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(54) **METHOD AND COMPOSITION FOR MAKING A WIRE**

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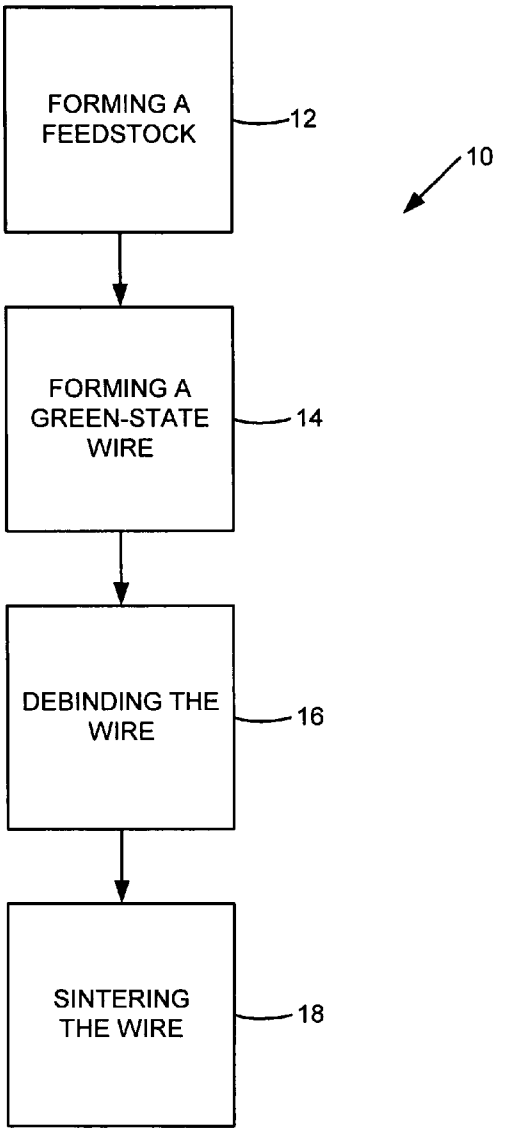
(57) **ABSTRACT**

A method for producing wires, such as welding or hardfacing wires, made of superalloys and other metals. In a disclosed embodiment, the method includes forming a green-state wire from a feedstock comprising a metal powder and a binder, such as by extruding the feedstock through a die orifice, and sintering the wire to effect consolidation and densification of the wire.



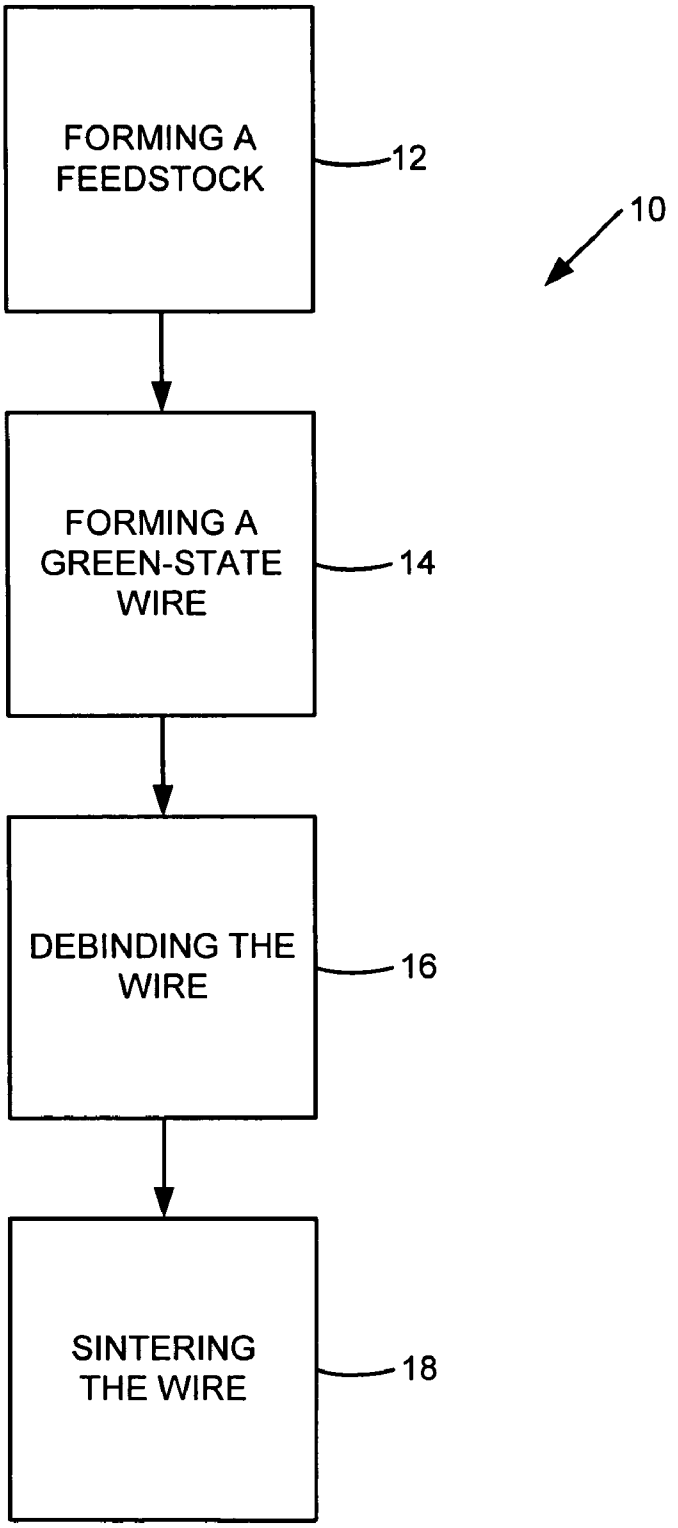

FORMING A FEEDSTOCK
12
10
FORMING A GREEN-STATE WIRE
14
DEBINDING THE WIRE
16
SINTERING THE WIRE
18

FIG. 1

METHOD AND COMPOSITION FOR MAKING A WIRE

BACKGROUND

[0001] Welding and hardfacing wires of superalloy and high temperature materials, such as René® 142 and alloy 718, are used to repair, rebuild, and manufacture gas turbine engines for aircraft and land-based applications and other parts used in structures that are subject to high working temperatures. Presently, such welding and hardfacing wires typically are manufactured by casting superalloy material into cast ingot having a diameter much larger than the final diameter of the wire. The cast ingot is then hot worked and extruded multiple times until the desired diameter of the wire is achieved (e.g., 0.045 inch). As can be appreciated, this process is time consuming and expensive.

[0002] Accordingly, there exists a need for a new and improved process for manufacturing welding and hardfacing wires, and in particular, such wires made from superalloy materials.

SUMMARY

[0003] The present disclosure concerns embodiments of a method for making wires, which method is particularly suited for making welding and hardfacing wires of superalloy materials used for manufacturing or repairing parts of aerospace structures, such as gas turbine aircraft engines. Such superalloys can include, but are not limited to, cobalt-based, titanium-based, iron-based, and nickel-based superalloys.

[0004] The method is accomplished by forming a "green"-state wire from a feedstock comprising a metal powder and a binder, such as by extruding the feedstock through a die. The green-state wire is then sintered to effect consolidation and densification of the wire. The wire can be further subjected to any of various processing techniques depending on the requirements of its intended application. The method can be used to form various types of wires, such as welding or hardfacing wires. Weld wires produced by the method can be used in various welding processes, such as TIG or MIG welding.

[0005] In particular embodiments, the feedstock is formed by mixing or blending the metal powder and the binder and heating the mixture to a temperature sufficient to cause the binder to melt and form a paste-like mixture. The mixture can be solidified and pelletized to create a plurality of feedstock pellets with thermoplastic properties. The feedstock pellets are loaded into an injection molding machine or another type of extrusion apparatus and are heated to a temperature sufficient to cause the binder to melt and form an extrudable, feedstock paste. The paste is extruded through a die of the extrusion apparatus to form a green-state wire. In other embodiments, the feedstock can be formed and extruded using an extrusion apparatus having mixing and extrusion capabilities so as to eliminate the intermediate step of solidifying and pelletizing the feedstock.

[0006] In other embodiments, the green-state wire can formed by methods other than extrusion through a die orifice. For example, in one embodiment, the green-state wire can be formed using rollers. In another embodiment, the green-state wire can be formed by injecting the feedstock into a mold. In still another embodiment, the feedstock can be flowed or otherwise placed into a die and then pressed into a green-state wire. Other types of molding processes that can be used to form the green-state wire include, without limitation, compression molding, transfer molding, and plunger molding.

[0007] After forming the green-state wire, it can be placed in the groove of a tray or mold to maintain its shape during subsequent processing. The wire can be chemically treated to remove at least a portion of the binder by immersing the wire in a suitable solvent, such as trichloroethylene or water. In an alternative embodiment, the binder can be partially or completely removed by thermal processing. After debinding, the wire is sintered at high temperature to effect consolidation and densification of the wire. Sintering also is effective to remove the remaining portion of the binder. In another embodiment, the extruded wire can be sintered without first being chemically or thermally treated to extract a portion of the binder.

[0008] If desired, the sintered wire can be subjected to further processing. For example, the wire can be further densified, such as via cold isostatic pressing or hot isostatic pressing, and/or the surface of the wire can be finished using conventional surface-finishing techniques, such as centerless grinding.

[0009] As noted above, conventional methods for manufacturing welding and hardfacing wires made of superalloys require multiple extrusion steps to achieve the final shape of the wire. An advantage of the present method is that the final shape of a wire can be achieved by a single molding or extrusion step, and therefore is less expensive and less time consuming than conventional methods.

[0010] The foregoing and other features and advantages of the invention will become more apparent from the following detailed description of several embodiments, which proceeds with reference to the accompanying figure.

BRIEF DESCRIPTION OF THE DRAWING

[0011] **FIG. 1** is a flowchart illustrating a method for making a wire, according to one embodiment.

DETAILED DESCRIPTION

[0012] As used herein, the singular forms "a,""an," and "the" refer to one or more than one, unless the context clearly dictates otherwise. As used herein, the term "includes" means "comprises." As used herein, the term "metal" is used generically to refer to both metals and metal alloys.

[0013] **FIG. 1** shows a flowchart, indicating generally at **10**, that illustrates a method for making a wire, according to one embodiment. As shown, the method generally includes forming a feedstock comprising a metal powder and a binder (indicated at **12**), forming a green-state wire (indicated at **14**), debinding the green-state wire (indicated at **16**), and sintering the wire (indicated at **18**).

[0014] The metal powder can be manufactured using conventional techniques, such as vacuum or inert gas melting of virgin raw materials or a combination of virgin materials and revert material, and then atomizing the metal to form a powder. The powder desirably is screened using a

screen having a mesh size of about −325, although smaller or larger mesh sizes also could be used.

[0015] The methods described herein are particularly useful for making welding and hardfacing wires of superalloys that typically are used for repairing, rebuilding, or manufacturing parts of aerospace structures. Such superalloys include, for example, cobalt-based superalloys, titanium-based superalloys (e.g., titanium aluminide, Ti-6-4), iron-based superalloys, and nickel-based superalloys (e.g., René® 142, René® 195, or alloy 718). The methods described herein also can be used to manufacture hardfacing wires from any of various hardfacing alloys or wires from more conventional metals, such as stainless steels (e.g., 17-4 PH stainless steel, 316 stainless steel, or 316 L stainless steel) or any of various other metals.

[0016] Any suitable binder can be used to form the feedstock. For example, the binder generally can comprise a plasticizer or an oil. Also, various water-soluble binders can be used. In certain embodiments, the binder comprises a plasticizer, a strengthener, a compatibilizer for the plasticizer and strengthener, and a surfactant. Without limitation, examples of plasticizers include paraffin wax, carnauba wax, polyethylene wax, or microcrystalline wax; examples of strengtheners include polypropylene, polystyrene, and polyacetal; examples compatibilizers include styrene-butadiene block copolymer (e.g., Kraton® commercially available from Shell) and ethyl vinyl acetate copolymer; and examples of surfactants include stearic acid, and zinc stearate.

[0017] In one embodiment, a binder typically has a composition in weight percent of about 45% to 55% plasticizer, 45% to 55% strengthener, 3% to 6% compatibilizer, and 0.25% to 0.5% surfactant, with 48.5% paraffin wax, 48.5% polypropylene, 3% styrene-butadiene, and 0.25% stearic acid being a specific example. The concentration of the metal powder and the binder in the feedstock can vary between about 50% to 70% by volume for each component.

[0018] To prepare the feedstock, a metal, in powder form, and a binder are mixed and heated to a temperature sufficient to cause the binder to melt and form a paste-like mixture. Any of various conventional mixers, such as a planetary mixer or equivalent mechanism, can be used to mix the metal powder and the binder. The temperature at which the mixture is heated depends on the composition of the binder. Generally, any temperature greater than room temperature may be sufficient to melt the binder. In one example, the binder composition described above is heated to a temperature of about 300° F. to 400° F., and more preferably 325° F. to 350° F. In particular embodiments, the feedstock is allowed to cool and form a solidified mass, which is then pelletized or otherwise fractionated to form a plurality of smaller, feedstock particles or pellets with thermoplastic properties.

[0019] In certain embodiments, the green-state wire is formed by extruding the feedstock, in the form of a paste, through the die orifice of an extruder. For example, in one specific implementation, the feedstock particles are loaded into an extruder, which can be a conventional barrel and ram extruder, an injection molding machine, or an equivalent mechanism, and the particles are heated at a temperature sufficient to cause the binder to melt and form an extrudable paste. The extrusion temperature can vary depending on the composition of the binder used. For example, a feedstock comprising a metal powder and a binder having the composition described above generally is heated to a temperature of about 300° F. to 400° F., and more preferably 325° F. to 350° F. to form an extrudable paste.

[0020] In an alternative embodiment, the feedstock can be transferred directly from the mixer to the extruder without the intermediate steps of solidifying and fractionating the feedstock into smaller particles. In still another embodiment, an extruder having mixing and extruding capabilities can be used. Thus, in the latter embodiment, the feedstock is formed by mixing the metal powder and binder in the extruder itself prior to extrusion.

[0021] In any event, the feedstock paste is extruded through the orifice of a die to form one or more green-state wires of a desired length. The size of the orifice can be selected to produce wires of any diameter. In certain embodiments, for example, welding or hardfacing wires having a diameter of about 0.015 to 0.100 inch are formed, such as typically used in TIG or MIG welding, although wires having a diameter greater than 0.100 inch or less than 0.015 inch also can be produced. Since sintering generally will cause the wires to densify, the size of the orifice is selected such that the diameter of the extruded wires is slightly greater than the required final diameter after sintering. The die orifice can be of any desirable geometric profile such as a circle, oval, triangle, square, rectangle, diamond, or various combinations thereof. The die may be provided with a single orifice or multiple orifices.

[0022] In other embodiments, the green-state wire can be formed by methods other than extrusion through a die orifice. For example, in one embodiment, the green-state wire can be formed using rollers. In another embodiment, the green-state wire can be formed by injecting the feedstock into a mold. In still another embodiment, the feedstock can be flowed or otherwise placed into a die and then pressed into a green-state wire. Other types of molding processes that can be used to form the green-state wire include, without limitation, compression molding, transfer molding, and plunger molding.

[0023] The green-state wires desirably are placed in respective grooves of a tray or similar structure so that the wires remain substantially straight during subsequent processing. Alternatively, subsequent processing of the wires can be carried out without placing the wires in such a tray. The tray can be made from any of various suitable materials, such as molybdenum, aluminum, or various ceramics, and can have various surface coatings, such as a spray-coating of yttria.

[0024] In particular embodiments, the unsintered, green-state wires are debound (indicated at **16** in **FIG. 1**) by immersing the tray of wires in a bath of a suitable solvent, such as trichloroethylene or water, to dissolve at least a portion of the binder in the wires. In lieu of or in addition to extracting the binder with solvent, the binder can be removed by thermal treatment. In one implementation, for example, the wires can be placed in a bath of a heated solvent. In another implementation, the binder can be removed by heat treating the wires in a furnace in lieu of or in addition to chemically treating the wires with a solvent. In the context of the present disclosure, "debinding" means to remove or extract at least a portion of the binder from the wires. Hence, debinding can include, but does not require,

removal of the entire binder phase from the wires. In some embodiments, for example, the solvent is effective to extract about 30% to 60% of the binder from the wires.

[0025] After debinding, the tray of wires is placed in a furnace or similar device for sintering. The specific sintering conditions can vary depending on the metal and the binder used. However, in general, sintering is carried out at a temperature of about 1800° F. to about 3000° F. for a period of about 0.5 to 10 hours for the materials noted above. In addition, the sintering temperature can be varied to achieve a desired wire density. The wire desirably (although not necessarily) is sintered to densify the wire to at least about 90% of the theoretical density of the metal, and more desirably to at least about 95% of the theoretical density of the metal.

[0026] In certain embodiments, the wires can be pre-heated at one or more temperature levels less than the final sintering temperature. In addition, the wires desirably are sintered under conditions that minimize oxidation of the wires. Such conditions can include, for example, sintering in a partial vacuum, in an atmosphere of an inert gas (e.g., argon or nitrogen), in a reducing atmosphere (e.g., a hydrogen atmosphere), or a combination of any of the foregoing conditions.

[0027] Sintering is effective to remove most, if not all, of the binder remaining in the wires after the debinding step. After sintering, the wires can be cooled in the furnace to a temperature of about 100° F., after which the wires can be removed from the furnace. If desired, an inert gas (e.g., argon) can be introduced into the furnace to facilitate cooling of the wires.

[0028] In an alternative embodiment, the extruded wires can be sintered without first subjecting the wires to a separate debinding step (e.g., the debinding step indicated at **16** in **FIG. 1**).

[0029] If desired, the sintered wires can be subjected to further processing. For example, the wires can be further densified by, for example, conventional hot isostatic pressing or conventional cold isostatic pressing. The wires can be ground using conventional techniques to further reduce their diameter. Also, the surfaces of the wires can be finished using conventional surface-finishing techniques, such as centerless grinding. Finally, the resulting wires as provided to the user can be straight or can be wound around a spool to form a continuous coil or spool of wire.

EXAMPLE 1

[0030] René® 142 powder was blended with 6% by weight of a binder. The binder had a composition in weight percent of about 48.5% wax, about 48.5% polypropylene, about 3% styrene-buta-diene, and about 0.25% stearic acid. The composition of René® 142 in this example comprised, in weight percent, about 1.30-1.70% Hf, about 11.45-12.05% Co, about 6.20-6.50% Ta, about 6.80-7.00% Cr, about 1.30-1.70% Mo, about 4.7-5.10% W, about 5.90-6.30% Al, about 2.60-3.00% Re, about 4.70-5.10% Ti, about 0.00-0.02% O and the balance Ni and incidental impurities. René® 142 can also have other compositions that vary slightly from the composition used in this example, such as described in U.S. Pat. No. 5,173,255.

[0031] The powder and binder were heated to about 325° F. to 350° F. and blended in a planetary mixture. The blend was allowed to cool to form a solidified mass, which was pelletized into a plurality of feedstock pellets. Pellets were loaded into the hopper of an injection molding machine and heated to a temperature of about 325° F. to form an extrudable paste. The injection molding machine had a 22-mm screw and barrel and was fitted with a die having a 0.070 inch diameter orifice. The feedstock paste was extruded through the die to form multiple welding/hardfacing wires having a diameter of about 0.070 inch and a length of about 24 inches. Pellets were also loaded into the barrel of a barrel-and-ram machine and heated at a temperature of about 325° F. to 350° F. The barrel-and-ram machine was fitted with a die having a 0.070 inch diameter orifice. The feedstock paste was extruded through the die to form multiple welding/hardfacing wires having a diameter of about 0.070 inch. The extruded weld wires were placed in the grooves of molybdenum trays having a spray coating of yttria.

[0032] The trays were placed in a bath of trichloroethylene heated to a temperature of about 155° F. for about 30 to 90 minutes, which removed about 40-50% of the binder. After debinding in the trichloroethylene, the trays were placed in a furnace for sintering. The conditions for sintering were as follows. The atmosphere inside furnace was evacuated using a vacuum pump, after which argon was introduced into the furnace until the pressure inside the furnace was about 3 torr. The temperature inside the furnace was increased from room temperature to about 500° F. at a rate of about 5° F./min. and held at about 500° F. for about 30 minutes, increased from 500° F. to about 1200° F. at a rate of about 2° F./min. and held at about 1200° F. for about 30 minutes, and increased from about 1200° F. to about 2230° F. at about 6° F./min. and held at about 2230° F. for about 15 minutes. At 2230° F., the pressure of the argon inside the furnace was increased to about 10 torr. The temperature of the furnace was further increased from about 2230° F. to about 2340° F. at a rate of about 40° F./min. and held at about 2340° F. for about 240 minutes to complete sintering of the wires.

[0033] Thereafter, the wires were allowed to cool inside the furnace to a temperature of about 1500° F., at which point the wires were cooled to a temperature of about 100° F. with high pressure argon introduced into the furnace. The furnace door was then opened to allow the wires to cool to room temperature.

[0034] The wires exhibited a theoretical density of about 95% and had a diameter of about 0.058 inch and a length of about 22 inches. The oxygen content in the wires was less than 100 PPM.

EXAMPLE 2

[0035] 17-4 stainless steel powder was blended with 6% by weight of a binder comprising in weight percent about 48.5% wax, about 48.5% polypropylene, about 3% styrene-buta-diene, and about 0.25% stearic acid. The powder and binder were heated to about 325° F. and blended in a planetary mixture. The feedstock was allowed to solidify and was pelletized. The pellets were loaded into the hopper an injection molding machine and heated to a temperature of about 325° F. The injection molding machine was fitted with a die having a 0.054 inch diameter orifice. The heated feedstock was extruded through the die to form multiple welding/hardfacing wires having a diameter of about 0.054

inch. The wires were placed in the grooves of a ceramic tray and a length of about 10 inches.

[0036] The tray and wires were immersed in a bath of trichloroethylene heated to a temperature of about 155° F. for about 30 to 90 minutes. Thereafter, the wires were sintered in an argon atmosphere at about 2480° F. for about 60 minutes. The sintered wires exhibited a density of about 7.6 g/cm3 (which is a theoretical density of about 98%) and had a diameter of about 0.04 inch and a length of about 10 inches.

EXAMPLE 3

[0037] Gamma titanium-aluminide powder was blended with 9.5% by weight of a binder. The binder had a composition of about 46.5% wax, about 48.0% polypropylene, about 5.0% thermoplastic elastomer, and about 0.5% stearic acid. The gamma titanium-aluminide in this example comprised, in weight percent, about 32-33.5% Al, about 4.5-5.1% Mb, about 2.4-2.7% Cr, and the balance titanium. Titanium aluminide can also have other compositions that vary from the composition used in this example.

[0038] The powder and binder were heated in a mixture to 325° F. to form a feedstock. The feedstock was allowed to solidify and was pelletized. The pellets were loaded in to a barrel of a barrel and ram machine and heated to a temperature of 325° F. The material was extruded to form several welding/hardfacing wires. Some of the binder was subsequently removed by chemically debinding, after which the wires were sintered at about 2500° F. for 10 hours.

[0039] The presently described methods and compositions have been shown in the described embodiments for illustrative purposes only. The methods and compositions may be subject to many modifications and changes without departing from the spirit or essential characteristics thereof.

We claim:

1. A method for making a wire comprising:

forming a green-state wire from a feedstock comprising a metal powder and a binder; and

sintering the green-state wire.

2. The method of claim 1, wherein the metal powder comprises a nickel-based superalloy.

3. The method of claim 1, wherein the binder comprises a plasticizer, a strengthener, a compatibilizer for the plasticizer and strengthener, and a surfactant.

4. The method of claim 1, wherein, prior to sintering, the green-state wire is debound by placing the wire in a bath of at least one solvent.

5. The method of claim 4, wherein the solvent comprises trichloroethylene.

6. The method of claim 5, wherein the trichloroethylene is at a temperature of about 155° F. and the green-state wire is placed in the bath of trichloroethylene for about 30 to 90 minutes.

7. The method of claim 1, wherein forming the green-state wire comprises extruding the feedstock to form the green-state wire.

8. The method of claim 7, wherein extruding the feedstock comprises:

heating the feedstock to a temperature sufficient to melt the binder and form an extrudable paste; and

extruding the paste to form the green-state weld wire.

9. The method of claim 8, wherein the feedstock is heated to a temperature of about from 300° F. to 500° F. to form the paste.

10. The method of claim 1, wherein forming the green-state wire comprises rolling the feedstock to form the green-state wire.

11. The method of claim 1, wherein forming the green-state wire comprises pressing the feedstock to form the green-state wire.

12. The method of claim 1, wherein forming the green-state wire comprises injection molding the feedstock to form the green-state wire.

13. The method of claim 1, wherein forming the green-state wire comprises compression molding the feedstock to form the green-state wire.

14. The method of claim 1, wherein forming the green-state wire comprises transfer molding the feedstock to form the green-state wire.

15. The method of claim 1, wherein forming the green-state wire comprises plunger molding the feedstock to form the green-state wire.

16. The method of claim 1, wherein the green-state wire is placed in a mold to maintain its shape during sintering.

17. The method of claim 1, wherein the feedstock is formed by mixing the metal powder and the binder, heating the metal powder and the binder to a temperature of about from 300° F. to 400° F. to form a paste, solidifying the paste, and fractionating the solidified paste to form a plurality of feedstock particles.

18. The method of claim 17, wherein forming the green-state wire comprises heating the feedstock particles to a temperature sufficient to cause the binder to melt and form an extrudable paste, and extruding the paste to form the green-state wire.

19. The method of claim 7, wherein extruding the feedstock comprises injection molding the feedstock through a die.

20. The method of claim 1, comprising sintering the unsintered wire to densify the wire to at least about 90% of the theoretical density of the metal.

21. The method of claim 1, wherein the sintered wire has a diameter of about 0.015 to 0.100 inch.

22. The method of claim 1, wherein the sintering is carried out at a temperature of about 2200° F. or greater for at least 4 hours.

23. The method of claim 1, wherein the sintering is carried out in an atmosphere containing an inert gas.

24. The method of claim 1, wherein a continuous spool of wire is formed from the sintered wire.

25. The method of claim 1, wherein the wire is a welding wire or a hardfacing wire.

26. The method of claim 1, wherein the metal powder is selected from the group comprising a nickel-based superalloy, a titanium-based superalloy, a cobalt-based superalloy, and an iron-based superalloy.

27. The method of claim 3, wherein the binder comprises wax, polypropylene, styrene-buta-diene, and stearic acid.

28. The method of claim 1, wherein the metal powder comprises a hardfacing alloy.

29. A method for making a wire comprising:

extruding a feedstock comprising a metal powder and a binder through a die to form an unsintered wire; and

sintering the unsintered wire.

30. The method of claim 29, wherein the wire is a welding wire or a hardfacing wire.

31. The method of claim 29, further comprising immersing the unsintered wire in a solvent to extract a portion of the binder from the wire.

32. The method of claim 29, wherein the metal powder is selected from the group comprising a nickel-based superalloy, a titanium-based superalloy, a cobalt-based superalloy, and an iron-based superalloy.

33. The method of claim 32, wherein the metal powder is a nickel-based superalloy and contains metals selected from the group consisting of tungsten, molybdenum, cobalt and tantalum.

34. The method of claim 33, wherein the metal powder comprises René® 142.

35. The method of claim 29, wherein the binder comprises a plasticizer, a strengthener, a compatibilizer for the plasticizer and strengthener, and a surfactant.

36. The method of claim 35, wherein the binder comprises wax, polypropylene, styrene-buta-diene, and stearic acid.

37. The method of claim 36, wherein the binder has a composition comprising in weight percent about 45% to 55% plasticizer, about 45% to 55% strengthener, about 3% to 6% compatibilizer, and about 0.25% to 0.5% surfactant.

38. The method of claim 29, wherein, prior to extruding the feedstock, the feedstock is formed by mixing the metal powder and the binder to form a mixture and heating the mixture to a temperature sufficient to melt the binder and form an extrudable paste.

39. The method of claim 29, comprising sintering the unsintered wire to densify the wire to at least about 95% of the theoretical density of the metal.

40. The method of claim 29, wherein the extruded wire is placed in a groove of a tray to maintain the shape of the wire during sintering.

41. A method for making a welding or hardfacing wire comprising:

forming a feedstock by mixing a metal powder and a binder, and heating the mixture to a temperature sufficient to cause the binder to melt, wherein the metal powder is selected from the group comprising a nickel-based superalloy, a titanium-based superalloy, a cobalt-based superalloy, and an iron-based superalloy, and the binder comprises wax, polypropylene, styrene-buta-diene, and stearic acid;

extruding the feedstock to form an unsintered wire;

placing the unsintered wire in a groove of a tray;

debinding the unsintered wire by immersing the tray and the wire in a bath of trichloroethylene; and

sintering the unsintered wire.

42. A composition for making a wire comprising:

at least one metal powder; and

a binder comprising wax, polypropylene, styrene-buta-diene, and stearic acid.

43. The composition of claim 42, wherein the at least one metal powder is selected from the group comprising a nickel-based superalloy, a titanium-based superalloy, a cobalt-based superalloy, and an iron-based superalloy.

44. The composition of claim 43, wherein the metal powder comprises René® 142.

45. The composition of claim 43, wherein the metal powder comprises René® 195.

46. The composition of claim 42, wherein the metal powder comprises a stainless steel.

47. The composition of claim 42, wherein the metal powder comprises a hardfacing alloy.

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