⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 229 478**
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: **86309337.3**

㉒ Date of filing: **01.12.86**

(51) Int.Cl.^{3}: **B 22 F 1/00**

㉚ Priority: **31.12.85 US 815429**

(43) Date of publication of application:
22.07.87 Bulletin 87/30

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

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(54) **Microcrystalline alloys prepared from solid state reaction amorphous or disordered metal alloy powders.**

(57) Microcrystalline alloys are synthesized by heat-treating amorphous or disordered metal alloy powder precursors which have been prepared under solid-state reaction conditions. The resultant microcrystalline alloys retain the same wide range of compositions present in the amorphous metal alloy powders. These microcrystalline alloys can be formed into solid shapes prior or subsequent to microcrystallization.

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MICROCRYSTALLINE ALLOYS PREPARED FROM SOLID STATE REACTION AMORPHOUS OR DISORDERED METAL ALLOY POWDERS

FIELD OF THE INVENTION

This invention relates to the preparation of microcrystalline alloys from amorphous or disordered metal alloy powder precursors. More specifically, this invention relates to the synthesis of microcrystalline alloys from amorphous or disordered metal alloy powders prepared by the interdiffusion of intimately mixed precursor materials during solid state reaction processes and novel microcrystalline compositions obtained therefrom.

BACKGROUND OF THE INVENTION

Microcrystalline alloys have become of interest in the area of structural and engineered materials due to their mechanical, physical, wear and corrosion resistant properties. These alloys are chracterized by many random nucleation sites, each having separate crystallinity, but whose growth has been inhibited, due to the growth of adjacent nucleation sites. This is different from true crystalline materials, which result from the continued growth of one nucleation site, forming a longer range, continuous ordered structure. The fine grained structure resulting from the numerous small nucleation sites is responsible for the improved mechanical and wear resistant properties of microcrystalline alloys, compared to polycrystalline materials. Microcrystalline alloys may possess high tensile strength, high thermal stability, and high ductility depending on the prevalent chracteristics of the elemental components of the individual microcrystalline alloy. These materials are of special interest for use as tool steel alloys, such as cutting tools, dies, and other similar metal products, which require high strength properties, as well as high temperature performance and oxidation resistance.

Microcrystalline alloys can be formed by heat-treating amorphous metal alloy powders at a temperature above the crystallization temperature of the powder. This is done for a period of time sufficient to produce the microcrystalline material, but not so long as to form a substantially crystalline material. The compositional range of the amorphous alloy material is retained during the microcrystallization heat-treatment, and present in the microcrystalline material formed. The composition and homogeneity of the amorphous or disordered metal alloy powder precursor, therefore, determine the degree to which various desired microcrystalline alloy characteristics, such as hardness, ductility and heat performance will exist in the resultant microcrystalline alloy.

The majority of amorphous metal alloy materials are prepared by rapid solidification processing (RSP) from a molten precursor phase. The amorphous metal alloy material is then heat-treated at a temperature above the crystallization temperature of the material for a time necessary to form its microcrystalline counterpart.

The RSP technique to form amorphous metal alloys has found great commercial success, as a variety of known alloys can be manufactured by this technique in various forms such as thin films, ribbons and wires. The technique involves subjecting a melt of the amorphous metal alloy composition to be made to rapid cooling rates on the order of 10^5-10^7°C/sec. One example of this method is taught by United States Patent No. 3,856,513 to Chen et al., which discloses directing a stream of the molten metal into the nip of rotating double rolls maintained at room temperature, which quenchs the metal in the form of an amorphous ribbon, thin film, wire, or platelet. To obtain an amorphous or disordered metal alloy powder from an RSP-prepared material requires mechanically reducing the amorphous metal alloy material as by chipping, crushing, grinding or ball milling. The resultant powder is then heat-treated at a temperature above the crystallization temperature of the amorphous metal alloy for a period of time necessary to cause microcrystallization to occur.

United States Patents Nos. 4,400,212 and 4,410,490 to Ray disclose the production of cobalt-chromium-carbon and cobalt-nickel-tungsten-carbon microcrystalline alloys, respectively, by the RSP method described above. United States Patent No. 4,473,402, also to Ray, discloses the consolidation, as by hot extrusion or cold pressing and sintering, of amorphous powder cobalt-chromium-carbide compositions prepared by the RSP technique to produce microcrystalline alloys. Ray reports a range of microcrystalline alloy material compositions which is wider than previously achieved composition ranges. This is due to the use of the RSP-rapid quench technique, which allows the direct stabilization of a high temperature phase, in this case an amorphous phase, from the melt state, to form the amorphous alloy. Stabilization by slower temperature reduction would yield a total or nearly total equilibrium state and may also cause crystallization to occur. Ray prepares his alloys, in all three patents, by melt spinning techniques. The resultant alloy is chemically homogeneous and in ribbon form, and must be comminuted to powder form prior to heat-treatment to produce the microcrystalline alloy. The comminution results in some loss of homogeneity in the resulting amorphous metal alloy powder, this decrease in homogeneity becoming a characteristic of the microcrystalline phase of the composition formed by this process.

The Journal of Materials Science, 16, 1981, at pages 2924-2930, contains two articles by Ray, "High Strength Microcrystalline Alloys Prepared by Devitrification of Metallic Glass," and "Devitrification/Hot Consolidation of Metallic Glass: A New Materials Technology via Rapid Solidification Processing." These articles disclose a process for crushing the amorphous metal alloy melt spun-RSP ribbons to powders and hot pressing the powders to the desired microcrystalline form. Microcrystallization occurs during the hot pressing process, combining a bulk forming process with the heat treating necessary to form the microcrystalline alloy.

The RSP process for making amorphous metal alloys, which has been discussed herein above, suffers from the disadvantage that the so-formed amorphous alloy is produced in a limited shape, that is as a thin-film such as a ribbon, wire or platelet. While there are a few direct uses for amorphous metal ribbons, most often a comminution step is required to obtain a more readily usable amorphous alloy powder, as is required to prepare microcrystalline alloys. The comminution step often results, to some extent, in a loss of homogeneity between the ribbon and powder stages. Further, comminution of the amorphous alloy, and subsequent recombination in a desired bulk shape, is a difficult process when it is realized that most amorphous metal alloys have high mechanical strengths and also possess high hardnesses.

While RSP techniques do somewhat increase the range of microcrystalline alloy compositions obtainable over that of a total equilibrium state system, the range remains rather narrow, as the melt phase of the amorphous alloy precursor material is not far removed from the equilibrium phase.

An alternative method to RSP techniques is the use of solid state reaction processes to produce amorphous or disordered metal alloy powders. Such a process is disclosed in International Application Number PCT/US84/00035, published under the Patent Cooperation Treaty, to Johnson et al. The process disclosed therein relates to the production of amorphous or fine crystalline materials by solid state reactions. This process comprises contacting two or more materials such that they undergo chemical reaction resulting in the diffusion of the materials into one another, and heating the materials at a temperature which permits the chemical reaction to occur, thus forming a metastable solid. Reacting at a temperature near the crystallization temperature may form a fine crystalline alloy. This process further requires that the phase formed have a lower free energy than the sum of the free energies of the starting components.

What is lacking in the area of microcrystalline alloy preparation from powders is a simple process for the direct formation of a large variety of microcrystalline alloy compositions from amorphous or disordered metal alloy powders. Especially lacking is a simple process that would synthesize amorphous metal alloy materials directly as powders which may undergo immediate heat treatment to produce microcrystalline alloys without loss of homogeneity.

Hence, it is one object of the present invention to provide novel microcrystalline alloy compositions.

It is another object of the present invention to provide a simple process for the preparation of a large variety of homogeneous microcrystalline alloy compositions.

These and additional objects of the present invention will become apparent in the description of the invention and examples that follow.

SUMMARY OF THE INVENTION

The present invention relates to a process for the synthesis of a microcrystalline alloy, comprising heat treating a substantially amorphous or disordered metal alloy powder, prepared by the interdiffusion of intimately mixed precursor materials during a solid state reaction process, at a temperature sufficiently above the crystallization temperature to form the microcrystalline alloy.

The invention further relates to a microcrystalline alloy prepared by heat-treating a substantially amorphous or disordered metal alloy powder, prepared by the interdiffusion of intimately mixed precursor materials during a solid state reaction process, at a temperature sufficiently above the crystallization temperature to form the microcrystalline alloy.

Also, the invention relates to a microcrystalline alloy characterized in that the free energy of the alloy is greater than that of a rapidly solidified material of about the same composition, and a process for producing the same.

DETAILED DESCRIPTION

In accordance with this invention, there are provided novel compositions of microcrystalline alloys synthesized from substantially amorphous or disordered metal alloy powder precursors prepared by solid state reaction methods. The phrase "microcrystalline alloy" as used herein refers to an alloy material characterized by a crystalline grain size of about 0.01 microns to about 1.0 microns. The phrase "amorphous metal alloy" connotes amorphous metal-containing alloys that may also comprise nonmetallic elements. The term "substantially" with respect to the amorphous metal alloy powder means that the powders used to prepare the microcrystalline alloys are at least 50 percent amorphous, preferably at least 80 percent amorphous, and most preferably about 100 percent amorphous.

The processes disclosed herein provide for the formation of microcrystalline alloys from amorphous or disordered metal alloy powder precursors prepared by solid state reaction methods. Solid state reaction preparation of the amorphous alloy produces the alloy in powder form, thus avoiding the need for comminution and increasing retention of the chemical homogeneity of the amorphous material in the subsequently produced microcrystalline alloy. These solid state reaction methods yield direct synthesis of amorphous or disordered metal alloy compositions in powder form far from the equilibrium composition. This highly non-equilibrium state influences the transformation from amorphous metal alloy powder to microcrystalline alloy in such a manner that these processes yield a microcrystalline alloy with increased compositional diversity and commensurate diversity with respect to physical properties.

The same processes which are disclosed herein to yield an atomic scale dispersement of atoms in a highly non-equilibrium state are amenable to the production of microcrystalline alloys or alloy compositions which are inaccessible by RSP technique due to the liquid immiscibility of the molten precursor state. A homogeneous and well-dispersed arrangement of the alloying atoms is obtainable in this type of solid state reaction synthesis, which cannot be obtained by RSP processing of immiscible molten metals. This is indicative of the expanded compositional variety of microcrystalline alloys that are feasible from amorphous metal alloy powder precursors prepared by the solid state reaction processes described herein.

The solid state reaction employed can vary depending on the desired alloy composition and properties. Some adaptable solid state reaction methods include chemical reduction reactions and thermal decomposition reactions. Each reaction method yields a powder alloy composition which is formed by the interdiffusion of the initial components absent the necessity of chemically reacting those initial components. This composition may be amorphous or be made amorphous by heat-treating at a temperature and pressure below that necessary for crystallization. The resultant amorphous or disordered powder, as taught herein, is suitable to undergo heat-treatment to the microcrystalline phase.

Solid state chemical reduction for the synthesis of amorphous or disordered metal alloy powder precursors is disclosed in United States Patent No. 4,537,625, entitled "Amorphous Metal Alloy Powders and Synthesis of Same by Solid State Chemical Reduction Reactions." This process comprises disposing a precursor compound in a liquid medium and reducing this compound to obtain a substantially amorphous metal alloy. More specifically, the process, as disclosed, involves dissolving the precursor compound in a solvent to form a solution and reducing the compound, which causes formation of a precipitate. This precipitate is an intimate mixture of the components of the amorphous metal alloy to be synthesized. The reduction, which preferably occurs in the absence of oxygen and at a temperature below crystallization temperature, can be accomplished by addition of a reducing agent to the solution, or by other reducing methods, such as electrochemical reduction or photocatalytic reduction. Subsequent heat-treatment at a temperature below the crystallization temperature of the amorphous metal alloy to be formed causes transition to the amorphous phase.

Solid state thermal decomposition is another method by which amorphous metal alloys may be formed. United States Patent No. 4,537,624, entitled "Amorphous Metal Alloy Powders and Synthesis of Same by Solid State Decomposition Reactions," teaches such a process. This process includes the step of thermally decomposing a precursor compound at a temperature below the crystallization temperature of the amorphous metal alloy to be formed. The decomposition of the precursor material may occur in a partial or full vacuum, or under an inert, reducing, or reactive atmosphere. The precursor components may alloy during the decomposition step if the temperature and timing are conducive to alloying of the given components. When alloying does not take place during the decomposition step, a powder which is an intimate mixture of the components of the alloy to be formed is obtained. This is then subsequently heat-treated, at a temperature sufficiently below the crystallization temperature of the alloy components, to form the amorphous phase.

The solid state reaction methods recited above yield amorphous or disordered metal alloy powders in a high non-equilibrium state. This high free energy state is characterized by higher molecular disorder than the melt phase employed with RSP for compounds having similar compositions. Solid state reactions produce stable amorphous or disordered alloy materials having much greater compositional diversity than can be obtained using RSP techniques which produce materials that generally consist of equilibrium phase compounds.

The resultant amorphous or disordered alloy powder, embodying variations in composition due to the high free energy of this material, is then heat-treated, in accordance with this disclosure, to form the microcrystalline alloy. Solid state reaction processes, such as those discussed above, increase the range of compositions that will exist in any given microcrystalline alloy. By increasing the range of compositions, a commensurate increase in the range of properties, characteristic to different compositions, is achieved, thus making solid state reactions desirable for microcrystalline alloy production.

The amorphous metal alloy powders, produced by the solid state reactions discussed above, or any other solid state reaction methods, can be compacted to a desired shape, or left in the powder form, and heat-treated to a temperature between about 0.6 and 0.95 of the solidus temperature of the amorphous or disordered metal alloy powder to produce the microcrystalline alloy. The heat-treatment process to the microcrystalline phase occurs over a period of from about 1 hour to about 1,000 hours, depending on the amorphous or disordered metal alloy composition used and the treatment temperature.

SPECIFIC EXAMPLES

The following examples are presented to more thoroughly explain the instant invention, but are not intended to be limitative thereof. The examples demonstrate the use of amorphous or disordered metal alloy powder precursors, prepared by solid state reaction methods, to produce microcrystalline alloys which have the desired properties characteristic of the amorphous or disordered metal alloy powder precursors.

Example 1

This example illustrates the formation of a microcrystalline alloy composition of iron-nickel-boron from an amorphous or disordered metal alloy powder prepared under solid state reduction conditions.

About 4 mmol of nickel chloride, $NiCl_2$ $6H_2O$, and about 16 mmol of iron chloride, $FeCl_2$ $4H_2O$, were dissolved in about 100 ml of distilled water to form a reaction solution, and then filtered into a 500 ml flask. The reaction solution was degassed with argon. An argon-degassed solution of about 50 mmol of $NaBH_4$, dissolved in about 100 ml of distilled water, was then added over about a one and one-quarter hour period. Immediately upon addition of the sodium borohydride solution, hydrogen gas was evolved from the solution and a black, magnetic precipitate was formed. After the addition was completed, the reaction solution was stirred for about 16 hours to insure that the reaction had gone to completion. The solution was cannulated away from the precipitate and the precipitate was then washed with two 50 ml portions of distilled water. The precipitate was then dried under a vacuum at about 60°C for about four hours. In this condition, the black precipitate powder reacts vigorously upon exposure to oxygen, and so should be maintained in the absence of oxygen.

The powder was then transferred under inert conditions to a quartz tube, which was sealed under vacuum, and was heat-treated at about 290°C for 264 hours. This produced a powder consisting substantially of amorphous material.

A portion of the powder was further heat-treated at about 900°C for one hour to produce a silver, cohesive agglomeration which reacted slightly upon exposure to oxygen.

X-ray diffraction data of the material indicated a microcrystalline alloy of the approximate composition Fe_8Ni_2B consisting of multiple phases.

Example 2

The procedure described in Example 1 was repeated with the exception that the heat-treatment of the amorphous or disordered metal alloy powder to form the microcrystalline alloy was carried out at about

600°C for about one hour. The resultant alloy was determined to be microcrystalline and to have about the same composition, Fe_8Ni_2B, as in Example 1. This illustrates that the temperature of this heat-treatment need only be sufficiently above the crystallization temperature, and that a broad range of temperatures beyond the crystallization temperature may be employed. This temperature range will vary, of course, depending on the elemental components of a given amorphous metal alloy powder precursor.

Example 3

About 9.10g (45.75 mmol) of $FeCl_2$ $4H_2O$ and 2.856g (12 mmol) of $CoCl_2$ $6H_2O$ were dissolved in 300 ml of distilled water. This solution was filtered into a 1 liter Schlenk flask and degassed with argon. Against a counterflow of argon, 1.623g of neodymium powder (11.25 mmol) was added. To this rapidly stirred suspension a degassed solution of 5.49g (144 mmol) of $NaBH_4$, in 200 ml of distilled water, was added dropwise over a 1 hour period. After stirring overnight, the solution was cannulated away from a black neodymium-containing precipitate mixture. This mixture was then washed with two 100 ml portions of distilled water and dried under vacuum at 60°C for 4 hours. Under vacuum, this material was heated to 200°C for 20.5 hours to remove any H_2 from the powder. The material was then sealed in a quartz tube and heat-treated at 840°C to produce a microcrystalline material of the composition $Nd_{15}Fe_{61}Co_{16}B_8$.

Example 4

In an argon filled dry box, 6.306g of a copper powder precipitate of high surface area, prepared by the reaction of $CuCl_2.2H_2O$ and $NaBH_4$ in water at room temperature under inert conditions, was added to a tetrahydrogenation solution of 0.246g of $W(CO)_6$ while stirring rapidly. The solvent was removed, and the resultant dry powder mixture was sealed under vacuum in a quartz tube.

The material was heat treated at 200°C for two hours followed by heating for 22 hours at 300°C. Elemental analysis indicated that the resultant powder, which had an atomic percent of $Cu_{99.3}W_{0.7}$, contained about 2.7 weight percent tungsten (calculated 2.0 weight percent tungsten). Only copper lines were observed by x-ray analysis. Subsequent heat-treatment of this disordered metal powder at elevated temperatures, above the crystallization temperature of the powder, produced a microcrystalline alloy of the same composition.

The above-described examples demonstrate the formation of microcrystalline alloy compositions from amorphous or disordered metal alloy powder precursors prepared by solid state reaction methods. This novel application of solid state reaction methods to form particulate precursor compounds as amorphous or disordered metal alloy powders, existing in a high free energy state, followed by microcrystallization heat-treatment processing, may facilitate retention of some of the highly disordered state of the system in the resultant microcrystalline alloy material. This increases compositional variation over prior known methods of microcrystalline alloy preparation, and is a simpler method than those previously utilized. Further, these materials and processing techniques may also make resultant materials useful as strengthening aids. Materials which could be altered to produce novel composites may include crystalline metal powders, ceramics and plastics.

The scope of this invention is intended to include modifications and variations commensurate with the scope of the appended claims. The parameters herein presented, such as temperatures above and below crystallization temperature and time periods appropriate to amorphous alloy and microcrystalline alloy formation, as well as the identified solid state reaction methods, are not intended to be limitative.

CLAIMS:

1. A process for the synthesis of a microcrystalline alloy, comprising heat-treating a substantially amorphous or disordered metal alloy powder prepared by a solid state reaction process at a temperature sufficiently above the crystallization temperature to form said microcrystalline alloy.

2. A process as claimed in claim 1 characterised in that the solid state reaction process is a chemical reduction reaction.

3. A process as claimed in claim 1 characterised in that the said solid state reaction process is a thermal decomposition reaction.

4. A process as claimed in any of claims 1 to 3 characterised in that the amorphous metal alloy powder is heat-treated at a temperature between about 0.6 and about 0.95 of the solidus temperature of said amorphous metal alloy powder.

5. A microcrystalline alloy prepared by heat-treating a substantially amorphous or disordered metal alloy powder prepared by a solid state reaction process at a temperature sufficiently above the crystallization temperature to form said microcrystalline alloy.

6. A microcrystalline alloy as claimed in claim 5 characterised in that the grain size of said microcrystalline alloy ranges from about 0.01 microns to about 1.0 microns.

7. A microcystalline alloy characterized in that the free energy of the alloy is greater than that of a rapidly solidified material of about the same composition.

8. A process for the synthesis of a microcrystalline alloy, comprising heat-treating a substantially amorphous metal alloy powder, prepared by a solid state reaction process and having a high non-equilibrium state, at a temperature sufficient above the crystallization temperature to transform said powder to said microcrystalline alloy, said microcrystalline alloy being characterized in that the highly non-equilibrium state of said amorphous metal alloy powder is retained in said microcrystalline alloy.

9. A process as claimed in claim 8 characterised in that the solid state reaction process is a chemical reduction reaction.

10. A process as claimed in claim 8 characterised in that the solid state reaction process is a thermal decomposition reaction.

11. A process as claimed in any of claims 8 to 10 characterised in that the amorphous metal alloy powder is heat-treated at a temperature between about 0.6 and about 0.95 of the solidus temperature of said amorphous metal alloy powder.

12. A microcrystalline alloy, characterised in that the free energy of the alloy is greater than that of a rapidly solidified material of about the same composition, synthesized by heat-treating a substantially amorphous metal alloy powder prepared by a solid state reaction process at a temperature sufficiently above the crystallization temperature to form said microcrystalline alloy.