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HIGH TEMPERATURE NICKEL BASE ALLOYS

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2 Sheets-Sheet 1

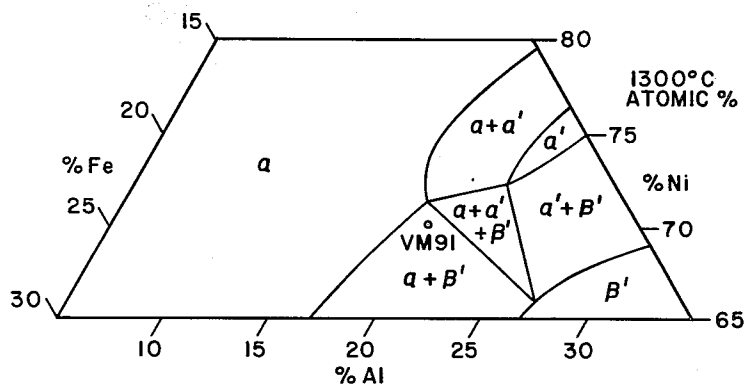


Fig. 1A

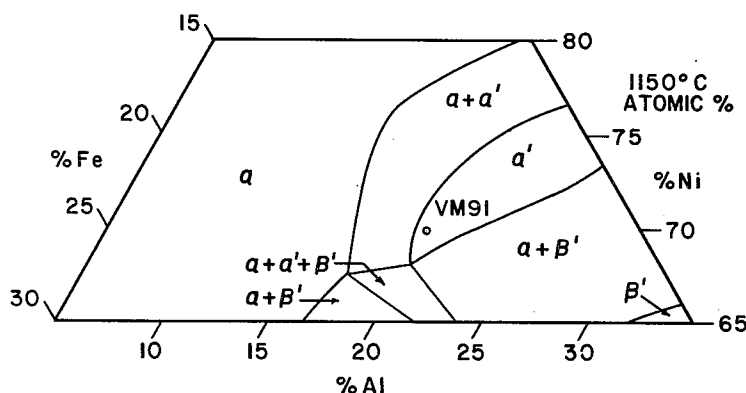


Fig. 1B

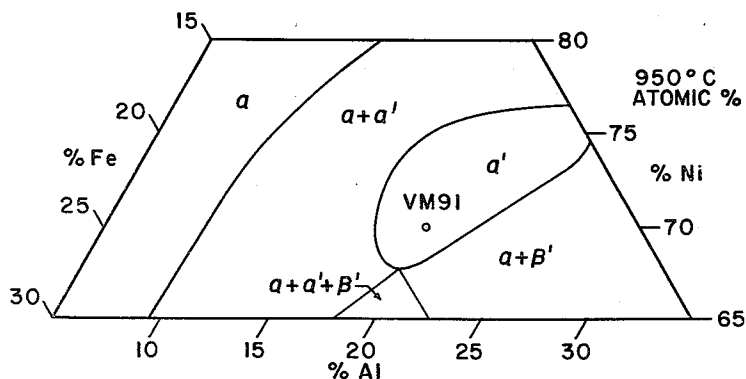


Fig. 1C

WITNESSES

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2 Sheets-Sheet 2

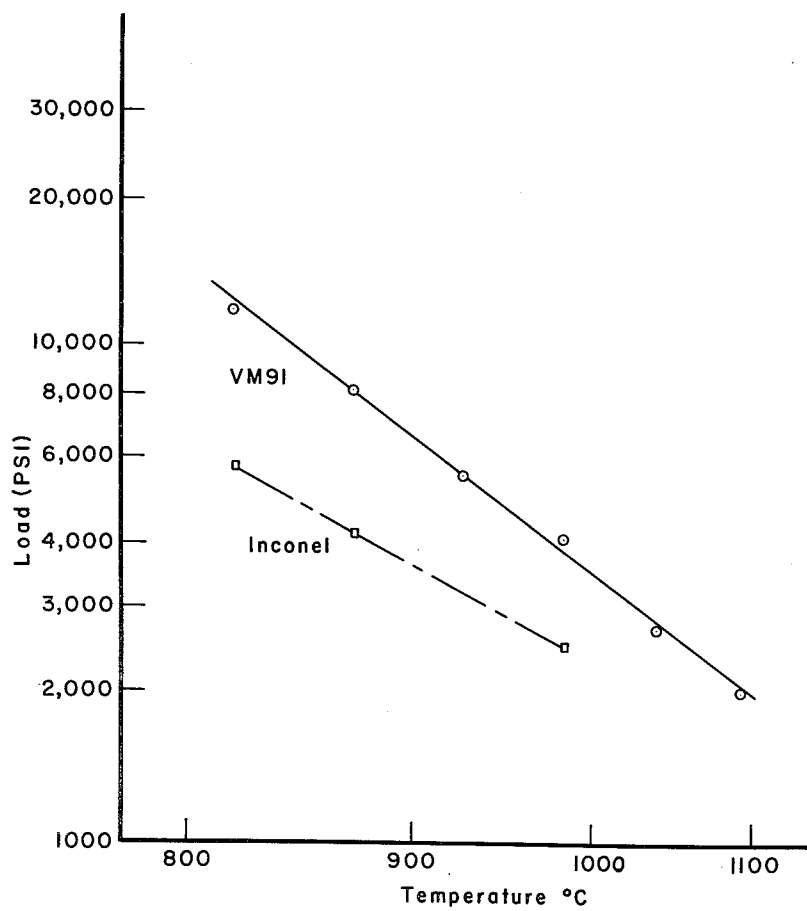


Fig. 2

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HIGH TEMPERATURE NICKEL BASE ALLOYS

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This invention relates to nickel base alloys having high strength at elevated temperatures, particularly alloys based on the Ni₃Al ordered structure, and methods of preparing such alloys.

There is a continuing need for alloys that can be cast or otherwise formed into members for employment at temperatures of 980° C. and higher. Such alloys may be used advantageously for the turbine blades of jet engines and gas turbines, and for heating elements.

In the past, the approach which has been used to provide high temperature strength alloys is the production of alloy structures which are extremely hard and strong at room temperature. This is done because, although the strength of the alloy may suffer great reduction at elevated temperatures, it is expected that the alloy will retain strength sufficient for the use intended. Such thermally unstable alloy structures have been produced in several ways; for example, by precipitation-hardening, by solid solution hardening, and by cold working. In these alloys strength is achieved through interference with dislocation glide, as by the finely dispersed particles in precipitation-hardened alloys, or by the local stress fields in cold-worked materials.

Among the alloys which have been examined with a view to high temperature application is the binary Ni₃Al of the nickel-aluminum system. Ni₃Al (α' phase) is an intermetallic compound or substitutional solid solution exhibiting a "superlattice" structure. The superlattice, or long-range ordered structure, is an arrangement of atoms in the crystal lattice in which the random distribution of solvent and solute atoms in the crystal ordinarily prevalent at higher temperatures, is replaced, at lower temperatures, by a regular or ordered arrangement of atoms on preferred lattice sites. The ordering energy of Ni₃Al is high, i.e., the order-disorder transformation occurs at temperatures well above half the melting point of the alloy. This alloy has not, however, proved a tractable material, and attempts at working the alloy have been unsuccessful, with low ductility at both room and elevated temperatures. Ni₃Al is a coarse-grained alloy, as obtained, in which fractures always occur at grain boundaries, although any one grain removed from the bulk material exhibits great ductility.

It is the object of this invention to provide improved ternary nickel base alloys containing iron and aluminum having superior high temperature properties including high ductility, utilizing the superlattice or long-range Ni₃Al ordering phenomenon.

It is a further object of this invention to achieve a method for producing ductile, high strength members usable at 980° C. from Ni₃Al base ternary alloys comprising hot working above the order-disorder transformation, and then solution treating.

A still further object of the invention is to provide improved corrosion resistant cutlery and other edged tools capable of keeping a sharp edge, from a ternary nickel base alloy containing predetermined amounts of iron and aluminum which alloy attains a high hardness on being worked to shape.

Other objects of the invention will become apparent as the description proceeds.

For a better understanding of the nature and objects of

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the invention, reference should be had to the following detailed description and drawings, in which:

FIGS. 1A, 1B and 1C show a portion of the phase diagram of the ternary Ni—Al—Fe system at temperatures of 1300° C., 1150° C. and 950° C., respectively.

FIG. 2 is a graph of the stress for 100 hour creep life for two alloys in which the load is plotted against temperature.

This invention relates to a ternary nickel base alloy comprising iron and aluminum in critical proportions, the alloy having an ordering energy level such that there is available a range of satisfactory hot working temperatures above the order-disorder transformation, and the alloy being capable of solution treatment to develop an ordered structure which is retained at elevated temperatures of 980° C. and higher, and having a fine grained structure which is highly ductile both at room temperature and at elevated temperatures of use. In particular, the alloy comprises as its essential ingredients, by weight, 79%–81% nickel, 9% to 11% aluminum, and the balance approximately 9% to 11% iron, and incidental impurities.

It has been discovered that the intergranular cracking which is characteristic of Ni₃Al can be substantially eliminated by introducing iron into the alloy to somewhat lower the ordering energy, and then processing the alloy to obtain a fine grain structure. The ternary with iron is one in which the Ni₃Al based field is extensive. It is of utmost importance in this invention, if the desired physical properties are to be secured, to obtain an alloy in which the ordered structure is retained at elevated temperatures, and which has a substantially fine grain structure.

Both casting and powder metallurgy techniques have been successfully used in the preparation of the alloys of this invention. Vacuum melting is employed in the casting technique to prevent oxidation of the aluminum additive. Also, if the alloy is cast, it must be hot-worked at a temperature above the ordering range to refine the grain structure. In the powder metallurgy technique, grain size is controlled by the size of the powder particles selected for compaction. An ordered structure is assured in all cases by a solution treatment at a temperature in the ordering range.

The following examples illustrate the preparation of the alloy of the present invention:

EXAMPLE I

Under vacuum there was melted a charge which had the following nominal analysis after casting:

	Wt., percent	Atomic, percent
Nickel.....	79	70
Aluminum.....	10	or 20
Iron.....	11	10

Trace elements in wt. percent:

Cobalt	} each less than .1%
Copper	
Silicon	
Boron	
Manganese	} each less than .01%
Gallium	
Gold	
Chromium	} each less than .001%
Silver	
Vanadium	
Magnesium	
Molybdenum	

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The alloy was prepared under vacuum to prevent oxidation of the aluminum. Electrolytic iron and nickel were first charged into a vacuum furnace and melted. This was followed by deoxidation with hydrogen and then the aluminum was carefully added. After casting and cooling, the ingot was hot rolled to a rod of a 0.5 inch diameter at approximately 1300° C. with relatively large reductions of from 10% to 25% reduction in area per pass. After the completion of the rolling operation, the rod was oil quenched. The rod was then further solution treated for 24 hours at 1150° C. The rod was of fine grained structure and was ready for use. Cold reduction of the hot worked rod subsequent to solution treatment, proved possible to produce .001 inch foil by cold rolling, and .020 inch diameter wire by swaging, with intermediate anneals in each case.

The alloy of the composition of this example disorders at approximately 1150° C. This temperature for the order-disorder transformation promises good high temperature properties at temperatures below about 1100° C., provided a fine grain structure can be obtained. The composition of this alloy was chosen because, as can be seen from the phase diagrams of FIG. 1 where in the alloy composition is expressed in atomic percent, the alloy has a two-phase structure at 1300° C. The hot rolling process, having as its purpose the production of a fine grained structure, is carried out in the (α + β') region. The (β') phase is generally segregated at the grain boundaries of the (α) phase grains, and thus serves to inhibit grain growth during the hot rolling operation. The hot rolled structure was reasonably fine grained at about ASTM No. 5. The purpose of the solution treatment is to dissolve the grain boundary (β') phase which imparts undesirable physical properties. During the solution treatment, grain growth does occur to a slight degree, but the grain size remains within serviceable limits. This sample is hereinafter designated as VM91.

EXAMPLE II

A mixture of electrolytic powders of nickel and a 50-50 weight percent master alloy of aluminum and iron, in the proportion of 80 weight percent nickel to 20 weight percent of the master alloy, was used to prepare an alloy of the approximate composition 80 nickel, 10 aluminum, 10 iron. The powders were composed of particles less than 44 microns in diameter. The mixture was thoroughly blended for 24 hours and then sieved through a 325 mesh screen to eliminate agglomerated powders. Using a compacting pressure of 30 t.s.i. (tons per square inch), the powders were compacted in the form of 3 inch long x 0.5 inch wide x 0.5 inch deep specimens. These specimens were surrounded by fine alumina powder and presintered at a temperature of 1125° C. for 4 hours in a hydrogen atmosphere with a dew point of -60° C. or lower. After sintering, the specimens were hot-coined at a temperature of 1250° C. This was accomplished by placing the specimen in a die keyed to the anvil of a forging hammer. After the specimen is positioned in the die cavity, the die is struck once by the hammer. The specimen is then permitted to cool in the die until it is no longer susceptible to high temperature oxidation. While at elevated temperatures, an argon atmosphere is maintained about the specimens. The coining operation was followed by sintering the specimen at 1325° C. for 4 hours.

Thereafter, some of the specimens were hot rolled at 1250° C. for reductions in thickness up to 25% between heatings. Other specimens were cold rolled. As the work-hardening rate of the alloy is very high, only a 10% reduction in thickness was applied and followed by anneals at 1250° C. for 15 minutes. Some specimens were cold rolled to a total of approximately 50% in thickness.

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EXAMPLE III

An alloy corresponding to the present invention was vacuum melted following the same general procedure as set forth in Example I, that is, melting electrolytic iron and nickel, hydrogen deoxidizing, carefully adding aluminum in the form of chips, and deoxidizing once again. The alloy was cast into a cylindrical ingot in a mold formed of a tube of plain carbon steel. Following solidification, the temperature of the ingot was raised to approximately 1260° C. and at that temperature the ingot and tube were extruded as a unit. Extrusion was followed by a solution treatment of the composite ingot for 2 hours at 1150° C. Thereafter, the plain carbon steel outer layer was stripped from the ingot. In the extrusion process a reduction in area was effected in a ratio of from 1 square inch to .03 square inch.

The heat is cast into a plain carbon steel tube to provide the ingot with a "can" which serves to protect the ingot during the extrusion process. Tubes of any ferrous base metal are suitable. The outermost fibers of an extruded member suffer the most distortion and oxidation in the process of extrusion. If the ingot is extruded without the protecting "can," an outer layer of the ingot may have to be removed before any further fabrication can be undertaken. With the "can" it is not the ingot but the tube which undergoes the severest working. It has also been found helpful to introduce a blanket of glass fibers into the press with the canned ingot to serve as a lubricant. After extrusion, the surface of the extruded member is treated to remove the jacket of ferrous metal and, if necessary, the nickel-aluminum iron alloy core machined to desired surface condition.

The extrusion temperature of 1260° C. is above the ordering temperature of this alloy. In the disordered condition, of course, the alloy is much more amenable to working. It is noteworthy that the melting point of this alloy is (1380° C.). The extrusion process is so rapid that grains of the material do not have time to grow and, as a result, a fine-grained structure is obtained. A grain size of ASTM No. 7 has been achieved after hot extrusion.

Tensile tests were conducted at room temperature and elevated temperature on alloys made in accordance with the processes described in Examples I through III. Results of these tests are set forth in the following table:

Table I

Condition	Temperature	Ult. Strength	.2% Yield	Total Percent Elong., Gauge Length=1"	Reduction of Area, percent
Cast and Wrought.	Room temp.	108,000	33,000	21	22
Powder.	do.	94,200	55,100	12.1	9.6
Extruded.	do.	111,600	51,300	12.3	8.7
Cast and Wrought.	1,000° C.	39,000	28,000	11	17
Powder.	980° C.	18,260	16,000	2.3	1.9
Extruded.	980° C.	35,100	31,050	14.5	13.5

Creep tests were carried out at 980° C. on alloys made in accordance with the processes disclosed in Examples I and III. The results of these tests appear in the following table:

Table II

Condition	Temperature, ° C.	Load (1,000 p.s.i.)	Life (hours)	Percent Elongation
Cast and Wrought.	980	5	30	23
Extruded.	980	5	43.5	15.4

In FIG. 2, the comparative stress rupture properties of an alloy made in accordance with this invention (VM91), and a precipitation-hardened nickel chromium base alloy comprising 80% nickel, 15% chromium, 5% iron (Inconel), are compared on the basis of 100 hour creep life at any given temperature up to 1100° C. It should be noted that VM91 shows definite superiority at all temperatures.

From the physical data presented, it should be clear that the alloys of the present invention show considerable promise for high temperature service. The alloy is metallurgically stable at a temperature of 980° C., and the ordered structure tends to suppress dislocation glide. A part of the iron can be replaced with up to 5% molybdenum and tungsten.

The alloys of the present invention are suitable for use as electrical resistance heating elements. They are superior in oxidation resistance and in strength at elevated temperatures to normally employed resistance element alloys. Heating elements of wires of a diameter of 0.020 inch of this alloy were made and found to be satisfactory.

While this alloy is primarily intended for service at elevated temperatures, certain of its properties command attention for application at room temperature. It has been found that this alloy has a very high work hardening rate, and that hardnesses in the range 500-550 D.P.H. are attained readily with a relatively small amount of working. Also, the alloy is highly corrosion resistant, and in this respect, it is equal to or better than stainless steel under the same conditions. For these reasons, the alloy of this invention is suitable for use in fabricating knife blades and other cutlery, other edged tools and cutting implements. As is well known, austenitic stainless steel, which is a common material presently used in making cutlery, fails to maintain a keen blade edge and dulls rapidly in use, and this deficiency is associated with the limited response of austenitic stainless steel to hardening treatment. Carbon steel, which hardens readily on heat treatment and tempering, will, of course, take a fine edge, but it is very susceptible to corrosion at room temperature. The present alloy, therefore, fills a need for a readily hardenable material capable of attaining high hardness, and hence maintaining a keen blade edge, while at the same time exhibiting great resistance to corrosion. These properties are particularly valuable for cutting, slicing, chopping, and grating blades in industrial food processing equipment where corrosion is an important consideration, and maintenance of keen blade edges is a problem costly in labor and shut-down time. The process of working the alloy to the desired cutter or blade shape of a thickness of, for example, 100 mils and less, is sufficient to develop a hardness of from 500 to 550 D.P.H. (diamond pyramidal hardness), and once worked to such thin shape, the cutter or blade can be sharpened to a long-lasting cutting edge. No additional heat treatment is required to develop the hardness of the cutters or knives made of the alloy of this invention. Thus a sheet of a thickness of less than 10 mils acquired a sharp edge which was suitable for cutting meat.

It will be understood that the above descriptions are illustrative only of the invention.

I claim as my invention:

1. A wrought member suitable for use in a high temperature environment consisting of an alloy composed of, by weight, 79% to 81% nickel, 9% to 11% aluminum, and the remainder iron except for incidental impurities, said alloy characterized in having a substantially fine-grain structure, ductility enabling the member to be cold worked, and an ordered crystalline lattice structure which is relatively stable up to a temperature of approximately 1150° C.

2. An extruded member consisting of a high temperature alloy comprising 79% to 81% nickel, 9% to 11%

aluminum, up to 5% of a metal selected from the group consisting of tungsten and molybdenum, and the remainder iron except for incidental impurities, said alloy characterized in having a fine grained, superlattice structure which is stable at temperatures up to approximately 1150° C.

3. An extruded member consisting of a high temperature alloy having a fine-grain structure, said alloy comprising 79% nickel, 10% aluminum, and the remainder iron except for incidental impurities, said alloy member having a fine-grained structure and exhibiting a highly stable ordered crystalline lattice structure having an order-disorder transformation temperature of approximately 1150° C.

4. A wrought member suitable for use in a high temperature environment consisting of an alloy having a fine-grain structure composed of, by weight, 79% nickel, 10% aluminum, and the remainder iron except for incidental impurities, said alloy having a fine-grained structure and characterized in having a highly stable ordered crystalline lattice structure which is retained up to a temperature of about 1150° C.

5. In a process for making a high temperature alloy ingot, the steps of, melting and casting under non-oxidizing conditions an alloy comprising from 79% to 81% nickel, from 9% to 11% aluminum, and the balance being iron except for incidental impurities, to provide an ingot of predetermined size and shape for extrusion, hot extruding the ingot above the order-disorder transformation temperature to obtain a fine-grained structure, and solution treating the extruded alloy ingot to develop an ordered lattice structure having substantial ductility.

6. In a process for making a high temperature alloy ingot, the steps of, melting and casting into a ferrous mold under non-oxidizing conditions an alloy comprising from 79% to 81% nickel, from 9% to 11% aluminum, and the balance being iron except for incidental impurities, to provide a composite member of predetermined size and shape, hot extruding the composite member above the order-disorder transformation temperature of said alloy to secure a fine-grained structure, solution treating the extruded composite member to develop an ordered lattice structure exhibiting substantial ductility, and stripping the ferrous mold from said alloy ingot.

7. A method for producing and processing a corrosion resistant and hardened nickel base alloy material suitable for fabrication into cutting implements having long-lasting cutting edges, comprising the steps of, melting and casting under non-oxidizing conditions an alloy comprising from 79% to 81% nickel, from 9% to 11% aluminum, and the balance being iron except for incidental impurities, to provide an ingot of predetermined size and shape for extrusion, hot extruding said ingot above the order-disorder transformation temperature to produce a fine-grained structure, solution treating said extruded ingot to develop an ordered lattice structure having substantial ductility, and working said ingot below the order-disorder transformation temperature to obtain a hardness in a range from 500 to 550 D.P.H.

8. A member suitable for use in a cutting implement, at least the cutting edge thereof consisting of a thin worked portion of an alloy composed of, by weight, 79% to 81% nickel, 9% to 11% aluminum, and the remainder iron except for incidental impurities; said thin worked portion having a fine-grain size and characterized in having good corrosion resistance and a relatively high work hardening rate, such that the thin worked portion has a hardness in the range of from 500 to 550 D.P.H.

9. A wrought member forming the cutting edge of a cutting implement consisting of an alloy composed of, by weight, 79% to 81% nickel, 9% to 11% aluminum, and the remainder iron except for incidental impurities; said member characterized in having good corrosion resistance

and a high hardness of from 500 to 550 D.P.H. produced by working.

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