

May 14, 1974

J. A. FORD ET AL

3,810,754

OXIDATION RESISTANT NICKEL BASE ALLOYS

Filed March 16, 1973

4 Sheets-Sheet 1

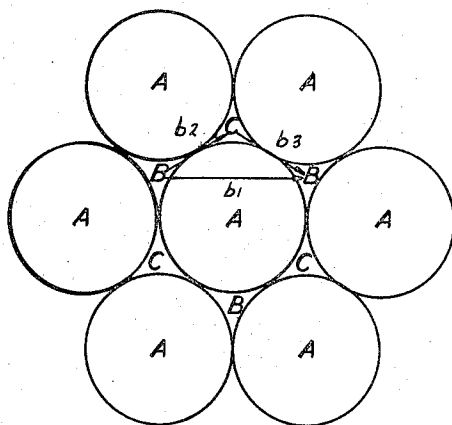


FIG-1

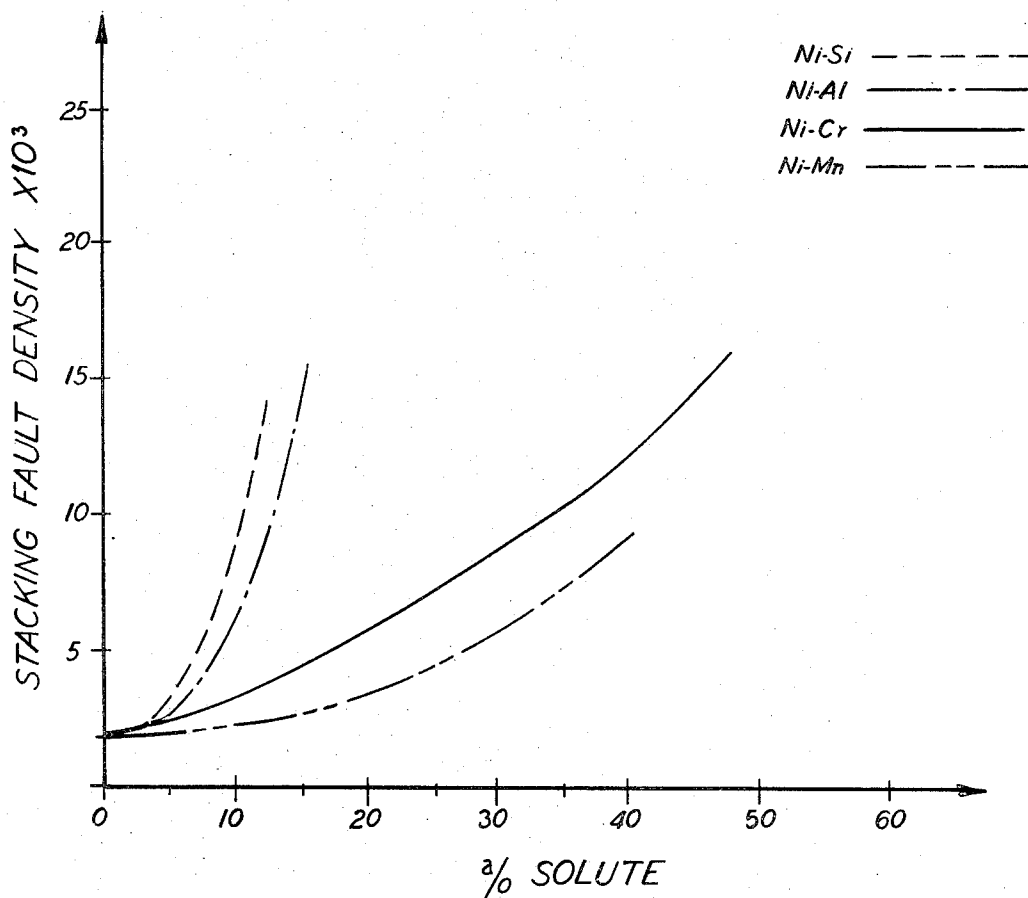


FIG-2

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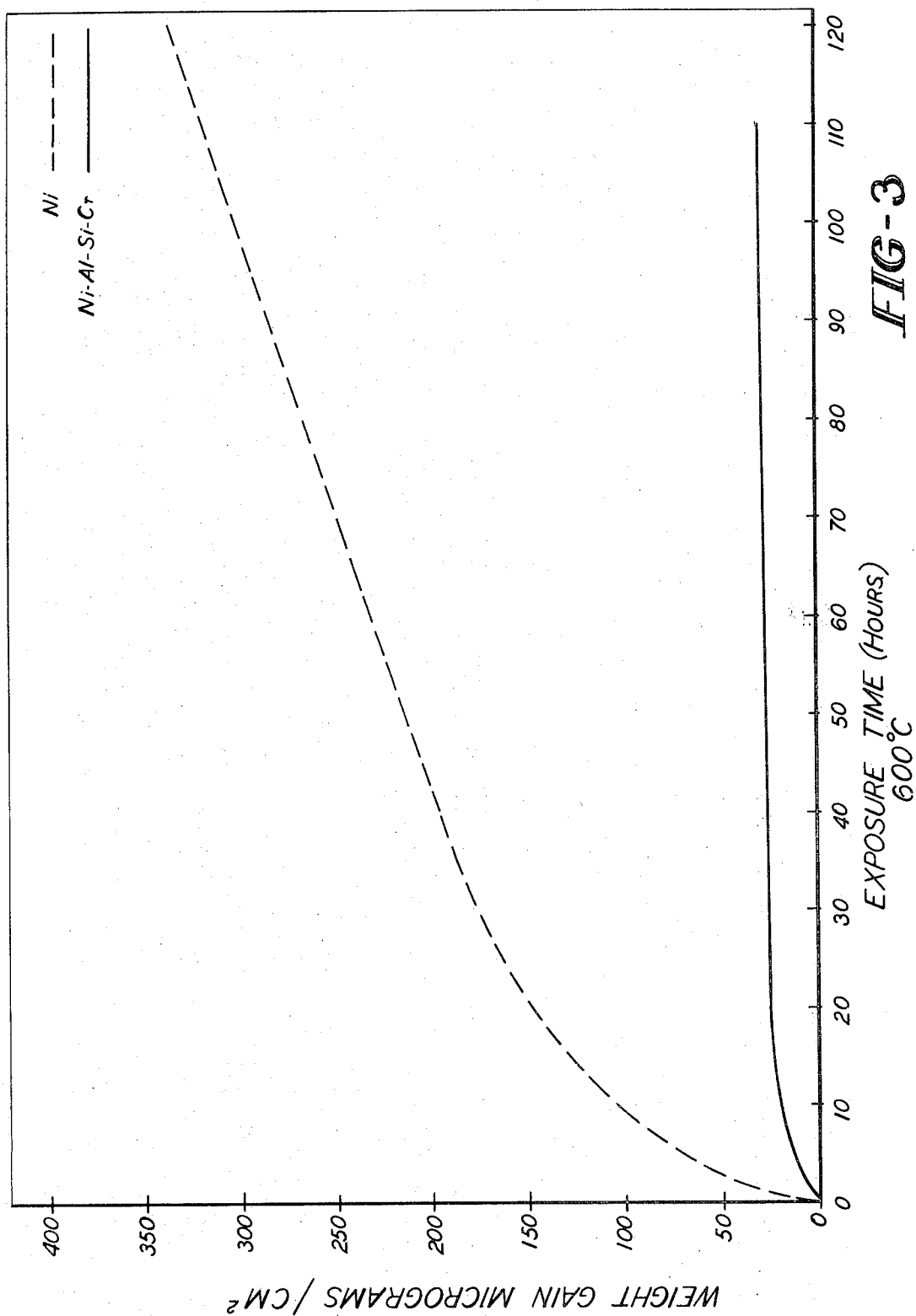
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OXIDATION RESISTANT NICKEL BASE ALLOYS

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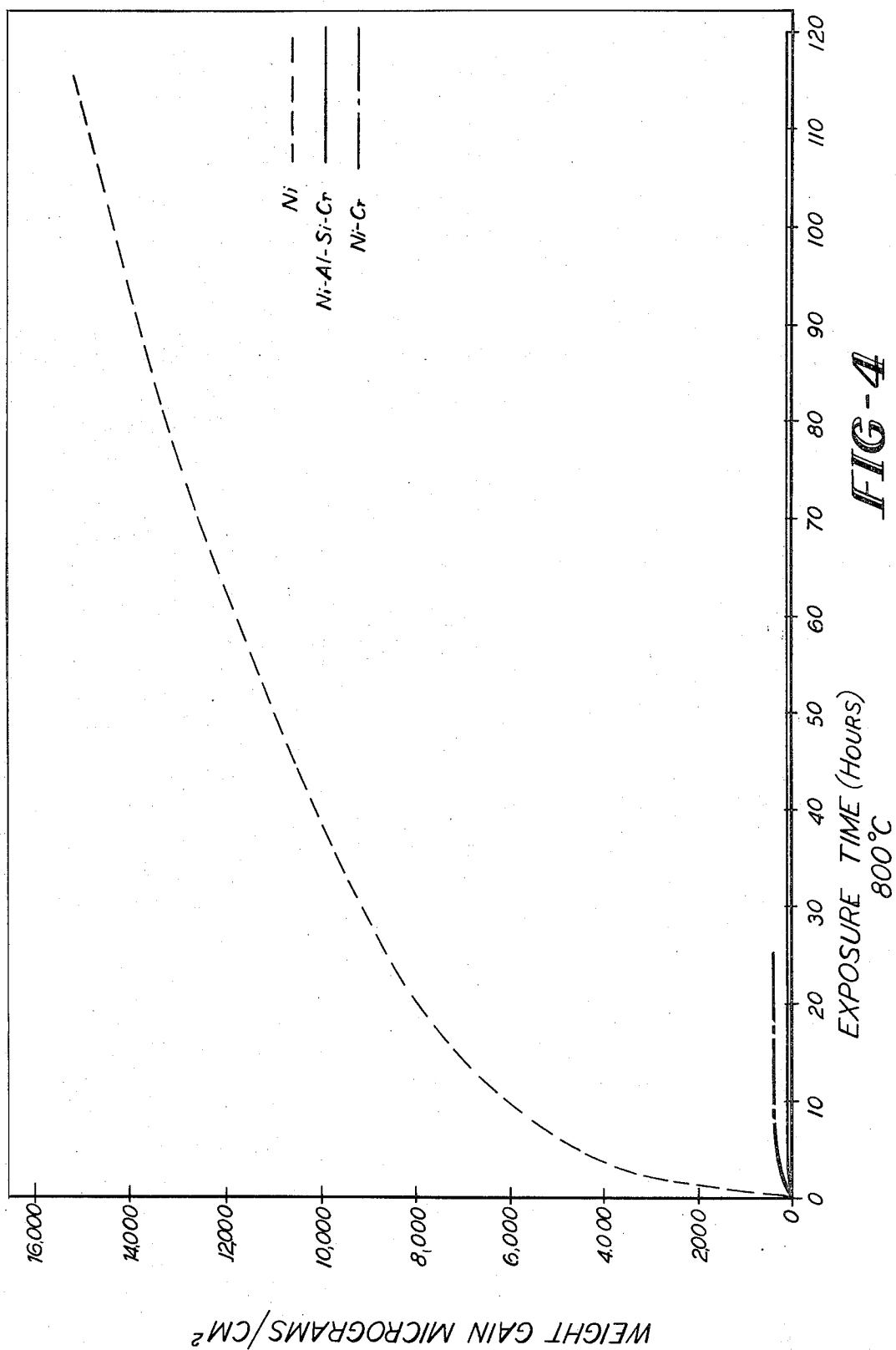
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OXIDATION RESISTANT NICKEL BASE ALLOYS

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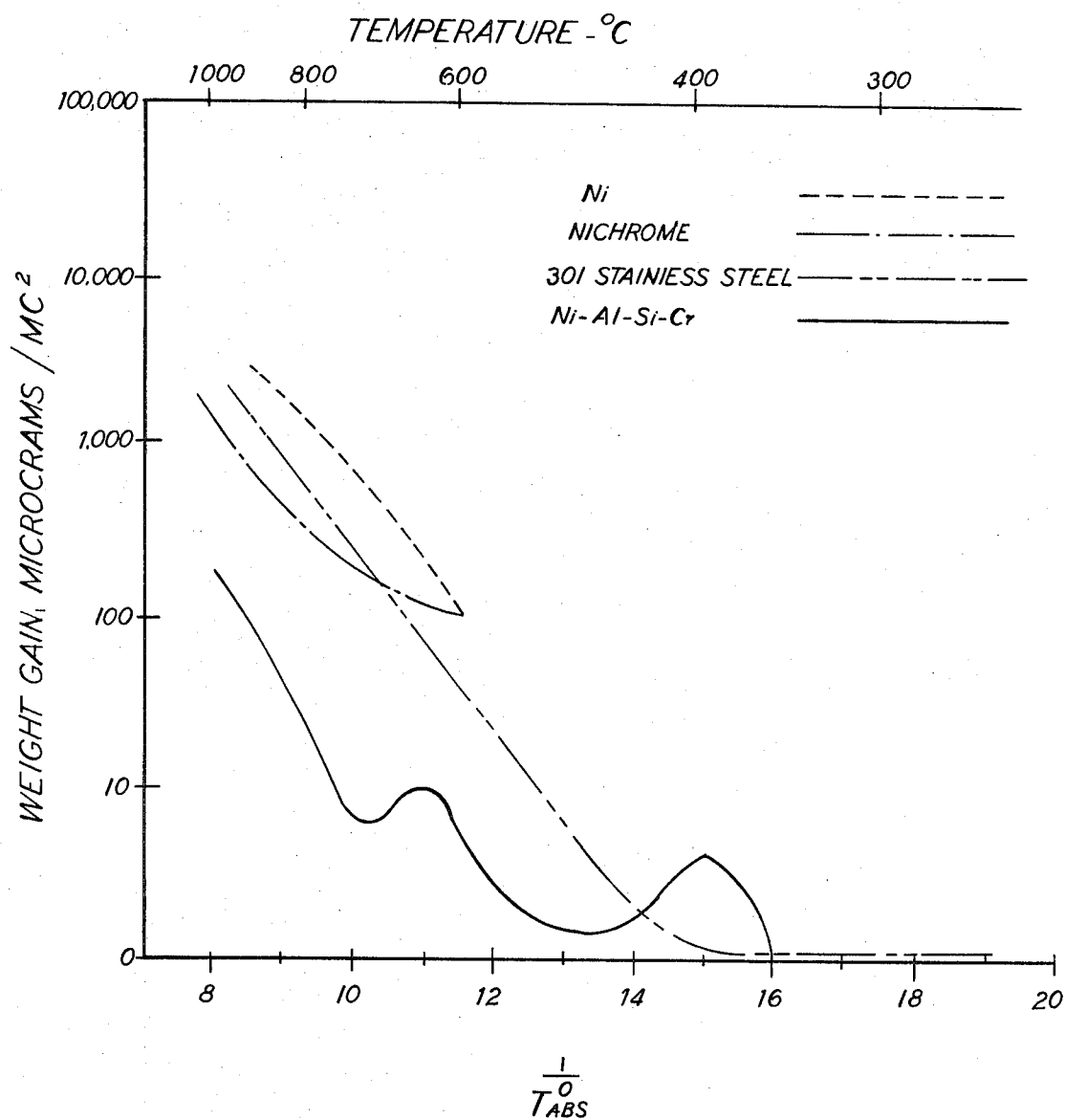


FIG-5

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OXIDATION RESISTANT NICKEL BASE ALLOYS
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4 Claims

ABSTRACT OF THE DISCLOSURE

Nickel base alloys containing alloying additions of aluminum, chromium and silicon are described which exhibit a unique and advantageous combination of high temperature mechanical properties and resistance to oxidation at high temperatures. In particular, the oxidation resistance of the alloys described is superior to that of pure nickel and other high nickel alloys such as Monel and Nichrome which are often used where oxidation is a problem. The oxidation resistance of these alloys is a result of the formation of a tenacious oxide film consisting essentially of the added alloying elements.

BACKGROUND OF THE INVENTION

Nickel alloys represent an important class of commercial alloys, and are commonly used in applications where high temperature strength and corrosion resistance are important. The art has long sought, and continues to actively seek new alloys in which these properties of high temperature strength and corrosion resistance are improved.

Typical nickel alloys, such as Monel (70% nickel, 30% copper), are found to be highly susceptible to form a high temperature corrosion known as oxidation-sulfidation, when exposed to high temperature gases containing oxygen and sulfur compounds. The mechanism of the oxidation-sulfidation attack in an intergranular one and the affected alloys crumble apart. The alloys of the present invention are highly resistant to this form of attack and also possess good mechanical properties at elevated temperatures.

SUMMARY OF THE INVENTION

The alloy of the present invention comprises a nickel base alloy containing carefully controlled quantities of aluminum, silicon and chromium, balance except for unavoidable impurities being nickel. Small quantities of manganese and magnesium may be added to aid in processing the alloy. These additions of aluminum, silicon and chromium are present in a nickel matrix and have been selected to reduce the stacking fault energy of nickel. The alloy additions have also been chosen for their effect on oxide formation. The alloys of the present invention attain numerous highly desirable advantages. The alloys of the present invention present a low fabrication cost since they are readily hot rollable and cold rollable.

As mentioned previously, a particular advantage possessed by these alloys is their extremely high resistance to deterioration under oxidation-sulfidation conditions at elevated temperatures. This resistance to high temperature corrosion makes the alloys of the present invention highly desirable in certain high temperature applications such as automotive exhaust systems, and catalytic converters, certain portions of jet engines and certain components in chemical process plants.

It is a primary object of the present invention to provide a nickel alloy having a high resistance to oxidation-sulfidation corrosion at elevated temperatures.

It is a further object of the present invention to provide a nickel alloy having good mechanical properties at elevated temperatures without relying on precipitation hardening effects such as gamma prime particle formation.

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Yet another object of the present invention is to provide a nickel base alloy characterized by relatively low cost and ease of manufacture.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the arrangement of the atoms on a close packed {111} plane in a face centered material such as nickel.

FIG. 2 shows the effect of certain alloying additions on a stacking fault density of nickel.

FIG. 3 shows a comparison of oxidation behavior of the alloys of the present invention with nickel at 600° C., .1 atm. O₂.

FIG. 4 shows a comparison of oxidation behavior of the alloys of the present invention with nickel at 800° C., .1 atm. O₂ and Nichrome (80 Ni, 20 Cr) also at 800° C., .1 atm. O₂.

FIG. 5 shows the oxidation behavior in air of the alloys of the present invention as compared with nickel AISI type 301 stainless steel, and Nichrome (80 Ni, 20 Cr) over a temperature range of 350 to 975° C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The alloys of the present invention achieve their remarkable combination of high temperature mechanical properties and high temperature corrosion resistance through the careful selection of alloying elements. Each of the alloying elements used contributes to the improvement of mechanical properties and corrosion resistance over that of pure nickel. This is achieved by selecting the alloying additions so that each alloying addition decreases the stacking fault energy of the alloy, thereby effecting the dislocation behavior of the alloy and increasing its mechanical strength. The alloying constituents also form complex oxides on the surface of the alloy at high temperatures. These oxides may be controlled and may be made extremely protective to the surface of the alloy by carefully controlling the concentration of the solute additions which form the oxides.

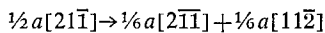
Metallic elements in solid form exhibit a regular repeating pattern, or crystal structure. Deformation of metallic materials can occur only by disruption of the regularity of the crystal structure. It is generally accepted in the metallurgical art that deformation of metallic crystals occurs by the propagation of individual defects or dislocations through the crystal. A metallic material exists in a particular crystal structure because of thermodynamic considerations. A particular crystal structure in which a material exists will have the lowest free energy of all possible crystal structures. Anything which disrupts the regularity of the crystal structure increases the free energy of the crystal. Any event which reduces the free energy of the crystal is thermodynamically favorable and will tend to occur.

Nickel and a nickel solid solution alloys crystallize in the face centered cubic crystal structure. This crystal structure may deform by slip or dislocation motion on close packed layers of atoms corresponding to the {111} planes. The slip deformation is accomplished by the motion of dislocations on these close packed {111} planes. The amount of slip accomplished by the motion of a dislocation is defined by the Burgers vector which in the face centered cubic structure is a $\frac{1}{2}a\langle 110 \rangle$. It has been shown that this unit dislocation, $\frac{1}{2}a\langle 110 \rangle$, can dissociate into so-called half-dislocations, or partial dislocations, resulting in a lower energy condition. Contained between these so-called half-dislocations will be a stacking fault.

The stacking fault may be best described and illustrated by considering how close packed {111} planes are

arranged in the face centered cubic structure. These planes are stacked on one another in the sequence ABCABCABC. The arrangement of atoms on one of these close packed planes is shown in FIG. 1 which is taken from "Dislocations and Plastic Flow in Crystals," by A. H. Cottrell, page 73, 1st edition, 1953. Referring to FIG. 1, the B and C plane atom positions are given by the letters B and C. Described in FIG. 1 as Vector Arrows are the unit dislocations b_1 and the respective half-dislocations b_2 and b_3 . It can be seen that if the atoms are regarded as spheres it would be easier for slip to occur along the path defined by b_2 and b_3 than along the path defined by b_1 . If slip occurs along a Vector such as b_2 between two of these close packed planes, i.e., if slip occurs by half-dislocation motion, a fault will be produced such that the stacking sequence becomes ABCACABC. This "stacking fault" causes the structure to assume a thin layer equivalent to a hexagonal close packed structure. It should be appreciated that the production of such a stacking fault will result in a small increase in the free energy of the crystal. This occurs because the arrangement of next nearest neighbor atoms in the face centered cubic structure has been changed.

Heidenreich and Shockley, "Report on Strength Of Solids" (London: Physical Society), 57 (1948), have suggested that a unit dislocation in the face centered cubic structure would dissociate into two half-dislocations. For example, in the case of a unit dislocation on a $\{111\}$ plane, the reaction



would occur. This reaction results in a lower energy for the two half-dislocations with respect to the original unit dislocation. These half-dislocations, because of their elastic self-energies, will repel one another and produce a sheet of stacking fault in the slip plane between them. The extent of the half-dislocation separation will be defined by the increase in lattice energy associated with the stacking fault. Under equilibrium conditions the half-dislocations will be separated by a distance which is defined by the following equation $r = \mu a^2 / 24\pi\epsilon$ where μ is the shear modulus, a the lattice parameter, and ϵ the fault energy.

Metallurgical elements each possess a particular stacking fault energy. For example, nickel exhibits a stacking fault energy of approximately 250 ergs. per square centimeter, while copper exhibits a stacking fault energy of approximately 30 ergs. per square centimeter. The addition of certain solute elements, namely those having appreciable solubility and valences higher than the solvent material will reduce the stacking fault energy of the solute and lead to larger separations of the partial dislocations. Another parameter related to stacking faults is the stacking fault probability. Stacking fault probability is the probability that a stacking fault will exist between any two neighboring $\{111\}$ layers. The stacking fault probability is inversely related to the stacking fault energy since a stacking fault is likely to form it, its formation involves a small amount of energy. The stacking fault density is the number of stacking faults actually present in the metal.

The effect of several alloying additions to nickel is shown in FIG. 2 which is taken from L. Delehouzee and A. Deruyttere, ACTA Metallurgica, vol. 15, May 1967. In FIG. 2 the ordinate depicts the concentration of the alloying element in atomic percent, and the abscissa depicts the stacking fault density.

Stacking faults have a pronounced effect on high temperature mechanical properties of metals. Recovery processes such as polygonization require that the dislocation cross slip, that is to say that the dislocations move in planes other than those in which they would normally move. In order for an extended dislocation to cross slip it must first recombine into one dislocation. The greater the distance between partial dislocations the less likely

such recombination is. The more difficult such dislocation motion is, the greater the high temperature strength is.

It can therefore be seen that materials having low stacking fault energies, those in which a high percentage of dislocations have formed stacking faults and those in which the stacking faults formed have a significant distance between partial dislocations, will have improved high temperature mechanical properties.

The alloys of the present invention comprise a nickel base containing from 2 to 6% aluminum, from .5 to 4% silicon and from 1 to 6% chromium. As shown in FIG. 2 these elements all increase the stacking fault density of nickel significantly.

As previously mentioned the alloy of the present invention possess a unique resistance to oxidation-sulfidation attack at high temperatures. This corrosion resistance is a result of the alloying additions of the present invention. The alloys of the present invention form an oxide coating when exposed to high temperatures. This oxide coating is extremely protective and is responsible for the surprising resistance of the alloy to oxidation-sulfidation attack.

The broad composition ranges which produce alloys having properties as claimed in the invention comprises from 2 to 6% aluminum, from .5 to 4% silicon, from 1 to 6% chromium, with the balance being essentially nickel. With this broad composition range there is a narrower preferred range over which the alloys of the present invention possess superior corrosion resistance properties. The preferred range is from 3 to 5% aluminum, from 3 to 5% chromium, from 2 to 3.5% silicon, with the balance being essentially nickel.

The lower composition ranges are selected on the basis of mechanical properties. Alloys containing less than the lower limit of the broad range of composition possess inferior mechanical properties. The upper composition ranges are selected on the basis of processing requirements. Above the upper limits of composition of the broad range, hot rolling and cold rolling of the alloy becomes difficult and uneconomical.

The alloys of the present invention possess a highly desirable combination of high temperature mechanical properties and high temperature oxidation resistance over the composition range from 2 to 6% aluminum, from .5 to 4% silicon, from 1 to 6% chromium with the balance being essentially nickel. The alloys of the present invention possess an exceptional combination of properties over a narrower preferred range of composition, from 3 to 5% aluminum, from 2 to 3.5% silicon, from 3 to 5% chromium, with the balance being essentially nickel. It is well known in the metallurgical art that the presence of even a trace amount of sulfur in high nickel alloys can cause great difficulty in hot rolling. This difficulty with sulfur may easily be overcome by the addition of up to .4% manganese to the alloy. This manganese addition has negligible effect upon the properties of the alloy and is necessitated only by processing considerations. Another minor element which may be added to the alloys of the present invention is magnesium which may be added for deoxidation of the alloy. The magnesium is added at the level of up to .1%. Because of the presence of aluminum in the alloy of the present invention which serves as a strong deoxidizer, the magnesium addition is optional and not absolutely required.

The present invention will be more readily understood from consideration of the following illustrative examples wherein all percentages are weight percentages unless otherwise indicated.

EXAMPLE 1

Three alloys of the following composition were prepared:

(1) Commercially pure nickel.

(2) 3% chromium, 2% silicon, 4% aluminum, balance nickel. Samples of these alloys were then oxidized in oxy-

gen at $\frac{1}{10}$ atmosphere pressure at a temperature of 600° C. Continuous measurements of weight change were made for time periods up to 120 hrs. In this type of experiment, the rate of oxidation is indicated by change in weight. The results are shown in FIG. 3. The results of this experiment clearly demonstrate the superior oxidation resistance of the alloys of the present invention over pure nickel. For example after 100 hrs. exposure the pure nickel had gained approximately 300 $\mu\text{g./cm.}^2$, while the alloy of the present invention had gained only 27 $\mu\text{g./cm.}^2$.

The alloys of the present invention have a demonstrated superiority of more than 10 to 1 in oxidation weight gain over pure nickel at 600° C.

EXAMPLE 2

Alloys of the same composition as those used for Example 1 and Nichrome (80 Ni, 20 Cr) were oxidized in oxygen at a pressure of $\frac{1}{10}$ atmosphere at 800° C. the results are shown in FIG. 4. Again the alloy of the present invention displayed a convincing superiority over nickel. At 25 hrs. the nickel sample had gained more than 8,500 $\mu\text{g./cm.}^2$, and the Nichrome had gained about 400 $\mu\text{g./cm.}^2$, however the alloy of the present invention had gained only 38 $\mu\text{g./cm.}^2$.

EXAMPLE 3

Alloys having the following compositions were prepared:

- (1) Commercially pure nickel.
- (2) 70% nickel, 30% copper (commonly known as Monel).
- (3) 3% chromium, 2% silicon, 4% aluminum, balance nickel.
- (4) 25% chromium, 20% nickel, 2% manganese, 1.5% silicon, .25% carbon (AISI grade 310 stainless steel).

These three alloys were tested in tension at 925° C. The tests were conducted at a cross head speed of 0.16 min.^{-1} to the yield point and then at 0.25 min.^{-1} to fracture. The results are tabulated below:

Alloy	UTS, ksl.	0.2% YS, ksl.	Elonga- tion percent
1.----- Nickel.-----	6.4	2.7	160
2.----- Monel.-----	6.5	4.0	56
3.----- Ni-Al-Si-Cu.-----	8.5	6.3	41
4.----- 310 S.S.-----	11.5	8.7	68

These results clearly indicate that the mechanical properties exhibited by the alloys of the present invention are comparable with those of conventional nickel and iron alloys used in high temperature applications where corrosion is a problem.

EXAMPLE 4

Samples of three alloys having the following compositions were prepared:

- (1) Nickel.
- (2) 17% chromium, 7% nickel, balance iron (AISI type 301 stainless steel).
- (3) 80% nickel, 20% chrome (commonly known as Nichrome).
- (4) 4% aluminum, 3% chromium, 2% silicon.

Samples of these alloys were oxidized for 2 hrs. in air at a variety of temperatures and their weight gain measured. FIG. 5 shows a comparison of these three alloys. The abscissa shows micrograms per square centimeter weight loss and the ordinate $1/T_{\text{ABS}}$. Again, the marked superiority of the present alloy is evident. Over the most of the temperature range tested, from 350 to 975° C., the alloy of the present invention displays significantly lower weight gain than pure nickel, Nichrome and type 301 stainless steel, a low cost austenitic grade of stainless steel commonly used in applications where high temperature oxidation is a problem. For example, at 800° C. the following weight gains were observed: for nickel 1400 $\mu\text{g./}$

cm.^2 ; for Nichrome 400 $\mu\text{g./cm.}^2$; for type 301 stainless steel 520 $\mu\text{g./cm.}^2$ and for the alloy of the present invention 20 $\mu\text{g./cm.}^2$.

As mentioned hereinabove, the alloys of the present invention have many applications. Other applications for which the alloys of the present invention are particularly suited include the fabrication of substrate structures for the support of catalysts and the construction of catalyst systems wherein a substrate comprising an alloy of the present invention has its surface composition changed, by plating or by mechanically bonding a layer of a catalytically active metal or alloy to the surface and said surface layer is subsequently oxidized to form a catalyst. Although particularly advantageous results are obtained through the use of the alloy of the present invention, for certain catalytic applications certain substituents of the alloy of the present invention may be omitted without an undue sacrifice of desirable properties. Specifically, it may be desirable to limit or omit the chromium addition because of the tendency for chromium to interfere with catalytic activity. Other materials, such as stainless steel and Monel tend to degrade and suffer from various forms of corrosion when used as catalytic substrates. The use of the alloy of the present invention eliminates these problems.

Although the alloys of the present invention are particularly suited for use as catalytic substrates as mentioned hereinabove their highly desirable combination of properties makes them suited for several other uses. The alloys of the present invention derive most of their favorable properties from the presence of controlled amounts of aluminum and silicon. Although chromium also improves the properties of the alloys of the present invention, it is less effective than aluminum and silicon and may be omitted for certain applications. In particular it may be economically desirable to eliminate chromium when the price of chromium rises above the price of nickel.

As previously noted, the oxidation resistance of the alloys of the present invention is due to the formation of an oxide film on the surface consisting largely of the alloying elements. As the data shown in FIGS. 3, 4 and 5 indicates, this oxide layer is extremely thin, that is a small weight gain is indicative of a thin layer. Such a thin tenacious oxide layer is uniquely suited for use in a formation of a metal-metal oxide-glass sealing system. The alloy is particularly suited for use in glass sealed semiconductors and similar applications. Because the alloys of the present invention contain no iron, they in addition are highly resistant to room temperature corrosion such as rusting. Conventional glass sealing alloys which contain high percentages of iron are subject to rust and stress corrosion, thereby limiting their usefulness.

Because of the low oxidation rate of the alloys of the present invention at high temperatures they are uniquely suited for use in high temperature heat exchanger applications. As the data presented in the present application in FIGS. 3, 4 and 5 indicates, the alloys of the present invention possess superior high temperature oxidation resistance when compared with commonly used grades of stainless steel. The thermal conductivity of the alloys of the present invention is comparable to or better than that of the commonly used grades of stainless steel. For these reasons the alloys of the present invention are particularly suited for use in high temperature heat exchangers.

The alloys of the present invention may also find use in applications where the presence of sea water, other aqueous fluids and even atmospheric exposure might cause corrosion problems. Because the alloys of the present invention are solid solution alloys, containing advantageous alloying elements as described above, they may be expected to possess a high degree of corrosion resistance in these environments.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present

embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A nickel base alloy having good mechanical properties at elevated temperatures and high resistance to oxidation and sulfidation at elevated temperatures, said alloy consisting essentially of from 2 to 6 percent aluminum, from .5 to 4 percent silicon, from 1 to 6 percent chromium, from 0.0 to .4 percent manganese, from 0.0 to 0.1 percent magnesium, balance nickel.

2. An alloy as in claim 1 wherein the aluminum content is from 3 to 5 percent.

3. An alloy as in claim 1 wherein the silicon content is from 2 to 3.5 percent.

4. An alloy as in claim 1 wherein the chromium content is from 3 to 5 percent.

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RICHARD O. DEAN, Primary Examiner