

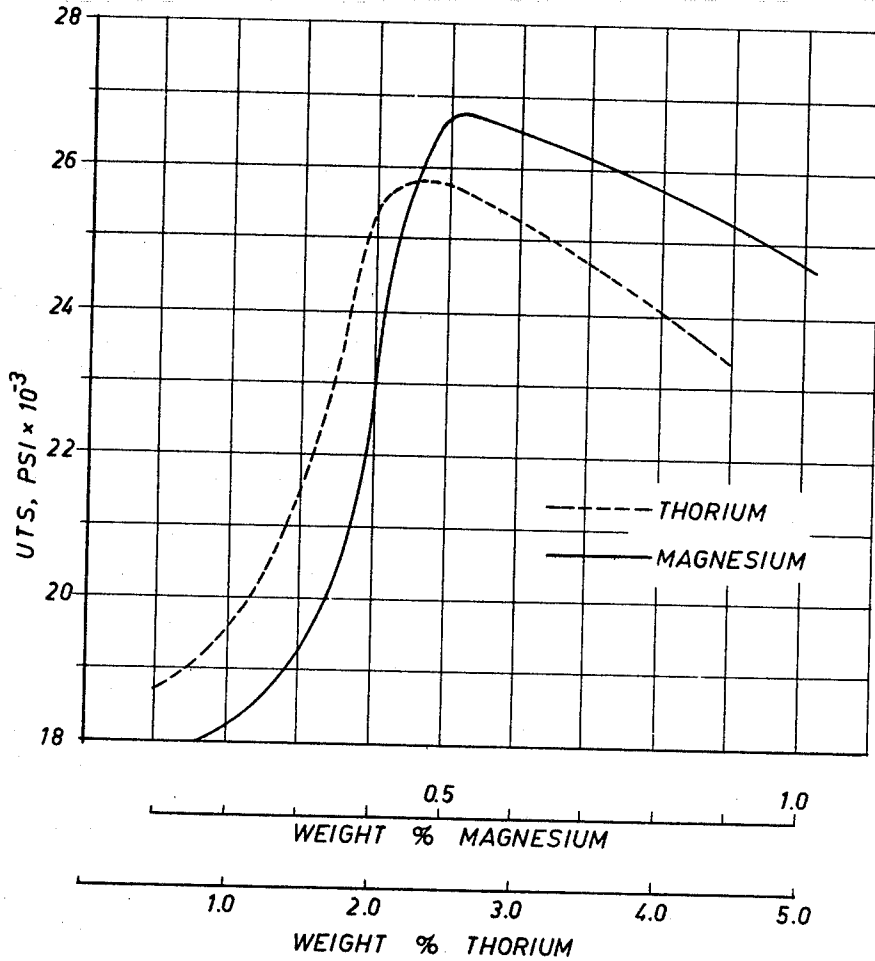
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DISPERSION STRENGTHENED NICKEL-CHROMIUM ALLOY COMPOSITION

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7 Claims

ABSTRACT OF THE DISCLOSURE

A powder metallurgy composition capable of fabrication into wrought dispersion strengthened nickel-chromium alloys by compacting, heating and working operations which composition contains nickel powder, chromium powder, uniformly distributed submicron sized refractory oxide particles and at least one additive metal powder, such as magnesium or yttrium, for example, which is capable of promoting homogenization of the nickel and chromium constituents of the powder mixture when the powder mixture is heated in the range of 1800° F. to 2200° F. during fabrication thereof by combining with oxygen in the powder mixture available for reaction therewith. The amount of additive metal is regulated such that all of it combines with reactive oxygen during fabrication of the powder, that is, no additive metal uncombined with oxygen occurs in the wrought product matrix.

This invention relates, in general, to dispersion strengthened nickel-chromium alloys. More particularly, it is concerned with novel powder metallurgy compositions for use in preparing such alloys, a novel method for producing wrought alloys of improved high temperature service characteristics and with the wrought alloys so formed.

Desirable service characteristics in high temperature resistant alloys are high tensile strength values, resistance to oxidation and superior stress-to-rupture life at elevated temperatures.

It is known that the incorporation of a dispersion of ultra-fine refractory oxide particles within a metal or alloy matrix can substantially improve the high temperature strength characteristics of the material. For example, using powder metallurgy techniques, dispersion strengthened nickel has been produced which has an ultimate tensile strength at 1600° F. of 29,000 p.s.i. as compared to about 8,000 p.s.i. for unmodified nickel. It is also known that the resistance of nickel to oxidation at elevated temperatures can be substantially improved by alloying it with about 15 to 40% chromium. It has long been considered desirable to incorporate a dispersed refractory oxide phase in nickel-chromium alloys so as to simulate the improvement in high temperature strength characteristics effected on pure nickel by the presence of a dispersed oxide phase while retaining the high temperature oxidation resistance inherent in nickel-chromium alloys. However, serious problems are encountered in producing dispersion strengthened wrought nickel-chromium alloys using conventional powder metallurgy techniques which involve handling and mixing of primary powders.

Firstly, difficulty is encountered in bringing about complete homogenization of the nickel-chromium matrix. One reason for this is that chromium powder particles, when exposed to air, become coated with layers of contaminant compounds. The contaminants include chromium oxides and nitrogen containing chromium compounds. These

layers reduce the ability of the chromium to diffuse into the nickel to give a well homogenized matrix when nickel-chromium powder mixtures are compacted, heated and worked. One characteristic of the lack of homogeneity, as shown by electron probe microanalysis, is the presence in the alloy product of numerous, small, localized areas which are rich in chromium and nitrogen and deficient in dispersion strengthening refractory oxides. The presence of these areas in the alloy is harmful to its high temperature service characteristics. Another problem which, it is believed, is attributable to chromium oxides contamination, is the agglomeration of the dispersed refractory oxide particles which further reduces the high temperature stability of the alloy product.

Accordingly, a principal object of this invention is to overcome the detrimental effects of contaminant compounds associated with chromium powders on the high temperature service characteristics of dispersion strengthened nickel-chromium and nickel-chromium base alloys produced by powder metallurgical methods.

Another object of this invention is to provide a powder metallurgy composition adapted to producing dispersion strengthened nickel-chromium alloys having improved high temperature service characteristics.

A further object of this invention is to provide a powder metallurgical method for producing alloys comprised of a homogeneous nickel-chromium matrix containing ultra-fine dispersed refractory oxides.

Still another object of this invention is the provision of wrought nickel-chromium alloys having excellent high temperature oxidation resistance and improved ultimate tensile strength values and stress-to-rupture life at elevated temperatures.

Generally speaking, these and other objects of the present invention are realized by the inclusion, in nickel-chromium base alloy powder compositions containing ultra-fine refractory oxides or substances capable of conversion to refractory oxides upon heating, of at least one additive metal powder which is capable of promoting homogenization by reacting with the contaminants associated with chromium in the powder composition and forming, in situ, a stable oxide compound having a free energy of formation at 1000° C. greater than 70 kilocalories per gram atom of oxygen in the oxide. More specifically, this invention provides powder metallurgy compositions composed of from 10 to 40 weight percent chromium, from 0.5 to 5 volume percent of at least one ultra-fine refractory oxide, from 0.05 to 5 weight percent of at least one additive metal, the oxide of which has a ΔF , at 1000° C. of at least 70 kilocalories per gram atom of oxygen and the balance nickel or nickel and other alloying agents capable of enhancing the high temperature service characteristics of nickel-chromium alloys.

The process of the invention contemplates compacting these novel powder compositions and heating the resulting compact in an inert or reducing atmosphere to a temperature below the melting point of nickel and preferably within the range of about 1800° F. to about 2200° F. and hot and cold working the heat treated compact to produce wrought, dispersion strengthened nickel-chromium base alloy products.

The wrought products of this invention have superior high temperature tensile strength, stress-to-rupture life and excellent high temperature oxidation resistance. They are characterized by having a completely homogenized nickel-chromium base alloy matrix which contains dispersed, sub-micron refractory oxides of one or more metals, at least a portion of such oxides being formed in situ by the combination, on heating, of an additive metal or metals with oxygen associated with the chromium oxides and with other oxygen within the powder compact available for combination therewith.

The invention is discussed in detail hereinafter as applied to nickel-chromium-refractory oxide compositions. However, it will be appreciated by those familiar with the art that the invention is applicable to dispersion strengthened nickel-chromium alloys containing additional modifying agents such as solution or precipitation hardeners which enhance the properties of conventional nickel-chromium alloys.

The nickel in the powder compositions of this invention may be any finely divided nickel powder. The particle size of the powder should be below about 5 microns and preferably below 1 micron. Finely divided nickel powders, such as those produced by direct reduction of nickel from aqueous media by reaction with hydrogen at elevated pressure and temperature, are well adapted for use in this invention.

It will be understood that care should be taken, in accordance with good powder metallurgical practice, to keep the content of impurities, such as carbon and sulphur, to a practical minimum in the various powders employed in this invention.

The refractory oxide constituent must be a thermally stable material having a melting point appreciably higher than the nickel-chromium alloy which is to comprise the matrix of the final wrought product; it must have low solubility in the matrix and must be substantially non-reactive with the matrix at normal and elevated temperatures. The refractory oxides which satisfy the foregoing conditions are well known in the art. Two refractory oxides which are preferred for the purposes of this invention are yttria and thoria. Other suitable oxides are calcia, magnesia, zirconia, silica, beryllia, hafnia, alumina, titania, uranium dioxide, lanthanum trioxide.

The refractory oxide constituent must be in a very finely divided form. The particles should be less than 100 millimicrons in size and preferably in the range of 10 to 30 millimicrons. Some refractory oxides in the desired size range are readily available in the form of colloidal aquasols. Aquasols of thoria and ceria, for example, are well known and commercially available. Thoria is a preferred refractory oxide because of its high melting point, high temperature stability and ready availability in the preferred size range.

The refractory oxides can be simply mixed with the nickel and chromium constituents such as dry mechanical mixing. For example, thoria, in the form of a colloidal aquasol can be mixed directly with nickel and/or chromium powder and the combined constituents mechanically blended to produce a uniform mixture. However, it is preferred to utilize composite powders in which ultra-fine refractory oxides are integrally associated with nickel particles. Methods are known by which such nickel-dispersoid powders can be produced. One such method is described in United States Pat. No. 2,853,398. Another method is described in co-pending United States Pat. application Ser. No. 543,495, filed Apr. 18, 1966, now Canadian Pat. No. 786,268. Nickel dispersoid powders produced by this latter process are preferred for use in the compositions of this invention. Powders produced by this process are comprised of submicron sized nickel particles formed into irregularly-shaped agglomerates generally about 0.5-1.0 micron in size and having ultra-fine refractory oxide particles firmly attached to the surfaces thereof.

The chromium content of the powder compositions of this invention can be provided as a finely divided powder or in the form of nickel coated composite powder such as is obtainable by the process of United States Pat. No. 2,853,403. It is desirable to utilize chromium powders which have been reasonably protected from exposure to air, so as to minimize nitrogen and oxygen contamination. A combined content of oxygen and nitrogen of less than 1.0% by weight is desirable. A particle size smaller than 200 mesh standard Tyler screen and preferably less than 325 mesh should be used. Chromium powders meeting

these specifications are readily available from commercial sources. The amount of chromium used will, of course, depend on the composition desired for the matrix of the final product. Chromium will add strength to a nickel-chromium alloy when a minimum of about 10% is present. It will substantially improve the oxidation resistance of the alloy when a minimum of 15% is present. The solubility limit of chromium in nickel is about 40%. Accordingly, the chromium content of the powder composition may vary from 10% to 40% by weight.

The additive metal or metals employed in the powder metallurgy compositions of this invention must be capable of reducing chromium oxides and combining with oxygen to form a solid oxide which is stable within the nickel-chromium alloy system. The additive metal must also be capable of preventing the formation of localized areas rich in chromium and nitrogen in the matrix of the final wrought alloy products. We have found that these requirements are met by metals which form oxides having a heat of formation at 1000° C. of 70 or more kilocalories per gram atom of oxygen in the oxide. More specifically, one or more of the following metals are particularly useful as additive metals for the purposes of this invention: magnesium, beryllium, thorium, titanium, calcium, zirconium, cerium, yttrium and hafnium. Magnesium is preferred as an additive metal because of its high oxygen to metal weight ratio which minimizes the amount of additive metal required to combine with all the oxygen in the compact available for reaction therewith.

According to a preferred embodiment of our invention, commercially available magnesium powder, which is substantially 100% minus 200 mesh standard Tyler screen and preferably substantially 100% minus 325 mesh, is used as the additive metal. The magnesium powder preferably should have a combined content of oxygen and nitrogen of less than 1.0% by weight.

The quantity of additive metal or metals to be included in the powder composition will vary depending on the type of additive metal employed and the amount of oxygen available in the powder compact to combine therewith. The bulk of the "available oxygen" will be comprised of the oxygen associated with the chromium oxides. However, there will be small additional amounts of oxygen introduced to the powder compact because of the deficiencies of the system. For example, the furnace atmosphere may contain minute quantities of oxygen and air may become entrapped within the compact during the compacting steps.

Useful improvement in the high temperature service characteristics of the nickel-chromium alloy product will result from the presence of from 0.2 to 1.0 times the amount of additive metal required to combine stoichiometrically with oxygen present in the powder composition as chromium oxides. It is preferred, however, to provide an amount of additive metal in excess of the stoichiometric amount noted above in order to ensure that other available oxygen present in the compact is also tied up. The amount of excess can be up to 10 times stoichiometric but in most cases will be less than 2 times this amount. The precise amount of additive metal required for optimum improvement of any given composition can be readily determined by simple experimentation. By conducting a series of test runs on a representative sample of the powder composition using varying amounts of additive metal and plotting ultimate tensile strength of the wrought product versus percentage of additive metal, a curve can be obtained the apex of which will indicate the optimum amount of additive metal. Typical curves obtained in this manner are shown in the accompanying drawing. Wrought products containing this optimum amount of additive metal will be substantially free of localized areas rich in chromium and nitrogen.

Generally, when commercially available chromium powder is used, the amount of additive metal will be

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within the broad range of 0.005 to 5.0% by weight of the composition. When magnesium is the additive metal, the amount required will be within the range of 0.10 to about 2.0 weight percent. For example, for a powder mixture suitable for forming a dispersion strengthened 77-20 nickel-chromium alloy containing 2.5 weight percent thoria as the dispersed oxide phase, the optimum magnesium content is about 0.4 to 1.0 weight percent. Where other additive metals are substituted, in whole or in part, for magnesium in a similar system, the amount of such metal or metals required can be readily calculated having regard to the atomic weight of the additive metal in the composition of the oxide it forms. For example, if thorium (atomic weight 232) were substituted for magnesium (atomic weight 24) about five times as much thorium would be required to tie up the same amount of available oxygen.

The process of this invention by which wrought dispersion strengthened nickel-chromium alloys having superior high temperature service characteristics are produced will now be described. In general, the process comprises the steps of forming a powder metallurgy composition containing nickel, chromium and ultra-fine refractory oxides in the desired proportions and providing therein at least one finely divided additive metal, the oxide of which has a heat of formation at 1000° C. of at least 70 kilocalories per gram atom of oxygen in the oxide, compacting the resulting powder mixture to form a self-sustaining green compact, heating said green compact to a temperature below the melting point of nickel and hot and cold working the compact as required to produce a completely homogenized nickel-chromium alloy matrix containing dispersed refractory oxides. The manner of preparation and the preferred proportions and properties of the constituents of the powder composition are described in detail hereinabove.

The powder is compressed by conventional procedures into compacts having a theoretical density of approximately 70%. Generally, a compacting load of about 30 tons per square inch is sufficient to form a "green" compact of sufficient strength to permit handling in the subsequent heating step.

The compact is then heated to a temperature below the melting point of nickel and preferably within the range of about 1800° F. to about 2200° F. in an inert or reducing atmosphere, preferably a hydrogen atmosphere. During this step, the additive metal reacts with the nitrogen and oxygen compounds associated with the chromium. We have found that heating to about 2000° F. for 15-30 minutes is sufficient to carry out the reactions substantially to completion. Several results arise from the presence of the additive metal in the alloy mix. Firstly, the oxygen and nitrogen containing compounds which surround the individual chromium particles are removed so that rapid and complete homogenization of the nickel and chromium occurs during heating and working resulting in improved high temperature strength and oxidation resistance. Secondly, minute particles of a stable oxide are formed in situ by the reaction of the additive metal and the available oxygen; these oxide particles are dispersed throughout the alloy and serve to supplement the dispersion strengthening effect of the refractory oxide initially present in the powder composition. Thirdly, the removal of chromium oxide inclusions by the additive metal diminishes agglomeration of the refractory oxide phase thereby increasing its effectiveness as a dispersion strengthening agent.

The hot compact is next worked to increase its density and strength. The working of metals is a well known art in the powder metallurgical field and there are many combinations of working cycles which may be used. We prefer to hot work the compact by first taking about a 50% thickness reduction with a single pass in a rolling mill to increase the density to approximately 100% theoretical. The substantially dense, hot-rolled strip is then heated

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in a hydrogen atmosphere at about 2000° F. for about 15 minutes to anneal it and complete the reaction of the additive metal with any remaining available oxygen. It is then subjected to a series of cold roll-anneal cycles to produce a final wrought alloy product of the desired dimensions and shape.

The invention is further illustrated by the following examples.

EXAMPLE 1

Nickel-thoria powder, obtained by hydrogen reduction from a basic nickel carbonate slurry was deoxidized by heating at 1400° F. for 15 minutes in a flowing hydrogen atmosphere. The powder particles were able to pass through a 325 mesh Tyler screen. The powder had an apparent density of 0.99 gm./cc. and a Fisher number of 0.53. "Fisher number" as used herein is the value obtained for average particle size by the Fisher Sub-sieve Sizer, following the procedure based on A.S.T.M. standard 13330-58T and using curves mathematically extrapolated from the curves supplied with the standard Fisher equipment to allow measurement of particles below 1 micron in size. The thoria particles which were attached to the surface of the powder particles were 10-20 millimicrons in size.

Following the deoxidizing treatment, the nickel-thoria powder was mechanically dry blended with chromium and magnesium powders to make a 30 gram batch with the composition: Chromium—20% by weight; magnesium—0.5% by weight; thoria—2.5% by weight and the balance nickel and incidental impurities. The chromium and magnesium powders were less than 44 microns in size, that is, they would pass through a 325 Tyler mesh screen. Blending of the powders was carried out in a twin-shell blender over a period of about 30 minutes.

The blended powders were then compacted to 70% theoretical density in a 1" x 3" double acting die using a load of about 33 tons per square inch. The green compact was heated to 2010° F. under a flowing hydrogen atmosphere. It was then hot-rolled once to effect a 30% reduction in thickness and then annealed at 2000° F. for 15 minutes in a flowing atmosphere of H₂. The annealed compact was hot rolled again to effect a further 30% reduction in thickness and to increase the density to about 100% of the theoretical. The strip was then cold rolled to obtain 10% thickness reduction and annealed at 2200° F. for 15 minutes in a flowing hydrogen atmosphere. The cold roll-anneal cycle was repeated seven times to produce a strip with a thickness of 0.02 inch. The final strip had an ultimate tensile strength at 1600° F. of 27,100 p.s.i. Electron probe microanalysis showed a completely homogenized nickel-chromium matrix. The magnesium was found to be present as magnesium oxide.

EXAMPLE 2

The procedure of Example 1 was repeated except that magnesium powder was not added to the nickel-thoria-chromium powder mix. The ultimate tensile strength of the final strip at 1600° F. was 19,800 p.s.i. Electron probe microanalysis showed that the matrix of the alloy product was not completely homogenized and that it contained numerous localized areas rich in chromium and nitrogen and deficient in dispersed refractory oxide.

Comparison of the results of Examples 1 and 2 shows the improvement obtained in the high temperature ultimate tensile strength of dispersion strengthened nickel-chromium alloys fabricated by powder metallurgical means from compositions containing an additive metal in accordance with the present invention.

EXAMPLE 3

In this example, the procedure of Example 1 was followed except that 0.3% by weight beryllium was used as the additive metal in place of magnesium. The alloy product strip had an ultimate tensile strength value at 1600° F. of 27,200 p.s.i.

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EXAMPLE 4

In this example, the procedure of Example 1 was followed except that 2.3% by weight yttria was used in place of the thoria. The alloy product strip had an ultimate tensile strength value at 1600° F. of 27,000 p.s.i.

EXAMPLE 5

In this example, the procedure of Example 1 was followed except that 5.0% by weight niobium powder sized to pass through a 325 Tyler mesh screen, was substituted for part of the nickel powder. The ultimate tensile strength of the final strip at 1600° F. was 32,300 p.s.i.

EXAMPLE 6

A comparison of the oxidation resistance of nickel, nickel-chromium, nickel-thoria-chromium and nickel-thoria-chromium-magnesia made according to the powder metallurgy procedure of Example 1 was carried out as follows: A 1.2 in. x 0.4 in. x .010 in. strip of each material was exposed to air while heated at a constant temperature of 1900° F. for a period of 100 hours. The weight gain of the material during this period was measured. The weight gain for the alloys was expressed as a ratio to the weight gained by pure nickel. The results are tabulated below:

TABLE 1.—COMPOSITION (WT. PERCENT)

Ni	Cr	ThO ₂	Mg	Ratio
100	-----	-----	-----	1.000
80	20	-----	-----	0.090
77.5	20	2.5	-----	0.025
77	20	2.5	0.5	0.006

EXAMPLE 7

To show the effect of the quantity of additive metal present in the powder composition on the properties of the wrought alloys fabricated therefrom, the procedure of Example 1 was repeated using varying amounts of magnesium and various amounts of thorium as the additive metals. The results are shown in graphical form in the accompanying drawing. It can be observed that ultimate tensile strengths increase rapidly with increasing amounts of additive metal until an optimum value is reached after which strengths begin to decrease again with increasing additive metal content.

Although we have described our invention with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example and the numerous changes in the details of the process may be resorted to without departing from the spirit and scope of the invention as hereafter claimed.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A composition capable of fabrication by powder metallurgy methods into wrought dispersion strengthened nickel-chromium base alloys having improved high temperature service characteristics, said composition consisting of a finely divided, uniform powder mixture contain-

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ing nickel particles, chromium particles, sub-micron sized refractory oxide particles and particles of at least one additive metal having an oxide with a free energy of formation at 1000° C. of at least 70 kilocalories per gram atom of oxygen in the oxide, said additive metal being provided in a sufficient amount to combine with oxygen available for reaction therewith in said powder mixture to promote homogenization of the nickel and chromium constituents when said mixture is heated in the range of 1800° F. to 2200° F. during the powder metallurgical fabrication thereof into solid wrought products but said amount being less than that which would result in the occurrence in such wrought product of additive metal uncombined with oxygen.

2. The composition claimed in claim 1 wherein said additive metal is at least one metal from the group consisting of beryllium, thorium, magnesium, titanium, calcium, zirconium, cerium, yttrium and hafnium.

3. The composition claimed in claim 2 wherein the refractory oxide is selected from the group consisting of thoria, yttria, calcia, magnesia, zirconia, silica, beryllia, hafnia, ceria, alumina, titania, uranium dioxide and lanthanum trioxide.

4. The composition claimed in claim 3 wherein the powder mixture contains from 10 to 40 weight percent chromium, from 0.5 to 5 volume percent of sub-micron refractory oxide particles, from 0.05 to 5 weight percent of additive metal and the balance nickel and incidental impurities.

5. The composition claimed in claim 1 wherein the powder mixture consists essentially of from 10 to 40 weight percent chromium powder having a particle size below about 44 microns, from 0.5 to 5 volume percent thoria particles having a particle size below about 100 millimicrons, from 0.25 to 2.0 weight percent magnesium powder having a particle size below about 44 microns and the balance nickel powder having a particle size below 1.0 micron.

6. The composition claimed in claim 5 wherein the thoria is in the form of discrete particles uniformly distributed in and mechanically separable from the nickel powder.

7. The composition claimed in claim 6 wherein the chromium contains a combined content of oxygen and nitrogen of less than 1% by weight and is present in amount within the range of 20 to 40% by weight, the thoria content is in the range of 2.0 to 4.0 volume percent, the magnesium content is in the range of 0.4 to 1.0% by weight and the balance is nickel and incidental impurities.

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