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(54) PROCESS FOR THE PRODUCTION OF REINFORCED METAL ALLOYS USING OXIDE DISPERSION

(57) The present invention belongs to the field of metal alloy production, specifically to a process for the production of metal alloys using metal powder atomisation in order to obtain reinforced alloys with dispersed oxides (Oxide Dispersion Strengthening or ODS). More particularly, the invention relates to a process for manufacturing an ODS metal alloy from a raw material consisting of a metal alloy and/or unoxidised metal elements, in solid state, wherein the process comprises the following steps:

- melting of the raw material;
- atomisation of the molten raw material;
- oxidation of the metal powder obtained after the atomisation step;
- heat compression of the oxidated powder obtained after the oxidation step, to form the powder into a part, at a temperature lower or equal to 1000°C;
- warm deformation of the part obtained after heat compacting, until achieving a thickness reduction of at least 85%;
- precipitation annealing of the warm deformed part, at a temperature comprised between 900-1200°C.

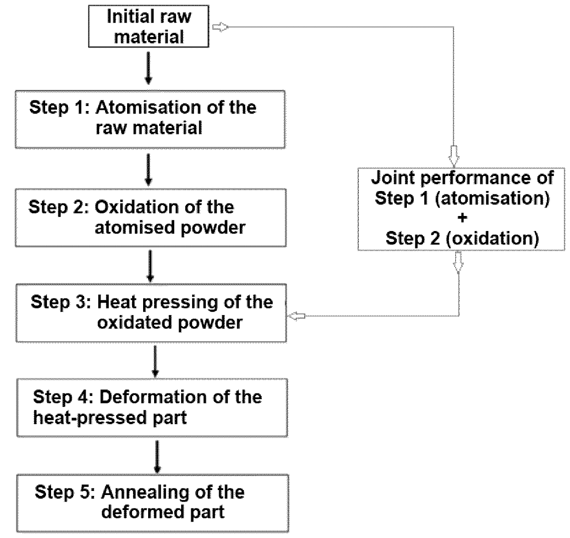

Fig. 1

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Description

Technical field

[0001] The present invention belongs to the field of metal alloy production, specifically to a process for the production of metal alloys using metal powder atomisation in order to obtain reinforced alloys with dispersed oxides (Oxide Dispersion Strengthening or ODS), and the invention relates to both the process and the devices for carrying it out.

Prior art

[0002] Reinforced metal alloys with dispersed oxides (Oxide Dispersion Strengthening or ODS) are highly functional materials in various technological fields.

[0003] Among them, ODS nickel alloys, i.e., reinforced with dispersed oxides, which exhibit high tenacity and mechanical strength at high temperatures, resistance to degradation or corrosion at high temperatures, as well as high creep properties, are of particular interest, making them optimal for applications such as turbine manufacturing or in the field of aeronautics.

[0004] Other alloys of high technological interest are ODS (Oxide Dispersion Strengthening) steels, structural materials for nuclear fission and nuclear fusion reactors, or reactors in chemical industries, among other applications. These ODS steels have good mechanical properties at high temperatures and high resistance to damage from neutron irradiation due to the presence of a high density of ultra-fine complex oxides (size less than 10 nm) that are very stable up to very high temperatures.

[0005] There are mainly two families of ODS steels:

- ODS steels with a high concentration of aluminium (Al), up to 5-6% by mass, initially developed for nuclear fission or applications where high resistance to oxidation at high temperatures is required.
- ODS steels without aluminium or with a very low concentration, developed specifically for nuclear fusion, although they have applications in other sectors.

[0006] By way of example, a typical composition of ODS steels developed for nuclear fusion is (% by mass): Fe-14Cr-2W-(0.3-0.5)Ti-(0.3-0.5)Y_2O_3. In them, the nanometric oxides are Y-Ti-O. It is also possible to find ODS steels in the literature in which said complex oxides are Y-Zr-O, Y-Al-O, Y-Hf-O, etc.

[0007] The conventional route to produce ODS metal alloys (reinforced with dispersed oxides) consists of the mechanical alloying of metal alloy powders (e.g., Fe-14Cr-2W-(0.3-0.5) Ti and Y_2O_3) to dissolve the oxide-forming element (e.g., yttrium) in the ferritic network. Alternatively, it is also possible to alloy the particles of the oxide-forming element (e.g., Y_2O_3 particles) with elemental powders of Fe, Cr, W and Ti. The state of the art contemplates encapsulating and compressing the alloyed powder by hot isostatic pressing (HIP) at high temperature, so that, for example, yttrium reacts with titanium and dissolved oxygen and forms Y-Ti-O nanoparticles.

[0008] The processes for the production of ODS metal alloys by mechanical alloying are widely known in the state of the art. Nevertheless, conventional mechanical alloying has a number of associated drawbacks:

- Introduction of pollutants during mechanical alloying, coming from the atmosphere, from the vials or from the grinding medium.
- Long processing times (mechanical alloying usually requires about 40 hours)
- Small batch manufacturing, due to the small dimensions of the containers in which mechanical alloying is carried out.
- High cost, associated with mechanical alloying.
- Limited reproducibility of the alloy grade, resulting in batch-to-batch differences.

[0009] The production of metal powders as precursors to metal alloys, with the dispersed oxide-forming elements (Ti, Y, Zr, Hf...) presents a number of challenges, among which the difficulties in retaining said elements are worth noting. Due to their high affinity for oxygen, at high temperatures or in liquid state, they react with any residual oxygen that may remain in the melting chamber of the atomisation unit, forming oxides that become part of the slag. The end result is a broth, and therefore a powder, totally or partially depleted in oxide-forming elements.

[0010] Furthermore, the processes for manufacturing ODS alloys from metal powders obtained through a simultaneous atomisation and oxidation process are also known in the state of the art. Nevertheless, such processes typically present a number of limitations. By way of example, some of these limitations on the simultaneous atomisation and oxidation processes are the impossibility of precisely controlling the quantity of oxygen introduced and its homogeneity during oxidation, and the difficulty of avoiding, at the end of the process, the formation of large stable oxides on old powder particle surfaces.

[0011] In summary, the limitations on these processes relate both to the manufacturing process itself and to the properties of ODS alloys due to the difficulty of obtaining an optimal distribution and size of the oxides in the ODS alloy.

[0012] The present invention aims to present a process for manufacturing ODS alloys that overcomes the limitations of the state-of-the-art processes and presents additional advantages.

Object of the invention

[0013] The present invention belongs to the field of metal alloy production, and describes a novel technology based on the atomisation and oxidation of metal alloys for the manufacture of ODS metal alloys.

[0014] More particularly, this invention describes a process for the production of ODS metal alloys, such as ODS nickel alloys or ODS steels, starting from a raw material that consists of the metal elements of interest and/or the metal alloy of interest without yet including the oxygen that will form part of the nanometric dispersed oxides that reinforce the alloy after the synthesis of the metal alloy, according to the present invention.

[0015] The process is characterised by the combination of five specific steps of atomisation, oxidation, heat compression, warm deformation, and annealing, to carry out the process for manufacturing metal alloys.

[0016] Furthermore, the process is also characterised by the following specific conditions: compression of the powder at high temperature (600-1000°C), warm deformation at high reductions greater than 85% of the thickness of the part obtained in the previous step, and precipitation annealing of the ODS alloy at temperatures between 900-1200°C.

[0017] As a result of the combination of these five steps and the specific conditions above, a process is obtained that is capable of manufacturing ODS metal alloys with greater purity, homogeneity, versatility, speed and production capacity than conventional processes. Furthermore, the ODS alloys obtained by the process of the present invention present stable oxides homogeneously dispersed in the alloy matrix, of an optimal size and distribution. Thus, the limitations on conventional state-of-the-art processes are overcome and advantages are provided with respect to the manufacturing process and the properties of the ODS alloys obtained. These steps and their specific parameters or conditions will be described in further detail in the detailed description of the invention.

[0018] Likewise, the devices that perform each of the steps of the process will be configured to perform said step, and will include certain specifications that ensure that the specific parameters or conditions characteristic of each step of the process are maintained.

[0019] These steps are briefly summarised below, and will be explained in further detail in the detailed description:

> **Step 1. Atomisation:** The raw material comprises a metal alloy and/or metal elements in an unoxidised elemental state, in solid state. The raw material initially melts at a temperature higher than the liquid formation temperature. The liquid, which is sprayed by a high pressure stream of gas (e.g., argon) is then made to flow. The gas breaks up the liquid flow and disperses the molten metal into small droplets, which when cooled form the metal powder.
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> **Step 2. Oxidation:** Heat treatment of the metal powder obtained in the previous step (atomisation) in an oxidising atmosphere, at a temperature that allows controlled surface oxidation of the metal powder. The fact of performing a specific step of oxidation, separately from the atomisation step, results in greater control and reproducibility of oxidation, and thus the gain in oxygen necessary for the stable oxide-forming elements to react completely to form complex oxides.
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> **Step 3. Heat compression:** This step applies high temperature and pressure to the oxidated powder of the metal alloy obtained in the oxidation step. Preferably, it consists of hot isostatic pressing (HIP) of the oxidated powder in a metal capsule. With this step, a metal part with a high density of the part is achieved, in other words, with a low presence of pores in its interior. Furthermore, the temperatures selected for this process maintain the metastable oxides on the old powder particle surfaces, so that the oxygen introduced in the previous step remains available to react with the stable oxide-forming elements in subsequent steps (warm deformation and annealing).
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> **Step 4. Warm deformation:** In this step, a deformation is applied to the metal alloy part, until achieving thickness reductions greater than 85% when warm, specifically at a temperature that is high enough to prevent the metal alloy part from cracking, but low enough to prevent the metal alloy from recrystallising. Warm deformation is preferably carried out by warm rolling. This deformation step helps to eliminate residual porosity and favours the reduction of grain size. In parallel, the metastable oxides partially decompose. Furthermore, the introduction of dislocations into the material during deformation results in the incipient formation of nanometric-sized oxides that are homogeneously distributed throughout the matrix.
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> **Step 5. Precipitation annealing:** After warm deformation (e.g., by warm rolling), an annealing heat treatment is applied at temperatures higher than the deformation temperature, so that the complete dissociation of metastable oxides (e.g., Cr and/or Fe oxides) that may remain on the old powder particle surfaces after deformation is promoted, the diffusion of stable oxide-forming elements (oxygen and, for example, Ti or Y) is promoted, and an additional precipitation of very stable nanometric oxides inside the ferrite grains is favoured. This annealing treatment is carried out at a temperature between 900-1200°C, requiring relatively low annealing times, which can be as low as only 5 minutes.

[0020] Optionally, in order to give the final metal part the desired shape and functionality, after the precipitation annealing step, said part can be machined using any technique known in the state of the art in order to give it the appropriate shape or functionality. Also optionally, additional annealing can be applied after machining, in order to eliminate any residual stress produced during machining, stresses that could cause the part to crack during subsequent use thereof. Since the oxides are stable after precipitation annealing, they are not affected by said treatment.

[0021] Optionally, the oxidation and atomisation steps can also be performed together, in the same step, by using at least one oxidising gas (e.g., a mixture of argon and oxygen) in the atomisation step, which makes it unnecessary to incorporate an additional oxidation step, with the consequent reduction in time, energy and resources for the manufacture of the ODS alloy according to the present invention.

[0022] Nevertheless, it should be noted that when atomisation is performed at a high temperature, very close to the melting temperature of the metal alloy, in contrast to the separate oxidation process that can be performed at a lower temperature, for example less than or equal to 400°C, it is not possible to have such precise control over the gain in oxygen during oxidation when it is done in conjunction with atomisation.

[0023] In summary, in a first embodiment of the invention, a process is provided for manufacturing an ODS metal alloy from a raw material consisting of a metal alloy and/or unoxidised metal elements, in solid state, wherein the process comprises the following steps:

- melting of the raw material;
- atomisation of the molten raw material;
- oxidation of the metal powder obtained after the atomisation step;
- heat compression of the oxidated powder obtained after the oxidation step, to form the powder into a part, at a temperature lower or equal to 1000°C;
- warm deformation of the part obtained after heat compression, until achieving a thickness reduction of at least 85%;
- precipitation annealing of the warm deformed part, at a temperature comprised between 900-1200°C.

[0024] In a second embodiment of the invention, atomisation is carried out at a temperature at least 160°C higher than the melting temperature of the metal elements in the raw material, preferably at a temperature between 160-240°C higher than the melting temperature of the metal elements in the raw material.

[0025] In a third embodiment of the invention, atomisation is carried out under vacuum conditions at least during part of the atomisation step.

[0026] In a fourth embodiment of the invention, oxidation takes place at a temperature less than or equal to 400°C, preferably less than or equal to 300°C, more preferably less than or equal to 250°C, and even more preferably between 150-250°C.

[0027] In a fifth embodiment of the invention, oxidation takes place in a furnace, preferably in a rotary drum furnace.

[0028] In a sixth embodiment of the invention, oxidation takes place simultaneously during the atomisation step, by using at least one oxidising gas during the atomisation step.

[0029] In a seventh embodiment of the invention, heat compression is carried out at a temperature between 600-1000°C.

[0030] In an eighth embodiment of the invention, warm deformation is carried out by warm rolling.

[0031] In a ninth embodiment of the invention, warm deformation is carried out in a succession of partial deformation steps, and the percentage of thickness reduction increases gradually after each partial deformation step.

[0032] In a tenth embodiment of the invention, a device is provided for carrying out the process according to any of the preceding embodiments, wherein the device comprises:

- melting means for melting the raw material,
- atomising means for atomising the molten raw material,
- oxidising means for oxidising the atomised powder,
- forming means for forming the oxidated powder by heat compression,
- deformation means configured to reduce the thickness of the formed part when warm, and
- annealing means configured to heat the deformed part.

[0033] In an eleventh embodiment of the invention, in the device for carrying out the process of the present invention:

- the melting means comprise a furnace with a vacuum atmosphere and/or non-oxidising atmosphere, and/or
- the atomising means comprise an atomiser, and/or
- the oxidation means comprise a furnace, preferably a rotary furnace, and even more preferably a rotary drum furnace, and/or
- the forming means by compression comprise a hot isostatic press (HIP), and/or
- the deformation means comprise a warm rolling mill, and/or
- the annealing means comprise a furnace.

[0034] In a twelfth embodiment, an ODS metal alloy product obtainable by the process according to any of the embodiments of the present invention is provided.

Description of the Figures

[0035]

Figure 1 shows a general diagram of the process steps comprising the process for manufacturing ODS metal alloys of the present invention.

Figure 2 shows a diagram of a particular embodiment of the manufacturing process of the present invention for an ODS steel.

Figure 3 presents two micrographs obtained with a scanning electron microscope (SEM) for an ODS steel according to the invention, with composition Fe-13.8Cr-2.0W-0.31Ti-0.27Y, with particle size <75 μm, oxidated up to 2500 ppm of oxygen, after hot isostatic pressing at 700°C and 140 MPa for 3 hours, and finally rolled according to the conditions that will be presented when reference is made to said Figure 3 in the description. Figure 3a presents 2000x magnification, while Figure 3b presents 100000x magnification.

Figure 4 presents two micrographs obtained with a scanning electron microscope (SEM) for the ODS steel according to the invention of Figure 3, which, after rolling, has additionally undergone heat treatment at 1100°C for 20 minutes. Figure 4a presents 1000x magnification, while Figure 4b presents 100000x magnification.

Detailed description of the invention

Raw material

[0036] To manufacture the ODS alloy according to the present invention, the process starts with a raw material consisting of a metal alloy and/or metal elements, both unoxidised.

[0037] The raw material in solid state can be presented in any form (metal parts, ingots, bars, briquettes, granules, powders, etc.) and will be initially melted before the atomisation step is performed.

[0038] More specifically, the starting raw material that can be used to perform the first step of atomisation of the molten raw material, according to the present invention, may consist of:

Option 1: An unoxidised metal alloy, or
Option 2: All the metal elements that the final alloy will contain, in an elemental form, or
Option 3: The metal elements of interest in an elemental state, but with a pre-alloying of the pre-alloyed oxide-forming metal elements.

[0039] For clarification, non-limiting examples of the 3 raw material options contemplated according to particular embodiments of the invention are presented below:

Option 1: start with an ingot having a very similar composition to the desired composition (for example Fe-14Cr-2W-0.30Ti-0.24Y). It is advisable to use a concentration of the metastable oxide-forming elements (Ti and Y in this case) greater than that which is desired in the final ODS alloy, in order to deal with losses of these elements when the alloy is in a liquid state, before atomising. This ingot can be produced, for example, by casting.

Option 2: all the alloying elements are introduced in an elemental form, including the stable oxide-forming elements, such as Ti, Y, Hf and Zr. An example of atomised ODS steel from the alloying elements introduced in elemental form is: Fe-14.0Cr-2.0W-0.23Y-0.32Zr. This option is more suitable for cases where it is possible to ensure a good vacuum level in the melting chamber (below 0.5 mbar), to ensure that the nanometric oxide-forming elements are not oxidised when forming the broth. For ODS steels with Y and Zr, it is possible to keep the losses of Y and Zr between 24 and 56% and Ti between 4 and 8% with respect to the quantity introduced, respectively.

Option 3: start with Fe, Cr and W in an elemental state, in the form of bars, blocks, briquettes, etc., and Y and Ti are introduced in pre-alloyed form, master alloy. The prealloy may be in the form of powder or solid blocks. It consists of a Fe base alloy (main element), where the concentration of Y and Ti depends on the final concentration of these elements in the ODS steel, and on the losses that occur during atomisation.

[0040] In the second and third options it is possible to add the elements most susceptible to oxidation, by means of an adder, which introduces said elements into the already formed broth, without deteriorating the atmosphere of the melting chamber.

[0041] A preferred embodiment of the raw material for manufacturing ODS steels according to the invention consists of ODS steels without aluminium or with a very low concentration (less than 0.03% by mass), preferably with Fe, Cr and W as base alloy components; and with Y as the stable oxide-forming element. Ti, Al, Zr or Hf is also included as a second (and optionally as a third) stable ODS oxide-forming element according to the process of the present invention.

[0042] Figure 1 presents a general diagram of the process for manufacturing ODS alloys according to the present invention. This diagram shows that, starting with the initial raw material that has been explained above, five process steps are performed, comprising a first step of atomisation, a second step of oxidation, a third step of heat compression, a fourth step of deformation of the formed part, and a fifth step of annealing the deformed step. Optionally, the first step of atomisation and the second step of oxidation can be performed together.

[0043] Figure 2 presents a diagram of a particular embodiment of the process of the invention, with particular devices to be used according to this embodiment to carry out each of the steps of the process of the present invention in order to obtain an ODS steel according to the process of the present invention, specifically the steps of atomisation of the molten raw material (1), oxidation of the metal powder obtained (2), heat compression of the powder into a part (3), warm deformation of the part (4), and annealing of the deformed part (5). The microstructure of the metal alloy powder and the metal part obtained according to the present invention in each step of the process is also shown schematically. In this particular example, it starts from the alloying elements of ODS steel in an elemental state, the atomisation (1) of the metal liquid is carried out in a confined flow atomiser (1.1), the amount of oxygen in the metal powder is adjusted by oxidation (2) in a heating device such as a furnace (2.1), heat compression (3) of the oxidated metal powder is carried out using hot isostatic pressing or HIP equipment (3.1) by compressing it, the formed part (4) is deformed by using a warm rolling mill (4.1), and lastly, precipitation annealing (5) of metal oxides is carried out in a heating device such as a furnace (5.1), obtaining the ODS alloy part of interest (6). Figure 2 also shows how the metastable oxides initially in the surface layer of the powder during the oxidation step (2), which occupy the grain boundaries (7.1) after the steps of heat compression (3) of the powder and warm deformation (4) of the formed part, decompose incipiently after warm deformation (4) and completely during annealing (5). During said annealing (5), the oxygen of the decomposed metastable oxides preferably segregates into the dislocations (7.2) generated during warm deformation (4) and finally forms stable oxides (7.3), after diffusing the oxide-forming elements also towards said dislocations (7.2).

[0044] The manufacturing process of the present invention can be carried out by means of a device with means configured to carry out each of the steps.

[0045] The manufacturing process of the present invention allows obtaining ODS metal alloys, such as ODS nickel alloys or ODS steels as non-limiting examples.

[0046] Therefore, the invention also relates to a product consisting of said ODS metal alloy.

[0047] Next, the steps of the process for manufacturing ODS alloys of the present invention are described, which uses the raw material described above as a starting material.

Step 1: Atomisation

[0048] During atomisation, the raw material consisting of metal elements and/or metal alloys according to options 1-3 described above must be in a liquid or molten state. The material will be melted by heating means, preferably a furnace with a vacuum atmosphere and/or non-oxidising atmosphere, in order to prevent the oxidation of the metals during their melting. To do so, in the event that the raw material is solid, initially the raw material is completely melted at a temperature higher than the melting temperature of the metals and/or alloy of the raw material, preferably at a temperature of at least 160°C above the melting temperature, and even more preferably at a temperature between 160-240°C above the melting temperature of said metals. In fact, it has been observed that using higher temperatures results in the evaporation of the metals, as well as unwanted oxidation of some alloying elements of the raw material. All of this leads to a loss of material and unwanted oxidation in this step.

[0049] Therefore, the molten raw material is that which is atomised. Atomisation can be carried out in any atomising device that guarantees the protective atmosphere, being, for example, a VIGA atomiser (vacuum and atomisation with inert gas), EIGA (electrode induction melting, without crucible, and gas atomisation), of plasma or centrifuge.

[0050] By way of non-limiting example, the device may also consist of an atomisation unit in which the melting of the raw material and the atomisation are carried out in different crucibles, using the so-called "tilt and pour" method. In this type of device, once the broth is obtained in the first crucible, said crucible is turned over and the liquid is poured into a second crucible, from which it is atomised.

[0051] Next, by way of non-limiting example, the atomisation process carried out in a PSI HERMIGA 75/3VI model atomiser, which is a confined flow atomiser, is described.

[0052] This atomiser has a convergent-divergent annular slit gas nozzle. Furthermore, it has independent melting and atomisation chambers, which can work under vacuum conditions to obtain high purity metal powders. In the melting chamber, an induction furnace melts the raw material contained in the alumina crucible. An alumina stopper rod prevents the broth from being poured into the atomisation chamber through the hole in the bottom of the crucible.

[0053] After melting the metals or metal alloy, for example, in a crucible, reaching the desired superheat temperature (e.g., about 200°C above liquid formation), the stopper rod is lifted and the liquid flows through the preheated guide tube, assisted by an overpressure exerted from the melting chamber, preferably an overpressure of less than 0.5 bar.

[0054] The high pressure atomising gas enters the atomisation unit through a pipe located on the side of the machine. The gas then enters the atomisation chamber through a continuous circular ring arranged around the nozzle for the metal broth. The atomiser is the most critical element of any atomisation unit and its main function is to expand and accelerate the atomising gas.

[0055] The gas is introduced under high pressure (e.g., at a pressure between 40-60 bar) and subsonic speed, and it flows through a convergent-divergent expansion nozzle, so that the gas accelerates in the convergent part of the same, reaching sonic conditions in the throat, and accelerating in the divergent part, until supersonic speeds are achieved at the outlet. This is how the atomising gas manages to increase its kinetic energy during its expansion before interacting with the metal jet.

[0056] Once the liquid metal has passed through the guide tube, the gas, at supersonic speed, instantly fragments the metal broth into small droplets that solidify in the atomisation chamber during flight, thus forming the powder particles.

[0057] The gas can be any inert gas that does not react with the metal or metal alloy, preferably pure argon with a purity greater than 99% by weight, or argon mixed with nitrogen.

[0058] Optionally, since the metals are very reactive at high temperatures, especially if they are in a liquid state, and in order to minimise the formation of oxides in the broth due to the presence of elements very similar to oxygen in said broth, and therefore the loss of alloying elements before atomisation, purges can be performed in the melting and atomisation chambers. To perform these purges, the introduction of high purity argon (H_2O <3 ppm, O_2 <2 ppm and C_nH_m < 0.5 ppm) and the creation of a vacuum, for example with a rotary pump (up to at least 0.5 mbar, preferably up to 0.01 mbar) are alternated.

[0059] Therefore, the incorporation of vacuum both during the melting of the metals and during at least part of the atomisation step minimises the formation of unwanted oxides and the consequent loss of alloying elements.

[0060] The powders obtained by the previous non-limiting example of the atomisation step are mainly spherical and contain a very thin surface layer of oxide, approximately 3 nm thick, due to the residual presence of oxygen in the atomisation chamber. To minimise the presence of oxides of the oxide-forming elements (for example, Y and/or Ti) inside the atomised powder particles, it is recommended that oxygen concentrations in the atomised powder be less than 100 ppm, preferably less than 50 ppm. In fact, to achieve such low oxidation values, it is important to correctly select the raw material and the atomising gas, minimise crucible degradation, and work with high vacuum levels.

[0061] After atomisation, the powder is sorted by sieving and the desired particle size is selected for the next oxidation step. The fraction of powder obtained depends on the particle size threshold selected for sieving. It is preferable to work with the finest powders possible, since during the next oxidation step it is of interest to reduce the distance that the oxygen must travel from the surface of the particle to the interior. However, the smaller the particle size, the smaller the fraction of powder that can be used. To that end, particle size threshold values after sieving that reach a compromise between both factors are preferred. By way of non-limiting examples, the particle size thresholds after sieving are preferably 100 μm, being able to be smaller than 45 μm and even smaller than 20 μm, thereby selecting powders with a size equal to or smaller than said threshold values.

Step 2: Oxidation

[0062] After selecting the appropriate fraction of powder, its surface is oxidated in a controlled manner by heating the metal powder in the presence of an oxidising gas.

[0063] The temperature and duration of each oxidation cycle depends on the particle size of the powder to be oxidised, the initial concentration of oxygen on its surface, the amount of powder to be oxidised, the type of oxidising atmosphere and its flow rate, and the desired final oxygen concentration. In turn, the oxygen concentration depends on the concentration of oxide-forming alloying elements.

[0064] The oxidation step of the present invention can be carried out at any time and temperature that allow the oxidation reaction to be carried out, although it is preferably carried out at a temperature less than or equal to 400°C, more preferably less than or equal to 300°C, even more preferably less than or equal to 250°C, and even more preferably between 150-250°C. In fact, it has been observed that performing oxidation at temperatures less than 400°C results in slower kinetics of the logarithmic oxidation reaction, which allows the oxidation to be controlled and therefore the quantity of oxygen incorporated into the metal alloy as well as the homogeneity of the oxidation.

[0065] Any type of heating device or furnace can be used to perform the oxidation of the metal powder obtained after atomisation, preferably and as a non-limiting example a rotary furnace, even more preferably a rotary drum furnace. In fact, the applicant of this Patent has no evidence that rotary furnaces have been used to perform oxidation heat treatments on metals or metal powders, as contemplated in the present invention. The preferred use of a rotary furnace in the present invention, even more preferably a rotary drum furnace, results in greater control and homogeneity of the oxidation reaction of the metal powder.

[0066] Therefore, in an even more preferred embodiment, the oxidation heat treatment is characterised by being carried out in a rotary furnace, for example, a rotary drum furnace, and at temperatures less than or equal to 400°C. This combination results in high control and adaptability of the metal oxides formed. In fact, it has been surprisingly observed that, under these oxidation conditions, the oxidation time is not so critical since the amount of oxygen incorporated into the metal powder in the form of metal oxides hardly varies with the oxidation time, which makes the oxidation process much more precise and versatile as to the oxidation time used.

[0067] Oxidation can be carried out by using oxidising gases, which could be pure oxygen O_2, a mixture of argon and O_2, conventional air, and even more preferably synthetic air (80% N_2 + 20% O_2). Said oxidising gas can be introduced into the furnace at any possible flow rate, preferably a flow rate of 5-10 L/min., and at any pressure that allows it to be introduced into the furnace, preferably at an overpressure of less than 0.5 bar, parameters that result in greater and more homogeneous oxidation.

[0068] Although the powder to be oxidised can have any size, it has been observed that greater and more homogeneous oxidation is obtained for powders with particle size less than 100 μm, even more preferably less than 75 μm.

[0069] In the case of carrying out the oxidation treatment in a rotary furnace, for example, a rotary drum furnace, oxidation can be carried out either statically (0 rpm) or by applying a rotary movement (preferably between 7-10 rpm).

[0070] These oxidation conditions are capable of obtaining optimal oxidation degrees for these ODS alloys, understood as metal powder oxidation values greater than 700 ppm of oxygen, preferably oxidation values greater than 1500 rpm, for example, between 1500-2500 ppm of oxygen.

[0071] Optionally, the oxidation and atomisation steps can also be performed together, in the same step, by using at least one oxidising gas (e.g., Ar + O_2) in the atomising gas, which makes it unnecessary to incorporate an additional oxidation step, with the consequent reduction in time, energy and resources for the manufacture of the ODS alloy according to the present invention.

[0072] Nevertheless, it should be noted that when atomisation is performed at a high temperature at least higher than the melting temperature of the metal alloy of the raw material, in contrast to the separate oxidation process that can be performed at a lower temperature, for example less than or equal to 400°C, it is not possible to have such precise control over the gain in oxygen during oxidation when it is done in conjunction with atomisation.

Step 3: Heat compression

[0073] After oxidation of the powder, heat compression thereof is carried out at a high temperature, to transform the powders into a formed metal part. Said compression is carried out at a high temperature between 600-1000°C. In a preferred non-limiting embodiment, heat compression of the powder is carried out using the hot isostatic pressing technique (HIP), at a high temperature between 600-1000°C. Alternatively, powder forming can be carried out by uniaxial compression or even by powder extrusion, or by forging.

[0074] The objective of this heat compression step is first to form the powder into the shape of a metal part, also considerably reducing its porosity.

[0075] In addition, it has been observed that this heat compression step, when carried out at a temperature between 600-1000°C, surprisingly results in the almost complete maintenance of metastable oxides in the formed metal part, which will be of great importance in the subsequent deformation steps up to high thickness reduction of the part (step 4) and annealing at high temperatures (step 5), allowing oxides of adequate distribution and size to form in the final ODS alloy, which result in suitable properties of the ODS alloys obtained according to the present invention. In fact, in the state of the art it is known that the use of compression at high temperatures above 900-1 000°C to sinter metal parts from metal powders, by means of hot isostatic pressing (HIP), results in the decomposition of metastable oxides and the formation of stable oxides of larger dimensions than desired and not homogeneously distributed. For this reason, an attempt is normally made to prevent the formation of oxides during heat compression. Moreover, in the method for obtaining reinforced alloys with dispersed oxides including mechanical alloying, high powder forming temperatures are also necessary to obtain the desired density of stable nanometric oxides.

[0076] To perform heat compression according to a non-limiting example of the present invention, the hot isostatic pressing (HIP) technique has been used. To do so, first, the metal powder is encapsulated in a capsule, for example, in a metal capsule of variable thickness between 1-3 mm and welded, for example, using the TIG (Tungsten Inert Gas) technique. This capsule can be cylindrical, or prismatic, in section, although it is usually square in section. The dimension of the capsule is the dimension that can accommodate the volume of powder to be contained and that adapts to the dimensions of the HIP press in which the hot pressing of the powder accommodated in the capsule will subsequently be carried out.

[0077] In order to obtain higher filling densities, it is possible to fill the capsule simultaneously with capsule vibration. Once the capsule is filled, it is necessary to remove the air, moisture and any volatile species adsorbed on the surface of the powder particles and on the inner walls of the capsule, using a vacuum system.

[0078] Lastly, the capsule is sealed and once the capsule is sealed, the HIP cycle is performed by simultaneously applying isostatic pressure and temperature. The cycle temperature can vary between 600 and 1000°C, which has been observed to allow metastable oxides to be maintained on the powder particle surfaces. In other words, relatively low consolidation temperatures prevent the dissociation of metastable oxides and the subsequent precipitation of large stable oxides, concentrated in the vicinity of the old powder particle surfaces. The applied pressure and maintenance time are such that they allow sufficient compression and densification of the powder, and the development of sintering necks between the particles, preferably a pressure between 100 and 150 MPa maintained for a time varying between 2 and 6 hours.

[0079] By way of non-limiting example, according to the process of the present invention, powders with particle size 20-45 μm were pressed by HIP, previously oxidated to 1000 ppm of oxygen, ODS steel of composition Fe-14.2Cr-2.0W-0.30Ti-0.18Y, under the following pressing conditions:

- HIP at 600°C and 140 MPa for 3 hours
- HIP at 900°C and 150 MPa for 2 hours

[0080] By using the previous heat compression step under the conditions described above, it has been observed that a consolidated metal part of high density is obtained from the metal powder, where relative densities of up to 95% can be obtained. In fact, since the residual porosity will be eliminated during the subsequent thermomechanical treatment, it is not necessary to obtain 100% dense materials after heat compression.

[0081] Furthermore, under these heat compression conditions, the metastable oxides of the old powder particle surfaces obtained after the previous oxidation step can also be maintained after the compression step.

Step 4: Warm deformation

[0082] The dense metal part of ODS alloy consolidated in the previous step is deformed when warm, in other words, at intermediate temperatures between the temperatures typical of cold and hot deformation processes. This deformation can be carried out, for example, by rolling, extrusion or forging, preferably by warm rolling. The deformation can be carried out on both the metal part, after removing the capsule from the previous hot isostatic compression step, and on the metal part still contained inside the capsule.

[0083] The term "warm deformation" according to the present invention refers to deformation that results in a reduced thickness of the deformed component, and that is carried out at a temperature higher than the temperature below which it is known that the alloy of interest would crack during deformation, but lower than the recrystallisation temperature of the alloy of interest.

[0084] Warm deformation according to the present invention can be carried out by any technique that results in a reduced thickness of the ODS alloy part on which the deformation is applied. As non-limiting examples, warm deformation can be carried out by rolling, extrusion, or forging, preferably by warm rolling.

[0085] On the one hand, through this deformation step, in addition to modifying the shape of the metal part, any residual porosity that may have remained after heat compression is eliminated, resulting in a 100% dense product.

[0086] Furthermore, this deformation results in microstructural refinement or reduction in the grain size of the ODS alloy matrix, which will be reflected in better mechanical properties of the final ODS alloy obtained.

[0087] In addition to all this, it has been surprisingly observed that the warm deformation of the ODS alloy after the compression of the previous step, when performed at high deformations or thickness reductions greater than 85% of the thickness of the part, results in the precipitation of a large number of homogeneously distributed nanometric oxides after deformation, which leads to obtaining ODS alloys with optimal properties such as their mechanical properties at a high temperature, resistance to radiation, and creep.

[0088] It has also been observed that, if warm deformation is carried out in a succession of partial deformation steps, where the percentage of thickness reduction increases gradually after each partial deformation step, this results in greater size optimisation and greater homogeneity and density of the precipitated nanometric oxides. In the particular case of warm rolling, this would correspond to the fact of gradually increasing the thickness reduction after each warm rolling pass of the part, that is, the fact that each subsequent rolling pass reduces the thickness more than the warm rolling step. Size optimisation refers to obtaining nanometric oxides of the smallest size possible. Nanometric oxide sizes smaller than 20 nm are considered to be optimal sizes according to the present invention. Greater homogeneity of nanometric oxides means a greater number of precipitated oxides distributed throughout the microstructure of the ODS alloy part.

[0089] As a non-limiting practical example, the deformation of 85% thickness reduction can be achieved by warm rolling. The rolling parameters to be used according to the present invention are broad and will depend on multiple factors, such as the relative density of the material after heat compression, the desired thickness reduction, the degree of refinement or reduction in grain size sought, or the density of precipitated nanometric oxides of interest.

[0090] By way of a non-limiting exemplary embodiment, the parameters used for warm rolling an ODS steel according to the present invention are presented, having composition Fe-13.8Cr-2.0W-0.31Ti-0.27Y, with particle size <75 μm, oxidated up to 2500 ppm of oxygen, and after HIP hot pressing at 700°C and 140 MPa for 3 hours:

- Time between passes: 10-30 seconds
- Number of passes: 26 passes
- Total thickness reduction: 92%
- Thickness reduction per pass with gradual increase from 5% per pass to 30% per pass.
- Initial rolling temperature: 770°C
- Final rolling temperature: 680°C

[0091] Surprisingly, after rolling within these rolling parameters up to a 92% reduction according to the previous non-limiting example, it has been observed that a very fine and homogeneous microstructure of the metal matrix is obtained (see Figure 3a), which is pore-free, in which most of the oxides on the old powder particle surfaces have dissolved, leaving only sub-micron-sized oxides. In fact, after warm rolling with the previous parameters, an incipient precipitation of very fine and homogeneous optimal oxides, with a particle size less than 20 nm, which is optimal is achieved and results, for example, in ODS alloys with better thermal and mechanical behaviour, as well as in ODS steels with better resistance to radiation. These oxides are observed in the micrographs obtained with a scanning electron microscope (SEM) in Figure 3a (2000x magnification) and in a more enlarged form in Figure 3b (100000x magnification), for an ODS steel of composition Fe-13.8Cr-2.0W-0.31 Ti-0.27Y.

Step 5: Precipitation annealing

[0092] After warm deformation, for example, after warm rolling, a final annealing treatment at temperatures higher than those applied during rolling and between 900-1200°C is applied to the deformed ODS alloy part.

[0093] It has been surprisingly observed that said final annealing heat treatment favours the oxidation and/or decomposition of particles rich in certain oxide-forming elements (e.g., Fe and Y in the case of ODS steels) that could remain after warm deformation, and an additional precipitation of complex nanometric oxides inside the metal grains of the ODS alloy (e.g., Y-Ti-O oxides in the Fe grains in the case of ODS steels). Furthermore, the formed oxides are very stable, which means that their composition, crystallographic structure and size do not change during use of the ODS alloy of the invention at different application temperatures. It has also been observed that the application of a precipitation annealing in the range 900-1200°C to the ODS alloy obtained according to the present invention does not result in recrystallisation of the alloy, since the ODS alloy after the deformation of the previous step is very resistant to recrystallisation at high temperatures. In fact, precipitation annealing is beneficial and not detrimental, as it results in additional and surprisingly fast precipitation of stable oxides, becoming as fast as only 5-20 minutes. This precipitation and stabilisation of the oxides after annealing results in an improvement in the mechanical properties of the ODS alloy at a high temperature, the resistance to radiation, and the creep properties of the ODS alloy.

[0094] Through this final annealing, microstructures of the ODS alloy are obtained, for example, ODS nickel or ODS steels, where the grains contain a dispersion of nanometric oxides rich in oxide-forming elements (e.g., Y and Ti, or Y and Zr, or Y and Hf). In fact, these multiple oxides anchor the dislocations even at high temperatures, resulting in ODS alloys with good mechanical behaviour and resistance to recrystallisation at high temperatures.

[0095] As a non-limiting example of precipitation annealing, according to the invention, a final annealing heat treatment was applied for 20 minutes at 1100°C to an ODS steel with composition Fe-13.8Cr-2.0W-0.31Ti-0.27Y, with particle size <75 μm, oxidated up to 2500 ppm of oxygen, after a HIP cycle at 700°C and 140 MPa for 3 hours, rolled according to the conditions described above. The micrographs obtained for said ODS steel by scanning electron microscope are presented in Figure 4a (1000x magnification) and Figure 4b (100000x magnification). Especially in Figure 4b, greater precipitation of nanometric oxides can be observed after annealing for the ODS steel both inside and on the grain boundaries (Figure 4b), compared to unannealed rolled ODS steel (Figure 3b). Therefore, it can be visually observed how the annealing treatment, in this particular non-limiting example at 1100°C for 20 minutes, favours the additional precipitation of the nanometric oxides of interest.

[0096] After performing this precipitation annealing, the part obtained can be treated using different optional treatments. By way of non-limiting examples, conventional machining of the ODS alloy part can be performed in order to give it the required form and functionality, as well as applying a final annealing heat treatment for reducing stresses after machining to allow the release of residual stresses introduced during machining.

[0097] Last but not least, this document only describes some of the embodiments of the present invention, and the person skilled in the art understands that other equivalent or alternative embodiments can also be carried out within the scope of the invention, as well as modifications that are equivalent or obvious. Therefore, the scope of the present invention will not be limited to the specific embodiments described herein.

Claims

1. A process for manufacturing an ODS metal alloy from a raw material consisting of a metal alloy and/or unoxidised metal elements, in solid state, wherein the process comprises the following steps:

    - melting of the raw material;
    - atomisation of the molten raw material;
    - oxidation of the metal powder obtained after the atomisation step;
    - heat compression of the oxidated powder obtained after the oxidation step, to form the powder into a part, at a temperature lower or equal to 1000°C;
    - warm deformation of the part obtained after heat compression, until achieving a thickness reduction of at least 85%;
    - precipitation annealing of the warm deformed part, at a temperature comprised between 900-1200°C.

2. The manufacturing process according to claim 1, wherein atomisation is carried out at a temperature 160°C higher than the melting temperature of the metal elements in the raw material, preferably at a temperature between 160-240°C higher than the melting temperature of the metal elements in the raw material.

3. The manufacturing process according to any of the preceding claims, wherein atomisation is carried out under vacuum conditions at least during part of the atomisation step.

4. The manufacturing process according to any of the preceding claims, wherein oxidation takes place at a temperature less than or equal to 400°C, preferably less than or equal to 300°C, more preferably less than or equal to 250°C, and even more preferably between 150-250°C.

5. The manufacturing process according to any of the preceding claims, wherein oxidation takes place in an oven, preferably a rotary drum oven.

6. The manufacturing process according to any of the preceding claims, wherein oxidation takes place simultaneously during the atomisation step, by using at least one oxidising gas during the atomisation step.

7. The manufacturing process according to any of the preceding claims, wherein heat compression is carried out at a temperature between 600-1000°C.

8. The manufacturing process according to any of the preceding claims, wherein warm deformation is carried out by warm rolling.

9. The manufacturing process according to any of the preceding claims, wherein warm deformation is carried out in a succession of partial deformation steps, and wherein the percentage of thickness reduction increases gradually after each partial deformation step.

10. A device for carrying out the process according to any of the preceding claims, wherein the device comprises:

- Melting means for melting the raw material,
- Atomising means for atomising the molten raw material,
- Oxidising means for oxidising the atomised powder,
- Forming means for forming the oxidated powder by heat compression,
- Deformation means configured to reduce the thickness of the formed part when warm, and
- Annealing means configured to heat the deformed part.

11. The device for carrying out the process according to claim 9, wherein:

- The melting means comprise a furnace with a vacuum atmosphere and/or non-oxidising atmosphere, and/or
- The atomising means comprise an atomiser, and/or
- The oxidation means comprise a furnace, preferably a rotary furnace, and even more preferably a rotary drum furnace, and/or
- The forming means by compression comprise a hot isostatic press (HIP), and/or
- The deformation means comprise a warm rolling mill, and/or
- The annealing means comprise a furnace.

12. An ODS metal alloy product obtainable by the process according to one of claims 1 to 9.

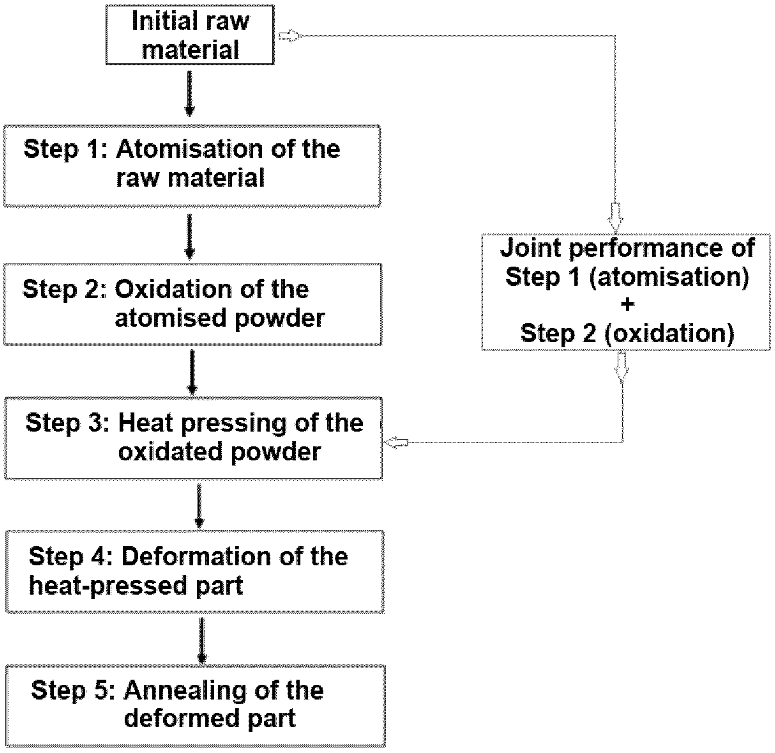
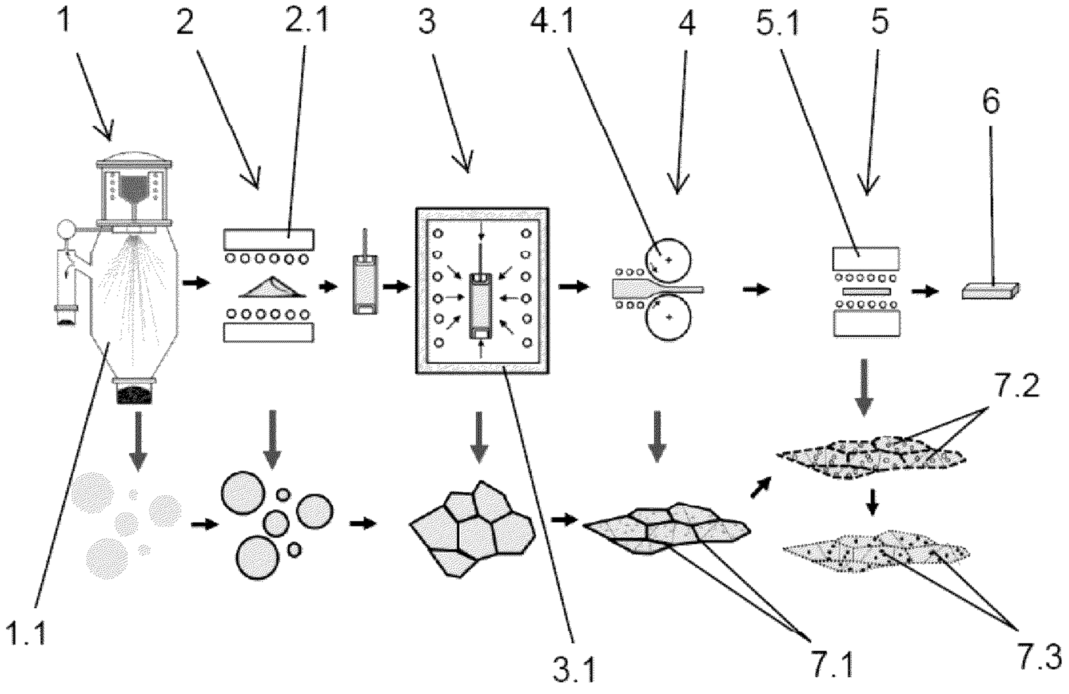

Initial raw material
Step 1: Atomisation of the raw material
Step 2: Oxidation of the atomised powder
Step 3: Heat pressing of the oxidated powder
Step 4: Deformation of the heat-pressed part
Step 5: Annealing of the deformed part
Joint performance of Step 1 (atomisation) + Step 2 (oxidation)

Fig. 1


1
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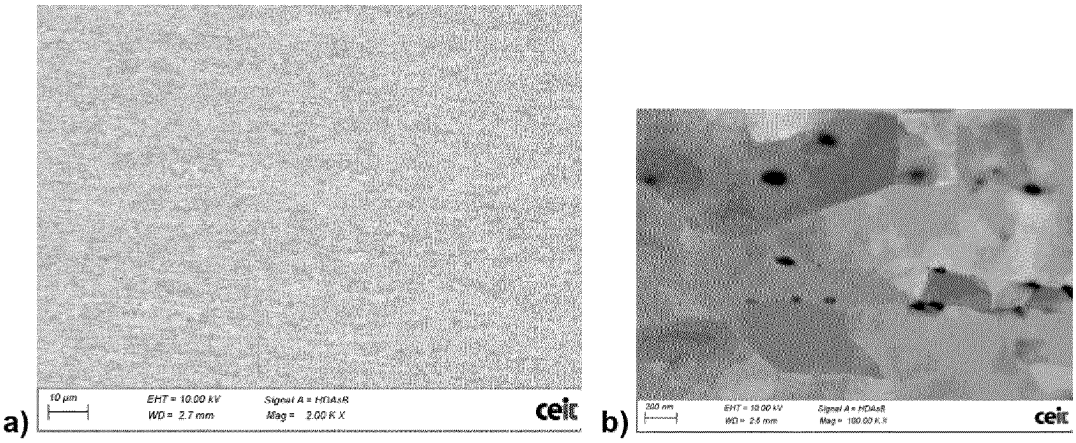
7.3

Fig. 2


a)
10 µm
EHT = 10.00 kV
WD = 2.7 mm
Signal A = HDAsB
Mag = 2.00 K X
ceit
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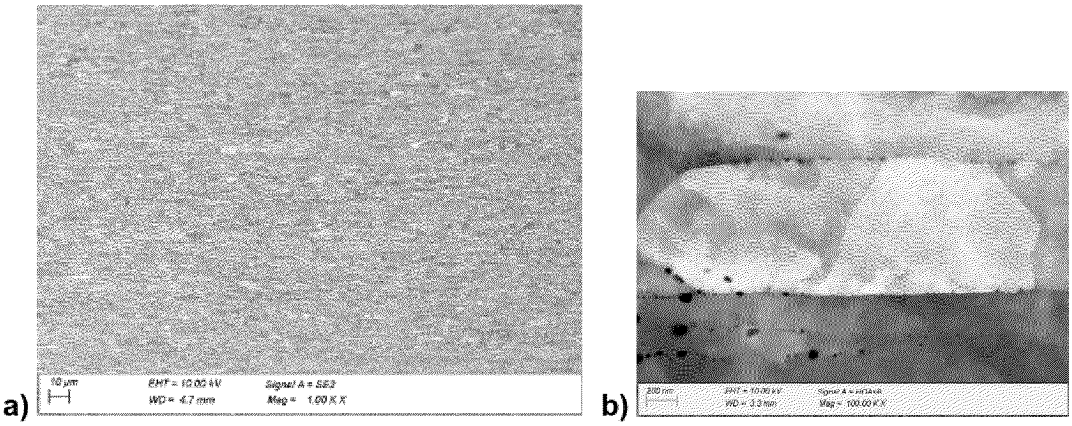
200 nm
EHT = 10.00 kV
WD = 2.6 mm
Signal A = HDAsB
Mag = 100.00 K X
ceit

Fig. 3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WD = 4.7 mm
Signal A = SE2
Mag = 1.00 K X
b)
200 nm
EHT = 10.00 kV
WD = 3.3 mm
Signal A = HDAsB
Mag = 100.00 K X

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2022/070010

A. CLASSIFICATION OF SUBJECT MATTER

C22C33/02 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, INVENES, WPI, XPESP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PAZOS, D. et al... ODS ferritic steels obtained from gas atomized powders through the STARS processing route: Reactive synthesis as an alternative to mechanical alloying. Nuclear Materials And Energy, 2018, N° 17, pages 1-8 Apartado 3.1 and 3.2.	1-12
A	RIEKEN, J. Gas atomized precursor alloy powder for oxide dispersion strengthened ferritic stainless steel. Proquest Dissertations And Theses; Thesis (ph.d.) Iowa State University, 2011., 2011 [on line][retrieved on 06/09/2022]. Retrieved from <URL: https://www.osti.gov/biblio/1048516/> pages 252 - 266.	1-12

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance.		
"E"	earlier document but published on or after the international filing date		
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"O"	document referring to an oral disclosure use, exhibition, or other means.	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents , such combination being obvious to a person skilled in the art
"P"	document published prior to the international filing date but later than the priority date claimed		
		"&"	document member of the same patent family

Date of the actual completion of the international search 23/09/2022	Date of mailing of the international search report **(28/09/2022)**
Name and mailing address of the ISA/ OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Facsimile No.: 91 349 53 04	Authorized officer B. Aragón Urueña Telephone No. 91 3493277

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2022/070010

C (continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GIL E. et al... ODS ferritic steels produced by an alternative route (STARS): microstructural characterisation after atomisation, HIPping and heat treatments . Powder Metallurgy, 2016, Vol. 59, Nº 5, pages 359-369	1-12
A	CN 110760760 A (NUCLEAR POWER INST CHINA) 07/02/2020, (abstract)	1-12

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

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Information on patent family members

International application No.

PCT/ES2022/070010

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Form PCT/ISA/210 (patent family annex) (January 2015)