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NICKEL ALLOY PRODUCT AND METHOD OF MAKING

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ABSTRACT OF THE DISCLOSURE

The invention is a high strength nickel alloy containing 1 to 20 percent by volume of intimately dispersed solid-insoluble second phase in a matrix of nickel or nickel alloy such as precipitation hardened alloy. The second phase is obtained by adding elements or compounds to nickel or nickel alloy in an amount in excess of their solid solubility in nickel. Elements or compounds which are only slightly soluble in nickel and form high melting compounds which have a useful liquid solubility are preferred. The alloy product is obtained by atomizing a substantially homogeneous melt, compacting the atomized particles and subjecting the compact to a wrought operation.

CROSS-REFERENCE TO RELATED APPLICATION

This is a divisional application based on application Ser. No. 650,210, filed June 30, 1967, and now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention relates to a novel nickel alloy and to the method of preparing a high strength wrought metal product therefrom.

The invention more particularly relates to nickel alloy that is strengthened by the introduction of elemental or compound additions in an amount that is miscible in molten nickel (at high temperatures at which the nickel is molten) but which exceeds the solid-solubility of the addition in solidified nickel metal. Such additions are made to nickel or to conventional nickel alloys including, particularly, precipitation hardened nickel alloys.

For the purposes of the specification and claims, the term nickel as used herein includes both nickel metal and nickel base alloys. Nickel base alloys are understood to be alloys in which the nickel content, by weight is greater than the content of any other single component of the alloy. Preferably the alloy comprises at least 35 percent, and more preferably at least 40 percent by weight of nickel.

(2) Description of the prior art

Nickel alloys have relatively low strength at room and moderate temperatures compared to steel. Conventionally, nickel has been strengthened by the addition of solid solution hardeners such as one or more of the metals chromium, iron, molybdenum, tungsten and cobalt in various combinations and in various proportions, e.g., up to about 30 percent in the case of cobalt and up to about 20 percent in the case of chromium as in the commercial Hastelloy alloys and Inconel alloys. Nickel alloys have been further improved by addition of such metals as aluminum, columbium and/or titanium separately or concurrently whereby precipitation hardening takes place,

normally during heat treating of the solidified metal. The added metals in this case provide for increasing the strength of the matrix metal through the phenomenon known as age hardening, and such metals are sometimes called age hardeners when added to nickel. In some instances the age hardening process may take place because atoms of age hardener metal, during heat treatment of the alloy, are fitted into the lattice of the matrix metal, albeit imperfectly, causing strain throughout a substantial zone, on the atomic level, at each such dislocative insertion of a foreign atom. More generally, as here, the process is believed to occur as a result of the precipitation of an extremely fine uniformly dispersed phase, the dispersed particles having sizes in the angstrom range. In any event, the precipitation hardened alloys tend to lose high strength properties during long exposure to elevated temperatures. During such exposure the atoms of age hardener that bring about age hardening become soluble in the solid metal and diffuse through the solid metal to a sufficient extent that the zones of precipitation hardening phase agglomerate into localized centers of particles of sufficiently gross nature that the strengthening expected from age hardening is not obtained.

Also known to the art is a high temperature nickel alloy that is made from a specially prepared intimate admixture of nickel and thorium oxide, but the alloy suffers from inferior strength properties at room temperature and slightly elevated temperatures because of inherent limitations in the method of preparation that preclude solid solution strengthening or precipitation hardening of the alloy.

OBJECTS OF THE INVENTION

It is a principal object of the present invention to provide a high strength nickel base alloy that exhibits desirably high strength at temperatures of the order of 1000 to about 2000° F., and especially at 1000 to about 1500° F. and maintains such high strength for a substantially longer period of time than the presently known workable and machineable nickel base alloys. Another object of the invention is to provide a method of preparing high strength wrought nickel products. A further object of the invention is to provide a method of preparing improved high temperature nickel alloys from known precipitation hardening alloys.

SUMMARY OF THE INVENTION

A high strength nickel base alloy is obtained upon combining up to 60 percent by weight of solid nickel alloy-soluble alloying additions either as single components or as mixtures but no single component exceeding the nickel content, up to about 20 percent by weight of precipitation hardening addition, from about 1 to about 20 percent by volume of at least one solid nickel alloy-insoluble second phase material and the balance at least about 35 percent by weight nickel. Ordinarily, the solid solution hardening addition is a metal selected from the group consisting of iron, chromium, cobalt, molybdenum, tungsten and mixtures thereof employed in a proportion not exceeding about 50 percent by weight but the proportion of any single metal added not exceeding the proportion of nickel in the alloy. The precipitation hardening addition is ordinarily in the range of about 1 to 15 percent by weight and more preferably is in the range of about 4 to 10 percent by weight. The solid-insoluble second phase material is selected from elements and compounds and combinations thereof that are miscible in molten nickel or nickel alloy but solid-insoluble in the solidified nickel.

Upon preparing the foregoing alloy, atomizing the alloy while it is in molten homogeneous form, compacting the atomized particles and subjecting the compact to a

wrought operation, a high strength, high temperature nickel alloy product is obtained.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, the properties of nickel, nickel alloyed with solid solution hardeners and nickel or nickel alloys containing age hardening elements can be improved by the addition of dispersion hardening material.

Sufficient dispersion hardening material is added to provide from 1 to 20 percent by volume of solid-insoluble second phase and more preferably 2 to 10 percent by volume of second phase in the solidified nickel metal.

Dispersion hardening is differentiated from precipitation hardening on the basis that the second phase formed on dispersion hardening (1) generally separates during solidification of the alloy, though it may separate from undercooled supersaturated solid solution as a consequence of working the alloy (2) is comprised of particles having dimensions in the micron range rather than the agstrom range, and (3) is substantially not solid-soluble in the matrix metal during conventional heat treatment of the alloy and therefore agglomeration tends to be minimal.

The dispersion hardening material should have appreciable liquid solubility but limited solid solubility and diffusivity so that after hot working, and preferably also after solution heat treatment of the dispersion hardened metal, the dispersion hardening material, once intimately dispersed in the solid metal, remains uniformly dispersed as particles less than about 5 microns in diameter, and preferably less than about 1 micron in diameter. The term diameter is intended to refer to the longest dimension of the particle in the event the particle is not equiaxed. The most preferred dispersion hardening materials are compounds that are stable in the matrix or base metal, that have very high melting temperatures, but limited solid solubility.

The second phase should be stable, i.e. it should agglomerate relatively slowly, if at all, in the nickel alloy. Materials that have high melting temperatures, above above 2500° F. and preferably above about 3500° F., tend to be stable. Another indicator of stability is solid solubility, which should be below about 5 percent by weight and more preferably below about 1 percent by weight. Also, the second phase should not significantly depress the solidus of the nickel or nickel alloy in order not to impair hot workability. There should be no melting of second phase at heat treatment temperatures, i.e., at temperatures of about 1800 to 2200° F.

For the purposes of the specification and claims, compounds formed by a metal and a metalloid are herein referred to as intermellatic compounds. Such compounds may be added per se to the molten nickel or formed in situ. Chemical compounds such as nickel sulfide may also be formed in situ.

The dispersion hardening material, whether it is functioning as an elemental substance, intermetallic compound, or other compound, should have sufficient liquid solubility to permit incorporation of useful proportions in the molten nickel. Therefore, liquid solubility should be at least 1 atomic percent and preferably at least 3 atomic percent.

Broadly speaking, the addition to the nickel source, i.e., nickel or nickel alloy, of dispersion hardening material in the form of one or more chemical elements or compounds in an amount that is miscible with the molten alloy but forms a second phase on solidification of the alloy or as a consequence of subsequent working, brings about the desired strengthening of the nickel alloy on thorough dispersion of the second phase according to the invention. The second phase may arise because the solid-solubility of the addition per se has been exceeded, or on account of interaction between different elements constituting the addition, or between the addition and the nickel of the alloy, to form one or more compounds present in an amount in excess of the solubility thereof.

Some elements which cause preciptation hardening when added in a lower concentration cause dispersion hardening when added in a higher concentration, or, when added concurrently with an interacting element or compound.

Suitable elements for addition that form nickelides of limited solid solubility include, for example, yttrium, scandium, cerium, and other rare earth metals, thorium, zirconium, and hafnium. Such elements have a solid solubility in nickel below about 5 atomic percent, and preferably below about 2 atomic percent.

Elements that react in nickel to form a phase having limited solid solubility are tabulated in the following Groups I and II. Each of the elements in Group I reacts with most of the elements in Group II to form the desired phase and vice versa.

Group I:	Group II:
titanium	carbon
zirconium	boron
rare earth metals	silicon
scandium	phosphorus
yttrium	arsenic
calcium	antimony

Examples of stable intermetallic compounds suitable for dispersion hardening according to the invention and formed as a consequence of such interaction are: TiC, Ca_3Sb_2, ThSi, CeSb, Zr_6Si_5 and Ti_5Si_3.

Preferred additions that bring about dispersion hardening in the nickel or nickel base alloy include, for example, thorium, rare earth metal, zirconium plus carbon, titanium plus silicon and titanium plus carbon.

To obtain the benefits of the solid-insoluble second phase material it is essential that the second phase material is finely and intimately dispersed throughout the solidified nickel metal. Atomizing is the key step in the preparation of improved alloy product. The homogeneous melt of nickel containing dispersion hardening material with or without solution hardening metals and precipitation hardening metals is atomized by dispersing the molten metal as fine droplets in an atomizing gas so that droplets solidify therein. If desired, the droplets may be projected against a relatively cold metal surface, preferably contacting the cold metal surface before the liquidus temperature has been reached in the droplets, in order to provide more rapid cooling and even finer distribution of the second phase material. In some cases, the alloy may supercool and solidify without separation of the second phase. In that event, the second phase will generally form and separate during or subsequent to wrought operations in which the atomized particles are employed.

On carrying out atomizing into a gas environment it is desirable to disperse the melt into droplets that on solidification provide pellets small enough to pass a No. 100 sieve (U.S. Sieve Series) although pellets as coarse as about 20 mesh are satisfactory. Use of such fine pellets assures sufficient dispersion of the second phase material during solidification of the pellet. The pellets may be collected in water below the gas enivornment but this is generally to be avoided since some surface oxidation of the pellets may occur. Such oxidation tends to interfere with bonding of the pellets during subsequent compacting and working.

Any number of known techniques may be used to consolidate the pellets. One technique frequently used is to cold press the pellets hydrostatically, can the compact under vacuum in a mild steel can, and extrude the composite at about 2000° F. with glass lubrication on a high speed press. The jacket is then removed by machining, pickling, or both. It has also been found that the pellets

can be canned directly without pre-compaction. Although conventional working techniques are used, it is desirable to avoid excessively high temperatures and long holding times since they cause agglomeration of the dispersed second phase and progressive loss of dispersion hardening. This also applies to any subsequent heat treatment.

The following examples serve to illustrate the invention and do not limit the scope thereof.

EXAMPLES

In a series of runs illustrating the method and composition of the invention nickel was alloyed with, variously, (1) titanium and silicon, (2) titanium and carbon, (3) aluminum and titanium, (4) aluminum, titanium and silicon, and (5) aluminum, titanium and carbon. In each case additions were made to molten nickel while it was at a temperature of about 3000° F. The homogeneous melt was atomized by allowing a thin stream of the molten metal to fall into a high pressure jet of argon. The solidified pellets were collected and found to be sufficiently fine enough to substantially pass a No. 20 sieve. In each case about ten pounds of pellets was placed in a can made by welding a juxtaposed circular piece of mild steel, as a cap, to one end of an 8 inch length of heavy-walled, extra strong, mild steel pipe having an inner diameter of 1.939 inches and an outer diameter of 2⅜ inches. Sufficient pellets were used to completely fill the can. Then the can was closed or capped by welding another circular piece of mild steel across the open end. The resulting closed can was then slid into about a 9 inch length of standard copper pipe having an inner diameter of 2½ inches and an outer diameter of 2⅞ inches, the closed can being substantially centered between the ends of the copper pipe. The extending ends of the copper pipe were peened over to hold the can in place. The assembly was then heated to about 1800 to 1900° F. and quickly inserted into the container of an extrusion press. The container had been preheated to about 900 to 1000° F. Extrusion was commenced as soon as possible, the assembly being extruded as a rod about one inch in diameter at a rate of about 5 feet per minute. The nickel alloy core was about ½ inch in diameter. Samples were cut from each rod and machined to remove the copper and steel jacket and prepare test bars. The so-obtained test bars were subjected to mechanical testing in order to obtain percent elongation and tensile yield strength and ultimate tensile strength values.

By way of comparison, commercial grade elemental nickel was similarly atomized, extruded and tested.

In further comparison tests aluminum and titanium additions were made to molten nickel and similarly atomized. The atomized pellets were transformed into extruded rod in the manner just described and the test bars obtained were subjected to mechanical testing. The results of the mechanical testing in each case and the compositions employed are listed in the following table. Each test bar was examined metallographically for the presence of second phase. The results of this test are also listed in the table along with the compounds theoretically expected, if any.

In Test No. 6, listed above, the aluminum and titanium, solid soluble at the concentration levels of the alloy of Test Comparison 2, formed a second phase with nickel that was solid-insoluble in the nickel alloy.

What is claimed is:

1. A wrought nickel base alloy product made by atomizing, compacting and working nickel base alloy, said alloy comprising up to about 60 percent by weight of a metal that serves as a solid nickel alloy-soluble hardening alloying addition, from about 1 to about 20 percent by volume of at least one solid nickel alloy-insoluble second phase material having a solid solubility in nickel below about 5 percent by weight and a melting temperature above about 1800 to 2200° F., from about 4 to 10 percent by weight of precipitated precipitation hardening alloying additions capable of solubilizing during heat treatment, and at least about 35 percent by weight of nickel, the alloy product being further characterized as containing the second phase dispersed therethrough as particles not exceeding about 5 microns in maximum dimension.

2. The wrought alloy product as in claim **1** in which the particle size of the dispersed second phase material does not exceed about 1 micron in maximum dimension.

3. The wrought alloy product as in claim **1** containing about 2 to 10 percent by volume of said second phase material.

4. The wrought alloy product as in claim **1** in which the second phase comprises a material selected from the group consisting of boron, rare earth metal, thorium, zirconium, titanium carbide, titanium silicide, aluminum titanium nickelide, thorium boride and zirconium carbide and combinations thereof.

5. The wrought alloy product as in claim **1** in which the solid nickel alloy-soluble hardening addition is a metal selected from the group consisting of iron, chromium, cobalt, molybdenum, tungsten and mixtures thereof.

6. The wrought alloy product as in claim **1** containing from about 5 to about 7.5 percent by weight of precipitation hardening alloying additions.

7. The wrought alloy product as in claim **1** in which the precipitation hardening alloying addition is a metal selected from the group consisting of aluminum, columbium, titanium and mixtures thereof.

8. The method of making the high strength product alloy product of claim **1** which comprises:

atomizing the alloy of claim **1**;

compacing the so-obtained atomized particles;

and subjecting the so-obtained compact to a wrought operation.

9. The method as in claim **8** in which the compact is canned under vacuum in a mild steel can before the wrought operation and the can is removed from the alloy after the wrought operation.

10. The method as in claim **8** in which the atomizing is carried out in a manner to obtain substantially only particles passing a No. 100 sieve (U.S. Sieve Series).

11. The method as in claim **8** in which the atomized alloy is placed in a mild steel can and the can and its contents are die-expressed whereby compacting and sub-

Test No.	Composition, by weight[1] Al	Ti	Si	C	Second phase	Physical properties at R.T. Percent E	TYS	TS	Physical properties at elevated temperatures Test temp.	Percent E	TYS	TS
Comparison 1	(Unalloyed nickel)				None	39	16	55	1,400	5	7.1	8.5
1		3	1		Titanium silicide	41	37	87	1,400	34	16	24
2		5		1	Titanium carbide	30	52	104	1,400	63	20	26
3	3	5	1		Titanium silicide	16	136	197	1,000	13		153
									1,400	18	30	50
4	3	7		1	Titanium carbide	15	120	184	1,400	31	25	42
5	4.5	8		1	Titanium carbide and aluminum titanium nickelide	1	152	162				
Comparison 2	3	2			None	32	36	79	1,400	31	12	19
6	4.5	3			Aluminum titanium nickelide	11	120	169				

[1]=Balance nickel.

NOTE.—Percent E=Percent elongation in two inches. TYS=Tensile yield strength in 1,000's of pounds per square inch. TS=Ultimate tensile strength in 1,000's of pounds per square inch. R.T.=Room temperature.

jecting the atomized alloy to a wrought operation are carried out substantially concurrently.

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