron and the chromium equivalent, calculated as the weight percent of chromium plus 6 plus the weight percent of aluminum minus 3, plus the weight percent of titanium, being so correlated as to fall within the area equivalent to that defined by E-W-T-S-R-Y-V-D-E in FIG. 4, and further comprising a refractory dispersoid in a small but effective amount for improved strength, said dispersoid having an average particle size of about 50 to 5000 Angstroms.

15. A mechanically alloyed metal powder according to claim **18**, comprising, by weight, about 15 to about 35% iron about 10 to about 20% chromium, about 4.3 to about 5.5% aluminum, up to about 0.6% titanium, and about 0.2 volume % to about 1 volume % of said refractory dispersoid.

16. A mechanically alloyed powder according to claim **14**, comprising up to about 2% of said refractory dispersoid.

17. A mechanically alloyed powder according to claim **14**, comprising about 3% of said refractory dispersoid.

18. A mechanically alloyed powder according to claim **14**, comprising about 10% of said refractory dispersoid.

19. An age-hardenable dispersion-strengthened alloy consisting essentially of, by weight, about 20 to about 50% iron, metallic aluminum in an amount not less than 3.75% and not exceeding about 6%, about 10 to about 30% chromium, about 0.1 to about 1% titanium, up to about 0.3% zirconium, up to 1% niobium, up to about 0.5% silicon, and the balance essentially nickel, the weight percents of said nickel and said iron and the chromium equivalent, calculated as the weight percent of chromium plus 6 plus the weight percent of aluminum minus 3, plus the weight percent of titanium being so correlated as to fall within the area equivalent to that defined by W-X-Y-Z-W in FIG. 4, and further comprising a refractory dispersoid in a small but effective amount for improved strength, said dispersoid having a fine average particle size.

20. An alloy according to claim **1** comprising at least about 20% iron.

21. A mechanically alloyed powder according to claim **14** comprising at least about 20% iron.

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