



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
17.04.2024 Bulletin 2024/16

(51) International Patent Classification (IPC):
C22C 19/03^(2006.01)

(21) Application number: **24152983.3**

(52) Cooperative Patent Classification (CPC):
(C-Sets available)
**C22C 19/03; B22F 1/12; C22C 1/0433;
C22C 1/053; C22C 1/059; C22C 1/1084;
C22C 19/007; B22F 2998/00; B22F 2998/10;
B22F 2999/00** (Cont.)

(22) Date of filing: **16.12.2014**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **27.12.2013 US 201361921380 P**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
14873424.7 / 3 087 210

(71) Applicant: **Raytheon Technologies Corporation**
Farmington, CT 06032 (US)

(72) Inventors:
• **CHIN, Herbert A.**
Hartford, OH 06103 (US)

• **REYNOLDS, Paul L.**
Hartford, OH 06103 (US)
• **MURON, Stephen P.**
Hartford, OH 06103 (US)
• **SCHLICHTING, Kevin W.**
Hartford, OH 06103 (US)
• **BENN, Raymond C.**
Hartford, OH 06103 (US)

(74) Representative: **Dehns**
St. Bride's House
10 Salisbury Square
London EC4Y 8JD (GB)

Remarks:
This application was filed on 19-01-2024 as a
divisional application to the application mentioned
under INID code 62.

(54) **HIGH-STRENGTH HIGH-THERMAL-CONDUCTIVITY WROUGHT NICKEL ALLOY**

(57) A nickel alloying process includes providing a
metal powder containing substantially unalloyed nickel,
forming a nickel alloy from the metal powder, removing

air and absorbed water from the nickel alloy, and hot
extruding the nickel alloy.

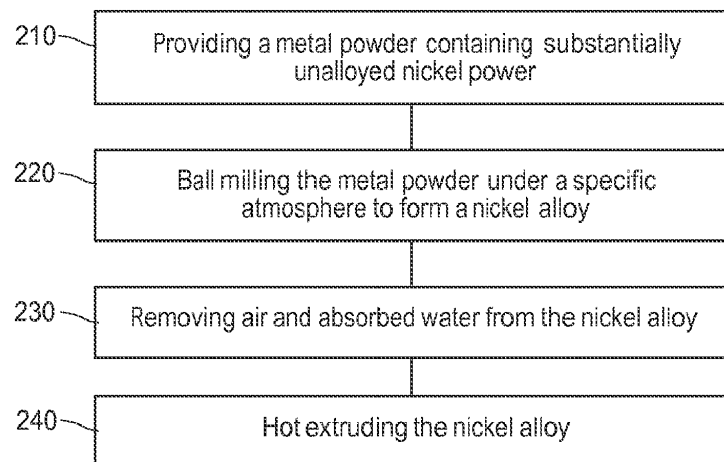


Fig. 2

(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets

B22F 2998/00, C22C 32/0026, C22C 32/0052,
C22C 32/0068;

B22F 2999/00, C22C 1/1084, B22F 2009/043,
B22F 2009/042

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 61/921,380 filed on December 27, 2013 and titled High Strength High Thermal Conductivity Wrought Nickel Alloy.

FIELD

[0002] The present disclosure relates generally to alloying metals, and, more particularly, to method for producing a nickel alloy with increased thermal conductivity combined with high temperature strength capability.

BACKGROUND

[0003] With each next generation of gas turbine engines comes increased performance, durability and reliability along with affordability. Those performance metrics are met with increased operating stresses, temperature and speed. These factors place ever increasing demands on Thermal Management System (TMS). A key component in the TMS is a heat exchanger for hot section air-to-air exchanges. The heat exchanger requires strength, temperature capability and high thermal conductivity along with manufacturability and cost. Conventional hot section heat exchanger materials are typically made of a nickel alloy for their high temperature capability and ease of fabrication. However, nickel alloys have significantly lower thermal conductivity as compared to pure nickel metal. Typical strengthening mechanisms used in those alloys, such as solid solution strengthening and precipitation hardening, cause significant electron scattering and markedly lower thermal conductivity. In some cases, the conventional nickel alloys have thermal conductivities 1/10th to 1/25th of that of pure nickel. But the relatively low strength of pure nickel makes it undesirable as an engineering or structural material.

[0004] As such, what is desired is one or more materials with high thermal conductivity and significant strength characteristics.

SUMMARY

[0005] Disclosed and claimed herein is a nickel alloying process which includes providing a metal powder containing substantially unalloyed nickel, forming a nickel alloy from the metal powder, removing air and absorbed water from the nickel alloy, and hot extruding the nickel alloy. In one embodiment, the metal powder is produced by blending a substantially unalloyed nickel powder with an incoherent particle powder. In one embodiment, the metal powder is produced by blending a nickel oxide powder proportionally with a nickel-aluminum alloy powder. In the above embodiments, the nickel alloy is formed by a ball milling process. In one embodiment, the metal pow-

der is a nickel-vanadium-carbon powder, and the nickel alloy is formed by a melting and rapid solidifying process.

[0006] Other aspects, features, and techniques will be apparent to one skilled in the relevant art in view of the following detailed description of the embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The drawings accompanying and forming part of this specification are included to depict certain aspects of the present disclosure. A clearer conception of the present disclosure, and of the components and operation of systems provided with the present disclosure, will become more readily apparent by referring to the exemplary, and therefore non-limiting, embodiments illustrated in the drawings, wherein like reference numbers (if they occur in more than one view) designate the same elements. The present disclosure may be better understood by reference to one or more of these drawings in combination with the description presented herein. It should be noted that the features illustrated in the drawings are not necessarily drawn to scale.

Fig. 1 is a plot diagram illustrating a weight fraction of phases, vanadium carbide (VC) and nickel metal as a function of temperature according one embodiment of the present disclosure.

Fig. 2 is a flow chart illustrating a process for producing a nickel alloy according to one embodiment of the present disclosure.

Figs. 3A-3C are flow charts illustrating details of the processes shown in Fig. 2 according to embodiments of the present disclosure.

DESCRIPTION

[0008] One aspect of the disclosure relates to processes of manufacturing high strength and high thermal conductivity wrought nickel alloy. Embodiments of the present disclosure will be described hereinafter with reference to the attached drawings.

[0009] One embodiment of the present disclosure provides a process to obtain higher strength in nickel alloys without significantly reducing the thermal conductivity of the alloys. In one embodiment, a process for forming a nickel alloy is based on dispersion strengthening of a nickel metal, in which a uniform ultra-fine dispersion of thermo-dynamically stable incoherent particles or precipitates is distributed in the nickel metal and produces increased strength by significantly inhibiting dislocation motion in the nickel. Specifically, Orowan Strengthening conditions are sought. The strength increase is generally proportional to the volume fraction (V_f) of the particles present in the nickel metal up to an appropriate limit. Key to dispersion strengthening is the size, distribution and V_f of the incoherent precipitates. Typically, a particle ra-

dus of about 10-20 nm, an interparticle spacing of about 100 nm or at least two times the particle size in a Vf of about 0.05 are conducive to Orowan Strengthening.

[0010] Particles of the aforementioned size range require a high magnification electron microscope to be observed. If they can be seen in an optical microscope at lower magnification, then they are described as non-metallic inclusions which are not suitable for engineering materials. Incoherent particles or precipitates covered in this disclosure include metal oxides, metal nitrides and metal carbides.

[0011] A necessary characteristic of the incoherent precipitates listed above is their thermodynamic stability up to the melting point of the nickel metal and resistance to coarsening over the thermo-mechanical processing range of the nickel metal during component fabrication and operation. Thermo-dynamic stability is reflected in high negative Gibbs free energy of formation, -AG.

[0012] A key to high thermal conductivity of the dispersion strengthened nickel is to limit any conventional alloying (solid solution strengthening and precipitation hardening) to less than 8 weight percent of combined alloying elements. In so doing, the nickel matrix will maintain its high thermal conductivity to nearly 90 W/m. K.

[0013] Fig. 1 is a plot diagram illustrating a weight fraction of phases, vanadium carbide (VC) and nickel metal as a function of temperature according one embodiment of the present disclosure. Line 110 represents pure Nickel, line 120 represents VC, and line 130 represents a liquid phase of the VC. The VC forms during the solidification from liquid to solid, and is stable from solidification to room temperature. Strength of the VC dispersion strengthened nickel metal can be adjusted according to the weight fraction of the VC dispersion in the nickel metal. Ni-2.15V-0.5C is an exemplary lower level VC weight fraction composition. -3V-0.7C is an exemplary higher level VC weight fraction. For these two alloys, alloy design involves compositions whereby there is a one-to-one ratio of vanadium to carbon as is accomplished by atomic percent and not by weight percent.

[0014] Fig. 2 is a flow chart illustrating a process for producing a nickel alloy according to one embodiment of the present disclosure. The process begins with providing a metal powder containing substantially unalloyed nickel powder in step 210. The substantially unalloyed nickel powder is to ensure a base metal with high thermal conductivity. A nickel alloy is formed in step 220 from the metal powder. In one embodiment, the nickel alloy is formed by a ball milling process under a specific atmosphere. The specific atmosphere can be gaseous and/or cryo-liquid, to promote repetitive cold-welding, deformation and fracturing of powder particles. In other embodiments, the ball milling process can be replaced by an attrition process for a similar result, as an attritor is a high energy ball mill.

[0015] The nickel alloy formed in step 220 is a composite powder in which average dispersoid interparticle spacing is approximately the same as welding inter-

space, i.e., a uniform microstructural spacing of ultra-fine dispersant. The nickel alloy is then placed in a suitable metal container and evacuated to remove air and absorbed water in step 230. Stainless steel can be used to make such metal container. Finally the resulting nickel alloy is hot extruded to full density in step 240. In order to control recrystallized grain size and shape of the nickel alloy, a subsequent thermomechanical processing may be employed. The nickel alloy produced according to the embodiment of the present disclosure possesses a desired microstructural condition for strength and high thermal conductivity.

[0016] Figs. 3A-3C are flow charts illustrating details of the processes shown in Fig. 2 according to embodiments of the present disclosure. Referring to Fig. 3 A, in one embodiment, the process of providing the metal powder of Fig. 2 begins with providing an unalloyed nickel powder in step 310. A selected incoherent particle powder is provided in step 320. The incoherent particle can be selected from metal oxides, metal nitrides and metal carbides. The metal oxides include but not limited to calcia, magnesia, alumina, ceria, silica, chromia, yttria and thoria and certain mixed oxides in forms of garnates, etc. The metal nitrides include but not limited to TiN, CrN, AlN, etc. The metal carbides include but not limited to vanadium carbide (VC), TiC, TaC, WC, HfC, etc.

[0017] Referring again to Fig. 3A, the unalloyed nickel powder and the selected incoherent particle powder are physically blended in step 330. The blended powder will then be ready for subsequent processing steps as shown in Fig. 2. It should be realized the unalloyed nickel powder used in step 310 can be replaced with a limited conventionally alloyed nickel. As an example, a conventionally mechanically alloy nickel alloy INCONEL MA 6000 is the product of the process shown in Fig. 2. However, its conventional alloy content as shown below is of significant proportion as to markedly debit the thermal conductivity of that alloy; 16 W/m.K for MA 6000 versus 90 W/m.K for Ni INCONEL MA 6000: Ni-0.06C-15.0Cr-4.5Al-2.3Ti-3.9W-1.5Fe-0.2N-0.57 total Oxygen with 1.1Y2O3 oxide dispersion.

[0018] Referring to Fig. 3B, in one embodiment, the process of providing the metal powder of Fig. 2 begins with providing a nickel oxide powder with ultra-fine oxide dispersion in step 340. A nickel and aluminum alloy powder is provided in step 350. The nickel and aluminum alloy powder can be made by conventional powder metallurgy methods, rotary atomization, or gas atomization. The nickel oxide powder is proportionally blended with a nickel and aluminum alloy powder in step 360. The proportion is determined by a need for the nickel oxide powder to react with the nickel-aluminum alloy powder to form nickel metal and aluminum oxide. Such reaction can be expressed as ((Ni + Al alloy powder) + (NiO oxide) reaction) -> Ni metal + Al2O3 oxide dispersion.

[0019] Referring to Fig. 3C, in one embodiment, the metal powder in step 210 of Fig. 2 is a nickel-vanadium-carbon powder provided in step 370. The nickel-vanadi-

um-carbon powder can be formulated with a certain level of VC dispersion in the nickel powder for a desired nickel alloy strength. Other nickel-refractory metal-carbon or metal-nitrogen powder can also be used. Such metal-carbon or metal-nitrogen powder can be formulated to subsequently form a dispersion of MC carbides (e.g. tungsten carbide or titanium carbide), metal nitrides, etc. There are a number of carbides that can be formed in metal alloys including Ni and Steels. Type depends on the alloying additions and their ratios. In MC carbides, the letter M represents metal and can be one or a mixture of metal alloying additions. Examples include but not limited to: WC, VC, TiC, HfC; Cr₇C₃, (Cr, Mo, Fe)₇C₃ and others; (Cr, Mo)₂₃C₆; Mo₂C and others; and Fe₃C. Their thermo-dynamic stabilities are in the order of (highest to lowest): MC, M₇C₃, M₂₃C₆, M₂C, M₃C. In embodiments of the present disclosure, MC carbides are preferred for their high thermo-dynamic stability to maintain dispersion strengthening to very high temperatures, while resisting coarsening.

[0020] Referring again to Fig. 3C, as a way to form the nickel alloy in step 220 of Fig. 2, the nickel-vanadium-carbon powder is melted in step 380, and then rapidly solidified in step 390. The rapid solidification may be implemented by rotary atomization using high specific heat inert quench gases like Helium, Hydrogen, or mixtures of these gases with more economical Argon or Nitrogen. Quench rate of 10⁵ degree Celsius/second or higher should be used to control the nucleation and precipitation of the uniform ultra-fine dispersion necessary for the strength of the resulting nickel alloy. For producing fine rapidly cooled powder high rotational speeds is preferred. The rapidly solidified powder should also be made to -240 mesh powder size fraction or finer to ensure that a desired rapid solidification rate can be obtained for a desired dispersion.

[0021] It should also be recognized that the methodology of the present disclosure for retaining good thermal conductivity of Ni, while increasing the high temperature strength, can be applied to situations where other physical properties of the metal base are retained and utilized at high temperatures. For example, conversely, the electrical resistivity of pure Ni is about 1/10th of such Ni-based alloys. Aside from heat, high temperature strength DS Ni in electrical/power applications has better electrical conductivity than Ni-base alloys, and may be used to improve related performance. Other physical properties like Coefficient of Thermal Expansion and Specific Heat stay approximately the same between Ni and most of its alloys (excluding certain Fe-Ni-base low CTE compositions), i.e., these properties do not adversely influence the present disclosure.

[0022] While this disclosure has been particularly shown and described with references to exemplary embodiments thereof, it shall be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit of the claimed embodiments.

Claims

1. A nickel alloying process comprising:
 - providing a metal powder containing substantially unalloyed nickel;
 - forming a nickel alloy from the metal powder;
 - removing air and absorbed water from the nickel alloy; and
 - hot extruding the nickel alloy.
2. The nickel alloying process of claim 1, wherein the providing the metal powder comprises providing the group consisting of a nickel-vanadium-carbon powder, a nickel-refractory metal-carbon powder and a nickel-refractory metal-nitrogen powder.
3. The nickel alloying process of claim 2, wherein the nickel-refractory metal-carbon powder is formulated to subsequently form a dispersion of metal carbides.
4. The nickel alloying process of claim 2, wherein the nickel-refractory metal-nitrogen powder is formulated to subsequently form a dispersion of metal nitrides.
5. The nickel alloying process of claim 1, wherein the forming the nickel alloy comprises melting the metal powder; and rapidly solidifying the melted metal powder.
6. The nickel alloying process of claim 5, wherein the melting is a vacuum induction melting.
7. The nickel alloying process of claim 5, wherein the rapidly solidifying is performed by rotary atomization using a high specific heat inert quench gas and high rotational speeds to produce fine rapidly cooled powder, preferably wherein the heat inert quench gas is selected from the group consisting of Helium, Hydrogen, Argon, Nitrogen and a combination thereof.

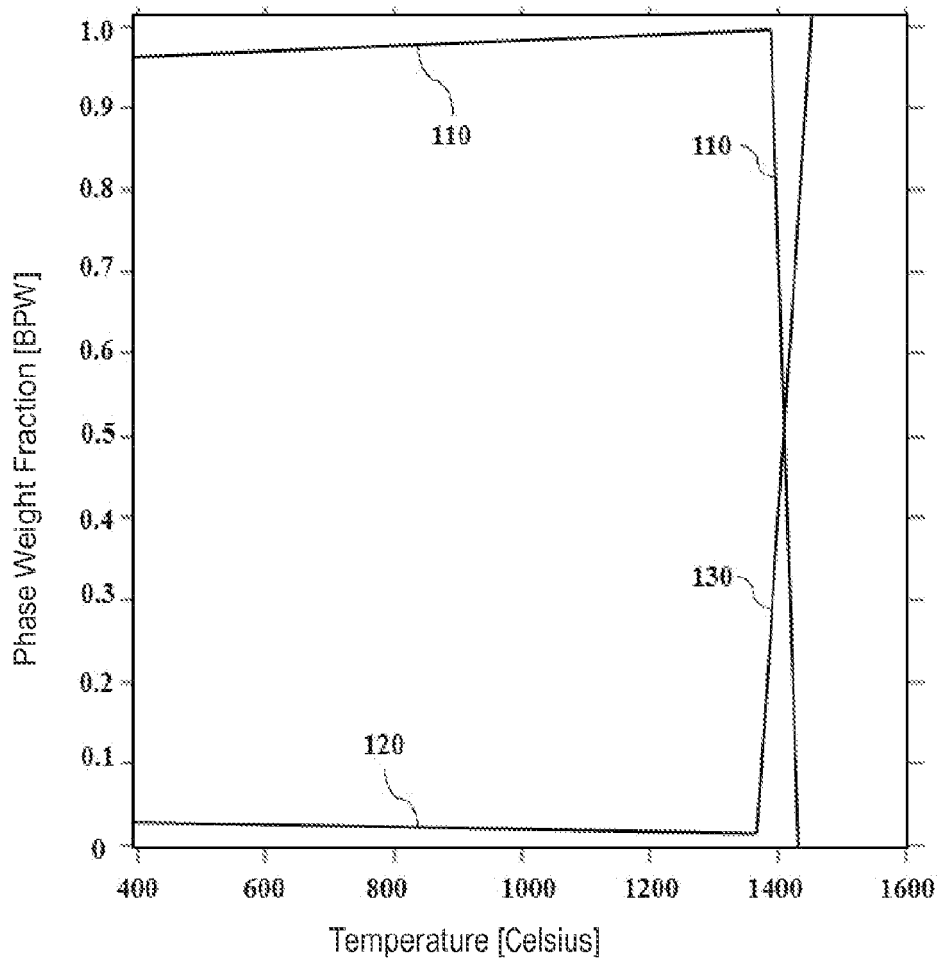


Fig. 1

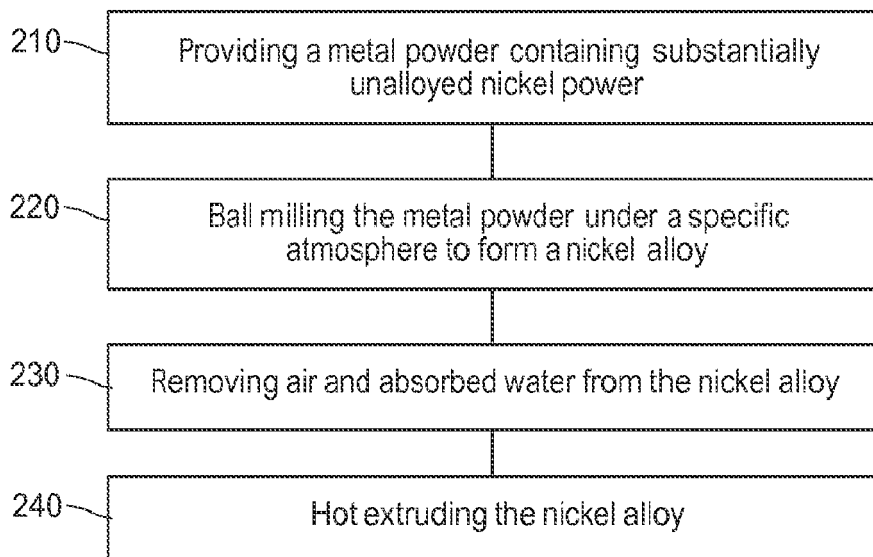


Fig. 2

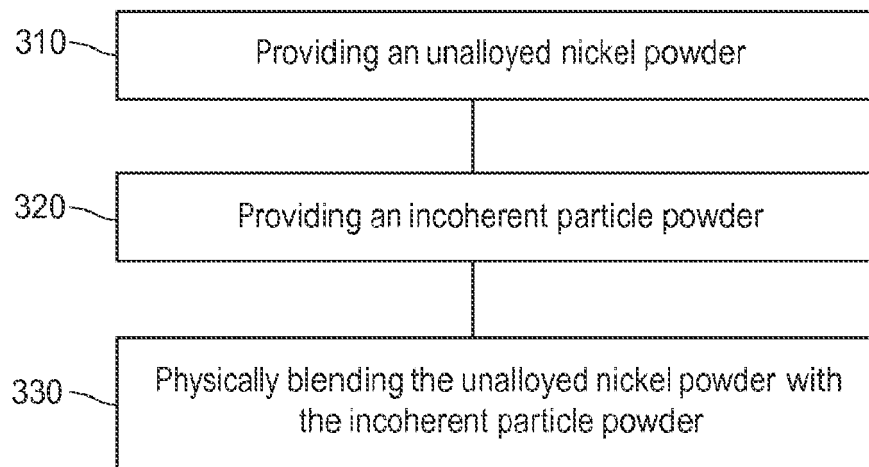


Fig. 3A

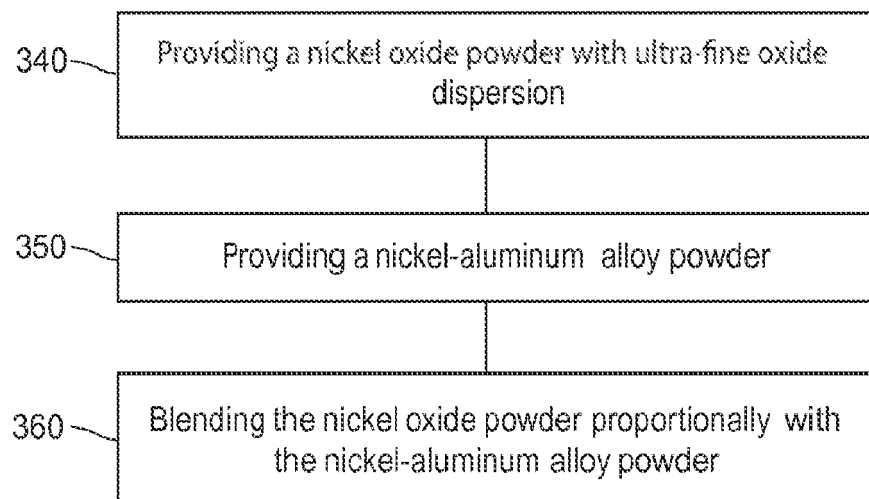


Fig. 3B

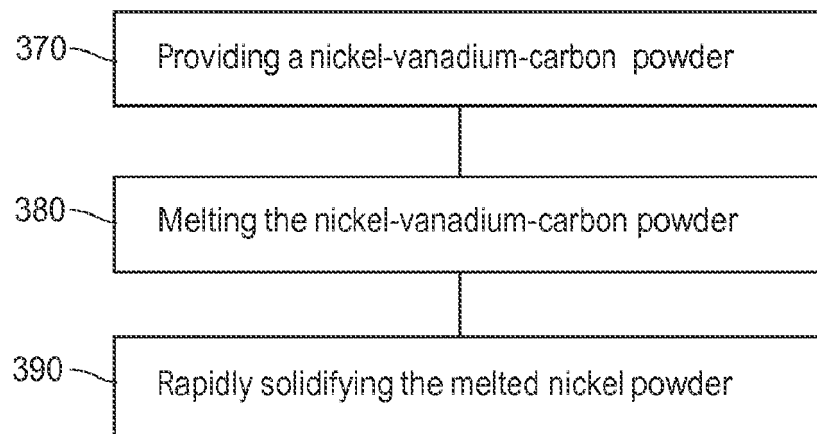


Fig. 3C

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 61921380 [0001]