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REFRACTORY ALLOYS CONTAINING A DISPERSED PHASE OF THORIA AND IN PROCESSES FOR THEIR PRODUCTION

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ABSTRACT OF THE DISCLOSURE

The alloys in question are refractory alloys of a nickel and/or cobalt and/or iron base containing chromium and a dispersed phase of thoria. In the process for preparing these alloys the starting material is an intimate mixture of the constituents, suitably purified. Porous agglomerates of this mixture are formed. Then these agglomerates are sintered in a halogenated (but not fluorinated) hydrogenated atmosphere.

The present invention relates on the one hand, to refractory alloys essentially comprising a metallic mass (pure metal or alloy) called in terms of the art "matrix," this matrix, whose base is nickel and/or cobalt and/or iron, containing, as additive element, in any case, chromium, and possibly in addition, tungsten, molybdenum, niobium, tantalum, titanium, zirconium, aluminum, etc., these refractory alloys furthermore containing, in the form of a dispersed phase, fine particles of thoria (THO_2) whose presence improves the characteristics of the matrix, in particular from the point of view of its resistance to plastic deformation at high temperatures; and on the other hand, to processes for the preparation of such alloys having a dispersed phase of thoria.

The chief object of the present invention is to provide alloys that fulfill the requirements of practice, and in particular, to provide alloys that are very homogeneous, exempt of chromium oxide (which is detrimental to the behaviour of the alloy at high temperatures), and that contain, at the final stage of their preparation, in a pure and fine form a quantity of thoria, dispersed in a homogeneous manner, corresponding substantially to the quantity of thoria used for the preparation of the alloys in question.

It appears appropriate, before discussing the principal feature of the invention, to recall that the processes of preparing metallic alloys having a dispersed phase of thoria use, as the starting material, an initial mixture of powders which is then subjected to a powder metallurgy treatment, this starting material being qualified hereafter as "initial mixture of powders."

The present invention comprises, principally, for preparing the alloys having a dispersed phase of thoria of the type in question, first of all, preparing an initial mixture of powders by intimately mixing, in a mechanical manner: on the one hand, at least one powder of at least one metal forming the base of the matrix of the alloy to be prepared, this powder containing in the dispersed state (and preferably in a proportion by weight of 1 to 10%) thoria, preferably fine (granulation of the order of 0.1 micron at the most) and pure, advantageously resulting from pyrolysis, at a temperature higher than 550° C. and preferably lower than 900° C., of a chelated compound of thorium whose anion comes from a diketone β, which compound can advantageously be thorium acetylacetoneate; on the other hand, preferably in a proportion by weight of 5 to 30%, a fine chromium powder, preferably the ultra-fine magneso-thermic chromium powder resulting

from a reduction by magnesium vapour of very fine chromium oxide powder (Cr_2O_3), this chromium powder being in any case practically exempt of impurities, in particular of oxygen; and finally, a fine powder of the metallic element or elements other than said base metal and the chromium when the matrix of the alloy should contain, in addition to this base metal and chromium, one or more complementary metallic elements; then, forming, with the initial mixture of powders thus prepared, agglomerated elements having a sufficient porosity (preferably higher than 20%) to permit a suitable gaseous circulation in the mass of these elements in the course of a subsequent treatment of diffusion by the intermediary of a halogenated gaseous phase, this treatment forming the following stage of the process of preparation of alloys of the type in question; and finally, with a view to assuring the transfer and/or the codiffusion of the metals present, sintering these agglomerated elements by disposing them in at least one partially gastight container placed in an enclosure heated to a temperature higher than 700° C. and preferably of the order of 900° C. to 1000° C. in which a hydrogenated atmosphere prevails, this container containing, in addition to the agglomerated elements in question, a reserve of chromium in the fragmented state and at least one relatively very stable halide other than a fluoride (this halide being preferably a chromous halide and more preferably still chromous chloride and/or chromous bromide), which relatively very stable halide then generates, by a reaction at the equilibrium resulting from a limited "in situ" reduction of this halide by the hydrogenated atmosphere in the heating enclosure penetrating in limited quantities into the partially gastight container, a halogenated gaseous phase at the equilibrium of reduction (exempt of fluorine) which penetrates into the mass of the porous aggglomerated elements and assures the diffusion of the chromium by transfer in halogenated gaseous phase (as well as, possibly, the diffusion of one or more other additive elements) in the base metal or metals of the alloy; due to which sintered pieces are obtained exempt of chromium oxide (which is detrimental to the high temperature behaviour of the alloy), these pieces having a remarkably homogeneous composition and structure, both with respect to the codiffusion and the proportions of the constituents of the alloy forming the matrix and with respect to the dispersion of the thoria whose quantity, in the final alloy, remains the same, and in the same state of dispersion as in the initial mixture of powders.

The invention comprises, apart from this principal feature, certain other features which are preferably used at the same time and which will be more explicitly described hereafter.

The invention is particularly applicable to the preparation of pieces of a refractory alloy, which are intended to be exposed to high temperatures, such as, in particular, blades, fixed or movable, of gas turbines.

The invention will be easily understood from the following specific description, given merely by way of example.

This specific description (given by way of example) relates to the preparation of a refractory metallic alloy comprising a matrix whose base is nickel and/or cobalt within any case as additive element chromium (in a proportion by weight of 5 to 30%) and possibly in addition, in the order of compatibility with the presence of thoria, turgsten, molybdenum, niobium, tantalum, titanium, zirconium, aluminum, etc., this matrix containing, dispersed in a homogeneous manner, thoria in a suitably divided state and in a proportion by weight of 1 to 10% (particles of granulation at the most of the order of 0.1 micron); the thoria is intended to improve the behaviour of the alloy when the alloy is intended for the preparation of pieces exposed to high tempera-

tures, such as, in particular, fixed or movable gas turbine blades.

In accordance with the principal feature of the invention, with a view to preparing the alloy in question, with its dispersed phase of thoria:

First, an initial mixture of powders is prepared by intimately mixing, in a mechanical manner: on the one hand, nickel and/or cobalt powder containing in the dispersed state thoria, preferably pure and fine (granulation of the order of 0.1 micron at the most); on the other hand, fine chromium powder (grains of granulation less than 50 microns) previously rendered exempt of impurities, in particular of oxygen; and furthermore, a fine powder of the metallic additive element or elements other than chromium when the matrix of the alloy should contain, as well as chromium, one or more complementary additive metallic elements;

Then, agglomerated elements are formed, with the initial mixture of powders thus prepared, these agglomerated elements having a sufficient porosity (preferably higher than 20) to permit a suitable gaseous circulation in the mass of these elements in the course of a subsequent treatment of diffusion by the intermediary of a halogenated gaseous phase, this treatment forming the following stage of the process of the preparation of the alloy of the type in question; and

Finally, with a view to assuring the codiffusion of the metals present, these agglomerated elements are sintered by disposing them in at least one partially gastight container placed in an enclosure heated to a temperature higher than 700° C. and preferably of the order of 900° C. to 1000° C. in which a hydrogenated atmosphere prevails, this container containing, as well as the agglomerated elements in question, a reserve of chromium in the fragmented state and at least one relatively very stable halide, other than a fluoride, which then generates, by a reaction at the equilibrium resulting from a limited "in situ" reduction of this halide by the hydrogenated atmosphere in the heating enclosure penetrating in limited quantities into the partially gastight container, a halogenated gaseous phase (exempt of fluorine) which penetrates into the mass of the porous agglomerated elements and assures the transfer and/or the codiffusion of the metals present.

In this manner, sintered pieces are obtained exempt of chromium oxide (which is detrimental to the high temperature behaviour of the alloy) these pieces having a remarkably homogeneous composition and structure, both with respect to the codiffusion and the proportions of the constituents of the alloy forming the matrix and with respect to the dispersion of the thoria whose content in the final alloy remains the same and in the same state of dispersion as in the initial mixture of powders.

A certain number of preferred embodiments of various characteristics of the principal feature of the invention mentioned hereabove will now be given.

First of all, with respect to the pure and fine thoria powder to be incorporated in the initial mixture of powders, it is preferably obtained according to the features of U.S. patent application No. 709,794 filed in the names Philippe Galmiche, Andre Hivert, Michel Marty on Mar. 1, 1968, corresponding to French patent application No. 97,105, now French Pat. No. 1,520,722, these features comprising essentially preparing the thoria by pyrolysis, at temperatures higher than 550° C. and preferably lower than 900° C., of a chelated compound of thoria whose anion comes from a diketone β, which compound can advantageously be thorium acetylacetoneate.

As for the chromium powder used for the formation of the initial mixture of powders, electrolytic chromium powder can be adopted, or better still, ultra-fine chromium powder obtained in a magneso-thermic manner, such a magneso-thermic chromium powder being advantageously obtained according to the features of French Pat. No.

1,123,326 and of its additions No. 70,936 and No. 79,879.

At present, whatever be the origin of the chromium powder adopted, it is advantageous, in order to assure that this chromium powder has the required purity, to use the features of U.S. Pat. No. 3,053,649 in the name Galmiche, granted Sept. 11, 1962, these features permitting, in particular, practically all trace of oxygen to be eliminated in the chromium powder and thus a subsequent pollution to be avoided, in the refractory alloy, of the dispersed phase of thoria by chromium oxide.

Finally, with respect to the relatively very stable halide (other than a fluoride) to be disposed in the partially gastight treatment container, preferably a chromous halide is adopted, especially chromous chloride and/or chromous bromide.

It will be supposed hereafter that, for the preparation of the refractory alloy whose base is nickel and/or cobalt containing in addition at least chromium and thoria in a dispersed form, not only is the principal feature of the invention applied, but also the preferred embodiments mentioned hereabove of certain characteristics of this principal feature are applied.

The various characteristics of that principal feature and of the preferred embodiments of the invention will now be reconsidered in a more detailed manner, together with comments.

Preparation of the nickel and/or cobalt powder containing dispersed thoria.—For this preparation, although any of the embodiments described in the above mentioned patent application No. 709,794 (French application No. 97,105, now French Pat. No. 1,150,722) can be used, it seems preferable to adopt one of the embodiments which brings into play at least one liquid phase, such an embodiment assuring the formation "in situ" of pure and fine thoria from thorium acetylacetoneate, this "in situ" formation thus taking place in the presence of nickel and/or cobalt powder or of a nickel and/or cobalt compound from which such nickel and/or cobalt powder can be obtained.

Thus a liquid phase (containing the thorium) is put in presence with a solid phase (containing the metal—in this case nickel and/or cobalt); to accomplish this, advantageously, a solution of thorium acetylacetoneate is used to wet a fine powder of nickel and/or cobalt or of a nickel and/or cobalt compound adapted to give a nickel and/or cobalt oxide reducible by pyrolysis effected in the zone of relatively low temperature suitable for the formation of pure and fine thoria by pyrolysis of thorium acetylacetoneate.

As the solvent for the thorium acetylacetoneate, the following can be used, in particular, ethanol, acetone, ether, or better still, acetylacetone.

The wetting thus achieved permits an intimate mixture of the constituents to be obtained. The pyrolysis that is then carried out at a temperature comprised between 550° C. and 900° C. has the effect of transforming the thorium acetylacetoneate into pure and fine thoria and, when the starting material was a powder of a nickel and/or cobalt compound, of transforming this compound directly into metal (in the case in which oxalates were used as the starting material, for example) or again into oxides reducible in hydrogen (in the case in which carbonates were used as the starting material, for example).

To give an idea, a quantitative example will now be given of this embodiment of preparation of a nickel and/or cobalt powder containing dispersed thoria.

Three kilograms of nickel and/or cobalt oxalate are introduced into a mixer provided with a heating device ("Werner" mixer for example) and, by cold rotation, 64 grams of thorium acetylacetoneate dissolved in 900 cubic centimeters of acetylacetone are incorporated into this oxalate.

The cold mixing is continued for one hour, then the temperature is progressively raised to 130° C., which

causes the volatilization of the solvent by ceaselessly renewing the surface contacts.

The dry powder thus obtained is placed in a nickel container and introduced into an adjustable temperature furnace capable of bringing this powder to a temperature of the order of 500° C. in four hours in an ordinary atmosphere, after which this temperature is maintained for one hour. After cooling, the powder is placed in a nickel cup and the pyrolysis is carried out in dry hydrogen at 700° C. for two hours.

In this manner is obtained an intimate mixture of powders of nickel and/or cobalt and of pure and fine thoria dispersed in a homogeneous manner.

Purification of the chromium powder.—This purification was effected according to the features of U.S. Pat. No. 3,053,649, that is to say, in particular, by putting the chromium powder, mixed with an inert diluent such as magnesia, in the presence of a halogenated atmosphere (exempt of fluorine) containing in addition a limited quantity of hydrogen, the purification treatment being conducted at a temperature comprised between 900° C. and 1400° C. for a duration greater than 30 minutes while avoiding (by an appropriate choice of the nature of the treatment containers, of the materials that are introduced in these containers, and of the gases possibly used in the treatment enclosure) the presence, in the treatment enclosure, of bodies adapted by their nature to influence unfavourably the reactions of purification that the process has precisely for its object to cause.

The application to the chromium powder of the features given in the above mentioned patent for purifying a powder of chromium permits a chromium powder to be finally obtained that is exempt of chromium oxide and that has very high characteristics of plasticity comparable to those of the nickel powder, such as plastified chromium powder lending itself particularly well, due to its good compressibility, to the subsequent preparation of agglomerated elements that are not fragile and are devoid of cracks.

Mixture in a mechanical manner of the nickel and/or cobalt powder containing dispersed thoria and of the plastified chromium powder.—This mixture is realized in an intimate manner in a mechanical way, by putting the powders to be mixed in a mixer, for example a screw type mixer, the mixing treatment being conducted cold for a duration of about 15 minutes.

Formation of the porous agglomerated elements from these mixtures.—These agglomerated elements are preferably in the form of compacts prepared under a relatively low pressure, of the order of 1 metric ton/square centimeter, in a manner to avoid cracking of these compacts at the output of the dies, and moreover, in a manner to obtain a sufficient porosity of the compacts in question, this preparation being advantageously effected by a process of hydrostatic compression.

Sintering in an atmosphere of chromous chloride and/or chromous bromide.—In the case in which nitrogen is tolerated, at least in small quantities, in the alloy to be prepared, it is convenient to use, for the preliminary formation of chromous chloride and/or chromous bromide, ammonium chloride and/or ammonium bromide both of which are in a powder form easy to manipulate.

On the other hand, in the case in which nitrogen is prohibited, even in small quantities, it is necessary to avoid compounds, such as ammonium halide, that contain this element. In this case, one can use, either bromine, or bromine chloride, or iodine chloride, or a mixture of at least two of these bodies; these bodies or mixtures are liquid or solid, hence convenient to handle.

By way of example, the sintering operation in a bromine-halogenated atmosphere at the equilibrium of reduction of the chromium bromide can be conducted in the following manner.

In a first operational stage a reactive mass is formed containing a small quantity of chromous bromide, that is to say bivalent chromium bromide, this formation being assured by a reaction between bromine and chromium in granules, these two constituents being heated in a reducing atmosphere (for example in hydrogen) to a temperature of the order of 1000° C.

The quantity of bromine is at the beginning of the order of 1 to 2% by weight of the quantity of chromium in granules, and these two constituents are placed in a nickel container that is partially gastight so as to permit limited gaseous exchanges between the interior of the container and the surrounding hydrogenated reducing atmosphere.

The reaction between the chromium and the bromine gives rise to the formation, at the periphery of the grains of chromium, of a mixture of bivalent chromium bromide and trivalent chromium bromide, this latter bromide being progressively reduced, at the temperature of treatment, to the state of bivalent chromium bromide. Thus, after cooling, a reserve of bivalent chromium bromide is obtained fixed on the granules of chromium, which reserve is then preferably preserved in tight containers in the presence of a desiccating substance, such as silica gel, due to the high hygroscopicity of vibalent chromium bromide.

Then the sintering treatment proper is carried out by placing the nickel-chromium-thoria compacts in the presence of, or even in contact with, the granules of chromium on which the bivalent chromium bromide is fixed, the whole being disposed in a nickel or nickel-chromium enclosure, partially gaslight, which is then heated in a hydrogenated reducing protecting atmosphere after elimination of the air initially contained in the enclosure.

This elimination of the air can be carried out by preliminary sweeping with argon or by evacuation followed by filling by argon.

Preferably, and in a general manner, the chromium granules containing the chromous halide are placed in a special container, of the same nature as the treatment container and advantageously covered by a grill, this special container being placed in a zone of the treatment container which, as a function of the configuration of the heating furnace, is heated the least quickly.

The sintering treatment is carried out for about one hour at a temperature of the order of 1000° C., after which cooling is carried out in a protective atmosphere, preferably at the exterior of the furnace with a view to accelerating the cooling.

In this manner, pieces are obtained of pearl grey aspect, well sintered, whose matrix is exclusively formed of a homogeneous nickel-chromium alloy.

Examination by X-ray diffraction of the pieces obtained in such conditions of sintering establishes the absence of any parasitic line indicative of the presence of free chromium or residual halides or other impurities.

In particular, the sintered products obtained are exempt of chromium oxide, and there is present in these products, all the thoria present before the sintering operation, and in the same state of dispersion.

It is interesting to note that the reactive masses comprising chromium and chromium chloride and/or chromium bromide can be used for several sucecssive operations without modification of the results, the only preservative measures to be taken being, either a simple periodic regeneration of these reactive masses by a "blank" operation analogous to the operation described with respect to the formation of the reactive mass, only bringing into play the addition, in one form or another, of a small quantity of appropriate halides or halogens, or periodic additions of anhydrous bivalent chromium chloride and/or chromium bromide, or again, when the special container mentioned previously is used, the renewal, after each operation, of the contents of this special container.

Everything that has just been described with respect to the sintering operation proper remains true if the nickel is

replaced by cobalt or again added to cobalt; needless to say additive elements other than chromium can be present in the sintered mass if the final alloy is intended to contain such other additive elements.

As a result of the present invention, whatever embodiment is adopted, a sintered refractory alloy is provided having a base of nickel and/or cobalt comprising chromium and dispersed thoria, this alloy being devoid of parasitic chromium oxide (whose detrimental presence, considered until the present invention as inevitable, was one of the major obstacles to the development of this type of alloy), in which the thoria is dispersed in a homogeneous manner in a pure and fine form, which permits, in particular, optimum characteristics to be obtained for the semiworked products obtained (generally by hot rolling then cold rolling) from the alloys in question.

Needless to say, the present invention is not limited to the various embodiments particularly described, as many modifications and changes can be made without departing from the spirit or scope of this invention.

What we claim is:

1. A process of manufacturing refractory alloys having a base selected from the group consisting of nickel, cobalt, iron, and alloys thereof; and chromium as an additive element, containing moreover, in the form of a dispersed phase, fine particles of thoria, which process comprises:

first, preparing an initial mixture of powders by intimately mixing, in a mechanical manner: on the one hand, at least one powder of at least one metal for the base of the matrix of the alloy to be manufactured, said powder containing, in the dispersed state, thoria, preferably fine (granulation of the order of 0.1 micron at the most) and pure, resulting advantageously from a pyrolysis, as a temperature higher than 550° C. and preferably lower than 900° C., of a chelated compound of thorium whose anion comes from a diketone β; on the other hand, some fine powder of chromium, preferably the ultra-fine magnesothermic chromium powder resulting from a reduction by magnesium vapour of very fine chromium oxide powder, this chromium powder being in any case practically exempt of impurities, in particular oxygen; and furthermore, a fine powder of the metallic element or elements other than said metal for the base and said chromium when the matrix of the alloy should contain, as well as this metal for the base and chromium, one or more complementary metallic elements;

then, forming, with the initial mixture of powders thus prepared, agglomerated elements having a sufficient porosity (preferably higher than 20%) to permit a suitable gaseous circulation in the mass of said elements in the course of a subsequent treatment of diffusion by the intermediary of a halogenated gaseous phase, said treatment constituting the following stage of the process of manufacturing the alloys of the type in question; and

finally, with a view to assuring the transfer and/or the codiffusion of the metals present, sintering said agglomerated elements by disposing them in at least one partially gastight container placed in an enclosure heated to a temperature higher than 700° C. and preferably of the order of 900° C. to 1000° C. in which a hydrogenated atmosphere prevails, said container containing, besides the agglomerated elements in question, a reserve of chromium in the fragmented state and at least one relatively very stable halide other than a fluoride, which relatively very stable halide then generates, by a reaction at the equilibrium resulting from a limited "in situ" reduction of said halide by the hydrogenated atmosphere in the heating enclosure penetrating in limited quantities into the partially gastight container, a halogenated gaseous phase at the equilibrium of reduction, in the absence of fluorine, which penetrates into the mass of the agglomerated elements and assures the diffusion of the chromium by transfer in halogenated gaseous phase in the metal or metals forming the base of the alloy.

2. A process according to claim **1**, wherein the proportion by weight of thoria in the initial mixture of powders is comprised between 1 and 10%.

3. A process according to claim **2**, wherein said chelated compound of thorium is thorium acetylacetoneate.

4. A process according to claim **3**, wherein the proportion by weight of the powder of chromium in the initial mixture of powders is comprised between 5 and 30%.

5. An alloy prepared according to claim **4.**

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